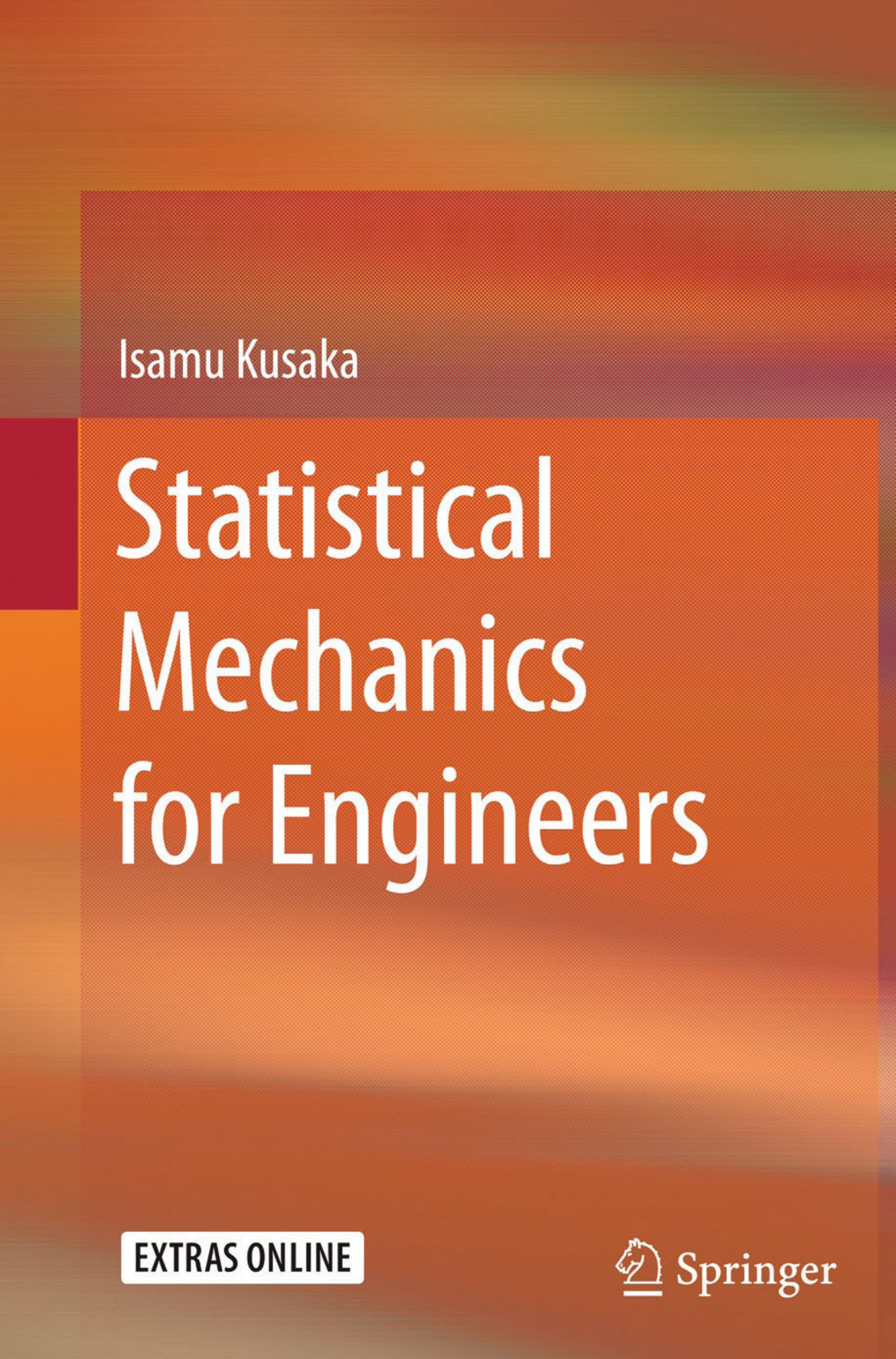

Isamu Kusaka

Statistical Mechanics for Engineers

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To the memory of the late Professor Kazumi Nishioka, to whom I owe everything I know about thermodynamics.

Preface

The purpose of writing this book is to explain basic concepts of equilibrium statistical mechanics to the first year graduate students in engineering departments. Why should an engineer care about statistical mechanics?

Historically, statistical mechanics evolved out of the desire to explain thermodynamics from fundamental laws of physics governing behavior of atoms and molecules. *If* a microscopic interpretation of the laws of thermodynamics were the only outcome of this branch of science, statistical mechanics would not appeal to those of us who simply wish to use thermodynamics to perform practical calculations. After all, validity of thermodynamics has long been established.

In thermodynamics, a concept of fundamental equations plays a prominent role. From one such equation many profound predictions follow in a completely general fashion. However, thermodynamics itself does *not* predict the explicit form of this function. Instead, the fundamental equation must be determined empirically for each system of our interest. Being a science built on a set of macroscopic observations, thermodynamics does not offer any systematic way of incorporating molecular level information, either. Thus, an approach based solely on thermodynamics is not sufficient if we hope to achieve desired materials properties through manipulation of nanoscale features and/or molecular level architecture of materials.

It is in this context that the method of statistical mechanics becomes important for us. Equilibrium statistical mechanics provides a general framework for constructing the fundamental equation from a molecular level description of the system of interest. It can also provide a wealth of molecular level insights that is otherwise inaccessible even experimentally. As such, it is becoming increasingly more relevant to engineering problems, requiring majority of engineering students to develop more than just a passing acquaintance with the basic results of this subject.

Because statistical mechanics is built on the basis of classical and quantum mechanics, some elementary knowledge of these subjects proves essential in order to access the existing textbooks on statistical mechanics in any meaningful manner. However, these subjects fall outside the expected background of engineering students. For some, these subjects are entirely foreign. This book is meant to fill in the gap felt by such students, who need to efficiently absorb only those essential back-grounds necessary to understand the basic ideas of statistical mechanics and quickly move onto more specific topics of their own interest.

My intention, therefore, is not to replace many excellent textbooks on statistical mechanics that exist today, but *to ease the transition* into such textbooks. Thus, I did not try to showcase various applications of statistical mechanics, of which there are many. Instead, the emphasis is on making the basic ideas of statistical mechanics accessible to the intended audience. The end result is this book, serving as a gentle introduction to the subject. By the end of this book, however, you will be well positioned to read more advanced textbooks including those with more specialized themes, some of which are listed in Appendix E.

In this book, I have chosen to present classical mechanical formulation of statistical mechanics. This is somewhat contrary to the prevailing wisdom that favors the mathematical simplicity of quantum statistical mechanics: Microstates in quantum mechanical systems can be counted, at least in principle. This is not so in classical mechanical systems *even in principle*. However, relevant concepts in quantum mechanics are far more abstract than those in classical mechanics and a proper understanding of the former requires that of the latter. A common compromise is to simply accept the discrete energy spectrum of bound quantum states. But, this leaves a rather uncomfortable gap in the students' knowledge. No less important is the fact that many applications of statistical mechanics in engineering problems take place within essentially the classical framework even though the fundamental laws of physics dictating the behavior of atoms are quantum mechanical in nature.

It seemed inappropriate to use a symbol that is either very different from established conventions or far detached from the meaning it is supposed to represent. The alternative has an unfortunate consequence that multiple meanings had to be given to a single symbol on occasion. In such cases, the context should always dictate what is meant by the particular symbol in question. In this regard, notation is no different from an ordinary language. To minimize a possible confusion, a list of frequently used symbols is provided at the end of each chapter.

Suggestions Before You Start

A prior exposure to undergraduate level thermodynamics will be very helpful as it provides you with a sense of direction throughout our journey ahead. I will also assume that you have a working knowledge of calculus. Specifically, you should know how to evaluate derivatives and integrals of functions of multiple variables. In case you need to regain some of these skills, I tried to include as much calculational details as reasonable. However, calculus is a perishable skill and a constant practice is essential in maintaining a certain level of proficiency. More importantly, "Mathematics is a language in which the physical world speaks to us."[1] That is, you cannot expect to understand the subject without penetrating through certain manipulative aspects first. I made no attempt to conceal this fact. It is up to you to fill in the missing steps of the calculations with a stack of papers and a pencil on your side.

Though this will *not* change the content of any given equation, it will profoundly change your relationship to that equation.

To help you learn new concepts, exercises are scattered throughout the book. Keeping with the above stated goal of this book, most of them require only a fairly straightforward (I hope) manipulation of equations and applications of concepts just learned. The primary reward for solving these problems is *not* the final answer per se but the *perspective you gain from working through them*. You are strongly urged to attempt as many of them as possible. So that the exercises will not become an undue hindrance to your progress, hints are given to a subset of them in Appendix G.

The materials covered in Chap. 1 through Chap. 5 form the core of this book and should be sufficient if you want to transition to more advanced textbooks as quickly as possible. Chapters 6 and 7 are concerned with thermodynamics and statistical mechanics of inhomogeneous fluids. So that you would not have to feel uncomfortable when consulting existing textbooks on statistical mechanics, Chap. 8 introduces key concepts from quantum mechanics and briefly illustrates their application in formulating statistical mechanics.

In the main body of the book, you will notice that some section headings bear a dagger (†). These sections are aimed at exploring issues prompted by questions from students in my graduate level courses on thermodynamics and statistical mechanics. Some of them provide detailed derivations of key results that are simply quoted in undaggered sections. Sections marked with double dagger (‡) cover materials that are considered standard by many, including myself. But, they can be brushed aside in view of our immediate goal. These optional sections were retained in the hope that they may spice up your journey through the book. Some are retained as a modest attempt at completeness. If you are pressed for time, or simply do not want to bother with them at this time, you can omit them without any guilt or loss of continuity until your curiosity compels you otherwise. On occasion, I do use certain results from these optional sections, but only with an explicit reference to the relevant sections. You can either choose to read the indicated section at that time, or simply accept the results quoted and move on. After all, learning is an iterative process and there is no need to absorb everything in your first attempt at the subject. Enjoy!

October 2014

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Acknowledgments

This book grew out of my graduate level courses on thermodynamics and statistical mechanics. Despite many inadequacies in earlier versions of the lecture notes, many students endured and enjoyed the experience. Intellectual curiosity and a sense of excitement they continued to express were the greatest driving force in my effort to explain the subject as clearly as I could.

Prof. Zhen-Gang Wang kindly allowed me to include one of his homework problems as an example in this book. The first three sections of Appendix A owe their organization to the undergraduate level course on fluid mechanics taught by Prof. Martin Feinberg. Ms. Yensil Park, Mr. Nicholas Liesen, and Mr. Robert Gammon Pitman, who were among the students in my course, found many persistent typos in a later version of the manuscript. Dr. Shunji Egusa read through a large portion of the manuscript and made many helpful suggestions to improve its overall readability. The ultimate responsibility, of course, resides with me. I am also indebted to Dr. Kenneth Howell and Ms. Abira Sengupta at Springer for their excellent support and strong commitment to this project. On a personal note, my wife gracefully endured my long held obsession with this work.

Contents

Chapter 1
Classical Mechanics

A macroscopic object we encounter in our daily life consists of an enormously large number of atoms. While the behavior of these atoms is governed by the laws of quantum mechanics, it is often acceptable to describe them by means of classical mechanics. In this chapter, we familiarize ourselves with the basic concepts of classical mechanics. From the outset, we assume that concepts such as mass, time, displacement, and force are understood on the basis of our everyday experiences without further elaboration. The role of classical mechanics, then is to explore the precise relationship among these objects in mathematical terms.

1.1 Inertial Frame

When describing physical phenomena, we need a frame of reference from which we make our observations. The mathematical expression of the laws of mechanics takes the simplest form when the frame is the so-called **inertial frame of reference**.

To understand what this is, imagine that you are sitting in front of your desk in your office in your building, and suppose that the desk is firmly secured to the floor and the surface of the desk is perfectly smooth and horizontal. If you place a billiard ball on the desk and remove your hand without giving any nudge to the ball, it will just sit there. If you are to give a gentle push, it will start rolling on the desk. It will continue to move in a straight line with a constant speed until it falls off at the edge of the desk. (We shall formally define the word "speed" in Sect. 1.2.1.)

These observations remain valid even if your office is housed in a train moving at a constant speed on a perfectly straight and leveled railroad track. A coordinate system attached to the desk, secured either to the building or to the train, is an example of inertial frames of reference, in which an object when subjected to no net force, either stands still or keeps on moving along a straight line at a constant speed.

However, if the train housing your office is to suddenly change direction, the ball, which was previously standing still with respect to the desk, will suddenly start moving without you doing anything to it. It is certainly more difficult to describe

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the behavior of the ball in such a frame of reference. In fact, the coordinate system attached to the desk, in this case, is no longer an inertial frame until the train resumes its motion along a straight line at a constant speed. Unless explicitly indicated otherwise, we shall always use an inertial frame of reference.

1.2 Mechanics of a Single Particle

Systems of our eventual interest consist of the order of 10^{24} atoms, if not more. Before we tackle the problem of describing their behavior, we shall first learn how to describe a motion of a single particle. This allows us to introduce the essential concepts and terminologies needed for the studies of many-particle systems.

1.2.1 Newton's Equation of Motion

Let us take some macroscopic object such as a ball, and imagine that the size of the object becomes smaller and smaller while maintaining its original mass. The limit of this imaginary process is a point carrying certain nonzero mass. Such a point is referred to as a **material point** or simply a **particle**.

The position $\boldsymbol{r}$ of a material point in space may change with time. This will be the case if, for example, you are to throw one such material point, for example, a ball. The time dependence of $\boldsymbol{r}$ is determined by **Newton's equation of motion**. In an inertial frame of reference, this equation takes a particularly simple form:

$$m\frac{\mathrm{d}^2\boldsymbol{r}}{\mathrm{d}t^2} = \boldsymbol{F} , \tag{1.1}$$

where t, m, and $\boldsymbol{F}$ denote, respectively, the time, the mass of the material point, and the net force acting on it. Conversely, if $\boldsymbol{r}$ of a particle is described by (1.1) in some frame of reference, the frame is an inertial frame.

In a Cartesian coordinate system, (1.1) can be written more explicitly as

$$m\frac{\mathrm{d}^2x}{\mathrm{d}t^2} = F_x , \quad m\frac{\mathrm{d}^2y}{\mathrm{d}t^2} = F_y , \quad \text{and} \quad m\frac{\mathrm{d}^2z}{\mathrm{d}t^2} = F_z , \tag{1.2}$$

where x, y, z are, respectively, the x-, y-, and z-components of the vector $\boldsymbol{r}$. Likewise for F_x, F_y, and F_z.

Example 1.1. Motion under no force: If $\boldsymbol{F}$ is zero at all time, then (1.1) tells us that

$$\frac{\mathrm{d}^2\boldsymbol{r}}{\mathrm{d}t^2} = \boldsymbol{0} , \tag{1.3}$$

which may be integrated to give

$$\frac{\mathrm{d}\boldsymbol{r}}{\mathrm{d}t} = \boldsymbol{c}_1 \quad \text{and} \quad \boldsymbol{r} = \boldsymbol{c}_1 t + \boldsymbol{c}_2 \, . \tag{1.4}$$

When no force is acting on the material point, the vector $\boldsymbol{v} := \mathrm{d}\boldsymbol{r}/\mathrm{d}t$, called the **velocity** of the material point, is seen to be independent of time. We also observe that the material point moves along a straight line, thus confirming what was said about inertial frames of reference in Sect. 1.1.

The constant vectors $\boldsymbol{c}_1$ and $\boldsymbol{c}_2$ may be determined from initial conditions. For example, if we know that the material point was at $\boldsymbol{r}_0$ at time $t = 0$ and that it was moving with the velocity $\boldsymbol{v}_0$ at $t = 0$, then substituting this information into (1.4), we obtain

$$\boldsymbol{c}_1 = \boldsymbol{v}_0 \quad \text{and} \quad \boldsymbol{c}_2 = \boldsymbol{r}_0 \, , \tag{1.5}$$

and hence

$$\frac{\mathrm{d}\boldsymbol{r}}{\mathrm{d}t} = \boldsymbol{v}_0 \quad \text{and} \quad \boldsymbol{r} = \boldsymbol{v}_0 t + \boldsymbol{r}_0 \, . \tag{1.6}$$

Example 1.2. Motion under gravity: Let us turn to a slightly more interesting problem of throwing a ball. If we ignore the friction between the ball and the air, the only force acting on the ball after it left your hand is the force of gravity $m\boldsymbol{g}$, where the gravitational acceleration $\boldsymbol{g}$ is a vector pointing toward the center of the earth. In this case, (1.1) becomes

$$m\frac{\mathrm{d}^2\boldsymbol{r}}{\mathrm{d}t^2} = m\boldsymbol{g} \, . \tag{1.7}$$

Assuming that $\boldsymbol{g}$ is constant, which is an excellent approximation over the time and the length scales involved in this example, the equation can be readily integrated to give

$$\boldsymbol{v} = \frac{\mathrm{d}\boldsymbol{r}}{\mathrm{d}t} = \boldsymbol{g}t + \boldsymbol{c}_1 \quad \text{and} \quad \boldsymbol{r} = \frac{1}{2}\boldsymbol{g}t^2 + \boldsymbol{c}_1 t + \boldsymbol{c}_2 \, , \tag{1.8}$$

where $\boldsymbol{c}_1$ and $\boldsymbol{c}_2$ are constant vectors. Unless $\boldsymbol{g}$ is parallel to $\boldsymbol{c}_1$ or $\boldsymbol{c}_1 = \boldsymbol{0}$, the trajectory of the particle is *not* a straight line.

As before, let $\boldsymbol{r} = \boldsymbol{r}_0$ and $\boldsymbol{v} = \boldsymbol{v}_0$ at $t = 0$. Then, $\boldsymbol{c}_1 = \boldsymbol{v}_0$ and $\boldsymbol{c}_2 = \boldsymbol{r}_0$. With the vectors $\boldsymbol{c}_1$ and $\boldsymbol{c}_2$ so determined, (1.8) completely determines $\boldsymbol{r}$ and $\boldsymbol{v}$ at any other value of t.

The two examples we have just seen point to a general scheme of classical mechanics. That is, if $\boldsymbol{F}$ is at most a known function of $\boldsymbol{r}$, $\boldsymbol{v}$, and t, then $\boldsymbol{r}$ and $\boldsymbol{v}$ of a particle at any time t are completely determined once they are specified at $t = 0$ or at any other instant of time for that matter. The pair of vectors $(\boldsymbol{r}, \boldsymbol{v})$ associated with a single particle at some instant of time is referred to as the **mechanical state** of that particle at that instant. It follows that the mechanical state of a particle is completely determined for all t if it is specified at some instant, say $t = 0$.[2]

The length $\|\boldsymbol{v}\| := \sqrt{\boldsymbol{v}\cdot\boldsymbol{v}} = \sqrt{{v_x}^2 + {v_y}^2 + {v_z}^2}$ of the velocity vector $\boldsymbol{v}$ is called the **speed**, where v_x, v_y, and v_z denote, respectively, the x-, y-, and z- components of the vector $\boldsymbol{v}$. We shall often write v instead of $\|\boldsymbol{v}\|$. Finally, $\mathrm{d}^2\boldsymbol{r}/\mathrm{d}t^2$ is the **acceleration**. For a brief review of vector algebra, see Appendix A.

We can now show that a frame of reference moving at a constant velocity with respect to an inertial frame is also an inertial frame. To see this, consider motion of a particle in two frames $\mathscr{O}$ and $\mathscr{O}'$, with respect to which the position vectors of the particle is $\boldsymbol{r}$ and $\boldsymbol{r}'$, respectively. Let $\boldsymbol{R}$ denote the position vector of the origin of $\mathscr{O}'$ with respect to that of $\mathscr{O}$. Then,

$$\boldsymbol{r} = \boldsymbol{r}' + \boldsymbol{R}\ . \tag{1.9}$$

If we suppose that $\mathscr{O}$ is an inertial frame, (1.1) holds for $\boldsymbol{r}$. Using (1.9), we find

$$m\frac{\mathrm{d}^2\boldsymbol{r}'}{\mathrm{d}t^2} = \boldsymbol{F} - m\frac{\mathrm{d}^2\boldsymbol{R}}{\mathrm{d}t^2}\ . \tag{1.10}$$

If the velocity $\mathrm{d}\boldsymbol{R}/\mathrm{d}t$ of $\mathscr{O}'$ with respect to $\mathscr{O}$ is constant, the second term on the right-hand side vanishes identically and we obtain

$$m\frac{\mathrm{d}^2\boldsymbol{r}'}{\mathrm{d}t^2} = \boldsymbol{F}\ , \tag{1.11}$$

indicating that $\mathscr{O}'$ is an inertial frame.

If $\mathscr{O}'$ is accelerating with respect to $\mathscr{O}$, then $\mathrm{d}^2\boldsymbol{R}/\mathrm{d}t^2$ must be retained in (1.10). At this point, however, our definition of inertial frames appears circular. In Newtonian mechanics, a force acting on a particle is defined by means of Newton's equation of motion in the form of (1.1). That is, the force is measured by the acceleration it produces.[3] Therefore, an observer in $\mathscr{O}'$ who is oblivious to the fact that his frame is not an inertial frame would simply compute the force $\boldsymbol{F}'$ acting on the particle as $m\mathrm{d}^2\boldsymbol{r}'/\mathrm{d}t^2$. This vector is, of course, equal to $\boldsymbol{F} - m\mathrm{d}^2\boldsymbol{R}/\mathrm{d}t^2$. But, this observer is under no obligation to separate $\boldsymbol{F}'$ into $\boldsymbol{F}$ and $-m\mathrm{d}^2\boldsymbol{R}/\mathrm{d}t^2$. Instead, he can insist that the frame $\mathscr{O}'$ is inertial and that the force acting on the particle is $\boldsymbol{F}'$, not $\boldsymbol{F}$. A tacit assumption made in Newtonian mechanics, therefore, is that forces can arise only through an effect a body produces onto another and that we can systematically either eliminate or account for such effects.

1.2.2 Work

If a particle experiences a displacement $\Delta\boldsymbol{r}$ under the influence of a force $\boldsymbol{F}$ and the force remained constant during the displacement, then the **work** W done *by* this

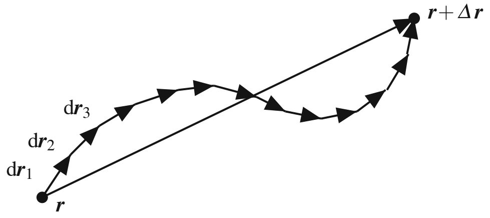

Fig. 1.1 The sum of infinitesimal displacements d$\boldsymbol{r}_i$ results in a net displacement $\int \mathrm{d}\boldsymbol{r} = \sum_{i=1}^{n} \mathrm{d}\boldsymbol{r}_i = \Delta\boldsymbol{r}$.

force *on* the particle is, by definition, the dot product of $\boldsymbol{F}$ and $\Delta\boldsymbol{r}$:

$$W := \boldsymbol{F}\cdot\Delta\boldsymbol{r}\,, \tag{1.12}$$

This definition does not preclude the situation in which other forces are also acting on the particle. In that case, (1.12) simply gives the work done by this particular force $\boldsymbol{F}$ alone and does not include the work done by the other forces.

It may be that $\boldsymbol{F}$ actually changes during the displacement. To allow for this more general situation, we define the work by the equation

$$W := \int \boldsymbol{F}\cdot\mathrm{d}\boldsymbol{r}\,, \tag{1.13}$$

where the integration is along the path taken by the particle. When $\boldsymbol{F}$ remains constant along the path, (1.13) may be written as

$$W = \boldsymbol{F}\cdot\int \mathrm{d}\boldsymbol{r}\,. \tag{1.14}$$

If we regard the integral as a “sum” of infinitesimal displacements d$\boldsymbol{r}_1$, d$\boldsymbol{r}_2$, d$\boldsymbol{r}_3$,…, the integral is equal to $\Delta\boldsymbol{r}$ as seen from Fig. 1.1, and (1.14) reduces to (1.12). Thus, (1.13) contains (1.12) as a special case.

Let us suppose, as illustrated in Fig. 1.2, that we lift a particle of mass m from $z = h_1$ to $z = h_2$ under gravity. In order to do this, we have to apply a force $\boldsymbol{F}$ just enough to overcome the force exerted on the particle by gravity $m\boldsymbol{g}$. In terms of components with respect to the coordinate system shown in Fig. 1.2, $m\boldsymbol{g} \doteq (0,0,-mg)$,[4] where the negative sign is needed because the force of gravity points in the negative z-direction. Thus, the force needed is $\boldsymbol{F} \doteq (0,0,mg+\varepsilon)$, where $\varepsilon > 0$. Since the displacement is in the positive z-direction, d$\boldsymbol{r} \doteq (0,0,\mathrm{d}z)$. Combining everything,

$$\begin{aligned} W &= \int \boldsymbol{F}\cdot\mathrm{d}\boldsymbol{r} = \int_{h_1}^{h_2}(mg+\varepsilon)\mathrm{d}z = (mg+\varepsilon)(h_2-h_1) \\ &\to mg(h_2-h_1) \quad \text{as} \quad \varepsilon\to 0\,. \end{aligned} \tag{1.15}$$

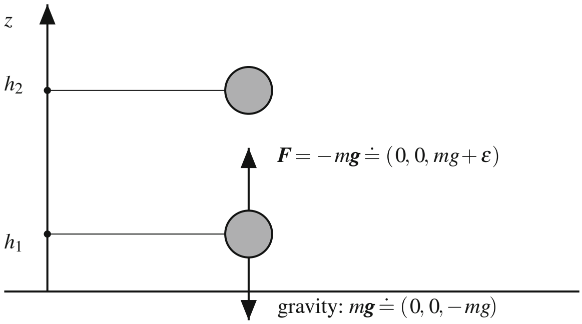

Fig. 1.2 A particle under gravity.

We define a new quantity

$$\psi(z) := mgz \tag{1.16}$$

and call it the **potential energy** of the particle due to gravity when it is at height z above the ground. With this definition, (1.15) becomes

$$W = \psi(h_2) - \psi(h_1) \,. \tag{1.17}$$

We also notice that

$$-\frac{\mathrm{d}\psi(z)}{\mathrm{d}z} = -mg \,, \tag{1.18}$$

that is, by taking the derivative of ψ with respect to z and putting a negative sign in front of it, we obtain the z-component of the force of gravity. This is a general feature of a potential energy as we shall see in the next subsection.

1.2.3 Potential Energy

More generally, potential energy can be introduced as follows. We suppose that the force $\boldsymbol{F}_c$ acting on a particle is a function of its position. As was the case with lifting of a particle under gravity in the previous section, the force $\boldsymbol{F} = -\boldsymbol{F}_c$ is needed to counter $\boldsymbol{F}_c$ and move the particle.[5] If the particle is made to move along a closed path, such as the one depicted in Fig. 1.3, the work done by the force $\boldsymbol{F}$ is given by

$$W = \oint \boldsymbol{F} \cdot \mathrm{d}\boldsymbol{r} \,, \tag{1.19}$$

where $\oint$ signifies the integration along a *closed* path. If this quantity is identically zero for *any* closed path, including those that does not necessarily pass through the points A, B, C, and D in the figure, then $\boldsymbol{F}_c$ is said to be **conservative**.

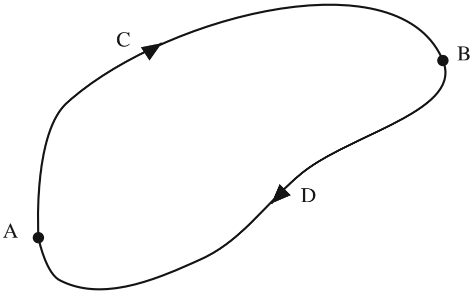

Fig. 1.3 A closed path along which the particle is moved.

The particular closed path *ACBDA* shown in Fig. 1.3 can be regarded as consisting of two parts, the path $A \to C \to B$ and the path $B \to D \to A$. Thus,

$$W = \int_{A\to C\to B} \boldsymbol{F}\cdot \mathrm{d}\boldsymbol{r} + \int_{B\to D\to A} \boldsymbol{F}\cdot \mathrm{d}\boldsymbol{r} =: W_{A\to C\to B} + W_{B\to D\to A} \ . \tag{1.20}$$

Now, suppose that we reverse the second part of the path and bring the particle from A to B through D. The infinitesimal displacement $\mathrm{d}\boldsymbol{r}$ on this reversed path $A \to D \to B$ will have the opposite sign to that on the original path $B \to D \to A$. But, the force $\boldsymbol{F}_c(\boldsymbol{r})$, and hence $\boldsymbol{F}(\boldsymbol{r})$, will remain unaffected by the reversal of the path. Thus,

$$W_{A\to D\to B} = -W_{B\to D\to A} \ , \tag{1.21}$$

and hence

$$W = W_{A\to C\to B} - W_{A\to D\to B} \ . \tag{1.22}$$

If $\boldsymbol{F}_c$ is conservative, then $W = 0$ and we have

$$W_{A\to C\to B} = W_{A\to D\to B} \ . \tag{1.23}$$

In other words, the work required to move a particle from point A to point B against the conservative force $\boldsymbol{F}_c$ is independent of the actual path taken and depends only on the positions of the end points A and B. Thus, the work can be written as

$$W_{A\to B} = \psi(\boldsymbol{r}_A, \boldsymbol{r}_B) \ , \tag{1.24}$$

without the superfluous references to C and D.

We refer to the quantity $\psi(\boldsymbol{r}_A, \boldsymbol{r}_B)$ as the **potential energy** of the particle at $\boldsymbol{r}_B$ with respect to the reference point $\boldsymbol{r}_A$. When $\psi(\boldsymbol{r}_A, \boldsymbol{r})$ is known for all $\boldsymbol{r}$ of interest, we can calculate the work required to move a particle between any pair of points. For example, we have

$$\begin{aligned} W_{X\to Y} &= W_{X\to A\to Y} = W_{X\to A} + W_{A\to Y} = -W_{A\to X} + W_{A\to Y} \\ &= -\psi(\boldsymbol{r}_A, \boldsymbol{r}_X) + \psi(\boldsymbol{r}_A, \boldsymbol{r}_Y) \ . \end{aligned} \tag{1.25}$$

Note that $\psi(\boldsymbol{r}_A,\boldsymbol{r})$ depends on our choice of $\boldsymbol{r}_A$. However, since $W_{X\to Y}$ depends only on $\boldsymbol{r}_X$ and $\boldsymbol{r}_Y$, any $\boldsymbol{r}_A$ dependence of ψ must cancel out in (1.25). Thus, as long as we are interested in computing the work required to move a particle between two points, the location of $\boldsymbol{r}_A$ is arbitrary.

Now, let us calculate the work required to move the particle by an infinitesimal distance from $\boldsymbol{r}$ to $\boldsymbol{r}+\mathrm{d}\boldsymbol{r}$. According to (1.25), the work is given by

$$\begin{aligned} W &= -\psi(\boldsymbol{r}_A,\boldsymbol{r})+\psi(\boldsymbol{r}_A,\boldsymbol{r}+\mathrm{d}\boldsymbol{r}) = \psi(\boldsymbol{r}_A,\boldsymbol{r}+\mathrm{d}\boldsymbol{r})-\psi(\boldsymbol{r}_A,\boldsymbol{r}) \\ &= \psi(\boldsymbol{r}_A,x+\mathrm{d}x,y+\mathrm{d}y,z+\mathrm{d}z)-\psi(\boldsymbol{r}_A,x,y,z)\,. \end{aligned} \tag{1.26}$$

Using equations from Appendix B.1, we expand the right-hand side into the Taylor series to obtain

$$W = \mathrm{d}\psi + \text{h.o.}, \tag{1.27}$$

where h.o. stands for the second- and higher order terms in dx, dy, and dz, and

$$\mathrm{d}\psi = \frac{\partial\psi}{\partial x}\mathrm{d}x+\frac{\partial\psi}{\partial y}\mathrm{d}y+\frac{\partial\psi}{\partial z}\mathrm{d}z =: \mathrm{d}\boldsymbol{r}\cdot\nabla\psi\,. \tag{1.28}$$

In the last step, we introduced a new symbol $\nabla\psi$. This vector is known as the **gradient** of ψ and may also be written as $\partial\psi/\partial\boldsymbol{r}$. In a Cartesian coordinate system, in which

$$\mathrm{d}\boldsymbol{r} \doteq (\mathrm{d}x,\mathrm{d}y,\mathrm{d}z), \tag{1.29}$$

we have

$$\nabla\psi \equiv \frac{\partial\psi}{\partial\boldsymbol{r}} \doteq \left(\frac{\partial\psi}{\partial x},\frac{\partial\psi}{\partial y},\frac{\partial\psi}{\partial z}\right)\,. \tag{1.30}$$

In other coordinate systems, components of d$\boldsymbol{r}$ are not $(\mathrm{d}x,\mathrm{d}y,\mathrm{d}z)$. Accordingly, the components of $\nabla\psi$ differ from those displayed here.

Comparing (1.12) and (1.28), we identify $\nabla\psi$ as the force $\boldsymbol{F}$ required to move the particle. It follows that

$$\boldsymbol{F}_c = -\nabla\psi\,, \tag{1.31}$$

which should be compared with (1.18).

In classical mechanics, we take a point of view that the physical reality at some instant t concerning a particle is defined completely by the pair of quantities $\boldsymbol{r}(t)$ and $\boldsymbol{v}(t)$. How these quantities evolve with time is determined by Newton's equation of motion, and hence by the force acting on the particle and initial conditions. It seems natural, then, to expect that the force $\boldsymbol{F}_c$ computed by (1.31) should not in any way depend on our *arbitrary* choice of $\boldsymbol{r}_A$.

Exercise 1.1. Show that

$$\nabla\psi(\boldsymbol{r}_{A'},\boldsymbol{r}) = \nabla\psi(\boldsymbol{r}_A,\boldsymbol{r})\,, \tag{1.32}$$

that is, the force $\boldsymbol{F}_c$ is indeed independent of the choice of $\boldsymbol{r}_A$. ///

In view of the indifference of both $W_{X\to Y}$ and $\boldsymbol{F}_c$ to our choice of $\boldsymbol{r}_A$, we shall suppress the explicit reference to $\boldsymbol{r}_A$ in the function ψ and denote the potential energy

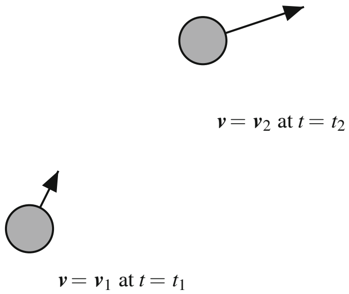

Fig. 1.4 Accelerating a particle.

simply as $\psi(\boldsymbol{r})$ even though its value certainly do depend on $\boldsymbol{r}_A$. From (1.24), we see that $\psi(\boldsymbol{r}_A, \boldsymbol{r}_A) = 0$. After dropping the first reference to $\boldsymbol{r}_A$ according to the convention just adopted, we obtain $\psi(\boldsymbol{r}_A) = 0$. We interpret this equation as identifying $\boldsymbol{r}_A$ as the reference point with respect to which $\psi(\boldsymbol{r})$ is computed.

1.2.4 Kinetic Energy

Let us calculate the work required to change the velocity of a particle of mass m from $\boldsymbol{v}_1$ at $t = t_1$ to $\boldsymbol{v}_2$ at time t_2 as illustrated in Fig. 1.4. The net force $\boldsymbol{F}$ exerted on it cannot be zero: Newton's equation of motion tells us that $\boldsymbol{v}$ remains constant otherwise. What we want to compute is the work done by this force, whether it is applied by you, some field of force such as gravity, or both. Using (1.1) in (1.13),

$$W = \int_{(t=t_1)}^{(t=t_2)} m \frac{\mathrm{d}^2\boldsymbol{r}}{\mathrm{d}t^2} \cdot \mathrm{d}\boldsymbol{r} \,. \tag{1.33}$$

Because $\boldsymbol{r}$ is a function of t, we have $\mathrm{d}\boldsymbol{r} = (\mathrm{d}\boldsymbol{r}/\mathrm{d}t)\mathrm{d}t$, which allows us to change the integration variables from $\boldsymbol{r}$ to t as

$$W = \int_{t_1}^{t_2} m \frac{\mathrm{d}^2\boldsymbol{r}}{\mathrm{d}t^2} \cdot \frac{\mathrm{d}\boldsymbol{r}}{\mathrm{d}t} \mathrm{d}t = \frac{1}{2} m \int_{t_1}^{t_2} \frac{\mathrm{d}}{\mathrm{d}t} \left(\frac{\mathrm{d}\boldsymbol{r}}{\mathrm{d}t} \cdot \frac{\mathrm{d}\boldsymbol{r}}{\mathrm{d}t} \right) \mathrm{d}t \,. \tag{1.34}$$

You can verify the second equality by evaluating the last member of the equation (with a help of the product rule of differentiation) to restore the second one. Since $\mathrm{d}\boldsymbol{r}/\mathrm{d}t = \boldsymbol{v}$,

$$W = \frac{1}{2} m \int_{t_1}^{t_2} \frac{\mathrm{d}}{\mathrm{d}t} (\boldsymbol{v} \cdot \boldsymbol{v}) \,\mathrm{d}t = \frac{1}{2} m [\boldsymbol{v} \cdot \boldsymbol{v}]_{t_1}^{t_2} = \frac{1}{2} m \left({v_2}^2 - {v_1}^2 \right) \,. \tag{1.35}$$

The resulting expression for W is seen to depend only on the mass of the particle and its velocities at t_1 and t_2. It is independent of the actual path taken by the particle,

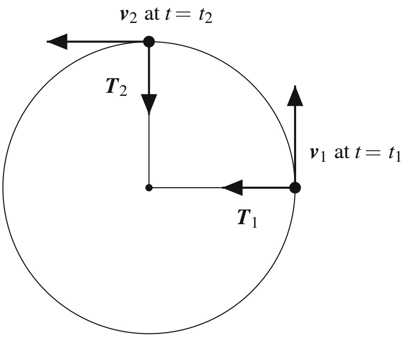

Fig. 1.5 In the case of a particle moving on a circle at a constant speed, the velocity $\boldsymbol{v}$ changes its direction without changing its length. A force is still needed to change the direction of $\boldsymbol{v}$ and is supplied, for example, by the tension $\boldsymbol{T}$ in a string to which the particle is attached. The work W done on the particle by $\boldsymbol{T}$, however, is zero.

that is, how $\boldsymbol{r}$ changed with t. In fact, we have made no assumption in this regard. In this sense, $mv^2/2$ is a reflection of an intrinsic property m of the particle and its instantaneous mechanical state, $\boldsymbol{v}$. The quantity $mv^2/2$ is called the **kinetic energy** of the particle.

From (1.34), we observe that $W \equiv 0$ if the acceleration $\mathrm{d}^2\boldsymbol{r}/\mathrm{d}t^2$ is always perpendicular to the velocity $\mathrm{d}\boldsymbol{r}/\mathrm{d}t$. Equation (1.35) then indicates that the length of the velocity vector remains constant. Such a motion can be observed directly if you attach a particle to one end of a (massless) string and swing it around the other end as shown in Fig. 1.5.

Exercise 1.2. In the derivation of (1.15), we tacitly assumed that the kinetic energy acquired by the particle is negligible. Validate this assumption in the limit of $\varepsilon \to 0$. You may assume that the particle is at rest initially at the height h_1. ///

1.2.5 Conservation of Energy

Let us consider a particle moving under the influence of a conservative force $-\nabla\psi$ and an additional external force $\boldsymbol{F}_{\mathrm{ext}}$. We calculate the work done on the particle by $\boldsymbol{F}_{\mathrm{ext}}$. In this case, Newton's equation of motion reads

$$m\frac{\mathrm{d}^2\boldsymbol{r}}{\mathrm{d}t^2} = -\nabla\psi(\boldsymbol{r}) + \boldsymbol{F}_{\mathrm{ext}} , \tag{1.36}$$

from which we have

$$W = \int_{(t=t_1)}^{(t=t_2)} \boldsymbol{F}_{\mathrm{ext}} \cdot \mathrm{d}\boldsymbol{r} = \int_{(t=t_1)}^{(t=t_2)} \left[m\frac{\mathrm{d}^2\boldsymbol{r}}{\mathrm{d}t^2} + \nabla\psi(\boldsymbol{r}) \right] \cdot \mathrm{d}\boldsymbol{r} . \tag{1.37}$$

Evidently, the two terms in the integrand can be integrated separately. The integration of the first term, as before, yields ${mv_2}^2/2 - {mv_1}^2/2$. The integration of the second term is almost immediate if we recall (1.28):

$$\int_{(t=t_1)}^{(t=t_2)} \nabla\psi(\boldsymbol{r})\cdot \mathrm{d}\boldsymbol{r} = \int_{(t=t_1)}^{(t=t_2)} \mathrm{d}\psi = \psi(\boldsymbol{r}_2) - \psi(\boldsymbol{r}_1)\ . \tag{1.38}$$

Note that we were able to compute the integral without knowing the path taken by the particle. This should not surprise you since ψ is a potential energy.

Combining the results, we arrive at the expression

$$W = \left[\frac{1}{2}m{v_2}^2 + \psi(\boldsymbol{r}_2)\right] - \left[\frac{1}{2}m{v_1}^2 + \psi(\boldsymbol{r}_1)\right]\ . \tag{1.39}$$

The kinetic energy plus the potential energy of a particle, that is,

$$E := \frac{1}{2}mv^2 + \psi(\boldsymbol{r})\ , \tag{1.40}$$

is called the **mechanical energy** or simply **energy** of the particle. According to (1.39), the change ΔE in the energy of a particle is equal to the work done on the particle by the external force $\boldsymbol{F}_{\mathrm{ext}}$:

$$\Delta E = W\ . \tag{1.41}$$

From (1.37), we see that $W = 0$ if $\boldsymbol{F}_{\mathrm{ext}} \equiv \boldsymbol{0}$. According to (1.41), this means that E remains constant. In other words, if a particle moves under the influence of a conservative force *alone*, then the energy of the particle does not change with time despite the fact that $\boldsymbol{r}$ and $\boldsymbol{v}$, upon which E depends, do change with time. Such a quantity is called a **constant of motion** or a **conserved quantity**. Mechanical energy is an example of constants of motion.

1.3 Mechanics of Many Particles

So far, we focused on the mechanics of a single particle, and treated a ball as if it is a material point. A more satisfactory description of the problem would treat the ball as a collection of many material points, each representing perhaps an atom making up the ball. These material points may also interact with each other as well as with an external field. **Newton's equation of motion** generalizes quite naturally to this case and we have

$$m_i \frac{\mathrm{d}^2\boldsymbol{r}_i}{\mathrm{d}t^2} = \boldsymbol{F}_i\ , \quad i = 1, \dots, N\ , \tag{1.42}$$

where N is the number of material points. As before, $\boldsymbol{r}_1, \dots, \boldsymbol{r}_N$ and $\boldsymbol{v}_1, \dots, \boldsymbol{v}_N$ at any time t are determined completely by these equations and initial conditions, that is, $\boldsymbol{r}_1, \dots, \boldsymbol{r}_N$ and $\boldsymbol{v}_1, \dots, \boldsymbol{v}_N$ at time $t = 0$. In keeping with the case of a single particle system, by a **mechanical state** of a system at some instant t, we shall understand the set of vectors ($\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N, \boldsymbol{v}_1, \ldots, \boldsymbol{v}_N$) referring to the positions and velocities of all the particles in the system at that moment. Thus, Newton's equations of motion, along with initial conditions, completely specify the mechanical state of a many-particle system at any other instant.

1.3.1 Mechanical Energy of a Many-Particle System

Let us calculate the work required to bring about a particular change in the mechanical state of a many-particle system.

If the system is subject to a conservative field ψ such as gravity, the ith particle experiences the force given by

$$-\nabla_i \psi(\boldsymbol{r}_i) \doteq \left(-\frac{\partial \psi}{\partial x_i}, -\frac{\partial \psi}{\partial y_i}, -\frac{\partial \psi}{\partial z_i}\right), \quad i = 1, \ldots, N \tag{1.43}$$

with x_i, y_i, and z_i denoting the x-, y-, and z-components of $\boldsymbol{r}_i$, respectively. The subscript i on ∇ indicates that the derivative is with respect to the position vector of the ith particle.

We assume that the interaction among the particles is characterized by a conservative force derivable from a single **potential energy** function $\phi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)$. That is

$$-\nabla_i \phi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) \doteq \left(-\frac{\partial \phi}{\partial x_i}, -\frac{\partial \phi}{\partial y_i}, -\frac{\partial \phi}{\partial z_i}\right), \quad i = 1, \ldots, N \tag{1.44}$$

gives the force exerted on the ith particle by all the other particles in the system. We arbitrarily set $\phi = 0$ when particles are separated sufficiently far away from each other that there is no interaction among them. If, in addition, the ith particle is subject to another external force $\boldsymbol{F}_{\mathrm{ext},i}$, (1.42) becomes

$$m_i \frac{\mathrm{d}^2 \boldsymbol{r}_i}{\mathrm{d}t^2} = -\nabla_i \psi(\boldsymbol{r}_i) - \nabla_i \phi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) + \boldsymbol{F}_{\mathrm{ext},i}, \quad i = 1, \ldots, N. \tag{1.45}$$

Thus, the work W done on the many-particle system by the external forces $\boldsymbol{F}_{\mathrm{ext},i}$ ($i = 1, \ldots, N$) is given by

$$W = \sum_{i=1}^{N} \int_{(t=t_1)}^{(t=t_2)} \boldsymbol{F}_{\mathrm{ext},i} \cdot \mathrm{d}\boldsymbol{r}_i = \sum_{i=1}^{N} \int_{(t=t_1)}^{(t=t_2)} \left[m_i \frac{\mathrm{d}^2 \boldsymbol{r}_i}{\mathrm{d}t^2} + \nabla_i \psi(\boldsymbol{r}_i) + \nabla_i \phi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) \right] \cdot \mathrm{d}\boldsymbol{r}_i. \tag{1.46}$$

The first two terms can be integrated as before and yield

$$\sum_{i=1}^{N} \left[\frac{1}{2} m_i {v_i}^2 + \psi(\boldsymbol{r}_i)\right]_{t_2} - \sum_{i=1}^{N} \left[\frac{1}{2} m_i {v_i}^2 + \psi(\boldsymbol{r}_i)\right]_{t_1}, \tag{1.47}$$

where we used the subscripts t_1 and t_2 to indicate that the expressions in the square brackets are to be computed at the initial state (at $t = t_1$) and the final state (at $t = t_2$), respectively. The last term of (1.46) can be computed by noting that

$$\sum_{i=1}^{N} \nabla_i \phi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) \cdot \mathrm{d}\boldsymbol{r}_i = \sum_{i=1}^{N} \left(\frac{\partial \phi}{\partial x_i} \mathrm{d}x_i + \frac{\partial \phi}{\partial y_i} \mathrm{d}y_i + \frac{\partial \phi}{\partial z_i} \mathrm{d}z_i \right) = \mathrm{d}\phi \ , \tag{1.48}$$

where the last step follows from (B.16) generalized to a function of $3N$ variables. Thus,

$$\sum_{i=1}^{N} \int_{(t=t_1)}^{(t=t_2)} \nabla_i \phi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) \cdot \mathrm{d}\boldsymbol{r}_i = \int_{(t=t_1)}^{(t=t_2)} \mathrm{d}\phi = \phi_2(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) - \phi_1(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) \ , \tag{1.49}$$

where the subscripts 1 and 2 on ϕ refer to the initial and the final states, respectively. Combining everything, we arrive at

$$W = \Delta E \ , \tag{1.50}$$

where we defined the **mechanical energy** of the many-particle system by

$$E = \sum_{i=1}^{N} \left[\frac{1}{2} m_i {v_i}^2 + \psi(\boldsymbol{r}_i) \right] + \phi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) \ , \tag{1.51}$$

in which

$$\sum_{i=1}^{N} \frac{1}{2} m_i {v_i}^2 \tag{1.52}$$

is the **kinetic energy** of the many-particle system. If the system evolves under the influence of conservative forces (derivable from ψ and ϕ) *alone*, that is, if $\boldsymbol{F}_{\mathrm{ext},i} \equiv 0$ for all $i = 1, \ldots, N$, then its mechanical energy is a constant of motion.

1.4 Center of Mass

In dealing with a many-particle system, it is often convenient to work with its **center of mass**, which is defined by

$$\boldsymbol{R} := \frac{1}{M} \sum_{i=1}^{N} m_i \boldsymbol{r}_i \ , \tag{1.53}$$

where $M := \sum_{i=1}^{N} m_i$ is the total mass of the system.

Exercise 1.3. Consider a collection of N particles under gravity. If we take the coordinate system so that the z-axis points vertically upward, then

$$\psi(\boldsymbol{r}_i) = m_i g z_i \tag{1.54}$$

and (1.51) reduces to

$$E = \sum_{i=1}^{N} \left[\frac{1}{2} m_i {v_i}^2 + m_i g z_i \right] + \phi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) . \tag{1.55}$$

Show that this expression can be written as

$$E = \frac{1}{2} M V^2 + M g Z + \sum_i \frac{1}{2} m_i {v_i}'^2 + \phi({\boldsymbol{r}_1}', \ldots, {\boldsymbol{r}_N}') , \tag{1.56}$$

where $\boldsymbol{V} := \mathrm{d}\boldsymbol{R}/\mathrm{d}t$ is the velocity of the center of mass, $V := \|\boldsymbol{V}\|$, Z is the z-component of $\boldsymbol{R}$, ${\boldsymbol{r}_i}' := \boldsymbol{r}_i - \boldsymbol{R}$, and ${\boldsymbol{v}_i}' := \mathrm{d}{\boldsymbol{r}_i}'/\mathrm{d}t$ for $i = 1, \ldots, N$. You will need to use the fact that ϕ depends on the relative positions of particles, not on their absolute position in space. ///

The first two terms of (1.56) is the mechanical energy the collection of N particles would have if all the particles were concentrated at $\boldsymbol{R}$ to form a single material point of mass M. The remaining term is the mechanical energy of the N particles computed in a (generally noninertial) coordinate system whose origin is attached to $\boldsymbol{R}$.

1.5 Hamilton's Principle

Mechanical behavior of a many-particle system is determined completely by (1.42) and initial conditions. However, for a system consisting of 10^{24} particles or more, which are of our principal interest, the actual solution of the equations of motion is practically impossible to obtain. More importantly, the solution contains far more detailed information than we possibly need. For example, you probably will not send your soup back in a restaurant on the basis that you do not like the position of a particular molecule in it. Our primary concern in this case will be in a much less detailed description of the system, such as its temperature, volume, and composition. Thus, our goal must be to extract such information on a system of many particles without ever solving (1.42). Newton's formulation of mechanics is not particularly useful for developing such a scheme. For that, we have to reformulate classical mechanics first, which is the subject of this section and, in fact, the rest of the chapter.

1.5.1 Lagrangian and Action

We define a quantity called **Lagrangian** L by

$$L := \text{(Kinetic Energy)} - \text{(Potential Energy)} . \tag{1.57}$$

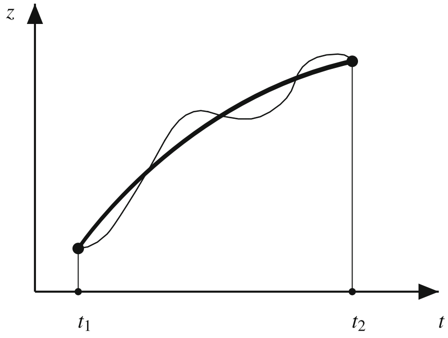

Fig. 1.6 The actual path $z(t)$ followed by the mechanical system (*thick curve*) and a varied path $z'(t) = z(t) + \delta z(t)$ (*thin wavy curve*). Note that $\delta z = 0$ at t_1 and t_2.

For example, the Lagrangian of a particle in a uniform gravitational field is given by

$$L = \frac{1}{2}m\dot{z}^2 - mgz\,, \tag{1.58}$$

where we took the z-axis vertically upward. We also introduced a short-hand notation $\dot{z} := \mathrm{d}z/\mathrm{d}t$ and assumed that the particle moves only in the z-direction. We see that, once z is known as a function of time t, we can find L as a function only of t. This function can then be integrated with respect to t over some interval of time $t_1 \le t \le t_2$, yielding the quantity called the **action integral** or action:

$$\mathscr{S}[z] := \int_{t_1}^{t_2} L(z,\dot{z})\mathrm{d}t\,. \tag{1.59}$$

The value of the action $\mathscr{S}$ depends on the form of the function $z(t)$. We express this dependence by means of the notation $\mathscr{S}[z]$.

Clearly, the value of $\mathscr{S}$ can be calculated not only for the actual path $z(t)$ followed by the mechanical system under consideration but also for any other path $z'(t)$, for which we obtain $\mathscr{S}[z']$. (z' is not to be confused with $\dot{z}$.) You might wonder if computation of $\mathscr{S}$ for any path other than the actual one serves any useful purpose at all. As we shall find out, however, such a computation leads to a useful and surprisingly simple (at least conceptually) way to characterize the actual path.

Now, let $z'(t) = z(t) + \delta z(t)$ so that $z'(t)$ differs only infinitesimally from the actual path $z(t)$ and calculate $\mathscr{S}[z+\delta z]$. (See Fig. 1.6.) **Hamilton's principle** states that, for any $\delta z(t)$,

$$\mathscr{S}[z+\delta z] - \mathscr{S}[z] = 0\,, \tag{1.60}$$

to the first order of $\delta z(t)$ *provided that*

$$z(t_1) = z'(t_1) \quad \text{and} \quad z(t_2) = z'(t_2)\,, \tag{1.61}$$

that is, the perturbed path $z'(t)$ coincides with the actual path $z(t)$ at the beginning and at the end of the time period over which we consider the time evolution of the system. This may be expressed as

$$\delta z(t_1) = \delta z(t_2) = 0\,. \tag{1.62}$$

The meaning of the phrase *to the first order of* δz is explained in Appendix B.1 and will be made clearer as we explore the consequence of Hamilton's principle.

First, we evaluate the difference

$$\mathscr{S}[z+\delta z] - \mathscr{S}[z] = \int_{t_1}^{t_2} \left[L\left(z+\delta z, \frac{\mathrm{d}}{\mathrm{d}t}(z+\delta z) \right) - L(z,\dot{z}) \right] \mathrm{d}t\,. \tag{1.63}$$

Recalling the definition of the short-hand notation we introduced earlier, we find

$$\frac{\mathrm{d}}{\mathrm{d}t}(z+\delta z) = \frac{\mathrm{d}z}{\mathrm{d}t} + \frac{\mathrm{d}}{\mathrm{d}t}(\delta z) = \dot{z} + \dot{\delta z}\,, \tag{1.64}$$

and hence

$$\mathscr{S}[z+\delta z] - \mathscr{S}[z] = \int_{t_1}^{t_2} \left[L(z+\delta z, \dot{z}+\dot{\delta z}) - L(z,\dot{z}) \right] \mathrm{d}t\,. \tag{1.65}$$

To extract the first-order term, we expand the integrand in the Taylor series:

$$L(z+\delta z, \dot{z}+\dot{\delta z}) - L(z,\dot{z}) = \frac{\partial L}{\partial z}\delta z + \frac{\partial L}{\partial \dot{z}}\dot{\delta z} + \text{h.o.}\,, \tag{1.66}$$

Bringing (1.66) into (1.65), we find

$$\mathscr{S}[z+\delta z] - \mathscr{S}[z] = \int_{t_1}^{t_2} \left(\frac{\partial L}{\partial z}\delta z + \frac{\partial L}{\partial \dot{z}}\dot{\delta z} \right) \mathrm{d}t + \text{h.o.} \tag{1.67}$$

The development up to this point might make you a bit uneasy. On the one hand, once the entire path $z(t)$ is specified, so is $\dot{z}(t) = \mathrm{d}z/\mathrm{d}t$. The same remark applies to the varied path as we have seen in (1.64). On the other hand, in (1.66), we considered the partial derivative of L with respect to z taken *while holding* $\dot{z}$ *constant.* Likewise for the partial derivative with respect to $\dot{z}$. That is, we are treating z and $\dot{z}$ as if they are independent. *Is this legitimate?* Given a function L that is expressed in terms of z and $\dot{z}$, this surely is a well-defined procedure mathematically, and there should be no doubt about the validity of (1.66), which is nothing but a Taylor series expansion. The real question, then is in what sense z and $\dot{z}$ can be regarded as independent. Why is L a function of both z and $\dot{z}$ and not a function of z alone? The reason is that, for a given value of z at any instant t, we can evidently assign different values to $\dot{z}$, thus obtaining various different mechanical states. In this sense, z and $\dot{z}$ at each instant are independent variables necessary to specify the mechanical state of the system at that instant. The Lagrangian is a function of the instantaneous mechanical state of the system, while the action depends on the entire path taken by the system between t_1 and t_2.

Applying the product rule of differentiation, we note that

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L}{\partial \dot{z}}\delta z\right) = \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L}{\partial \dot{z}}\right)\delta z + \frac{\partial L}{\partial \dot{z}}\delta\dot{z}\,. \tag{1.68}$$

Integrating both sides of the equation with respect to t, we find

$$\left[\frac{\partial L}{\partial \dot{z}}\delta z\right]_{t_1}^{t_2} = \int_{t_1}^{t_2}\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L}{\partial \dot{z}}\right)\delta z\mathrm{d}t + \int_{t_1}^{t_2}\frac{\partial L}{\partial \dot{z}}\delta\dot{z}\mathrm{d}t\,, \tag{1.69}$$

which is just an integration by parts of the integrand $(\partial L/\partial\dot{z})\delta\dot{z}$. The left-hand side of this equation is identically zero because of (1.62). Thus, we may rewrite (1.67) as

$$\mathscr{S}[z+\delta z] - \mathscr{S}[z] = \int_{t_1}^{t_2}\left[\frac{\partial L}{\partial z} - \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L}{\partial \dot{z}}\right)\right]\delta z\mathrm{d}t + \mathrm{h.o.} \tag{1.70}$$

By definition, the variation of $\mathscr{S}$ up to the first order of δz refers to the quantity

$$\delta\mathscr{S} := \int_{t_1}^{t_2}\left[\frac{\partial L}{\partial z} - \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L}{\partial \dot{z}}\right)\right]\delta z\mathrm{d}t\,. \tag{1.71}$$

Hamilton's principle demands that this expression vanish for *any* δz. Hence

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L}{\partial \dot{z}}\right) - \frac{\partial L}{\partial z} = 0 \quad \text{for all } t_1 \le t \le t_2\,. \tag{1.72}$$

That (1.72) is sufficient in order for (1.71) to vanish should be obvious. To see that (1.72) is also necessary, suppose that (1.72) did not hold at some instant t^*. This means that the left-hand side of (1.72) is either positive or negative at t^*. Suppose that it is negative. Then, the integrand occurring in (1.71) will be positive at t^*. *Provided that the integrand is a continuous function of* t, it remains positive over some interval containing t^*. Then, we could fine-tune δz over this interval and make (1.71) false. If we demand that $\delta\mathscr{S}$ vanish for *any* δz, nonzero value of the integrand in (1.71) cannot be allowed. Equation (1.72) is called **Lagrange's equation of motion**.

Exercise 1.4. Show that, for the Lagrangian given by (1.58), (1.72) reduces to Newton's equation of motion. ///

1.5.2 Generalized Coordinates

In deriving Lagrange's equation of motion, no use was made of the fact that z is one of the Cartesian coordinates. All what we required was that the configuration of the system can be specified by z and that L is a (twice) differentiable function of z and $\dot{z}$. Any such variable will do.

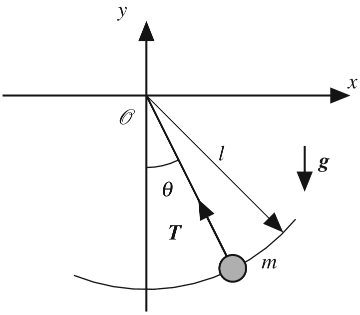

Fig. 1.7 A pendulum oscillating in the xy-plane. The length l of the rod is constant.

As an example, consider a simple pendulum in Fig. 1.7, which consists of a massless rigid rod of length l and a particle of mass m attached at the end of the rod. For simplicity, we assume that the particle is confined to the xy-plane. Once we specify θ, the coordinates (x,y) of the particle are completely determined:

$$x = l\sin\theta \quad \text{and} \quad y = -l\cos\theta \,. \tag{1.73}$$

Thus, we know the time evolution of the pendulum once we find θ as a function of t.

How do we find $\theta(t)$ then? If we can somehow express L as a function of θ and $\dot\theta$, we can use this $L(\theta,\dot\theta)$ in (1.59) to find the action:

$$\mathscr{S}[\theta] := \int_{t_1}^{t_2} L(\theta,\dot\theta)\mathrm{d}t \,. \tag{1.74}$$

But, this is just (1.59) with z replaced by θ. So, by demanding that $\delta\mathscr{S} = 0$ with respect to arbitrary perturbation $\delta\theta$, we should arrive at

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L}{\partial\dot\theta}\right) - \frac{\partial L}{\partial\theta} = 0 \,, \tag{1.75}$$

which is an equation for $\theta(t)$.

We observe that the *form* of Lagrange's equation of motion as given by (1.72) remains unchanged by going from the Cartesian coordinate system to any other coordinate system. It should be carefully noted, however, that the functional *form* of L and hence the resulting equation of motion, in which partial derivatives of L are carried out explicitly, do depend on the variable used.

Example 1.3. Simple two-dimensional pendulum: To derive the differential equation for $\theta(t)$ from (1.75) in the case of the simple pendulum, we need to find the expressions for the kinetic and the potential energies of the system first. From (1.73), we see that

$$\dot{x} = l\dot{\theta}\cos\theta \quad \text{and} \quad \dot{y} = l\dot{\theta}\sin\theta \ . \tag{1.76}$$

So, the kinetic energy of the particle is given by

$$\frac{1}{2}m\left(\dot{x}^2 + \dot{y}^2\right) = \frac{1}{2}ml^2\dot{\theta}^2 \ , \tag{1.77}$$

while the potential energy is

$$mgy = -mgl\cos\theta \ , \tag{1.78}$$

and hence

$$L = \frac{1}{2}ml^2\dot{\theta}^2 + mgl\cos\theta \ . \tag{1.79}$$

Taking the required partial derivatives, we find

$$\frac{\partial L}{\partial\dot{\theta}} = ml^2\dot{\theta} \quad \text{and} \quad \frac{\partial L}{\partial\theta} = -mgl\sin\theta \ . \tag{1.80}$$

Substituting these expressions in (1.75), we arrive at

$$ml^2\ddot{\theta} + mgl\sin\theta = 0 \ . \tag{1.81}$$

Thus,

$$\ddot{\theta} = -\frac{g}{l}\sin\theta \ . \tag{1.82}$$

When θ is small, $\sin\theta \approx \theta$ and hence

$$\ddot{\theta} = -\frac{g}{l}\theta \ , \tag{1.83}$$

which is the equation of motion of a harmonic oscillator with the general solution given by

$$\theta(t) = c_1\cos\omega t + c_2\sin\omega t \ , \tag{1.84}$$

where $\omega = \sqrt{g/l}$. Under the initial conditions that $\theta = \theta_0$ and $\dot{\theta} = 0$ at $t = 0$, we obtain $c_1 = \theta_0$ and $c_2 = 0$.

One advantage of formulating mechanics in terms of Lagrange's equation of motion rather than Newton's is based on the fact that the choice of coordinates is arbitrary as long as they can uniquely specify the configuration of the system. To see why this is a good thing, let us try to analyze the same problem using Newton's equation of motion.

Since the pendulum is confined to the xy-plane, we need the x- and y-components of the equation:

$$m\ddot{x} = -T\sin\theta \quad \text{and} \quad m\ddot{y} = T\cos\theta - mg\ , \tag{1.85}$$

the solution of which must satisfy the constraint that the length l of the pendulum does not change:

$$x^2 + y^2 = l^2 = \text{const.} \tag{1.86}$$

In (1.85), $T = \|\boldsymbol{T}\|$ is the length of the unknown force vector $\boldsymbol{T}$ required to enforce the constraint. Thus, $\boldsymbol{T}$ must be found as a part of the solution. In contrast, $\boldsymbol{T}$ simply does not arise in Lagrange's equation of motion, because the constraint was automatically taken care of by choosing θ as a single variable to specify the configuration of the system. That is, x and y given by (1.73) automatically satisfy (1.86).

It is also worth pointing out that, in Newtonian mechanics, we work directly with vectors such as force, position, and velocity. In contrast, we deal primarily with scalars, such as kinetic and potential energies and Lagrangian in Lagrangian mechanics. This often leads to a simpler treatment of the same problem.

A variable needed to specify the configuration of the system, such as θ, is called a **generalized coordinate**. We refer to its time derivative, $\dot{\theta}$ here, as a **generalized velocity**.

Exercise 1.5. Show that (1.85) reduces to (1.82). ///

1.5.3 Many Mechanical Degrees of Freedom

The number of generalized coordinates necessary to specify the configuration of a system is called the number of **mechanical degrees of freedom**. In the above example, it was one. A **mechanical state** of the system having f mechanical degrees of freedom is specified by f generalized coordinates, $q_1, \ldots, q_f$, and f generalized velocities, $\dot{q}_1, \ldots, \dot{q}_f$. Accordingly, L is a function of these $2f$ variables and the action is given by

$$\mathscr{S}[q_1,\ldots,q_f] = \int_{t_1}^{t_2} L(q_1,\ldots,q_f,\dot{q}_1,\ldots,\dot{q}_f,t)\mathrm{d}t\ , \tag{1.87}$$

where we also allowed for the possibility that L changes even if $q_1, \ldots, q_f$ and $\dot{q}_1, \ldots, \dot{q}_f$ remained constant. Such time dependence is said to be *explicit*. In contrast, the time dependence of L through its dependence on $q_1, \ldots, q_f$ and $\dot{q}_1, \ldots, \dot{q}_f$ is said to be *implicit*. The **explicit time dependence** arises if, for example, the external field such as an electric field varies with time either according to some prescription or stochastically but in a manner that is *independent* of the mechanical state of the system. We exclude a field that changes with time in a manner that depends on the state of the system. In this latter case, the field and the system taken together must be studied as a single mechanical system.

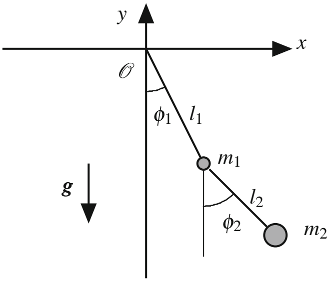

Fig. 1.8 A coplanar double pendulum oscillating in the xy-plane. Both l_1 and l_2 are constant.

The explicit time dependence of L does not play any role when considering the variations of $q_1, \dots, q_f$ at each instant of time between given t_1 and t_2 because the field is common to both actual and varied paths.

When applying the stationarity condition of $\mathscr{S}$, that is, $\delta\mathscr{S} = 0$, the variations of $q_1, \dots, q_f$ are entirely arbitrary except that the variations must vanish at $t = t_1$ and t_2. As one such variation, we may consider a variation, in which only δq_i is nonzero and $\delta q_j \equiv 0$ for $j \neq i$. Even for this rather special variation, Hamilton's principle demands that $\delta\mathscr{S} = 0$. This gives

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L}{\partial \dot{q}_i}\right) - \frac{\partial L}{\partial q_i} = 0\,. \tag{1.88}$$

Letting i vary from 1 to f, we arrive at

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L}{\partial \dot{q}_i}\right) - \frac{\partial L}{\partial q_i} = 0\,, \quad i = 1, \dots, f\,. \tag{1.89}$$

What we have shown is that (1.89) is necessary in order for $\delta\mathscr{S}$ to vanish with respect to arbitrary variations of $q_1, \dots, q_f$. Equation (1.89) is also sufficient for $\delta\mathscr{S} = 0$. (Take a moment to think about this.)

In arriving at (1.89), we made use of the fact that q_i's are all capable of independent variations. If the number of q_i's exceeds f, they are not independent. Thus, by demanding that $\delta q_j \equiv 0$ for $j \neq i$, we may be imposing a constraint on the possible values of δq_i. In this case, Hamilton's principle does not necessarily lead to (1.89).

Example 1.4. Coplanar double pendulum: Let us find a Lagrangian of a coplanar double pendulum placed in a uniform gravitational field as depicted in Fig. 1.8.

The configuration of the system is uniquely determined if we specify the position of the particles (x_1, y_1) and (x_2, y_2). In terms of these variables, we have

$$L = \frac{1}{2}m_1({\dot{x}_1}^2 + {\dot{y}_1}^2) - m_1 g y_1 + \frac{1}{2}m_2({\dot{x}_2}^2 + {\dot{y}_2}^2) - m_2 g y_2 \ . \tag{1.90}$$

However, since the particles are attached to the rods, x_1, y_1, x_2, and y_2 are not independent and we cannot derive Lagrange's equations of motion directly from the Lagrangian given by (1.90).

Instead, we note that x_1, y_1, x_2, and y_2 are completely determined by specifying two variables ϕ_1 and ϕ_2. In other words, the mechanical degrees of freedom of the system is two and we should be able to find two Lagrange's equations of motion from a Lagrangian expressed in terms of ϕ_1, ϕ_2, $\dot{\phi}_1$, and $\dot{\phi}_2$. From Fig. 1.8, we note the following relations:

$$\begin{aligned} x_1 &= l_1 \sin\phi_1 \ , \\ y_1 &= -l_1 \cos\phi_1 \ , \\ x_2 &= l_1 \sin\phi_1 + l_2 \sin\phi_2 \ , \\ y_2 &= -l_1 \cos\phi_1 - l_2 \cos\phi_2 \ . \end{aligned} \tag{1.91}$$

Taking the time derivative,

$$\begin{aligned} \dot{x}_1 &= l_1 \dot{\phi}_1 \cos\phi_1 \ , \\ \dot{y}_1 &= l_1 \dot{\phi}_1 \sin\phi_1 \ , \\ \dot{x}_2 &= l_1 \dot{\phi}_1 \cos\phi_1 + l_2 \dot{\phi}_2 \cos\phi_2 \ , \\ \dot{y}_2 &= l_1 \dot{\phi}_1 \sin\phi_1 + l_2 \dot{\phi}_2 \sin\phi_2 \ . \end{aligned} \tag{1.92}$$

Using these relations in (1.90), we find

$$\begin{aligned} L = {} & \frac{1}{2}(m_1 + m_2){l_1}^2{\dot{\phi}_1}^2 + \frac{1}{2}m_2{l_2}^2{\dot{\phi}_2}^2 + m_2 l_1 l_2 \dot{\phi}_1 \dot{\phi}_2 \cos(\phi_1 - \phi_2) \\ & + (m_1 + m_2) g l_1 \cos\phi_1 + m_2 g l_2 \cos\phi_2 \ , \end{aligned} \tag{1.93}$$

where we used the identity:

$$\cos(\alpha + \beta) = \cos\alpha \cos\beta - \sin\alpha \sin\beta \ . \tag{1.94}$$

This L can be used in (1.89) to find Lagrange's equations of motion for $\phi_1(t)$ and $\phi_2(t)$.

Exercise 1.6. Consider a pendulum consisting of a massless harmonic spring and a particle of mass m attached at the end of the spring as shown in Fig. 1.9. The spring constant and the natural length of the spring are k and l_0, respectively.

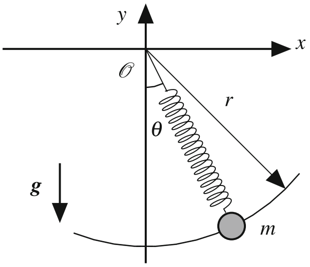

Fig. 1.9 A pendulum suspended by a harmonic spring.

a. Let $\boldsymbol{e}_r$ denote a unit vector pointing from the origin to the particle. Whether we are stretching the spring ($r > l_0$) or compressing it ($r < l_0$), the force exerted by the spring on the particle is given by

$$\boldsymbol{F} = -k(r - l_0)\boldsymbol{e}_r \,. \tag{1.95}$$

(Draw a diagram to convince yourself of this point.) Use this expression to show that the potential energy of the harmonic spring is given by

$$\psi(r) = \frac{1}{2}k(r - l_0)^2 \,. \tag{1.96}$$

b. Using θ and r as your generalized coordinates, find the Lagrangian of the system. You may assume that the motion of the spring and the particle is confined to the xy-plane. ///

Exercise 1.7. A system consists of two particles, one at $\boldsymbol{r}_1$ and the other at $\boldsymbol{r}_2$. They interact via a potential energy ϕ which depends only on their relative position $\boldsymbol{r} := \boldsymbol{r}_1 - \boldsymbol{r}_2$. Using the position vector $\boldsymbol{R}$ of the center of mass

$$\boldsymbol{R} = \frac{m_1\boldsymbol{r}_1 + m_2\boldsymbol{r}_2}{m_1 + m_2} \tag{1.97}$$

and $\boldsymbol{r}$ as your generalized coordinates, show that

$$L = \frac{1}{2}M\dot{R}^2 + \frac{1}{2}\mu\dot{r}^2 - \phi(\boldsymbol{r}) \,, \tag{1.98}$$

where $M := m_1 + m_2$, $\dot{R}^2 := \|\dot{\boldsymbol{R}}\|^2 = \dot{\boldsymbol{R}} \cdot \dot{\boldsymbol{R}}$, and likewise for $\dot{r}^2$. The quantity

$$\mu := \frac{m_1 m_2}{m_1 + m_2} \tag{1.99}$$

is the so-called **reduced mass**. Why is it more convenient to work with $\boldsymbol{R}$ and $\boldsymbol{r}$ than with $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$? ///

Given a mechanical system, its Lagrangian is determined only to an additive function $\mathrm{d}F/\mathrm{d}t$. In fact, if L_1 denotes a Lagrangian of a mechanical system with f degrees of freedom, the new function

$$L_2 := L_1 + \frac{\mathrm{d}F(q_1,\ldots,q_f,t)}{\mathrm{d}t} \tag{1.100}$$

also serves as a Lagrangian of the same system.

The validity of this claim is immediately obvious if we integrate (1.100) with respect to time. In fact, if

$$\mathscr{S}_i[q_1,\ldots,q_f] := \int_{t_1}^{t_2} L_i(q_1,\ldots,q_f,\dot{q}_1,\ldots,\dot{q}_f,t)\mathrm{d}t\ , \tag{1.101}$$

then

$$\begin{aligned}\mathscr{S}_2[q_1,\ldots,q_f] = \mathscr{S}_1[q_1,\ldots,q_f] + F(q_1(t_2),\ldots,q_f(t_2),t_2) \\ -F(q_1(t_1),\ldots,q_f(t_1),t_1)\ .\end{aligned} \tag{1.102}$$

Since $\delta q_i(t_1) = \delta q_i(t_2) = 0$ for all $i = 1, \ldots, f$, we see that $\delta\mathscr{S}_2 = \delta\mathscr{S}_1$. Thus, if $\delta\mathscr{S}_1 = 0$, then $\delta\mathscr{S}_2 = 0$ for *the same set of functions* $q_1(t), \ldots, q_f(t)$, which is then the solution of Lagrange's equations of motion whether they are derived from L_1 or L_2. Alternatively, you can validate the claim through a more explicit computation of various derivatives as illustrated in the next exercise.

Exercise 1.8. Use (1.100) to compute

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L_2}{\partial \dot{q}_i}\right) - \frac{\partial L_2}{\partial q_i}$$

and show that it is zero if and only if

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L_1}{\partial \dot{q}_i}\right) - \frac{\partial L_1}{\partial q_i} = 0\,.$$

This being the case for $i = 1, \ldots, f$, the same set of functions $q_1(t), \ldots, q_f(t)$ found by solving Lagrange's equations of motion obtained from L_1 also satisfies those derived from L_2. ///

1.6 Momentum and Energy: Definitions

The quantity

$$p_i := \frac{\partial L}{\partial \dot{q}_i} \tag{1.103}$$

is called the **generalized momentum** conjugate to the generalized coordinate q_i. When q_i is one of the Cartesian coordinates, then its conjugate momentum is called the **linear momentum**. Thus, the linear momentum of the ith particle in the system is given by

$$\boldsymbol{p}_i = \frac{\partial L}{\partial \dot{\boldsymbol{r}}_i} = \frac{\partial L}{\partial \boldsymbol{v}_i} \,. \tag{1.104}$$

We recall from Sect. 1.2.3 that this is just a compact way of writing

$$p_x = \frac{\partial L}{\partial v_x} \,, \quad p_y = \frac{\partial L}{\partial v_y} \,, \quad \text{and} \quad p_z = \frac{\partial L}{\partial v_z} \,, \tag{1.105}$$

where we omitted the subscript i for brevity. We define the **energy function**

$$h := \sum_{i=1}^{f} \frac{\partial L}{\partial \dot{q}_i} \dot{q}_i - L \,. \tag{1.106}$$

As seen in the following example, h is often equal to the mechanical energy, that is, the sum of the kinetic and the potential energies.

Example 1.5. Energy function of a particle: Consider a particle of mass m moving in an external field ψ. Using a Cartesian coordinate system, we have

$$L = \frac{1}{2} m v^2 - \psi(\boldsymbol{r}) \,. \tag{1.107}$$

From (1.104),

$$\boldsymbol{p} = \frac{\partial L}{\partial \boldsymbol{v}} = m\boldsymbol{v} \,. \tag{1.108}$$

According to (1.106),

$$h = \boldsymbol{p} \cdot \boldsymbol{v} - L = m v^2 - \frac{1}{2} m v^2 + \psi(\boldsymbol{r}) = \frac{1}{2} m v^2 + \psi(\boldsymbol{r}) \,. \tag{1.109}$$

At least in this example, therefore, the energy function h is nothing but the mechanical energy defined by (1.40).

If you prefer, you can work directly with the components of various vectors. Thus, we start by writing (1.107) as

$$L = \frac{1}{2} m \left({v_x}^2 + {v_y}^2 + {v_z}^2 \right) - \psi(\boldsymbol{r}) \,. \tag{1.110}$$

From (1.105),

$$p_x = \frac{\partial L}{\partial v_x} = m v_x \,, \quad p_y = \frac{\partial L}{\partial v_y} = m v_y \,, \quad \text{and} \quad p_z = \frac{\partial L}{\partial v_z} = m v_z \,, \tag{1.111}$$

which is just (1.108). According to (1.106),

$$\begin{aligned} h &= (p_x v_x + p_y v_y + p_z v_z) - L \\ &= m{v_x}^2 + m{v_y}^2 + m{v_z}^2 - \frac{1}{2}m\left({v_x}^2 + {v_y}^2 + {v_z}^2\right) + \psi(\boldsymbol{r}) \\ &= \frac{1}{2}m\left({v_x}^2 + {v_y}^2 + {v_z}^2\right) + \psi(\boldsymbol{r})\,. \end{aligned} \tag{1.112}$$

So, is h always equal to E? Disappointingly, the answer is no. As an example, consider the following exercise.

Exercise 1.9. For L_1 and L_2 in (1.100), show that

$$h_2 = h_1 - \frac{\partial F}{\partial t}\,. \tag{1.113}$$

That is, if $h_1 = E$, then $h_2 \neq E$ unless $\partial F/\partial t \equiv 0$. ///

In the next section, marked with a dagger (†) for an optional reading, we examine the condition under which $h = E$. The conclusion is that, for a broad range of applications of classical mechanics we are going to encounter, $h = E$ holds. Thus, unless stated otherwise, we shall assume this equality and speak only of the energy E.

To conclude this section, let us deduce one immediate consequence of (1.106). We consider two mechanical systems, A and B, and suppose that they are sufficiently far away from each other that they evolve independently. However, there is nothing in principle that prevents us from treating them as a single composite system. It is clear that Lagrange's equations of motion for the composite system can be derived from the Lagrangian $L := L_a + L_b$, in which L_a depends only on q_i's and $\dot{q}_i$'s pertaining to system A and does not depend on those pertaining to system B. Similarly for L_b. This means that Lagrangian is an additive quantity. From (1.106), it follows that energy also is an additive quantity.

1.7 †Energy Function and Energy

Consider a collection of N particles subject to an external field ψ. Using a Cartesian coordinate system, we have

$$E = \sum_{i=1}^{N}\left[\frac{1}{2}m_i{v_i}^2 + \psi(\boldsymbol{r}_i, t)\right] + \phi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)\,, \tag{1.114}$$

where we allowed for the explicit time dependence of ψ. As in Exercise 1.3, ϕ is the potential energy due to the mutual interaction among particles.

Suppose that we introduced a set of generalized coordinates $q_1,\dots,q_f$ that are related to $\boldsymbol{r}_1, \dots, \boldsymbol{r}_N$ by the following set of equations:

$$\boldsymbol{r}_i = \boldsymbol{r}_i(q_1,\dots,q_f,t)\ , \quad i = 1,\dots,N\ . \tag{1.115}$$

If there is no constraint on $\boldsymbol{r}_i$'s, then $f = DN$, where D is the dimensionality of the space in which the particles move. Otherwise, $f < DN$. In (1.73), for example, $f = 1$, $D = 2$, and $N = 1$. Following the approach we took in Example 1.3, we proceed to express L in terms of q_i's and $\dot{q}_i$'s. First, we note that

$$\boldsymbol{v}_i = \frac{\mathrm{d}\boldsymbol{r}_i}{\mathrm{d}t} = \sum_{j=1}^{f} \frac{\partial \boldsymbol{r}_i}{\partial q_j}\dot{q}_j + \frac{\partial \boldsymbol{r}_i}{\partial t}\ . \tag{1.116}$$

Thus,

$$v_i{}^2 = \boldsymbol{v}_i \cdot \boldsymbol{v}_i = \sum_{j=1}^{f}\sum_{k=1}^{f} A_i^{jk}\dot{q}_j\dot{q}_k + 2\sum_{j=1}^{f} B_i^j \dot{q}_j + C_i\ , \tag{1.117}$$

where we defined

$$A_i^{jk} := \frac{\partial \boldsymbol{r}_i}{\partial q_j}\cdot\frac{\partial \boldsymbol{r}_i}{\partial q_k}\ , \quad B_i^j := \frac{\partial \boldsymbol{r}_i}{\partial q_j}\cdot\frac{\partial \boldsymbol{r}_i}{\partial t}\ , \quad \text{and} \quad C_i := \frac{\partial \boldsymbol{r}_i}{\partial t}\cdot\frac{\partial \boldsymbol{r}_i}{\partial t}\ . \tag{1.118}$$

Using (1.117), we see that the kinetic energy of the system is given by

$$\frac{1}{2}\sum_{i=1}^{N} m_i v_i{}^2 = \frac{1}{2}\sum_{i=1}^{N} m_i \left[\sum_{j=1}^{f}\sum_{k=1}^{f} A_i^{jk}\dot{q}_j\dot{q}_k + 2\sum_{j=1}^{f} B_i^j\dot{q}_j + C_i\right]\ . \tag{1.119}$$

Because of (1.115), $\boldsymbol{r}_i$'s in ψ and ϕ are now functions of $q_1,\dots,q_f$ and t. Thus, the total potential energy may be written as

$$\sum_{i=1}^{N} \psi(\boldsymbol{r}_i,t) + \phi(\boldsymbol{r}_1,\dots,\boldsymbol{r}_N) =: U(q_1,\dots,q_f,t)\ . \tag{1.120}$$

So, the Lagrangian, when expressed in terms of $q_1,\dots,q_f$ is

$$L = \frac{1}{2}\sum_{i=1}^{N} m_i \left[\sum_{j=1}^{f}\sum_{k=1}^{f} A_i^{jk}\dot{q}_j\dot{q}_k + 2\sum_{j=1}^{f} B_i^j\dot{q}_j + C_i\right] - U(q_1,\dots,q_f,t)\ . \tag{1.121}$$

It follows that

$$\frac{\partial L}{\partial \dot{q}_n} = \sum_{i=1}^{N} m_i \left[\sum_{j=1}^{f} A_i^{jn}\dot{q}_j + B_i^n\right]\ , \tag{1.122}$$

where we used the fact that $A_i^{jk} = A_i^{kj}$. (Take a moment to convince yourself of (1.122). You can set $N = 1$ and $f = 2$, for example, and compute $\partial L/\partial \dot{q}_1$ explicitly. This should give you some idea about the essential steps involved.) Using (1.106), we arrive at

$$h = \sum_{n=1}^{f} \frac{\partial L}{\partial \dot{q}_n} \dot{q}_n - L = \sum_{i=1}^{N} m_i \left[\sum_{j=1}^{f} \sum_{n=1}^{f} A_i^{jn} \dot{q}_j \dot{q}_n + \sum_{n=1}^{f} B_i^n \dot{q}_n \right] - L$$

$$= \frac{1}{2} \sum_{i=1}^{N} m_i \left[\sum_{j=1}^{f} \sum_{k=1}^{f} A_i^{jk} \dot{q}_j \dot{q}_k - C_i \right] + U(q_1, \dots, q_f, t) \,. \tag{1.123}$$

But, according to (1.119) and (1.120), the total mechanical energy of the system is

$$E = \frac{1}{2} \sum_{i=1}^{N} m_i \left[\sum_{j=1}^{f} \sum_{k=1}^{f} A_i^{jk} \dot{q}_j \dot{q}_k + 2 \sum_{j=1}^{f} B_i^j \dot{q}_j + C_i \right] + U(q_1, \dots, q_f, t) \,. \tag{1.124}$$

Evidently, *if* $B_i^j \equiv 0$ and $C_i \equiv 0$ for all $i = 1, \dots, N$, then $h = E$. In view of (1.118), this implies that $\boldsymbol{r}_i$'s do not depend *explicitly* on t. So, if the relation between $\boldsymbol{r}_i$'s and q_i's is of the form of

$$\boldsymbol{r}_i = \boldsymbol{r}_i(q_1, \dots, q_f) \,, \quad i = 1, \dots, N \tag{1.125}$$

in place of (1.115), then the energy function coincides with the mechanical energy of the system.

1.8 Conservation Laws and Symmetry

As a mechanical system evolves according to the equations of motion, its generalized coordinates and velocities change. If we construct a function of these variables, its value will, in general, change with them. However, the value of a certain combination of the generalized coordinates and velocities may remain constant. Such a quantity is called a **constant of motion** or a **conserved quantity**. We have already encountered one such quantity, that is, energy, in Sects. 1.2.5 and 1.3.1. Constants of motions are of great interest since they allow us to extract certain information about the mechanical behavior of the system without actually solving the equations of motion.

In general, the Lagrangian of a mechanical system is a function of generalized coordinates and generalized velocities. It may also depend explicitly on time. In certain problems, however, it may so happen that L remains unchanged when these variables undergo certain changes. As we shall see below, this, in turn, points to an existence of some conserved quantity.

Let us start by looking at a somewhat trivial example. We suppose that L is independent of q_i. Then,

$$\frac{\partial L}{\partial q_i} \equiv 0 \,. \tag{1.126}$$

From Lagrange's equation of motion,

$$\frac{\mathrm{d}p_i}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L}{\partial \dot{q}_i}\right) = \frac{\partial L}{\partial q_i} \equiv 0 \,. \tag{1.127}$$

Thus, if L is independent of q_i, then, its conjugate momentum p_i is a constant of motion. Now you are ready to look at something a little more profound.

1.8.1 Conservation of Linear Momentum

Let us consider a mechanical system A consisting of N particles. In the absence of any constraint that reduces the mechanical degrees of freedom, its Lagrangian is given by

$$L^A = L(\boldsymbol{r}_1,\dots,\boldsymbol{r}_N,\dot{\boldsymbol{r}}_1,\dots,\dot{\boldsymbol{r}}_N,t) \,, \tag{1.128}$$

Given this system A, imagine that we created its *identical* copy B, and placed system B some distance away from system A. These systems are then related by a linear translation, say by $\Delta\boldsymbol{r}$. Thus, the position $\boldsymbol{r}_i'$ (with respect to the same origin as system A) of the ith particle in system B is given by

$$\boldsymbol{r}_i' = \boldsymbol{r}_i + \Delta\boldsymbol{r} \,, \quad i = 1,\dots,N \,. \tag{1.129}$$

By "identical copy," we also mean that

$$\dot{\boldsymbol{r}}_i' = \dot{\boldsymbol{r}}_i \,, \quad i = 1,\dots,N \,, \tag{1.130}$$

that is, $\dot{\boldsymbol{r}}_i$'s remain unaffected by the linear translation. Now the question is this: What is the relationship between the Lagrangians L^A and L^B of these two systems? Here, it should be clearly noted that the comparison is between L^A when system A alone is present and L^B when system B alone is present. Thus, there is no interaction between A and B.

Since these two systems are identical in all respect except for its position in space, we have no reason to evaluate L^B any differently from L^A. That is, we use the same function L to evaluate L^A and L^B, the only difference being in the values assumed by its arguments:

$$L^B = L(\boldsymbol{r}_1 + \Delta\boldsymbol{r},\dots,\boldsymbol{r}_N + \Delta\boldsymbol{r},\dot{\boldsymbol{r}}_1,\dots,\dot{\boldsymbol{r}}_N,t) \,. \tag{1.131}$$

If these two systems are far a way from any source of external field, there will be nothing that can distinguish the region occupied by system A and that by system B. This is referred to as the **homogeneity of space**. Less formally, one may say that "here" is as good as any other place. Therefore, we should expect that $L^B = L^A$. That is, the value of L remains unaffected by a linear translation by $\Delta\boldsymbol{r}$. Such an L is said to be *translationally invariant*.

As an example, we recall the system considered in Sect. 1.3.1, which has a translationally invariant L if $\psi \equiv 0$, that is, in the absence of an external field. Clearly, ψ remains zero even after a displacement by $\boldsymbol{\Delta r}$ of the mechanical system. The kinetic energy of the system depends only on mass and velocity of each particle. So, it remains unaffected as well. Likewise for the potential energy ϕ due to interaction among particles, which depends only on their relative position. Thus, $L^A = L^B$.

We now explore the consequence of the translational invariance of L. It is sufficient to restrict ourselves to an infinitesimal translation and replace $\boldsymbol{\Delta r}$ by $\boldsymbol{\delta r}$. From (1.128) and (1.131), we find

$$L^B - L^A = \sum_{i=1}^{N} \left(\frac{\partial L}{\partial \boldsymbol{r}_i} \cdot \boldsymbol{\delta r} \right) + \text{h.o.}, \tag{1.132}$$

where we recall that

$$\frac{\partial L}{\partial \boldsymbol{r}_i} \doteq \left(\frac{\partial L}{\partial x_i}, \frac{\partial L}{\partial y_i}, \frac{\partial L}{\partial z_i} \right) \quad \text{and} \quad \boldsymbol{\delta r} \doteq (\delta x, \delta y, \delta z)\,, \tag{1.133}$$

and hence

$$\frac{\partial L}{\partial \boldsymbol{r}_i} \cdot \boldsymbol{\delta r} = \frac{\partial L}{\partial x_i}\delta x + \frac{\partial L}{\partial y_i}\delta y + \frac{\partial L}{\partial z_i}\delta z\,. \tag{1.134}$$

From Lagrange's equations of motion and (1.104), we have

$$\frac{\partial L}{\partial \boldsymbol{r}_i} = \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L}{\partial \dot{\boldsymbol{r}}_i} \right) = \frac{\mathrm{d}\boldsymbol{p}_i}{\mathrm{d}t}\,. \tag{1.135}$$

Thus, the first-order term of (1.132), which we denote by δL, is given by

$$\delta L := \sum_{i=1}^{N} \left(\frac{\mathrm{d}\boldsymbol{p}_i}{\mathrm{d}t} \cdot \boldsymbol{\delta r} \right) = \boldsymbol{\delta r} \cdot \sum_{i=1}^{N} \frac{\mathrm{d}\boldsymbol{p}_i}{\mathrm{d}t} = \boldsymbol{\delta r} \cdot \frac{\mathrm{d}}{\mathrm{d}t}\left(\sum_{i=1}^{N} \boldsymbol{p}_i \right)\,, \tag{1.136}$$

where we pulled $\boldsymbol{\delta r}$ out of the summation since it is common to all particles and hence is independent of i.

If L is translationally invariant, δL must be identically zero for *any* $\boldsymbol{\delta r}$, from which we deduce

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\sum_{i=1}^{N} \boldsymbol{p}_i \right) \equiv \boldsymbol{0}\,. \tag{1.137}$$

It follows that the **total linear momentum** defined by

$$\boldsymbol{P} := \sum_{i=1}^{N} \boldsymbol{p}_i \tag{1.138}$$

is a constant of motion. In this way, the conservation of the total linear momentum is seen to be a consequence of the translational invariance of L, and hence of the homogeneity of space.

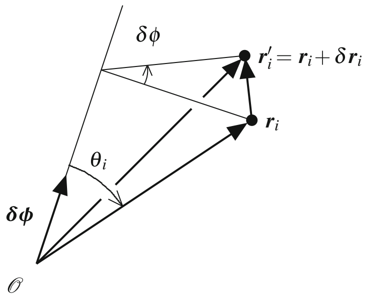

Fig. 1.10 Change in $\boldsymbol{r}_i$ upon rotation.

It may be that L is invariant with respect to translation in a direction parallel to the xy-plane, but not in the z-direction. This will be the case, for example, for a mechanical system moving in a uniform gravitational field if the z-axis is chosen to align with the gravitational acceleration $\boldsymbol{g}$. By considering the displacement $\boldsymbol{\delta r}$ that is parallel to the xy-plane, we observe that the x- and y- components of $\boldsymbol{P}$ are still constants of motion in this case. The z-component, however, is not. You can easily confirm this by allowing an object to free fall toward the floor: P_z of the object will continue to change with time.

1.8.2 ‡Conservation of Angular Momentum

Suppose that system B is related to system A by an infinitesimal rotation around some axis by $\delta\phi$. Again we expect that $L^A = L^B$. This is a consequence of the **isotropy of space**, that is, all directions in space are equivalent.

We need to relate $\boldsymbol{r}_i$'s and $\dot{\boldsymbol{r}}_i$'s of system B to those of system A. From Fig. 1.10, we see that

$$\|\delta\boldsymbol{r}_i\| = r_i \sin\theta_i \delta\phi \ , \tag{1.139}$$

where θ_i is the angle between the axis of rotation and $\boldsymbol{r}_i$. Let us denote by $\boldsymbol{\delta\phi}$ the vector of length $\delta\phi$ that points toward the direction a right-hand screw advances upon rotation by $\delta\phi$. Note that $\boldsymbol{\delta\phi}$ is *not* a variation of some vector $\boldsymbol{\phi}$. Rather, it is a vector of infinitesimal length $\|\boldsymbol{\delta\phi}\|$, where the "length" is an angle measured in radian in this case. Since $\delta\boldsymbol{r}_i$ is perpendicular to the plane including $\boldsymbol{r}_i$ and $\boldsymbol{\delta\phi}$, we see that $\delta\boldsymbol{r}_i$ is parallel to the vector $\boldsymbol{\delta\phi} \times \boldsymbol{r}_i$, where "×" denotes the cross product of two vectors. (See Appendix A.6 for a brief review.) Combining this observation with (1.139), we arrive at

$$\delta\boldsymbol{r}_i = \boldsymbol{\delta\phi} \times \boldsymbol{r}_i \ , \tag{1.140}$$

The same argument applies for $\dot{\boldsymbol{r}}_i$ as well, leading to

$$\delta\dot{\boldsymbol{r}}_i = \boldsymbol{\delta\phi} \times \dot{\boldsymbol{r}}_i \ . \tag{1.141}$$

Thus, to the first order of $\delta\phi$, $L^B - L^A$ is given by

$$\delta L = \sum_{i=1}^{N} \left[\frac{\partial L}{\partial \boldsymbol{r}_i} \cdot \delta \boldsymbol{r}_i + \frac{\partial L}{\partial \dot{\boldsymbol{r}}_i} \cdot \delta \dot{\boldsymbol{r}}_i \right] = \sum_{i=1}^{N} \left[\frac{\partial L}{\partial \boldsymbol{r}_i} \cdot \boldsymbol{\delta\phi} \times \boldsymbol{r}_i + \frac{\partial L}{\partial \dot{\boldsymbol{r}}_i} \cdot \boldsymbol{\delta\phi} \times \dot{\boldsymbol{r}}_i \right] . \tag{1.142}$$

Using (1.89) and (1.104),

$$\delta L = \sum_{i=1}^{N} \left[\frac{\mathrm{d}}{\mathrm{d}t} \left(\frac{\partial L}{\partial \dot{\boldsymbol{r}}_i} \right) \cdot \boldsymbol{\delta\phi} \times \boldsymbol{r}_i + \frac{\partial L}{\partial \dot{\boldsymbol{r}}_i} \cdot \boldsymbol{\delta\phi} \times \dot{\boldsymbol{r}}_i \right] = \sum_{i=1}^{N} \left(\dot{\boldsymbol{p}}_i \cdot \boldsymbol{\delta\phi} \times \boldsymbol{r}_i + \boldsymbol{p}_i \cdot \boldsymbol{\delta\phi} \times \dot{\boldsymbol{r}}_i \right) . \tag{1.143}$$

With the help of a vector identity (A.32), we may rewrite this as

$$\delta L = \boldsymbol{\delta\phi} \cdot \sum_{i=1}^{N} \left(\boldsymbol{r}_i \times \dot{\boldsymbol{p}}_i + \dot{\boldsymbol{r}}_i \times \boldsymbol{p}_i \right) = \boldsymbol{\delta\phi} \cdot \frac{\mathrm{d}}{\mathrm{d}t} \left(\sum_{i=1}^{N} \boldsymbol{r}_i \times \boldsymbol{p}_i \right) . \tag{1.144}$$

Since $\delta L \equiv 0$ for any $\boldsymbol{\delta\phi}$, we conclude that the **total angular momentum** defined by

$$\boldsymbol{M} := \sum_{i=1}^{N} \boldsymbol{r}_i \times \boldsymbol{p}_i \tag{1.145}$$

is a constant of motion. We see that the conservation of total angular momentum follows from the *rotational invariance* of L, and hence from the isotropy of space.

Exercise 1.10. Motion of a particle subject to a central field, that is, one in which the potential energy depends only on the distance from some particular point in space, is confined to a plane containing that point. Why? ///

1.8.3 Conservation of Energy

Returning now to a general mechanical system with f mechanical degrees of freedom, we suppose that its L does not depend *explicitly* on time:

$$L = L(q_1, \ldots, q_f, \dot{q}_1, \ldots, \dot{q}_f) . \tag{1.146}$$

Since q_i and $\dot{q}_i$ are functions of t, L still depends on t. But such a time dependence is said to be *implicit*. Using the chain rule,

$$\frac{\mathrm{d}L}{\mathrm{d}t} = \sum_{i=1}^{f} \frac{\partial L}{\partial q_i} \dot{q}_i + \sum_{i=1}^{f} \frac{\partial L}{\partial \dot{q}_i} \ddot{q}_i . \tag{1.147}$$

We can rewrite the first term on the right-hand side using Lagrange's equation of motion (1.89) and write

$$\frac{\mathrm{d}L}{\mathrm{d}t} = \sum_{i=1}^{f}\left[\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L}{\partial \dot{q}_i}\right)\dot{q}_i + \frac{\partial L}{\partial \dot{q}_i}\ddot{q}_i\right] = \sum_{i=1}^{f}\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L}{\partial \dot{q}_i}\dot{q}_i\right) , \tag{1.148}$$

from which we find

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\sum_{i=1}^{f}\frac{\partial L}{\partial \dot{q}_i}\dot{q}_i - L\right) = 0 . \tag{1.149}$$

Recalling (1.106) and our assumption that $h = E$, we see that the energy is a conserved quantity.

What will happen if we allowed for an *explicit* time dependence of L? This will be the case if there is a time-dependent external field. Carrying out the same analysis while retaining $\partial L/\partial t$, we observe that (1.149) is replaced by

$$\frac{\mathrm{d}E}{\mathrm{d}t} = -\frac{\partial L}{\partial t} . \tag{1.150}$$

Clearly, E is a constant of motion if and *only if* $\partial L/\partial t \equiv 0$.

Exercise 1.11. Derive (1.150). ///

The procedure we used to deduce the law of conservation of energy admits the following curious interpretation. Suppose you conducted a certain experiment today and plan on repeating the *identical* experiment tomorrow. Within mechanics, this means that you start the experiment from the identical initial conditions as specified by the generalized coordinates and velocities. You should naturally expect to find the identical outcome.[6] So, you have no reason to change the form of the function L between today (t^A) and tomorrow (t^B). You would also expect that its value remains the same for an identical mechanical state. In other words, each instant of time is equivalent to any other. This is referred to as the **homogeneity of time**. We demand, therefore, that the relation

$$L(q_1,\dots,q_f,\dot{q}_1,\dots,\dot{q}_f,t^A) = L(q_1,\dots,q_f,\dot{q}_1,\dots,\dot{q}_f,t^B) , \tag{1.151}$$

hold for *any* t^A and t^B. It follows that

$$\frac{\partial L}{\partial t} \equiv 0 . \tag{1.152}$$

Equation (1.150) then indicates that E is a constant of motion. Energy is a constant of motion because "now" is as good as any other instant of time.

One might argue that the outcome of the two experiments should be identical even if there is a time-dependent external field. But, this is so only if timing of the two experiments is properly chosen to make sure that they are in sync with the time-dependent external field in an identical manner. In other words, (1.151) holds only for properly chosen pairs of t^A and t^B. From this, we *cannot* deduce (1.152).

Example 1.6. Symmetry and constants of motion: Suppose that a system consisting of many particles moves in an external field generated by fixed sources uniformly distributed on an infinite plane, say, the xy-plane (on which $z = 0$). In this case, L is invariant with respect to (1) translation in t, (2) translation parallel to the xy-plane, and, if you read Sect. 1.8.2, (3) rotation around any axis perpendicular to the xy-plane. So, the energy, the x- and y-components of the linear momentum, and the z-component of the angular momentum are constants of motion.

If the source of the field is confined to $x > 0$, the system is invariant only with respect to (1) translation in t and (2) translation along the y-axis. So, constants of motion are the energy and the y-component of the linear momentum.

1.9 Hamilton's Equations of Motion

Lagrange's equations of motion are the relationships among the partial derivatives of L with respect to its independent variables $q_1, \ldots, q_f$ and $\dot{q}_1, \ldots, \dot{q}_f$. When supplemented with initial conditions, these equations of motion tell us how $q_1, \ldots, q_f$ and $\dot{q}_1, \ldots, \dot{q}_f$ evolve with time. Thus, we may say that the function L, *if* expressed in terms of $q_1, \ldots, q_f, \dot{q}_1, \ldots, \dot{q}_f$, and t, contains within it the mechanical behavior of the system in its entirety.

Suppose now that, for whatever reason, we wanted to describe mechanics of the system using $p_1, \ldots, p_f$ instead of $\dot{q}_1, \ldots, \dot{q}_f$ as our independent variables. This may require a new function to replace L. We would certainly want our new approach to be equally useful as the Lagrangian-based approach. We can ensure this by demanding that this new function *contains the same information as the Lagrangian.* In other words, we demand not only that we can construct this function from the Lagrangian, but also that we can recover the original Lagrangian from it. That way, even in the worst case scenario in which equations of motion cannot be derived *directly* from the new function, we can at least derive Lagrange's equations of motion by first finding the Lagrangian from our new function.

Our goal then is to replace $\dot{q}_i$ by $p_i = \partial L/\partial \dot{q}_i$ while preserving the information content of L. There is a mathematical procedure called **Legendre transformation** designed just for this purpose. A brief introduction to this method is given in Appendix C, in which we present the Legendre transformation of a function of a single variable. In contrast, we are now interested in replacing multiple variables, $\dot{q}_1, \ldots, \dot{q}_f$, by $p_1, \ldots, p_f$. In the next section, we show in detail how this can be accomplished by replacing one variable at a time, thus performing the Legendre transformation f times. Here, we take for granted that the transformation described in Appendix C generalizes naturally to the case of simultaneous replacement of multiple variables and proceed as follows:

Step 1: Given the Lagrangian

$$L(q_1,\dots,q_f,\dot{q}_1,\dots,\dot{q}_f,t)\ , \tag{1.153}$$

calculate p_i by (1.103) for $i = 1, \dots, f$, thus finding $p_1, \dots, p_f$ as functions of $q_1, \dots, q_f$ and $\dot{q}_1, \dots, \dot{q}_f$:

$$p_i = p_i(q_1,\dots,q_f,\dot{q}_1,\dots,\dot{q}_f)\ ,\ i = 1,\dots,f\ . \tag{1.154}$$

Step 2: Solve these f equations for $\dot{q}_1, \dots, \dot{q}_f$ to express them as functions of q_1, $\dots$, q_f and $p_1, \dots, p_f$:

$$\dot{q}_i = \dot{q}_i(q_1,\dots,q_f,p_1,\dots,p_f)\ ,\ i = 1,\dots,f\ . \tag{1.155}$$

Step 3: Express

$$H := \sum_{i=1}^{f} p_i\dot{q}_i - L \tag{1.156}$$

as a function of $q_1, \dots, q_f$ and $p_1, \dots, p_f$. This makes H the negative of the **Legendre transform** of L. The function

$$H(q_1,\dots,q_f,p_1,\dots,p_f,t) \tag{1.157}$$

is called the **Hamiltonian** of the system. From (1.103) and (1.106), we see that Hamiltonian is the energy (function) of the system expressed as a function of q_1, $\dots$, q_f and $p_1, \dots, p_f$.

By construction, L and H contain the same information. But, before we can accept the Hamiltonian as a useful concept, we must be able to derive from H the equations of motion that relate $q_1, \dots, q_f$ and $p_1, \dots, p_f$ to their time derivatives. From (1.156),

$$\mathrm{d}H = \sum_{i=1}^{f}(p_i\mathrm{d}\dot{q}_i + \dot{q}_i\mathrm{d}p_i) - \mathrm{d}L\ . \tag{1.158}$$

From (1.153),

$$\mathrm{d}L = \sum_{i=1}^{f}\left(\frac{\partial L}{\partial q_i}\mathrm{d}q_i + \frac{\partial L}{\partial \dot{q}_i}\mathrm{d}\dot{q}_i\right) + \frac{\partial L}{\partial t}\mathrm{d}t = \sum_{i=1}^{f}(\dot{p}_i\mathrm{d}q_i + p_i\mathrm{d}\dot{q}_i) + \frac{\partial L}{\partial t}\mathrm{d}t\ , \tag{1.159}$$

where we used (1.89) and (1.103). Combining (1.158) and (1.159)

$$\mathrm{d}H = \sum_{i=1}^{f}(-\dot{p}_i\mathrm{d}q_i + \dot{q}_i\mathrm{d}p_i) - \frac{\partial L}{\partial t}\mathrm{d}t\ . \tag{1.160}$$

On the other hand, (1.157) indicates that

$$\mathrm{d}H = \sum_{i=1}^{f} \left(\frac{\partial H}{\partial q_i} \mathrm{d}q_i + \frac{\partial H}{\partial p_i} \mathrm{d}p_i \right) + \frac{\partial H}{\partial t} \mathrm{d}t \ . \tag{1.161}$$

Comparing (1.160) and (1.161), we conclude that

$$\frac{\partial H}{\partial p_i} = \dot{q}_i \ , \quad \frac{\partial H}{\partial q_i} = -\dot{p}_i \ , \quad \text{and} \quad \frac{\partial H}{\partial t} = -\frac{\partial L}{\partial t} \ , \quad i = 1, \ldots, f \ . \tag{1.162}$$

The first two of these equations, expressing $\dot{q}_1, \ldots, \dot{q}_f$ and $\dot{p}_1, \ldots, \dot{p}_f$ in terms of $q_1, \ldots, q_f$, $p_1, \ldots, p_f$, and t are called **Hamilton's equations of motion**. The last equation is an identity relating the partial derivatives of H and L with respect to t but plays no role in determining the time evolution of $q_1, \ldots, q_f$ and $p_1, \ldots, p_f$.

Because $H = E$, it seems we have two symbols referring to the same quantity. We emphasize, however, that the Hamiltonian H refers to the energy of a mechanical system *expressed as a function of generalized coordinates* $q_1, \ldots, q_f$ *and their conjugate momenta* $p_1, \ldots, p_f$. In contrast, the energy expressed as a function of other variables is not a Hamiltonian. Such a function will be denoted by E. On occasion, we also use E to refer to the *value* of H when $q_1, \ldots, q_f$ and $p_1, \ldots, p_f$ assume certain values.

Example 1.7. Particle moving in a conservative field: Consider a particle of mass m moving in a conservative potential field $\psi(\boldsymbol{r})$ with velocity $\boldsymbol{v}$. The kinetic energy of the particle is given by

$$\frac{1}{2} m \boldsymbol{v} \cdot \boldsymbol{v} \ , \tag{1.163}$$

and hence

$$L = \frac{1}{2} m \boldsymbol{v} \cdot \boldsymbol{v} - \psi(\boldsymbol{r}) \ . \tag{1.164}$$

By definition, the momentum $\boldsymbol{p}$ that is conjugate to $\boldsymbol{v}$ is

$$\boldsymbol{p} = \frac{\partial L}{\partial \boldsymbol{v}} = m\boldsymbol{v} \ , \tag{1.165}$$

and hence

$$\boldsymbol{v} = \frac{\boldsymbol{p}}{m} \ . \tag{1.166}$$

The Hamiltonian is obtained as follows:

$$H = \boldsymbol{p} \cdot \boldsymbol{v} - L = \boldsymbol{p} \cdot \frac{\boldsymbol{p}}{m} - \frac{1}{2} m \frac{\boldsymbol{p}}{m} \cdot \frac{\boldsymbol{p}}{m} + \psi(\boldsymbol{r}) = \frac{\boldsymbol{p} \cdot \boldsymbol{p}}{2m} + \psi(\boldsymbol{r}) \ . \tag{1.167}$$

From Hamilton's equations of motion,

$$\dot{\boldsymbol{r}} = \frac{\partial H}{\partial \boldsymbol{p}} = \frac{\boldsymbol{p}}{m} \quad \text{and} \quad \dot{\boldsymbol{p}} = -\frac{\partial H}{\partial \boldsymbol{r}} = -\frac{\partial \psi}{\partial \boldsymbol{r}} \, . \tag{1.168}$$

Eliminating $\boldsymbol{p}$ from these two equations, we arrive at

$$m\ddot{\boldsymbol{r}} = -\frac{\partial \psi}{\partial \boldsymbol{r}} \, , \tag{1.169}$$

which is Newton's equation of motion of the particle.

Exercise 1.12. Translate the above example using components of the vectors involved. ///

Exercise 1.13. By taking the partial derivative of (1.156) with respect to t while holding q_1, …, q_f and p_1, …, p_f constant, directly establish the third equation in (1.162). ///

Exercise 1.14. We obtained (1.162) from (1.153), (1.156), (1.157), and Lagrange's equations of motion. Since Lagrangian and Hamiltonian are equivalent ways of encoding the mechanical behavior of the system, it should be possible to reverse this process. Combining (1.162) with (1.153), (1.156), and (1.157), derive Lagrange's equations of motion. ///

1.10 †Routhian

Given the Lagrangian as in (1.153), we have

$$p_1 = \frac{\partial L}{\partial \dot{q}_1} = p_1(q_1, \dots, q_f, \dot{q}_1, \dots, \dot{q}_f, t) \, , \tag{1.170}$$

which may be solved for $\dot{q}_1$ to yield

$$\dot{q}_1 = \dot{q}_1(q_1, \dots, q_f, p_1, \dot{q}_2, \dots, \dot{q}_f, t) \, . \tag{1.171}$$

Using this equation, we express a new function

$$R_1 := L - p_1 \dot{q}_1 \tag{1.172}$$

as a function of q_1, …, q_f, p_1, $\dot{q}_2$, …, $\dot{q}_f$, and t:

$$R_1 = R_1(q_1, \dots, q_f, p_1, \dot{q}_2, \dots, \dot{q}_f, t) \, . \tag{1.173}$$

A partial Legendre transformation, such as R_1, is called a **Routhian** and is an equally valid encoding of the mechanical behavior of the system as L and H.

Before we can proceed to the next round of Legendre transformation, in which we replace $\dot{q}_2$ by p_2, we need to evaluate $\partial R_1/\partial \dot{q}_2$. From (1.172), we see that

$$\begin{aligned} \mathrm{d}R_1 &= \mathrm{d}L - p_1 \mathrm{d}\dot{q}_1 - \dot{q}_1 \mathrm{d}p_1 \\ &= \sum_{i=1}^{f} \frac{\partial L}{\partial q_i}\mathrm{d}q_i + \sum_{i=1}^{f} \frac{\partial L}{\partial \dot{q}_i}\mathrm{d}\dot{q}_i + \frac{\partial L}{\partial t}\mathrm{d}t - p_1 \mathrm{d}\dot{q}_1 - \dot{q}_1 \mathrm{d}p_1 \\ &= \sum_{i=1}^{f} \frac{\partial L}{\partial q_i}\mathrm{d}q_i + \sum_{i=2}^{f} \frac{\partial L}{\partial \dot{q}_i}\mathrm{d}\dot{q}_i + \frac{\partial L}{\partial t}\mathrm{d}t - \dot{q}_1 \mathrm{d}p_1 , \end{aligned} \tag{1.174}$$

where we used (1.103). It follows that

$$\frac{\partial R_1}{\partial \dot{q}_2} = \frac{\partial L}{\partial \dot{q}_2} = p_2 . \tag{1.175}$$

It is important to note that the partial derivative on the left is evaluated by holding $q_1, \dots, q_f, p_1, \dot{q}_3, \dots, \dot{q}_f$, and t constant. In contrast, that on the right is for constant $q_1, \dots, q_f, \dot{q}_1, \dot{q}_3, \dots, \dot{q}_f$, and t.

The left most expression of (1.175) gives p_2 as a function of $q_1, \dots, q_f, p_1, \dot{q}_2, \dots, \dot{q}_f$, and t. When this is solved for $\dot{q}_2$, we obtain

$$\dot{q}_2 = \dot{q}_2(q_1, \dots, q_f, p_1, p_2, \dot{q}_3, \dots, \dot{q}_f, t) . \tag{1.176}$$

Using this equation, we now express

$$R_2 := R_1 - p_2\dot{q}_2 = L - p_1\dot{q}_1 - p_2\dot{q}_2 \tag{1.177}$$

as a function of $q_1, \dots, q_f, p_1, p_2, \dot{q}_3, \dots, \dot{q}_f$, and t. The resulting function is another Routhian. Continuing in this way, we finally arrive at

$$R_f := L - \sum_{i=1}^{f} p_i\dot{q}_i = R_f(q_1, \dots, q_f, p_1, \dots, p_f, t) . \tag{1.178}$$

Now that all of $\dot{q}_1, \dots, \dot{q}_f$ are replaced by $p_1, \dots, p_f$, we do not refer to R_f as a Routhian. Instead, it is the negative of the Hamiltonian H.

Exercise 1.15. Derive the following set of equations of motion from the Routhian R_n:

$$\frac{\partial R_n}{\partial q_i} = \dot{p}_i , \quad \frac{\partial R_n}{\partial p_i} = -\dot{q}_i , \quad i = 1, \dots, n , \tag{1.179}$$

and

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial R_n}{\partial \dot{q}_i}\right) - \frac{\partial R_n}{\partial q_i} = 0 , \quad i = n+1, \dots, f . \tag{1.180}$$

///

Equations of motion derived from a Routhian find practical applications in an analysis of the stability of a steady motion.

1.11 Poisson Bracket

Quantities such as the energy and the total linear momentum of a system are called **dynamical variables**. More generally, we define a dynamical variable A as a function of the instantaneous state of the mechanical system, which is specified by q^f and p^f:

$$A(q^f, p^f, t) \,. \tag{1.181}$$

Here we allowed for an explicit time dependence of A. We also introduced a new notation in which q^f and p^f stand for $q_1, \ldots, q_f$ and $p_1, \ldots, p_f$, respectively. Note carefully the distinction between q^f and q_f. The former is the collective notation just introduced, while the latter refers to the fth generalized coordinate.

As the coordinates and momenta change in accordance with the laws of mechanics, the value of A will, in general, change as well. It is straightforward to find the expression for the time rate of change of A. Differentiating (1.181) with respect to time, we find

$$\frac{\mathrm{d}A}{\mathrm{d}t} = \sum_{i=1}^{f} \left(\frac{\partial A}{\partial q_i} \dot{q}_i + \frac{\partial A}{\partial p_i} \dot{p}_i \right) + \frac{\partial A}{\partial t} \,. \tag{1.182}$$

Using Hamilton's equations of motion, we may rewrite the right-hand side as

$$\frac{\mathrm{d}A}{\mathrm{d}t} = \sum_{i=1}^{f} \left(\frac{\partial A}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial H}{\partial q_i} \frac{\partial A}{\partial p_i} \right) + \frac{\partial A}{\partial t} \,. \tag{1.183}$$

We introduce the **Poisson bracket** of two dynamical variables A and B, which is defined by

$$\{A, B\} := \sum_{i=1}^{f} \left(\frac{\partial A}{\partial q_i} \frac{\partial B}{\partial p_i} - \frac{\partial B}{\partial q_i} \frac{\partial A}{\partial p_i} \right) , \tag{1.184}$$

and write (1.183) more compactly as

$$\frac{\mathrm{d}A}{\mathrm{d}t} = \{A, H\} + \frac{\partial A}{\partial t} \,. \tag{1.185}$$

By definition, A is a **constant of motion** if $\mathrm{d}A/\mathrm{d}t \equiv 0$. It should be noted that the definition does *not* demand $\partial A/\partial t$ to be zero. Thus, a dynamical variable can be a constant of motion even if it has an explicit time dependence. The Hamiltonian is an exception to this rule. In fact, if we set $A = H$ in (1.185),

$$\frac{\mathrm{d}H}{\mathrm{d}t} = \{H, H\} + \frac{\partial H}{\partial t} = \frac{\partial H}{\partial t} \,. \tag{1.186}$$

So, H is a constant of motion if and only if H does not depend explicitly on time.

As another example of dynamical variables, let us consider q_k. Using (1.185), we find

$$\dot{q}_k = \{q_k, H\} + \frac{\partial q_k}{\partial t} \,. \tag{1.187}$$

As in (1.183), the partial derivative with respect to t is taken while holding q^f and p^f constant. Thus, $\partial q_k/\partial t = 0$ and we obtain

$$\dot{q}_k = \{q_k, H\} . \tag{1.188}$$

Similarly, by setting $A = p_k$, we find

$$\dot{p}_k = \{p_k, H\} . \tag{1.189}$$

As seen in Exercise 1.16, (1.188) and (1.189) are nothing but Hamilton's equations of motion.

We note that, since q's and p's are independent variables, we have $\partial p_k/\partial q_i \equiv 0$ and $\partial q_k/\partial p_i \equiv 0$ regardless of the values of i and k. On the other hand, $\partial q_k/\partial q_i$ is unity if $i = k$ and zero if $i \neq k$, that is,

$$\frac{\partial q_k}{\partial q_i} = \delta_{ik} \quad \text{and} \quad \frac{\partial p_k}{\partial p_i} = \delta_{ik} , \tag{1.190}$$

where δ_{ik} is the **Kronecker delta**, which takes the value unity if $i = k$ and zero otherwise.

Exercise 1.16. Let A be a dynamical variable of a mechanical system with f degrees of freedom, that is, $A = A(q^f, p^f, t)$. Evaluate $\{q_j, A\}$ and $\{p_j, A\}$. Then, show that (1.188) and (1.189) are Hamilton's equations of motion. ///

Exercise 1.17. Using (1.190), show that

$$\{q_i, q_j\} = 0 , \quad \{q_i, p_j\} = \delta_{ij} , \quad \text{and} \quad \{p_i, p_j\} = 0 . \tag{1.191}$$

///

The Poisson bracket satisfies a number of identities:

$$\{A, A\} = 0 , \tag{1.192}$$

$$\{c, A\} = 0 , \tag{1.193}$$

$$\{A, B + C\} = \{A, B\} + \{A, C\} , \tag{1.194}$$

$$\{A, BC\} = B\{A, C\} + \{A, B\}C , \tag{1.195}$$

where c is a real number. Through a straightforward but lengthy computation, one can prove **Jacobi's identity**:

$$\{A, \{B, C\}\} + \{B, \{C, A\}\} + \{C, \{A, B\}\} = 0 . \tag{1.196}$$

With the help of this identity, we can show that, if A and B are constants of motion, then so is $\{A, B\}$. This is known as the **Poisson theorem**, which, on occasion, allows us to generate a new constant of motion from known constants of motion.

Exercise 1.18. Prove the Poisson theorem.

a. For simplicity, first assume that neither A nor B depends explicitly on time.
b. Generalize the theorem when A and B may depend explicitly on time. ///

Finally, there appears to be no general agreement on the sign of the Poisson bracket. For example, Ref. [3] defines it as

$$\{A, H\} = \sum_{i=1}^{f} \left(\frac{\partial A}{\partial p_i} \frac{\partial H}{\partial q_i} - \frac{\partial H}{\partial p_i} \frac{\partial A}{\partial q_i} \right) , \tag{1.197}$$

which has the opposite sign to what we defined.

1.12 Frequently Used Symbols

$A := B$, the symbol A is defined by the expression B.
$A =: B$, the expression A defines the symbol B.
$\boldsymbol{a} \doteq (a_x, a_y, a_z)$, the x-, y-, z-components of the vector $\boldsymbol{a}$ are a_x, a_y, and a_z, respectively.
$\|\boldsymbol{a}\|$, length of the vector $\boldsymbol{a}$.
$\mathrm{d}\phi$, the first order term of $\Delta\phi$.
$\Delta\phi$, change in ϕ including the higher order terms.

f , the number of mechanical degrees of freedom.
$\boldsymbol{g}$, gravitational acceleration.
h , energy function.
h.o. , higher order terms of Taylor series expansion, typically second order and higher.
m , mass of a particle.
p_i , generalized momentum conjugate to q_i.
p^f , collective notation for $p_1, \ldots, p_f$.
$\boldsymbol{p}_i$, linear momentum of the ith particle.
q_i , the ith generalized coordinate.
q^f , collective notation for $q_1, \ldots, q_f$.
$\boldsymbol{r}_i$, position vector of the ith particle.
t , time.
$\boldsymbol{v}_i$, velocity vector of the ith particle.

E , mechanical energy.
$\boldsymbol{F}$, force.
H , Hamiltonian.
L , Lagrangian.
M , total mass of a many-particle system.
$\boldsymbol{M}$, total angular momentum of a many-particle system.
$\boldsymbol{P}$, total linear momentum of a many-particle system.

R , Routhian.
$\boldsymbol{R}$, position of the center of mass.
$\boldsymbol{V}$, velocity of the center of mass.
W , work.

$\mathscr{S}$, action.

$\delta q(t)$, infinitesimal variation of some function $q(t)$ at time t.
δ_{ij} , Kronecker delta.
μ , reduced mass.
ϕ , potential energy due to interparticle interactions.
ψ , potential energy due to an external field.

References and Further Reading

1. Goldstein H (1980) Classical Mechanics, 2nd edn. Addison-Wesley, Reading, Massachusetts
   The book has much to recommend and it is in fact one of the standard references on classical mechanics. For a detailed discussion of what we saw in this chapter, see Chaps. 1, 2, and 8. For a discussion on the relation between the energy function and the mechanical energy, see pp. 60-61. The corresponding discussion regarding the Hamiltonian and the mechanical energy is in pp. 349-351. For Routhian and its application, see Sect. 8.3. Note that his Routhian is the negative of ours. Various properties of the Poisson bracket are given in Chap. 9.
2. Lanczos C (1986) The variational principles of mechanics. Dover, New York
   A very detailed, yet highly accessible and engaging, discussion of the variational principles including Hamilton's principle.
3. Landau L D, Lifshitz E M (1973) Mechanics, 3rd edn. Pergamon Press, New York
   A very short account on classical mechanics. The book is full of unusual insights, though not everything they say is immediately obvious. Their Poisson bracket is the negative of ours.
4. Tolman R C (1979) The principles of statistical mechanics. Dover, New York
   Chapter 2 gives a short review of classical mechanics including topics we have omitted.

Chapter 2
Thermodynamics

We know from experience that a macroscopic system behaves in a relatively simple manner. For example, when liquid water is heated under atmospheric pressure, it will boil at 100 °C. If the vapor so produced is cooled at the same pressure, it will condense at 100 °C. These statements hold true regardless of the initial conditions from which the body of water under consideration has evolved. This situation is in stark contrast to that in classical mechanics, in which initial conditions play a far more prominent role. In fact, our experience tells us that results of measurements we make of a macroscopic body are quite insensitive to the detailed microscopic state of the body. Thermodynamics is built on this empirical observation and systematically elucidates interconnections among these *insensitive observations*. In this chapter, we review the framework of thermodynamics before attempting to interpret it from the classical mechanical point of view in Chaps. 3 and 4.

2.1 The First Law of Thermodynamics

A macroscopic system, such as a glass of water, consists of many molecules. While behavior of molecules is subject to the laws of quantum mechanics rather than those of classical mechanics, the latter framework can still provide a useful approximation in many situations. On the basis of conservation of energy we saw in the previous chapter, we may conclude that the work W' done on the system, which is a collection of molecules in this case, is equal to the change ΔE in its total energy:

$$\Delta E = W' . \tag{2.1}$$

In writing this equation, it is assumed that the number of mechanical degrees of freedom remains fixed while the work is performed on the system. In thermodynamics, a system that does not exchange particles with the surroundings is called a **closed system** or a **body**. In contrast, an **open system** allows for particles to freely

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pass through its boundary, thereby changing its number of mechanical degrees of freedom. For a moment, we focus only on closed systems.

Our everyday experience tells us, however, that a change in the apparent state of the system can be brought about without exerting any work on it. For example, by immersing a piece of heated steel in a glass of cold water, we can cause the state of the water to change. It becomes warmer and, if the steel is sufficiently hot, the water may even start to boil. From this observation, we infer that its energy content has also changed. At the molecular scale, this may be understood as a result of kinetic energy being transferred from iron atoms to water molecules through collisions among them. The kinetic energy is also constantly redistributed within the piece of steel. It appears then that the process we are observing belongs to the realm of classical mechanics. While this is true aside from the abovementioned quantum nature of atomistic processes, a full description of the process from this mechanistic point of view demands that we be capable of knowing the position and velocity of each constituent particle in the system (a glass of water in this case) and in the surroundings (a block of steel) at some instant of time and that the equations of motion can be integrated from the initial conditions so determined. Even if this is somehow possible, it is not clear if the microscopic description we would obtain is particularly useful.

Thus, when we perform a macroscopic observation, which does not inquire into the molecular-level details of a process, we must acknowledge that there are two types of processes. Firstly, there are those processes for which the force and the resulting displacement can be identified at a macroscopic level. In this case, we can readily compute ΔE by means of (2.1). Then, there are other processes, such as those we have considered above, for which the relevant forces and displacements are detectable only at a microscopic level. In such a situation, we, as a macroscopic observer, cannot compute ΔE by means of (2.1).

It is then sensible to use separate notations and words referring to these two modes of affecting the energy content of the system. From this point on, we shall use the term **work** to mean the mode of energy transfer into a system in which the force and the resulting displacement are measurable at a macroscopic level. We use the symbol W to denote the work in this narrower sense of the word. The other mode of energy transfer is called **heat** and is denoted by the symbol Q. Thus, heat embraces all modes of energy transfer we cannot express in a form of a macroscopic force and the resulting macroscopic displacement. By means of the newly introduced quantities, (2.1) becomes

$$\Delta E = W + Q \,. \tag{2.2}$$

The principle of conservation of energy, when expressed in this form, is called the **first law of thermodynamics**.

Of course, (2.2) would not be very useful unless we can compute Q for a given process despite our inability to identify the relevant forces and displacements at the microscopic level. This question of quantifying Q will be taken up in the next section.

The state of a system defined in terms of the coordinates and momenta of all particles in the system is called the "microscopic state" or **microstate** of the system. In contrast, we use the phrase "macroscopic state," or **macrostate** for short, to refer to the state in which the system appears to us when making observations that are insensitive to the microscopic details. Thus, *the notion of heat arises when we describe the behavior of the system in terms of macrostates as opposed to microstates*.

In thermodynamics, we are primarily interested in the "internal state of the system" and not in its macroscopic motion in space or change in its position relative to an external field. Accordingly, the kinetic energy due to translational motion of the system as a whole and the potential energy due to an external field are subtracted off from E, and we focus only on what is left, which is called the **internal energy** of the system and is denoted by U.

If we consider a system enclosed by rigid walls that are fixed in space, the location of its center of mass fluctuates at a microscopic level as a result of interaction between the system and its surroundings. Because of this, the procedure just described is not well defined if applied within the context of microscopic description of the system. However, the change in the kinetic or the potential energy due to such fluctuation is generally too small to be detectable by *macroscopic measurements*. Within the accuracy of such measurements, the separation of E into U and the rest will be a well-defined procedure.

In Sect. 1.6, we saw that E is an additive quantity. Since both the kinetic and potential energies we are considering here are additive, U also is an **additive quantity**. For a homogeneous body, U is also an **extensive quantity**. That is, U is proportional to the size of the system. To see this, we may imagine dividing the homogeneous body into two equal parts. If each part is still macroscopic, the interaction between them makes a negligible contribution to U. By the additivity of the internal energy, U of the whole system is equal to twice the internal energy of one of the parts.

Provided that neither the heat nor the work affects the translational motion of the system as a whole or its position in the external field, we may rewrite (2.2) as

$$\Delta U = W + Q \,. \tag{2.3}$$

Given two macrostate A and B accessible to a system, there are many distinct ways of bringing it from one to the other. The amount of work W involved usually depends on exactly how the change is brought about. We express this fact by saying that W is path dependent. A path-dependent quantity is called a **path function**.

Based on the classical mechanical notion of energy, however, we expect that the energy of a system has a uniquely determined value for a given macrostate of the system. Such a quantity, the value of which is determined *only* by the macrostate in question, is called a **state function**. Consequently, the energy difference $\Delta U := U_b - U_a$ between the two states is path independent. According to (2.3), then Q must be a path function.

We note that the classical mechanical work W' is, as seen from (2.1), path independent. In defining W, we have focused only on macroscopic forces and macroscopic displacements and lost track of the processes occurring at the microscopic level. This is what makes W a path function.

We will often be concerned with infinitesimal changes, in which W and Q are infinitesimally small. Using $đW$ and $đQ$ to denote, respectively, the amount of work done on and heat added to the system, and replacing ΔU by $\mathrm{d}U$ to indicate that only the leading term of ΔU is retained, we write (2.3) as

$$\mathrm{d}U = đW + đQ \tag{2.4}$$

for an infinitesimal process. As with W and Q, and in contrast to $\mathrm{d}U$, both $đW$ and $đQ$ are path-dependent quantities. We use the notation $đ$ to emphasize this fact.

Typically, the work term for an infinitesimal change is given by

$$đW = -P\mathrm{d}V \ , \tag{2.5}$$

where P and V are the pressure and volume of the system, respectively. In Sect. 2.3, we examine how this expression arises and under what conditions.

2.2 Quantifying Heat

The notion of heat was introduced as a result of our inability to track the detailed mechanism of energy transfer at the microscopic level. Therefore, it is not clear if heat can be quantified at all. How do we compute Q if it is defined as everything that cannot be expressed as force times displacement?

For expediency, we accept the following statement: Using a purely classical mechanical device, it is always possible to change the state of a system between two distinct macrostates A and B.

In other words, at least one of the two changes, from A to B *or* from B to A, can always be realized. By a purely **classical mechanical device**, we imply our ability to track all of its generalized coordinates and momenta. As a result, the device does not exchange heat with the system, but it can exchange work with the system. This means that the difference in energy between any two states can be measured in terms of force and the displacement. For example, if the change from A to B is achievable, we have

$$U_b - U_a = W_{\mathrm{cm}} \ , \tag{2.6}$$

where W_{cm} is the work done on the system by the purely classical mechanical device. Having determined the energy difference, we can compute the heat Q received by the system during *any* process that brings the system from A to B. In fact, from (2.3),

$$Q = (U_b - U_a) - W = W_{\mathrm{cm}} - W \ , \tag{2.7}$$

where W is the work done on the system during the process that involves an exchange of heat.

2.3 ‡A Typical Expression for $đW$

Suppose that an external body exerts a force $\boldsymbol{t}\mathrm{d}A$ on the system through a surface element of area $\mathrm{d}A$ on the boundary of the system. Further, let $\mathrm{d}\boldsymbol{l}$ denote the infinitesimal displacement experienced by the surface element. The work done by the force $\boldsymbol{t}\mathrm{d}A$ is then $\mathrm{d}\boldsymbol{l}\cdot(\boldsymbol{t}\mathrm{d}A)$. Repeating this computation for each of the surface elements, into which the system boundary A is divided, and adding together the results, we arrive at the total work done on the system:

$$đW = \int_A \mathrm{d}\boldsymbol{l}\cdot(\boldsymbol{t}\mathrm{d}A)\,, \tag{2.8}$$

where the integral is over the boundary A. If a part of the boundary is held fixed, then $\mathrm{d}\boldsymbol{l} = \boldsymbol{0}$ for that part of the boundary.

The stress vector $\boldsymbol{t}$ is given in terms of the stress tensor $\hat{T}$ as

$$\boldsymbol{t} = \boldsymbol{n}\cdot\hat{T}\,, \tag{2.9}$$

where $\boldsymbol{n}$, called the outward unit normal, is a unit vector perpendicular to $\mathrm{d}A$ and pointing away from the system. By definition,

$$\hat{T} = -P\hat{I} + \hat{T}_v\,, \tag{2.10}$$

where $\hat{I}$ is the unit tensor and $\hat{T}_v$ is referred to as the extra (or viscous) stress tensor.

We recall that $\hat{T}_v$ for Newtonian fluids is proportional to the *rate* of deformation. (The explicit expression for $\hat{T}_v$ is of no importance in the present discussion. For further details, consult Ref. [5], for example.) The key observation here is that, if any imbalance of force at any point on the system boundary is infinitesimally small, then the boundary moves very slowly and $\hat{T}_v$ will be negligibly small. Thus,

$$\hat{T} = -P\hat{I}\,. \tag{2.11}$$

Since $\boldsymbol{a}\cdot\hat{I} = \boldsymbol{a}$ for any vector $\boldsymbol{a}$, we have

$$\boldsymbol{n}\cdot\hat{T} = \boldsymbol{n}\cdot(-P\hat{I}) = -P\boldsymbol{n}\cdot\hat{I} = -P\boldsymbol{n}\,. \tag{2.12}$$

So,

$$đW = \int_A \mathrm{d}\boldsymbol{l}\cdot(-P\boldsymbol{n})\mathrm{d}A\,. \tag{2.13}$$

If P is uniform over the boundary A of the system, this may be written as

$$đW = -P\int_A \mathrm{d}\boldsymbol{l}\cdot\boldsymbol{n}\mathrm{d}A\,. \tag{2.14}$$

But, as seen from Fig. 2.1, $\mathrm{d}\boldsymbol{l}\cdot\boldsymbol{n}\mathrm{d}A$ is the volume swept out by the surface element $\mathrm{d}A$ as it moves by $\mathrm{d}\boldsymbol{l}$. When this quantity is added together for all such surface elements, the end result is the net change in the volume of the system. In this way, we arrive at (2.5).

We note that solids can sustain nonzero $\hat{T}_v$ even if the boundary does not move at all. This is because, according to Hooke's law, which is an excellent approximation

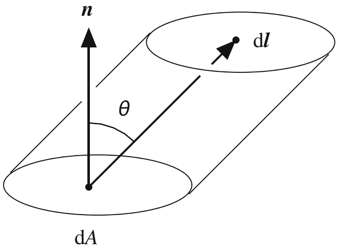

Fig. 2.1 The volume of the column swept out by the surface element dA as it moves by d$\boldsymbol{l}$ is given by $\mathrm{d}\boldsymbol{l}\cdot\boldsymbol{n}\mathrm{d}A = \mathrm{d}A\|\mathrm{d}\boldsymbol{l}\|\cos\theta$, in which $\boldsymbol{n}$ is the outward unit normal of dA and $\|\mathrm{d}\boldsymbol{l}\|\cos\theta$ is the height of the column.

for many solids as long as the deformation is sufficiently small, $\hat{T}_v$ in a solid is proportional *not* to the rate of deformation but to the size of deformation itself. We can still apply (2.5) to a solid under hydrostatic pressures, for which $\hat{T}_v \equiv 0$.

2.4 The Second Law of Thermodynamics

The content of the **second law of thermodynamics** is the following: There is a *state function* of a system called **entropy** S. The value of S can change as a result of both interactions with the surroundings and internal processes. Denoting the change associated with these processes by $đS_e$ and $đS_i$, respectively, we have

$$\mathrm{d}S = đS_e + đS_i \,. \tag{2.15}$$

For *closed* systems, $đS_e$ is given by

$$đS_e = \frac{đQ}{T} \tag{2.16}$$

where T is the **absolute temperature** and is a positive number. Thus, $đS_e$ can be positive, negative, or zero depending on the sign of $đQ$. A process for which $đQ \equiv 0$ is called an **adiabatic process**. In contrast,

$$đS_i \geq 0 \tag{2.17}$$

regardless of whether the system is closed or open. For processes occurring in a closed system, therefore, we have

$$\mathrm{d}S \geq \frac{đQ}{T} \,. \tag{2.18}$$

As shown more explicitly later in Example 2.1, the equality in (2.17) and (2.18) holds only for **reversible processes**. A process is called reversible if the sequence of states visited by the system can be traversed in an opposite direction by an infinitesimal change in the boundary conditions. As an example, we may think of a very slow expansion and compression of a gas enclosed in a thermally insulated cylinder fitted with a frictionless piston. The gas will expand if the external pressure is infinitesimally smaller than that of the gas. By an infinitesimal increase in the external pressure, the process can be reversed. Heat transfer due to an infinitesimal temperature difference is another example.

As is the case with the internal energy, entropy is an additive quantity. To see this, we may consider a composite system consisting of subsystems, each at its own uniform temperature. For each of them, we can assign a reference state at which its entropy is zero. Using a combination of reversible adiabatic processes and reversible heat transfer, we can bring a subsystem from its reference state to the actual state of interest and compute the change in its entropy by means of (2.18) with equality. The entire process in which this is done, one subsystem after another, may be regarded as a single process in which the composite system is brought to the state of interest from its reference state. As long as the interaction among subsystems can be ignored, the resulting change in entropy of the composite system is equal to the sum of the entropy change for each of the subsystems. **Additivity** of S, when applied to a homogeneous body implies that entropy of the body is proportional to its size. In other word, S is an **extensive quantity**. This property of S are in stark contrast with such quantities as T and P, which are independent of the size of the system and is said to be **intensive**.

As we shall see later, classification of thermodynamic quantities into extensive and intensive variables is of fundamental importance in thermodynamics. Without it, one cannot derive important equations such as the Euler relation and the Gibbs–Duhem relation. (See Sects. 2.10, 2.11, 6.4, and 6.5.)

We will be concerned primarily with the consequence of the second law and the properties of entropy as summarized above and will not inquire how the law can be established solely on the basis of macroscopic observations. An interested reader should consult Ref. [2].

2.5 Equilibrium of an Isolated System

When a system is isolated from the surroundings and thus left undisturbed, it eventually reaches a particularly simple state, in which no further change is observed in any *macroscopic* quantities we can measure of the system. This final state is called an **equilibrium state**. The second law of thermodynamics leads to a precise formulation of the condition of equilibrium of an isolated system in terms of entropy.

Since $đQ = 0$ for an isolated system, (2.18) reduces to

$$\mathrm{d}S \geq 0 \,. \tag{2.19}$$

That is, during a spontaneous internal process that brings the system eventually to a state of equilibrium, the entropy of the system does not decrease. At the same time, the internal energy of the system remains constant since $đW$ is also zero for an isolated system.

It seems unlikely that the entropy of a *finite* isolated system can increase indefinitely. Instead, we expect the entropy of the system to eventually reach the maximum possible value consistent with the given values of U, V, the total mass, and any other constraints that might be imposed on the system. Once the system reached this state of maximum entropy, any further change would require the entropy to decrease, which is impossible for an isolated system. Evidently, the same argument applies when S is only a local maximum. The entropy being (local) maximum is thus *sufficient* for an isolated system to be in equilibrium.

To establish its *necessity* for equilibrium, we may consider a system that is not at the state of maximum entropy under a given set of constraints. In this case, those processes that result in an increase of S are still possible while the processes in the opposite direction are not. Thus, we expect that the state of the system under consideration is not one of equilibrium.

In this way, we are led to accept the following formulation of the condition of equilibrium:

Condition of Equilibrium 1 *For the equilibrium of an isolated system, it is necessary and sufficient that the entropy of the system is (local) maximum under a set of constraints imposed on the system.*

For a more careful discussion aimed at establishing the necessity and the sufficiency of the condition, see pp. 58–61 of Ref. [3].

According to the second law, processes resulting in a decrease of the entropy are impossible for an isolated system. From a point of view of statistical mechanics, which provides a microscopic interpretation of the second law, this is not entirely accurate. In fact, the probability of finding the system with entropy S' which is less than the equilibrium value S is proportional to

$$e^{(S'-S)/k_B} , \tag{2.20}$$

where $k_B = 1.3806 \times 10^{-23}$ J/K is the **Boltzmann constant**. That the entropy of an isolated system can actually decrease by spontaneous fluctuation is directly responsible for the initial stage of the so-called first-order phase transition, the examples of which include freezing of a supercooled liquid, sudden boiling of superheated liquid, and condensation of supersaturated vapor. These phases of temporary existence, such as the supercooled liquid, superheated liquid, and supersaturated vapor, are said to be **metastable** and correspond to a *local* maximum of the entropy.

2.6 Fundamental Equations

The concept of fundamental equation is essential to thermodynamics. As we shall see, by merely accepting its existence and assuming that it meets some modest mathematical requirements, we can establish surprising interrelations among seemingly unrelated quantities almost effortlessly.

2.6.1 Closed System of Fixed Composition

For a moment, we restrict ourselves to reversible precesses occurring in a closed system. For simplicity, we also assume that there is no chemical reaction in the system so that the number of moles of species i, to be denoted by N_i, is constant for each species $(i = 1, \ldots, c)$. Under these conditions, we may rewrite (2.4) using (2.5) and (2.18) to obtain

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V\ . \tag{2.21}$$

As of now, we have accepted the validity of this equation only for reversible processes during which $N_1, \ldots, N_c$ of the system remain constant. We now argue that it applies to irreversible processes as well.

The key idea here is that, as long as we limit ourselves to an isolated system that is in *equilibrium* and *homogeneous*, its entropy S is a function only of U, V, and N_1, $\ldots$, N_c:

$$S = S(U, V, N_1, \ldots, N_c)\ . \tag{2.22}$$

This is so because the value of S, in the case of an isolated system in equilibrium, is determined by it being the maximum possible value for given values of U, V, and N_1, $\ldots$, N_c. Equation (2.22) is an example of **fundamental equations** of the system.

The restriction on homogeneity stems from our use of (2.5). In the case of an inhomogeneous system, there may be no single value of P. Thus, the work done on the system by an infinitesimal displacement of an infinitesimal portion of the system boundary depends on the position of this surface element. In order to specify the state of the system, then, one generally has to specify the shape of the system boundary, and not just its volume.

For the processes under consideration, N_1, $\ldots$, N_c are constant. Suppose now that we have changed the values of U and V by some infinitesimal amounts $\mathrm{d}U$ and $\mathrm{d}V$, respectively. The value of S in this new state is simply

$$S(U + \mathrm{d}U, V + \mathrm{d}V, N_1, \ldots, N_c)\ . \tag{2.23}$$

To the first order, therefore, the resulting change in S is given by

$$\mathrm{d}S = \left(\frac{\partial S}{\partial U}\right)_{V,N} \mathrm{d}U + \left(\frac{\partial S}{\partial V}\right)_{U,N} \mathrm{d}V\ , \tag{2.24}$$

where we used (B.16) and included N in the subscripts to remind us that the derivatives are taken while holding all of N_1, $\ldots$, N_c constant.

Note that (2.24) is obtained by applying (2.22) to the states before and after the infinitesimal change. Thus, so long as the system is in equilibrium and homogeneous both *before and after* the change and N_1, $\ldots$, N_c remain unaffected, (2.24) applies to *any* process including irreversible ones.

According to (2.21), however,

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}U + \frac{P}{T}\mathrm{d}V \tag{2.25}$$

for a reversible process. A comparison between (2.24) applied for a reversible process and (2.25) gives

$$\frac{1}{T}=\left(\frac{\partial S}{\partial U}\right)_{V,N} \quad \text{and} \quad \frac{P}{T}=\left(\frac{\partial S}{\partial V}\right)_{U,N} . \tag{2.26}$$

The differential coefficients on the right-hand side are obtained by comparing the values of S for infinitesimally different two equilibrium states. Since S is a state function, the partial derivatives depend only on the values of $\mathrm{d}U$ or $\mathrm{d}V$, but not on how these changes are brought about. Therefore, (2.26) holds regardless of the nature of the process.

Combining (2.24) and (2.26) and noting that neither depends on the process being reversible, we conclude that (2.25), and hence (2.21), hold for *any* infinitesimal change that is occurring in a closed system without affecting $N_1, \ldots, N_c$.

We emphasize that, given a pair of initial and final states, values of $đQ$ and $đW$ do depend on the actual path taken, since they are path functions. In particular, $đQ \neq T\mathrm{d}S$ and $đW \neq -P\mathrm{d}V$ for irreversible processes. Only the sum of these two, $\mathrm{d}U = đW + đQ$, is independent of the path and is given by (2.21). We illustrate these points with the following example.

Example 2.1. Gas in a cylinder: Let us consider a gas enclosed in a cylinder that is fitted with a frictionless piston. We suppose that the gas is initially in equilibrium and has a uniform temperature T and pressure P. Then, we induce a change in the state of the gas by changing the external pressure acting on the piston to P_e and by changing the wall temperature of the cylinder to T_a.

The gas will expand if $P_e < P$ while it will be compressed if $P_e > P$. In both cases, the work $đW$ done *on* the system by the surroundings is given by

$$đW = -P_e\mathrm{d}V = -P\mathrm{d}V + (P - P_e)\mathrm{d}V . \tag{2.27}$$

Since temperature varies continuously across interfaces, T_a is also the temperature of the gas in the immediate vicinity of the wall. According to (2.16), the heat $đQ$ received by the system during this process is

$$đQ = T_a\, đS_e , \tag{2.28}$$

which is positive if $T_a > T$ and negative if $T_a < T$.

Unless $P_e = P$ *and* $T_a = T$, the process will momentarily make the system inhomogeneous. Nevertheless, after the process has completed and the system is left alone for a while, it will reach a new state of equilibrium and the state function S, and hence $\mathrm{d}S$, will have definite values. Let us introduce this $\mathrm{d}S$ in our expression for $đQ$. Using (2.15),

$$đQ = T\, đS_e + (T_a - T)\, đS_e = T(\mathrm{d}S - đS_i) + (T_a - T)\, đS_e . \tag{2.29}$$

We observe that the values of $đW$ and $đQ$ cannot be determined solely by those of T, P, $\mathrm{d}V$, and $\mathrm{d}S$. This is expected: $đW$ and $đQ$ are path functions. What we saw in this section is that their sum, $đW + đQ$, is nevertheless completely determined by these and is given by

$$đW + đQ = \mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V \ . \tag{2.30}$$

It follows that

$$-P\mathrm{d}V + (P - P_e)\mathrm{d}V + T(\mathrm{d}S - đS_i) + (T_a - T)\,đS_e = T\mathrm{d}S - P\mathrm{d}V \ . \tag{2.31}$$

Thus,

$$T\,đS_i \equiv (T_a - T)\,đS_e + (P - P_e)\mathrm{d}V \ . \tag{2.32}$$

This result is entirely consistent with (2.17). If $T_a > T$, then $đS_e = đQ/T_a > 0$, while $đS_e < 0$ if $T_a < T$. Thus, the first term is positive unless $T = T_a$. Likewise, we see that the second term is positive unless $P = P_e$. The conclusion is that $đS_i = 0$ if and *only if* $T = T_a$ *and* $P_e = P$, that is, if and only if the process is reversible.

Finally, we note that (2.21) actually holds even when we allow for chemical reactions. This is to be expected since the equation is merely an expression of the first law of thermodynamics, that is, conservation of energy but applied to a system in equilibrium. An explicit demonstration, however, must wait until our formalism is fully developed. We shall visit this issue in Sect. 2.9.4.

2.6.2 Open System

Because an open system allows for particles of some of the species to freely pass through its boundary, some of $N_1, \ldots, N_c$ are no longer constant. Thus, the most general expression for $\mathrm{d}S$ is

$$\mathrm{d}S = \left(\frac{\partial S}{\partial U}\right)_{V,N} \mathrm{d}U + \left(\frac{\partial S}{\partial V}\right)_{U,N} \mathrm{d}V + \sum_{i=1}^{c} \left(\frac{\partial S}{\partial N_i}\right)_{U,V,N_{j\neq i}} \mathrm{d}N_i \ , \tag{2.33}$$

where the first two partial derivatives are given by (2.26). In the last partial derivative, U, V, and all of $N_1, \ldots, N_c$ except for N_i are held constant. Following the convention, we write

$$-\frac{\mu_i}{T} := \left(\frac{\partial S}{\partial N_i}\right)_{U,V,N_{j\neq i}} \tag{2.34}$$

and refer to μ_i as the **chemical potential** of species i. The quantity μ_i was first introduced by Gibbs, who referred to this quantity simply as potential. Combining

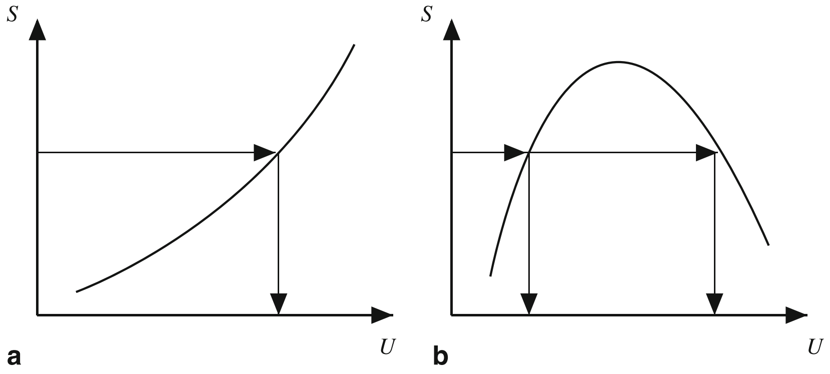

Fig. 2.2 The function $S = S(U)$, for some fixed values of $V, N_1, \dots, N_c$, can be inverted to give $U = U(S)$ since $1/T = (\partial S/\partial U)_{V,N} > 0$, and hence the function is monotonic as indicated in **a**. If $1/T$ changes its sign as in **b**, there may be multiple values of U for a given value of S and the function $S = S(U)$ cannot be inverted.

everything, we arrive at

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}U + \frac{P}{T}\mathrm{d}V - \sum_{i=1}^{c} \frac{\mu_i}{T}\mathrm{d}N_i \; , \tag{2.35}$$

which is often referred to as the **fundamental property relation** or the fundamental equation in differential form.

Recall that T of a system is a positive quantity. Consequently, S increases monotonically with increasing U. As indicated in Fig. 2.2, this has an important implication that (2.22) can be solved for U, yielding

$$U = U(S, V, N_1, \dots, N_c) \; . \tag{2.36}$$

It is graphically clear that the process can be reversed. That is, (2.22) and (2.36) are equivalent ways of expressing the same set of information regarding the thermodynamic behavior of the system. In view of this equivalence, the function in (2.36) is also a fundamental equation.

Solving (2.35) for $\mathrm{d}U$, we obtain

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \sum_{i=1}^{c} \mu_i \mathrm{d}N_i \; , \tag{2.37}$$

which is simply an alternative way of writing the fundamental property relation. From this, we obtain

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} , \quad -P = \left(\frac{\partial U}{\partial V}\right)_{S,N} , \quad \text{and} \quad \mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_{j\neq i}} , \; i = 1, \dots, c \; . \tag{2.38}$$

Exercise 2.1. A pure gas is well described by the fundamental equation

$$S = aN + NR \ln \frac{U^{3/2}V}{N^{5/2}} . \tag{2.39}$$

a. Find the equation of state of the gas in the form of

$$P = P(T, V, N) . \tag{2.40}$$

b. Show that

$$U = \frac{3}{2} PV . \tag{2.41}$$

c. Show that

$$PV^{5/3} = \text{const.} \tag{2.42}$$

holds during an adiabatic reversible expansion of the gas.

d. An isolated cylinder made of adiabatic and rigid wall is divided into two compartments of equal volume by a frictionless piston. One of the compartments contains the gas well described by (2.39) and the other compartment is evacuated. If the piston is linked to an external work source and allowed to move very slowly until the gas fills the entire chamber, show that

$$U_2 = 2^{-2/3} U_1 , \tag{2.43}$$

where the subscripts 1 and 2 refer to the initial and the final states, respectively. ///

Exercise 2.2. The fundamental equation of a pure system is given by

$$S = a(UVN)^b , \tag{2.44}$$

where a is a positive constant. The system is held at $P = 0.3$ MPa:

a. What is the value of b?
b. Find the value of U/V.
c. Find the value of μ in J/mol when $N/V = 0.1$ (mol/cm^3). ///

2.6.3 Heat Capacities

The **constant volume heat capacity** C_V is the ratio of the infinitesimal amount of heat $đQ$ injected into the system to the resulting infinitesimal increase $\mathrm{d}T$ in its temperature when the system is held at constant volume and $N_1, \dots, N_c$:

$$C_V := \frac{đQ}{\mathrm{d}T} , \quad V, N_1, \dots, N_c \text{ const.} \tag{2.45}$$

The heat capacity per mole of the material

$$\underline{C}_V := C_V \Bigg/ \sum_{i=1}^{c} N_i \tag{2.46}$$

is the **constant volume molar heat capacity**. Similarly, we define the **constant pressure heat capacity** C_P by

$$C_P := \frac{đQ}{\mathrm{d}T}\,, \quad P, N_1, \ldots, N_c \text{ const.} \tag{2.47}$$

and the **constant pressure molar heat capacity** $\underline{C}_P$ by

$$\underline{C}_P := C_P \Bigg/ \sum_{i=1}^{c} N_i \tag{2.48}$$

Heat capacity of a unit mass of the material is referred to as the **specific heat**.

Exercise 2.3.

a. Show that

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} = T\left(\frac{\partial S}{\partial T}\right)_{V,N} . \tag{2.49}$$

b. Show that

$$C_P = \left(\frac{\partial U}{\partial T}\right)_{P,N} + P\left(\frac{\partial V}{\partial T}\right)_{P,N} = \left(\frac{\partial H}{\partial T}\right)_{P,N} , \tag{2.50}$$

in which $H := U + PV$ is the **enthalpy**. The partial derivative $(\partial V/\partial T)_{P,N}$ is related to the **coefficient of thermal expansion** α by

$$\alpha := \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,N} . \tag{2.51}$$

///

2.6.4 ‡Ideal Gas

Later in optional sections, we require a few key results regarding properties of an ideal gas of fixed N_1, …, N_c. For convenience, we summarize them here while highlighting the key concepts we have introduced so far.

At the molecular level, an ideal gas is characterized by a lack of interaction among molecules. This is, of course, an idealization, which becomes increasingly more accurate with decreasing density and increasing temperature. Because a given molecule does not feel the presence of others, its energy is independent of density, and hence of V. Thus, the internal energy of an ideal gas of fixed N_1, …, N_c is a

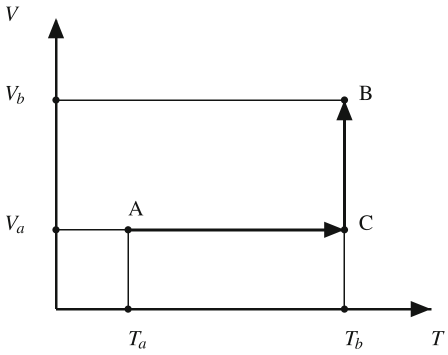

Fig. 2.3 A thermodynamic path bringing the system from state A to B.

function only of T. Exercise 2.23 provides a purely thermodynamic justification of this statement.

We wish to compute the changes U and S experience between states A and B that are specified by (T_a, V_a) and (T_b, V_b), respectively. For simplicity, we assume that C_V is constant in what follows.

To facilitate the computation, let us imagine bringing the system from A to B along the path shown in Fig. 2.3, in which we indicate the intermediate state C at (T_b, V_a). This does not affect the final answer since U and S are state functions.

For the constant volume process A→C, we can use (2.49) to write

$$\mathrm{d}U = C_V \mathrm{d}T \tag{2.52}$$

and hence

$$U_c - U_a = C_V (T_b - T_a) \,. \tag{2.53}$$

Applying (2.25) to a constant volume process,

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}U = \frac{C_V}{T}\mathrm{d}T \,, \tag{2.54}$$

yielding

$$S_c - S_a = C_V \ln \frac{T_b}{T_a} \,. \tag{2.55}$$

For the constant temperature process C→B, U remains constant:

$$U_b - U_c = 0 \,. \tag{2.56}$$

Setting $\mathrm{d}U = 0$ in (2.25), we find

$$\mathrm{d}S = \frac{P}{T}\mathrm{d}V = \frac{NR}{V}\mathrm{d}V \tag{2.57}$$

and

$$S_b - S_c = NR \ln \frac{V_b}{V_a} \,, \tag{2.58}$$

where $R = 8.3145$ J/mol K is the **gas constant**. We also used the equation of state, $PV = NRT$, of the ideal gas, where N temporarily denotes $\sum_{i=1}^{c} N_i$.

Combining everything,

$$U_b - U_a = C_V(T_b - T_a) \tag{2.59}$$

and

$$S_b - S_a = C_V \ln \frac{T_b}{T_a} + NR \ln \frac{V_b}{V_a} \; . \tag{2.60}$$

We emphasize that (2.59) and (2.60) apply for any pair of states A and B and for any process regardless of whether the process goes through state C or not.

Now, let us suppose that the process A→B occurred adiabatically and reversibly. In this case, $\mathrm{d}S \equiv 0$ and (2.21) reduces to

$$\mathrm{d}U = -P\mathrm{d}V \; . \tag{2.61}$$

When this is combined with (2.52), we find

$$C_V \mathrm{d}T = -\frac{NRT}{V}\mathrm{d}V \; . \tag{2.62}$$

Integrating this equation from state A to state B,

$$C_V \ln \frac{T_b}{T_a} = -NR \ln \frac{V_b}{V_a} \; . \tag{2.63}$$

This is nothing but (2.60) applied to an adiabatic reversible process, for which $S_b = S_a$. Eliminating temperatures by means of the equation of state, we obtain

$$\frac{P_b}{P_a} = \left(\frac{V_b}{V_a}\right)^{-\gamma} , \tag{2.64}$$

where

$$\gamma := 1 + \frac{NR}{C_V} \; . \tag{2.65}$$

Exercise 2.4. Show that

$$C_P = C_V + NR \tag{2.66}$$

for an ideal gas. It follows that

$$\gamma = C_P / C_V \; . \tag{2.67}$$

///

Exercise 2.5. From (2.52) and the ideal gas equation of state, we see that

$$U = \frac{C_V}{NR} PV + \text{const.} \tag{2.68}$$

Applying this equation to an adiabatic reversible process, directly establish (2.64).

///

2.6.5 †Heat Flow into an Open System

Now that we have seen how (2.21) for a closed system generalizes to (2.37) for an open system, it is natural to ask how (2.4) and (2.18) written for a closed system should be generalized. There is no fundamental requirement imposing a unique solution to this question. Instead, it is a matter of convention. In this section, we shall limit ourselves to reversible processes and consider a few such conventions.

Convention 1: We can take a point of view that adding molecules to or extracting them from a system is a form of work and generalize (2.4) to read

$$\mathrm{d}U = đW_1 + đQ_1 + đW_{\mathrm{mol}} , \tag{2.69}$$

where we use the subscript 1 to indicate the infinitesimal work and heat under the current convention. For reversible processes, $đW_{\mathrm{mol}}$ is given by

$$đW_{\mathrm{mol}} = \sum_{i=1}^{c} \mu_i \mathrm{d}N_i \tag{2.70}$$

and is called **quasi-static chemical work**. Under this convention, we retain the original meanings of work and heat, and write

$$đW_1 = -P\mathrm{d}V \quad \text{and} \quad đQ_1 = T\mathrm{d}S . \tag{2.71}$$

Convention 2: We recall that heat was defined as a mode of energy transfer that cannot be characterized as a macroscopic force times macroscopic displacement. Conduction of heat between bodies occurs when molecules moving about due to thermal motion exchange mechanical energy through collisions. Diffusive flux of molecules is also driven by thermal motion of molecules. That is, conduction and diffusion are both macroscopic manifestations of molecular level processes that do not involve macroscopic force or displacement. From this point of view, the concept of heat should be enlarged to include both heat conduction and diffusive molecular flux. That is, we retain (2.4):

$$\mathrm{d}U = đW_2 + đQ_2 \tag{2.72}$$

and write

$$đW_2 = -P\mathrm{d}V \quad \text{and} \quad đQ_2 = T\mathrm{d}S + \sum_{i=1}^{c} \mu_i \mathrm{d}N_i . \tag{2.73}$$

Convention 3: The second equation in (2.73) can be rewritten in a somewhat more illuminating manner using a thermodynamic identity to be established later in Exercise 2.24:

$$\mu_i = \overline{H}_i - T\overline{S}_i . \tag{2.74}$$

Here $\overline{H}_i$ and $\overline{S}_i$ are, respectively, the partial molar enthalpy and partial molar entropy to be introduced in Sect. 2.15. Using (2.74), we define heat as

$$đQ_3 := đQ_2 - \sum_{i=1}^{c} \overline{H}_i \mathrm{d}N_i = T\mathrm{d}S - T\sum_{i=1}^{c} \overline{S}_i \mathrm{d}N_i \,. \tag{2.75}$$

With this new definition of heat, (2.72) now reads

$$\mathrm{d}U = đW_2 + đQ_3 + \sum_{i=1}^{c} \overline{H}_i \mathrm{d}N_i \,. \tag{2.76}$$

Enthalpy is sometimes called the heat function. Thus, the last term of (2.76) may be interpreted as the heat brought into the system by the flow of molecules. Similarly, when (2.75) is written as

$$\mathrm{d}S = \frac{đQ_3}{T} + \sum_{i=1}^{c} \overline{S}_i \mathrm{d}N_i \,, \tag{2.77}$$

the last term suggests the flow of entropy associated with the flow of molecules. This is a very satisfying state of affair, at least psychologically.

Convention 1 is used in Ref. [1]. Conventions 3 is often adopted in textbooks on transport phenomena. Obviously, it is important to check which convention is being used in any given application. Any equation containing heat will have a different *appearance* depending on the convention.

2.7 Role of Additional Variables

In Sect. 2.5, we accepted the maximum of S under the existing constraints as both necessary and sufficient for equilibrium of an isolated system. Among other things, U and V of an isolated system are held constant. If we assume that c species in the system do not undergo chemical reactions, then the number of moles of each species, that is, all of $N_1, \ldots, N_c$, are fixed as well.

It is at this point that our formulation might appear inconsistent to you. In fact, according to (2.22), S is a function of U, V, and N_1, ..., N_c only, all of which are fixed in an isolated system without chemical reactions. It is thus legitimate to wonder just what is meant by S being maximum when all of its arguments are fixed.

We need to remember, however, that (2.22) holds only for a homogeneous system in equilibrium. If the system is inhomogeneous or not in equilibrium, specification of its state may require not only those variables already listed but also some *additional variables*. Examples may include those variables characterizing spatial variation of composition, density, or temperature. If there is a macroscopic motion within the system, the velocity field throughout the system must also be given in order to fully specify the state of the system.

What the condition of equilibrium tells us is that *these additional variables, if allowed to vary, are determined so as to maximize S*. If a chemical reaction does take place in the system, then $N_1, \ldots, N_c$ can change in a manner that is consistent

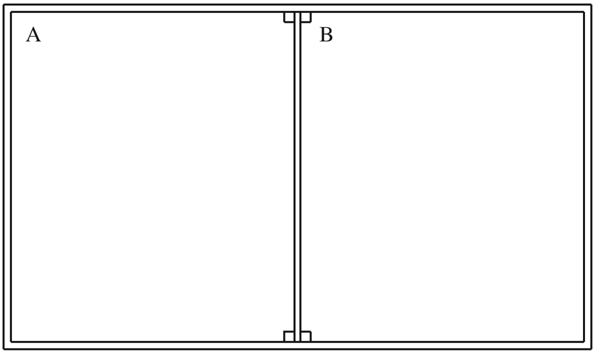

Fig. 2.4 A system consisting of two compartments. The system as a whole is isolated, while the properties of the wall separating the compartments can be modified as needed.

with the stoichiometry of the reaction. At equilibrium, the extent of reaction, once again, is determined by the condition that S is maximum.

To make the role of the additional variables clearer, we consider an example shown in Fig. 2.4. The system we consider is isolated from the surroundings by an adiabatic and rigid partition impermeable to all species. The interior of the box is divided into two compartments by a partition, whose property can be changed as needed. Initially, we suppose that the partition is adiabatic, rigid, impermeable to all species, and held fixed in place by stops. In this case, each compartment will eventually reach a state of equilibrium on its own independent of what is happening in the other compartment. When this final state of equilibrium is reached, the entropy of each compartment is a function of *its* U, V, N_1, ..., N_c. Since entropy is an additive quantity, the total entropy S of the composite system is given by

$$S = S^a(U^a, V^a, N_1^a, \ldots, N_c^a) + S^b(U^b, V^b, N_1^b, \ldots, N_c^b) , \tag{2.78}$$

where the superscripts a and b label the respective compartment and we assumed that each compartment is homogeneous. Since the internal energy, volume, and the number of particles are all additive quantities, we have

$$U^a + U^b = U , \quad V^a + V^b = V , \quad \text{and} \quad N_1^a + N_1^b = N_1 , \ i = 1, \ldots, c . \tag{2.79}$$

Using (2.79) in (2.78),

$$\begin{aligned} S &= S^a(U^a, V^a, N_1^a, \ldots, N_c^a) + S^b(U - U^a, V - V^a, N_1 - N_1^a, \ldots, N_c - N_c^a) \\ &= S(U, V, N_1, \ldots, N_c; U^a, V^a, N_1^a, \ldots, N_c^a) . \end{aligned} \tag{2.80}$$

The quantities U^a, V^a, and $N_1^a, \ldots, N_c^a$ are examples of the additional variables. They are needed since the composite system taken as a whole, although in equilibrium, is not homogeneous.

Now, suppose that the partition suddenly became **diathermal**, allowing heat to pass from one compartment to the other. (The Greek prefix “dia” means “across”or “through.”) This implies that U^a is now free to change and, according to (2.80), S can change also even though $U, V, N_1, \ldots, N_c, V^a$, and $N_1^a, \ldots, N_c^a$ are all held constant. The content of the second law is that the equilibrium value of U^a is determined to maximize S for given values of $U, V, N_1, \ldots, N_c, V^a$, and $N_1^a, \ldots, N_c^a$. If the partition is made both movable and permeable to all species as well as being diathermal, all the quantities with superscript a in (2.80) can change. Their equilibrium values are again determined by the condition that S is maximum. (Such a partition is actually relevant in applications of thermodynamics. See Sect. 2.12.) The entire argument can be generalized to cases with more than two compartments.

2.8 Entropy Representation

We are now ready to formulate the condition of equilibrium in quantitative terms. The second law also tells us the direction of a spontaneous process as the system evolves toward the state of equilibrium.

2.8.1 Condition of Equilibrium

To proceed generally, let us suppose that r variables $X_1, \ldots, X_r$ are required in addition to $U, V, N_1, \ldots, N_c$ to fully specify the state of the system. Of these r variables, we assume that only the first m variables are free to change. In (2.80), for example, $r = c+2$. If the partition between the two compartments is diathermal, rigid, impermeable to all species, and is held fixed in place, then $m = 1$ and $X_1 = U^a$. On the other hand, if the partition is diathermal, movable, and permeable to all species, then $m = r = c+2$.

If an isolated system is in equilibrium, then its entropy S is maximum for given values of $U, V, N_1, \ldots, N_c$, and $X_{m+1}, \ldots, X_r$. This condition, in turn, determines the values of $X_1, \ldots, X_m$ at equilibrium. Thus, if we denote the latter by $X_1^{\mathrm{eq}}, \ldots, X_m^{\mathrm{eq}}$, then we may express the condition of equilibrium by saying that

$$\begin{aligned}\Delta S = {} & S(U,V,N_1,\ldots,N_c;X_1^{\mathrm{eq}}+\delta X_1,\ldots,X_m^{\mathrm{eq}}+\delta X_m;X_{m+1},\ldots,X_r) \\ & - S(U,V,N_1,\ldots,N_c;X_1^{\mathrm{eq}},\ldots,X_m^{\mathrm{eq}};X_{m+1},\ldots,X_r) \leq 0\,. \end{aligned} \tag{2.81}$$

holds for any possible values of $\delta X_1, \ldots, \delta X_m$.

We note that, after the infinitesimal changes denoted by $\delta X_1, \ldots, \delta X_m$ are made, the system, in general, will no longer be in equilibrium. That is, unless we confine $X_1, \ldots, X_m$ to their new values, they will simply return to their initial values $X_1^{\mathrm{eq}}, \ldots, X_m^{\mathrm{eq}}$ to maximize S. The system may not be even homogeneous both before and after the change. This is to be contrasted with the situation considered in (2.35), in

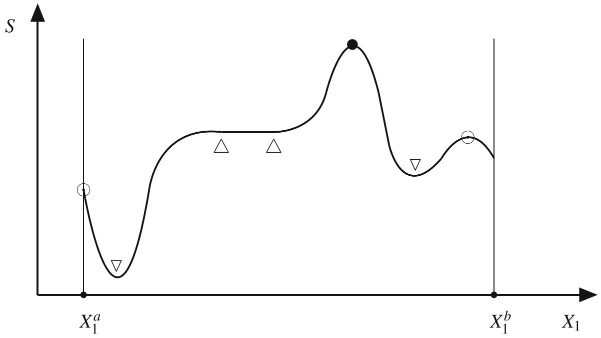

Fig. 2.5 Various possible states of equilibrium when X_1 is confined to the interval $\left[X_1^a, X_1^b\right]$. The system is in stable (●), metastable ($\odot$), unstable ($\triangledown$), and neutral equilibrium (between the two $\triangle$).

which the system was supposed to be homogeneous and in equilibrium *both* before and after the infinitesimal change. To make the distinction clear, we used the symbol δ for the infinitesimal changes occurring in (2.81) and refer to them as **variations**. We shall continue to use d as before to denote infinitesimal changes considered in writing (2.35) and refer to them as **differentiations**.

In what follows, we retain only up to the first-order terms in (2.81) and adopt the following statement as the condition of equilibrium:

Condition of Equilibrium 2 *For the equilibrium of an isolated system, it is necessary and sufficient that*

$$(\delta S)_{U,V,N_1,\ldots,N_c;X_{m+1},\ldots,X_r} \leq 0 \tag{2.82}$$

for all possible variations of $X_1, \ldots, X_m$ *consistent with given constraints.*

The subscripts U, V, N_1, $\ldots$, N_c, X_{m+1}, $\ldots$, X_r remind us that the variations cannot affect the values of these (constrained) variables. However, the set of variables showing up in this list must be modified to suite the particular situation at hand. For example, if we allow for chemical reactions, N_1, $\ldots$, N_c may change, but their variations must satisfy a set of equations expressing the constraint on the number of atoms of each element.

In practice, it may be very difficult to explore *all* possible variations and we will have to limit ourselves to a subset of all that are possible. The resulting conditions of equilibrium, therefore, will be *necessary but not sufficient* for equilibrium.

It is important, at least conceptually, to realize that both (2.81) and (2.82) allow for S to exhibit a kink (with a discontinuous first derivative) at the maximum. The maximum of S may also occur at an end point of the interval over which $X_1, \ldots, X_m$ can vary. In such cases, the system is in equilibrium even though $\delta S \neq 0$. According to (2.82), a minimum entropy state is also an equilibrium state as long as $\delta S = 0$. We illustrate these situations in Fig. 2.5 and classify them according to their stability with respect to perturbations.

Such perturbations may result due to outside influences which is so extremely minute that the system can otherwise be considered isolated. For example, your "isolated" system securely anchored to the floor of your building may experience small vibrations from time to time due to traffic outside. Even if the system is perfectly isolated from the rest of the universe, small inhomogeneity of density is constantly evolving throughout the system as the molecules move about. This is an example of spatially varying perturbation, which may be denoted as $\delta X_{\boldsymbol{r}}$ with $\boldsymbol{r}$ indicating the position dependence.

For simplicity, we let $m = 1$ in Fig. 2.5, that is, only X_1 is free to change. Then, • denotes a **stable equilibrium** state. This is because the system will return to this original state even after experiencing perturbations in X_1. States marked by ⊙ differ from the • state in that the system is stable only for small perturbations but not for sufficiently large perturbation in X_1. We call such a state **metastable**. The states marked by ▽ are in equilibrium. But the equilibrium is **unstable** because the system moves away from it as a result of even the slightest perturbation in X_1. Over the interval between the two △ where S is constant, the system is said to be in **neutral equilibrium**. In this case, there is no tendency for the system to return to the original state after an infinitesimal perturbation. But, there is not tendency to move away from it, either.

As we shall see shortly, there are other ways to express the condition of equilibrium. The current formulation, in which entropy plays a prominent role, is called the **entropy representation**.

2.8.2 Equality of Temperature

To illustrate the use of the condition of equilibrium, let us continue on the example in Sect. 2.7. We assume that the partition separating the two compartments is diathermal, rigid, impermeable to all species, and held in place by stops. Equations (2.80) and (2.82) provide a practical means of determining the value of the additional variable U^a at equilibrium.

According to (2.78), $S = S^a + S^b$, and hence

$$\delta S = \delta S^a + \delta S^b \,. \tag{2.83}$$

Using (2.35), we may rewrite this equation as

$$\delta S = \frac{1}{T^a}\delta U^a + \frac{1}{T^b}\delta U^b \,. \tag{2.84}$$

Since

$$U^a + U^b = U = \text{const.}\,, \tag{2.85}$$

and hence $\delta U^b = -\delta U^a$, (2.84) reduces to

$$\delta S = \left(\frac{1}{T^a} - \frac{1}{T^b}\right)\delta U^a \,. \tag{2.86}$$

Now, (2.82) demands that $\delta S \leq 0$ for any value of δU^a. Provided that δU^a can be either positive or negative, it follows that

$$T^a = T^b \,, \tag{2.87}$$

which is the condition of equilibrium of the composite system.

From (2.26), we see that T^a is a function of U^a, V^a, and $N_1^a, \ldots, N_c^a$. Likewise for T^b. Thus, (2.85) and (2.87) serve as the set of equations to determine U^a and U^b provided that the value of the constant U is known. Once U^a and U^b are found from these equations, then the temperature $T^a = T^b$ of the composite system in equilibrium can be computed from (2.26).

Strictly speaking, (2.87) is necessary for equilibrium but not sufficient since we have not considered *all* possible variations. For example, variations that disturbs homogeneity in either of the compartments were not considered. Such a concern is best addressed in terms of the stability of the equilibrium.

Finally, suppose that we remove the stops on the left of the partition but keep those on the right. In this case, V^a is incapable of a positive variation and $\delta V^a \leq 0$. From this, one can only deduce that $P^a/T^a \geq P^b/T^b$ at equilibrium. For a diathermal partition, we have $T^a = T^b$ and hence $P^a \geq P^b$. When this inequality is satisfied, clearly, the partition will not move to the left. It will not move to the right either because of the remaining stops. The composite system is thus in equilibrium even if P^a may differ from P^b.

Exercise 2.6. Suppose that the stops holding the partition are now removed and that the partition, besides being diathermal, just became permeable to species 1 while still impermeable to other species. Show that $T^a = T^b$, $P^a = P^b$, and $\mu_1^a = \mu_1^b$ hold at equilibrium. ///

Exercise 2.7. [7] The fundamental equation of a particular binary mixture is given by

$$S = aN + NR\ln\frac{U^{3/2}V}{N^{5/2}} - N_1R\ln\frac{N_1}{N} - N_2R\ln\frac{N_2}{N} \,, \quad N := N_1 + N_2 \,, \tag{2.88}$$

where a is an unspecified constant and R is the gas constant.

An isolated system is divided into two compartments A and B of equal volume by an adiabatic, rigid, and impermeable partition fixed in place by stops. Initially, compartment A is filled with $N_1 = 10$ mol of pure species 1 at $T^a = 300$ K while compartment B is filled with $N_2 = 4$ mol of pure species 2 at $T^b = 400$ K:

a. The partition suddenly became diathermal, while remaining rigid, impermeable, and held fixed in place by stops. After the system reached a new state of equilibrium, what is the temperature in each compartment?
b. The partition became permeable to species 1 in addition to being diathermal, while remaining rigid, impermeable to species 2, and held fixed in place by stops. After the system reached a new state of equilibrium, what is the final number of moles of species 1 in each compartment? What about the temperature? ///

2.8.3 Direction of a Spontaneous Process

In addition to identifying the state of equilibrium, the second law also determines the direction of a spontaneous process occurring in an isolated system.

In the example considered in Sect. 2.8.2, let us suppose that $T^a > T^b$ at the moment when the adiabatic partition became suddenly diathermal. Then we ask which of the two compartments receives heat as the composite system evolves toward a new state of equilibrium, at which $T^a = T^b$. You know the answer intuitively, of course. The purpose of this discussion is to make an argument based on the principle of thermodynamics.

From (2.86), we have

$$\mathrm{d}S = \left(\frac{1}{T^a} - \frac{1}{T^b}\right)\mathrm{d}U^a , \tag{2.89}$$

where we use "d" to indicate an infinitesimal change *without* implying that the *composite* system is in equilibrium either before or after the change. Instead, "d" in this equation denotes the infinitesimal change during a spontaneous process occurring in the system as it evolves toward equilibrium. Each compartment, taken separately, is assumed to be in equilibrium at all time. This assumption will be satisfactory if the change occurs very slowly.

By assumption, $T^a > T^b$ initially and the quantity in the brackets is negative. For a spontaneous process in the composite system that is isolated, $\mathrm{d}S$ must be positive. According to (2.89), $\mathrm{d}U^a < 0$ and hence $\mathrm{d}U^b = -\mathrm{d}U^a > 0$, that is, the heat flows from compartment A to B.

Just like a difference in temperature drives the heat flow between the two compartments, a difference in pressure drives the repartitioning of the volume between them. Similarly, a difference in the chemical potential of one of the species drives the flow of particles of that species. Chemical potentials also play a crucial role when chemical reactions can take place. You are invited to explore these remarks in detail in the following exercises.

Exercise 2.8. Consider an isolated system consisting of two compartments separated by a diathermal and rigid partition impermeable to all species and fixed by stops. Show that, when the stops are removed, the partition moves from the higher pressure compartment to the lower pressure compartment. You may assume that the temperatures of the two compartments are equal at all time. ///

Exercise 2.9. Consider an isolated system consisting of two compartments separated by a diathermal and rigid partition permeable to molecules of species 1 but not to the others. The partition is held fixed in place. Show that molecules of species 1 flow from the higher chemical potential compartment to the lower chemical potential compartment. You may assume that the temperatures of the two compartments are equal at all time. ///

Exercise 2.10. Consider an isolated and homogeneous ternary system ($c = 3$) consisting of species A_1, A_2, and A_3, in which the following chemical reaction can take place:

$$c_1A_1 + c_2A_2 \rightleftarrows c_3A_3 , \tag{2.90}$$

where c_1, c_2, and c_3 are some positive constants.

a. Show that

$$c_1\mu_1 + c_2\mu_2 = c_3\mu_3 \tag{2.91}$$

at equilibrium.

b. Show that the reaction proceeds from left to right if

$$c_1\mu_1 + c_2\mu_2 > c_3\mu_3 \ . \tag{2.92}$$

///

2.8.4 †Very Short Remark on the Stability of Equilibrium

In order for the composite system to eventually come to equilibrium through the spontaneous process considered in Sect. 2.8.3, the temperature must increase with an inflow of energy and decrease with an outflow of energy. This same condition is also necessary for the stability of a body with uniform temperature throughout. That is, if, by fluctuation, heat flows from one region to another, the temperature of a part receiving the heat must increase while the temperature of a region losing the heat must decrease. Otherwise, the ever-increasing inequality of temperature would drive the system further away from the original state. Thus, for the stability of any system, it is necessary that

$$\left(\frac{\partial T}{\partial U}\right)_{V,N} > 0 \,, \tag{2.93}$$

which, in view of (2.49), implies that

$$C_V > 0 \ . \tag{2.94}$$

We can develop a graphical approach to the question of stability. As an example, let us take an isolated homogeneous system and define the entropy density $s := S/V$ and the internal energy density $u := U/V$. Since S is an extensive quantity, we have

$$s = S(u, 1, N_1/V, \ldots, N_c/V) \ , \tag{2.95}$$

which simply states that the system containing U/V of the internal energy and N_i/V moles of species i in unit volume has $1/V$ times the entropy of the original system containing U of internal energy and N_i moles of species i in volume V. It follows that, for fixed values of V, and N_1, …, N_c, the quantity s is a function only of u.

If $s = s(u)$ is concave up as shown in Fig. 2.6, the system is unstable with respect to separation into two homogeneous parts with distinct values of the internal energy density.

To see why, let us consider a homogeneous system having the internal energy U_0 and consisting of N_i moles of species i in volume V. We denote its entropy density by s_0 and its internal energy density by u_0. Then, the system is represented by the

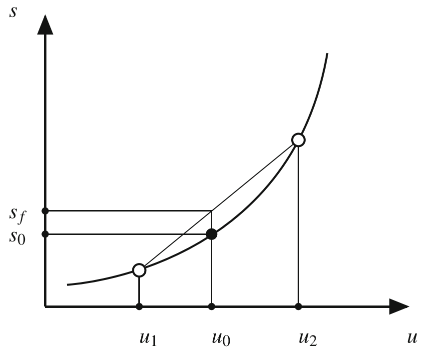

Fig. 2.6 If the curve $s = s(u)$ for a homogeneous body is concave up, the body is unstable with respect to the spontaneous separation into two homogeneous parts. Because of how the graph is drawn, the system can further increase its entropy by moving the *open circles* away from each other in such a way that the overall energy density remains at u_0.

filled circle in Fig. 2.6. Now, suppose that the system separated into two parts, one having the internal energy density u_1 and the other u_2 such that $u_1 < u_0 < u_2$ as represented by the open circles in Fig. 2.6. Then, the entropy density of the system at this final state is given by s_f in the figure. This is because the entropy density at the final state should be somewhere on the straight line connecting the two open circles, while the overall internal energy density must be u_0 because the system as a whole is isolated. If $s(u)$ is concave up, clearly, $S_f - S_0 = V(s_f - s_0) > 0$ and the process occurs spontaneously.

Exercise 2.11. Justify the graphical method given above for locating s_f through an explicit computation. ///

Exercise 2.12. By considering the sign of the second derivative:

$$\left(\frac{\partial^2 S}{\partial U^2}\right)_{V,N}, \tag{2.96}$$

show that the constant volume heat capacity C_V defined by (2.49) is negative if $S = S(U)$ is concave up. Thus, $C_V > 0$ is necessary for the stability of a thermodynamic system. ///

2.9 Energy Representation

While the second law leads directly to the entropy representation of the condition of equilibrium, this is by no means the only possible formulation. Nor is it the most convenient. To explore alternatives, we begin by looking into the energy represen-

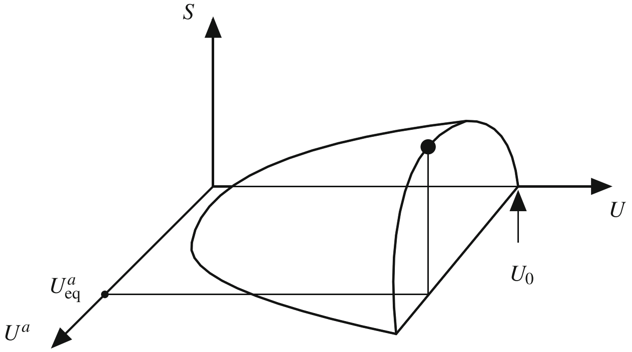

Fig. 2.7 Graphical representation of S of the composite system considered in Sect. 2.8.2. In drawing this graph, all the variables occurring in (2.80), except for U and U^a, are fixed. The equilibrium value of U^a, which we denote here by U^a_{eq}, is determined so that S takes the maximum possible value consistent with the given value, U_0, of the internal energy of the composite system. The equilibrium state is then indicated by the *filled circle*.

tation, in which the internal energy plays a central role in characterizing a state of equilibrium. Other possibilities are considered in Sect. 2.13.

2.9.1 Condition of Equilibrium

It is instructive to envision the approach to an equilibrium state graphically. For this purpose, let us revisit the example discussed in Sects. 2.8.2 and 2.8.3 and depict S of the composite system as a function of U and U^a as shown in Fig. 2.7.

Because the composite system is isolated, U is fixed at a constant value, say U_0. As the system evolves toward the equilibrium state, at which $T^a = T^b$ and $U^a = U^a_{\text{eq}}$, its representative point moves along the curve defined by the intersection between the surface of S and the $U = U_0$ plane until it reaches the maximum S state indicated by $\bullet$ in Fig. 2.7. If this trajectory is projected onto the US-plane as shown in Fig. 2.8, the representative point is seen to move vertically upward until it meets the S versus U curve, at which $S = S_0$. From the latter figure, we observe that the same equilibrium state, that is, the point (U_0, S_0) can also be regarded as the state of *minimum* internal energy for a given value (S_0) of the entropy.

This suggests the following formulation, called the **energy representation**, of the condition of equilibrium as an alternative to the entropy representation:

Condition of Equilibrium 3 *For the equilibrium of an isolated system, it is necessary and sufficient that*

$$(\delta U)_{S,V,N_1,\ldots,N_c;X_{m+1},\ldots,X_r} \geq 0 \qquad (2.97)$$

for all possible variations of $X_1, \ldots, X_m$ *consistent with given constraints.*

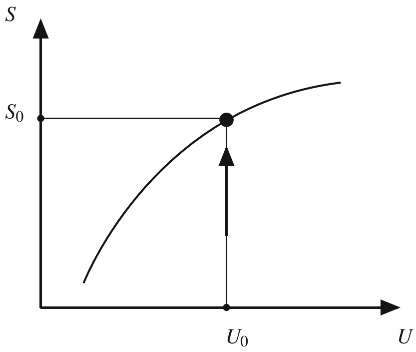

Fig. 2.8 Projection onto the US-plane of the locus of the maximum entropy as a function of U. The *vertical arrow* at U_0 indicates the trajectory of the system during evolution toward equilibrium as observed in the US-plane. The *filled circle* indicates the state of equilibrium after the partition became diathermal.

As is the case with *Condition of Equilibrium* 2, subscripts on δU must be modified according to the problem at hand. The same remark applies to all criteria of equilibrium we encounter later.

To illustrate the use of *Condition of Equilibrium 3* in a more concrete setting, we examine the same problem you considered in Exercise 2.6, that is, we deduce the equations that must be satisfied at equilibrium when the partition between the two subsystems is diathermal, movable, and permeable only to species 1.

Since the internal energy is an additive quantity, we have

$$U = U^a(S^a, V^a, N_1^a, \dots, N_c^a) + U^b(S^b, V^b, N_1^b, \dots, N_c^b) , \tag{2.98}$$

and hence

$$\delta U = \delta U^a + \delta U^b . \tag{2.99}$$

Applying (2.37) to each compartment, we can rewrite (2.99) as

$$\delta U = T^a \delta S^a - P^a \delta V^a + \mu_1^a \delta N_1^a + T^b \delta S^b - P^b \delta V^b + \mu_1^b \delta N_1^b , \tag{2.100}$$

where we note that $\delta N_2^a = \dots = \delta N_c^b \equiv 0$ since the partition is impermeable to species 2, ..., c.

Equation (2.97) requires that we minimize U for a given value of S, while allowing for S^a and S^b to change:

$$S^a + S^b = S = \text{const.} \tag{2.101}$$

Since the composite system is isolated, we also have

$$V^a + V^b = V = \text{const.} \quad \text{and} \quad N_1^a + N_1^b = N_1 = \text{const.} \tag{2.102}$$

Using (2.101) and (2.102), we rewrite (2.100) as

$$\delta U = (T^a - T^b)\delta S^a - (P^a - P^b)\delta V^a + (\mu_1^a - \mu_1^b)\delta N_1^a \,. \tag{2.103}$$

For equilibrium of the composite system, it is necessary that this quantity be nonnegative for *all* possible values of δS^a, δV^a, and δN_1^a, from which we deduce that $T^a = T^b$, $P^a = P^b$, and $\mu_1^a = \mu_1^b$. For example, (2.103) must be nonnegative even when δV^a and δN_1^a are both zero and δS^a takes an arbitrary value, which leads to the conclusion that $T^a = T^b$.

Suppose that the partition, besides being diathermal and movable, is now made permeable to all species. It is straightforward to show that, at equilibrium, $T^a = T^b$, $P^a = P^b$, and $\mu_i^a = \mu_i^b$ for $i = 1, \ldots, c$.

2.9.2 Reversible Work Source

Looking at (2.97), you may object to the indicated increase of U because the system under consideration is isolated. Nevertheless, according to Fig. 2.8, *Condition of Equilibrium 3* is equivalent to *Condition of Equilibrium 2* in Sect. 2.8.1. We can give two distinct interpretations of (2.97).

In one interpretation, the variation is regarded as representing an act of comparing the values of U of many copies of the system, each having the same values of S, V, N_1, …, N_c, and X_{m+1}, …, X_r, but differing by the values of X_1, …, X_m. Equation (2.97) then identifies the system with minimum U as being in equilibrium.

An alternative, more physical, interpretation is possible. We may suppose that the increase in U is brought about by means of a purely classical mechanical device which is linked to the otherwise isolated system and induces changes in $X_1, \ldots, X_m$. As discussed in Sect. 2.2, such a device does not exchange heat with the system. Since the variation is taken while maintaining S constant, the process must occur reversibly. The mechanical device capable of inducing the variation reversibly is called the **reversible work source**.

If we take the second view point, then from the conservation of energy, the reversible work imparted on the system by the reversible work source is given by

$$\delta W^{\text{rev}} = (\delta U)_{S,V,N_1,\ldots,N_c;X_{m+1},\ldots,X_r} \,. \tag{2.104}$$

This observation leads to yet another formulation of the condition of equilibrium:

Condition of Equilibrium 4 *For the equilibrium of an isolated system, it is necessary and sufficient that*

$$(\delta W^{\text{rev}})_{S,V,N_1,\ldots,N_c;X_{m+1},\ldots,X_r} \geq 0 \tag{2.105}$$

for all possible variations of X_1, …, X_m consistent with given constraints.

As we shall see later, this formulation applies not only to an isolated system but also to other kinds of systems, for example, a system held at a constant temperature by virtue of thermal contact with the surroundings.

Condition of Equilibrium 4 has a direct physical interpretation. To see if a system, isolated or otherwise, is in equilibrium, we connect it to a reversible work source and let the latter perturb the state of the system by varying the values of $X_1, \dots, X_m$. If, to the first order of variation, a nonnegative work is required for any such perturbation, then from this observation, we conclude that the initial unperturbed system was in equilibrium.[8]

We can now establish the equivalence of *Conditions of Equilibrium 2 and 3* without resorting to Fig. 2.8. Suppose that (2.97) holds and that we exerted work reversibly on the otherwise isolated system to induce a required change in $X_1, \dots, X_m$. This does not affect S but U may change. According to (2.97), however, U cannot decrease. If U remains unchanged, then the variation just considered satisfies (2.82) with equality. If U increases, it can be brought back to its initial value by removing the extra energy in the form of heat from the system while holding the values of $X_1, \dots, X_m$ at those in the varied state, that is, $X_1 + \delta X_1, \dots, X_m + \delta X_m$. The combined result of the two step process is a decrease of S without affecting U. Thus, if (2.97) holds for all possible variations, so does (2.82). To prove the converse, suppose that (2.97) is violated by some variation, that is, $\delta U < 0$ for this variation. The reversible work source then receives work, which can be converted to heat, using friction for example, and injected back into the system. This will restore U to its original value but will increase S. The combined result of the two step process is a variation that violates (2.82).

2.9.3 †Condition of Perfect Equilibrium

In the absence of any internal constraints $X_{m+1}, \dots, X_r$, the condition of equilibrium can be formulated as follows:

Condition of Equilibrium 5 *For the equilibrium of an isolated system subject to no internal constraint, it is necessary and sufficient that*

$$\delta U \geq T\delta S - P\delta V + \sum_{i=1}^{c} \mu_i \delta N_i \tag{2.106}$$

for all possible variations of S, V, $N_1, \dots, N_c$, and $X_1, \dots, X_m$.

This seems rather surprising since (2.106) looks very much like (2.37), which is essentially the first law of thermodynamics. The system we have in mind is a body that is homogeneous initially and enclosed in a container without any internal partitions. As an example of variations in $X_1, \dots, X_m$, one may consider fluctuations in local density that upset the homogeneity. A state of equilibrium that prevails when there is no internal constraints is called the **perfect equilibrium** state. With a slight modification to (2.106), this formulation of the condition of perfect equilibrium becomes an important starting point for thermodynamics of inhomogeneous systems as we shall see in Chap. 6.

To see that (2.106) is sufficient for equilibrium, suppose that (2.106) holds for any variations of S, V, $N_1, \ldots, N_c$, and $X_1, \ldots, X_m$. Then, $\delta U \geq 0$ for any variations of $X_1, \ldots, X_m$ that *do not* affect the values of S, V, and $N_1, \ldots, N_c$. This is just (2.97) written without $X_{m+1}, \ldots, X_r$, which are absent for the situation under consideration.

The necessity of (2.106) takes a little more effort to establish. As in (2.80),

$$U = U(S, V, N_1, \ldots, N_c; X_1, \ldots, X_m) . \tag{2.107}$$

in general. Thus, when S, V, $N_1, \ldots, N_c$, and $X_1, \ldots, X_m$ are perturbed by infinitesimal amounts, the resulting variation in δU is given by

$$\begin{aligned}\delta U = &\left(\frac{\partial U}{\partial S}\right)_{V,N,X} \delta S + \left(\frac{\partial U}{\partial V}\right)_{S,N,X} \delta V + \sum_{i=1}^{c} \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_{j\neq i},X} \delta N_i \\ &+ \sum_{i=1}^{m} \left(\frac{\partial U}{\partial X_i}\right)_{S,V,N,X_{j\neq i}} \delta X_i ,\end{aligned} \tag{2.108}$$

where we abbreviated the subscripts $N_1, \ldots, N_c$ and $X_1, \ldots, X_m$ to just N and X, respectively.

Comparing (2.108) against (2.104), we see immediately that

$$\delta W^{\text{rev}} = \sum_{i=1}^{m} \left(\frac{\partial U}{\partial X_i}\right)_{S,V,N,X_{j\neq i}} \delta X_i . \tag{2.109}$$

If the system is initially in perfect equilibrium, this quantity is nonnegative as demanded by (2.105). Therefore, dropping the last term of (2.108), we arrive at

$$\delta U \geq \left(\frac{\partial U}{\partial S}\right)_{V,N,X} \delta S + \left(\frac{\partial U}{\partial V}\right)_{S,N,X} \delta V + \sum_{i=1}^{c} \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_{j\neq i},X} \delta N_i . \tag{2.110}$$

Now, can we say that

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N,X} ? \tag{2.111}$$

This looks very much like the expression for T in (2.38). In arriving at that expression, however, we considered a differentiation, that is, the system was assumed to be in equilibrium both before and after the change. In other words, $X_1, \ldots, X_m$ were allowed to adjust themselves in order to maintain the equilibrium. This is why X does not show up as a subscript in (2.38). Going back to the definition of partial derivative, therefore, we can express T as given by (2.38) as

$$\begin{aligned}T = \left(\frac{\partial U}{\partial S}\right)_{V,N} = \lim_{\Delta S \to 0} \frac{1}{\Delta S} &\left[U(S + \Delta S, V, N_1, \ldots, N_c; X_1 + \Delta X_1, \ldots, X_m + \Delta X_m)\right. \\ &\left. - U(S, V, N_1, \ldots, N_c; X_1, \ldots, X_m)\right] ,\end{aligned} \tag{2.112}$$

where ΔX_i denotes the adjustment the system makes to X_i in order to maintain the equilibrium when S is changed by ΔS. Expanding the internal energy difference into the Taylor series,

$$T = \lim_{\Delta S \to 0} \frac{1}{\Delta S} \left[\left(\frac{\partial U}{\partial S} \right)_{V,N,X} \Delta S + \sum_{i=1}^{m} \left(\frac{\partial U}{\partial X_i} \right)_{S,V,N,X_{j \neq i}} \Delta X_i \right] , \tag{2.113}$$

where we dropped the higher order terms that vanish more rapidly than ΔS.

Now, suppose that the system is *initially* in equilibrium and that each X_i is capable of **reversible variation**, in the sense that both negative and positive values of δX_i are possible for each i. (Our usage of the word "reversible" in this context is due to Gibbs and differs from our earlier usage of the same word pertaining to processes.) Then, (2.105) and (2.109) lead to

$$\left(\frac{\partial U}{\partial X_i} \right)_{S,V,N,X_{j \neq i}} = 0 \, , \; i = 1, \ldots, m \, . \tag{2.114}$$

This is now introduced into (2.113) to give

$$T = \left(\frac{\partial U}{\partial S} \right)_{V,N,X} . \tag{2.115}$$

This proof is due to Ref. [4]. Similarly,

$$-P = \left(\frac{\partial U}{\partial V} \right)_{S,N,X} \quad \text{and} \quad \mu_i = \left(\frac{\partial U}{\partial N_i} \right)_{S,V,N_{j \neq i},X} , \quad i = 1, \ldots, m \, . \tag{2.116}$$

Because of (2.114), the last term of (2.108) is identically zero and (2.110) holds with equality. Therefore, by virtue of (2.115) and (2.116), we obtain

$$\delta U = T \delta S - P \delta V + \sum_{i=1}^{c} \mu_i \delta N_i \, , \tag{2.117}$$

which is a special case of (2.106).

What if one of ΔX_1, ..., ΔX_m, say ΔX_1, cannot take a positive value? Because the system is initially in equilibrium, the partial derivative

$$\left(\frac{\partial U}{\partial X_1} \right)_{S,V,N,X_{j \neq 1}} \tag{2.118}$$

cannot be positive. In fact, if it were positive, then the system could lower U by decreasing X_1, in contradiction to the assumption that the system was in equilibrium initially. It may be that the partial derivative, which is to be evaluated at the initial state, happens to be zero. In this case, we have (2.114) holding for all i including $i = 1$ and we once again obtain (2.117).

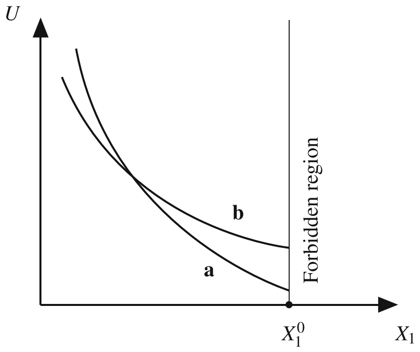

Fig. 2.9 The function $U = U(X_1)$. Suppose that X_1 cannot exceed X_1^0 and the slope of U at $X_1 = X_1^0$ is negative initially as indicated by curve **a**. As illustrated by curve **b**, the slope remains negative even after an infinitesimal change is made to S. Then, $X_1 = X_1^0$ at equilibrium both before and after the change. So, $\Delta X_1 = 0$.

On the other hand, if the partial derivative is negative, ΔX_1 occurring in (2.113), that is, the adjustment the system makes to X_1 in response to the change in S must be zero. This is because an infinitesimal change in S cannot induce a finite change in the value of the partial derivative, which thus remains negative even after the change. The underlying assumption here is that the partial derivative is a continuous function of S. Figure 2.9 illustrates the situation. In this way, we see that (2.115) and (2.116) hold in this case as well. When these equations are substituted into (2.110), we arrive at (2.106).

In this case, however, the inequality sign in (2.106) cannot be dropped. To see this, let us consider a variation of X_1. By assumption, δX_1 can only be negative. But, its coefficient $(\partial U/\partial X_1)_{S,V,N,X_{j\neq 1}}$ is also negative. Thus, the contribution to δU from any nonzero δX_1 is always positive. Note carefully the difference between ΔX_1 and δX_1 in this discussion. The former is the adjustment the *system* makes to maintain equilibrium, while the latter is the change in X_1 *we* impose on the system by means of the reversible work source.

2.9.4 †Closed System with a Chemical Reaction

We remarked in Sect. 2.6.1 that (2.21) holds even in the presence of chemical reactions provided that the system is homogeneous and in equilibrium both before and after the infinitesimal change, during which the system remains closed. We are now ready to see why this is so.

For simplicity, we allow only a single chemical reaction:

$$c_1A_1 + c_2A_2 \rightleftarrows c_3A_3 \tag{2.119}$$

among three species A_1, A_2, and A_3. The positive constants c_1, c_2, and c_3 are called the stoichiometric coefficients. There may be more species present in the system in addition to these three species. But, their numbers of moles are fixed. In contrast, N_1, N_2, and N_3 can change, but only in compliance with the stoichiometry of the reaction:

$$\delta N_1 = -\frac{c_1}{c_3}\delta N_3 \quad \text{and} \quad \delta N_2 = -\frac{c_2}{c_3}\delta N_3 \tag{2.120}$$

as you saw in Exercise 2.10.

If the system prior to variation is in equilibrium, (2.106) applies and

$$\delta U \geq T\delta S - P\delta V + \left(-\frac{c_1}{c_3}\mu_1 - \frac{c_2}{c_3}\mu_2 + \mu_3\right)\delta N_3 \tag{2.121}$$

must hold true for any possible values of δS, δV, and δN_3. In particular, it must hold even if $\delta S = 0$ and $\delta V = 0$. Provided that δN_3 is capable of assuming both positive and negative values, we find that

$$-\frac{c_1}{c_3}\mu_1 - \frac{c_2}{c_3}\mu_2 + \mu_3 = 0\,. \tag{2.122}$$

Thus,

$$c_1\mu_1 + c_2\mu_2 = c_3\mu_3\,, \tag{2.123}$$

which is the condition of equilibrium for the reaction under consideration. Substituting (2.123) back into (2.121), we find that

$$\delta U \geq T\delta S - P\delta V\,. \tag{2.124}$$

If we assume that X_1, ..., X_m are all capable of reversible variations in the sense defined in the previous subsection, the inequality may be replaced by equality. Furthermore, if we restrict ourselves to such variations as to leave the system homogeneous and in equilibrium, δ can be replaced by d. Thus we finally arrive at

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V\,, \tag{2.125}$$

which is just (2.21).

2.9.5 †Maximum Work Principle

We can take advantage of the tendency of a system to evolve toward a state of equilibrium and extract a useful work. For this purpose, we connect the system to an external agency and suppose that the composite system, consisting of the system and the external agency attached to it, as a whole, is isolated. We show that, in this setting, the maximum amount of work is extracted by the external agency when the process is carried out reversibly.

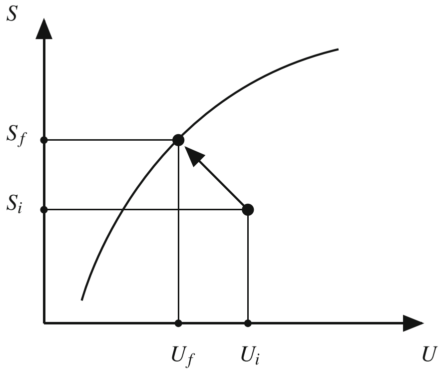

Fig. 2.10 Graphical illustration of the maximum work principle. The work extracted, $U_i - U_f$, is maximum when the arrow connecting the initial state to the final state points horizontally to the left so that $S_f - S_i = 0$. In the absence of the external agency, $U_f = U_i$ and the arrow would point vertically upward as in Fig. 2.8.

Let us first plot the equilibrium value of S of the system as a function of its U as shown in Fig. 2.10. If the system is not in equilibrium, its representative point lies below this curve because S of the system is not the maximum possible for a given value of U. Let us therefore suppose that the representative point is initially at (U_i, S_i).

If the system is allowed to relax toward equilibrium in the absence of the external agency, then as in Fig. 2.8, the representative point will simply move vertically upward until it hits the curve $S(U)$.

We now suppose instead that the system is linked to the external agency. From the conservation of energy, the work W extracted by the latter during the approach to equilibrium is given by

$$W = U_i - U_f \ , \tag{2.126}$$

where U_i and U_f denote the internal energy of the system at the beginning and the end of the equilibration process, respectively. *If the process is such as not to affect the entropy of the external agency*, we have

$$S_f - S_i \geq 0 \ . \tag{2.127}$$

Because the composite system, with the external agency attached, is isolated, this means that the process is spontaneous. From Fig. 2.10, it is evident that the maximum amount of work is extracted when the equality holds in (2.127), that is if the process occurred reversibly. This is the **maximum work principle**.

As an example of the external agency whose entropy remains unaffected, we may consider a purely classical mechanical device that can exchange energy with the system only in the form of work. A so-called **cycle**, which by definition, repeatedly returns to its original state is another example.

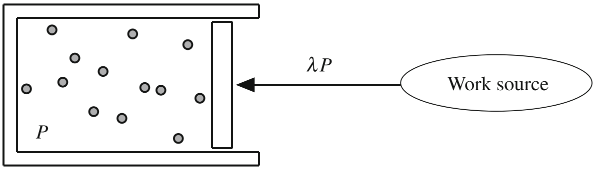

Fig. 2.11 The work source extracts work from an adiabatic expansion of an ideal gas. The expansion is reversible when $\lambda = 1$ and irreversible otherwise.

Example 2.2. Adiabatic expansion of an ideal gas: Suppose that an ideal gas is confined to a cylinder made of a rigid and adiabatic wall and is fitted with a piston. See Fig. 2.11. The space outside the cylinder is vacuum and our aim is to extract work using the tendency of the gas to expand. To do this, we connect the work source to the system so that it exerts a pressure λP on the piston. Here P is the pressure inside the cylinder and λ is a constant. In order for the expansion to occur, $\lambda < 1$.

For the process considered, $đQ = 0$, and hence

$$\mathrm{d}U = đW = -\lambda P \mathrm{d}V \; . \tag{2.128}$$

In order for this quantity to be negative so that we can extract positive work, $\lambda > 0$ and we assume that this is the case in what follows.

Using the equation of state of an ideal gas and recalling from Sect. 2.6.4 that $\mathrm{d}U = C_V \mathrm{d}T$,

$$C_V \mathrm{d}T = -\frac{\lambda NRT}{V} \mathrm{d}V \; , \tag{2.129}$$

which is now integrated to give

$$\ln \frac{T_f}{T_i} = -\frac{\lambda NR}{C_V} \ln \frac{V_f}{V_i} \; . \tag{2.130}$$

Applying (2.59), we find that the work extracted from the process is

$$U_i - U_f = C_V T_i \left[1 - \left(\frac{V_i}{V_f} \right)^{\lambda NR/C_V} \right] , \tag{2.131}$$

while it follows from (2.60) that

$$S_f - S_i = (1-\lambda) NR \ln \frac{V_f}{V_i} \; . \tag{2.132}$$

Remembering that $V_f/V_i > 1$ for an expansion, we see that $S_f - S_i$ is maximum at $\lambda = 0$ (free expansion) and decreases monotonically with increasing λ until it reaches the minimum value zero at $\lambda = 1$ (a reversible process). In contrast,

$U_i - U_f$ is zero for the free expansion and increases monotonically until it reaches the maximum value for the reversible expansion.

We can also extract work from the natural tendency for two bodies in thermal contact to reach a common temperature by means of a **heat engine**. This is a device that visits a given set of multiple states in a cyclic fashion and in so doing, it receives heat from the higher temperature body, converts a part of the energy into work, and expels the rest in the form of heat into the lower temperature body. After completing one cycle, the heat engine itself returns to the original state while the temperature difference between the bodies decreases. The heat engine is an example of a cycle.

Analogously, we can also operate what might be called a **material engine** between two bodies having the same temperature but different values of the chemical potentials for some of the species, say species 1. In this case, the engine receives heat and molecules of species 1 from higher chemical potential body and delivers them to the lower chemical potential body while extracting work from the process.

These possibilities are considered in the following two examples on the ground of the general principle. Each example is followed by an exercise, in which you are asked to consider the inner working of reversible engines in some detail.

Example 2.3. Heat engine: Consider two homogeneous bodies H and L at thermal contact that are initially at different temperatures T_h and T_l, respectively. To extract work, we break the thermal contact and insert a heat engine HE between H and L. The system now consists of H, L, and HE, and our goal is to figure out the amount of work this composite system delivers to a work source when the latter is linked to HE. We note that the work source is purely a classical mechanical device described in Sect. 2.2 and does not exchange heat with the composite system.

We restrict ourselves to processes occurring without affecting the volume of H or that of L. We also suppose that only a very small amount of heat and work are involved during a single cycle of HE so that T_h and T_l may be regarded as constant. Then, denoting by $đQ_h$ the amount per cycle of heat transferred from H to HE, we have

$$-đQ_h = \mathrm{d}U_h = T_h \mathrm{d}S_h \,, \tag{2.133}$$

and hence

$$\mathrm{d}S_h = -\frac{đQ_h}{T_h} \,. \tag{2.134}$$

Similarly, if $đQ_l$ is the amount per cycle of heat transferred from HE to L,

$$đQ_l = \mathrm{d}U_l = T_l \mathrm{d}S_l \,, \tag{2.135}$$

and hence

$$\mathrm{d}S_l = \frac{đQ_l}{T_l} . \tag{2.136}$$

Since HE returns to its original state at the end of one cycle, $\mathrm{d}S_{he} = 0$. So, for the composite system, we have

$$\mathrm{d}S = \mathrm{d}S_h + \mathrm{d}S_l = -\frac{đQ_h}{T_h} + \frac{đQ_l}{T_l} . \tag{2.137}$$

According to the first law, the work $đW$ delivered to the work source is

$$đW = -(\mathrm{d}U_h + \mathrm{d}U_l) = đQ_h - đQ_l , \tag{2.138}$$

where we note that $\mathrm{d}U_{he} = 0$.

Now, let $đQ_l := \lambda\, đQ_h$ and rewrite these equations as

$$\mathrm{d}S = \left(\frac{\lambda}{T_l} - \frac{1}{T_h}\right) đQ_h \quad \text{and} \quad đW = (1-\lambda)\, đQ_h . \tag{2.139}$$

For spontaneous processes, we have $\mathrm{d}S \geq 0$. Since we are interested in the amount of work that can be extracted from such processes, we demand that $đW \geq 0$. These considerations lead to

$$\frac{T_l}{T_h} \leq \lambda \leq 1 . \tag{2.140}$$

When $\lambda = 1$, $đW = 0$ and $đQ_h = đQ_l$, and the process is seen to be identical to the direct heat conduction between H and L through a diathermal wall. In contrast, the maximum of $đW$ occurs when $\lambda = T_l/T_h$, and is given by

$$đW = \left(1 - \frac{T_l}{T_h}\right) đQ_h . \tag{2.141}$$

In this case, $\mathrm{d}S = 0$ and the process is reversible.

This example demonstrates the existence of an upper limit of the **efficiency** η of *any* heat engines:

$$\eta := \frac{đW}{đQ_h} \leq 1 - \frac{T_l}{T_h} . \tag{2.142}$$

Exercise 2.13. As an example of reversible heat engines operating between the higher temperature body H at T_h and the lower temperature one L at T_l, consider a **Carnot cycle**. The engine uses a working fluid confined to a cylinder fitted with a frictionless piston. The wall of the cylinder is rigid and impermeable to all species. The wall is also adiabatic except that one side of the wall, denoted by Σ_T, can be made either adiabatic or diathermal as needed. The heat engine undergoes the following sequence of processes:

a. The engine containing the working fluid at T_h is brought to thermal contact with H through diathermal Σ_T and expands isothermally and reversibly at T_h while extracting heat Q_h from H.
b. The wall Σ_T becomes adiabatic and the fluid expands reversibly until its temperature reaches T_l.
c. The fluid is brought to thermal contact with L through diathermal Σ_T and is compressed isothermally and reversibly while rejecting heat Q_l to L.
d. The wall Σ_T becomes adiabatic again and the fluid is compressed reversibly until its temperature reaches T_h.

Assuming that the working fluid is an ideal gas, show that $W = (1 - T_l/T_h)Q$ by means of an explicit computation of work and heat involved in each step. ///

Example 2.4. Material engine: Consider two homogeneous mixtures H and L both at the same temperature T and suppose that the chemical potential of species 1 in H and that in L, denoted by μ_h and μ_l, respectively, satisfy $\mu_h > \mu_l$. If they are brought in contact through a wall permeable to species 1, molecules of 1 will flow from H to L. Instead of the permeable wall, we will insert a material engine ME in between. Once again, we are interested in the amount of work the composite system consisting of H, L, and ME delivers to the work source.

We suppose that only a very small amount of heat and material transfer is involved during one cycle of the engine, leaving T, μ_h, and μ_l constant. For the heat and material transfer from H to ME, we have

$$\mathrm{d}U_h = T\mathrm{d}S_h - \mu_h \mathrm{d}N\,, \tag{2.143}$$

where dN is the number of moles of species 1 being transferred to ME. Similarly,

$$\mathrm{d}U_l = T\mathrm{d}S_l + \mu_l \mathrm{d}N\,. \tag{2.144}$$

Note that ME gives up as many molecules of species 1 to L as it has received from H. Otherwise, there will be an accumulation or depletion of the molecules in ME and it will not qualify as a cycle.

Combining these equations,

$$đW = -(\mathrm{d}U_h + \mathrm{d}U_l) = -T\mathrm{d}S + (\mu_h - \mu_l)\mathrm{d}N\,, \tag{2.145}$$

where $\mathrm{d}S = \mathrm{d}S_h + \mathrm{d}S_l$ is the increment in entropy of the composite system per single cycle since $\mathrm{d}S_{mc} = 0$ as in the previous example. The maximum of $đW$ occurs when $\mathrm{d}S = 0$ and is given by $(\mu_h - \mu_l)\mathrm{d}N$.

Exercise 2.14. In analogy to Carnot cycle, let us consider a reversible material engine operating between two mixtures H and L. We suppose that they are at the same temperature T and denote the chemical potential of species 1 in H and that in L by μ_h and μ_l, respectively, where $\mu_h > \mu_l$. As the working fluid, we use a pure ideal gas of species 1 confined to a cylinder fitted with a frictionless piston. The cylinder is made of a rigid wall that is diathermal and impermeable to all species. However, one side of the wall, which we call Σ_μ, can be made either permeable or impermeable to species 1 as needed. In each of the following steps, expansion or compression is performed both isothermally and reversibly:

a. The engine containing the working fluid at μ_h is brought to thermal contact with H through the permeable Σ_μ and expands while extracting ΔN moles of species 1 from H.
b. The wall Σ_μ becomes impermeable and the fluid expands until the chemical potential of species 1 becomes μ_l.
c. The fluid is brought to thermal contact with L through Σ_μ, which now is made permeable to species 1. The fluid is compressed while rejecting ΔN moles of species 1 to L.
d. The wall Σ_μ is made impermeable again and the fluid is compressed until the chemical potential becomes μ_h.

Noting that

$$\mu(T,P) = \mu^\circ(T) + RT\ln P \tag{2.146}$$

for a pure ideal gas, show that $W = (\mu_h - \mu_l)\Delta N$. Not surprisingly, this is actually the work extracted from an isothermal and reversible expansion of ΔN moles of an ideal gas from the pressure P_h, at which $\mu = \mu_h$, to P_l at which $\mu = \mu_l$. ///

2.10 Euler Relation

We note that the variables occurring in (2.36) are all extensive quantities. That is, they are all proportional to the "size" of the system. This can be expressed more precisely as

$$U(\lambda S, \lambda V, \lambda N_1, \ldots, \lambda N_c) = \lambda U(S, V, N_1, \ldots, N_c)\ , \tag{2.147}$$

where λ is a positive constant. A function that satisfies such a relation is called a homogeneous function of degree one. This leads to the following important equation called the **Euler relation**:

$$U = TS - PV + \sum_{i=1}^{c} \mu_i N_i\ . \tag{2.148}$$

As we see in Sect. 2.15, (2.148) is a mathematical consequence of (2.147) and can be derived without making any further reference to the physical situation beyond what has been made so far. Nevertheless, it is of some interest to consider an alternative, physically more appealing, derivation of (2.148).

Let us consider a large homogeneous body. Within this body, we choose a small part enclosed by the smaller circle in Fig. 2.12 as our system. Note that this act of choosing the system is purely a thought process and does not involve us putting in any physical wall. In other words, the partition separating the system from the rest

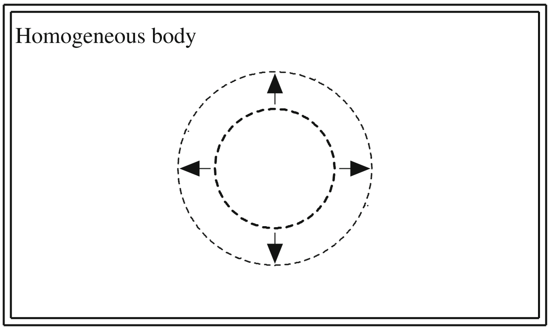

Fig. 2.12 A system taken inside a homogeneous body is indicated by the *smaller circle*. The *larger circle* represents the system after the infinitesimal change we considered in writing (2.150). Note that the expansion of the system boundary has no effect on the physical state of the matter anywhere in the homogeneous body.

of the homogeneous body is diathermal, permeable to all species, and has no effect either on the state or the property of the homogeneous body.[9]

Let u, s, and n_i denote, respectively, the densities of internal energy, the entropy, and the number of moles of species i in the homogeneous body. Then, U, S, and N_i of the system are given by

$$U = uV\ , \quad S = sV\ , \quad \text{and} \quad N_i = n_iV\ , \quad i = 1,\dots,c\ , \tag{2.149}$$

where V is the volume of the system.

Now, let us consider a process in which the partition is enlarged to contain a larger part of the homogeneous body. Once again, this is a thought process and has no impact on the physical state of the body including the values of u, s, and n_1, ..., n_c. But, U, S, and N_1, ..., N_c of the system do change. If we denote by $V + \mathrm{d}V$ the volume of the system after the change, which is indicated in Fig. 2.12 by the larger circle, we have

$$\begin{aligned} U + \mathrm{d}U &= u(V + \mathrm{d}V)\ , \quad S + \mathrm{d}S = s(V + \mathrm{d}V)\ , \\ N_i + \mathrm{d}N_i &= n_i(V + \mathrm{d}V)\ , \quad i = 1,\dots,c\ . \end{aligned} \tag{2.150}$$

Comparing (2.149) and (2.150), we find

$$\mathrm{d}U = u\mathrm{d}V\ , \quad \mathrm{d}S = s\mathrm{d}V\ , \quad \text{and} \quad \mathrm{d}N_i = n_i\mathrm{d}V\ , \quad i = 1,\dots,c\ , \tag{2.151}$$

which is now substituted into (2.37) to yield

$$u\mathrm{d}V = Ts\mathrm{d}V - P\mathrm{d}V + \sum_{i=1}^{c} \mu_i n_i \mathrm{d}V\ . \tag{2.152}$$

Multiplying both sides by $V/\mathrm{d}V$, we arrive at (2.148).

2.11 Gibbs–Duhem Relation

Suppose that the state of the system is altered by infinitesimal changes made to the independent variables S, V, and $N_1, \ldots, N_c$. In general, this will be accompanied by the corresponding changes in the dependent variables U, T, P, and $\mu_1, \ldots, \mu_c$. If the system is homogeneous and in equilibrium both before and after the change is made, (2.148) must hold for both of these states. Thus, applying (2.148) to the system after the change, we write

$$U + \Delta U = (T + \Delta T)(S + \mathrm{d}S) - (P + \Delta P)(V + \mathrm{d}V) + \sum_{i=1}^{c} (\mu_i + \Delta \mu_i)(N_i + \mathrm{d}N_i) , \tag{2.153}$$

where U is the internal energy of the system before the change, and ΔU is the change in the internal energy due to the change in the independent variables. (As explained in Appendix B.1, $\Delta U = \mathrm{d}U + \mathrm{d}^2U/2 + \mathrm{d}^3U/6 + \cdots$, in which the first-order term $\mathrm{d}U$ dominates the remaining higher order terms.) Using (2.37) and (2.148) applied for the initial state, we obtain

$$\Delta U = \mathrm{d}U + S\Delta T - V\Delta P + \sum_{i=1}^{c} N_i \Delta \mu_i + \mathrm{d}S\Delta T - \mathrm{d}V\Delta P + \sum_{i=1}^{c} \mathrm{d}N_i \Delta \mu_i . \tag{2.154}$$

Retaining only the first-order terms, that is, ignoring such terms as $\mathrm{d}S\Delta T$ and replacing ΔU, ΔT, ΔP, and $\Delta \mu_i$, by $\mathrm{d}U$, $\mathrm{d}T$, $\mathrm{d}P$, and $\mathrm{d}\mu_i$, respectively, we find

$$S\mathrm{d}T - V\mathrm{d}P + \sum_{i=1}^{c} N_i \mathrm{d}\mu_i = 0 , \tag{2.155}$$

which is known as the **Gibbs–Duhem relation** and indicates that T, P, and $\mu_1, \ldots, \mu_c$ cannot be varied independently.

Dividing (2.155) by V,

$$\mathrm{d}P = s\mathrm{d}T + \sum_{i=1}^{c} n_i \mathrm{d}\mu_i , \tag{2.156}$$

from which we find

$$\left(\frac{\partial P}{\partial T}\right)_{\mu} = s \quad \text{and} \quad \left(\frac{\partial P}{\partial \mu_i}\right)_{T,\mu_{j\neq i}} = n_i . \tag{2.157}$$

The first equation, for example, is obtained by setting $\mathrm{d}\mu_1 = \cdots = \mathrm{d}\mu_c = 0$ in (2.156) and dividing both sides by $\mathrm{d}T$.

2.12 ‡Gibbs Phase Rule

In thermodynamics, the word **phase** refers to a homogeneous body without any regard to its size. Thermodynamic state of a phase can be specified once the values of s and $n_1, \dots, n_c$ are fixed. Homogeneous bodies with identical values of these variables are the same phase regardless of their size. Those with distinct values of these variables constitute distinct phases.

Multiple phases can coexist at equilibrium. By heating water under atmospheric pressure, you can achieve liquid–vapor coexistence of water in a kettle at 100°C. If you pour enough sugar into a glass of water, you can observe the coexistence between aqueous sugar solution and sugar crystals.

Experience shows, however, that we cannot maintain the liquid–vapor coexistence of water if we fix the pressure and change the temperature from 100°C. You can certainly achieve the coexistence at temperatures other than 100°C, but only by properly adjusting the pressure. Why should this be?

The interface between coexisting phases may be regarded as a partition that is diathermal, movable, and permeable to all species. Continuing with the example of pure water, therefore, we have

$$T^l = T^v\,, \quad P^l = P^v\,, \quad \text{and} \quad \mu^l = \mu^v \tag{2.158}$$

as the condition of equilibrium, where the superscripts l and v refer to the liquid and the vapor phases, respectively. Now, suppose that we perturb the state of the system by changing its temperature, for example. If the phase coexistence is to subsist, (2.158) must hold after the change also:

$$T^l + \mathrm{d}T^l = T^v + \mathrm{d}T^v\,, \quad P^l + \mathrm{d}P^l = P^v + \mathrm{d}P^v\,, \quad \text{and} \quad \mu^l + \mathrm{d}\mu^l = \mu^v + \mathrm{d}\mu^v\,. \tag{2.159}$$

It follows that

$$\mathrm{d}T^l = \mathrm{d}T^v\,, \quad \mathrm{d}P^l = \mathrm{d}P^v\,, \quad \text{and} \quad \mathrm{d}\mu^l = \mathrm{d}\mu^v\,. \tag{2.160}$$

As we have seen in the previous section, these infinitesimal quantities are subject to the Gibbs–Duhem relation:

$$s^l\mathrm{d}T - \mathrm{d}P + n^l\mathrm{d}\mu = 0 \quad \text{and} \quad s^v\mathrm{d}T - \mathrm{d}P + n^v\mathrm{d}\mu = 0\,, \tag{2.161}$$

where we dropped the superscripts from $\mathrm{d}T$, $\mathrm{d}P$, and $\mathrm{d}\mu$ as they are common to both phases. If we hold P constant as we change T, (2.161) reduces to

$$s^l\mathrm{d}T + n^l\mathrm{d}\mu = 0 \quad \text{and} \quad s^v\mathrm{d}T + n^v\mathrm{d}\mu = 0\,. \tag{2.162}$$

Unless the ratio s^l/n^l happens to be equal to s^v/n^v, these equations demand that both $\mathrm{d}T$ and $\mathrm{d}\mu$ be zero. That is, if we want to perturb the state of the system while maintaining the vapor–liquid coexistence, we cannot possibly hold P constant. Instead, (2.161) uniquely determines the necessary change one must make to P for a given value of $\mathrm{d}T$. The same set of equations also determine the value of $\mathrm{d}\mu$.

In the case of sugar crystals in a glass of water, the condition of equilibrium is given by

$$T^c = T^l\ , \quad P^c = P^l\ , \quad \mu_s^c = \mu_s^l, \qquad \text{and} \quad \mu_w^c \geq \mu_w^l\ , \tag{2.163}$$

where the superscripts c and l refer to the crystal and liquid phases, respectively. The subscript s denotes sugar while w refers to water. The inequality in the last relation cannot be dropped since the crystal is, by assumption, pure sugar, and the number of water molecules in the crystal is incapable of a negative variation. Considering an infinitesimal change that maintains the coexistence, we have

$$\mathrm{d}T^c = \mathrm{d}T^l\ , \quad \mathrm{d}P^c = \mathrm{d}P^l\ , \quad \mathrm{d}\mu_s^c = \mathrm{d}\mu_s^l\ , \tag{2.164}$$

while

$$\mu_w^c + \mathrm{d}\mu_w^c \geq \mu_w^l + \mathrm{d}\mu_w^l\ , \tag{2.165}$$

which cannot be simplified further. The Gibbs–Duhem relations for the phases can then be written as

$$s^l\mathrm{d}T - \mathrm{d}P + n_s^l\mathrm{d}\mu_s + n_w^l\mathrm{d}\mu_w^l = 0 \quad \text{and} \quad s^c\mathrm{d}T - \mathrm{d}P + n_s^c\mathrm{d}\mu_s = 0\ . \tag{2.166}$$

Thus, in order to maintain the coexistence, only two of the four infinitesimal quantities $\mathrm{d}T$, $\mathrm{d}P$, $\mathrm{d}\mu_s$, and $\mathrm{d}\mu_w^l$ can be specified independently and only within the confines of the inequality (2.165).

The above consideration can be generalized for coexistence among M phases of c component mixture, for which

$$s^I\mathrm{d}T - \mathrm{d}P + \sum_{i=1}^{c} n_i^I\mathrm{d}\mu_i = 0\ , \quad I = 1,\dots,M\ , \tag{2.167}$$

where the superscripts I labeling the phase should not be confused with exponents. We note that (2.167) provides M equations among $c+2$ infinitesimal quantities $\mathrm{d}T$, $\mathrm{d}P$, and $\mathrm{d}\mu_1, \dots, \mathrm{d}\mu_c$. Thus, only $c+2-M$ of them can be specified independently. This result is known as the **Gibbs phase rule**.

The examples we considered above are consistent with the predictions of the Gibbs phase rule. In the case of vapor–liquid coexistence of water, $M=2$, $c=1$, and hence $c+2-M=1$, indicating that only one of $\mathrm{d}T$, $\mathrm{d}P$, and $\mathrm{d}\mu$ can be specified as we please. For crystal–solution coexistence, $M=2$, $c=2$, and hence $c+2-M=2$.

We note that the phase rule is obtained using the Gibbs–Duhem relation, which is a consequence of (2.37). The validity of the latter equation depends, among other things, on (2.5). But, this equation does not apply to a solid under a nonhydrostatic stress. Thus, when a solid phase is involved, the phase rule we derived applies only if the solid is under a hydrostatic pressure. During the initial stage of the first-order phase transition, the so-called critical nucleus, a small fragment of the new phase, forms in a bulk metastable phase. While the nucleus and the metastable phase are in (unstable) equilibrium, the phase rule does not apply here, either. This is because the nucleus is inhomogeneous and its fundamental equation cannot be written in the form of (2.37). (See Sect. 6.7.3.)

2.13 Free Energies

While isolated systems are conceptually the simplest to consider, rarely in our everyday life do we actually encounter such a system. Far more common is a system whose temperature, for example, is actively maintained through an interaction with some external body. It is therefore of practical importance to develop thermodynamics for systems that are not isolated.

In this section, we present the details only for a closed system held at constant temperature and volume. The analysis, however, can be generalized straightforwardly to other systems and you are invited to explore them in the exercises collected toward the end of this section.

2.13.1 Fixing Temperature

Before we proceed further, we need to know what exactly is meant by temperature being fixed. We recall that $1/T = (\partial S/\partial U)_{V,N}$, which is a function of U, V, N_1, $\ldots$, N_c. Therefore, once the values of these independent variables are fixed, as is the case with any isolated system, the temperature is also fixed. This will be fine as far as we are concerned only with a state of equilibrium. In formulating condition of equilibrium, however, we must compare two states differing infinitesimally by the values of the additional variables as seen from (2.81). When the values of $X_1, \ldots, X_m$ are changed from the equilibrium values in an isolated system, there is no guarantee that the system temperature remain unchanged. Moreover, when we talk about a system held at a given temperature, we presume our ability to set that temperature as we please. Thus, we should demand that the temperature occur in our formulation not as a dependent variable but as an independent variable.

One simple way to fix the temperature of a system is to immerse it in a large body of liquid with uniform temperature and allow for exchange of heat between the two. If the body is much larger than the system itself, the temperature of the body will remain unchanged despite the energy exchange with the system. Such a body is called a **heat bath**.

2.13.2 Condition of Equilibrium

Because we are interested in the condition of equilibrium of the system but not that of the heat bath, we make a few simplifying assumptions about the bath. In addition to being sufficiently large, we assume that the relaxation time of the heat bath is extremely short. That is, the heat bath reestablishes equilibrium very quickly after it is disturbed by exchanging energy with the system. This allows us to assume that the heat bath is always in equilibrium.

Now, suppose that the composite system consisting of the heat bath and the system of interest, as a whole, is isolated. If the composite system is in equilibrium, then the system is evidently in equilibrium at the temperature T of the heat bath. Conversely, if the system is in equilibrium at T, the composite system is also in equilibrium by virtue of the assumptions made of the heat bath. Thus, for equilibrium of the system, it is necessary and sufficient that

$$\delta U^{\mathrm{comp}} = \delta U + \delta U^{B} \geq 0 \tag{2.168}$$

for any possible variation of the state of the composite system. Here the superscripts comp and B denote the composite system and the heat bath, respectively.

Applying (2.37) to the heat bath,

$$\delta U^{B} = T \delta S^{B} \,. \tag{2.169}$$

Since $S^{\mathrm{comp}} = S + S^{B}$ is constant as indicated in *Condition of Equilibrium 3*, $\delta S^{B} = -\delta S$, and hence

$$\delta U^{B} = -T \delta S \,, \tag{2.170}$$

which is now substituted into (2.168) to give

$$\delta U^{\mathrm{comp}} = \delta U - T\delta S = \delta(U - TS) = \delta F \,, \tag{2.171}$$

where we used the fact that the variations considered do not affect T by virtue of the first assumptions made of the heat bath. We also introduced a new quantity called the **Helmholtz free energy** through the equation:

$$F := U - TS \,. \tag{2.172}$$

Note that, when considering all possible variations, the system temperature T was fixed through exchange of heat with the heat bath. Remembering that V and N_1, $\ldots, N_c$ were also fixed and denoting, as before, any other constraints by means of the constant values of $X_{m+1}, \ldots, X_r$, we arrive at the following condition of equilibrium:

Condition of Equilibrium 6 *For equilibrium of a closed system held at a given temperature T and volume V, it is necessary and sufficient that*

$$(\delta F)_{T,V,N_1,\ldots,N_c;X_{m+1},\ldots,X_r} \geq 0 \tag{2.173}$$

holds for any possible variation of the state of the system.

From (2.171) and the discussion in Sect. 2.9.2, we have

$$\delta F = \delta U^{\mathrm{comp}} = \delta W^{\mathrm{rev}} \,. \tag{2.174}$$

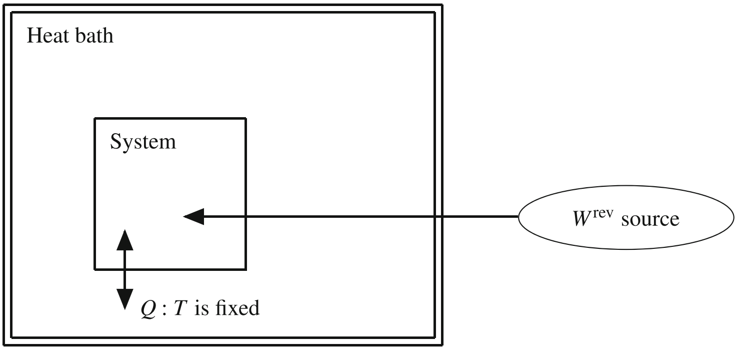

Fig. 2.13 The system of interest in contact with a heat bath. The reversible work source is connected only to the system and not to the heat bath.

Thus, *Condition of Equilibrium 4* applies also to the current situation provided that the subscript S is replaced by T in (2.105). We emphasize that the reversible work source is connected only to the system of interest and not to the heat bath as shown in Fig. 2.13. This is because the reversible work source does not exchange heat with other bodies. Thus, δW^{rev} in (2.174) is the work done on the system when it is allowed to exchange heat with the heat bath as needed in order to keep its temperature constant.

2.13.3 Direction of a Spontaneous Process

The Helmholtz free energy cannot increase for spontaneous processes occurring in the system. To see this, we start by noting that

$$\mathrm{d}S^{\text{comp}} = \mathrm{d}S + \mathrm{d}S^B = \mathrm{d}S + \frac{1}{T}\mathrm{d}U^B \,. \tag{2.175}$$

Because the composite system is isolated, $\mathrm{d}U^B = -\mathrm{d}U$:

$$\mathrm{d}S^{\text{comp}} = \mathrm{d}S - \frac{1}{T}\mathrm{d}U = \frac{\mathrm{d}(TS-U)}{T} = -\frac{\mathrm{d}F}{T} \,. \tag{2.176}$$

For spontaneous processes in the composite system, $\mathrm{d}S^{\text{comp}} \geq 0$, and hence $\mathrm{d}F \leq 0$.

Applying (2.174) for a finite (as opposed to infinitesimal) constant temperature process, we have

$$\Delta F = W^{\text{rev}} \,. \tag{2.177}$$

Likewise, (2.176) gives

$$\Delta S^{\text{comp}} = -\frac{\Delta F}{T} \tag{2.178}$$

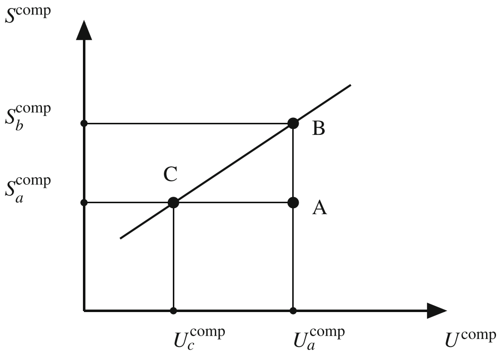

Fig. 2.14 The entropy change $\Delta S^{\text{comp}} = S_b^{\text{comp}} - S_a^{\text{comp}}$ for the spontaneous process A→B is related to the energy difference $W^{\text{rev}} = U_c^{\text{comp}} - U_a^{\text{comp}}$ by (2.179).

for a finite process of constant T. Combining (rather blindly) these equations, we obtain

$$\Delta S^{\text{comp}} = -\frac{W^{\text{rev}}}{T} \,. \tag{2.179}$$

We examine the validity of this equation closely in the next subsection. Accepting (2.179) for a moment, suppose that W^{rev} is positive so that ΔS^{comp} is negative. Identifying $S' - S$ in (2.20) with ΔS^{comp} and using (2.179), we conclude that the probability that the system undergoes the unfavorable finite change as a result of spontaneous fluctuation is given by

$$e^{-W^{\text{rev}}/k_BT} \,. \tag{2.180}$$

You will frequently encounter (2.180) when studying activated processes such as nucleation. If W^{rev} is negative, then ΔS^{comp} is positive and the process occurs spontaneously.

2.13.4 †W^{rev} and a Spontaneous Process

At this point, you may be feeling a little uncomfortable with (2.179). In fact, (2.176) pertains to a spontaneous process, while (2.174) is written for a process that is carried out reversibly by means of a reversible work source. So, δF in (2.174) and $\mathrm{d}F$ in (2.176) refer to *different processes*. Is it really admissible to combine these two equations to get (2.179)? How do we know that these two quantities have the same value when they refer to different processes?

Figure 2.14 helps us answer this question. Because of the first assumption regarding the heat bath, the slope $\partial S^{\text{comp}}/\partial U^{\text{comp}} = 1/T$ is constant and S^{comp} is a linear function of U^{comp}.

If we prepare the composite system in state A and simply let it evolve, it will eventually reach state B. The resulting change in entropy is

$$\Delta S^{\mathrm{comp}} = S_b^{\mathrm{comp}} - S_a^{\mathrm{comp}} > 0 \,. \tag{2.181}$$

Since the slope of the line is $1/T$, this same quantity is given by

$$\Delta S^{\mathrm{comp}} = \frac{U_a^{\mathrm{comp}} - U_c^{\mathrm{comp}}}{T} \,. \tag{2.182}$$

But, $U_a^{\mathrm{comp}} - U_c^{\mathrm{comp}} > 0$ is the reversible work we would be able to extract from the composite system during the spontaneous process *if* it were to be carried out reversibly, thus leaving the composite system in state C instead of B. Now, W^{rev} denotes the work done *on* the composite system, and hence

$$W^{\mathrm{rev}} = U_c^{\mathrm{comp}} - U_a^{\mathrm{comp}} < 0 \,. \tag{2.183}$$

Combining the last two equations, we arrive at (2.179).

Conversely, if the composite system is initially at state B and a spontaneous fluctuation brings it to state A,

$$\Delta S^{\mathrm{comp}} = S_a^{\mathrm{comp}} - S_b^{\mathrm{comp}} < 0 \,. \tag{2.184}$$

Using Fig. 2.14, we find that this same quantity is given by

$$\Delta S^{\mathrm{comp}} = -\frac{U_a^{\mathrm{comp}} - U_c^{\mathrm{comp}}}{T} \,, \tag{2.185}$$

in which $U_a^{\mathrm{comp}} - U_c^{\mathrm{comp}} > 0$ is the reversible work required to bring the composite system to state A *but starting from state C instead of B*.

It is worth emphasizing that (2.179) holds only if B and C are equilibrium states and state A lies directly below B *and* directly to the right of C.

Fluctuations occurring in a stable system or those that initiate the eventual decay of a metastable system toward a more stable state are examples of process B→A. Using (2.179), we can, if desired, estimate ΔS^{comp} by means of a thought experiment in which the composite system is brought from C to A along a reversible path.[10]

Equation (2.179), when combined with (2.174) and (2.176), implies that

$$F_b - F_a = F_c - F_a \,, \tag{2.186}$$

leading us to expect that any difference between states B and C is confined solely to the heat bath. In fact, the composite system can be brought from state B to C by removing heat from the heat bath. Since the heat bath is extremely large, this has no impact on the state of the system of our interest. Disregarding the difference between states B and C, one may say that *a spontaneous process proceeds in such a direction as to deliver positive work to the reversible work source*.[11]

2.13.5 Fundamental Equation

We note that when F defined by (2.172) is expressed in terms of T, V, and $N_1, \dots, N_c$, the resulting function

$$F = F(T, V, N_1, \dots, N_c) \tag{2.187}$$

is the **Legendre transform** of the internal energy U expressed in terms of S, V, and $N_1, \dots, N_c$. Since the latter is a fundamental equation of the system, (2.187) also qualifies as a fundamental equation. (When the transformation is used in thermodynamics, the condition that $\mathrm{d}^2y/\mathrm{d}x^2$ be of a definite sign in the notation of Sect. C.1 is related to the stability of the system. See Exercises 2.3a and 2.12.)

To arrive at the differential form of the fundamental equation, consider infinitesimal changes in T, V, and $N_1, \dots, N_c$, which induce the corresponding changes in the quantities occurring in (2.172):

$$F + \Delta F = U + \Delta U - (T + \mathrm{d}T)(S + \Delta S) \,. \tag{2.188}$$

Using (2.172), we cancel F on the left-hand side and $U - TS$ on the right to obtain

$$\Delta F = \Delta U - T\Delta S - S\mathrm{d}T - \mathrm{d}T\Delta S \,. \tag{2.189}$$

Retaining the first-order terms only,

$$\mathrm{d}F = \mathrm{d}U - T\mathrm{d}S - S\mathrm{d}T \,. \tag{2.190}$$

Now we use (2.37) and arrive at

$$\mathrm{d}F = -S\mathrm{d}T - P\mathrm{d}V + \sum_{i=1}^{c} \mu_i \mathrm{d}N_i \,, \tag{2.191}$$

which is the differential form of the fundamental equation we seek.

From (2.187), we have

$$\mathrm{d}F = \left(\frac{\partial F}{\partial T}\right)_{V,N} \mathrm{d}T + \left(\frac{\partial F}{\partial V}\right)_{T,N} \mathrm{d}V + \sum_{i=1}^{c} \left(\frac{\partial F}{\partial N_i}\right)_{T,V,N_{j\neq i}} \mathrm{d}N_i \,. \tag{2.192}$$

Since the last two equations hold for any values of $\mathrm{d}T$, $\mathrm{d}V$, and $\mathrm{d}N_1, \dots, \mathrm{d}N_c$, we find

$$-S = \left(\frac{\partial F}{\partial T}\right)_{V,N} , \quad -P = \left(\frac{\partial F}{\partial V}\right)_{T,N} ,$$
$$\text{and} \quad \mu_i = \left(\frac{\partial F}{\partial N_i}\right)_{T,V,N_{j\neq i}} , \quad i = 1, \dots, c \,, \tag{2.193}$$

which are to be contrasted with (2.38).

Exercise 2.15. Show that

$$\left(\frac{\partial F/T}{\partial T}\right)_{V,N} = -\frac{U}{T^2} . \tag{2.194}$$

This identity is known as the **Gibbs–Helmholtz equation**. Following essentially the same approach, you can also show that

$$\left(\frac{\partial G/T}{\partial T}\right)_{P,N} = -\frac{H}{T^2} , \tag{2.195}$$

where G and H are, respectively, the Gibbs free energy and the enthalpy to be introduced in Sect. 2.13.6. This is also called the Gibbs–Helmholtz equation. ///

2.13.6 *Other Free Energies*

The relevant free energy when discussing equilibrium of a closed system held at constant temperature and pressure is the **Gibbs free energy** defined by

$$G := U - TS + PV . \tag{2.196}$$

To see why, attempt the following exercise.

Exercise 2.16. Formulate the condition of equilibrium for a closed system held at constant temperature and pressure. Then, using (2.196), obtain the equations corresponding to (2.176), (2.191), and (2.193). ///

Using (2.148) in (2.196), we find that

$$G = \sum_{i=1}^{c} \mu_i N_i . \tag{2.197}$$

One of the major goals in mixture thermodynamics is to predict μ_i as a function of T, P, and mole fractions $x_1, \dots, x_{c-1}$, where

$$x_i := N_i \bigg/ \sum_{i=1}^{c} N_i . \tag{2.198}$$

Since

$$x_c = 1 - \sum_{i=1}^{c-1} x_i , \tag{2.199}$$

we do not include x_c in the list of independent variables. If functions

$$\mu_i = \mu_i(T, P, x_1, \ldots, x_{c-1}) \,, \quad i = 1, \ldots, c \tag{2.200}$$

can be constructed for each species in a mixture, then G will be known as a function of T, P, and N_1, ..., N_c. But, this function is a fundamental equation of the mixture. From this point of view, various activity coefficient models, which are widely used for correlating phase equilibria data involving liquid phases, represent an effort to construct fundamental equations of mixtures. The following exercise explores the simplest example of such model mixtures.

Exercise 2.17. A mixture in which μ_i of each species is given by

$$\mu_i(T, P, x_1, \ldots, x_{c-1}) = \mu_i^\circ(T) + RT\,(\ln P + \ln x_i) \,, \quad i = 1, \ldots, c \tag{2.201}$$

is called an **ideal gas mixture**. Suppose that a composite system made of two compartments, each containing the gas well described by (2.201), is held at some T and P by a heat bath and movable pistons.

a. Initially, compartment A contained 3 mol of species 1 and 1 mol of species 2, while compartment B contained no species 1 and 2 mol of species 2. Find the number of moles of species 1 in compartment B after they are brought into contact through the diathermal, rigid, and immovable partition permeable to the first but not to the second species and a new state of equilibrium is established.
b. Do the same when compartment A initially contained 3 mol of species 1 but no species 2. The initial numbers of moles in compartment B are the same as in part a.
c. In each case considered above, plot G/RT against the number of moles of species 1 in compartment B. ///

There are other commonly used free energies. For example, when

$$\Omega := U - TS - \sum_{i=1}^{c} \mu_i N_i \tag{2.202}$$

is expressed as a function of T, V, and μ_1, ..., μ_c, it is another fundamental equation. This is commonly known as the **grand potential**. The grand potential is particularly useful in describing open systems. If a system is open to species 1 but not to the others, the appropriate choice of the free energy is

$$\chi := U - TS - \mu_1 N_1 \tag{2.203}$$

to be expressed as a function of T, V, μ_1, and N_2, ..., N_c. A free energy of this type is often called a **semi-grand potential**. Finally, **enthalpy**, defined by

$$H := U + PV \,, \tag{2.204}$$

is also a fundamental equation when it is expressed as a function of S, P, and $N_1, \ldots, N_c$. Thus, enthalpy is a free energy characterizing a system held at constant entropy, pressure, and the number of moles of each species.

Exercise 2.18. Show that

$$\left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_{j\neq i}} = \left(\frac{\partial F}{\partial N_i}\right)_{T,V,N_{j\neq i}} = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_{j\neq i}} = \left(\frac{\partial H}{\partial N_i}\right)_{S,P,N_{j\neq i}} . \tag{2.205}$$

///

Exercise 2.19. Use (2.202) as a starting point to derive (2.157). ///

The existence of a multitude of free energies prompts the following question: For a system consisting of c components, how many fundamental equations can we come up with? Let us start from the internal energy expressed in terms of S, V, and $N_1, \ldots, N_c$. A new free energy is constructed by replacing some of these variables by the corresponding intensive quantities, for example, S by T, V by $-P$, or, μ_i by N_i. (See Sect. 2.15 for an explicit demonstration that μ_i is an intensive quantity.) For each of the extensive variables, we may either choose to keep it or replace it. The choice we make for a given variable is independent of those we make for the others. Apparently, therefore, there are 2^{c+2} distinct free energies.

Of these, the choice of replacing every extensive quantity by the corresponding intensive variable does not work. The first sign of trouble is that the quantity defined by

$$\Upsilon := U - TS + PV - \sum_{i=1}^{c} \mu_i N_i \tag{2.206}$$

is, according to the Euler relation, identically zero. There are more convincing reasons why Υ does not qualify as a free energy. Firstly, when all the extensive quantities are replaced by the corresponding intensive quantities, information regarding the size of the system is permanently lost. Secondly, T, P, $\mu_1, \ldots, \mu_c$, which are to be used as the independent variables, are *not* independent of each other as seen from the Gibbs–Duhem relation.

In this way, we see that the total of $2^{c+2} - 1$ fundamental equations can be constructed. If we include those functions we obtain by starting from the entropy expressed as a function of U, V, and $N_1, \ldots, N_c$, we will find the same number of fundamental equations, known as **Massieu functions**, examples of which include $-F/T$, $-G/T$, and $-\Omega/T$. In total, therefore, there are $2(2^{c+2} - 1)$ fundamental equations all pertaining to the same system. Of course, only a few of them, such as those we have mentioned already, will be of any use in practice.

Exercise 2.20. You might still feel a slight discomfort with the above discussion of Υ. After all, we did follow the well-defined procedure of the Legendre transformation, did we not? Why should it ever fail? To put your mind at ease, attempt to find the Legendre transformation

$$\Upsilon := \Omega + PV \tag{2.207}$$

of the grand potential

$$\Omega = \Omega(T, V, \mu_1, \ldots, \mu_c) \,. \tag{2.208}$$

Exactly where does the procedure break down? ///

2.14 ‡Maxwell Relation

We recall the following result from calculus. Let $f = f(x,y)$ be a scalar-valued function of two variables x and y. If both

$$\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right) \quad \text{and} \quad \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right) \tag{2.209}$$

are continuous in some domain, then

$$\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right) = \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right) \tag{2.210}$$

in that same domain. For example, let $f = x^2 y + x \ln y$. Then,

$$\frac{\partial f}{\partial x} = 2xy + \ln y \quad \text{and} \quad \frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right) = 2x + \frac{1}{y} \,, \tag{2.211}$$

while

$$\frac{\partial f}{\partial y} = x^2 + \frac{x}{y} \quad \text{and} \quad \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right) = 2x + \frac{1}{y} \,. \tag{2.212}$$

As advertised, we ended up with the same function regardless of the order of taking the derivatives.

By applying this result from calculus to various free energies, we can obtain numerous **Maxwell relations**. Each Maxwell relation predicts an equality between a pair of seemingly unrelated partial derivatives, reflecting completely different physical situations. From the first two of (2.193), for example, we see that

$$-\left(\frac{\partial S}{\partial V}\right)_{T,N} = \frac{\partial^2 F}{\partial T \partial V} = -\left(\frac{\partial P}{\partial T}\right)_{V,N} \,, \tag{2.213}$$

and hence

$$\left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial P}{\partial T}\right)_{V,N} \,. \tag{2.214}$$

Since $T\mathrm{d}S = đQ$ for a reversible process, the left-hand side of this equation is related to the heat absorbed by the system upon expansion at constant T and N_1, ..., N_c. On the other hand, the right-hand side is related to the increase in P upon heating at constant V and N_1, ..., N_c. It will be difficult to anticipate that these quantities pertaining to these distinct physical processes are related in this simple manner. Yet, we have reached this conclusion by admitting only the existing of a fundamental equation and some basic mathematical properties about it. In particular, we made no reference to any specific material from which the system is made. Here lies the power of thermodynamics. Equation (2.214) holds for *any* homogeneous body in equilibrium.

Exercise 2.21. Derive the following Maxwell relations:

a.

$$-\left(\frac{\partial S}{\partial N_i}\right)_{T,V,N_{j\neq i}} = \left(\frac{\partial \mu_i}{\partial T}\right)_{V,N} . \tag{2.215}$$

b.

$$-\left(\frac{\partial P}{\partial N_i}\right)_{T,V,N_{j\neq i}} = \left(\frac{\partial \mu_i}{\partial V}\right)_{T,N} . \tag{2.216}$$

c.

$$-\left(\frac{\partial S}{\partial P}\right)_{T,N} = \left(\frac{\partial V}{\partial T}\right)_{P,N} . \tag{2.217}$$

d.

$$-\left(\frac{\partial S}{\partial N_i}\right)_{T,P,N_{j\neq i}} = \left(\frac{\partial \mu_i}{\partial T}\right)_{P,N} . \tag{2.218}$$

e.

$$\left(\frac{\partial V}{\partial N_i}\right)_{T,P,N_{j\neq i}} = \left(\frac{\partial \mu_i}{\partial P}\right)_{T,N} . \tag{2.219}$$

///

Exercise 2.22. For a c component system, how many Maxwell relations are there? ///

Exercise 2.23. Using the ideal gas equation of state $PV = NRT$, show that

$$\left(\frac{\partial U}{\partial V}\right)_{T,N} = 0 \, , \tag{2.220}$$

that is U of an ideal gas is independent of its volume. ///

2.15 ‡Partial Molar Quantities

Let $\theta = \theta(T,P,N_1,\dots,N_c)$ be an extensive quantity. That is

$$\theta(T,P,\lambda N_1,\dots,\lambda N_c) = \lambda\theta(T,P,N_1,\dots,N_c) \, , \tag{2.221}$$

where λ is a positive number. The **partial molar quantity** $\overline{\theta}_i$ is defined by

$$\overline{\theta}_i(T,P,N_1,\ldots,N_c) := \left(\frac{\partial\theta}{\partial N_i}\right)_{T,P,N_{j\neq i}} . \tag{2.222}$$

One particularly important example of $\overline{\theta}_i$ is the partial molar Gibbs free energy:

$$\overline{G}_i(T,P,N_1,\ldots,N_c) = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_{j\neq i}} , \tag{2.223}$$

which is nothing but the chemical potential of species i. As other examples of partial molar quantities, we rewrite the last two equations in Exercise 2.21 as

$$\overline{S}_i = -\left(\frac{\partial\mu_i}{\partial T}\right)_{P,N} \quad \text{and} \quad \overline{V}_i = \left(\frac{\partial\mu_i}{\partial P}\right)_{T,N} , \tag{2.224}$$

respectively.

Partial molar quantities are intensive. To see why this might be so, we first recall the Gibbs–Duhem relation, (2.155), which reduces to

$$S\mathrm{d}T - V\mathrm{d}P + N\mathrm{d}\mu = 0 \tag{2.225}$$

for a single component system. Upon division by N, we find

$$\mathrm{d}\mu = -\underline{S}\mathrm{d}T + \underline{V}\mathrm{d}P , \tag{2.226}$$

where $\underline{S} := S/N$ and $\underline{V} := V/N$. For any changes in T and P, the corresponding change in μ is given by (2.226). Since neither $\underline{S}$ nor $\underline{V}$ depends on the size of the system, it follows that the chemical potential of a single component system is independent of the size of the system. Thus, it is an intensive quantity.

It seems natural to expect that the same conclusion hold when we move to a multicomponent system. But, because chemical potentials are just a particular example of partial molar quantities, we are lead to expect that the partial molar quantities are, in general, intensive quantities.

Now we verify this expectation. We start by noting that (2.221) holds for any positive value of N_i. Thus, when we take the partial derivative of (2.221) with respect to N_i, the equality still holds.[12] Thus,

$$\frac{\partial\theta(T,P,M_1,\ldots,M_c)}{\partial M_i}\frac{\partial M_i}{\partial N_i} = \lambda\frac{\partial\theta(T,P,N_1,\ldots,N_c)}{\partial N_i} , \tag{2.227}$$

where $M_i := \lambda N_i$, and hence $\partial M_i/\partial N_i = \lambda$. From (2.222), the partial derivative on the left-hand side of (2.227) is the partial molar quantity $\overline{\theta}_i$ of the system containing M_i moles of species i. Thus, we have

$$\overline{\theta}_i(T,P,M_1,\ldots,M_c) = \overline{\theta}_i(T,P,N_1,\ldots,N_c) . \tag{2.228}$$

Since λ is arbitrary, this equation holds even if we set $\lambda = 1/\sum_i N_i$:

$$\overline{\theta}_i(T,P,x_1,\dots,x_{c-1}) = \overline{\theta}_i(T,P,N_1,\dots,N_c)\ , \tag{2.229}$$

where $x_i = N_i/\sum_i N_i$ is the mole fraction of the ith species. Note that only $c-1$ of the mole fractions are independent because $\sum_i x_i \equiv 1$. *According to (2.229), $\overline{\theta}_i$ is an intensive quantity.*

Next, we consider the partial derivative of (2.221) with respect to λ:

$$\sum_{i=1}^{c} \frac{\partial\theta(T,P,M_1,\dots,M_c)}{\partial M_i}\frac{\partial M_i}{\partial\lambda} = \theta(T,P,N_1,\dots,N_c)\ . \tag{2.230}$$

Since $\partial M_i/\partial\lambda = N_i$, we find

$$\sum_{i=1}^{c} \overline{\theta}_i(T,P,x_1,\dots,x_{c-1})N_i = \theta(T,P,N_1,\dots,N_c)\ . \tag{2.231}$$

Essentially, the identical approach can be used to derive (2.148). In view of this, (2.231) is often referred to as the **generalized Euler relation** .

If we set $\theta = G$, (2.231) becomes

$$G(T,P,N_1,\dots,N_c) = \sum_{i=1}^{c} \overline{G}_i(T,P,x_1,\dots,x_{c-1})N_i\ , \tag{2.232}$$

which is just (2.197) since $\overline{G}_i = \mu_i$. To get something new, let $\theta = V$. Then,

$$V(T,P,N_1,\dots,N_c) = \sum_{i=1}^{c} \overline{V}_i(T,P,x_1,\dots,x_{c-1})N_i\ , \tag{2.233}$$

or dividing by $\sum_i N_i$,

$$\underline{V}(T,P,N_1,\dots,N_c) = \sum_{i=1}^{c} \overline{V}_i(T,P,x_1,\dots,x_{c-1})x_i\ . \tag{2.234}$$

Equations like this occur very often in mixture thermodynamics.

Just like the Gibbs–Duhem relation followed from the Euler relation in Sect. 2.11, we can derive the generalized Gibbs–Duhem relation from the generalized Euler relation using the identical approach. The only difference is in the symbols we use.

As in Sect. 2.11, suppose that the state of the system has changed as a result of infinitesimal changes of T, P, and $N_1, \dots, N_c$. Both θ and $\overline{\theta}_1, \dots, \overline{\theta}_c$ will change as a result. Applying (2.231) to the state after the change, we may write

$$\theta + \Delta\theta = \sum_{i=1}^{c} (\overline{\theta}_i + \Delta\overline{\theta}_i)(N_i + \mathrm{d}N_i)\ . \tag{2.235}$$

From this, we subtract (2.231) applied to the state prior to the infinitesimal change and obtain

$$\Delta\theta = \sum_{i=1}^{c} \overline{\theta}_i \mathrm{d}N_i + \sum_{i=1}^{c} N_i \Delta\overline{\theta}_i + \sum_{i=1}^{c} \Delta\overline{\theta}_i \mathrm{d}N_i \,. \tag{2.236}$$

Retaining the first-order terms only,

$$\mathrm{d}\theta = \sum_{i=1}^{c} \overline{\theta}_i \mathrm{d}N_i + \sum_{i=1}^{c} N_i \mathrm{d}\overline{\theta}_i \,. \tag{2.237}$$

But, since θ is a function of T, P, and $N_1, \ldots, N_c$,

$$\mathrm{d}\theta = \theta_T \mathrm{d}T + \theta_P \mathrm{d}P + \sum_{i=1}^{c} \overline{\theta}_i \mathrm{d}N_i \,, \tag{2.238}$$

where

$$\theta_T := \left(\frac{\partial\theta}{\partial T}\right)_{P,N} \quad \text{and} \quad \theta_P := \left(\frac{\partial\theta}{\partial P}\right)_{T,N} \,. \tag{2.239}$$

Combining (2.237) and (2.238), we finally arrive at

$$0 = -\theta_T \mathrm{d}T - \theta_P \mathrm{d}P + \sum_{i=1}^{c} N_i \mathrm{d}\overline{\theta}_i , \tag{2.240}$$

which is called the **generalized Gibbs–Duhem relation**.

Once again, let $\theta = G$. Then, (2.240) becomes

$$0 = -G_T \mathrm{d}T - G_P \mathrm{d}P + \sum_{i=1}^{c} N_i \mathrm{d}\mu_i \,. \tag{2.241}$$

But, since

$$G_T := \left(\frac{\partial G}{\partial T}\right)_{P,N} = -S \quad \text{and} \quad G_P := \left(\frac{\partial G}{\partial P}\right)_{T,N} = V \,, \tag{2.242}$$

(2.241) is nothing but the usual Gibbs–Duhem relation.

Exercise 2.24. Establish (2.74). ///

2.16 Graphical Methods

In this section, we discuss a few graphical methods you will encounter in later chapters. From a computational point of view, the accuracy expected of such methods is not very high. Yet, they do have intuitive appeal and thus help us understand certain key concepts in thermodynamics. On occasion, they can also help diagnose difficulties that may arise in practical computations.

2.16.1 Pure Systems: $\underline{F}$ Versus $\underline{V}$ (Constant T)

Recall the definition of the Helmholtz free energy in (2.172). Using (2.148), we find

$$F := U - TS = -PV + \mu N \,. \tag{2.243}$$

for a single component system, where N is the number of moles in the system. Dividing both sides by N, we obtain

$$\underline{F} := \frac{F}{N} = -P\underline{V} + \mu \,, \tag{2.244}$$

where $\underline{V} := V/N$. We now show that

$$-P = \left(\frac{\partial \underline{F}}{\partial \underline{V}}\right)_T \,. \tag{2.245}$$

To see this, we apply (2.191) to a single component system and restricting our attention to processes in which T and N are held constant:

$$\mathrm{d}F = -P\mathrm{d}V \,. \tag{2.246}$$

Dividing both sides by N,

$$\mathrm{d}\underline{F} = -P\mathrm{d}\underline{V} \,, \tag{2.247}$$

where we note that $(\mathrm{d}V)/N = \mathrm{d}(V/N)$ since N is held fixed. Likewise for $(\mathrm{d}F)/N$. Dividing both sides of (2.247) by $\mathrm{d}\underline{V}$ and recalling that the equation holds only for constant T and N processes, we arrive at

$$-P = \left(\frac{\partial \underline{F}}{\partial \underline{V}}\right)_{T,N} = \left(\frac{\partial \underline{F}}{\partial \underline{V}}\right)_T \,. \tag{2.248}$$

In the last step, we used the fact that $\underline{F}$ is a molar quantity and hence is independent of N. Alternatively, we could proceed more mechanically as follows:

$$-P = \left(\frac{\partial F}{\partial V}\right)_{T,N} = \left(\frac{\partial F/N}{\partial V/N}\right)_{T,N} = \left(\frac{\partial \underline{F}}{\partial \underline{V}}\right)_{T,N} = \left(\frac{\partial \underline{F}}{\partial \underline{V}}\right)_T \,. \tag{2.249}$$

Equations (2.244) and (2.245) lead to the graphical construction illustrated in Fig. 2.15. Specifically, suppose that the isotherm is produced at some temperature T of interest. If we draw the tangent line at some particular value of $\underline{V}$, say $\underline{V}^*$, the negative of the slope is the pressure P^* at $(T, \underline{V}^*)$. The intercept of the tangent line on the $\underline{F}$-axis (on which $\underline{V} = 0$) is computed as

$$\underline{F}^* - \left(\frac{\partial \underline{F}}{\partial \underline{V}}\right)_T \bigg|_{\underline{V}=\underline{V}^*} \underline{V}^* = \underline{F}^* + P^*\underline{V}^* = \mu^* \,, \tag{2.250}$$

where we used (2.244). That is, the intercept is the chemical potential at $(T, \underline{V}^*)$.

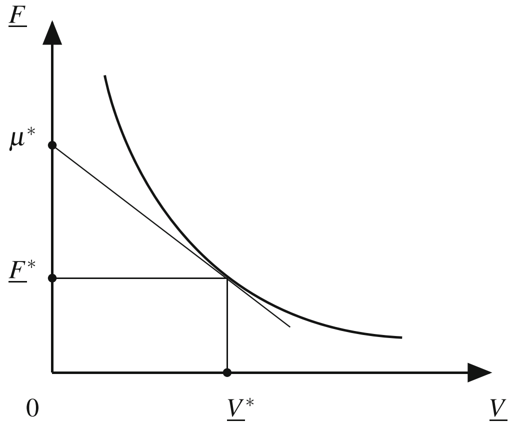

Fig. 2.15 Graphical construction involving an $\underline{F}$ versus $\underline{V}$ isotherm.

2.16.1.1 Gibbs–Duhem Relation at Constant T: Interpretation

Now, let us imagine what happens to the tangent line in Fig. 2.15 if we move $\underline{V}^*$ to the right. We see that, as the tangent line rolls on the curve, the intercept on the $\underline{F}$-axis (μ^*) decreases while the slope ($-P^*$) increases. In other words, at a given temperature, a decrease in μ is accompanied by a decrease in P. This is actually a consequence of the Gibbs–Duhem relation (2.155), which reduces to

$$\mathrm{d}\mu = \underline{V}\mathrm{d}P\,, \quad T \text{ const.} \tag{2.251}$$

for constant T processes in a pure system. In this way, the Gibbs–Duhem relation acquires a graphical interpretation.

2.16.1.2 †Gibbs–Duhem Relation at Constant T: Derivation

It is somewhat amusing to turn the above observation around and derive (2.251) graphically. Let us draw two tangent lines to the $\underline{F}$-$\underline{V}$ isotherm, one at $\underline{V}^*$ and the other at $\underline{V} = \underline{V}^* + \mathrm{d}\underline{V}$ as shown in Fig. 2.16. The negative of the slope and the intercept on the $\underline{F}$-axis of the second tangent line are the pressure and the chemical potential at $(T, \underline{V}^* + \mathrm{d}\underline{V})$, which we denote by $P^* + \Delta P$ and $\mu^* + \Delta\mu$, respectively.

If we shift this second tangent line vertically upward till it passes through the point of tangent (A_1) of the first tangent line at $\underline{V} = \underline{V}^*$, the intercept of the resulting line is

$$\mu^* + \Delta'\mu = \underline{F}^* + (P^* + \Delta P)\underline{V}^*\,. \tag{2.252}$$

Using (2.250), we find that

$$\Delta'\mu = \underline{V}^*\Delta P\,. \tag{2.253}$$

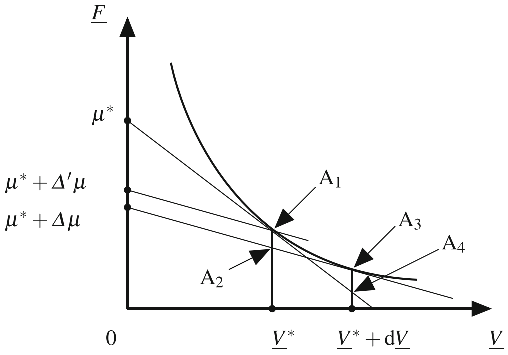

Fig. 2.16 Graphical derivation of the Gibbs–Duhem relation for a constant T process in a pure system.

We now show that the difference between $\Delta'\mu$ and $\Delta\mu$ is zero to the first order of $d\underline{V}$. In fact,

$$\Delta'\mu - \Delta\mu = (\mu^* + \Delta'\mu) - (\mu^* + \Delta\mu) = \mathrm{A_1A_2} \propto \mathrm{A_3A_4} \;, \tag{2.254}$$

where $\mathrm{A_1A_2}$ is the length of the line segment connecting points $\mathrm{A_1}$ and A_2. Likewise for $\mathrm{A_3A_4}$. But,

$$\mathrm{A_3A_4} = \underline{F}(\underline{V}^* + d\underline{V}) - \left[\underline{F}(\underline{V}^*) + \left(\frac{\partial \underline{F}}{\partial \underline{V}} \right)_T \bigg|_{\underline{V}=\underline{V}^*} d\underline{V} \right] = \text{h.o.} \tag{2.255}$$

Thus, retaining up to the first-order term in (2.253), we have

$$d\mu = \underline{V}^* dP \tag{2.256}$$

for a constant T process. Since the equality holds for any $\underline{V}^*$, (2.251) is now established.

2.16.2 Binary Mixtures: $\underline{G}$ Versus x_1 (Constant T and P)

From (2.148) and (2.196), we have

$$G := U - TS + PV = \mu_1 N_1 + \mu_2 N_2 \tag{2.257}$$

for a binary mixture. Dividing both sides by $N := N_1 + N_2$, we obtain

$$\underline{G} = \mu_1 x_1 + \mu_2 x_2 \;, \tag{2.258}$$

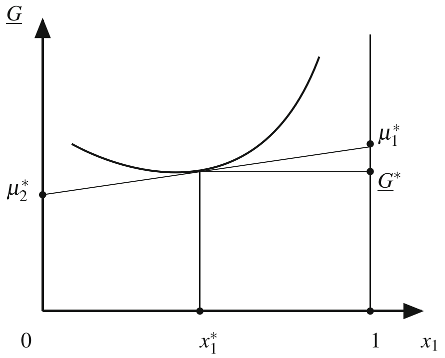

Fig. 2.17 Graphical construction involving a $\underline{G}$ versus x_1 plot at constant (T,P).

where $\underline{G} := G/N$ and $x_i := N_i/N$. To see the physical meaning of the slope of the $\underline{G}$ versus x_1 plot, we recall from Exercise 2.16 that

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P + \mu_1\mathrm{d}N_1 + \mu_2\mathrm{d}N_2 \tag{2.259}$$

and consider constant T and P processes in which $N := N_1 + N_2$ is also held constant. This somewhat unusual constraint does not necessarily imply any chemical reaction between species 1 and 2. It simply states that, whenever species 1 enters the system, the equal number of moles of species 2 needs to be extracted from it. For such processes,

$$\mathrm{d}G = (\mu_1 - \mu_2)\mathrm{d}N_1\ , \quad T,P,N \text{ const.} \tag{2.260}$$

Dividing both sides by N,

$$\mathrm{d}\underline{G} = (\mu_1 - \mu_2)\mathrm{d}x_1\ , \quad T,P \text{ const.} \tag{2.261}$$

where $\underline{G} := G/N$ and $x_1 := N_1/N$. We also dropped the reference to N being constant since $\underline{G}$ is a molar quantity and hence, in this case, is a function of T, P, and x_1 only. Dividing (2.261) by $\mathrm{d}x_1$, we find

$$\left(\frac{\partial \underline{G}}{\partial x_1}\right)_{T,P} = \mu_1 - \mu_2\ . \tag{2.262}$$

This motivates the graphical method illustrated in Fig. 2.17. We draw a tangent line to the $\underline{G}$ versus x_1 curve for given (T,P) at the mole fraction $x_1 = x_1^*$. Its intercept on the $\underline{G}$-axis (at $x_1 = 0$) is μ_2 of the mixture at (T,P,x_1^*), which we denote by μ_2^*. In fact,

$$\underline{G}^* - \left(\frac{\partial \underline{G}}{\partial x_1}\right)_{T,P}\Bigg|_{x_1=x_1^*} x_1^* = \underline{G}^* - (\mu_1^* - \mu_2^*)x_1^* = \mu_2^*\ , \tag{2.263}$$

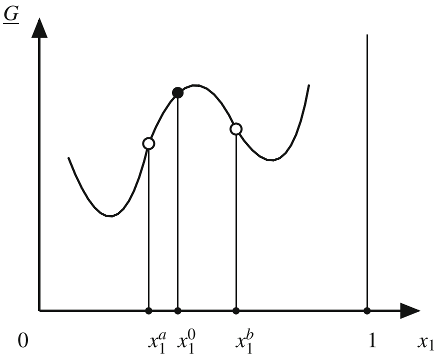

Fig. 2.18 $\underline{G}$ versus x_1 plot at constant (T,P) showing two inflection points indicated by the *open circles*.

where we used (2.258) and the identity $x_1 + x_2 \equiv 1$. Similarly, the intercept on the vertical line at $x_1 = 1$ is μ_1 of the same mixture:

$$\underline{G}^* + \left(\frac{\partial \underline{G}}{\partial x_1}\right)_{T,P}\bigg|_{x_1=x_1^*}(1 - x_1^*) = \underline{G}^* + (\mu_1^* - \mu_2^*)x_2^* = \mu_1^* \,. \tag{2.264}$$

2.16.2.1 Gibbs–Duhem Relation at Constant T and P: Interpretation

As in Sect. 2.16.1.1, the above graphical method provides a graphical interpretation of the Gibbs–Duhem relation applied to constant (T,P) processes in a binary mixture:

$$x_1 \mathrm{d}\mu_1 + x_2 \mathrm{d}\mu_2 = 0\,, \quad T,P\,\text{const.} \tag{2.265}$$

In fact, imagine how the intercepts at $x_1 = 0$ and $x_1 = 1$ move as the tangent line rolls on the $\underline{G}$ versus x_1 plot with increasing x_1. From the figure, it is clear that μ_1 increases while μ_2 decreases. But, that is exactly what (2.265) indicates.

The $\underline{G}$ versus x_1 plot may contain inflection points as shown in Fig. 2.18. As x_1 passes through the inflection point at x_1^a in the figure, μ_1 goes through a local maximum, while μ_2 goes through a local minimum. Beyond this inflection point, the curve will be concave down, and μ_1 now decreases while μ_2 increases. In this way, we see that $\mathrm{d}\mu_1$ and $\mathrm{d}\mu_2$ either have opposite signs or they are simultaneously zero. Again, this behavior is consistent with (2.265).

As we shall see in Sect. 2.16.2.3, a binary mixture is unstable with respect to phase separation if its $\underline{G}$ versus x_1 curve is concave down. Thus, x_1^a marks the onset of instability. In Fig. 2.18, the curve develops another inflection point at x_1^b. For $x_1 > x_1^b$, the curve is concave up and the mixture regains its stability.

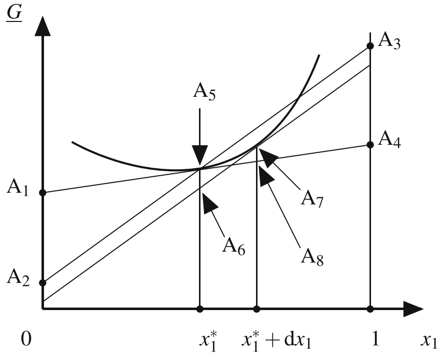

Fig. 2.19 Graphical derivation of the Gibbs–Duhem relation for a constant (T, P) process in a binary mixture.

2.16.2.2 †Gibbs–Duhem Relation at Constant T and P: Derivation

As in Sect. 2.16.1.2, let us derive (2.265) graphically. For this purpose, we draw another tangent line at $x_1 = x_1^* + \mathrm{d}x_1$ as illustrated in Fig. 2.19. Its intercepts on the $\underline{G}$-axis is the chemical potential of species 2 at $(T, P, x_1 + \mathrm{d}x_1^*)$, which we denote by $\mu_2^* + \Delta\mu_2$. The intercept on the vertical line $x_1 = 1$ is the chemical potential of species 1 at the same condition and is denoted by $\mu_1^* + \Delta\mu_1$.

Now, we shift the tangent line at $x_1 = x_1^* + \mathrm{d}x_1$ vertically upward so that it passes through the point of tangent (A_5 in Fig. 2.19) of the tangent line at $x_1 = x_1^*$. We denote the intercepts of this shifted tangent line at $x_1 = 0$ (A_2) and $x_1 = 1$ (A_3) by $\mu_2(x_1^*) + \Delta'\mu_2$ and $\mu_1(x_1^*) + \Delta'\mu_1$, respectively. From Fig. 2.19, we note that the two triangles $\triangle A_1A_2A_5$ and $\triangle A_4A_3A_5$ are similar. Thus,

$$\frac{A_1A_2}{A_3A_4} = \frac{\mu_2^* - (\mu_2^* + \Delta'\mu_2)}{(\mu_1^* + \Delta'\mu_1) - \mu_1^*} = \frac{x_1^*}{1 - x_1^*} , \tag{2.266}$$

from which we find

$$x_1^*\Delta'\mu_1 + x_2^*\Delta'\mu_2 = 0 . \tag{2.267}$$

From the figure, we observe that

$$\Delta'\mu_i - \Delta\mu_i = A_5A_6 \propto A_7A_8 , \quad i = 1, 2 . \tag{2.268}$$

But,

$$A_7A_8 = \underline{G}(x_1^* + \mathrm{d}x_1) - \left[\underline{G}(x_1^*) + \left(\frac{\partial \underline{G}}{\partial x_1} \right)_{T,P} \bigg|_{x_1 = x_1^*} \mathrm{d}x_1 \right] = \text{h.o.} , \tag{2.269}$$

and hence

$$\Delta'\mu_i = \Delta\mu_i + \text{h.o.} , \quad i = 1, 2 , \tag{2.270}$$

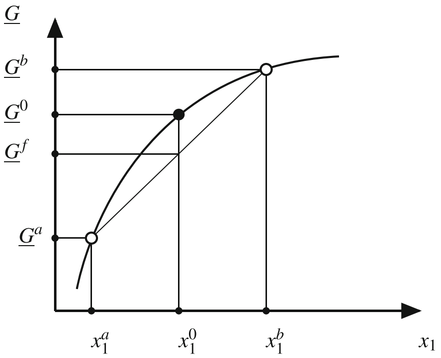

Fig. 2.20 $\underline{G}$ versus x_1 plot at constant T and P.

which in turn allows us to rewrite (2.267) as

$$x_1^* \Delta\mu_1 + x_2^* \Delta\mu_2 = \text{h.o.} \tag{2.271}$$

Retaining the first-order terms only, we obtain

$$x_1^* \mathrm{d}\mu_1 + x_2^* \mathrm{d}\mu_2 = 0 \,. \tag{2.272}$$

Since this equality holds for any x_1^* as long as T and P are fixed, we finally arrive at (2.265).

2.16.2.3 Phase Separation

A binary mixture of a given mole fraction is unstable with respect to phase separation if $\underline{G}$ versus x_1 plot is concave down at that mole fraction. For example, the molar Gibbs free energy of a binary mixture at x_1^0 in Fig. 2.20 is $\underline{G}^0$. By separating into phase A with mole fraction x_1^a and phase B with x_1^b, the molar Gibbs free energy decreases to $\underline{G}^f$.

As you saw in Exercise 2.16, a closed system held at constant T and P evolves toward the direction of decreasing G. So, the phase separation we just considered is a spontaneous process and the initial phase is unstable.

As in Exercise 2.11, the graphical construction for $\underline{G}^f$ can be justified as follows. First, the Gibbs free energy G^f of the composite system consisting of phases A and B is given by

$$G^f = N\underline{G}^f = N^a \underline{G}^a + N^b \underline{G}^b \,, \tag{2.273}$$

where N is the total number of moles of molecules in the system and includes molecules of both species. We denote the total number of moles in phase A by N^a and that in phase B by N^b. Clearly,

$$N = N^a + N^b \,. \tag{2.274}$$

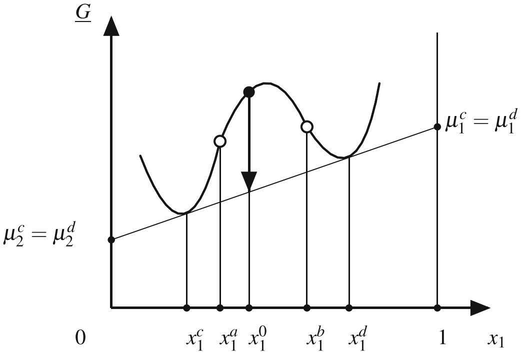

Fig. 2.21 The common tangent construction to find the mole fractions, x_1^c and x_1^d, at phase coexistence. The mixture is unstable between two inflection points (*open circles*) at x_1^a and x_1^b.

Considering the total number of moles of species 1 in the entire system, we obtain

$$x_1^0 N = x_1^a N^a + x_1^b N^b \, . \tag{2.275}$$

From (2.273) and (2.274), we find

$$\underline{G}^f = \frac{N^a}{N}\underline{G}^a + \frac{N^b}{N}\underline{G}^b = \underline{G}^a + (\underline{G}^b - \underline{G}^a)\frac{N^b}{N} \, , \tag{2.276}$$

while (2.274) and (2.275) gives

$$\frac{N^b}{N} = \frac{x_1^0 - x_1^a}{x_1^b - x_1^a} \, . \tag{2.277}$$

Thus,

$$\underline{G}^f = \underline{G}^a + \frac{\underline{G}^b - \underline{G}^a}{x_1^b - x_1^a}(x_1^0 - x_1^a) \tag{2.278}$$

in agreement with the graphical construction.

Because of the way the diagram is drawn, $\underline{G}$ versus x_1 plot is concave down at x_1^a and x_1^b. So, both phases A and B are still unstable. If $\underline{G}$ actually is concave down everywhere between $x_1 = 0$ and $x_1 = 1$, then the system will split into two pure phases. In reality, however, it is likely that the curve will eventually turn around and become concave up toward both ends of the x_1-axis (at $x_1 = 0$ and $x_1 = 1$).

2.16.2.4 Phase Coexistence

If the mole fraction x_1^0 of the system sits between two inflection points of the $\underline{G}$ versus x_1 plot as shown in Fig. 2.21, the mixture will separate into two phases. The mole fractions of these coexisting phases, which we denote by x_1^c and x_1^d, can be found by means of the **common tangent construction** illustrated in Fig. 2.21. According to this method, we draw a tangent line having two points of contact. The mole fractions of the coexisting phases are then given by those of the points of tangent.

Why? Recall that the intercept at $x_1 = 0$ of the tangent line gives you μ_2, while that at $x_1 = 1$ gives you μ_1. So, from the figure, we see that $\mu_1^c = \mu_1^d$ and $\mu_2^c = \mu_2^d$. Since the curve is for given T and P, clearly, $T^c = T^d$ and $P^c = P^d$. So, the composite system consisting of the two phases is in equilibrium. The equilibrium is stable because $\underline{G}$ is concave up at these mole fractions.

As indicated by the downward arrow in the Fig. 2.21, $\underline{G}$ decreases upon phase separation. The length of this arrow is the **driving force of phase separation**. As in (2.277),

$$\frac{N^d}{N} = \frac{x_1^0 - x_1^c}{x_1^d - x_1^c} , \tag{2.279}$$

where $N = N_c + N_d$ is the total number of moles in the system. Thus,

$$\frac{N^c}{N} = 1 - \frac{N_d}{N} = \frac{x_1^d - x_1^0}{x_1^d - x_1^c} . \tag{2.280}$$

Thus,

$$N^c(x_1^0 - x_1^c) = N^d(x_1^d - x_1^0) . \tag{2.281}$$

This result is known as the **lever rule**. The amount of each phase, as measured by the total number of moles, satisfies the condition of the mechanical balance of a lever with fulcrum at x_1^0 and loads N^c and N^d at x_1^c and x_1^d, respectively.

Between x_1^c and x_1^a, the phase is not unstable, but its free energy can be lowered by undergoing phase separation (into x_1^c and x_1^d). The phase is thus metastable. Likewise for a phase between x_1^b and x_1^d.

2.17 Frequently Used Symbols

c , the number of species.
k_B , Boltzmann constant, 1.3806×10^{-23} J/K.
n_i , N_i/V. We often drop the subscript for a pure system.
s , S/V.
u , U/V.
x_i , mole fraction of species i.

C_P , constant pressure heat capacity.
$\underline{C}_P$, constant pressure molar heat capacity.
C_V , constant volume heat capacity.
$\underline{C}_V$, constant volume molar heat capacity.
E , total energy.

F , Helmholtz free energy.
G , Gibbs free energy.
H , enthalpy.
N_i , the number of moles of species i. We often drop the subscript for a pure system.
P , pressure.
Q , heat.
R , gas constant. 8.3145 J/mol K
S , entropy.
T , absolute temperature.
U , internal energy.
V , volume.
W , work.
W^{rev} , work done by a reversible work source.
X_i , ith additional variable needed to specify the state of a system not in equilibrium.

α , coefficient of thermal expansion.
γ , C_P/C_V.
μ_i , chemical potential of species i. We often drop the subscript for a pure system.
θ , extensive quantity.
$\overline{\theta}$, partial molar quantity defined by $(\partial\theta/\partial N_i)_{T,P,N_{j\neq i}}$.
$\underline{\theta}$, molar quantity defined by $\theta/\sum_{i=1}^{c} N_i$.
Ω , grand potential.

References and Further Reading

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2. Fermi E (1956) Thermodynamics. Dover, New York
   One thing that is missing from Callen as well as from the current chapter is the concept of entropy introduced through purely macroscopic considerations. Fermi's book fills this gap very nicely. Entropy is covered in the first 60 pages or so. His definition of an adiabatic process differs from ours in that he demands the process to be reversible as well.
3. Gibbs J W (1993) The Scientific Papers of J. Willard Gibbs, Volume I. Thermodynamics. Ox Bow, Connecticut
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   Highly readable and thoughtfully written introduction to fluid mechanics.

Chapter 3
Classical Statistical Mechanics

According to classical mechanics, equations of motion supplemented by initial conditions uniquely determine the subsequent evolution of a given system. For typical systems of our interest, however, the number of mechanical degrees of freedom is of the order of 10^{24}. One cannot possibly write down 10^{24} equations of motion, much less solve them. It is also impossible to specify the initial conditions for such a system with a required accuracy. Moreover, even if we could somehow accomplish all of this, it would be entirely impossible to comprehend the resulting list of coordinates and momenta at any instant. Despite a hopeless scenario this observation might suggest, behavior of a macroscopic system is surprisingly regular as we have seen in thermodynamics. It is as if laws governing behavior of a macroscopic system are quite different from those governing its behavior at a microscopic level. In this chapter, we examine the connection between these two distinct ways of looking at a macroscopic system.

3.1 Macroscopic Measurement

Suppose that we measure the value of a dynamical variable A of some macroscopic body at time t. Is the outcome $A_{\mathrm{expt}}(t)$ equal to the value of A at time t? That is, can we write

$$A_{\mathrm{expt}}(t) = A(q^f(t), p^f(t), t)\ ? \tag{3.1}$$

For example, we might wish to measure the length of an object consisting of N particles (atoms) as in Fig. 3.1. One possible definition for the dynamical variable representing the desired length is

$$l(\boldsymbol{r}^N(t), \boldsymbol{p}^N(t)) = \max_{i,j} \left| x_i(t) - x_j(t) \right| \ . \tag{3.2}$$

I. Kusaka, *Statistical Mechanics for Engineers*,
DOI 10.1007/978-3-319-13809-1_3

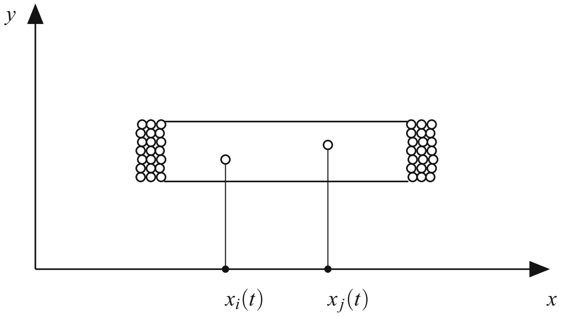


Fig. 3.1 Measurement of the length of a bar.

That is, we define the *instantaneous* length of the object as the maximum difference in the x coordinates of the particles comprising the object. In analogy to the notation q^f and p^f we introduced in Chap. 1, $\boldsymbol{r}^N$ and $\boldsymbol{p}^N$ in (3.2) collectively denote the position vectors and the linear momenta of particles in the system, respectively.

If we observe the time evolution of l, however, we will find that l fluctuates as a result of particles bouncing around in the object. The characteristic time scale for this kind of molecular motion is of the order of 10^{-12} s. See Example 3.1, for example. To measure the length, we can simply place a scale bar next to the object and read the scale with the naked eye. The characteristic time scale for such a measurement is of the order of 10^{-2} s at best. Even if we take a picture to "freeze the motion," the time duration of the measurement will be no shorter than 10^{-4} s or so.

Thus, what we obtain as a result of this measurement is not the instantaneous value $l(t)$ assumed by the dynamical variable, rather it is a time average of $l(t)$. So, a proper expression for $l_{\mathrm{expt}}(t)$ is

$$l_{\mathrm{expt}}(t) = \lim_{\tau\to\infty} \frac{1}{\tau} \int_t^{t+\tau} l(\boldsymbol{r}^N(t'),\boldsymbol{p}^N(t'))\mathrm{d}t' \;, \tag{3.3}$$

where $\tau \to \infty$ simply means that τ, being comparable with the characteristic time scale of a macroscopic measurement, is extremely large compared to the characteristic time scale of molecular motion.

For a general dynamical variable A, therefore, we write

$$A_{\mathrm{expt}}(t) = \lim_{\tau\to\infty} \frac{1}{\tau} \int_t^{t+\tau} A(q^f(t'),p^f(t'),t')\mathrm{d}t' \;, \tag{3.4}$$

Taking an average consolidates a multitude of complexity embodied in the full specification of $q^f(t)$ and $p^f(t)$. The apparent regularity we associate with the behavior of macroscopic bodies is a result of this consolidation.

It is instructive to consider a simple, if somewhat artificial, example. Let

$$A(q^f,p^f,t) = A_0 + \sum_{i=1} A_i \sin\frac{2\pi t}{T_i} \;, \tag{3.5}$$

where A_0, A_i, and T_i are some constants. The second term on the right-hand side is a superposition of sine waves each with the period T_i and amplitude A_i. Because of this term, A will fluctuate with time in a complex manner. (For an extensive quantity pertaining to a macroscopic body, we typically have $|A_i/A_0| \sim 1/\sqrt{N}$ for all $i \geq 1$ as discussed in Sect. 4.1.) Let us calculate the result of measuring this A. From (3.4), we obtain

$$\begin{aligned} A_{\text{expt}}(t) &= \lim_{\tau\to\infty} \frac{1}{\tau} \int_t^{t+\tau} \left(A_0 + \sum_{i=1} A_i \sin \frac{2\pi t'}{T_i} \right) \mathrm{d}t' \\ &= A_0 - \lim_{\tau\to\infty} \frac{1}{\tau} \sum_{i=1} \frac{A_i T_i}{2\pi} \left[\cos \frac{2\pi t'}{T_i} \right]_t^{t+\tau} . \end{aligned} \tag{3.6}$$

Note that the magnitude of $\cos(2\pi t'/T_i)$ is at most 1. Thus, the fluctuating part of A does not contribute to A_{expt} unless T_i is of the order of τ, that is, only extremely slow modes of fluctuation can survive the time averaging implicit in macroscopic measurements and more rapid fluctuations are "hidden" from macroscopic measurements.

Even though these rapid fluctuations are hidden in the sense just indicated, their effect may be felt at a macroscopic level. Heat is a notable mechanism through which such hidden modes of fluctuation manifest themselves at a macroscopic level.

In principle, (3.4) provides a prescription for predicting the value of $A_{\text{expt}}(t)$ for the system of interest "simply" by solving the equations of motion. This is the basic idea behind the molecular dynamics simulation method, in which equations of motion are solved numerically for systems containing a large number of particles interacting through effective potentials that are designed to mimic the actual molecular interactions. One can easily deal with systems containing $10^4 \sim 10^5$ or even larger number of particles. In pursuing this approach, one must first identify appropriate dynamical variables corresponding to various macroscopic quantities of interest. For certain quantities, such as temperature, entropy, free energies, and chemical potentials, however, it is not immediately obvious what they should be. The role of statistical mechanics, in part, is to provide microscopic interpretations and *microscopic expressions* for various quantities we deal with in a macroscopic description of our world.

Example 3.1. Vibration of a monomer in liquid water: To estimate a characteristic time scale of the vibrational motion of molecules, let us focus on liquid water and suppose that a molecule in the liquid phase may be regarded as a rigid spherical particle confined to a rigid spherical cavity of radius $R_l = (3/4\pi n_l)^{1/3}$, where n_l is the number density of molecules. For liquid water at 298.15 K, $R_l = 1.928$ Å. If we approximate the effective radius R_w of a water molecule by the Lennard–Jones radius used in a model potential of water, such as the TIP4P model potential, $R_w \approx 1.577$ Å. The magnitude of the x-component of the velocity, on average, is given by $\sqrt{k_B T/m}$ as seen

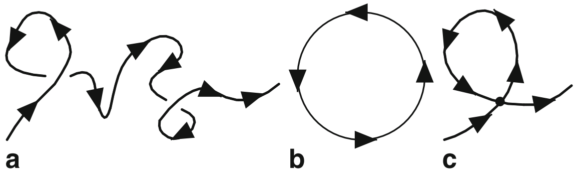


Fig. 3.2 **a** and **b** are examples of possible phase trajectories, while **c** is an impossible phase trajectory.

from (3.170). At 298.15 K, this gives $v_x = 371.0$ (m/s). Assuming that a given molecule is bouncing around between $x = R_l$ and $x = -R_l$ at this velocity, the period of the vibrational motion is $4(R_l - R_w)/v_x = 3.78 \times 10^{-12}$ s.

3.2 Phase Space

The mechanical state of a system is specified by giving numerical values to $2f$ variables, q^f and p^f. If we consider a space spanned by the axis $q_1, \ldots, q_f$ and $p_1, \ldots, p_f$, then the mechanical state of the system will be represented by a point in this $2f$ dimensional space. This space is called the **phase space**, and the point representing the state of the system is called the **phase point**. As the mechanical system evolves with time, $q_1, \ldots, q_f$ and $p_1, \ldots, p_f$ will also change, and the phase point will move along a path, which is referred to as the **phase trajectory**. Trajectories in Fig. 3.2a, b are examples of possible phase trajectories, with the latter representing a periodic motion.[13] However, trajectory in Fig. 3.2c indicates an impossible phase trajectory. According to what we saw in Chap. 1, if the system is at a particular point in the phase space at some instant of time t_0, its position in this space at any other time $t \neq t_0$ is completely determined by the equations of motion. Trajectory c violates this principle.[14]

Example 3.2. Free fall of a particle: Consider a free fall of a particle of mass m from the height h at $t = 0$. Taking the z-axis as vertically upward from the ground and setting the initial velocity to zero, we find

$$z(t) = -\frac{1}{2}gt^2 + h \quad \text{and} \quad \dot{z} = -gt \; . \tag{3.7}$$

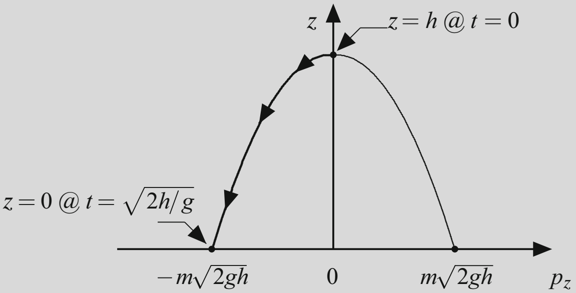
Thus,

$$p_z(t) = m\dot{z} = -mgt \; . \tag{3.8}$$

Eliminating t from the equations for $z(t)$ and $p_z(t)$, we find

$$z = -\frac{1}{2}g\left(-\frac{p_z}{mg}\right)^2 + h = -\frac{{p_z}^2}{2m^2 g} + h\,. \tag{3.9}$$

This is, then, the equation for the phase trajectory. Because the particle is moving toward the negative z-direction, only the portion with $p_z \leq 0$ in the following diagram is relevant.



Setting $z = 0$ in (3.7), we see that the particle hit the ground at $t = \sqrt{2h/g}$. According to (3.8),

$$p_z = -mg\sqrt{\frac{2h}{g}} = -m\sqrt{2gh} \tag{3.10}$$

at this very moment.

Exercise 3.1. A particle is confined to a potential well $\phi(x) = kx^2/2$ $(k > 0)$. Assuming that the particle moves in the x-direction only, draw its phase trajectory. ///

3.3 Ensemble Average

Suppose that we observe a system over a long duration of time that commences at time t and ends at $t + \tau$. During τ, the system evolves according to the equations of motion and passes through various regions in the phase space. As shown in Fig. 3.3 for the case of $f = 1$, we take an infinitesimal volume element $\mathrm{d}q^f \mathrm{d}p^f$ around a phase point (q^f, p^f) and denote by $\Delta t(q^f, p^f, t)$ the total amount of time the system spent in this volume element. Then, we define ρ by

$$\rho(q^f, p^f, t)\mathrm{d}q^f \mathrm{d}p^f := \lim_{\tau\to\infty} \frac{\Delta t(q^f, p^f, t)}{\tau}\,. \tag{3.11}$$

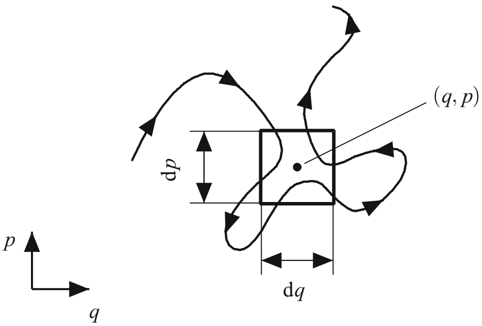


Fig. 3.3 A phase trajectory passing through a volume element $\mathrm{d}q\mathrm{d}p$ centered around a phase point (q,p) in a two-dimensional phase space during a time duration τ.

The quantity $\rho \mathrm{d}q^f \mathrm{d}p^f$ is the probability of finding the system inside the volume element if it is observed at some instant of time t', which we choose arbitrarily with uniform probability between t and $t+\tau$. We can easily see that $\rho \mathrm{d}q^f \mathrm{d}p^f$ satisfies the usual requirements of probability. Firstly, because $\Delta t \geq 0$, we have $\rho \geq 0$ everywhere in the phase space. Secondly, because the system is always found somewhere in the phase space, the summation of Δt for all the volume elements yields τ:

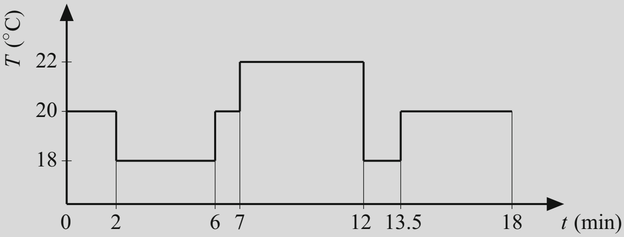
$$\int \rho(q^f,p^f,t)\mathrm{d}q^f \mathrm{d}p^f = 1 , \tag{3.12}$$

where the integration is over the *entire phase space*. Because of the probabilistic interpretation of $\rho \mathrm{d}q^f \mathrm{d}p^f$, we may write the long-time average of the dynamical variable $A(q^f,p^f,t)$ as

$$A_{\text{expt}}(t) = \int A(q^f,p^f,t)\rho(q^f,p^f,t)\mathrm{d}q^f \mathrm{d}p^f . \tag{3.13}$$

For the reason that becomes clear in Sect. 3.5, the expression on the right is referred to as the **ensemble average**, or the **thermal average**, of the dynamical variable A. To help you convince yourself of the validity of (3.13), consider the following example.

Example 3.3. Temperature of a house as experienced by a moving object: Suppose that you picked up a thermometer and walked around in your house, visiting multiple times three of the rooms, kept at different temperatures. The temperature reading from the thermometer, as a function of time, may look like this:



What is the average temperature T_{expt} you have experienced? Equation (3.4) applied to this problem gives

$$T_{\text{expt}} = \frac{1}{18}\left[(20\times 2)+(18\times 4)+(20\times 1)+(22\times 5)+(18\times 1.5)+(20\times 4.5)\right] . \tag{3.14}$$

Evidently, this expression can be rewritten somewhat more compactly as

$$T_{\text{expt}} = \frac{1}{18}\left[18\times(4+1.5)+20\times(2+1+4.5)+22\times 5\right] . \tag{3.15}$$

To make it look more like (3.13), let T_i and Δt_i denote the temperature of room i and the total amount of time you spent in room i, respectively. From the graph shown above, we can construct the following table:

i	T_i (°C)	Δt_i (min)
1	18	5.5
2	20	7.5
3	22	5

Then, the above equation for T_{expt} becomes

$$T_{\text{expt}} = \frac{1}{\tau}\sum_{i=1}^{3} T_i \Delta t_i = \sum_{i=1}^{3} T_i \rho_i , \tag{3.16}$$

where $\tau = 18$(min) and $\rho_i := \Delta t_i/\tau$. This expression for T_{expt} should be compared against (3.13).

We note that the value of ρ, at fixed q^f and p^f, can depend on t, because Δt we obtain from our measurement may very well depend on when we commence our measurement. The explicit time dependence of A indicated in (3.13) deserves some comment, however.

Note that the explicit time dependence can arise in a dynamical variable if the system is subject to a time-dependent external field. If the field changes very rapidly during the time interval Δt, then in general, we cannot expect (3.13) to hold. To see this, one might consider a somewhat artificial example in which A is independent of

q^f and p^f but depends explicitly on time as

$$A(q^f, p^f, t') = \begin{cases} 1 \text{ if } t \leq t' < t + \varepsilon \\ 0 \text{ otherwise,} \end{cases} \tag{3.17}$$

where $\varepsilon \ll \tau$. In this case, $A_{\text{expt}}(t) \approx 0$ from (3.4). But according to (3.13), in which the integrand is evaluated at time t, $A_{\text{expt}}(t) = 1$. In writing (3.13), therefore, it is tacitly assumed that the change in A due to its *explicit* time dependence occurs sufficiently slowly during τ. In other words, we are allowing only for external fields that changes very slowly. On the other hand, rapid variations that may be exhibited by A due to its *implicit* dependence, that is, the change in A due to changes in q^f and p^f with t, is captured by the dependence of ρ on q^f and p^f.

3.4 Statistical Equilibrium

So far, all we have done is to rewrite (3.4) using a newly defined quantity ρ. But, to compute ρ from (3.11), we still have to solve the equations of motion. So, why do we even bother with the quantity ρ?

By expressing A_{expt} by means of ρ, we are hoping that we could somehow come up with an educated guess for the functional form of ρ *without ever having to solve the equations of motion*. It will be very difficult to do this for the most general situations. However, if we restrict our attention only to systems in *equilibrium*, maybe we can come up with a sensible guess for ρ without too much difficulty.

Of course, you note that we have converted the problem of evaluating the one-dimensional integral in (3.4) along with the solution of $2f$-coupled first-order differential equations into that of evaluating $2f$-dimensional integral as given by (3.13). How should that make the actual calculation of A_{expt} any easier? For example, this $2f$-dimensional integral is often evaluated numerically by means of Monte Carlo simulation. The required computational effort is comparable to that of molecular dynamics.

However, and this is the point: By introducing the new quantity ρ, we have completely changed the nature of the problem. This, in turn, allows for a completely new set of logical deductions and physical insights to operate, enabling us to introduce reasonable approximations in a manner unimaginable if we insist on solving the equations of motion as required by (3.4). Even more importantly, it is now possible to find explicit expressions for entropy and free energies in terms of functions of q^f and p^f as we shall see.

Because we have decided to limit our considerations to systems in equilibrium, we should first define precisely what is meant by equilibrium. We say that the system is in **statistical equilibrium** if and only if $\mathrm{d}A_{\text{expt}}/\mathrm{d}t = 0$ at any instant of time for *any* dynamical variable A that does *not* depend *explicitly* on time. For such A, the total time derivative of (3.13) can be evaluated as follows. First, we recall the definition of the derivative:

$$\frac{\mathrm{d}A_{\mathrm{expt}}(t)}{\mathrm{d}t} = \lim_{\Delta t \to 0} \frac{1}{\Delta t} \left[A_{\mathrm{expt}}(t+\Delta t) - A_{\mathrm{expt}}(t) \right] . \tag{3.18}$$

Using (3.13), we find

$$\begin{aligned} \frac{\mathrm{d}A_{\mathrm{expt}}(t)}{\mathrm{d}t} = \lim_{\Delta t \to 0} \frac{1}{\Delta t} \bigg[&\int A(q^f,p^f)\rho(q^f,p^f,t+\Delta t)\mathrm{d}q^f\mathrm{d}p^f \\ &- \int A(q^f,p^f)\rho(q^f,p^f,t)\mathrm{d}q^f\mathrm{d}p^f \bigg] . \end{aligned} \tag{3.19}$$

Since both integrals are taken over the entire phase space, they can be combined to give

$$\frac{\mathrm{d}A_{\mathrm{expt}}(t)}{\mathrm{d}t} = \lim_{\Delta t \to 0} \frac{1}{\Delta t} \int A(q^f,p^f) \left[\rho(q^f,p^f,t+\Delta t) - \rho(q^f,p^f,t) \right] \mathrm{d}q^f\mathrm{d}p^f . \tag{3.20}$$

For a small enough Δt, the change in ρ during the time duration Δt may be written as

$$\rho(q^f,p^f,t+\Delta t) - \rho(q^f,p^f,t) = \frac{\partial \rho(q^f,p^f,t)}{\partial t}\Delta t \tag{3.21}$$

with sufficient accuracy. Introducing this expression in (3.20), we obtain

$$\frac{\mathrm{d}A_{\mathrm{expt}}(t)}{\mathrm{d}t} = \int A(q^f,p^f) \frac{\partial \rho(q^f,p^f,t)}{\partial t} \mathrm{d}q^f\mathrm{d}p^f . \tag{3.22}$$

At equilibrium, this quantity must vanish at any instant of time for *any* choice of A. Thus, the necessary and sufficient condition for statistical equilibrium is that

$$\frac{\partial \rho(q^f,p^f,t)}{\partial t} = 0 \tag{3.23}$$

holds everywhere in the phase space at any instant. In other words, ρ does not depend explicitly on t.

3.5 Statistical Ensemble

Recall that we constructed ρ by observing a single system over a long duration of time starting at time t. This ρ, and hence A_{expt} calculated by means of (3.13), will in general depend on t. When this time dependence is absent for any A_{expt} that corresponds to a dynamical variable A without an explicit time dependence, we say that the system is in statistical equilibrium. While this definition of equilibrium makes good physical sense, (3.23) that followed from it does not appear to offer any useful insight toward an educated guess for the functional form of ρ. For this reason, we introduce the following construction.

First, we create a large number, say $\mathscr{N}$, of copies of the original system. Copies have the identical mechanical construction to the original. If there are time-dependent external fields, their time dependence are common to all copies. In other words, the *functional form* of the Hamiltonian of a copy is identical to that of the original *including* the explicit time dependence. Such a collection of $\mathscr{N}$ copies is called the **statistical ensemble**.

At a given instant t, each copy of the ensemble has a representative point, as specified by $(q^f(t), p^f(t))$, in the phase space. While all copies in the ensemble are characterized by the same functional form of the Hamiltonian, we do not require that their mechanical states, and hence the corresponding phase points in the phase space, at any instant should coincide. Instead, we construct the statistical ensemble so that the number of copies whose mechanical state falls within the infinitesimal volume element $\mathrm{d}q^f\mathrm{d}p^f$ taken around (q^f, p^f) is given by

$$\mathscr{N}\rho(q^f, p^f)\mathrm{d}q^f\mathrm{d}p^f \ . \tag{3.24}$$

That is, the number density of copies in the phase space at (q^f, p^f) is $\mathscr{N}\rho(q^f, p^f)$.

It should be emphasized that a given copy in the ensemble does *not* interact with the other copies in the ensemble. Each copy has its own representative point in the phase space and moves along its own phase trajectory according to the equations of motion pertaining only to that copy.

If we take a fixed control volume in the phase space, the number of copies found in it may change with time as some copies leave the control volume while others enter it. However, once we put $\mathscr{N}$ copies in the phase space and watch what happens to them, no copy will simply disappear from the phase space, nor will a new one appear spontaneously out of nothing. This implies that the number density $\mathscr{N}\rho$ of the copies satisfies the equivalent of mass balance or the equation of continuity from fluid mechanics in the phase space. This observation leads to an important theorem, which guide us in our search for the equilibrium distribution as we shall see next.

3.6 Liouville's Theorem

Let us start by reviewing the equation of continuity from fluid mechanics in ordinary three-dimensional space. (The current derivation is adopted solely for the sake of expediency. For a physically more natural derivation of the equation of continuity, see Chap. 3 of Ref. [6].)

Consider a control volume V fixed in space at all time. The total number of particles within V at a given moment t is given by

$$\int_V \rho(\boldsymbol{r},t)\mathrm{d}\boldsymbol{r} \, , \tag{3.25}$$

where $\rho(\boldsymbol{r},t)$ temporarily denotes the number density of particles such as molecules at position $\boldsymbol{r}$ at time t. If we exclude the possibility of chemical reactions, the rate of change of this integral can be expressed in terms of the flux across the boundary A of V:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_V \rho(\boldsymbol{r},t)\mathrm{d}\boldsymbol{r} = -\oint_A \rho(\boldsymbol{r},t)\boldsymbol{v}(\boldsymbol{r},t)\cdot\boldsymbol{n}(\boldsymbol{r})\mathrm{d}A\,, \tag{3.26}$$

where $\boldsymbol{n}$ is the outward unit normal and $\boldsymbol{v}$ is the average velocity of the particles passing through the surface element $\mathrm{d}A$.

Because our control volume remains fixed at all time, the total time derivative on the left-hand side can be brought inside the integral sign, where it becomes a partial derivative for the integrand is a function of $\boldsymbol{r}$ as well. Furthermore, by means of the divergence theorem, the surface integral in (3.26) may be converted into a volume integral, thus yielding

$$\int_V \left[\frac{\partial \rho}{\partial t} + \nabla\cdot(\rho\boldsymbol{v})\right]\mathrm{d}\boldsymbol{r} = 0\,. \tag{3.27}$$

Because this equation holds for any choice of the control volume V,

$$\frac{\partial \rho}{\partial t} + \nabla\cdot(\rho\boldsymbol{v}) = 0 \tag{3.28}$$

must hold everywhere at any instant. Writing out the divergence term $\nabla\cdot(\rho\boldsymbol{v})$ using a Cartesian coordinate system, we have

$$\frac{\partial \rho}{\partial t} + \frac{\partial(\rho v_x)}{\partial x} + \frac{\partial(\rho v_y)}{\partial y} + \frac{\partial(\rho v_z)}{\partial z} = 0\,. \tag{3.29}$$

where the subscripts label the respective components of $\boldsymbol{v}$.

In the phase space, the coordinates are $q_1, \dots, q_f$ and $p_1, \dots, p_f$ instead of x, y, and z. Instead of the components v_x, v_y, and v_z, of the average velocity $\boldsymbol{v}$, we have $\dot{q}_1, \dots, \dot{q}_f$ and $\dot{p}_1, \dots, \dot{p}_f$ for the components of the average velocity of phase points. Finally, $\mathscr{N}\rho$ takes the place of ρ. Thus, by analogy to (3.29), we have

$$\frac{\partial(\mathscr{N}\rho)}{\partial t} + \sum_{i=1}^{f}\left[\frac{\partial(\mathscr{N}\rho\dot{q}_i)}{\partial q_i} + \frac{\partial(\mathscr{N}\rho\dot{p}_i)}{\partial p_i}\right] = 0\,. \tag{3.30}$$

Noting that $\mathscr{N}$ is a constant independent of q^f, p^f, and t, and using Hamilton's equations of motion (1.162), we find

$$\begin{aligned} 0 &= \frac{\partial \rho}{\partial t} + \sum_{i=1}^{f}\left[\frac{\partial}{\partial q_i}\left(\rho\frac{\partial H}{\partial p_i}\right) - \frac{\partial}{\partial p_i}\left(\rho\frac{\partial H}{\partial q_i}\right)\right] \\ &= \frac{\partial \rho}{\partial t} + \sum_{i=1}^{f}\left(\frac{\partial \rho}{\partial q_i}\frac{\partial H}{\partial p_i} + \rho\frac{\partial^2 H}{\partial q_i \partial p_i} - \frac{\partial H}{\partial q_i}\frac{\partial \rho}{\partial p_i} - \rho\frac{\partial^2 H}{\partial p_i \partial q_i}\right)\,. \end{aligned} \tag{3.31}$$

Since the second derivatives are independent of the order of differentiation, we arrive at

$$\frac{\partial \rho}{\partial t} + \sum_{i=1}^{f} \left(\frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial H}{\partial q_i} \frac{\partial \rho}{\partial p_i} \right) = 0 \,. \tag{3.32}$$

Recalling the definition of the Poisson bracket (1.184), we may rewrite (3.32) as

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = \frac{\partial \rho}{\partial t} + \{\rho, H\} = 0 \,, \tag{3.33}$$

where the first equality is an example of (1.185). Equation (3.33) is known as **Liouville's theorem** and indicates that ρ is a constant of motion. (Our usage of this phrase is slightly inappropriate here. Constant of motion usually refers to a dynamical variable pertaining to a single mechanical system rather than to a collection of them.)

According to (3.23), therefore, the necessary and sufficient condition of statistical equilibrium is that ρ be a constant of motion that *does not depend explicitly on time*. For this to be the case, it is sufficient (but not necessary) that ρ is a function of constants of motion that are not, themselves, explicit functions of time. In fact, let $\{A_1, \ldots, A_n\}$ be a set of such constants of motion and suppose that

$$\rho = \rho(A_1, \ldots, A_n). \tag{3.34}$$

Then, because A_i does not depend explicitly on t,

$$\frac{\partial \rho}{\partial t} = \sum_{i=1}^{n} \frac{\partial \rho}{\partial A_i} \frac{\partial A_i}{\partial t} = 0 \tag{3.35}$$

and, because A_i is a constant of motion,

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = \sum_{i=1}^{n} \frac{\partial \rho}{\partial A_i} \frac{\mathrm{d}A_i}{\mathrm{d}t} = 0 \tag{3.36}$$

as required by (3.23) and (3.33), respectively.

As we have seen, Liouville's theorem simply states that the number of copies in a statistical ensemble is conserved. This is a general requirement ρ must satisfy *regardless* of whether the system is in statistical equilibrium or not. Statistical equilibrium imposes an additional requirement (3.23), which is quite distinct from (3.33). Because of (3.33), one often expresses (3.23) as

$$\{\rho, H\} = 0 \,. \tag{3.37}$$

We observe that any set of two equations taken from (3.23), the second equality in (3.33), and (3.37), is equivalent to any other such set.

3.7 Significance of H

Accepting (3.34) as our guiding principle in our search for the equilibrium distribution, we still have to decide on the set of dynamical variables. In the absence of a time-dependent external field, a system of f mechanical degrees of freedom has $2f-1$ independent constants of motion, each without an explicit time dependence. (See the next section.) The mechanical energy E, the total linear momentum $\boldsymbol{P}$, and the total angular momentum $\boldsymbol{M}$ are notable examples of such constants. (See (1.106), (1.138), and (1.145) for definitions.) Functions of these constants are also constants of motion. Among the multitude of constants, how do we choose our dynamical variable in terms of which to express ρ?

In Sect. 1.8, we saw that conservation laws of E, $\boldsymbol{P}$, and $\boldsymbol{M}$ followed from a very general consideration regarding symmetry of space and time. In particular, it was unnecessary to refer to any specific details of the mechanical system. As such, conservation laws of these quantities are of very general character. In our search for a general theory applicable to *all* systems in equilibrium, the claim that they should serve a critical role is extremely compelling.

Typically, we are interested in macroscopic bodies at rest and E is the only relevant dynamical variable. Therefore, using H instead of E to emphasize its dependence on q^f and p^f, we suppose that

$$\rho = \rho(H)\,. \tag{3.38}$$

The justification of this hypothesis ultimately rests on the agreement between predictions of our theory and experimental observations.

3.8 †The Number of Constants of Motion

Let us see how many *independent* constants of motion are associated with a given mechanical system. We assume that the system is subject to no time-dependent external field.

We start by noting that the solution of Hamilton's equations of motion may be written as

$$q_i(t) = \mathscr{F}_{q_i}(t-t_0, a^f, b^f) \quad \text{and} \quad p_i(t) = \mathscr{F}_{p_i}(t-t_0, a^f, b^f)\,, \quad i = 1, \dots, f\,, \tag{3.39}$$

where we introduced a temporary notation $\mathscr{F}_x$ to indicate functional dependence of the quantity x on the variables listed in the brackets. The first equation indicates, for example, that q_i at time t depends only on the time that has passed since some arbitrary chosen instant t_0 and the values q^f and p^f assumed at t_0, which we denote by a^f and b^f, respectively. In the absence of a time-dependent external field, the time dependence of q^f and p^f occurs only through $t-t_0$.

If the set of $2f$ equations (3.39) is solved for $2f$ variables $a_1, \dots, a_f$, $b_1, \dots, b_{f-1}$, and $t - t_0$, we obtain

$$\begin{aligned} a_i &= \mathscr{F}_{a_i}(q^f, p^f, b_f)\,, \quad i = 1, \dots, f \\ b_i &= \mathscr{F}_{b_i}(q^f, p^f, b_f)\,, \quad i = 1, \dots, f-1 \\ t_0 &= t - \mathscr{F}_{t-t_0}(q^f, p^f, b_f)\,. \end{aligned} \tag{3.40}$$

Thus, $a_1, \dots, a_f$, $b_1, \dots, b_{f-1}$, and t_0 are all functions of q^f and p^f that remain constant, that is, they are constants of motion. Excluding t_0, which depends explicitly on t, we are left with $2f - 1$ constants of motion with no explicit time dependence. Insofar as their values can be specified independent of each other, $\mathscr{F}_{a_1}, \dots, \mathscr{F}_{a_f}$ and $\mathscr{F}_{b_1}, \dots, \mathscr{F}_{b_{f-1}}$ are independent functions.

Example 3.4. Free fall of a particle: Let us see how the above general scheme works for the problem of free-falling particle in Example 3.2. As the initial condition, we suppose that $z = z_0$ and $v_z = v_0$ at $t = t_0$. In terms of the notation adopted above, we have

$$q_1 = z\,, \quad p_1 = p_z\,, \quad a_1 = z_0\,, \quad \text{and} \quad b_1 = v_0\,. \tag{3.41}$$

Since $f = 1$, we expect to find $2 \times 1 - 1 = 1$ constant of motion.

Now, in place of (3.39), we have

$$\begin{aligned} z &= -\frac{1}{2}g(t-t_0)^2 + v_0(t-t_0) + z_0 \\ p_z &= -mg(t-t_0) + mv_0\,. \end{aligned} \tag{3.42}$$

Solving these equations for z_0 and $t - t_0$, we find

$$z_0 = z + \frac{1}{2m^2 g}\left({p_z}^2 - m^2 {v_0}^2\right) \quad \text{and} \quad t - t_0 = \frac{mv_0 - p_z}{mg}\,. \tag{3.43}$$

The first equation gives z_0 as a function of the time-dependent coordinate z and the momentum p_z but displays no explicit time dependence.

Rearranging the equation a little, we arrive at

$$mgz_0 + \frac{1}{2}m{v_0}^2 = mgz + \frac{{p_z}^2}{2m}\,, \tag{3.44}$$

which is recognized as the mechanical energy E. According to this equation, E is also a constant of motion. However, E is given in terms of z_0 and hence is not independent of z_0. So, the number of independent constants of motion with no explicit time dependence is just one as advertised.

3.9 Canonical Ensemble

At this point, we need to come up with an explicit expression for ρ. Let us suppose then that

$$\rho(q^f,p^f) = \frac{1}{C}e^{-\beta H(q^f,p^f)} \tag{3.45}$$

and see where it will take us. In Sect. 3.11, we see that there is actually a compelling reason for choosing this particular form of ρ. Nevertheless, (3.45) is a hypothesis, the ultimate justification of which must be sought through experimental scrutiny. The constant C is determined by the normalization condition of ρ:

$$C = \int e^{-\beta H(q^f,p^f)}\mathrm{d}q^f\mathrm{d}p^f \ , \tag{3.46}$$

where the integration extends over all phase space. For applications we have in mind, there is usually no upper limit to values H can assume while H is bounded from below. (The potential energy of interaction between two atoms takes the minimum possible value when the distance between the atoms is of the order of the atomic diameter. When they are squeezed closer together, the potential energy increases indefinitely.) In order for the integral in (3.46) to exist, therefore, the constant β must be positive. The statistical ensemble characterized by (3.45) is called the **canonical ensemble**.

Note that copies with different values of energy are present in the canonical ensemble. But, ρ was constructed from a phase trajectory along which H is constant. We shall come back to this point in Sect. 3.11. For now, we simply accept the canonical ensemble as given and explore its implications. We start by looking for physical meaning of β and C in this section.

We define the internal energy U of a system by

$$U := \langle H\rangle = \int H(q^f,p^f)\rho(q^f,p^f)\mathrm{d}q^f\mathrm{d}p^f = \frac{1}{C}\int H(q^f,p^f)e^{-\beta H(q^f,p^f)}\mathrm{d}q^f\mathrm{d}p^f \ , \tag{3.47}$$

where we introduced a new notation for the **ensemble average** we encountered earlier:

$$\langle A\rangle := \int A(q^f,p^f)\rho(q^f,p^f)\mathrm{d}q^f\mathrm{d}p^f = \frac{1}{C}\int A(q^f,p^f)e^{-\beta H(q^f,p^f)}\mathrm{d}q^f\mathrm{d}p^f \ . \tag{3.48}$$

Recalling (3.13), we have

$$\langle A\rangle = A_{\mathrm{expt}} \ . \tag{3.49}$$

As with (3.13), this identity is a consequence of our construction of the statistical ensemble.

We recall from thermodynamics that

$$\mathrm{d}U = T\mathrm{d}S + \text{work term.} \tag{3.50}$$

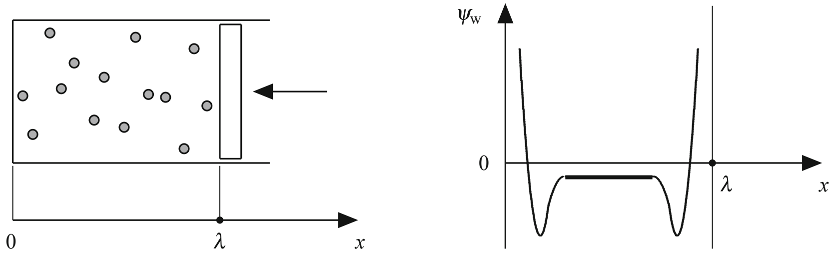


Fig. 3.4 Gas particles confined to a cylinder. Each particle is subject to the external field generated by the walls of the cylinder. The figure on the *right* illustrates the net field ψ_w produced by the vertical wall on the left and the piston on the right.

If we can develop an expression for dU based on (3.47) for a process involving work, we should be able to relate T and S to statistical mechanical quantities such as ρ, β, and C. This forms a basis for exploring a link between thermodynamics and the microscopic description of matter based on mechanics.

First, we introduce a few notations. Let $\Theta = \beta^{-1}$ and rewrite (3.45) as

$$H = -\Theta \ln \rho - \Theta \ln C \, . \tag{3.51}$$

Upon taking the average, we find

$$U = -\Theta \langle \ln \rho \rangle - \Theta \ln C = \Theta \eta + \alpha \, , \tag{3.52}$$

where we used the fact that $\langle A \rangle = A$ if A is independent of q^f and p^f. We also defined

$$\eta := -\langle \ln \rho \rangle \quad \text{and} \quad \alpha := -\Theta \ln C \, . \tag{3.53}$$

From (3.52),

$$\mathrm{d}U = \eta \mathrm{d}\Theta + \Theta \mathrm{d}\eta + \mathrm{d}\alpha \, . \tag{3.54}$$

Equation (3.54) with three terms on the right cannot be compared directly with (3.50). We also need to relate quantities on the right-hand side of (3.54) with the work. To this end, let us consider the example shown in Fig. 3.4 illustrating N gas particles confined to a cylinder. By moving the piston, we can exert work on the gas. Since we require the ability to control λ at will, we choose the gas particles as our statistical mechanical system and regard *the piston as a movable source of an external field*, which, together with the field generated by the fixed walls, confines the particles to the cylinder. So, the value of λ is common to all members of the statistical ensemble. The Hamiltonian of the system is given by

$$H = \sum_{i=1}^{N} \frac{\|\boldsymbol{p}_i\|^2}{2m} + \phi(\boldsymbol{r}^N) + \psi(\boldsymbol{r}^N, \lambda) \, , \tag{3.55}$$

where ϕ is the potential energy due to mutual interaction among the particles and ψ is the net external field generated by the piston and the other walls of the cylinder.

The point here is that we can perform work on the system by changing λ and that the Hamiltonian is a function of λ.

From (3.46), we see that C is a function of $\Theta = \beta^{-1}$ and λ, and hence

$$\mathrm{d}C = \left(\frac{\partial C}{\partial \Theta}\right)_\lambda \mathrm{d}\Theta + \left(\frac{\partial C}{\partial \lambda}\right)_\Theta \mathrm{d}\lambda \ . \tag{3.56}$$

Now, using (3.53) and (3.56), we find

$$\mathrm{d}\alpha = -\mathrm{d}\Theta \ln C - \frac{\Theta}{C}\mathrm{d}C = \left[\frac{\alpha}{\Theta} - \frac{\Theta}{C}\left(\frac{\partial C}{\partial \Theta}\right)_\lambda\right]\mathrm{d}\Theta - \frac{\Theta}{C}\left(\frac{\partial C}{\partial \lambda}\right)_\Theta \mathrm{d}\lambda \ . \tag{3.57}$$

Using (3.46), we can rewrite the partial derivatives in a little more illuminating form:

$$\frac{1}{C}\left(\frac{\partial C}{\partial \Theta}\right)_\lambda = \frac{1}{C}\frac{\partial}{\partial \Theta}\int e^{-H/\Theta}\mathrm{d}q^f\mathrm{d}p^f \ . \tag{3.58}$$

Since Θ appears only as the denominator in the exponent, $\partial/\partial\Theta$ can be brought inside the integral:

$$\frac{1}{C}\left(\frac{\partial C}{\partial \Theta}\right)_\lambda = \frac{1}{C}\int \frac{\partial}{\partial \Theta} e^{-H/\Theta}\mathrm{d}q^f\mathrm{d}p^f = \frac{1}{C}\int \frac{H}{\Theta^2} e^{-H/\Theta}\mathrm{d}q^f\mathrm{d}p^f = \frac{U}{\Theta^2} \ , \tag{3.59}$$

where we used (3.47). Similarly,

$$\begin{aligned}\frac{1}{C}\left(\frac{\partial C}{\partial \lambda}\right)_\Theta &= \frac{1}{C}\frac{\partial}{\partial \lambda}\int e^{-H/\Theta}\mathrm{d}q^f\mathrm{d}p^f = \frac{1}{C}\int \frac{\partial}{\partial \lambda} e^{-H/\Theta}\mathrm{d}q^f\mathrm{d}p^f \\ &= \frac{1}{C}\int -\frac{1}{\Theta}\frac{\partial H}{\partial \lambda} e^{-H/\Theta}\mathrm{d}q^f\mathrm{d}p^f \ ,\end{aligned} \tag{3.60}$$

where the partial derivative in the integrand is for fixed q^f and p^f. Using (3.48),

$$\frac{1}{C}\left(\frac{\partial C}{\partial \lambda}\right)_\Theta = -\frac{1}{\Theta}\left\langle \frac{\partial H}{\partial \lambda}\right\rangle \ . \tag{3.61}$$

Substituting (3.59) and (3.61) in (3.57) and using (3.52), we obtain

$$\mathrm{d}\alpha = \frac{1}{\Theta}(\alpha - U)\mathrm{d}\Theta + \left\langle \frac{\partial H}{\partial \lambda}\right\rangle \mathrm{d}\lambda = -\eta \mathrm{d}\Theta + \left\langle \frac{\partial H}{\partial \lambda}\right\rangle \mathrm{d}\lambda \ . \tag{3.62}$$

This equation can be brought into (3.54) to yield

$$\mathrm{d}U = \Theta \mathrm{d}\eta + \left\langle \frac{\partial H}{\partial \lambda}\right\rangle \mathrm{d}\lambda \ . \tag{3.63}$$

We identify the term proportional to the displacement, $\mathrm{d}\lambda$, as the work term. Because η depends on λ, a term proportional to $\mathrm{d}\lambda$ is implicit in $\mathrm{d}\eta$. In essence, the work in thermodynamics is *defined* to be $\langle \partial H/\partial\lambda \rangle \mathrm{d}\lambda$. This definition seems very reasonable since $-\partial H/\partial\lambda$ is the x-component of the force exerted on the piston by the gas molecules. The appearance of thermal average is also natural provided that the characteristic time scale over which the work is performed is considerably larger than that of typical molecular motions.

Upon comparison between (3.50) and (3.63), we finally arrive at

$$\Theta \mathrm{d}\eta = T\mathrm{d}S\,. \tag{3.64}$$

This equation implies that $\Theta \propto T$ and $\mathrm{d}\eta \propto \mathrm{d}S$. The proportionality constant between $\mathrm{d}S$ and $\mathrm{d}\eta$ is quite arbitrary and the most logical choice for the constant perhaps is just unity. However, for a historical reason, we introduce the Boltzmann constant k_B and write (3.64) as

$$\Theta \mathrm{d}\eta = k_B T\mathrm{d}(S/k_B)\,. \tag{3.65}$$

This suggests that we set

$$T = \frac{\Theta}{k_B} \tag{3.66}$$

and

$$S = k_B\eta + \text{const.} = -k_B\langle \ln\rho\rangle + \text{const.} \tag{3.67}$$

Since we are usually interested only in a entropy difference, we set the constant rather arbitrarily to zero. For an in-depth discussion on this choice, see Chap. 3 of Ref. [4]. In any case, we now have

$$S = k_B\eta = -k_B\langle \ln\rho\rangle\,. \tag{3.68}$$

Equations (3.66) and (3.68) are, then, the statistical mechanical expressions for T and S, respectively.

Equation (3.68) is due to Gibbs, and is known as **Gibbs's entropy formula**. From (3.66), we note that changing the choice of the constant k_B in (3.65) simply amounts to changing the scale for measuring the temperature. Since $\Theta = \beta^{-1}$ and k_B are both positive, T must be positive as well. With the identification

$$\beta := \frac{1}{k_B T}\,, \tag{3.69}$$

the expression $e^{-\beta H}$ is called the **Boltzmann factor**.

Equation (3.66) makes it clear that T is *not* an average of some dynamical variable. Instead, it is a parameter characterizing the distribution of the members of the statistical ensemble over states of different energy values. Later, we see that T is proportional to the average kinetic energy per particle. However, this does *not* imply that T is *defined* in terms of the average kinetic energy. The average becomes computable only *after* we specify T.

We note that

$$\alpha = U - \Theta\eta = U - TS \tag{3.70}$$

is the Helmholtz free energy F. Thus, combining (3.53) and (3.66), we finally arrive at

$$F = -k_B T\ln C\,. \tag{3.71}$$

As exciting all these results are, (3.71) turns out to be not quite correct. To see why this is so, however, we have to temporarily accept (3.71) and explore its consequences. It is only by comparing the predictions of (3.71) against other areas of our experience that we are able to uncover the fatal flaw hidden in (3.71). Until Sect. 3.12, where we introduce corrections to both (3.68) and (3.71), we pretend as if everything is fine and press on.

Exercise 3.2.

a. Show that

$$U = -\frac{\partial \ln C}{\partial \beta} \, . \tag{3.72}$$

This is the statistical mechanical version of the **Gibbs–Helmholtz equation** derived in Exercise 2.15.

b. Show that

$$\frac{\partial^2 \ln C}{\partial \beta^2} = \left\langle (H - \langle H \rangle)^2 \right\rangle \, . \tag{3.73}$$

c. Show that

$$\frac{\partial^2 \ln C}{\partial \beta^2} = k_B T^2 C_V \, . \tag{3.74}$$

Combining parts b and c, we see that C_V is related to the characteristic width of fluctuation of H. ///

Exercise 3.3. Using (3.45) and (3.68), derive (3.71). ///

3.10 Simple Applications of Canonical Ensemble

To gain some familiarity with the formalism we have developed so far, we shall consider several simple model systems and compute a few of their thermodynamic properties using the canonical ensemble.

3.10.1 Rectangular Coordinate System

Example 3.5. Particle in a box: Consider a particle of mass m confined to a rectangular box of dimension $L_x \times L_y \times L_z$. The Hamiltonian of the system may be written as

$$H(\boldsymbol{r},\boldsymbol{p}) = \frac{p^2}{2m} + \psi_{\mathrm{w}}(\boldsymbol{r}) \, , \tag{3.75}$$

where $p^2 = \|\boldsymbol{p}\|^2$ and ψ_{w} is the potential energy arising from the interaction between the particle and the wall of the box. In this problem, we assume a simple form for it:

$$\psi_{\mathrm{w}}(\boldsymbol{r}) = \begin{cases} 0 & \text{if } \boldsymbol{r} \text{ is in the box,} \\ \infty & \text{otherwise.} \end{cases} \tag{3.76}$$

The corresponding Boltzmann factor is given by

$$e^{-\beta H(\boldsymbol{r},\boldsymbol{p})} = \begin{cases} e^{-\beta p^2/2m} & \text{if } \boldsymbol{r} \text{ is in the box,} \\ 0 & \text{otherwise.} \end{cases} \tag{3.77}$$

The normalization constant C is obtained by integrating this expression over all phase space:[15]

$$C = \int e^{-\beta H} \mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{p} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-\beta H} \mathrm{d}x\mathrm{d}y\mathrm{d}z\mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z \,. \tag{3.78}$$

Let us start by considering the innermost integral:

$$\int_{-\infty}^{\infty} e^{-\beta H} \mathrm{d}x \,. \tag{3.79}$$

Since the integrand vanishes outside the box, it is sufficient to integrate from 0 to L_x. Over this interval, the integrand is independent of x. Thus,

$$\int_{-\infty}^{\infty} e^{-\beta H} \mathrm{d}x = L_x e^{-\beta H} \,. \tag{3.80}$$

When this expression is brought back into (3.78) and the integration with respect to y and z are performed in the similar manner, we find that

$$C = V \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-\beta H} \mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z \,, \tag{3.81}$$

where $V := L_x L_y L_z$ is the volume of the box. Next, we note that

$$p^2 = {p_x}^2 + {p_y}^2 + {p_z}^2 \,, \tag{3.82}$$

and hence

$$C = V \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-\beta {p_x}^2/2m} e^{-\beta {p_y}^2/2m} e^{-\beta {p_z}^2/2m} \mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z \,. \tag{3.83}$$

When performing the innermost integral with respect to p_x, we may regard p_y and p_z as constant. Thus,

$$C = V \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-\beta {p_y}^2/2m} e^{-\beta {p_z}^2/2m} \left[\int_{-\infty}^{\infty} e^{-\beta {p_x}^2/2m} \mathrm{d}p_x \right] \mathrm{d}p_y\mathrm{d}p_z \,. \tag{3.84}$$

Since the quantity in the square bracket is independent of p_y and p_z, it can be pulled out of the integrals with respect to p_y and p_z. The remaining two-dimensional integral can be performed similarly to yield

$$C = V\left[\int_{-\infty}^{\infty} e^{-\beta {p_x}^2/2m}\mathrm{d}p_x\right]\left[\int_{-\infty}^{\infty} e^{-\beta {p_y}^2/2m}\mathrm{d}p_y\right]\left[\int_{-\infty}^{\infty} e^{-\beta {p_z}^2/2m}\mathrm{d}p_z\right] . \tag{3.85}$$

Using the formula established in Exercise 3.4 to carry out the integrals, we obtain

$$C = V\left(\frac{2\pi m}{\beta}\right)^{3/2} . \tag{3.86}$$

By means of (3.71), we find

$$F = -k_B T\left[\ln V + \frac{3}{2}\ln\left(\frac{2\pi m}{\beta}\right)\right] . \tag{3.87}$$

This equation gives F as a function of T, V, and $N = 1$, and hence is a fundamental equation of the system. Other thermodynamic properties of the system can be obtained just by taking partial derivatives. For example, the pressure P is given by

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{k_B T}{V} , \tag{3.88}$$

which is recognized as the ideal gas equation of state applied to a system containing only a single particle. The internal energy follows from (3.72):

$$U = -\frac{\partial \ln C}{\partial \beta} = \frac{3}{2\beta} = \frac{3}{2}k_B T . \tag{3.89}$$

From (2.49),

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2}k_B . \tag{3.90}$$

These nontrivial results were obtained straightforwardly once the multidimensional integral in (3.78) was evaluated. It is doubtful that we would be so successful if we insisted on solving the equations of motion of the particle instead.

Exercise 3.4. Derive the following equality:

$$I(a) := \int_0^{\infty} e^{-ax^2}\mathrm{d}x = \frac{1}{2}\sqrt{\frac{\pi}{a}} . \tag{3.91}$$

Using this result, show that

$$\int_0^{\infty} x^2 e^{-ax^2}\mathrm{d}x = \frac{1}{4}\sqrt{\frac{\pi}{a^3}} \quad \text{and} \quad \int_0^{\infty} x^4 e^{-ax^2}\mathrm{d}x = \frac{3}{8}\sqrt{\frac{\pi}{a^5}} . \tag{3.92}$$

///

Example 3.6. Three-dimensional harmonic oscillator: Consider a particle of mass m bound to the origin by a harmonic potential $\psi(\boldsymbol{r}) = kr^2/2$. Using a Cartesian coordinate system, we specify the position of the particle by x, y, and z. The conjugate momenta are just the components of the linear momentum, that is, p_x, p_y, and p_z. Thus, the system Hamiltonian is

$$H(\boldsymbol{r},\boldsymbol{p}) = \frac{1}{2m}\left({p_x}^2 + {p_y}^2 + {p_z}^2\right) + \frac{1}{2}k\left(x^2 + y^2 + z^2\right) = \frac{p^2}{2m} + \frac{1}{2}kr^2 \,. \quad (3.93)$$

The normalization constant C is given by

$$C = \int e^{-\beta H(\boldsymbol{r},\boldsymbol{p})}\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{p} = \int e^{-\beta p^2/2m} e^{-\beta kr^2/2}\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{p} \,. \quad (3.94)$$

Noting that the result of carrying out the integration with respect to $\boldsymbol{r}$ is independent of $\boldsymbol{p}$, we have

$$C = \left[\int e^{-\beta p^2/2m}\mathrm{d}\boldsymbol{p}\right]\left[\int e^{-\beta kr^2/2}\mathrm{d}\boldsymbol{r}\right] . \quad (3.95)$$

These integrals can be evaluated using the Cartesian coordinate system as in Example 3.5. However, the numerical values of these integrals should be independent of the choice of the coordinate system we use. It is actually easier to evaluate them using the spherical coordinate system. For example,

$$\int e^{-\beta kr^2/2}\mathrm{d}\boldsymbol{r} = \int_0^\infty e^{-\beta kr^2/2} 4\pi r^2 \mathrm{d}r = \left(\frac{2\pi}{\beta k}\right)^{3/2} . \quad (3.96)$$

The first equality is justified because the integrand depends only on r and the volume of the spherical shell defined by two radii r and $r + \mathrm{d}r$ is, to the first order of $\mathrm{d}r$, given by $4\pi r^2 \mathrm{d}r$. The second equality follows from a formula from Exercise 3.4. Evaluating the second integral in (3.95) similarly, we arrive at

$$C = \left(\frac{2\pi m}{\beta}\right)^{3/2}\left(\frac{2\pi}{\beta k}\right)^{3/2} , \quad (3.97)$$

Since $C \propto \beta^{-3}$, we have $\ln C = -3\ln\beta + \text{const}$. Thus,

$$U = 3k_BT \quad \text{and} \quad C_V = 3k_B \,. \quad (3.98)$$

Exercise 3.5. Suppose that the Hamiltonian H of the system of N particles is given by

$$H(\boldsymbol{r}^N,\boldsymbol{p}^N) = \sum_{i=1}^N \frac{\|\boldsymbol{p}_i\|^2}{2m_i} + \phi(\boldsymbol{r}^N) \,. \quad (3.99)$$

Show that the probability $\rho(\boldsymbol{p}_1)\mathrm{d}\boldsymbol{p}_1$ that particle 1 has the linear momentum within the volume element $\mathrm{d}\boldsymbol{p}_1$ taken around $\boldsymbol{p}_1$ is given by

$$\rho(\boldsymbol{p}_1)\mathrm{d}\boldsymbol{p}_1 = \frac{1}{(2\pi m_1 k_B T)^{3/2}} \exp\left(-\frac{\|\boldsymbol{p}_1\|^2}{2m_1 k_B T}\right) \mathrm{d}\boldsymbol{p}_1 \,. \tag{3.100}$$

This is the well-known **Maxwell–Boltzmann distribution**, which is more often expressed as

$$\rho(\boldsymbol{v}_1)\mathrm{d}\boldsymbol{v}_1 = \left(\frac{m_1}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{m_1\|\boldsymbol{v}_1\|^2}{2k_B T}\right) \mathrm{d}\boldsymbol{v}_1 \,, \tag{3.101}$$

where we used $\mathrm{d}\boldsymbol{p}_1 = \mathrm{d}p_{1x}\mathrm{d}p_{1y}\mathrm{d}p_{1z} = {m_1}^3\mathrm{d}v_{1x}\mathrm{d}v_{1y}\mathrm{d}v_{1z} = {m_1}^3\mathrm{d}\boldsymbol{v}_1$. It is worth emphasizing that the Maxwell–Boltzmann distribution holds regardless of the form of the potential energy term $\phi(\boldsymbol{r}^N)$. ///

3.10.2 Equipartition Theorem

Looking back at Examples 3.5 and 3.6, we notice something interesting. In particular, each quadratic term, such as x^2 and ${p_x}^2$, in the Hamiltonian leads to a factor of $\beta^{-1/2}$ in C. In view of (3.72), this means that each quadratic term makes a contribution of $k_BT/2$ and $k_B/2$ to U and C_V, respectively.

This observation can be generalized straightforwardly. Thus, suppose that q_1 occurs in Hamiltonian as a quadratic term and appears nowhere else:

$$H(q^f, p^f) = a{q_1}^2 + h(q_2, \cdots, q_f, p_1, \cdots, p_f) \,. \tag{3.102}$$

If $e^{-\beta H}$ decays sufficiently fast with increasing $|q_1|$, the limits of integration for q_1 that is occurring in (3.46) can be extended to cover from $-\infty$ to ∞. Then, the $a{q_1}^2$ term gives rise to a factor of $(\pi/\beta a)^{1/2}$ in C.

Exercise 3.6. For a system described by the Hamiltonian given by (3.102), show that

$$\langle a{q_1}^2 \rangle = \frac{1}{2} k_B T \,. \tag{3.103}$$

///

More generally, if

$$H(q^f, p^f) = \sum_{i=1}^{f} \left(a_i {q_i}^2 + b_i {p_i}^2\right) \,, \tag{3.104}$$

and the limits of integration can be similarly extended to from $-\infty$ to ∞ for all q^f and p^f, then,

$$U = f k_B T, \quad \text{and} \quad C_V = f k_B \,. \tag{3.105}$$

This is called the **equipartition theorem** or the **principle of equipartition of energy** to indicate that U, on average, is partitioned equally among each mechanical degrees of freedom.

3.10.3 Spherical Coordinate System

In Example 3.6, we wrote down the expression for H using the Cartesian coordinate system and used the spherical coordinate system only in the last step when computing the multidimensional integrals for C. It is instructive to rework the same problem using the spherical coordinate system from the beginning.

Example 3.7. Three-dimensional harmonic oscillator: spherical coordinate system: We start from the Lagrangian:

$$L(\boldsymbol{r},\dot{\boldsymbol{r}}) = \frac{1}{2m}\left(\dot{x}^2+\dot{y}^2+\dot{z}^2\right) - \frac{1}{2}kr^2 \,. \tag{3.106}$$

In a spherical coordinate system,

$$x = r\sin\theta\cos\phi, \quad y = r\sin\theta\sin\phi, \quad z = r\cos\theta \,. \tag{3.107}$$

Taking the time derivative of these expressions, we find

$$\begin{aligned}\dot{x} &= \dot{r}\sin\theta\cos\phi + r\dot{\theta}\cos\theta\cos\phi - r\dot{\phi}\sin\theta\sin\phi \\ \dot{y} &= \dot{r}\sin\theta\sin\phi + r\dot{\theta}\cos\theta\sin\phi + r\dot{\phi}\sin\theta\cos\phi \\ \dot{z} &= \dot{r}\cos\theta - r\dot{\theta}\sin\theta \,. \end{aligned} \tag{3.108}$$

Using these expressions, we find[16]

$$\dot{x}^2+\dot{y}^2+\dot{z}^2 = \dot{r}^2 + r^2\dot{\theta}^2 + r^2\dot{\phi}^2\sin^2\theta \,. \tag{3.109}$$

Thus, in terms of the generalized coordinates r, θ, ϕ, and the corresponding generalized velocities $\dot{r}$, $\dot{\theta}$, and $\dot{\phi}$, the Lagrangian is given by

$$L = \frac{1}{2}m\left(\dot{r}^2 + r^2\dot{\theta}^2 + r^2\dot{\phi}^2\sin^2\theta\right) - \frac{1}{2}kr^2 \,. \tag{3.110}$$

By definition (1.103), the corresponding generalized momenta are

$$p_r = \frac{\partial L}{\partial \dot{r}} = m\dot{r}, \quad p_\theta = \frac{\partial L}{\partial \dot{\theta}} = mr^2\dot{\theta}, \quad p_\phi = \frac{\partial L}{\partial \dot{\phi}} = mr^2\dot{\phi}\sin^2\theta \,. \tag{3.111}$$

The Hamiltonian follows from (1.156) and is given by

$$H = \sum_i p_i \dot{q}_i - L = \frac{{p_r}^2}{2m} + \frac{{p_\theta}^2}{2mr^2} + \frac{{p_\phi}^2}{2mr^2 \sin^2\theta} + \frac{1}{2}kr^2 . \tag{3.112}$$

According to (3.46), the normalization constant C is given by

$$C = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} e^{-\beta H} \mathrm{d}\phi \mathrm{d}\theta \mathrm{d}r \mathrm{d}p_\phi \mathrm{d}p_\theta \mathrm{d}p_r , \tag{3.113}$$

in which ϕ, θ, and r are the generalized coordinates in this problem with the corresponding generalized momentum given by p_ϕ, p_θ, and p_r, respectively. Carrying out the integrations with respect to p_ϕ, p_θ, and p_r by means of the formula from Exercise 3.4, we find

$$C = \int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} \left(\frac{2\pi m}{\beta}\right)^{1/2} \left(\frac{2\pi mr^2}{\beta}\right)^{1/2} \left(\frac{2\pi mr^2 \sin^2\theta}{\beta}\right)^{1/2} \times e^{-\frac{1}{2}\beta kr^2} \mathrm{d}\phi \mathrm{d}\theta \mathrm{d}r . \tag{3.114}$$

But, because $\sin\theta \geq 0$ for $0 \leq \theta \leq \pi$, we have $(\sin^2\theta)^{1/2} = \sin\theta$. Thus,

$$C = \left(\frac{2\pi m}{\beta}\right)^{3/2} \int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} e^{-\frac{1}{2}\beta kr^2} r^2 \sin\theta \mathrm{d}\phi \mathrm{d}\theta \mathrm{d}r . \tag{3.115}$$

We observe that the Jacobian $r^2 \sin\theta$ of the coordinate transformation from (x, y, z) to (r, θ, ϕ) appeared naturally *without us having to put it in by hand*. Evaluating the integrals over ϕ, θ, and r in this order, we find

$$C = \left(\frac{2\pi m}{\beta}\right)^{3/2} \left(\frac{2\pi}{\beta k}\right)^{3/2} \tag{3.116}$$

in agreement with the result we found in Example 3.6.

Exercise 3.7. Counting the number of quadratic terms in (3.93), we conclude from the equipartition theorem that $U = 3k_BT$. Doing the same in (3.112), one might conclude that $U = 2k_BT$. Resolve this apparent contradiction. ///

Exercise 3.8. As a model for a diatomic molecule, take a pair of particles of mass m_1 and m_2 connected by a massless rigid rod of length l:

a. Calculate the normalization constant C for the system consisting of a single diatomic molecule confined to a cubic box of volume V. You may assume that $V^{1/3} \gg l$. Why is this assumption convenient?
b. What is the constant volume heat capacity C_V of the system?

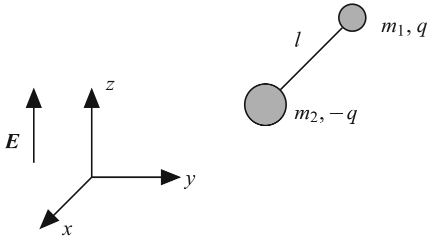


Fig. 3.5 A simple model of a polar molecule.

c. Replace the rigid rod by a harmonic spring of natural length l and spring constant k, and then redo the calculation. To make the computation analytically tractable, assume that $e^{-\beta k l^2/2} \approx 0$. ///

Exercise 3.9. Continuing with the rigid diatomic molecule from Exercise 3.8, suppose that the particles m_1 and m_2 carry electric charges q and $-q$, respectively. (See Fig. 3.5.) In the presence of a static electric field $\boldsymbol{E}$, the additional term $-\boldsymbol{m}_e \cdot \boldsymbol{E}$ is needed in the Hamiltonian of the molecule, where the dipole moment $\boldsymbol{m}_e$ is a vector of length ql pointing from m_2 to m_1:

a. Evaluate C of the molecule confined to a cubic box of volume V.

b. Show that

$$\frac{\partial \ln C}{\partial \boldsymbol{E}} = \beta \langle \boldsymbol{m}_e \rangle \, . \tag{3.117}$$

c. Show that

$$\frac{\partial E}{\partial \boldsymbol{E}} = \frac{\boldsymbol{E}}{E} \, , \tag{3.118}$$

where $E := \|\boldsymbol{E}\|$ should not be confused with energy.

d. Show that

$$\langle \boldsymbol{m}_e \rangle = m_e \mathscr{L}(\beta m_e E) \boldsymbol{e} \, , \tag{3.119}$$

where $\boldsymbol{e}$ is the unit vector pointing in the direction of the field and

$$\mathscr{L}(x) := \coth x - \frac{1}{x} = \frac{\cosh x}{\sinh x} - \frac{1}{x} \tag{3.120}$$

is the **Langevin function**.

In part a, the computation will be considerably easier if you align the z-axis with $\boldsymbol{E}$ as shown in Fig. 3.5. Since our choice of the coordinate system is arbitrary, this leads to no loss of generality. ///

3.10.4 †General Equipartition Theorem

In this section, we consider a more general form of the equipartition theorem. In particular, we establish that

$$\left\langle q_i \frac{\partial H}{\partial q_i} \right\rangle = k_B T \quad \text{and} \quad \left\langle p_i \frac{\partial H}{\partial p_i} \right\rangle = k_B T \ . \tag{3.121}$$

For example, let

$$H = \frac{1}{2m}\left({p_x}^2 + {p_y}^2 + {p_z}^2\right) \ . \tag{3.122}$$

According to (3.121),

$$k_B T = \left\langle p_x \frac{\partial H}{\partial p_x} \right\rangle = \left\langle \frac{{p_x}^2}{m} \right\rangle \tag{3.123}$$

in agreement with the more restricted form of the theorem discussed in Sect. 3.10.2.

To prove (3.121), let us first consider the following partial derivative:

$$\frac{\partial}{\partial q_1}\left(q_1 e^{-\beta H}\right) = e^{-\beta H} - \beta q_1 \frac{\partial H}{\partial q_1} e^{-\beta H} \ . \tag{3.124}$$

Integrating this expression over the entire phase space,

$$\int \left[q_1 e^{-\beta H}\right]_{q_1=-\infty}^{q_1=\infty} \mathrm{d}q_2 \cdots \mathrm{d}q_f \mathrm{d}p^f = C - \beta \int q_1 \frac{\partial H}{\partial q_1} e^{-\beta H} \mathrm{d}q^f \mathrm{d}p^f \ . \tag{3.125}$$

If the Hamiltonian is such that the Boltzmann factor vanishes for sufficiently large values of $|q_1|$, then the left-hand side of this equation is zero, yielding

$$k_B T = \frac{1}{C} \int q_1 \frac{\partial H}{\partial q_1} e^{-\beta H} \mathrm{d}q^f \mathrm{d}p^f = \left\langle q_1 \frac{\partial H}{\partial q_1} \right\rangle \ . \tag{3.126}$$

Likewise for the other q's. Carrying out the similar analysis with p_i, we obtain the second of (3.121).

3.11 Canonical Ensemble and Thermal Contact

In this section, we shall return to the question posed at the beginning of Sect. 3.9. On the one hand, ρ was determined by observing a single system for a long duration of time. During such an observation, the energy of the system should remain constant. On the other hand, the canonical ensemble contains the copies with various values of the energy. Does this mean that the canonical ensemble, despite its apparent success we saw in the previous sections, is purely an artificial construction with no counterpart in the real-world situation?

Let us go back to (3.45). This equation tells us that if we wanted to predict macroscopic behavior of a system by means of a canonical ensemble, we must first specify its temperature. Under an observational situation in which we wish to specify and control temperature, however, we must allow for an exchange of energy between the system and the surroundings. As a result, the energy of the system does not, in general, remain constant. So, the fact that the canonical ensemble contains the copies with various values of the energy does not invalidate this ensemble. Rather, it suggests that the ensemble may be relevant in describing the behavior of a system in *thermal contact* with the surroundings. In fact, under a modest set of assumptions, we can show that the canonical ensemble is the only possible ensemble one can construct for such cases.

First, we need to introduce the notion of a **weak interaction**. Let us consider an isolated system $\mathscr{S}_t$, in which we take a subsystem $\mathscr{S}_s$ enclosed by a rigid wall impermeable to particles. The other part of $\mathscr{S}_t$ will be referred to as the surroundings and denoted by $\mathscr{S}_r$. Quite generally then, the Hamiltonian H_t of $\mathscr{S}_t$ can be written as

$$H_t(q^{m+n}, p^{m+n}) = H_s(q^m, p^m) + H_r(q^n, p^n) + H_{\text{int}}(q^{m+n}, p^{m+n}) \,, \tag{3.127}$$

where m and n denote the numbers of mechanical degrees of freedom of $\mathscr{S}_s$ and $\mathscr{S}_r$, respectively. The last term H_{int} arises from the interaction between $\mathscr{S}_s$ and $\mathscr{S}_r$.

We note that this division of $\mathscr{S}_t$ into $\mathscr{S}_s$ and $\mathscr{S}_r$ would be purely formal and quite useless if H_{int} is of a comparable magnitude to either H_s or H_r. On the other hand, if H_{int} is identically zero, then we might as well imagine $\mathscr{S}_s$ and $\mathscr{S}_r$ as sitting at the opposite ends of a galaxy, and there will be very little motivation for us to study them simultaneously by regarding them as constituting a composite system $\mathscr{S}_t$. The situation we are interested in is somewhere in between.

With this in mind, the interaction between $\mathscr{S}_s$ and $\mathscr{S}_r$ is said to be *weak* if (1) H_{int} is of a negligible magnitude compared to H_s and H_r for typical values of their arguments to justify the approximation,

$$H_t(q^{m+n}, p^{m+n}) \approx H_s(q^m, p^m) + H_r(q^n, p^n) \tag{3.128}$$

but, at the same time, (2) it is still sufficient to ensure exchange of energy between $\mathscr{S}_s$ and $\mathscr{S}_r$ over a long duration of time.

Now, suppose that $\mathscr{S}_s$ consists of subsystems A and B and denote the numbers of mechanical degrees of freedom of these subsystems by m_a and m_b, respectively. Clearly, $m = m_a + m_b$. Furthermore, suppose that the interaction between A and B is also weak in the sense just defined. Then, we may write

$$H_s(q^m, p^m) \approx H_a(q^{m_a}, p^{m_a}) + H_b(q^{m_b}, p^{m_b}) \,, \tag{3.129}$$

where we note that H_a depends only on the generalized coordinates and the conjugate momenta pertaining to the mechanical degrees of freedom of subsystem A. Likewise for H_b. Thus, when Hamilton's equations of motion are obtained from H_s, we should find out that those equations of motion dictating the time evolution of (q^{m_a}, p^{m_a}) are decoupled from those governing (q^{m_b}, p^{m_b}).

This approximate independence between the two subsystems implies that

$$\rho_s \approx \rho_a \rho_b \, , \tag{3.130}$$

and hence that

$$\ln \rho_s \approx \ln \rho_a + \ln \rho_b \, . \tag{3.131}$$

We recall from Sect. 3.6 that ρ is a function of constants of motion. Here we see that $\ln \rho$ is also additive. These requirements will be met if $\ln \rho$ is a linear function of constants of motion which are themselves additive. We note that energy is such a quantity and that the linear dependence of $\ln \rho$ on energy already indicates the canonical distribution.[17]

To see this more explicitly, let us suppose that ρ is a function of H only. If statistical mechanics is to have any predictive ability at all, this function $\rho(H)$ cannot be specific to each system we happen to choose for our study. Instead, we demand that the form of the function $\rho(H)$ is independent of a particular system under consideration. Thus, letting

$$\rho = af(H) \, , \tag{3.132}$$

where a is a system-dependent constant that can be determined by the normalization condition of ρ, we write

$$a_s f(H_a + H_b) = a_a f(H_a) a_b f(H_b) \, . \tag{3.133}$$

Differentiating this equation with respect to H_a, we find

$$a_s f'(H_a + H_b) = a_a f'(H_a) a_b f(H_b) \, , \tag{3.134}$$

while differentiation with respect to H_b yields

$$a_s f'(H_a + H_b) = a_a f(H_a) a_b f'(H_b) \, . \tag{3.135}$$

From these two equations,

$$\frac{f'(H_a)}{f(H_a)} = \frac{f'(H_b)}{f(H_b)} \, , \tag{3.136}$$

which must hold regardless of the values of H_a and H_b. Note that the left-hand side depends only on H_a, while the right-hand side depends only on H_b, indicating that they can only be a constant. For example, we may arbitrarily fix H_a at 1J, and then allow H_b to change. Even then the equation must hold true since it holds for *any* values of H_a and H_b. Likewise, we can fix H_b and allow H_a to change. In any event, the expressions in (3.136) are equal to some constant, which we denote by $-\beta$. Upon integration, then we find

$$f(x) = be^{-\beta x} \, , \tag{3.137}$$

where b is a constant. When this expression is substituted into (3.132) and ab is determined by the normalization condition of ρ, we find that

$$\rho_a = {C_a}^{-1} e^{-\beta H_a}\,, \quad \rho_b = {C_b}^{-1} e^{-\beta H_b}\,, \quad \text{and} \quad \rho_s = {C_s}^{-1} e^{-\beta H_s}\,, \tag{3.138}$$

which is the canonical distribution as advertised.

That β is common to subsystems A and B is quite consistent with our earlier conclusion that $\beta = (k_B T)^{-1}$. At equilibrium, the subsystems A and B both in contact with the same surroundings should have the same temperature. As noted already in Sect. 3.9, β must be positive in order for the integral for C to converge, an observation consistent with β being $(k_B T)^{-1}$.

If we substitute (3.138) into (3.130) and use (3.129), we arrive at the conclusion that

$$C_s = C_a C_b\,. \tag{3.139}$$

Or, equivalently,

$$\ln C_s = \ln C_a + \ln C_b\,, \tag{3.140}$$

which in light of (3.71) indicates that the Helmholtz free energy is an additive quantity.

It is significant that the additivity of the free energy relies on the interaction between the two subsystems A and B being sufficiently weak. This is the case if A and B are both macroscopic and the intermolecular potential between the molecules of A and those of B are sufficiently short ranged as to affect only those molecules near the boundary of the subsystems. Then, the interaction amounts to a surface effect, which is usually negligible for a macroscopic body.

If you look back at our derivation of Liouville's theorem in Sect. 3.6, which guided our search for ρ, you might wonder, however. Did we not write down equations of motion for the system assuming that it was isolated? Then, in our search for ρ of a system in thermal contact with the surroundings, why can we still accept the conclusion drawn from Liouville's theorem and limit our search of ρ to the functions of H alone?

But, we recall that the interaction between the system and the surroundings were supposed to be sufficiently weak. So, over a time interval that is not too long, the system behaves like an isolated system to a sufficient degree of accuracy. The equations of motion obtained by ignoring H_{int}, and hence Liouville's theorem, will be sufficiently accurate over such a time interval. If many segments of phase trajectory from many such intervals of time are combined together, we expect to end up with a canonical distribution.

Exercise 3.10. What is the role of the surroundings $\mathscr{S}_r$ in arriving at (3.138)? ///

Exercise 3.11. Show that the entropy as given by Gibbs's entropy formula is additive. ///

3.12 Corrections from Quantum Mechanics

As pointed out at the end of Sect. 3.9, our formula (3.71) for F is not quite correct as it stands. In this section, we see why this is so and then introduce necessary corrections.

3.12.1 A System of Identical Particles

Suppose that we have N noninteracting identical particles in a rectangular box of dimension $L_x \times L_y \times L_z$. The Hamiltonian is given by

$$H(\boldsymbol{r}^N,\boldsymbol{p}^N) = \sum_{i=1}^{N} \frac{\|\boldsymbol{p}_i\|^2}{2m} + \psi_{\mathrm{w}}(\boldsymbol{r}^N) , \tag{3.141}$$

where ψ_{w} is the wall potential as in Example 3.5. With $\boldsymbol{p}_i \doteq (p_{ix}, p_{iy}, p_{iz})$, we have $\|\boldsymbol{p}_i\|^2 = {p_{ix}}^2 + {p_{iy}}^2 + {p_{iz}}^2$. Thus,

$$C = \int e^{-\beta H(\boldsymbol{r}^N,\boldsymbol{p}^N)} \mathrm{d}\boldsymbol{r}^N \mathrm{d}\boldsymbol{p}^N = V^N \left(\frac{2\pi m}{\beta}\right)^{3N/2} . \tag{3.142}$$

(If this result is not obvious to you, set $N = 2$ and evaluate C following Example 3.5.) Combining (3.71) and (3.142), we obtain

$$F = -k_B T \left[\frac{3N}{2} \ln(2\pi m k_B T) + N \ln V\right] \tag{3.143}$$

for the Helmholtz free energy of the system. The pressure of the system follows from

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{N k_B T}{V} , \tag{3.144}$$

which is the ideal gas equation of state.

Our expression for F, however, is not quite correct. To see this, let us rewrite (3.143) as

$$F = a_1(T)N + a_2(T)N \ln V , \tag{3.145}$$

where a_1 and a_2 are some functions of T. Now, we recall from (3.140) and also from thermodynamics that F is extensive, that is,

$$F(T,\lambda V,\lambda N) = \lambda F(T,V,N) , \tag{3.146}$$

which is in direct conflict with the result just obtained. Equally disturbing is the fact that (3.145) fails to satisfy the Euler relation as you can easily verify by writing the latter as

$$F = -PV + \mu N . \tag{3.147}$$

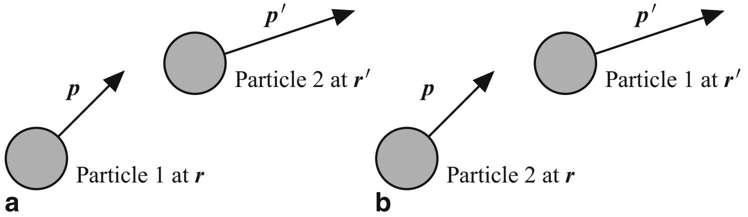


Fig. 3.6 In classical mechanics, **a** and **b** represent two distinct microstates $(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{p}_1,\boldsymbol{p}_2) = (\boldsymbol{r},\boldsymbol{r}',\boldsymbol{p},\boldsymbol{p}')$ and $(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{p}_1,\boldsymbol{p}_2) = (\boldsymbol{r}',\boldsymbol{r},\boldsymbol{p}',\boldsymbol{p})$, respectively. According to quantum mechanics, they represent the same state.

Statistical mechanics as we have developed it so far cannot coexist with thermodynamics!

What went wrong? The problem is *not* with our development of statistical mechanics. Rather, it is with our starting point, that is, classical mechanics. The difficulty lies in the fact that the behavior of molecules is governed not by classical mechanics but by quantum mechanics. To address the difficulty with (3.143), we simply borrow a few relevant facts from quantum mechanics.

In classical mechanics, particles are distinguishable even if they look exactly the same. At $t = 0$, we can mentally label all the molecules in the system and measure their positions and velocities. Then, the equations of motion will tell us precisely which particle is where at any other instant. Thus, for any particle we pick at a later time, we know the label we have given it at the earlier time even if we were not paying any attention to the system in between. According to quantum mechanics, however, this simply cannot be done *even in principle*. In the quantum mechanical world, identical particles are *fundamentally indistinguishable*, that is, neither a computational nor an experimental means of distinguishing them can ever be constructed.

Recall that C was introduced as the normalization constant. By writing

$$C = \int e^{-\beta H(\boldsymbol{r}^N,\boldsymbol{p}^N)} \mathrm{d}\boldsymbol{r}^N \mathrm{d}\boldsymbol{p}^N \,, \tag{3.148}$$

we hoped to sum the unnormalized probability $e^{-\beta H}\mathrm{d}\boldsymbol{r}^N\mathrm{d}\boldsymbol{p}^N$ over all possible states. According to quantum mechanics, however, this amounts to counting each state many times.

To figure out exactly how many times, consider a system of just two particles. In the integral

$$C = \int e^{-\beta H} \mathrm{d}\boldsymbol{r}_1 \mathrm{d}\boldsymbol{r}_2 \mathrm{d}\boldsymbol{p}_1 \mathrm{d}\boldsymbol{p}_2 \,, \tag{3.149}$$

the configurations shown in Fig. 3.6a and b are both included. But, quantum mechanics tells us to count these classical mechanically distinct two states as a single state. Since these two states have the identical value of the Boltzmann factor, they contribute equally to C. The same consideration applies to any other pair of

N	Exact	(3.152)	(3.153)
1	0	−0.8106	−1
2	0.6931	0.6518	−0.6137
3	1.7917	1.7641	0.29584
4	3.1781	3.1573	1.5452
5	4.7875	4.7708	3.0472
10	15.104	15.096	13.026
50	148.48	148.48	145.60
100	363.74	363.74	360.52
1000	5912.1	5912.1	5907.8
10000	82109	82109	82103

Table 3.1 Accuracy of the approximate formulae, (3.152) and (3.153), for computing $\ln N!$.

classical mechanically distinct, but quantum mechanically identical, states. Thus, we should really be writing the normalization constant as

$$C' = \frac{1}{2}\int e^{-\beta H}\mathrm{d}\boldsymbol{r}_1\mathrm{d}\boldsymbol{r}_2\mathrm{d}\boldsymbol{p}_1\mathrm{d}\boldsymbol{p}_2\ . \tag{3.150}$$

What happens if we have three particles? To answer this, we note that Fig. 3.6b was obtained from Fig. 3.6a simply by switching the labels "1" and "2" attached to the two particles, and the number 2 which divides C can be understood as the number of distinct ways of labeling the particles in the system. When we have three particles, there are $3! = 3\cdot 2\cdot 1 = 6$ distinct ways of labeling them. (Using the labels 1, 2, and 3 once and only once.)

Generalizing this result to a system of N identical particles, we conclude that the number of distinct permutations of N particles is $N! := N(N-1)(N-2)\cdots 3\cdot 2\cdot 1$. So, we should have defined the normalization factor by

$$C' = \frac{1}{N!}\int e^{-\beta H(\boldsymbol{r}^N,\boldsymbol{p}^N)}\mathrm{d}\boldsymbol{r}^N\mathrm{d}\boldsymbol{p}^N\ . \tag{3.151}$$

For a sufficiently large N, the following approximate relation, called **Stirling's formula**, holds.

$$\ln N! \approx N\ln N - N + \frac{1}{2}\ln(2\pi N) \tag{3.152}$$

$$\approx N\ln N - N\ . \tag{3.153}$$

The accuracy of these approximate formulae is illustrated in Table 3.1. In statistical mechanics, the typical values of N are in the order of 10^{24} and (3.153) is seen to be quite sufficient.

Using (3.153), we can show that the Helmholtz free energy defined by

$$F := -k_B T\ln C' \tag{3.154}$$

is an extensive quantity for a system of N noninteracting identical particles.

Exercise 3.12. Prove this statement. ///

Exercise 3.13. Provide a plausibility argument to support (3.153). ///

What if N is not large enough to ensure the accuracy of Stirling's formula? In this case, even with the $N!$ factor, the Helmholtz free energy of the system is not extensive. This is not a cause for a concern, though. If two small systems are brought together, the energy of their mutual interaction can be comparable with the energy of either one of them alone. As discussed in Sect. 3.11, there is no reason to expect the free energy to be extensive in such cases.

As of now, we shall officially retire (3.71). You do not need (3.154) beyond this point, either. In its place, we introduce the correct formula for F in (3.167). That is the equation you need to remember and use.

3.12.2 Implication of the Uncertainty Principle

There is another important quantum mechanical effect, which we have ignored up to this point. Contrary to the underlying assumption of classical mechanics, the **Heisenberg uncertainty principle** states that both $\boldsymbol{r}$ and $\boldsymbol{p}$ of a particle cannot be determined simultaneously with absolute precision. Instead, quantum mechanics places a *fundamental limit* on the precision that is achievable in our measurement.

Focusing only on the x-component, let $(\Delta x)_{QM}$ denote the uncertainty[18] associated with the measured value of x. Likewise, $(\Delta p_x)_{QM}$ is the uncertainty associated with the measured value of p_x. Naturally, we would like to make both $(\Delta x)_{QM}$ and $(\Delta p_x)_{QM}$ as small as possible. However, the uncertainty principle demands that, for a *simultaneous* measurement of x and p_x, they satisfy

$$(\Delta x)_{QM}(\Delta p_x)_{QM} \gtrsim h\,, \tag{3.155}$$

where the quantity $h = 6.626 \times 10^{-34}$ (J·s) is the **Planck constant** having the dimension of *action* as in action integral. The similar relations hold for the y- and z- components of $\boldsymbol{r}$ and $\boldsymbol{p}$. Even though h is very small, it is not zero. If we are to determine x with absolute certainty, that is, if $(\Delta x)_{QM} = 0$, then we have absolutely no idea what p_x is at that very moment. We emphasize that this limitation is not due to practical difficulties in manufacturing a measuring device, but that it is a consequence of the principles of quantum mechanics.

To explore the consequence of (3.155), let us consider a system of a single particle confined to a one-dimensional container. In its phase space, suppose we take a box of area h. Classical mechanically, there are infinitely many distinct states in this box, and the integration

$$\int_{p_x-(\Delta p_x)_{QM}/2}^{p_x+(\Delta p_x)_{QM}/2} \int_{x-(\Delta x)_{QM}/2}^{x+(\Delta x)_{QM}/2} e^{-\beta H(x,p_x)} \mathrm{d}x\mathrm{d}p_x \tag{3.156}$$

adds up the Boltzmann factor for all of these states. According to quantum mechanics, however, it is meaningless to try to distinguish these states. Thus, the integration should be replaced by a single Boltzmann factor.

Because the area h of the box is actually quite small, the Boltzmann factor remains essentially constant within the box. (We could of course make $(\Delta x)_{QM}$ extremely small causing $(\Delta p_x)_{QM}$ to be extremely large, and vice versa. Such a choice of a box must be excluded in order for our argument to hold.) So, in place of (3.156), we can simply write

$$e^{-\beta H(x^*,p_x{}^*)} \tag{3.157}$$

without being precise about the values of x^* and p^* except to note that (x^*,p^*) should be somewhere in the box of area h:

$$x-\frac{(\Delta x)_{QM}}{2}\le x^*\le x+\frac{(\Delta x)_{QM}}{2} \quad \text{and} \quad p_x-\frac{(\Delta p_x)_{QM}}{2}\le p_x{}^*\le p_x+\frac{(\Delta p_x)_{QM}}{2}\ . \tag{3.158}$$

Due to the smallness of h, we can replace (3.157) by its average taken inside the box:

$$\frac{1}{h}\int_{p_x-(\Delta p_x)_{QM}/2}^{p_x+(\Delta p_x)_{QM}/2}\int_{x-(\Delta x)_{QM}/2}^{x+(\Delta x)_{QM}/2} e^{-\beta H(x,p_x)}\mathrm{d}x\mathrm{d}p_x \tag{3.159}$$

without introducing a noticeable change in the end result. Computationally, this is a much easier quantity to handle than (3.157).

The uncertainty relation holds for any pair of a generalized coordinate and its conjugate momentum. Thus, generalizing the above consideration to the case of a mechanical system having f degrees of freedom, we may regard a volume element of size h^f in the phase space as containing a single state, and write the normalization constant as

$$Z=\frac{1}{h^f}\int e^{-\beta H(q^f,p^f)}\mathrm{d}q^f\mathrm{d}p^f\ . \tag{3.160}$$

As we saw in the previous section, if there are identical particles in the system and the integration over q^f and p^f induces $\mathscr{P}$ distinct permutations of identical particles, we have

$$Z=\frac{1}{h^f\mathscr{P}}\int e^{-\beta H(q^f,p^f)}\mathrm{d}q^f\mathrm{d}p^f\ . \tag{3.161}$$

The quantity Z is called the **canonical partition function** and is *dimensionless*.

For a system of N identical particles in a three-dimensional space, we have $h^f\mathscr{P}=h^{3N}N!$, and hence the partition function is given by

$$Z=\frac{1}{h^{3N}N!}\int e^{-\beta H(\boldsymbol{r}^N,\boldsymbol{p}^N)}\mathrm{d}\boldsymbol{r}^N\mathrm{d}\boldsymbol{p}^N\ . \tag{3.162}$$

The actual uncertainty relation reads

$$\langle\Delta x\rangle_{QM}\langle\Delta p_x\rangle_{QM}\ge\frac{h}{4\pi} \tag{3.163}$$

as we shall see in Sect. 8.7.2. However, 4π does not factor in here. The $1/h^{3N}N!$ factor is chosen so that the quantum mechanical partition function agrees with our Z in the so called classical limit. See Sect. 8.16.5 for details.

We emphasize that the correction factor $1/h^f\mathscr{P}$ (or $1/h^{3N}N!$) arises from quantum mechanical considerations and is quite foreign to purely classical mechanical view of the world. This makes an intuitive interpretation of such *hybrid formula* as (3.161) and (3.162) difficult to obtain. In fact, any such attempt, if taken too literally, leads to contradiction with the correct quantum mechanical interpretation. Nevertheless, we find it convenient to interpret $\int$ as "the sum over states" as before and regard

$$e^{-\beta H(q^f,p^f)}\frac{\mathrm{d}q^f\mathrm{d}p^f}{h^f\mathscr{P}}\,, \tag{3.164}$$

as the unnormalized probability of finding the system within the infinitesimal volume element $\mathrm{d}q^f\mathrm{d}p^f$ in the phase space taken around the phase point (q^f,p^f). Dividing (3.164) by the normalization factor Z, we see that

$$\rho(q^f,p^f)\mathrm{d}q^f\mathrm{d}p^f=\frac{1}{Z}e^{-\beta H(q^f,p^f)}\frac{\mathrm{d}q^f\mathrm{d}p^f}{h^f\mathscr{P}} \tag{3.165}$$

is the normalized probability of finding the system within the infinitesimal volume element $\mathrm{d}q^f\mathrm{d}p^f$.

The breakdown of Z into the sum over states and the unnormalized probability is not unique. We note, however, that the probability given by (3.165) is dimensionless while the probability *density* ρ as defined by this equation carries the dimension of 1/(action)^f. This is what one should expect.

The ensemble average $\langle A\rangle$ of a dynamical variable A is now given by

$$\langle A\rangle=\frac{1}{Z}\int A(q^f,p^f)e^{-\beta H(q^f,p^f)}\frac{\mathrm{d}q^f\mathrm{d}p^f}{h^f\mathscr{P}}\,. \tag{3.166}$$

Since $Z=C/h^f\mathscr{P}$, the correction factor $h^f\mathscr{P}$ drops out when computing the ensemble average and (3.48) requires no modification. However, (3.71) must be corrected. Introducing the correction factor $h^f\mathscr{P}$ into C, we have

$$F=-k_BT\ln Z\,. \tag{3.167}$$

in place of (3.71). As seen from the following exercise, we have

$$S=-k_B\langle\ln(h^f\mathscr{P}\rho)\rangle\,. \tag{3.168}$$

The latter is identical to (3.68) except for the $h^f\mathscr{P}$ factor.

Exercise 3.14. Using (3.165), (3.167), and the definition $F:=U-TS$, show that S is given by (3.168). ///

3.12.3 Applicability of Classical Statistical Mechanics

We introduced the $1/h^{3N}N!$ factor based on quantum mechanical considerations. By simply grafting quantum concepts onto the classical mechanical framework, however, we cannot possibly expect to arrive at a theory that agrees with quantum mechanical predictions on *all* accounts. It is therefore important for us to know when we can expect classical statistical mechanics, with the factor $1/h^{3N}N!$, to be an acceptable mode of description.

First, we define

$$(\Delta p_x)_{SM} := \left\langle (p_x - \langle p_x \rangle)^2 \right\rangle^{1/2} , \tag{3.169}$$

which may be considered as the purely statistical mechanical uncertainty in p_x. For a classical mechanical particle in a box,

$$\frac{1}{2}k_B T = \left\langle \frac{{p_x}^2}{2m} \right\rangle . \tag{3.170}$$

as we saw in Example 3.5. You can also easily convince yourself that $\langle p_x \rangle = 0$ since the probability density ρ is an even function of p_x. Thus,

$$(\Delta p_x)_{SM} = \sqrt{mk_B T} . \tag{3.171}$$

Given that this statistical mechanical uncertainty is always present in systems of our interest, we have no reason to require the quantum mechanical uncertainty $(\Delta p_x)_{QM}$ to be any smaller than this. At the same time, we probably do not want $(\Delta p_x)_{QM}$ to be much larger than $(\Delta p_x)_{SM}$, either. Otherwise, predictions of classical statistical mechanics would be of little use. Demanding, therefore, that they are of comparable magnitude, we may rewrite (3.155) as

$$(\Delta x)_{QM} \approx \frac{h}{\sqrt{mk_B T}} \approx \frac{h}{\sqrt{2\pi m k_B T}} =: \Lambda , \tag{3.172}$$

where the quantity Λ, defined by the expression proceeding it, is known as the **thermal wavelength**.

The classical approach would be acceptable if Λ is much smaller than the diameter of particles in the system since in that case, *for all practical purposes* we know "exactly" where our particles are. Assuming a typical value of 2×10^{-10} m for the diameter of an atom, this requirement translates to $T \gg 2$ K for argon and $T \gg 20$ K for helium.

Exercise 3.15. By making an appropriate change to the normalization constant C you have computed in Exercise 3.8a, compute the partition function Z for the rigid diatomic molecule. ///

Exercise 3.16. As a model for an ideal gas, consider a collection of N noninteracting identical particles confined to a container of volume V:

a. Compute the partition function Z of the ideal gas.
b. Derive expressions for internal energy, pressure, and chemical potential of the ideal gas. ///

Exercise 3.17. A binary ideal gas mixture consisting of $2N$ particles of species A and N particles of species B is confined to a container of volume V made of diathermal, rigid, and impermeable wall, and is maintained at constant T. Find the reversible work required to isothermally separate the mixture into pure A and B occupying $V/3$ and $2V/3$, respectively. ///

3.13 †A Remark on the Statistical Approach

In the traditional approach to statistical mechanics, the notion of statistical ensemble and that of an ensemble average are introduced independent of a long-time average. The equivalence between these two kinds of average,

$$\langle A \rangle = A_{\text{expt}} , \tag{3.173}$$

is then adopted as a hypothesis. Any attempt to justifying this hypothesis on the basis of classical mechanics leads to a very difficult problem called the **ergodic problem**.

For us, (3.173) is a consequence of how we constructed our statistical ensemble. This, however, *does not* mean that we have circumvented the ergodic problem. In fact, we have not shown how our observation of a single mechanical system over the time period τ should lead to ρ that is given by (3.45).

We recall that $\tau \to \infty$ in (3.11) only meant that τ is much longer than the characteristic time scale of vibrational molecular motion. The actual value of τ we had in mind is comparable with a duration of a typical measurement, say 10^{-4} s or so. Certainly, this is not sufficiently long for a given molecule, in a glass of water for example, to fully explore all possible positions (and momentum) accessible to it. Diffusive exploration by this molecule throughout the entire glass takes much longer than 10^{-4} s. Nevertheless, the Boltzmann factor $e^{-\beta H}$ is nonzero for all possible positions of this molecule with finite H. Despite this contradiction, our statistical approach is apparently very successful. Why is that?

We can offer at least two qualitative explanations. Firstly, our macroscopic measurement is not fine enough to distinguish two molecules of the same species. Quantum mechanics actually preclude this possibility. Thus, we are concerned only with those dynamical variables that are invariant with respect to permutation of *identical* molecules. The value of a dynamical variable A evaluated at two distinct phase points

$$(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3,\dots,\boldsymbol{r}_N,\boldsymbol{p}_1,\boldsymbol{p}_2,\boldsymbol{p}_3,\dots,\boldsymbol{p}_N) \quad \text{and} \quad (\boldsymbol{r}_2,\boldsymbol{r}_1,\boldsymbol{r}_3,\dots,\boldsymbol{r}_N,\boldsymbol{p}_2,\boldsymbol{p}_1,\boldsymbol{p}_3,\dots,\boldsymbol{p}_N) , \tag{3.174}$$

for example, should be equal.

Secondly, macroscopic measurements are usually not sufficiently sensitive. Thus, even if the phase trajectory is perturbed slightly, our measurement lacks the sensitivity to detect the resulting change in A.

These observations suggest that the appropriate construction of the probability density ρ is not quite what we saw in Sect. 3.3. Instead, we proceed as follows: Given a phase trajectory of a mechanical system, we consider all possible permutations of the coordinates of the identical particles and then "smear out" the trajectories thus obtained to give them a nonzero thickness. Whether our newly constructed ρ leads to (3.45) is still an open question, of course.

We shall take a pragmatic point of view in what follows. We accept (3.45) and (3.173) as the fundamental hypothesis of our theory. The hypothesis should be deemed appropriate if the theory produces predictions in agreement with the outcome of experiments. This is how physical theories are constructed elsewhere.

3.14 ‡Expressions for P and μ

In statistical mechanics, T is a parameter characterizing a statistical ensemble. Nevertheless, it is possible to express T as a thermal average of a dynamical variable. In fact, the equipartition theorem implies that

$$T = \frac{2}{3k_BN}\left\langle \sum_{i=1}^{N} \frac{\|\boldsymbol{p}_i\|^2}{2m} \right\rangle \tag{3.175}$$

for a system of N identical particles confined to a three-dimensional box. In a similar manner, we can express other intensive quantities, P and μ, as thermal averages of some dynamical variables in a canonical ensemble even though they are parameters characterizing statistical ensembles as we shall see in Chap. 4.

In this section, we derive expressions for P and μ for a system of N identical particles with the Hamiltonian

$$H = \sum_{i=1}^{N} \frac{\|\boldsymbol{p}_i\|^2}{2m} + \phi(\boldsymbol{r}^N) , \tag{3.176}$$

in which ϕ is the potential energy due to interparticle interactions. The canonical partition function of the system is given by

$$Z = \frac{1}{h^{3N}N!}\int e^{-\beta H(\boldsymbol{r}^N,\boldsymbol{p}^N)} d\boldsymbol{r}^N \mathrm{d}\boldsymbol{p}^N = \frac{1}{\Lambda^{3N}N!}\int e^{-\beta\phi(\boldsymbol{r}^N)}\mathrm{d}\boldsymbol{r}^N , \tag{3.177}$$

where we carried out the momentum integration, that is, the integration with respect to $\boldsymbol{p}^N$. The remaining integral

$$\int e^{-\beta\phi(\boldsymbol{r}^N)}\mathrm{d}\boldsymbol{r}^N \tag{3.178}$$

is called the **configurational integral**.

3.14.1 ‡Pressure

Recalling (2.193), we have

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = k_B T\left(\frac{\partial \ln Z}{\partial V}\right)_{T,N} . \tag{3.179}$$

In (3.178), V appears in the limits of integration with respect to $\boldsymbol{r}^N$. To facilitate the computation of the partial derivative, we assume that the system is a cube of side length $L = V^{1/3}$ and introduce a new set of variables by

$$\boldsymbol{r}_i =: L\boldsymbol{s}_i\,, \quad i = 1,\ldots,N\,. \tag{3.180}$$

We note that

$$\mathrm{d}\boldsymbol{r}_i = \mathrm{d}x_i\mathrm{d}y_i\mathrm{d}z_i = L^3\mathrm{d}s_{ix}\mathrm{d}s_{iy}\mathrm{d}s_{iz} = V\mathrm{d}\boldsymbol{s}_i \tag{3.181}$$

with s_{ix} denoting the x-component of $\boldsymbol{s}_i$ and similarly for s_{iy} and s_{iz}. Thus,

$$Z = \frac{V^N}{\Lambda^{3N}N!}\int e^{-\beta\phi(L\boldsymbol{s}_1,\ldots,L\boldsymbol{s}_N)}\mathrm{d}\boldsymbol{s}^N =: \frac{V^N}{\Lambda^{3N}N!}Q_N\,, \tag{3.182}$$

where the integration is over the unit cube, that is, the cube of side length 1. We see that the V dependence of Z is now made explicit in the factor V^N and in the potential energy ϕ. From (3.179) and (3.182),

$$P = k_B T\left[\frac{N}{V} + \frac{1}{Q_N}\left(\frac{\partial Q_N}{\partial V}\right)_{T,N}\right] = P^{\mathrm{id}} - \left\langle\frac{\partial\phi}{\partial V}\right\rangle , \tag{3.183}$$

where $P^{\mathrm{id}} := k_B TN/V$ is the ideal gas contribution to P and $\partial\phi/\partial V$ is evaluated for fixed $\boldsymbol{s}^N$. Invoking the chain rule, we find

$$\frac{\partial\phi}{\partial V} = \frac{\mathrm{d}L}{\mathrm{d}V}\frac{\partial\phi}{\partial L} = \frac{L}{3V}\sum_{i=1}^{N}\frac{\partial\boldsymbol{r}_i}{\partial L}\cdot\nabla_i\phi(\boldsymbol{r}^N) = \frac{1}{3V}\sum_{i=1}^{N}\boldsymbol{r}_i\cdot\nabla_i\phi(\boldsymbol{r}^N)\,, \tag{3.184}$$

where

$$\nabla_i\phi \doteq \left(\frac{\partial\phi}{\partial x_i}, \frac{\partial\phi}{\partial y_i}, \frac{\partial\phi}{\partial z_i}\right) \tag{3.185}$$

is the negative of the net force exerted on the ith particle by the other particles in the system. Defining the internal **virial** by

$$\mathscr{V} := -\frac{1}{3}\sum_{i=1}^{N}\boldsymbol{r}_i\cdot\nabla_i\phi\,, \tag{3.186}$$

we have

$$P = P^{\mathrm{id}} + \frac{\langle\mathscr{V}\rangle}{V}\,. \tag{3.187}$$

It is convenient and often acceptable to assume the **pairwise additivity** of ϕ. That is, we assume that ϕ may be written as

$$\phi(\boldsymbol{r}^N) = \frac{1}{2} \sum_{j=1}^{N} {\sum_{k=1}^{N}}' v(r_{jk}) \,, \tag{3.188}$$

where v is called the **pair potential** and $'$ on the second summation sign indicates that the $k = j$ term is excluded from the sum. We also defined

$$\boldsymbol{r}_{jk} := \boldsymbol{r}_j - \boldsymbol{r}_k \tag{3.189}$$

and made the usual assumption that the potential energy of interaction between jth and kth particles depends only on the distance $r_{jk} := \|\boldsymbol{r}_{jk}\|$ between them.

In order to compute $\nabla_i \phi$ in the internal virial, we must first isolate $\boldsymbol{r}_i$-dependent terms in (3.188). These are the terms corresponding to either $j = i$ or $k = i$. So, the quantity of our interest is

$$\frac{1}{2} \sum_{k \neq i} v(r_{ik}) + \frac{1}{2} \sum_{j \neq i} v(r_{ji}) \,. \tag{3.190}$$

The first term is obtained by retaining only the $j = i$ term in the summation over j and noting that the condition $k \neq j$ on the second sum translates to $k \neq i$ for this term. Similarly for the second term. Since k in the first term of (3.190) is just a dummy index, it can be replaced by j without affecting its value. We also note that $r_{ji} = r_{ij}$ in the second term. So, we can rewrite (3.190) as

$$\sum_{j \neq i} v(r_{ij}) \,, \tag{3.191}$$

which is just the sum of v for all the pairwise interactions involving the ith particle. This is exactly what the phrase "pairwise additivity" suggests. In any case, we now have

$$\nabla_i \phi(\boldsymbol{r}^N) = \sum_{j \neq i} \nabla_i v(r_{ij}) \,, \tag{3.192}$$

indicating simply that the net force exerted on the ith particle by the rest of the particles in the system is given by the sum of the individual contribution from each particle.

The expression $\nabla_i v(r_{ij})$ can be evaluated as follows. From (3.189) and

$${r_{ij}}^2 = {x_{ij}}^2 + {y_{ij}}^2 + {z_{ij}}^2 \,, \tag{3.193}$$

we see that

$$2 r_{ij} \frac{\partial r_{ij}}{\partial x_i} = 2 x_{ij} \frac{\partial x_{ij}}{\partial x_i} = 2 x_{ij} \,. \tag{3.194}$$

So,

$$\frac{\partial r_{ij}}{\partial x_i} = \frac{x_{ij}}{r_{ij}} . \tag{3.195}$$

Noting the similar relations for $\partial r_{ij}/\partial y_i$ and $\partial r_{ij}/\partial z_i$, we have

$$\nabla_i r_{ij} = \frac{\boldsymbol{r}_{ij}}{r_{ij}} , \tag{3.196}$$

Thus, by means of the chain rule, we have

$$\nabla_i v(r_{ij}) = \frac{\mathrm{d}v(r_{ij})}{\mathrm{d}r_{ij}} \frac{\boldsymbol{r}_{ij}}{r_{ij}} . \tag{3.197}$$

Combining everything,

$$\sum_{i=1}^{N} \boldsymbol{r}_i \cdot \nabla_i \phi = \sum_{i=1}^{N} \sum_{j=1}^{N}{}' \frac{\mathrm{d}v(r_{ij})}{\mathrm{d}r_{ij}} \frac{\boldsymbol{r}_{ij}}{r_{ij}} \cdot \boldsymbol{r}_i = \sum_{i=1}^{N} \sum_{j=1}^{N}{}' \frac{\mathrm{d}v(r_{ji})}{\mathrm{d}r_{ji}} \frac{\boldsymbol{r}_{ji}}{r_{ji}} \cdot \boldsymbol{r}_j . \tag{3.198}$$

Adding the last two alternative expressions for the same quantity and noting that $\boldsymbol{r}_{ji} = -\boldsymbol{r}_{ij}$ while $r_{ij} = r_{ji}$, we find

$$\sum_{i=1}^{N} \boldsymbol{r}_i \cdot \nabla_i \phi = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N}{}' \frac{\mathrm{d}v(r_{ij})}{\mathrm{d}r_{ij}} r_{ij} . \tag{3.199}$$

So, for a pairwise additive potential, the internal virial is

$$\mathscr{V} = -\frac{1}{6} \sum_{i=1}^{N} \sum_{j=1}^{N}{}' \frac{\mathrm{d}v(r_{ij})}{\mathrm{d}r_{ij}} r_{ij} \tag{3.200}$$

and we finally arrive at the desired expression for P:

$$P = P^{\mathrm{id}} - \frac{1}{6V} \left\langle \sum_{i=1}^{N} \sum_{j=1}^{N}{}' \frac{\mathrm{d}v(r_{ij})}{\mathrm{d}r_{ij}} r_{ij} \right\rangle . \tag{3.201}$$

3.14.2 ‡Chemical Potential

According to (2.193),

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V} . \tag{3.202}$$

Since the number of molecules can only be a nonnegative integer, the partial derivative with respect to N is not well defined. Since $N \approx 10^{24} \gg 1$, we may write

$$\mu = F(T,V,N+1) - F(T,V,N) = -k_BT \ln \frac{Z_{N+1}}{Z_N} \,, \tag{3.203}$$

where the subscripts $N+1$ and N refer to the number of molecules in the system. (In Chap. 2, we used N to denote the number of *moles*. In this chapter, the same symbol represents the number of *molecules* in the system. This difference simply translates to the change in units of μ. This is why we have k_B instead of the gas constant R in (3.203).)

To evaluate the ratio Z_{N+1}/Z_N, let

$$\Delta(\boldsymbol{r}^{N+1}) := \phi(\boldsymbol{r}^{N+1}) - \phi(\boldsymbol{r}^N) \tag{3.204}$$

denote the change in the potential energy when the $N+1$th particle is added to the system of N particles at the position $\boldsymbol{r}_{N+1}$. Then,

$$\begin{aligned}\frac{Z_{N+1}}{Z_N} &= \frac{1}{\Lambda^3(N+1)} \frac{\int e^{-\beta\phi(\boldsymbol{r}^{N+1})} \mathrm{d}\boldsymbol{r}^{N+1}}{\int e^{-\beta\phi(\boldsymbol{r}^N)} \mathrm{d}\boldsymbol{r}^N} \\ &= \frac{1}{\Lambda^3(N+1)} \frac{\int e^{-\beta\phi(\boldsymbol{r}^N)} \left[\int e^{-\beta\Delta} \mathrm{d}\boldsymbol{r}_{N+1}\right] \mathrm{d}\boldsymbol{r}^N}{\int e^{-\beta\phi(\boldsymbol{r}^N)} \mathrm{d}\boldsymbol{r}^N} \\ &= \frac{V}{\Lambda^3(N+1)} \left\langle \frac{1}{V} \int e^{-\beta\Delta} \mathrm{d}\boldsymbol{r}_{N+1} \right\rangle \,,\end{aligned} \tag{3.205}$$

where we suppressed $\boldsymbol{r}^{N+1}$ dependence of Δ, a convention we shall continue to follow throughout the remainder of this section. Using this expression in (3.203), we see that

$$\mu = -k_BT \ln \frac{V}{\Lambda^3(N+1)} - k_BT \ln \left\langle \frac{1}{V} \int e^{-\beta\Delta} \mathrm{d}\boldsymbol{r}_{N+1} \right\rangle \,, \tag{3.206}$$

in which

$$-k_BT \ln \frac{V}{\Lambda^3(N+1)} \tag{3.207}$$

is the chemical potential of an ideal gas. This expression is obtained by applying (3.203) to the ideal gas and should be compared against

$$\mu^{\mathrm{id}} = -k_BT \ln \frac{V}{\Lambda^3 N} \tag{3.208}$$

which follows from (3.202). (See Exercise 3.16b.) Equation (3.206) is the basis of **Widom's test particle insertion method**, a common approach for estimating the chemical potential in molecular simulation.

We now derive an alternative expression for the chemical potential. For this purpose, let us define

$$\phi(\lambda) := \phi(\boldsymbol{r}^N) + \lambda\Delta \ . \tag{3.209}$$

Clearly,

$$\phi(0) = \phi(\boldsymbol{r}^N) \quad \text{and} \quad \phi(1) = \phi(\boldsymbol{r}^{N+1}) \ . \tag{3.210}$$

If we define

$$Z(\lambda) := \frac{1}{\Lambda^{3N} N!} \int e^{-\beta\phi(\lambda)} \mathrm{d}\boldsymbol{r}^{N+1} \ , \tag{3.211}$$

we see that

$$Z(0) = VZ_N \quad \text{and} \quad Z(1) = \Lambda^3 (N+1) Z_{N+1} \ , \tag{3.212}$$

where we used (3.177). It follows that

$$\ln \frac{Z_{N+1}}{Z_N} = \ln \frac{V}{\Lambda^3(N+1)} + \ln \frac{Z(1)}{Z(0)} \ . \tag{3.213}$$

But,

$$\ln \frac{Z(1)}{Z(0)} = \ln Z(1) - \ln Z(0) = \int_0^1 \left(\frac{\partial \ln Z(\lambda)}{\partial \lambda} \right)_{\beta,V,N} \mathrm{d}\lambda \tag{3.214}$$

From (3.211),

$$\left(\frac{\partial \ln Z(\lambda)}{\partial \lambda} \right)_{\beta,V,N} = -\beta \langle \Delta \rangle_\lambda \ , \tag{3.215}$$

where $\langle \cdots \rangle_\lambda$ is the thermal average when the interparticle potential energy is $\phi(\lambda)$. Using (3.213) – (3.215) in (3.203), we obtain

$$\mu = -k_B T \ln \frac{V}{\Lambda^3(N+1)} + \int_0^1 \langle \Delta \rangle_\lambda \mathrm{d}\lambda \ . \tag{3.216}$$

This is an example of the **thermodynamic integration method**, in which a thermodynamic quantity is expressed in terms of an integration of some thermal average.

The connection between (3.206) and (3.216) can be made clearer by considering an intermediate approach between them. Thus, let

$$\lambda_i := \frac{i}{k} \ , \quad i = 0, \dots, k \tag{3.217}$$

so that $\lambda_0 = 0$ and $\lambda_k = 1$. Then,

$$\frac{Z(1)}{Z(0)} = \frac{Z(\lambda_k)}{Z(\lambda_0)} = \frac{Z(\lambda_k)}{Z(\lambda_{k-1})} \frac{Z(\lambda_{k-1})}{Z(\lambda_{k-2})} \cdots \frac{Z(\lambda_{i+1})}{Z(\lambda_i)} \cdots \frac{Z(\lambda_1)}{Z(\lambda_0)} \ . \tag{3.218}$$

But,

$$\frac{Z(\lambda_{i+1})}{Z(\lambda_i)} = \frac{\int e^{-\beta\phi(\lambda_{i+1})} \mathrm{d}\boldsymbol{r}^{N+1}}{\int e^{-\beta\phi(\lambda_i)} \mathrm{d}\boldsymbol{r}^{N+1}} = \langle e^{-\beta\Delta/k} \rangle_{\lambda_i} \ . \tag{3.219}$$

For a sufficiently large k, $e^{-\beta\Delta/k} \approx 1 - \beta\Delta/k$, and hence

$$\frac{Z(\lambda_{i+1})}{Z(\lambda_i)} \approx 1 - \frac{\beta}{k}\langle\Delta\rangle_{\lambda_i} . \tag{3.220}$$

Because $\ln(1-x) \approx -x$ if $|x| \ll 1$, we have

$$\ln\frac{Z(1)}{Z(0)} \approx \sum_{i=0}^{k-1} \ln\left(1 - \frac{\beta}{k}\langle\Delta\rangle_{\lambda_i}\right) \approx -\sum_{i=0}^{k-1} \frac{\beta}{k}\langle\Delta\rangle_{\lambda_i} \approx -\beta\int_0^1 \langle\Delta\rangle_\lambda \mathrm{d}\lambda , \tag{3.221}$$

which is just (3.214) and we recover (3.216). One may say that the test particle insertion method, if broken down to a series of "partial particle insertions," reduces to the thermodynamic integration method.

3.15 †Internal Energy

In Sect. 3.9, we identified the average Hamiltonian $\langle H\rangle$ with the internal energy U. However, U is usually defined as a part of $\langle H\rangle$ reflecting only the internal state of the system. The kinetic energy due to its macroscopic translational motion as a whole and the potential energy due to its position in an external field are excluded in defining U.

Let us examine in details what is involved in this separation. What we have in mind is a collection of N particles that are held together either by intermolecular forces or by a container. In the latter case, we shall regard the particles making up the container as a part of the system. Then, the system as a whole experiences a translational motion under the influence of an external field ψ.

3.15.1 †*Equilibrium in Motion?*

It might be argued that a system in motion is not in equilibrium. However, a system in motion in one frame of reference is also at rest in another. If there is no time-dependent external field in the second, the system will eventually reach equilibrium. Our goal here is to describe that equilibrium from the first frame of reference with respect to which the system is in macroscopic motion.

Let us choose an inertial frame $\mathscr{O}^a$, with respect to which the system is moving, and write down its Lagrangian L^a as

$$L^a = \sum_{i=1}^{N} \frac{1}{2} m_i \|\boldsymbol{v}_i^a\|^2 - \sum_{i=1}^{N} \psi(\boldsymbol{r}_i^a, m_i) - \phi(\boldsymbol{r}_1^a, \ldots, \boldsymbol{r}_N^a) , \tag{3.222}$$

where we use the superscript a to signify that the quantities bearing them are evaluated in $\mathscr{O}^a$. From the outset, we assume that ψ has the following special form

$$\psi(\boldsymbol{r}_i, m_i) = -m_i \boldsymbol{b} \cdot \boldsymbol{r}_i \,, \tag{3.223}$$

where $\boldsymbol{b}$ is a constant. In the case of the gravitational field, $\boldsymbol{b} = \boldsymbol{g}$, for example.

Exercise 3.18. Find equations of motion for the particles. ///

By definition, (1.103), the momentum $\boldsymbol{p}_i^a$ conjugate to $\boldsymbol{r}_i^a$ is given by

$$\boldsymbol{p}_i^a := \frac{\partial L^a}{\partial \boldsymbol{v}_i^a} = m_i \boldsymbol{v}_i^a \,. \tag{3.224}$$

The Hamiltonian follows from (1.156) as

$$H^a := \sum_{i=1}^{N} \boldsymbol{p}_i^a \cdot \boldsymbol{v}_i^a - L^a = \sum_{i=1}^{N} \frac{\|\boldsymbol{p}_i^a\|^2}{2m_i} + \sum_{i=1}^{N} \psi(\boldsymbol{r}_i^a, m_i) + \phi(\boldsymbol{r}_1^a, \ldots, \boldsymbol{r}_N^a) \,. \tag{3.225}$$

Note that the Hamiltonian also bears the superscript a because it is expressed in terms of the position and the momenta of particles as measured in $\mathscr{O}^a$.

If we assume a canonical distribution, can we say that

$$\rho^a = \frac{e^{-\beta H^a}}{Z^a} \,? \tag{3.226}$$

Because of the macroscopic motion with respect to $\mathscr{O}^a$, when our system occupies a certain region in $\mathscr{O}^a$, it does so only once and only for a brief interval of time. From this observation, it might seem that ρ^a vanishes everywhere in the phase space because Δt in (3.11) becomes vanishingly small in comparison to τ. This is not quite correct. We must remember that τ is supposed to be very long only in comparison to the time scale of molecular motion but comparable with the time scale of our measurement. *If* $l/\|\boldsymbol{V}\| \gg \tau$, where l is the characteristic length scale of the system and $\boldsymbol{V}$ is the velocity of the system, the system may be regarded as occupying essentially the same region in $\mathscr{O}^a$ over the duration τ and ρ^a takes nonzero values over the corresponding region of the phase space. However, this region of nonzero ρ^a continues to move in the phase space in accordance with the translational motion of the system in $\mathscr{O}^a$.

The immediate conclusion is that (3.23), or $\partial \rho^a/\partial t \equiv 0$, is not an appropriate definition for statistical equilibrium. How do we define statistical equilibrium of our system then? It is also unsatisfactory that we have to impose an upper limit on the velocity of the macroscopic motion when discussing statistical equilibrium.

We note that the motion we are considering can be eliminated entirely in a suitably chosen frame of reference. So, the difficulty we have just described is only apparent and can be made to disappear by introducing a new coordinate system $\mathscr{O}$ that *moves with the system*. One might say, then, that the system is in statistical equilibrium if there is a frame of reference in which $\partial \rho/\partial t \equiv 0$.

We expect equilibrium to eventually prevail in $\mathscr{O}$ if there is no time-dependent field in $\mathscr{O}$. Assuming that there is a thermal contact between the system and its surroundings, ρ at equilibrium will be given by the canonical distribution. Thus, we will first have to find the Hamiltonian H of the system that is appropriate for $\mathscr{O}$. Then, the only remaining problem is that of translating ρ in $\mathscr{O}$ back to ρ^a in $\mathscr{O}^a$. This is the plan we follow.

3.15.2 †From a Stationary to a Moving Frame

We denote the velocity of $\mathscr{O}$ with respect to $\mathscr{O}^a$ by $\boldsymbol{V}(t)$. The time dependence of $\boldsymbol{V}$ is included because the system, in general, experiences acceleration with respect to $\mathscr{O}^a$ in the presence of an external field. This implies that $\mathscr{O}$ is not an inertial frame in general.

In order to find the Lagrangian L and the Hamiltonian H written for $\mathscr{O}$, we need to figure out the relationship between the position $\boldsymbol{r}^a$ and the velocity $\boldsymbol{v}^a$ of a particle in $\mathscr{O}^a$ on the one hand and their counterparts, $\boldsymbol{r}$ and $\boldsymbol{v}$ in $\mathscr{O}$, on the other. Clearly,

$$\boldsymbol{r}^a = \boldsymbol{r} + \boldsymbol{R} \,, \tag{3.227}$$

where $\boldsymbol{R}$ is the position of the origin of $\mathscr{O}$ as measured in $\mathscr{O}^a$. To find the relation between $\boldsymbol{v}^a$ and $\boldsymbol{v}$, suppose that, after a time duration $\mathrm{d}t$, the position of the particle in $\mathscr{O}^a$ is $\boldsymbol{r}^a + \mathrm{d}\boldsymbol{r}^a$. The location of this same particle in $\mathscr{O}$ may be denoted by $\boldsymbol{r} + \mathrm{d}\boldsymbol{r}$. At the same time, however, $\mathscr{O}$ itself has moved by $\boldsymbol{V}\mathrm{d}t$. Thus, applying (3.227) to the varied state,

$$\boldsymbol{r}^a + \mathrm{d}\boldsymbol{r}^a = (\boldsymbol{r} + \mathrm{d}\boldsymbol{r}) + (\boldsymbol{R} + \boldsymbol{V}\mathrm{d}t) \,. \tag{3.228}$$

Subtracting (3.227) from (3.228), and then dividing the resulting equation by $\mathrm{d}t$, we find

$$\boldsymbol{v}^a = \boldsymbol{v} + \boldsymbol{V} \,, \tag{3.229}$$

which could have been obtained simply by taking the time derivative of (3.227). Equation (3.227) and $t^a = t$ taken together is called a **Galilean transformation**.

Substituting (3.227) and (3.229) into (3.222), we find

$$L^a = \sum_{i=1}^{N} \frac{1}{2} m_i \|\boldsymbol{v}_i\|^2 - \sum_{i=1}^{N} \psi(\boldsymbol{r}_i, m_i) - \phi(\boldsymbol{r}^N) + \boldsymbol{V} \cdot \sum_{i=1}^{N} m_i \boldsymbol{v}_i + \frac{1}{2} M \|\boldsymbol{V}\|^2 + M\boldsymbol{b} \cdot \boldsymbol{R} \,, \tag{3.230}$$

where we used (3.223) to rewrite the external field term. As in Sect. 1.4, $M := \sum_i m_i$ is the total mass of the system.

We now *assume* that $\boldsymbol{R}$ and $\boldsymbol{V}$ may be regarded as explicit functions of t only. That is, we suppose that they do not depend on $\boldsymbol{r}_1^a, \ldots, \boldsymbol{v}_N^a$. Whether this actually is the case depends on how we choose $\boldsymbol{R}$ and will be discussed in Sect. 3.15.3. Under this assumption, the right-hand side of (3.230) is a function of t and the variables pertaining only to $\mathscr{O}$, and hence it may be used as the Lagrangian L in $\mathscr{O}$

from which equations of motion appropriate for $\mathscr{O}$ can be derived. These equations should be equivalent to those obtained from L^a for $\mathscr{O}^a$. In fact, since $L^a \equiv L$ for any mechanical state of the system at any instant, the action integral $\mathscr{S}^a$ computed in $\mathscr{O}^a$ is numerically equal to the action integral $\mathscr{S}$ in $\mathscr{O}$. Thus, the stationarity condition of the former coincides with that of the latter.

Exercise 3.19. Verify this statement by deriving equations of motion from (3.230) and comparing your results against what you found in Exercise 3.18. ///

For this choice of L, (1.104) yields

$$\boldsymbol{p}_i = \frac{\partial L}{\partial \boldsymbol{v}_i} = m_i(\boldsymbol{v}_i + \boldsymbol{V}) \; . \tag{3.231}$$

Recalling (1.156), we have

$$H = \sum_{i=1}^{N} \frac{\|\boldsymbol{p}_i\|^2}{2m_i} + \sum_{i=1}^{N} \psi(\boldsymbol{r}_i, m_i) + \phi(\boldsymbol{r}^N) - \boldsymbol{V}\cdot\boldsymbol{P} - M\boldsymbol{b}\cdot\boldsymbol{R} \; , \tag{3.232}$$

where $\boldsymbol{P} := \sum_{i=1}^{N} \boldsymbol{p}_i$ is, by (1.138), the total linear momentum of the system. We observe that unless $\boldsymbol{R}$ is constant and hence $\boldsymbol{V} \equiv \boldsymbol{0}$, this H depends explicitly on time. It is not at all clear if such a system can reach equilibrium even to an observer in $\mathscr{O}$. It is possible, however, to use somewhat different expressions for L and H.

First, we recall that the last two terms of (3.230) are, by our assumption, functions of t only, and hence can be expressed as the total time derivative of some function of t. By Exercise 1.8, they can be dropped without affecting the resulting equations of motion. Next, we rewrite the term linear in $\boldsymbol{V}$ in (3.230) by noting that

$$\boldsymbol{V}\cdot\boldsymbol{v}_i = \frac{\mathrm{d}}{\mathrm{d}t}(\boldsymbol{V}\cdot\boldsymbol{r}_i) - \frac{\mathrm{d}\boldsymbol{V}}{\mathrm{d}t}\cdot\boldsymbol{r}_i \; . \tag{3.233}$$

The first term on the right-hand side can be dropped from the Lagrangian for the same reason. In this way, we see that the Lagrangian L may be redefined as

$$L := \sum_{i=1}^{N} \frac{1}{2} m_i \|\boldsymbol{v}_i\|^2 - \sum_{i=1}^{N} \psi(\boldsymbol{r}_i, m_i) - \phi(\boldsymbol{r}^N) - \frac{\mathrm{d}\boldsymbol{V}}{\mathrm{d}t}\cdot\sum_{i=1}^{N} m_i\boldsymbol{r}_i \; . \tag{3.234}$$

Exercise 3.20. Derive equations of motion using this Lagrangian. ///

With this Lagrangian, we have

$$\boldsymbol{p}_i = \frac{\partial L}{\partial \boldsymbol{v}_i} = m_i\boldsymbol{v}_i \tag{3.235}$$

and

$$H = \sum_{i=1}^{N} \frac{\|\boldsymbol{p}_i\|^2}{2m_i} + \sum_{i=1}^{N} \psi(\boldsymbol{r}_i, m_i) + \phi(\boldsymbol{r}^N) + \frac{\mathrm{d}\boldsymbol{V}}{\mathrm{d}t}\cdot\sum_{i=1}^{N} m_i\boldsymbol{r}_i \; . \tag{3.236}$$

Because of (3.235), the first term of this H is the kinetic energy of the system *as measured in* $\mathscr{O}$. This situation should be contrasted to that in (3.232), for which such an interpretation does not hold due to the presence of $\boldsymbol{V}$ in (3.231).

Up to this point, our choice of $\boldsymbol{R}$ was quite arbitrary. When discussing macroscopic motion of a collection of particles, it is often convenient to place $\mathscr{O}$ at the center of mass of the system. One often points to this choice of the coordinate system when defining the internal energy of a moving system in thermodynamics.

In this case, $\boldsymbol{R}$ is equal to the position of the center of mass as measured in $\mathscr{O}^a$, which we denote by $\boldsymbol{R}_{\mathrm{cm}}$:

$$\boldsymbol{R} \equiv \boldsymbol{R}_{\mathrm{cm}} = \frac{1}{M}\sum_{i=1}^{N} m_i \boldsymbol{r}_i^a = \frac{1}{M}\sum_{i=1}^{N} m_i(\boldsymbol{r}_i + \boldsymbol{R}_{\mathrm{cm}}) \,, \tag{3.237}$$

where we recall that a container, if present, must be included in computing $\boldsymbol{R}_{\mathrm{cm}}$. From this equation, it follows that

$$\sum_{i=1}^{N} m_i \boldsymbol{r}_i \equiv \boldsymbol{0} \tag{3.238}$$

and that

$$\sum_{i=1}^{N} \psi(\boldsymbol{r}_i, m_i) \equiv 0 \,. \tag{3.239}$$

When these results are substituted into (3.234) and (3.236), we find

$$L = \sum_{i=1}^{N} \frac{1}{2} m_i \|\boldsymbol{v}_i\|^2 - \phi(\boldsymbol{r}^N) \quad \text{and} \quad H = \sum_{i=1}^{N} \frac{\|\boldsymbol{p}_i\|^2}{2m_i} + \phi(\boldsymbol{r}^N) \,. \tag{3.240}$$

These equations indicate that the effect of the external field vanishes in a coordinate system that moves with the center of mass of the system. It should be emphasized that we reached this conclusion *only* for the external field having the form of (3.223) and only by making a rather special choice of L in (3.234). Nevertheless, (3.240) represent a very satisfying state of affair. Both L and H are well defined without any reference to the motion of $\mathscr{O}$ relative to some inertial frame $\mathscr{O}^a$ that is external to $\mathscr{O}$.

For a given mechanical state of the system, the value of H^a evaluated by (3.225) and that of H given by (3.240) are, in general, different. This is not surprising and, in fact, is expected on the basis of Exercise 1.9. It is straightforward to show that

$$H^a = H + \frac{1}{2} M \|\boldsymbol{V}_{\mathrm{cm}}\|^2 + \psi(\boldsymbol{R}_{\mathrm{cm}}, M) \,, \tag{3.241}$$

where $\boldsymbol{V}_{\mathrm{cm}} := \mathrm{d}\boldsymbol{R}_{\mathrm{cm}}/\mathrm{d}t$. In this form, we can clearly see the separation of H^a into something "intrinsic" to the system and the remaining terms due to its macroscopic motion.

Exercise 3.21. Verify (3.241). ///

Now that $\mathscr{O}$ moves with $\boldsymbol{R}_{\text{cm}}$, the region of nonzero ρ will be stationary in the phase space for $\mathscr{O}$ and the condition of equilibrium may be expressed as $\partial\rho/\partial t \equiv 0$. For a system in thermal contact with the surroundings, we have $\rho \propto e^{-\beta H}$ with H given by (3.240).

In writing the statistical distribution ρ for an observer in $\mathscr{O}$, however, we must remember that the center of mass of the system is fixed at its origin. As a result, $\boldsymbol{r}^N$ must satisfy (3.238), and hence are not all independent. Because the equation holds at all t, it also holds upon taking the time derivative. These constraints are most easily imposed by means of the Dirac δ-function:

$$\rho_{\text{cm}}(\boldsymbol{r}^N,\boldsymbol{p}^N) = \delta[\cdots]\frac{1}{Z_{\text{cm}}}\frac{e^{-\beta H}}{h^{3(N-1)}\mathscr{P}}\ , \tag{3.242}$$

where we introduced a shorthand notation

$$\delta[\cdots] := \delta\left(\frac{\sum_{i=1}^N m_i\boldsymbol{r}_i}{M}\right)\delta\left(\sum_{i=1}^N \boldsymbol{p}_i\right) \tag{3.243}$$

for the product of two Dirac δ-functions. (See Appendix D.4 for the definition of the three-dimensional δ-function.) As before, $\mathscr{P}$ is the number of distinct permutations of identical particles if there are any and the subscript cm remind us of the constraints on the center of mass. Because of the constraints, the mechanical degrees of freedom of the system is reduced by 3 from the original value of $3N$. This accounts for the factor $h^{3(N-1)}$ in place of now familiar h^{3N}. Finally, the normalization constant is given by

$$Z_{\text{cm}} = \frac{1}{h^{3(N-1)}\mathscr{P}}\int \delta[\cdots]e^{-\beta H}\mathrm{d}\boldsymbol{r}^N\mathrm{d}\boldsymbol{p}^N\ . \tag{3.244}$$

3.15.3 †Back to the Stationary Frame

With the expression of ρ_{cm} now in hand, we can determine ρ_{cm}^a as follows. We first note that the quantity

$$\rho_{\text{cm}}(\boldsymbol{r}^N,\boldsymbol{p}^N)\mathrm{d}\boldsymbol{r}^N\mathrm{d}\boldsymbol{p}^N \tag{3.245}$$

represents the probability of finding the system within the infinitesimal volume element $\mathrm{d}\boldsymbol{r}^N\mathrm{d}\boldsymbol{p}^N$ taken around the phase point $(\boldsymbol{r}^N,\boldsymbol{p}^N)$ of the phase space for $\mathscr{O}$. But, as seen from (3.224), (3.227), (3.229), and (3.235), the Jacobian of transformation from $(\boldsymbol{r}_1^a,\ldots,\boldsymbol{p}_N^a)$ to $(\boldsymbol{r}^N,\boldsymbol{p}^N)$ is unity, that is, the volume occupied by $\mathrm{d}\boldsymbol{r}^N\mathrm{d}\boldsymbol{p}^N$ in the phase space for $\mathscr{O}$ is equal to the volume occupied by $\mathrm{d}\boldsymbol{r}_1^a\cdots\mathrm{d}\boldsymbol{p}_N^a$ in the phase space for $\mathscr{O}^a$. It follows that the probability (3.245) can also be written as

$$\rho_{\text{cm}}^a(\boldsymbol{r}_1^a,\ldots,\boldsymbol{p}_N^a)\mathrm{d}\boldsymbol{r}_1^a\cdots\mathrm{d}\boldsymbol{p}_N^a \tag{3.246}$$

with ρ^a_{cm} given simply by ρ_{cm} expressed in terms of $\boldsymbol{r}^a_1,\dots,\boldsymbol{p}^a_N$. Thus,

$$\rho^a_{\mathrm{cm}}(\boldsymbol{r}^a_1,\dots,\boldsymbol{p}^a_N) = \delta^a[\cdots]\frac{1}{Z^a_{\mathrm{cm}}}\frac{e^{-\beta(H^a-E_{\mathrm{mm}})}}{h^{3(N-1)}\mathscr{P}}\,, \tag{3.247}$$

where we defined

$$\delta^a[\cdots] := \delta\left(\frac{\sum_{i=1}^N m_i\boldsymbol{r}^a_i}{M} - \boldsymbol{R}_{\mathrm{cm}}(t)\right)\delta\left(\sum_{i=1}^N \boldsymbol{p}^a_i - \boldsymbol{P}_{\mathrm{cm}}(t)\right) \tag{3.248}$$

with $\boldsymbol{P}_{\mathrm{cm}} = M\boldsymbol{V}_{\mathrm{cm}}$ and

$$E_{\mathrm{mm}} = \frac{1}{2}M\|\boldsymbol{V}_{\mathrm{cm}}\|^2 + \psi(\boldsymbol{R}_{\mathrm{cm}},M) \tag{3.249}$$

is the energy due to macroscopic motion as observed in $\mathscr{O}^a$. The normalization of ρ^a_{cm} leads to

$$Z^a_{\mathrm{cm}} = \frac{1}{h^{3(N-1)}\mathscr{P}}\int \delta^a[\cdots]e^{-\beta(H^a-E_{\mathrm{mm}})}\mathrm{d}\boldsymbol{r}^a_1\cdots\mathrm{d}\boldsymbol{p}^a_N\,, \tag{3.250}$$

which is equal to Z_{cm} numerically. The δ-functions ensure that only those phase points consistent with the given functions $\boldsymbol{R}_{\mathrm{cm}}(t)$ and $\boldsymbol{P}_{\mathrm{cm}}(t)$ are accounted for.

We still have to show that $\boldsymbol{R}_{\mathrm{cm}}(t)$ and $\boldsymbol{V}_{\mathrm{cm}}(t)$ may be regarded as some prescribed function depending only on t. Using the equations of motion derived in Exercise 3.18, we obtain

$$\boldsymbol{V}_{\mathrm{cm}}(t) = \boldsymbol{b}t + \boldsymbol{c}_0 \quad \text{and} \quad \boldsymbol{R}_{\mathrm{cm}}(t) = \frac{1}{2}\boldsymbol{b}t^2 + \boldsymbol{c}_0 t + \boldsymbol{c}_1\,, \tag{3.251}$$

where $\boldsymbol{c}_0$ and $\boldsymbol{c}_1$ are constant vectors to be determined by $\boldsymbol{V}_{\mathrm{cm}}$ and $\boldsymbol{R}_{\mathrm{cm}}$ at time $t = 0$. Given these initial conditions, the subsequent evolution of $\boldsymbol{R}_{\mathrm{cm}}$ and $\boldsymbol{V}_{\mathrm{cm}}$ is given by (3.251), and hence they are explicit functions of t only. This is what we needed to show.

Because of the interaction between the system and the surroundings, the actual time evolution of $\boldsymbol{R}_{\mathrm{cm}}$ and $\boldsymbol{V}_{\mathrm{cm}}$ deviates from the predictions of (3.251) in a manner that depends on $\boldsymbol{r}^N$ and $\boldsymbol{p}^N$. Strictly speaking, therefore, the assumption we introduced after (3.230) does not hold and the separation of $\langle H\rangle$ into U_{cm} and E_{mm} must be regarded as an approximation.

Exercise 3.22. Derive (3.251). ///

Finally, when the contribution of the macroscopic motion is separated out, we define the internal energy U_{cm} as $\langle H\rangle$ computed with respect to ρ_{cm}:

$$U_{\mathrm{cm}} = -\frac{\partial \ln Z_{\mathrm{cm}}}{\partial\beta}\,. \tag{3.252}$$

Since ρ_{cm} and ρ^a_{cm} are numerically equal, this may also be written as

$$U_{\mathrm{cm}} = -\frac{\partial \ln Z^a_{\mathrm{cm}}}{\partial \beta} \tag{3.253}$$

We note that U_{cm} reflects the average behavior of $3(N-1)$ mechanical degrees of freedom. The macroscopic motion of the center of mass accounts for the remaining three degrees of freedom.

3.16 †Equilibrium of an Accelerating Body

If we enclose a system of N particles in a rigid container and make the container move in the manner we prescribe, the system will, in general, experience acceleration. Insofar as the acceleration is prescribed, it is common to all members of the ensemble. If we limit our consideration to a *constant* linear acceleration, its effect will be seen to manifest itself as a *time-independent* external field. This allows for a statistical equilibrium to establish. The same holds for a *uniform* rotation as observed in centrifugation. In this section, we shall derive the appropriate expressions for the statistical weight ρ for these cases. We attach a moving coordinate system $\mathscr{O}$ to the container. Because the container is then fixed in $\mathscr{O}$, there is no need to include the container in our definition of the system.

3.16.1 †Linear Translation

We may take (3.236) as our starting point and rewrite it using (3.223):

$$H = H_0 + \sum_{i=1}^{N} \psi(\boldsymbol{r}_i, m_i) + \boldsymbol{A} \cdot \sum_{i=1}^{N} m_i \boldsymbol{r}_i = H_0 + (\boldsymbol{A} - \boldsymbol{b}) \cdot \sum_{i=1}^{N} m_i \boldsymbol{r}_i \,, \tag{3.254}$$

where $\boldsymbol{A} := \mathrm{d}\boldsymbol{V}/\mathrm{d}t$ is the acceleration of the container and

$$H_0 := \sum_{i=1}^{N} \frac{\|\boldsymbol{p}_i\|^2}{2m_i} + \phi\left(\boldsymbol{r}^N\right) \tag{3.255}$$

is the part of the Hamiltonian that appears *intrinsic* to an observer in $\mathscr{O}$ as was pointed out following (3.236).

We see from (3.254) that the effect of the acceleration $\boldsymbol{A}$ of the container manifest itself as an *effective* external field and acts only to modify the existing external field ψ. *If* $\boldsymbol{A}$ does not depend on t, that is, for a constant linear acceleration, H has no explicit time dependence and we expect the system to reach a statistical equilibrium. We note that the coordinate system $\mathscr{O}$ is attached to the container wall and not to

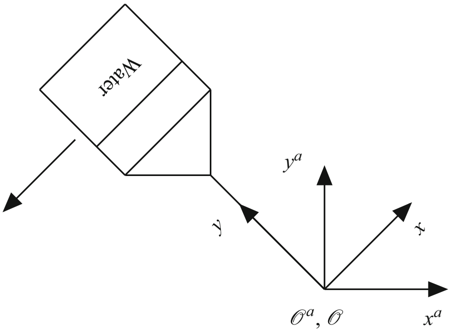


Fig. 3.7 A rotating bucket of water as observed from the inertial frame $\mathscr{O}^a$ and the frame $\mathscr{O}$ that rotates with the bucket.

the center of mass of the particles. This means that the constraint (3.243) is absent here. Instead of (3.242), therefore, we have

$$\rho\left(\boldsymbol{r}^N, \boldsymbol{p}^N\right) = \frac{1}{Z}\frac{e^{-\beta H}}{h^{3N}\mathscr{P}} \quad \text{and} \quad Z = \frac{1}{h^{3N}\mathscr{P}}\int e^{-\beta H} \mathrm{d}\boldsymbol{r}^N \mathrm{d}\boldsymbol{p}^N \tag{3.256}$$

for a system in thermal contact with the surroundings.

3.16.2 †Rotation

Let us consider the case of rotation without any linear translation. Once again, we adopt a frame of reference $\mathscr{O}$ that is attached to the container rotating with respect to the inertial frame $\mathscr{O}^a$. For simplicity, we assume that these two frames share the same origin. Figure 3.7 illustrates the situation.

The frame $\mathscr{O}$ clearly is not an inertial frame: A particle at rest in the rotating frame is accelerating with respect to the inertial frame. In general, the effect of acceleration is felt as **apparent forces**. In the case of rotation, they are the **centrifugal force**, the **Coriolis force**, and the **Euler force** as we shall see in Example 3.8. This last terminology is due to Ref. [2].

It is clear that an external field ψ that is time independent in $\mathscr{O}^a$ *varies with time* in $\mathscr{O}$ in general. In this section, therefore, we assume that the effect of ψ is negligible in comparison to the intermolecular forces *and* the apparent forces.

Again, we need to establish the relationship between the velocity vector of a particle as measured in $\mathscr{O}^a$ and that in $\mathscr{O}$. For this purpose, suppose that the position vector of a particle, as measured in $\mathscr{O}$, changed from $\boldsymbol{r}$ to $\boldsymbol{r}+\mathrm{d}\boldsymbol{r}$ during a time duration $\mathrm{d}t$. If we denote the same vectors as observed in $\mathscr{O}^a$ by $\boldsymbol{r}^a$ and $\boldsymbol{r}^a + \mathrm{d}\boldsymbol{r}^a$, respectively, then,

$$\boldsymbol{r} = \boldsymbol{r}^a \tag{3.257}$$

because both $\boldsymbol{r}$ and $\boldsymbol{r}^a$ refer to the same arrow in space. But the final vector $\boldsymbol{r}+\mathrm{d}\boldsymbol{r}$ is not equal to $\boldsymbol{r}^a+\mathrm{d}\boldsymbol{r}^a$ because of the rotation of $\mathscr{O}$ with respect to $\mathscr{O}^a$. We stress that $\mathrm{d}\boldsymbol{r}^a$ is the change *as observed in* $\mathscr{O}^a$ of the vector $\boldsymbol{r}^a$. This change is brought about by two contributions, one is the change $\mathrm{d}\boldsymbol{r}$ as observed in $\mathscr{O}$ of the vector $\boldsymbol{r}$ and the other is the rotation of $\mathscr{O}$ with respect to $\mathscr{O}^a$. This is why $\mathrm{d}\boldsymbol{r}^a \neq \mathrm{d}\boldsymbol{r}$.

To make things easier, let us first suppose that $\boldsymbol{r}$ remained constant in $\mathscr{O}$. Denoting the rotation of $\mathscr{O}$ with respect to $\mathscr{O}^a$ by $\mathbf{d}\boldsymbol{\phi}$ as we have done in Sect. 1.8.2, we see that

$$\mathrm{d}\boldsymbol{r}^a = \mathbf{d}\boldsymbol{\phi} \times \boldsymbol{r}\,, \tag{3.258}$$

and hence

$$\boldsymbol{r}^a + \mathrm{d}\boldsymbol{r}^a = \boldsymbol{r} + \mathbf{d}\boldsymbol{\phi} \times \boldsymbol{r}\,. \tag{3.259}$$

If $\boldsymbol{r}$ did not remain constant but became $\boldsymbol{r}+\mathrm{d}\boldsymbol{r}$, we have only to replace $\boldsymbol{r}$ by $\boldsymbol{r}+\mathrm{d}\boldsymbol{r}$ and obtain

$$\boldsymbol{r}^a + \mathrm{d}\boldsymbol{r}^a = (\boldsymbol{r}+\mathrm{d}\boldsymbol{r}) + \mathbf{d}\boldsymbol{\phi} \times (\boldsymbol{r}+\mathrm{d}\boldsymbol{r})\,. \tag{3.260}$$

Now we cancel $\boldsymbol{r}^a$ and $\boldsymbol{r}$ using (3.257) and divide the resulting expression by $\mathrm{d}t$ to arrive at

$$\boldsymbol{v}^a = \boldsymbol{v} + \boldsymbol{\Omega} \times \boldsymbol{r}\,, \tag{3.261}$$

where we ignored the higher order term $\mathbf{d}\boldsymbol{\phi} \times \mathrm{d}\boldsymbol{r}$. The new vector $\boldsymbol{\Omega} := \mathbf{d}\boldsymbol{\phi}/\mathrm{d}t$ is called the **angular velocity** of $\mathscr{O}$ with respect to $\mathscr{O}^a$.

Using (3.257) and (3.261) in (3.222) with $\psi \equiv 0$, we find

$$L^a = \sum_{i=1}^{N} \frac{1}{2} m_i \|\boldsymbol{v}_i\|^2 - \phi\left(\boldsymbol{r}^N\right) + \sum_{i=1}^{N} m_i \boldsymbol{v}_i \cdot \boldsymbol{\Omega} \times \boldsymbol{r}_i + \sum_{i=1}^{N} \frac{1}{2} m_i \|\boldsymbol{\Omega} \times \boldsymbol{r}_i\|^2\,. \tag{3.262}$$

Example 3.8. Apparent forces: Let $N=1$ in (3.262):

$$L^a = \frac{1}{2} m \|\boldsymbol{v}\|^2 + m\boldsymbol{v} \cdot \boldsymbol{\Omega} \times \boldsymbol{r} + \frac{1}{2} m \|\boldsymbol{\Omega} \times \boldsymbol{r}\|^2\,, \tag{3.263}$$

from which we derive Lagrange's equation of motion of the particle in $\mathscr{O}$. This allows us to identify the expressions for the apparent forces.

From (3.263),

$$\frac{\partial L^a}{\partial \boldsymbol{v}} = m\boldsymbol{v} + m\boldsymbol{\Omega} \times \boldsymbol{r}\,. \tag{3.264}$$

To compute $\partial L^a/\partial \boldsymbol{r}$, we make use of (A.32):

$$\frac{\partial}{\partial \boldsymbol{r}}(\boldsymbol{v} \cdot \boldsymbol{\Omega} \times \boldsymbol{r}) = \frac{\partial}{\partial \boldsymbol{r}}(\boldsymbol{r} \cdot \boldsymbol{v} \times \boldsymbol{\Omega}) = \boldsymbol{v} \times \boldsymbol{\Omega}\,. \tag{3.265}$$

We also note that

$$\|\boldsymbol{\Omega} \times \boldsymbol{r}\|^2 = \|\boldsymbol{\Omega}\|^2 \|\boldsymbol{r}\|^2 \sin^2\theta = \|\boldsymbol{\Omega}\|^2 \|\boldsymbol{r}\|^2 (1-\cos^2\theta) = \|\boldsymbol{\Omega}\|^2 \|\boldsymbol{r}\|^2 - (\boldsymbol{\Omega} \cdot \boldsymbol{r})^2\,. \tag{3.266}$$

Thus,

$$\frac{1}{2}\frac{\partial\|\boldsymbol{\Omega}\times\boldsymbol{r}\|^2}{\partial\boldsymbol{r}} = \|\boldsymbol{\Omega}\|^2\boldsymbol{r} - (\boldsymbol{\Omega}\cdot\boldsymbol{r})\boldsymbol{\Omega} = \|\boldsymbol{\Omega}\|^2(\boldsymbol{r}-\boldsymbol{r}_\parallel) = \|\boldsymbol{\Omega}\|^2\boldsymbol{r}_\perp\ , \tag{3.267}$$

where we defined

$$\boldsymbol{r}_\parallel := \frac{\boldsymbol{\Omega}}{\|\boldsymbol{\Omega}\|}\|\boldsymbol{r}\|\cos\theta \quad \text{and} \quad \boldsymbol{r}_\perp := \boldsymbol{r}-\boldsymbol{r}_\parallel\ . \tag{3.268}$$

Geometrically, this decomposes $\boldsymbol{r}$ into a part ($\boldsymbol{r}_\parallel$) that is parallel to $\boldsymbol{\Omega}$ and the other ($\boldsymbol{r}_\perp$) that is perpendicular to $\boldsymbol{\Omega}$ as seen from Fig. 3.8.

From Lagrange's equation of motion, we obtain

$$m\dot{\boldsymbol{v}} + m\dot{\boldsymbol{\Omega}}\times\boldsymbol{r} + m\boldsymbol{\Omega}\times\boldsymbol{v} = m\boldsymbol{v}\times\boldsymbol{\Omega} + m\|\boldsymbol{\Omega}\|^2\boldsymbol{r}_\perp\ . \tag{3.269}$$

Solving for $m\dot{\boldsymbol{v}}$,

$$m\dot{\boldsymbol{v}} = 2m\boldsymbol{v}\times\boldsymbol{\Omega} + m\|\boldsymbol{\Omega}\|^2\boldsymbol{r}_\perp - m\dot{\boldsymbol{\Omega}}\times\boldsymbol{r}\ . \tag{3.270}$$

In this equation, the terms on the right are the apparent forces. From the left, they are the Coriolis force, the centrifugal force, and the Euler force. Being perpendicular to $\boldsymbol{v}$, the Coriolis force does not perform any work on the particle.

Coming back to (3.262), we simply adopt it as the Lagrangian L in $\mathscr{O}$ without further modifications. Thus,

$$\boldsymbol{p}_i := \frac{\partial L}{\partial\boldsymbol{v}_i} = m_i(\boldsymbol{v}_i + \boldsymbol{\Omega}\times\boldsymbol{r}_i) = m_i\boldsymbol{v}_i^a = \boldsymbol{p}_i^a\ , \tag{3.271}$$

and hence

$$H := \sum_{i=1}^N \boldsymbol{p}_i\cdot\boldsymbol{v}_i - L = \sum_{i=1}^N \boldsymbol{p}_i^a\cdot(\boldsymbol{v}_i^a - \boldsymbol{\Omega}\times\boldsymbol{r}_i) - L^a\ . \tag{3.272}$$

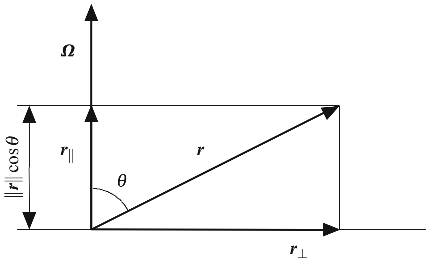


Fig. 3.8 Decomposition of $\boldsymbol{r}$ into $\boldsymbol{r}_\perp$ and $\boldsymbol{r}_\parallel$.

Since the first and the third terms taken together is H^a, it may be replaced by the expression given in (3.225), where we recall that $\psi \equiv 0$ in this section. Noting once again that $\boldsymbol{r}_i^a = \boldsymbol{r}_i$ and $\boldsymbol{p}_i^a = \boldsymbol{p}_i$, we find

$$H = \sum_{i=1}^{N} \frac{\|\boldsymbol{p}_i\|^2}{2m_i} + \phi(\boldsymbol{r}^N) - \sum_{i=1}^{N} \boldsymbol{p}_i \cdot \boldsymbol{\Omega} \times \boldsymbol{r}_i \,. \tag{3.273}$$

Using the vector identity (A.32) and the definition (1.145) of the total angular momentum, we have

$$\sum_{i=1}^{N} \boldsymbol{p}_i \cdot \boldsymbol{\Omega} \times \boldsymbol{r}_i = \boldsymbol{\Omega} \cdot \sum_{i=1}^{N} \boldsymbol{r}_i \times \boldsymbol{p}_i = \boldsymbol{\Omega} \cdot \boldsymbol{M} \,, \tag{3.274}$$

and hence

$$H = \sum_{i=1}^{N} \frac{\|\boldsymbol{p}_i\|^2}{2m_i} + \phi(\boldsymbol{r}^N) - \boldsymbol{\Omega} \cdot \boldsymbol{M} \,. \tag{3.275}$$

When $\boldsymbol{\Omega}$ is independent of time, the rotation is said to be uniform. For a *uniform rotation*, H has no explicit time dependence and the system is expected to reach equilibrium eventually. The statistical distribution is then given by

$$\rho(\boldsymbol{r}^N, \boldsymbol{p}^N) = \frac{1}{Z} \frac{e^{-\beta H}}{h^{3N} \mathscr{P}} \quad \text{and} \quad Z = \frac{1}{h^{3N} \mathscr{P}} \int e^{-\beta H} \mathrm{d}\boldsymbol{r}^N \mathrm{d}\boldsymbol{p}^N \,. \tag{3.276}$$

While $\boldsymbol{p}_i$ is the generalized momentum conjugate to $\boldsymbol{r}_i$, it is *not* the mechanical momentum $m_i \boldsymbol{v}_i$ an observer in $\mathscr{O}$ would compute based on the values of $\boldsymbol{v}^N$ measured in that frame. The situation is entirely analogous to (3.231). To extract from H an energy term this observer would compute, we use (3.271) to eliminate $\boldsymbol{p}_i$ from (3.275) in favor of the **mechanical momentum** defined by $\boldsymbol{\pi}_i := m_i \boldsymbol{v}_i$. This leads to

$$E = \sum_{i=1}^{N} \frac{\|\boldsymbol{\pi}_i\|^2}{2m_i} + \phi(\boldsymbol{r}^N) - \sum_{i=1}^{N} \frac{1}{2} m_i \|\boldsymbol{\Omega} \times \boldsymbol{r}_i\|^2 =: E_0 + \psi_{\mathrm{cp}} \,, \tag{3.277}$$

where

$$E_0 := \sum_{i=1}^{N} \frac{\|\boldsymbol{\pi}_i\|^2}{2m_i} + \phi(\boldsymbol{r}^N) \quad \text{and} \quad \psi_{\mathrm{cp}} := -\sum_{i=1}^{N} \frac{1}{2} m_i \|\boldsymbol{\Omega} \times \boldsymbol{r}_i\|^2 \,. \tag{3.278}$$

The expression (3.277) is numerically equal to H in (3.275) but it is not a Hamiltonian since E is given in terms of the *mechanical* rather than the *generalized* momenta. Nevertheless, the expression is illuminating. In particular, E_0 is the energy an observer in $\mathscr{O}$ would compute based on the values of $\boldsymbol{r}^N$ and $\boldsymbol{\pi}^N$ measured in this frame without any regard to the fact that $\mathscr{O}$ is rotating. Equation (3.277) also makes it clear that the effect of rotation of our coordinate system manifests itself only through the *apparent external field* ψ_{cp} called the **centrifugal potential energy**.

Exercise 3.23. Verify (3.277). ///

Because of its intuitive appeal, it will be desirable to use E rather than H to express the statistical distribution. To find the functional form of this distribution, let

$$\rho'(\boldsymbol{r}^N,\boldsymbol{\pi}^N)\mathrm{d}\boldsymbol{r}^N\mathrm{d}\boldsymbol{\pi}^N \tag{3.279}$$

denote the probability of finding the system of interest within the infinitesimal volume element $\mathrm{d}\boldsymbol{r}^N\mathrm{d}\boldsymbol{\pi}^N$ taken around the point $(\boldsymbol{r}^N,\boldsymbol{\pi}^N)$ in the space spanned by $2N$ vectors $\boldsymbol{r}^N$ and $\boldsymbol{\pi}^N$. From (3.271), we see that the Jacobian of the coordinate transformation from $(\boldsymbol{r}^N,\boldsymbol{p}^N)$ to $(\boldsymbol{r}^N,\boldsymbol{\pi}^N)$ is unity. As in Sect. 3.15.3, this implies that ρ' is simply ρ expressed in terms of $\boldsymbol{r}^N$ and $\boldsymbol{\pi}^N$. From (3.276), we arrive at

$$\rho'(\boldsymbol{r}^N,\boldsymbol{\pi}^N)=\frac{1}{Z'}\frac{e^{-\beta(E_0+\psi_{\mathrm{cp}})}}{h^{3N}\mathscr{P}} \quad \text{and} \quad Z':=\frac{1}{h^{3N}\mathscr{P}}\int e^{-\beta(E_0+\psi_{\mathrm{cp}})}\mathrm{d}\boldsymbol{r}^N\mathrm{d}\boldsymbol{\pi}^N\,. \tag{3.280}$$

3.17 Frequently Used Symbols

$\langle A\rangle$, ensemble average of a dynamical variable A.

f , the number of mechanical degrees of freedom.
h , Planck constant. 6.626×10^{-34} (J·sec).
k_B , Boltzmann constant, 1.3806×10^{-23} J/K.
m_i , mass of the ith particle.
p_i , generalized momentum conjugate to q_i.
p^f , collective notation for $p_1,\ldots,p_f$.
$\boldsymbol{p}_i$, linear momentum of the ith particle.
$\boldsymbol{p}^N$, collective notation for $\boldsymbol{p}_1,\ldots,\boldsymbol{p}_N$.
q_i , the ith generalized coordinate.
q^f , collective notation for $q_1,\ldots,q_f$.
$\boldsymbol{r}_i$, position vector of the ith particle.
$\boldsymbol{r}^N$, collective notation for $\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N$.
t , time.
$\boldsymbol{v}_i$, velocity vector of the ith particle.
$\boldsymbol{v}^N$, collective notation for $\boldsymbol{v}_1,\ldots,\boldsymbol{v}_N$.

A , a generic dynamical variable.
C , normalization constant for ρ.
C_V , constant volume heat capacity.
F , Helmholtz free energy.
H , Hamiltonian.
L , Lagrangian.
M , total mass of a many-particle system.

N , total number of particles in a system.
S , entropy.
T , absolute temperature.
U , internal energy.
V , volume.
Z , canonical partition function.

$\mathscr{N}$, total number of copies in a statistical ensemble.
$\mathscr{P}$, the number of permutations of identical particles.
$\mathscr{V}$, internal virial.

β , $1/k_BT$.
$\delta(x)$, Dirac δ-function.
ρ , statistical weight.
$\boldsymbol{\pi}$, mechanical momentum.
ϕ , potential energy due to interparticle interactions.
ψ , potential energy due to an external field.

Λ , thermal wavelength $h/\sqrt{2\pi m k_B T}$ of a particle of mass m.
$\boldsymbol{\Omega}$, angular velocity.

References and Further Reading

1. Gibbs J W (1981) Elementary principles in statistical mechanics. Ox Bow Press, Connecticut
Our Sect. 3.9 followed Chap. 4 of the book, where the canonical ensemble was introduced. The same chapter demonstrates the relationship between statistical mechanics and thermodynamics and provides further motivation for the canonical ensemble.
2. Lanczos C (1986) The variational principles of mechanics. Dover, New York
The phrase “Euler force” is introduced in p. 103.
3. Landau L D, Lifshitz E M (1980) Statistical physics: Part 1, 3rd edn. Pergamon Press, New York
In developing the basic principles of statistical mechanics, we loosely followed Chap. 1 of the book. Our treatment of a rotating body is based on their treatment of the subject, in particular, Sects. 26 and 34.
4. Schrödinger E (1989) Statistical thermodynamics. Dover, New York
Chapter 3 of the book provides a detailed discussion on the meaning of setting the constant term in (3.67) to zero. He uses Boltzmann’s entropy formula rather than that of Gibbs. But, the former can be derived from the latter as we shall see later.
5. Tolman R C (1979) The principles of statistical mechanics. Dover, New York
For an extended discussion on the statistical approach and its validity, see Chap. 3. A brief summary is in Sect. 25.
6. Whitaker S (1992) Introduction to fluid mechanics. Krieger Publishing Company, Florida
It is far more natural and physically compelling to write down laws of physics, such as the conservation of mass, Newton’s equation of motion, and the first law of thermodynamics, for a (possibly moving and deforming) body than to do so for a control volume fixed in space. A derivation of the equation of continuity from this more satisfactory stand point is found in Chap. 3.

Chapter 4
Various Statistical Ensembles

A canonical ensemble describes a system held at a constant temperature. From the canonical partition function follows the Helmholtz free energy. As we saw in thermodynamics, however, it is highly desirable to be able to describe a system held under a different set of constraints, such as constant temperature and pressure or constant temperature and chemical potentials of some species. These situations call for different free energies in thermodynamics, to which correspond different statistical ensembles in statistical mechanics. In this chapter, we construct such ensembles and illustrate their applications with several simple examples. Our first task is to establish the notion of microcanonical ensemble, which is suitable for describing an isolated system. The other ensembles of more practical importance, including the canonical ensemble, can be derived straightforwardly from the microcanonical ensemble.

4.1 Fluctuations in a Canonical Ensemble

A system held at a constant temperature is constantly exchanging energy with the surroundings, which serves as a heat bath. As a result, the energy of the system will fluctuate with time. Let us first figure out the magnitude of this fluctuation. A good measure is given by

$$\Delta_{\mathrm{rms}}H := \left\langle (H - \langle H \rangle)^2 \right\rangle^{1/2} . \tag{4.1}$$

In fact, $\Delta_{\mathrm{rms}}H$ is zero if and only if H is identically equal to $\langle H \rangle$, and increases as the deviation of H from the average becomes more probable. Because of the square root, $\Delta_{\mathrm{rms}}H$ also has the dimension of energy.

Recall from Exercise 3.2 that

$$\langle H \rangle = -\frac{\partial \ln Z}{\partial \beta} \quad \text{and} \quad \left\langle (H - \langle H \rangle)^2 \right\rangle = \frac{\partial^2 \ln Z}{\partial \beta^2} . \tag{4.2}$$

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DOI 10.1007/978-3-319-13809-1_4

For an ideal gas of N noninteracting identical particles, we have

$$Z = \frac{V^N}{N!\Lambda^{3N}} , \tag{4.3}$$

where $\Lambda \sim \sqrt{\beta}$. Thus,

$$\langle H \rangle = \frac{3N}{2\beta}, \quad \left\langle (H - \langle H \rangle)^2 \right\rangle = \frac{3N}{2\beta^2} , \tag{4.4}$$

and hence

$$\frac{\Delta_{\rm rms} H}{\langle H \rangle} \sim \sqrt{\frac{1}{N}} . \tag{4.5}$$

For a macroscopic system of $N \sim 10^{24}$, this quantity is 10^{-12}. If we let $\langle H \rangle = 1$ J for the sake of illustration, then the magnitude of fluctuation $\Delta_{\rm rms} H$ is of the order of 10^{-12} J. Such an extremely small quantity cannot be measured by an instrument whose intended range is of the order of 1 J.

Equations similar to (4.5) hold quite generally for any extensive quantities of a homogeneous macroscopic body. To see this, let G be such an extensive quantity and denote by N the total number of particles in the body. We divide the body into M equal parts and denote the value of the extensive quantity pertaining to the ith part by g_i. Since G is an extensive quantity, we may write

$$G = \sum_{i=1}^{M} g_i . \tag{4.6}$$

In writing this equation, we are actually assuming that each part is still sufficiently large that the contribution to G from the interaction among adjacent parts can be ignored.[19] The assumption is justified since we are interested only in macroscopic systems here and N can be taken as large as we desire. Taking the average of (4.6), we find

$$\langle G \rangle = \sum_{i=1}^{M} \langle g_i \rangle = \sum_{i=1}^{M} g = Mg , \tag{4.7}$$

where we used the fact that the original system is homogeneous and hence $g := \langle g_i \rangle$ is common for all i. Let us next figure out the magnitude of fluctuation of G. First, we calculate

$$(G - \langle G \rangle)^2 = \left(\sum_{i=1}^{M} g_i - Mg \right)^2 = \left[\sum_{i=1}^{M} (g_i - g) \right]^2 , \tag{4.8}$$

where we used (4.7). Now,

$$\left[\sum_{i=1}^{M} (g_i - g) \right]^2 = \sum_{i=1}^{M} (g_i - g) \sum_{j=1}^{M} (g_j - g) = \sum_{i=1}^{M} \sum_{j=1}^{M} (g_i - g)(g_j - g) . \tag{4.9}$$

Taking the average, we find

$$(\Delta_{\mathrm{rms}}G)^2 = \sum_{i=1}^{M}\sum_{j=1}^{M}\langle(g_i-g)(g_j-g)\rangle\ . \tag{4.10}$$

We have already assumed that the interaction among the adjacent parts is sufficiently weak, implying that we may regard each part as statistically independent of the adjacent ones. Thus, if $i \neq j$,

$$\langle(g_i-g)(g_j-g)\rangle = \langle g_i-g\rangle\langle g_j-g\rangle = 0\ . \tag{4.11}$$

However, if $i = j$,

$$\langle(g_i-g)(g_j-g)\rangle = \langle(g_i-g)^2\rangle =: (\Delta_{\mathrm{rms}}\,g)^2 \tag{4.12}$$

and (4.10) becomes

$$(\Delta_{\mathrm{rms}}G)^2 = M(\Delta_{\mathrm{rms}}\,g)^2\ . \tag{4.13}$$

Combining (4.7) and (4.13), we arrive at

$$\frac{\Delta_{\mathrm{rms}}G}{\langle G\rangle} \sim \sqrt{\frac{1}{M}}\ . \tag{4.14}$$

If we fix the number of particles included in each of the parts, into which we divided our original system, then $M \sim N$, and hence

$$\frac{\Delta_{\mathrm{rms}}G}{\langle G\rangle} \sim \sqrt{\frac{1}{N}} \tag{4.15}$$

as advertised.

4.2 Microcanonical Ensemble

Equation (4.5) indicates that the distribution of the system energy is sharply peaked around $\langle H\rangle$ for macroscopic systems with $N \sim 10^{24}$. This being the case, the canonical ensemble can be approximated by a new ensemble, called **microcanonical ensemble**, in which all the copies have practically the same energy.

4.2.1 Expression for ρ

To define a statistical ensemble precisely, we must give an explicit expression for ρ. For this purpose, let us start from a canonical ensemble and then imagine selecting from the ensemble only those copies whose energy lies within an extremely narrow semi-open interval $(E-\Delta E, E]$. (That is, H of a copy must satisfy $E-\Delta E < H \leq E$.) Those copies so selected form the microcanonical ensemble. Now, we recall that copies in the original canonical ensemble are distributed in the phase space according to the density ρ which depends only on the energy of the system. Since $\Delta E/E$ is extremely small, we can regard ρ within the interval $(E-\Delta E, E]$ as constant without any noticeable loss of accuracy. The microcanonical ensemble constructed from the canonical ensemble is therefore characterized by

$$\rho(q^f,p^f)\mathrm{d}q^f\mathrm{d}p^f = \begin{cases} \frac{1}{C_M}\frac{\mathrm{d}q^f\mathrm{d}p^f}{h^f\mathscr{P}} & \text{if } E-\Delta E < H(q^f,p^f) \leq E \\ 0 & \text{otherwise.} \end{cases} \tag{4.16}$$

Aside from the normalization factor, this expression for ρ when $E-\Delta E < H \leq E$ follows from (3.165) by replacing the Boltzmann factor $e^{-\beta H}$ by a constant.

There is nothing special about our choice of the interval for H. We could have very well chosen $[E-\Delta E, E)$ instead. The particular choice we made here, however, will affect the definition of $\mathscr{W}(E)$ and our choice for the step function to be introduced in what follows. The reason for using a half-open interval becomes clear in (4.23).

If we take a phase point A, the number of copies in the ensemble whose representative phase points fall inside the volume element $\mathrm{d}q^f\mathrm{d}p^f$ taken around A is given by $\mathscr{N}\rho(q^f,p^f)\mathrm{d}q^f\mathrm{d}p^f$, where $\mathscr{N}$ is the total number of copies in the ensemble. According to (4.16), if the $\mathrm{d}q^f\mathrm{d}p^f$ lies entirely inside the region $E-\Delta E < H(q^f,p^f) \leq E$, this number is $\mathscr{N}\mathrm{d}q^f\mathrm{d}p^f/h^f\mathscr{P}C_M$ regardless of exactly where A is located. On the other hand, if $\mathrm{d}q^f\mathrm{d}p^f$ is taken entirely outside the indicated region, the number is strictly zero. Thus, the copies in the ensemble are distributed with uniform density in the region of the phase space corresponding to $(E-\Delta E, E]$. In other words, all states satisfying $E-\Delta E < H(q^f,p^f) \leq E$ are equally probable. This result is known as the **principle of equal weight**.

We arrived at this principle by applying a canonical ensemble to a macroscopic system. In a more common approach to statistical mechanics, one starts with a microcanonical ensemble. In this case, the principle plays a more central role of being the logical foundation of statistical mechanics.

We recall that ρ must be normalized:

$$\int \rho(q^f,p^f)\mathrm{d}q^f\mathrm{d}p^f = 1\,. \tag{4.17}$$

Substituting (4.16), we find

$$C_M = \frac{1}{h^f\mathscr{P}}\int_{E-\Delta E<H\leq E}\mathrm{d}q^f\mathrm{d}p^f\,. \tag{4.18}$$

We refer to C_M as the **microcanonical partition function**. Note that the integral in (4.18) is the volume of the region in the phase space (or the phase volume for short) that is compatible with $E-\Delta E < H \leq E$, while $h^f\mathscr{P}$ is the phase volume occupied by a single (quantum mechanically distinct) state. Thus, C_M is the number of states consistent with the condition that $E-\Delta E < H \leq E$.

We introduced a microcanonical ensemble as an approximation to a canonical ensemble. Thus, it is sensible to expect that Gibbs's entropy formula continues to apply to the microcanonical ensemble. Using (4.16) in (3.168) and noting that $x \ln x \to 0$ as $x \to 0$,[20] we have

$$-S/k_B = \int \rho \ln(h^f \mathscr{P} \rho) \mathrm{d}q^f \mathrm{d}p^f = \int \rho \ln \frac{1}{C_M} \mathrm{d}q^f \mathrm{d}p^f = \ln \frac{1}{C_M} \, . \tag{4.19}$$

The last step follows from (4.17) and the fact that C_M is a constant. This is the famous **Boltzmann's entropy formula**:

$$S = k_B \ln C_M \, . \tag{4.20}$$

4.2.2 Choice of ΔE

It is clear from (4.18) that, once the functional form of H is specified and the integration is carried out, the resulting C_M and hence S depend on f, E, ΔE, and the limits of integrations. Because the integration in (4.18) includes only those microstates compatible with $E - \Delta E < H \leq E$ and $\Delta E/E$ is extremely small, the internal energy may be identified with E:

$$U := \langle H \rangle \approx E \, . \tag{4.21}$$

For a system of N particles contained in a three-dimensional box, $f = 3N$ and the limits of integrations for their coordinates usually show up only in the form of the system volume V in the final expression for C_M. This being the case,

$$S = S(U, V, N, \Delta E) \, . \tag{4.22}$$

Of all these quantities, upon which S can depend, ΔE alone does not have any corresponding quantity in thermodynamics. We now show that the value of ΔE can be taken quite arbitrarily within a reasonable bound with no quantitative consequence to the value of S. Thus, S is practically a function only of U, V, and N.

To see that S is in fact insensitive to ΔE, let $\mathscr{W}(E,V,N)$ denote the number of states satisfying $H \leq E$ for given values of V and N. Clearly,

$$C_M(E,V,N,\Delta E) = \mathscr{W}(E,V,N) - \mathscr{W}(E - \Delta E, V, N) \, . \tag{4.23}$$

Because ΔE is extremely small compared to E, we expand the second $\mathscr{W}$ into a Taylor series to obtain

$$\begin{aligned} C_M(E,V,N,\Delta E) &\approx \mathscr{W}(E,V,N) - \left[\mathscr{W}(E,V,N) - \frac{\partial \mathscr{W}}{\partial E} \Delta E \right] \\ &= \frac{\partial \mathscr{W}}{\partial E} \Delta E =: \overline{\Omega}(E,V,N) \Delta E \, , \end{aligned} \tag{4.24}$$

where

$$\overline{\Omega}(E,V,N) := \frac{\partial \mathscr{W}}{\partial E} \tag{4.25}$$

is the **density of states**. This terminology is quite appropriate since an integration of $\overline{\Omega}$ over a certain interval of energy yields the total number of states whose energy falls within that interval.

Using (4.20), we obtain

$$S = k_B \ln \overline{\Omega}(E,V,N)\Delta E\ , \tag{4.26}$$

which is still a function of E, V, N, and ΔE.

Based on the consideration that led us to microcanonical ensemble, it seems quite reasonable to set $\Delta E = E/\sqrt{N}$, for which the entropy is evaluated as

$$S_1 = k_B \ln \overline{\Omega}(E,V,N)\frac{E}{\sqrt{N}}\ . \tag{4.27}$$

An extreme choice for ΔE would be E itself. For this choice, the Taylor series expansion used in arriving at (4.24) cannot be justified. Nevertheless, if we proceed blindly, we find

$$S_2 = k_B \ln \overline{\Omega}(E,V,N)E\ . \tag{4.28}$$

Thus,

$$\frac{S_2 - S_1}{k_B N} = \frac{1}{2N}\ln N\ . \tag{4.29}$$

For a macroscopic body with $N \sim 10^{24}$, this quantity is approximately 3×10^{-23} even though the two choices for ΔE differ by a factor of $\sqrt{N} \sim 10^{12}$. For macroscopic systems, therefore, the precise value of ΔE is unimportant. What happens if N is not large enough? In this case, the use of microcanonical ensemble is of little interest. The ensemble was introduced only as an approximation applicable for a large N.

4.2.3 Isolated System

In a microcanonical ensemble, all copies of the ensemble have nearly the same amount of energy. If we recall how ρ was constructed from the long-time behavior of a single system, this implies that its energy fluctuates very little. In fact, the width of this fluctuation relative to the energy itself is of the order of $1/\sqrt{N}$ and E of the system is a constant within the accuracy of any practical means of measuring E. We recall that the energy of an isolated system is a constant of motion. Thus, a microcanonical ensemble is a natural choice for describing a system that can be regarded as isolated within the accuracy of experiments.

This correspondence between a microcanonical ensemble and an isolated system is quite satisfactory from the point of view of thermodynamics. We recall that entropy played a prominent role in the condition of equilibrium of an isolated system. Moreover, S expressed in terms of (U,V,N) is a fundamental equation of thermodynamics. Because S is practically independent of ΔE, (4.22) indicates that S is obtained directly as a function of just these variables.

One might argue that ΔE should be identically zero for a truly isolated system. While this might be so, the system we intend to study must be subjected to experimental measurements by necessity. Because ΔE is extremely small compared to E itself, the very attempt to measure something about the system will generally affect the system energy by an amount far exceeding ΔE. At the same time, we have no interest in predicting the behavior of a system if no measurement will ever be performed on it. In this sense, a truly isolated system never really arises as a subject of our study. Instead, ΔE is nonzero for isolated systems of our interest.

4.3 Phase Integral in Microcanonical Ensemble

The phase integral for C_M extends only over a portion of the phase space consistent with the condition $E - \Delta E < H \leq E$ as we see from (4.18). It is very awkward to work with a phase integral whose limits are given in terms of the system energy. For the subsequent development, it is desirable, and indeed possible, to rewrite the phase integral so that the integral is over all phase space.

We first note that the phase integral

$$\int_{H \leq E} \mathrm{d}q^f \mathrm{d}p^f \tag{4.30}$$

is the phase volume of the region satisfying $H(q^f, p^f) \leq E$. If we divide this quantity by $h^f \mathscr{P}$, which represents the phase volume occupied by a single microstate, we obtain the number of states with $H(q^f, p^f) \leq E$. That is,

$$\mathscr{W}(E,V,N) = \frac{1}{h^f \mathscr{P}} \int_{H \leq E} \mathrm{d}q^f \mathrm{d}p^f = \frac{1}{h^f \mathscr{P}} \int \theta\left(E - H(q^f, p^f)\right) \mathrm{d}q^f \mathrm{d}p^f \,, \tag{4.31}$$

where θ is the step function defined by (D.2). See Fig. 4.1 to justify its use here.

Following the definition of $\overline{\Omega}(E)$ given by (4.24), we now have to differentiate $\mathscr{W}$ with respect to E. Because the integral is taken over all phase space, the only E dependence of $\mathscr{W}$ is in the step function θ, giving rise to the Dirac δ-function as shown in Appendix D:

$$\begin{aligned} \overline{\Omega}(E,V,N) = \frac{\partial \mathscr{W}}{\partial E} &= \frac{1}{h^f \mathscr{P}} \int \frac{\partial}{\partial E} \theta\left(E - H(q^f, p^f)\right) \mathrm{d}q^f \mathrm{d}p^f \\ &= \frac{1}{h^f \mathscr{P}} \int \delta\left(E - H(q^f, p^f)\right) \mathrm{d}q^f \mathrm{d}p^f \,. \end{aligned} \tag{4.32}$$

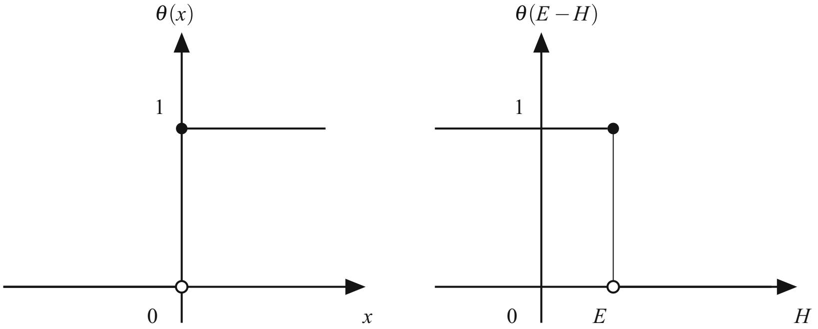


Fig. 4.1 Step function. If $H > E$, $E-H < 0$ and hence $\theta(E-H) = 0$. If $H \le E$, $E-H \ge 0$ and $\theta(E-H) = 1$.

Substituting this expression into (4.24), we find that

$$C_M = \frac{1}{h^f \mathscr{P}} \int \delta\left(E - H(q^f, p^f)\right) \Delta E \mathrm{d}q^f \mathrm{d}p^f \ . \tag{4.33}$$

In essence, we replaced the limits of the phase integral in (4.18) by a δ-function in the integrand.

Example 4.1. Irreversible expansion of an ideal gas: Consider an isolated system consisting of two compartments of equal volume V that are separated by rigid and impermeable partition held fixed in place. Suppose that, at the initial state, one of the compartments is filled with N noninteracting identical particles while the other compartment is empty. If the partition is removed, the gas will expand and fill the entire volume $2V$. Insofar as this process is irreversible, we expect that the entropy of the system at the final state is larger than that at the initial state. Let us compute the change in entropy by means of (4.33).

At the initial state, the Hamiltonian of the system is given by

$$H(\boldsymbol{r}^N, \boldsymbol{p}^N) = \begin{cases} \sum_{i=1}^N |\boldsymbol{p}_i|^2 / 2m \text{ if } \boldsymbol{r}_i \in V \text{ for all } i \\ \infty \qquad\qquad\quad \text{otherwise.} \end{cases} \tag{4.34}$$

Setting $\mathscr{P} = N!$ and $f = 3N$ we write (4.33) as

$$C_M^i = \frac{1}{N! h^{3N}} \int \delta\left(E - H(\boldsymbol{r}^N, \boldsymbol{p}^N)\right) \Delta E \mathrm{d}\boldsymbol{r}^N \mathrm{d}\boldsymbol{p}^N \ . \tag{4.35}$$

Because we are concerned only with a finite value of E, the integrand is zero if H is infinity, that is, if any one of the particle goes outside the volume V. It follows that the integration over coordinates should be confined to the volume

V and H is then a function of momenta only. Thus,

$$C_M^i = \frac{1}{N!h^{3N}} \int_{\boldsymbol{r}^N \in V} \left[\int \delta\left(E - H(\boldsymbol{p}^N)\right) \Delta E \mathrm{d}\boldsymbol{p}^N \right] \mathrm{d}\boldsymbol{r}^N , \tag{4.36}$$

where $\boldsymbol{r}^N \in V$ denotes the condition that all the particles are inside V. We have also chosen to perform first the integration with respect to momenta. But, the result of this integration is independent of coordinates. So,

$$C_M^i = \frac{V^N}{N!h^{3N}} \int \delta\left(E - H(\boldsymbol{p}^N)\right) \Delta E \mathrm{d}\boldsymbol{p}^N . \tag{4.37}$$

In this problem, there is no need to compute this integral as we will see shortly. Nevertheless, such a simple system as an ideal gas should surely be "easy" to handle and you are invited to carry out the actual computation in Exercise 4.3.

At the final state, particles can be anywhere inside the volume $2V$. Repeating the above computation, but with V replaced by $2V$, we find

$$C_M^f = \frac{(2V)^N}{N!h^{3N}} \int \delta\left(E - H(\boldsymbol{p}^N)\right) \Delta E \mathrm{d}\boldsymbol{p}^N . \tag{4.38}$$

The change in entropy upon removal of the partition, therefore, is given by

$$S^f - S^i = k_B \ln C_M^f - k_B \ln C_M^i = k_B \ln \frac{C_M^f}{C_M^i} = N k_B \ln 2 , \tag{4.39}$$

which is positive as expected.

Note that C_M^f is the number of distinct microstates consistent with the given values of E, N, and the volume $2V$. We also recall that all these C_M^f states are equally probable. Among these states, however, some have all the particles confined to the original volume V. The number of such states is just C_M^i.

(To see this more clearly, suppose that the system is a one-dimensional box of length $2L$ and let $N = 2$. The integration over coordinates is then given by

$$\begin{aligned} \int_{-L}^{L}\int_{-L}^{L} \mathrm{d}x_1 \mathrm{d}x_2 = & \int_{-L}^{0}\int_{-L}^{0} \mathrm{d}x_1 \mathrm{d}x_2 + \int_{-L}^{0}\int_{0}^{L} \mathrm{d}x_1 \mathrm{d}x_2 \\ & + \int_{0}^{L}\int_{-L}^{0} \mathrm{d}x_1 \mathrm{d}x_2 + \int_{0}^{L}\int_{0}^{L} \mathrm{d}x_1 \mathrm{d}x_2 . \end{aligned} \tag{4.40}$$

The first term on the right corresponds to the situation in which both particles occupy the left half of the box.)

Thus, the probability $p^<$ that all the particles are found within the original volume V in the final state is given by

$$p^< = \frac{C_M^i}{C_M^f} = e^{(S_i - S_f)/k_B} \,. \tag{4.41}$$

This is an example of (2.20). For $N = 10^{24}$, $p^< = 2^{-10^{24}} \approx 10^{-0.3\times 10^{24}}$, an extremely small number. For all practical purposes, the process of expansion of the gas is irreversible. However, if $N = 4$, then $p^< = 2^{-4}$ and a spontaneous reversal of the process is not too unlikely. In this way, *the irreversible approach to an equilibrium state acquires a probabilistic interpretation*.

Exercise 4.1. Consider an isolated system consisting of two compartments of equal volume that are separated by a diathermal, rigid, impermeable partition held fixed in place. Initially, one of the compartments is filled with N noninteracting identical particles of species A, while the other is filled with N noninteracting identical particles of species B. If the partition is removed and a new state of equilibrium is reached, what is the increase in the total entropy? What would be the increase in the entropy if species A and B happen to be the same? ///

In the following two exercises, we find an explicit expression for $\mathscr{W}$ and $\overline{\Omega}$ for an ideal gas. Exercise 4.2 introduces a new mathematical tool, which will be used in Exercise 4.3.

Exercise 4.2. The **Gamma function** is defined by

$$\Gamma(s) := \int_0^\infty x^{s-1} e^{-x} \mathrm{d}x \quad (s > 0) \,. \tag{4.42}$$

Prove the following identities:

a.

$$\Gamma(s+1) = s\Gamma(s) \,. \tag{4.43}$$

b.

$$\Gamma(n+1) = n! \,, \tag{4.44}$$

where n is a positive integer.

c.

$$\Gamma\left(n + \frac{1}{2}\right) = \frac{\sqrt{\pi}(2n)!}{2^{2n} n!} \,. \tag{4.45}$$

///

Exercise 4.3. Following the steps indicated below, evaluate the partition function C_M for a system of N noninteracting identical particles confined to a box of volume V:

a. Calculate

$$I_n := \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e^{-({x_1}^2+\cdots+{x_n}^2)} \mathrm{d}x_1 \cdots \mathrm{d}x_n \,. \tag{4.46}$$

b. Let U_n be the volume of the unit sphere in n-dimensional space. Then, the volume of the n-dimensional sphere of radius r is $U_n r^n$. Use this fact to express I_n in terms of U_n.

c. Show that U_n is given by

$$U_n = \frac{\pi^{n/2}}{\Gamma(n/2+1)} \,. \tag{4.47}$$

Check the validity of the formula for $n = 2$ and $n = 3$.

d. Show that

$$\mathscr{W}(E,V,N) = \frac{V^N}{N!} \left(\frac{2mE}{h^2} \right)^{3N/2} \int \theta \left(1 - \sum_{i=1}^{N} s_i^2 \right) \mathrm{d}\mathbf{s}^N \,. \tag{4.48}$$

e. Evaluate C_M. ///

4.4 †Adiabatic Reversible Processes

Suppose that a system is subject to an external field, such as the one generated by a piston in Fig. 3.4, for example. The system is otherwise isolated. We know from thermodynamics that, if this external field varies very slowly, the process proceeds reversibly and the entropy S of the system remains constant. Our goal in this section is to provide a statistical mechanical demonstration of this fact.

As before, Hamiltonian of the system depends on the parameter λ denoting the position of the external body. We suppose that λ changes by an infinitesimal amount $\Delta\lambda$ over a long duration of time τ commencing at time t. Then, the total change in H can be expressed as

$$H(t+\tau) - H(t) = \int_t^{t+\tau} \frac{\mathrm{d}H}{\mathrm{d}t'} \mathrm{d}t' \,. \tag{4.49}$$

From (1.186), we have

$$\frac{\mathrm{d}H}{\mathrm{d}t} = \frac{\partial H}{\partial t} \,. \tag{4.50}$$

For the process we are considering, the explicit time dependence of H arises solely from the time dependence of the parameter λ. Thus,

$$\frac{\partial H}{\partial t} = \frac{\partial H}{\partial \lambda} \frac{\mathrm{d}\lambda}{\mathrm{d}t} \,. \tag{4.51}$$

Using this expression in (4.49), we obtain

$$H(t+\tau) - H(t) = \int_t^{t+\tau} \frac{\partial H}{\partial \lambda} \frac{\mathrm{d}\lambda}{\mathrm{d}t'} \mathrm{d}t' \,. \tag{4.52}$$

If λ changes at a constant rate, $\mathrm{d}\lambda/\mathrm{d}t'$ may be written as $\Delta\lambda/\tau$, thus yielding

$$H(t+\tau)-H(t)=\frac{\Delta\lambda}{\tau}\int_t^{t+\tau}\frac{\partial H}{\partial\lambda}\mathrm{d}t' \,. \tag{4.53}$$

Because the change is supposed to occur very slowly, we let $\tau\rightarrow\infty$ and recall (3.4) to write[21]

$$H(t+\tau)-H(t)=\Delta\lambda\left\langle\frac{\partial H}{\partial\lambda}\right\rangle \,. \tag{4.54}$$

In a microcanonical ensemble, all copies in the ensemble have nearly identical energies. Thus, with very high degree of accuracy, we can write

$$H(t+\tau)=\langle H(t+\tau)\rangle=U(t+\tau) \quad \text{and} \quad H(t)=\langle H(t)\rangle=U(t) \,. \tag{4.55}$$

as in (4.21). Thus, (4.54) finally becomes

$$U(t+\tau)-U(t)=\mathrm{d}\lambda\left\langle\frac{\partial H}{\partial\lambda}\right\rangle \,, \tag{4.56}$$

where we replaced $\Delta\lambda$ by the usual notation $\mathrm{d}\lambda$ to indicate the infinitesimal change. Since the microcanonical ensemble is obtained as an approximation to canonical ensemble, there is nothing that prevents us from using (3.63), which in light of (4.56) indicates that $\mathrm{d}S=0$.

The key assumption in arriving at this result was that the process occurs very slowly. But, $\tau\rightarrow\infty$ only means that τ is much larger compared to the characteristic time scale of molecular motions. Thus, the very slow process we considered here can be quite rapid when measured in a time scale of experiments. In fact, many textbooks on thermodynamics contend that $\mathrm{d}S\approx 0$ during a very *rapid* expansion or compression of a gas. There, the process is said to be rapid if no appreciable heat flow is involved between the system and the surroundings. These rapid processes are still very slow compared to the characteristic time scale of molecular motions.

4.5 Canonical Ensemble

We introduced microcanonical ensemble as an approximation to canonical ensemble. Historically, though, microcanonical ensemble was the first to be formulated. This is because an isolated system is the most natural system to consider in classical mechanics. From the point of view of practical applications, an isolated system is a rather rare occurrence. So, it is nice to have statistical ensembles suitable for describing systems in contact with their surroundings.

The situation is exactly the same as that in thermodynamics. There, the second law was formulated first for an isolated system. Then, various free energies were obtained by means of Legendre transformation of the energy representation.

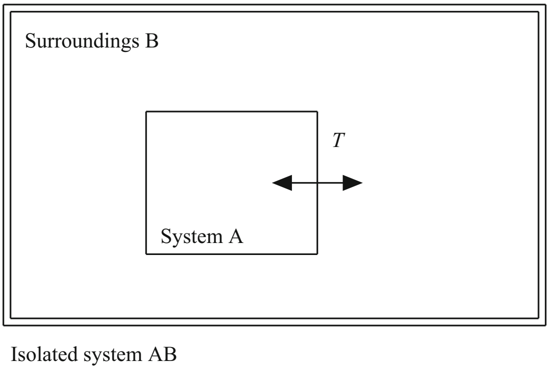


Fig. 4.2 The system of interest A is held at a constant temperature T by exchanging energy with the surroundings B. The composite system AB is isolated from the rest of the universe by means of an adiabatic, rigid, and impermeable wall.

Similarly, various statistical ensembles can be derived from the microcanonical ensemble. For this reason, the microcanonical ensemble is important conceptually despite the computational awkwardness you saw in Exercise 4.3.

4.5.1 Closed System Held at a Constant Temperature

Let us take a closed system A held at a constant temperature T. The number of particles N in A and the volume of A are both constant. But the system is allowed to exchange energy with the surroundings, which is assumed to be macroscopic. As we saw in Sect. 2.13.1, this thermal contact is what maintains the temperature of the system at a desired value.

Due to the energy exchange with the surroundings, the energy E_a of A fluctuates over time. Our immediate goal is to find the probability $p(E_a)\mathrm{d}E_a$ that the energy of A lies somewhere in the interval $(E_a - \mathrm{d}E_a, E_a]$. We use microcanonical ensemble for this purpose.

As we have indicated already, a microcanonical ensemble is suitable for describing an isolated system, which system A is not. In order to make the microcanonical ensemble applicable to the current situation, we construct a composite system AB consisting of A and the macroscopic surroundings B, and then isolate AB from the rest of the universe by means of an adiabatic, rigid, and impermeable wall as shown in Fig. 4.2. We shall assume that the interaction between A and B is sufficiently weak in the sense that

$$H_{ab} \approx H_a + H_b \, . \tag{4.57}$$

Because the composite system AB is isolated, the microcanonical ensemble applies. As in (4.16), we have

$$E_{ab} - \Delta E < H_{ab} \leq E_{ab} \tag{4.58}$$

for the allowed values of H_{ab}.

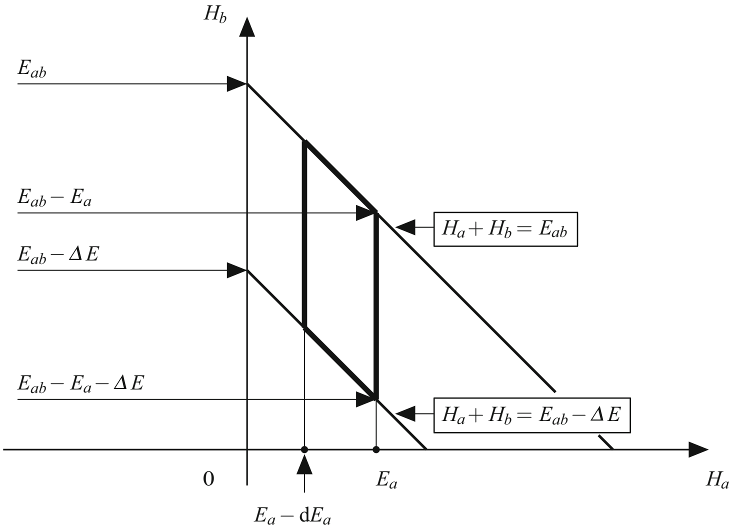


Fig. 4.3 The parallelogram region defined by four lines $H_a+H_b=E_{ab}$, $H_a+H_b=E_{ab}-\Delta E$, $H_a=E_a$, and $H_a=E_a-\mathrm{d}E_a$ contains all the microstates accessible to the composite system AB that are consistent with (4.58) and (4.59).

We recall that all the microstates of AB consistent with this condition on H_{ab} are equally probable. Thus, to compute $p(E_a)\mathrm{d}E_a$, we need to figure out the total number of microstates of AB that are consistent with both (4.58) *and* the condition

$$E_a-\mathrm{d}E_a<H_a\leq E_a\,. \tag{4.59}$$

The desired probability is this number divided by the total number of microstates of AB, which is simply $\overline{\Omega}_{ab}(E_{ab})\Delta E$.

Now, the number of microstates accessible to A under the condition (4.59) is simply

$$\overline{\Omega}_a(E_a)\mathrm{d}E_a\,, \tag{4.60}$$

where we suppressed the dependence of $\overline{\Omega}_a$ on the system volume and the number of mechanical degrees of freedom of the system as they are constant in this case. But, when A is at a particular microstate with a given energy, B can still be in various different microstates that are consistent with the remaining energy left to it.

As seen in Fig. 4.3, the conditions (4.58) and (4.59) specify the allowed values of H_b. The figure indicates that the interval for H_b depends on the exact value of H_a. This leads to a complication in figuring out the number of microstates accessible to system B. However, for sufficiently small $\mathrm{d}E_a$, we may replace the parallelogram indicated by thick solid lines by the rectangle defined by $H_a=E_a$, $H_a=E_a-\mathrm{d}E_a$, $H_b=E_{ab}-E_a$, and $H_b=E_{ab}-E_a-\Delta E$. Thus, we may write

$$E_{ab}-E_a-\Delta E<H_b\leq E_{ab}-E_a\,. \tag{4.61}$$

Accordingly, the number of microstates accessible to B that are consistent with both the conditions (4.58) and (4.59) is given by

$$\overline{\Omega}_b(E_{ab}-E_a)\Delta E\ . \tag{4.62}$$

The total number of microstates accessible to the composite system AB as a whole is then the product of (4.60) and (4.62):

$$\overline{\Omega}_a(E_a)\mathrm{d}E_a\overline{\Omega}_b(E_{ab}-E_a)\Delta E\ . \tag{4.63}$$

So, the desired probability is

$$p(E_a)\mathrm{d}E_a=\frac{\overline{\Omega}_b(E_{ab}-E_a)\Delta E\overline{\Omega}_a(E_a)\mathrm{d}E_a}{\overline{\Omega}_{ab}(E_{ab})\Delta E}\ . \tag{4.64}$$

The normalization condition of $p(E_a)$ leads to

$$\overline{\Omega}_{ab}(E_{ab})\Delta E=\int\overline{\Omega}_b(E_{ab}-E_a)\Delta E\overline{\Omega}_a(E_a)\mathrm{d}E_a\ , \tag{4.65}$$

where the integration is with respect to all possible values of E_a. This result is quite natural. In order to find out the total number of microstates accessible to AB, we first figure out the number of microstates accessible to AB when H_a is within a certain interval indicated by (4.59). This gives (4.63). Once the number of microstates is obtained for all the other intervals of width $\mathrm{d}E_a$, we can simply add up the results to obtain the total number of microstates.

4.5.2 Canonical Distribution

As it is, (4.64) is not very useful for practical computations. As we saw in Exercise 4.3, $\overline{\Omega}$ is a very awkward function to work with. To transform (4.64) a bit further, we recall Boltzmann's entropy formula (4.26) and write

$$\overline{\Omega}_b(E_{ab}-E_a)\Delta E=e^{\ln\overline{\Omega}_b(E_{ab}-E_a)\Delta E}=e^{S_b(E_{ab}-E_a)/k_B}\ . \tag{4.66}$$

Expanding $S_b(E_{ab}-E_a)$ in a Taylor series, we find

$$S_b(E_{ab}-E_a)=S_{b0}-\left.\frac{\partial S_b(E_b)}{\partial E_b}\right|_0 E_a+\text{h.o.}=S_{b0}-\frac{E_a}{T}+\text{h.o.}\ , \tag{4.67}$$

where the subscript 0 on S_b and its derivative indicates that they are to be computed under the condition that $E_b=E_{ab}$, while T defined in the last step is the temperature of the surroundings B when its energy is E_{ab}.

At this point, we note that the surroundings B can be chosen arbitrarily large compared to A, and hence the numbers of mechanical degrees of freedom of these two systems can be made to satisfy $f_a \ll f_b$. This implies that $E_{ab} \gg E_a$ for all reasonable values of E_a and hence T is quite insensitive to the exact value of E_a. This being the case, T can be referred to as the temperature of B regardless of the exact value of E_a and we can safely ignore the higher order terms in the Taylor series expansion of S_b.[22]

Recalling that $\beta := 1/k_BT$, we can rewrite (4.66) as

$$\overline{\Omega}_b(E_{ab} - E_a)\Delta E = e^{S_{b0}/k_B} e^{-\beta E_a} \,, \tag{4.68}$$

in terms of which (4.64) and (4.65) become

$$p(E_a)\mathrm{d}E_a = \frac{e^{S_{b0}/k_B} e^{-\beta E_a} \overline{\Omega}_a(E_a)\mathrm{d}E_a}{\overline{\Omega}_{ab}(E_{ab})\Delta E} \tag{4.69}$$

and

$$\overline{\Omega}_{ab}(E_{ab})\Delta E = e^{S_{b0}/k_B} \int \overline{\Omega}_a(E_a) e^{-\beta E_a} \mathrm{d}E_a \,, \tag{4.70}$$

respectively.

In what follows, we will be concerned only with system A. Thus, we drop the subscript a without a risk of confusion. Combining the last two equations,

$$p(E)\mathrm{d}E = \frac{1}{Z} \overline{\Omega}(E) e^{-\beta E} \mathrm{d}E \,, \tag{4.71}$$

in which

$$Z := \int \overline{\Omega}(E) e^{-\beta E} \mathrm{d}E \tag{4.72}$$

is the **canonical partition function** .[23] In Sect. 4.5.3, we see that (4.72) agrees with (3.162).

The free energy associated with this ensemble, by definition, is the **Helmholtz free energy**:

$$F = -k_BT \ln Z \,. \tag{4.73}$$

This definition, along with (2.172), leads to Gibbs's entropy formula as you will see in Exercise 4.5. Note that $\overline{\Omega}$ is a function of E, the volume V, and the number of mechanical degrees of freedom f of the system. When it is multiplied by the Boltzmann factor and integrated with respect to E, the final answer Z and hence F will be functions of T, V, and f. That is, (4.73) is a fundamental equation of the system.

We recall that $\overline{\Omega}(E)$ is the density of states. So, $\overline{\Omega}(E)\mathrm{d}E$ is the number of microstates of system A within the interval $(E - \mathrm{d}E, E]$. We already remarked that each of these microstates are equally probable.[24] Accordingly, (4.71) has the following interpretation. The factor $e^{-\beta E}/Z$ is the probability that the system A is at a *particular* microstate with energy somewhere in the interval $(E - \mathrm{d}E, E]$. But, there are $\overline{\Omega}(E)\mathrm{d}E$ equally probable microstates within this interval. Therefore, the probability that the energy of system A is in the interval $(E - \mathrm{d}E, E]$, irrespective of which particular microstate it is in, is given by (4.71).

Finally, our development up to this point is based entirely on classical mechanics, except for the $1/h^f \mathscr{P}$ factor originating from quantum mechanical considerations. Nevertheless, a fully quantum mechanical formulation also leads to (4.71) and (4.72). That is, they are valid regardless of the underlying mechanics. See Chap. 8 for details.

Example 4.2. Harmonic oscillator: In Exercise 3.8, you computed the constant volume heat capacity C_V of a diatomic molecule. The result was that, if the chemical bond connecting the two atoms is perfectly rigid, then, $C_V = \frac{5}{2}k_B$. The equipartition theorem indicates that, of this amount, $\frac{3}{2}k_B$ reflects the translational degrees of freedom of the center of mass of the molecule, while the remaining k_B comes from the rotation of the molecule around its center of mass. On the other hand, if the chemical bond is modeled as a harmonic spring, $C_V = \frac{7}{2}k_B$. The additional k_B comes from the vibrational motion (stretching and compressing) of the spring.

Experimentally, it is found that $C_V = \frac{5}{2}k_B$ for many (but not all) molecules at room temperature. Should we believe, then, that the chemical bond is absolutely rigid? So, if we are to pull on the atoms, then, the molecule will stay rigid until it suddenly snaps? This does not sound reasonable at all. Just as puzzling is the following observation: Physically, we expect that the harmonic spring will approach the rigid rod if the spring constant k is made infinitely large. However,

$$\lim_{k\to\infty} \frac{7}{2}k_B \neq \frac{5}{2}k_B \,. \tag{4.74}$$

This rather unsatisfactory state of affair stems from the fact that the chemical bond must be described *not* by classical mechanics but by quantum mechanics. (The same remark applies to both translational and rotational degrees of freedom of the molecule. At room temperature, however, the classical treatment proves sufficiently accurate. For details, see Chap. 8 of Ref. [1], for example.)

According to quantum mechanics, the energy E of the harmonic oscillator, a particle of mass m attached to a spring with spring constant k, can take only a discrete set of values as prescribed by the formula:

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) , \quad n = 0, 1, 2, \dots , \tag{4.75}$$

where

$$\omega := \sqrt{\frac{k}{m}} \quad \text{and} \quad \hbar := \frac{h}{2\pi} \,. \tag{4.76}$$

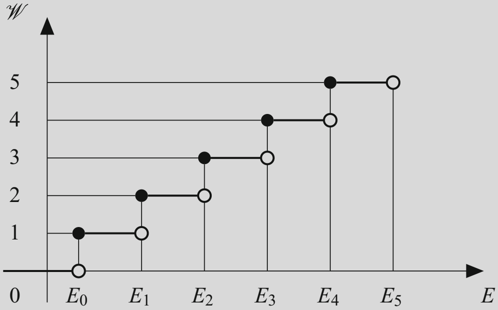
(See Sect. 8.14 for a derivation of this result.) In the case of a diatomic molecule consisting of atoms of mass m_1 and m_2, $m := m_1 m_2/(m_1 + m_2)$ is the reduced mass.

As remarked above, (4.72) is still applicable even for a quantum mechanical system. To compute Z, then, all we have to do is to figure out $\overline{\Omega}(E)$. It is actually easier to compute $\mathscr{W}(E)$, the number of states whose energy is *less than or equal to* E, and then obtain $\overline{\Omega}(E)$ as the partial derivative of $\mathscr{W}(E)$ with respect to E.

To find $\mathscr{W}(E)$, we proceed as follows. If E is less than E_0, there is no quantum mechanical state. Thus $\mathscr{W}(E) = 0$ if $E < E_0$. But, there is a single quantum state at $E = E_0$ and then another at $E = E_1$. Thus, $\mathscr{W}(E) = 1$ if $E_0 \leq E < E_1$. Likewise, $\mathscr{W}(E) = 2$ if $E_1 \leq E < E_2$. In this way, we end up with

$$\mathscr{W}(E) = \sum_{n=0}^{\infty} \theta(E - E_n) \ . \tag{4.77}$$

The graph of $\mathscr{W}(E)$ looks like this:



Taking the derivative with respect to E, we find

$$\overline{\Omega}(E) = \frac{\partial \mathscr{W}(E)}{\partial E} = \sum_{n=0}^{\infty} \delta(E - E_n) \ . \tag{4.78}$$

Substituting this expression in (4.72),

$$Z = \int_0^{\infty} \sum_{n=0}^{\infty} \delta(E - E_n) e^{-\beta E} \mathrm{d}E = \sum_{n=0}^{\infty} \int_0^{\infty} \delta(E - E_n) e^{-\beta E} \mathrm{d}E \ , \tag{4.79}$$

where the lower limit of the integration can be anything as long as it is less than E_0 since $\overline{\Omega}(E) \equiv 0$ for $E < E_0$. Using (D.15), we find

$$Z = \sum_{n=0}^{\infty} e^{-\beta E_n} = \sum_{n=0}^{\infty} e^{-\beta \hbar \omega \left(n + \frac{1}{2}\right)} = e^{-\beta \hbar \omega / 2} \sum_{n=0}^{\infty} \left(e^{-\beta \hbar \omega}\right)^n \ . \tag{4.80}$$

To carry out the indicated summation, we recall (B.25). Setting $r = e^{-\beta \hbar \omega}$, which is less than unity since $\beta \hbar \omega > 0$, we find

$$Z = \frac{e^{-\beta \hbar \omega / 2}}{1 - e^{-\beta \hbar \omega}} \ . \tag{4.81}$$

Thus,

$$\ln Z = -\frac{\beta\hbar\omega}{2} - \ln\left(1 - e^{-\beta\hbar\omega}\right) \tag{4.82}$$

and

$$U = -\frac{\partial \ln Z}{\partial \beta} = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} . \tag{4.83}$$

So, the heat capacity of the quantum harmonic oscillator is given by

$$C_{\mathrm{ho}} = \frac{\partial U}{\partial T} = \frac{\mathrm{d}\beta}{\mathrm{d}T}\frac{\partial U}{\partial \beta} = -\frac{1}{k_B T^2}\frac{-(\hbar\omega)^2 e^{\beta\hbar\omega}}{\left(e^{\beta\hbar\omega} - 1\right)^2} = k_B(\beta\hbar\omega)^2\frac{e^{\beta\hbar\omega}}{\left(e^{\beta\hbar\omega} - 1\right)^2} . \tag{4.84}$$

Let us define Θ_v by

$$\beta\hbar\omega = \frac{1}{T}\frac{\hbar}{k_B}\sqrt{\frac{k}{m}} =: \frac{\Theta_v}{T} \tag{4.85}$$

and write

$$C_{\mathrm{ho}} = k_B\left(\frac{\Theta_v}{T}\right)^2 \frac{e^{\Theta_v/T}}{\left(e^{\Theta_v/T} - 1\right)^2} . \tag{4.86}$$

Suppose that $\Theta_v/T \ll 1$, which occurs if T is large, m is large, or k is small. Then,

$$e^{\Theta_v/T} \approx 1 + \frac{\Theta_v}{T} + \frac{1}{2}\left(\frac{\Theta_v}{T}\right)^2 , \tag{4.87}$$

and hence to the first order of Θ_v/T,

$$C_{\mathrm{ho}} \approx k_B\left(\frac{\Theta_v}{T}\right)^2 \frac{1 + \Theta_v/T}{[1 + \Theta_v/T + 1/2(\Theta_v/T)^2 - 1]^2} = k_B \tag{4.88}$$

in agreement with the classical result. With some extra work, we can find that

$$C_{\mathrm{ho}} \approx k_B\left[1 - \frac{1}{12}\left(\frac{\Theta_v}{T}\right)^2\right] . \tag{4.89}$$

If, on the other hand, $\Theta_v/T \gg 1$, then $e^{\Theta_v/T} \gg 1$, and we have

$$C_{\mathrm{ho}} \approx k_B\left(\frac{\Theta_v}{T}\right)^2 \frac{e^{\Theta_v/T}}{\left(e^{\Theta_v/T}\right)^2} = k_B\left(\frac{\Theta_v}{T}\right)^2 e^{-\Theta_v/T} , \tag{4.90}$$

which becomes vanishingly small in the low T limit. Temperature dependence of C_{ho} is illustrated in Fig. 4.4.

We note that Θ_v is a material property. Some representative values, along with the value of C_{ho}/k_B computed from (4.86), are given in Table 4.1.

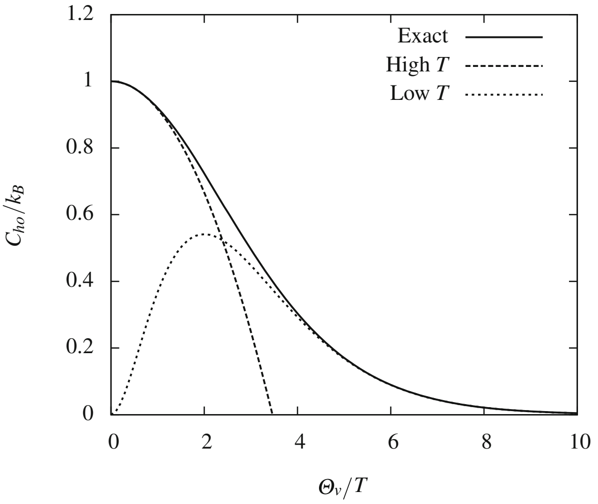


Fig. 4.4 Temperature dependence of the heat capacity C_{ho} of a quantum harmonic oscillator. "Exact, " "High T," and "Low T" refer to (4.86), (4.89), and (4.90), respectively. A classical treatment of the harmonic oscillator gives $C_{\text{ho}}/k_B = 1$ as you saw in Exercise 3.8c.

Thus, except for Cl_2 and I_2, the vibrational motion makes a negligible contribution to C_V at room temperature. This is why the rigid chemical bond model works so well in predicting C_V for many (but not all) diatomic molecules. At the room temperature, the vibrational degrees of freedom of the chemical bond is still frozen.

Quantum mechanical treatment of the rotational degrees of freedom of a symmetric diatomic molecule, such as H_2 in the table, requires a special consideration. See Ref. [1] for details.

Exercise 4.4. Prove (4.89). ///

	Θ_v (K)	C_{ho}/k_B at 300 K
H_2	6215	4.32×10^{-7}
HCl	4227	1.51×10^{-4}
N_2	3374	1.65×10^{-3}
CO	3100	3.47×10^{-3}
Cl_2	810	0.563
I_2	310	0.916

Table 4.1 Representative examples of Θ_v values and C_{ho} at 300 K. The entries for Θ_v are adapted from *Statistical Mechanics* by Donald McQuarrie, and are reprinted with permission from University Science Books, all rights reserved [2].

4.5.3 Classical Canonical Partition Function

The quantity Z defined by (4.72) is actually the canonical partition function introduced earlier. Using the expression for $\overline{\Omega}(E)$ given by (4.32) in (4.72):

$$\begin{aligned} Z &= \int \left[\frac{1}{h^f \mathscr{P}} \int \delta\left(E - H(q^f,p^f)\right) \mathrm{d}q^f \mathrm{d}p^f \right] e^{-\beta E} \mathrm{d}E \\ &= \frac{1}{h^f \mathscr{P}} \int \left[\int \delta\left(E - H(q^f,p^f)\right) e^{-\beta E} \mathrm{d}E \right] \mathrm{d}q^f \mathrm{d}p^f \\ &= \frac{1}{h^f \mathscr{P}} \int e^{-\beta H(q^f,p^f)} \mathrm{d}q^f \mathrm{d}p^f \ , \end{aligned} \tag{4.91}$$

which is (3.161). Since Z is the normalization constant and $\int$ represents the sum over states, this result implies that the probability of finding a system within an infinitesimal volume element $\mathrm{d}q^f \mathrm{d}p^f$ taken around (q^f, p^f) is given by

$$\rho(q^f,p^f)\mathrm{d}q^f \mathrm{d}p^f = \frac{1}{Z} e^{-\beta H(q^f,p^f)} \frac{\mathrm{d}q^f \mathrm{d}p^f}{h^f \mathscr{P}} \ , \tag{4.92}$$

which is (3.165). Unlike (4.71) and (4.72), the validity of (4.91) and (4.92) is limited to classical mechanical systems only.

Exercise 4.5. We now have two definitions for the Helmholtz free energy, one is (2.172) from thermodynamics and the other is (4.73). Consolidate them using (4.71). A similar attempt for (4.92) lead to (3.168) as you saw in Exercise 3.14. ///

4.5.4 Applicability of Canonical Ensemble

Looking back at our derivation, we can list two important assumptions made in arriving at the canonical ensemble. First, we assumed that the interaction between A and B is sufficiently weak. As discussed in Sect. 3.11, an interaction is said to be sufficiently weak if it allows exchange of energy between A and B *and* if the Hamiltonian of the composite system AB can be expressed as in (4.57). Second, we assumed that the number of the mechanical degrees of freedom of the surroundings f_b is much larger than that of the system of interest f_a. These are the only assumptions we made. Nowhere in our derivation have we assumed that f_a is large. Provided that these two conditions are met, the canonical ensemble is generally applicable even if $f_a = 1$.

Finally, let us remark on the statistical mechanical meaning of T. Because of exchange of energy between subsystem A and the surroundings B, the energy of system A fluctuates with time. Without the detailed knowledge of this interaction, it is not possible to predict how E_a evolves with time. Nevertheless, if the behavior of A is observed for a long interval of time, the resulting distribution of the energy

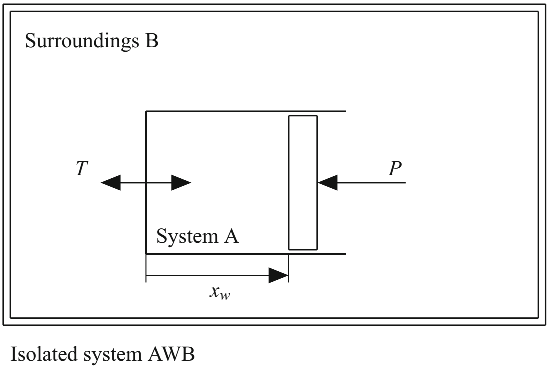


Fig. 4.5 The system of interest A is held at constant temperature T and pressure P due to exchange of energy and repartitioning of volume with the surroundings B. The composite system AWB is isolated from the rest of the universe by means of an adiabatic, rigid, and impermeable wall.

$p(E_a)$ is given by (4.71). The temperature T appears here simply as a *parameter* characterizing this distribution.

4.6 ‡Isothermal–Isobaric Ensemble

In this section, we derive an appropriate ensemble for describing a closed system held at a given temperature T and a pressure P. Our system A is the region inside a cylinder fitted with a piston. The quantity of interest is the probability $p(E_a, V_a)\mathrm{d}E_a\mathrm{d}V_a$ that A has the energy in $(E_a - \mathrm{d}E_a, E_a]$ and the volume in $(V_a, V_a + \mathrm{d}V_a]$. As with our derivation of canonical ensemble, we use a microcanonical ensemble as our starting point. Thus, we consider the composite system AWB consisting of system A, the piston W, and the surrounding B, and then isolate AWB from the rest of the universe by means of an adiabatic, rigid, and impermeable wall. See Fig. 4.5. Under the usual assumption of weak interaction, the Hamiltonian H_{awb} of the composite system may be written as

$$H_{awb} = H'_a + H'_b + K_w + \phi_{aw} + \phi_{bw} \, , \tag{4.93}$$

where we use $'$ to indicate that H'_a contains the generalized coordinates and their conjugate momenta pertaining only to the degrees of freedom of system A but not to the degrees of freedom of the piston. Likewise for H'_b. $K_w := p_w^2/2m_w$ is the kinetic energy of the piston, ϕ_{aw} denotes the potential energy due to the interaction between system A and the piston, and likewise for ϕ_{bw}. Now, we set $H_a := H'_a + \phi_{aw}$ and $H_b := H'_b + \phi_{bw}$ and write

$$H_{awb} = H_a + H_b + K_w \, . \tag{4.94}$$

Applying (4.32) to the composite system AWB, we see that the total number of microstates accessible to the composite system as a whole is given by

$$\overline{\Omega}_{awb}(E_{awb})\Delta E = \int \delta(E_{awb} - H_{awb})\Delta E \frac{\mathrm{d}q^{f_a}\mathrm{d}p^{f_a}}{h^{f_a}\mathscr{P}_a} \frac{\mathrm{d}x_w\mathrm{d}p_w}{h} \frac{\mathrm{d}q^{f_b}\mathrm{d}p^{f_b}}{h^{f_b}\mathscr{P}_b} , \tag{4.95}$$

where x_w and p_w refer to the position and the linear momentum of the piston, respectively. Using (D.26),

$$\begin{aligned}\delta(E_{awb} - H_{awb}) &= \delta(E_{awb} - H_a - H_b - K_w) \\ &= \int \delta(E_{awb} - E_a - K_w - H_b)\delta(E_a - H_a)\mathrm{d}E_a .\end{aligned} \tag{4.96}$$

Substituting this expression into (4.95), we identify

$$\overline{\Omega}_a(E_a,x_w) = \int \delta(E_a - H_a)\frac{\mathrm{d}q^{f_a}\mathrm{d}p^{f_a}}{h^{f_a}\mathscr{P}_a} \tag{4.97}$$

as the density of states for A. The indicated x_w dependence arises through that of H_a. Similarly,

$$\overline{\Omega}_b(E_{awb} - E_a - K_w, x_w) = \int \delta(E_{awb} - E_a - K_w - H_b)\frac{\mathrm{d}q^{f_b}\mathrm{d}p^{f_b}}{h^{f_b}\mathscr{P}_b} . \tag{4.98}$$

It follows that

$$\overline{\Omega}_{awb}(E_{awb})\Delta E = \iiint \overline{\Omega}_b(E_{awb} - E_a - K_w, x_w)\Delta E\, \overline{\Omega}_a(E_a,x_w)\mathrm{d}E_a \frac{\mathrm{d}x_w\mathrm{d}p_w}{h} . \tag{4.99}$$

In this equation, $\overline{\Omega}_b\Delta E$ is the number of microstates for system B when its energy is in the interval $(E_{awb} - E_a - K_w - \Delta E, E_{awb} - E_a - K_w]$ and piston W is at x_w. Similarly, $\overline{\Omega}_a\mathrm{d}E_a$ is the number of microstates for system A when its energy is in $(E_a - \mathrm{d}E_a, E_a]$ with the piston at x_w. According to (4.99), $\mathrm{d}x_w\mathrm{d}p_w/h$ is then the number of microstates for the piston when its phase point is somewhere in the infinitesimal phase volume $\mathrm{d}x_w\mathrm{d}p_w$. This result is consistent with the interpretation we have given to the quantum mechanical correction factor due to the Heisenberg uncertainty principle.

As before, we use Boltzmann's entropy formula

$$\overline{\Omega}_b(E_{awb} - E_a - K_w, x_w)\Delta E = e^{S_b(E_{awb}-E_a-K_w,x_w)/k_B} \tag{4.100}$$

and expand S_b in Taylor series:

$$S_b(E_{awb} - E_a - K_w, x_w) = S_{b0} - \left.\frac{\partial S_b}{\partial E_b}\right|_0 (E_a + K_w) + \left.\frac{\partial S_b}{\partial x_w}\right|_0 x_w + \mathrm{h.o.}, \tag{4.101}$$

where the subscript 0 on S_b and its partial derivatives indicates that they are to be computed at $E_b = E_{awb}$ and $x_w = 0$, that is, system A has zero volume and zero energy.

That such a situation is extremely unlikely to occur for nonempty system A is of no concern for us here. The indicated state servers only as a reference point around which to perform the Taylor series expansion of S_b, the entropy of system B. All we need is that S_b is well defined and differentiable at that state.

The first partial derivative in this equation is just $1/T$. In order to transform the second partial derivative into something familiar, let $A_w := V_a/x_w$ denote the cross sectional area of the cylinder. Then,

$$\left.\frac{\partial S_b}{\partial x_w}\right|_0 x_w = \left.\frac{\partial S_b}{\partial (A_w x_w)}\right|_0 A_w x_w = \left.\frac{\partial S_b}{\partial V_a}\right|_0 V_a = -\left.\frac{\partial S_b}{\partial V_b}\right|_0 V_a = -\frac{P}{T} V_a \,. \tag{4.102}$$

Thus, ignoring the higher order terms, we have

$$S_b(E_{awb} - E_a - K_w, x_w) = S_{b0} - \frac{E_a + K_w}{T} - \frac{PV_a}{T} \,. \tag{4.103}$$

Combining the results, we rewrite (4.99) as

$$\overline{\Omega}_{awb}(E_{awb})\Delta E = \iiint e^{S_{b0}/k_B} e^{-\beta E_a - \beta K_w - \beta P V_a} \overline{\Omega}_a(E_a, V_a) \mathrm{d}E_a \frac{\mathrm{d}x_w \mathrm{d}p_w}{h} \,. \tag{4.104}$$

Performing the integration with respect to p_w and replacing $\mathrm{d}x_w$ by $\mathrm{d}V_a/A_w$, we obtain

$$\overline{\Omega}_{awb}(E_{awb})\Delta E = e^{S_{b0}/k_B} \int e^{-\beta P V_a} \int \overline{\Omega}_a(E_a, V_a) e^{-\beta E_a} \frac{\mathrm{d}E_a \mathrm{d}V_a}{A_w \Lambda_w} \,, \tag{4.105}$$

where $\Lambda_w := h/\sqrt{2\pi m_w k_B T}$ is the thermal wavelength of the piston W. Because the $1/\Lambda_w$ factor arose upon the integration of $e^{-\beta K_w} \mathrm{d}x_w \mathrm{d}p_w/h$ with respect to p_w, $\mathrm{d}x_w/\Lambda_w = \mathrm{d}V_a/A_w\Lambda_w$ may be conveniently interpreted as the number of microstates accessible to the piston W when it is found somewhere between x_w and $x_w + \mathrm{d}x_w$ regardless of its momentum.

By carrying out the integrations with respect to E_a and V_a only over intervals of infinitesimal widths $\mathrm{d}E_a$ and $\mathrm{d}V_a$, we find the number of microstates accessible to the composite system AWB when H_a and V_A are within these infinitesimal intervals:

$$e^{S_{b0}/k_B} e^{-\beta P V_a} \overline{\Omega}_a(E_a, V_a) e^{-\beta E_a} \frac{\mathrm{d}E_a \mathrm{d}V_a}{A_w \Lambda_w} \,. \tag{4.106}$$

The desired probability, $p(E_a, V_a)\mathrm{d}E_a \mathrm{d}V_a$, is obtained by dividing this expression by (4.105).

Once again, we can drop the subscript a without a risk of confusion. Thus,

$$p(E, V)\mathrm{d}E\mathrm{d}V = \frac{1}{Y} e^{-\beta P V} \overline{\Omega}(E, V) e^{-\beta E} \frac{\mathrm{d}E \mathrm{d}V}{A_w \Lambda_w} \,, \tag{4.107}$$

where we defined the **isothermal–isobaric partition function** by

$$Y := \int e^{-\beta PV} \int \overline{\Omega}(E,V) e^{-\beta E} \frac{\mathrm{d}E\mathrm{d}V}{A_w \Lambda_w} \,. \tag{4.108}$$

The free energy associated with this ensemble is, by definition, the **Gibbs free energy**:

$$G := -k_B T \ln Y \,. \tag{4.109}$$

Recall that $\overline{\Omega}$ is a function of E, V, and the number of mechanical degrees of freedom f. When this is multiplied by the Boltzmann factor and $e^{-\beta PV}$ and then integrated with respect to E and V, we obtain a function of T, P, and f. The Gibbs free energy G also depends on this same set of variables. Equation (4.109) is therefore a fundamental equation of the system.

In (4.108), the integration with respect to V extends over all possible values. Because the surrounding can be made arbitrarily large, the upper limit of the integration over V is usually set to ∞. This is acceptable if the integrand vanishes sufficiently fast, which is usually the case if $P > 0$. On the other hand, the lower limit is set to zero, the theoretical minimum. Except for an ideal gas, $\overline{\Omega}(E,V)$ becomes negligibly small with increasing N/V unless E is extremely large. For example, imagine a densely packed liquid phase, in which there is little room for a molecule to move around. But, if E is very large, the Boltzmann factor effectively kills off the integrand and the integration with respect to V from $V = 0$ to ∞ is finite.

The integral

$$\int \overline{\Omega}(E,V) e^{-\beta E} \mathrm{d}E \tag{4.110}$$

in (4.108) is the canonical partition function Z of system A when its volume is V. The partition function Y is the Laplace transform of Z.

Using (4.32) in (4.108), we arrive at

$$Y = \frac{1}{h^f \mathscr{P}} \int_0^\infty e^{-\beta PV} \int e^{-\beta H(q^f,p^f)} \mathrm{d}q^f \mathrm{d}p^f \frac{\mathrm{d}V}{A_w \Lambda_w} \,. \tag{4.111}$$

Interpreting the integral signs as the sum over microstates, we identify

$$\rho(q^f,p^f,V)\mathrm{d}q^f \mathrm{d}p^f \mathrm{d}V = \frac{1}{Y} e^{-\beta PV} e^{-\beta H(q^f,p^f)} \frac{\mathrm{d}q^f \mathrm{d}p^f}{h^f \mathscr{P}} \frac{\mathrm{d}V}{A_w \Lambda_w} \tag{4.112}$$

as the probability that the piston W defines volume between V and $V + \mathrm{d}V$ and system A has its phase point somewhere in the phase volume $\mathrm{d}q^f \mathrm{d}p^f$ centered around (q^f,p^f).

Exercise 4.6. Deduce Gibbs entropy formula by combining (2.196), (4.107), and (4.109). Do the same using (4.112). ///

Because of the $1/A_w \Lambda_w$ factor, the isothermal-isobaric partition function is dimensionless. It is customary, however, to avoid an explicit reference to the piston, and redefine the partition function Y by

$$Y := \int e^{-\beta PV} \int \overline{\Omega}(E,V) e^{-\beta E} \mathrm{d}E \mathrm{d}V \,. \tag{4.113}$$

Using (4.32), we arrive at

$$Y = \frac{1}{h^f \mathscr{P}} \int_0^\infty e^{-\beta PV} \int e^{-\beta H(q^f,p^f)} \mathrm{d}q^f \mathrm{d}p^f \mathrm{d}V \,. \tag{4.114}$$

This partition function has the dimension of volume. When the Gibbs free energy is calculated as $-k_B T \ln Y$ using this dimensional Y, its numerical value depends on the unit used to measure length. A change in the unit of length amounts to an addition of a constant to the Gibbs free energy. This is of no consequence when discussing the difference in the Gibbs free energy between two states. We also note that $p(E,V)\mathrm{d}E\mathrm{d}V$ given by (4.107) remains unaffected when we drop the $1/A_w \Lambda_w$ factor. We have kept the factor up to this point since such a notion as the number of microstates becomes very difficult to conceive of otherwise.

Exercise 4.7. Find the partition functions Y (without $A_w \Lambda_w$) for an ideal gas, modeled as a system of N noninteracting identical particles. You need to recall the definition and properties of the Gamma function from Exercise 4.2. ///

Example 4.3. A system of three rods:[25] As shown in Fig. 4.6, a chain of three rod-shape molecules is confined to a cylinder of cross sectional area A fitted with a piston and is held under a constant temperature T and pressure P. The sequence of molecules ABC cannot be changed, but each molecule can take two distinct orientations, that is, horizontal (A and C in Fig. 4.6) and vertical (B in Fig. 4.6). The length of the molecule is l and the width is w. System energy E is always 0 independent of the orientations of the molecules. Let us find the equation of state, that is, an equation relating the average length $\langle L \rangle$ of the system to T and P.

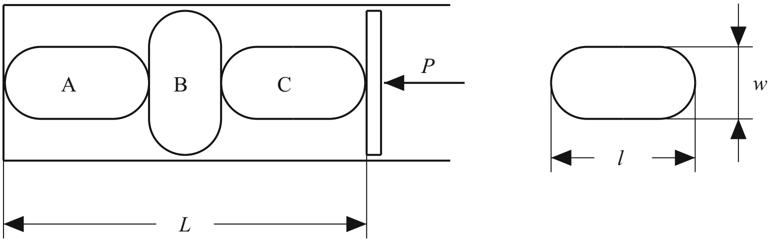


Fig. 4.6 A system of three rods held at a constant temperature and pressure.

The following orientations of molecules (A,B,C) are possible:

$$\begin{aligned}
&(w,w,w) && L=3w\,, \\
&(l,w,w)\,,\ (w,l,w)\,,\ (w,w,l) && L=2w+l\,, \\
&(l,l,w)\,,\ (l,w,l)\,,\ (w,l,l) && L=w+2l\,, \\
&(l,l,l) && L=3l\,,
\end{aligned}$$

where we also included the corresponding values of L. The energy is zero regardless of the configuration. Thus, the density of states is given by

$$\begin{aligned}
&\overline{\Omega}(E,L) \\
&=\delta(E)\left[\delta(L-3w)+3\delta(L-2w-l)+3\delta(L-w-2l)+\delta(L-3l)\right]\,.
\end{aligned} \tag{4.115}$$

To see this, we note that $\overline{\Omega}(E,L)$, upon integration over some domain on the EL-plane, gives the number of states within that domain. Thus, the point $(E,L)=(0,3w)$, if included, should contribute 1 to the integral while the point $(E,L)=(0,2w+l)$ should yield 3 upon integration. Equation (4.115) is compatible with this requirement.

Using (4.115) in (4.113),

$$\begin{aligned}
Y &= \int_0^\infty e^{-\beta PV}\int \overline{\Omega}(E,L)e^{-\beta E}\,\mathrm{d}E\,\mathrm{d}V \\
&= \int_0^\infty e^{-\beta PAL}\left[\delta(L-3w)+3\delta(L-2w-l)\right. \\
&\qquad\qquad \left.+3\delta(L-w-2l)+\delta(L-3l)\right]A\,\mathrm{d}L \\
&= A(x^3+3x^2y+3xy^2+y^3)=A(x+y)^3\,,
\end{aligned} \tag{4.116}$$

where $x := e^{-\beta PAw}$ and $y := e^{-\beta PAl}$. Finally,

$$\langle V\rangle = -\left(\frac{\partial \ln Y}{\partial \beta P}\right)_\beta = -\frac{3}{x+y}\left[\left(\frac{\partial x}{\partial \beta P}\right)_\beta + \left(\frac{\partial y}{\partial \beta P}\right)_\beta\right] = \frac{3A(wx+ly)}{x+y}\,. \tag{4.117}$$

Dividing by A, we find

$$\langle L\rangle = \frac{3(wx+ly)}{x+y}\,, \tag{4.118}$$

which is the desired equation of state.

If you prefer, you can stick to the formalism we used in Example 4.2 and work with $\mathscr{W}(E,L)$, which is the number of states with the energy less than or equal to E *and* the length less than or equal to L. Note that no states are allowed unless $E=0$. So, $\mathscr{W}$ is zero if $E<0$ and positive if $E\geq 0$. This implies that $\mathscr{W}$ is proportional to $\theta(E)$.

Let $w < l$ and assume that $E = 0$. If $L < 3w$, $\mathscr{W} = 0$, while $\mathscr{W} = 1$ if $3w \leq L < 2w + l$. Proceeding similarly with larger values of L, we get

$$\begin{aligned}\mathscr{W}(E,L) = \theta(E)\,[&\theta(L-3w)+3\theta(L-2w-l)\\&+3\theta(L-w-2l)+\theta(L-3l)]\ .\end{aligned} \tag{4.119}$$

Note that the product $\theta(E)\theta(L-3w)$ is nonzero only if $E \geq 0$ and $L \geq 3w$. A similar remark applies to other products in (4.119). Equation (4.115) follows from

$$\overline{\Omega}(E,L) = \frac{\partial^2 \mathscr{W}}{\partial E \partial L}\ . \tag{4.120}$$

To see that this is a proper way to compute $\overline{\Omega}(E,L)$, note that

$$\begin{aligned}\int_{E_1}^{E_2}\int_{L_1}^{L_2}\overline{\Omega}(E,L)\mathrm{d}L\mathrm{d}E &= \int_{E_1}^{E_2}\left[\frac{\partial\mathscr{W}(E,L_2)}{\partial E} - \frac{\partial\mathscr{W}(E,L_1)}{\partial E}\right]\mathrm{d}E\\ &= \mathscr{W}(E_2,L_2) - \mathscr{W}(E_1,L_2) - \mathscr{W}(E_2,L_1) + \mathscr{W}(E_1,L_1)\ ,\end{aligned} \tag{4.121}$$

which may be recognized as the number of states with $E_1 < E \leq E_2$ *and* $L_1 < L \leq L_2$. You can convince yourself of this by drawing rectangles on the EL-plane.

Exercise 4.8. Generalize Example 4.3 for a system of N rods. ///

4.7 Grand Canonical Ensemble

In this section, we shall consider an open system which can exchange energy and particles of a given species with the surroundings. By means of this exchange, the temperature and the chemical potential of that species in the system are held at constant values.

Our formulation generalizes quite straightforwardly to a system open to multiple species, but the notation becomes quite unmanageable. Thus, we refrain from exploring this more general situation here. The formulation we present does *not* exclude mixtures as long as the other species are confined to the system of our interest.

As before, the quantity of interest is the probability $p(E_a,N_a)\mathrm{d}E_a$ that system A contains N_a particles and has the energy in $E_a - \mathrm{d}E_a < H_a \leq E_a$. The expression for the probability will be found using microcanonical ensemble. Once again, we construct a composite system AB consisting of the system of interest A and the surroundings B, and then isolate AB from the rest of the universe by means of an adiabatic, rigid, and impermeable wall as shown in Fig. 4.7.

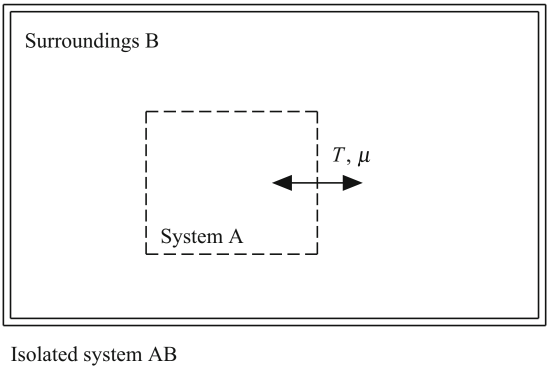


Fig. 4.7 The system of interest A is held at a constant temperature T and chemical potential μ due to exchange of energy and particles with the surroundings B. The composite system AB is isolated from the rest of the universe by means of an adiabatic, rigid, and impermeable wall.

The argument that led to (4.64) generalizes directly to the current situation simply by noting that $\overline{\Omega}_a$, $\overline{\Omega}_b$, and hence p now depends on N_a as well as on E_a:

$$p(E_a,N_a)\mathrm{d}E_a = \frac{\overline{\Omega}_b(E_{ab}-E_a,N_{ab}-N_a)\Delta E\,\overline{\Omega}_a(E_a,N_a)\mathrm{d}E_a}{\overline{\Omega}_{ab}(E_{ab},N_{ab})\Delta E} \,. \tag{4.122}$$

The normalization condition of $p(E_a,N_a)$ leads to

$$\overline{\Omega}_{ab}(E_{ab},N_{ab})\Delta E = \sum_{N_a}\int \overline{\Omega}_b(E_{ab}-E_a,N_{ab}-N_a)\Delta E\,\overline{\Omega}_a(E_a,N_a)\mathrm{d}E_a \,, \tag{4.123}$$

where the integral is taken over all possible values of E_a and the summation is over all possible values of N_a. The bounds on N_a will be specified later. We can interpret (4.123) by following the argument similar to the one given to (4.65).

In order to transform (4.122) to a more convenient form, we define the chemical potential μ of a particle in the surroundings by

$$-\frac{\mu}{T} := \left.\frac{\partial S_b(E_b)}{\partial N_b}\right|_0 \,, \tag{4.124}$$

where we introduced the subscript 0 to indicate that quantities bearing them are to be computed at $E_b = E_{ab}$ and $N_b = N_{ab}$, that is, the surroundings have all the energy and particles of the composite system.

If the number of mechanical degrees of freedom of B is much larger than that of A, then the Taylor series expansion of $S_b(E_{ab}-E_a,N_{ab}-N_a)$ will be sufficiently accurate when only the first-order terms in E_a and N_a are retained. This gives

$$\overline{\Omega}_b(E_{ab}-E_a,N_{ab}-N_a)\Delta E = e^{S_{b0}/k_B}e^{-\beta E_a+\beta\mu N_a} \,, \tag{4.125}$$

in terms of which we rewrite (4.123) as

$$\overline{\Omega}_{ab}(E_{ab},N_{ab})\Delta E = e^{S_{b0}/k_B}\sum_{N_a} e^{\beta\mu N_a}\int \overline{\Omega}_a(E_a,N_a)e^{-\beta E_a}\mathrm{d}E_a \ . \tag{4.126}$$

As with other ensembles, we drop the subscript a here and substitute the last two equations into (4.122):

$$p(E,N)\mathrm{d}E = \frac{1}{\Xi}e^{\beta\mu N}\overline{\Omega}(E,N)e^{-\beta E}\mathrm{d}E \ , \tag{4.127}$$

where

$$\Xi = \sum_N e^{\beta\mu N}\int \overline{\Omega}(E,N)e^{-\beta E}\mathrm{d}E \tag{4.128}$$

is the **grand canonical partition function**. The free energy associated with this ensemble, by definition, is the **grand potential**:[26]

$$\Omega := -k_B T\ln\Xi \ . \tag{4.129}$$

Recall that $\overline{\Omega}$ is a function of E, V, N, and the number f of any remaining mechanical degrees of freedom. Any other species, if present in the system, afford an example of such remaining degrees of freedom. Thus, Ξ and Ω are functions of T, V, μ, and f. Equation (4.129) is then a fundamental equation of the system.

For a classical mechanical system of identical particles, (4.128) may be written as

$$\Xi = \sum_N \frac{e^{\beta\mu N}}{h^{3N}N!}\int e^{-\beta H(\boldsymbol{r}^N,\boldsymbol{p}^N)}\mathrm{d}\boldsymbol{r}^N\mathrm{d}\boldsymbol{p}^N \ . \tag{4.130}$$

We interpret $\sum_N\int$ as the sum over states. Then,

$$\rho(\boldsymbol{r}^N,\boldsymbol{p}^N,N)\mathrm{d}\boldsymbol{r}^N\mathrm{d}\boldsymbol{p}^N = \frac{1}{\Xi}e^{\beta\mu N}e^{-\beta H(\boldsymbol{r}^N,\boldsymbol{p}^N)}\frac{\mathrm{d}\boldsymbol{r}^N\mathrm{d}\boldsymbol{p}^N}{h^{3N}N!} \tag{4.131}$$

is the probability that system A contains N particles and is found inside the phase volume $\mathrm{d}\boldsymbol{r}^N\mathrm{d}\boldsymbol{p}^N$ taken around the phase point $(\boldsymbol{r}^N,\boldsymbol{p}^N)$.

Exercise 4.9. Combine (2.202), (4.127), and (4.129) to deduce Gibbs's entropy formula. Do the same using (4.131). ///

In arriving at these results, we assumed that the number of mechanical degrees of freedom of system B is much larger than that of system A. This implies that the upper limit of the summation over N should be kept sufficiently small compared to the total number of particles in the composite system. However, the surroundings can be made arbitrarily large. Moreover, for a finite system volume V, $\overline{\Omega}(E,N)$ becomes negligibly small with increasing N unless E is extremely large, and the Boltzmann factor kills off the integrand. Thus, it is customary to set the upper limit of the summation to ∞. Equation (4.128) may be regarded as a *discrete* version of the Laplace transform of the canonical partition function Z.

Let us look at the other end. In principle, system A can become empty. So, the lower limit must be set to $N = 0$. What is the value of the summand in this case? If we just look at (4.130), the answer is unclear because there is no variable with respect to which to perform the integration. Let us step back a little and note that

$$\int p(E,0)\mathrm{d}E \tag{4.132}$$

is the probability that system A is empty, which, as we have just noted, can be nonzero. On the other hand, we expect that $p(E,0)$ should be zero unless E is equal to zero (or whatever any other value we assign to the vacuum):

$$p(E,0) = 0 \quad \text{if } E \neq 0 \,. \tag{4.133}$$

These two equations mean that $p(E,0)$ must be proportional to the δ-function $\delta(E)$. Now, it is quite sensible to demand that, when considering system A alone, the number of microstates accessible to A when it is empty should be just one. That is, once the system boundary is fixed, there should be only one kind of vacuum:

$$\int \overline{\Omega}(E,0)\mathrm{d}E = 1 \,. \tag{4.134}$$

We see from (4.127) that $\overline{\Omega}(E,0)$ is proportional to $p(E,0)$, and hence to $\delta(E)$. From (4.134), we conclude that

$$\overline{\Omega}(E,0) = \delta(E) \,, \tag{4.135}$$

which can be used in the $N = 0$ term in (4.128) to yield

$$e^{\beta\mu\cdot 0}\int \overline{\Omega}(E,0)e^{-\beta E}\mathrm{d}E = 1 \,. \tag{4.136}$$

So, the $N = 0$ term is unity. Because (4.130) was obtained from (4.128), this conclusion holds for the $N = 0$ term in (4.130) as well.

Example 4.4. Ideal gas: Let us find the partition functions Ξ for a pure ideal gas, defined as a system of noninteracting identical particles. From (4.130),

$$\Xi = \sum_{N=0}^{\infty} \frac{e^{\beta\mu N}}{h^{3N}N!}\int e^{-\beta H}\mathrm{d}\boldsymbol{r}^N\mathrm{d}\boldsymbol{p}^N = \sum_{N=0}^{\infty} \frac{V^N e^{\beta\mu N}}{\Lambda^{3N}N!} = \sum_{N=0}^{\infty} \frac{1}{N!}\left(\frac{Ve^{\beta\mu}}{\Lambda^3}\right)^N \,. \tag{4.137}$$

Using (B.5), we find

$$\Xi = \exp\left[\frac{Ve^{\beta\mu}}{\Lambda^3}\right] \,. \tag{4.138}$$

The quantity

$$z := \frac{e^{\beta\mu}}{\Lambda^3} \tag{4.139}$$

occurring in (4.138) is referred to as the **absolute fugacity**. For an ideal gas, this quantity is just the number density of particles:

$$z = \frac{N}{V} \quad \text{(ideal gas only).} \tag{4.140}$$

To see this, we recall (2.202) and the Euler relation (2.148) to obtain

$$\Omega = -PV \quad \text{(homogeneous system only).} \tag{4.141}$$

Since (2.148) holds only for a homogeneous body, the same restriction applies to this identity. Of course, an instantaneous configuration of particles will never be homogeneous. But, in writing thermodynamic identity such as (4.141), we are concerned only with the average behavior over a long duration of time. When interaction between the particles and the system wall can be ignored, and if there is no external field, all points in the system are equivalent and a fluid phase will be homogeneous, again upon long-time averaging.

Using (4.138),

$$-PV = -k_B T \ln \Xi = -k_B T z V \ . \tag{4.142}$$

Recalling the ideal gas equation of state, $PV = Nk_BT$, we arrive at (4.140). For an explicit derivation of the equation of state, see Exercise 4.11.

Example 4.5. Probability of a cavity formation: A gas consisting of a large number (N) of noninteracting identical particles is held at a constant temperature T and occupies a macroscopic volume V. If we focus on a very small region of space of volume v taken inside V, where $v \ll V$, the number of particles in v will fluctuate with time. Let us find the probability p_0 that v contains no particle at all.

Approach 1: The Hamiltonian of the macroscopic V may be written as the sum of two Hamiltonians one pertaining only to the particles in v and the other only to $V - v$. This implies that the interaction between regions v and $V - v$ is sufficiently weak. Because V is much larger than v, region $V - v$ acts as a reservoir of the energy and the particles for region v, allowing us to describe region v by a grand canonical ensemble. The relevant partition function is

$$\Xi = \sum_{n=0}^{\infty} e^{\beta\mu n} \int \overline{\Omega}(E,n) e^{-\beta E} \mathrm{d}E = \exp\left[\frac{v e^{\beta\mu}}{\Lambda^3}\right] . \tag{4.143}$$

We recall that the n-th term in the summation is the unnormalized probability of finding n particles in v and that Ξ is the normalization constant.

The desired probability, therefore, is obtained by dividing the $n = 0$ term by Ξ. But, the term in question is just one. So,

$$p_0 = \frac{1}{\Xi} = \exp\left[-\frac{ve^{\beta\mu}}{\Lambda^3}\right] . \tag{4.144}$$

Equation (4.142) applied to region v gives

$$-Pv = -k_BT \ln \Xi , \tag{4.145}$$

Thus,

$$p_0 = \frac{1}{\Xi} = e^{-Pv/k_BT} , \tag{4.146}$$

in which we recognize Pv as the reversible work required to create a cavity of volume v in a gas held at the pressure P. This result is an example of (2.180).

Approach 2: We can treat the entire gas phase in V using a canonical ensemble, for which the relevant partition function is

$$Z = \frac{1}{N!}\frac{V^N}{\Lambda^{3N}} , \tag{4.147}$$

where N is the total number of particles in V. Only a subset of all microstates embraced by Z is consistent with the condition that v being empty. The partition function computed under this condition is

$$Z_0 = \frac{1}{N!}\frac{(V-v)^N}{\Lambda^{3N}} . \tag{4.148}$$

Thus,

$$p_0 = \frac{Z_0}{Z} = \left(1 - \frac{v}{V}\right)^N \tag{4.149}$$

Let us take the limit of $N \to \infty$ while holding $n_v := N/V$ constant. This is known as the **thermodynamic limit**. With the help of (B.24), we see that p_0 approaches

$$e^{-n_v v} \tag{4.150}$$

in this limit. But, this is just (4.146) because of the ideal gas equation of state. Note that the use of grand canonical ensemble in Approach 1 implies the thermodynamic limit for region $V - v$.

Exercise 4.10. For Ξ given by (4.128),

a. Show that

$$\langle N \rangle = \left(\frac{\partial \ln \Xi}{\partial \beta\mu}\right)_{\beta,V} . \tag{4.151}$$

b. Show that

$$\langle N^2\rangle - \langle N\rangle^2 = \left(\frac{\partial^2 \ln \Xi}{\partial \beta\mu^2}\right)_{\beta,V} . \tag{4.152}$$

The notation is a bit clumsy here, but the derivative is twice with respect to $\beta\mu$.

c. Show that

$$\left(\frac{\partial^2 \ln \Xi}{\partial \beta\mu^2}\right)_{\beta,V} = \frac{k_B T \kappa_T \langle N\rangle^2}{V} , \tag{4.153}$$

where

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N} \tag{4.154}$$

is the **isothermal compressibility**. ///

Combining (4.152) and (4.153), we obtain

$$\frac{\langle N^2\rangle - \langle N\rangle^2}{\langle N\rangle^2} = \frac{k_B T n_v \kappa_T}{\langle N\rangle} , \tag{4.155}$$

where $n_v := \langle N\rangle/V = 1/\underline{V}$. But, since $k_B T n_v \kappa_T$ is an intensive quantity, (4.155) implies that

$$\frac{\Delta_{\mathrm{rms}} N}{\langle N\rangle} \sim \sqrt{\frac{1}{\langle N\rangle}} , \tag{4.156}$$

which is just another example of (4.15).

Exercise 4.11. In this chapter, we found expressions for partition functions C_M, Z, Y, and Ξ of a pure ideal gas. Assuming that N is large, find the relationships among:

a. T, U, and N
b. T, P V, and N
c. e^{μ/k_BT}, V, N, and Λ

for each ensemble. Verify that, for large N, the results are independent of the choice of the ensemble. (Omit Y if you skipped Sect. 4.6.) ///

Exercise 4.12. So far, we discussed canonical, isothermal–isobaric (Sect. 4.6),and grand canonical ensembles. They are suitable for describing a system held at constant (T,V,N), (T,P,N), and (T,V,μ), respectively. In this problem, you are invited to explore the possibility of constructing a statistical ensemble suitable for a system held at constant (T,P,μ).

By a simple generalization of the expressions for Z, Y, and Ξ, it seems reasonable to expect that the partition function X for this ensemble is given by

$$X(T,P,\mu) = \int_0^\infty e^{-\beta PV} \sum_{N=0}^{\infty} \frac{e^{\beta\mu N}}{h^{3N} N!} \int e^{-\beta H(\boldsymbol{r}^N,\boldsymbol{p}^N)} \mathrm{d}\boldsymbol{r}^N \mathrm{d}\boldsymbol{p}^N \mathrm{d}V \tag{4.157}$$

in the case of a classical system of identical particles.

a. What is the probability $\rho(\boldsymbol{r}^N, \boldsymbol{p}^N, V, N)\mathrm{d}\boldsymbol{r}^N\mathrm{d}\boldsymbol{p}^N\mathrm{d}V$ of finding the system with N particles, with volume in the interval $(V, V + \mathrm{d}V]$, and within an infinitesimal volume element $\mathrm{d}\boldsymbol{r}^N\mathrm{d}\boldsymbol{p}^N$ taken around the phase point $(\boldsymbol{r}^N, \boldsymbol{p}^N)$?
b. Using Gibbs's entropy formula, evaluate the *numerical value* of $-k_BT\ln X$. Is this ensemble useful at all? Why or why not?
c. Suppose that the system is an ideal gas. Does X for the ideal gas agree with what you found in part b? If not, provide a possible explanation for the disagreement.

///

4.8 Frequently Used Symbols

$\langle A \rangle$, ensemble average of a dynamical variable A.

f , the number of mechanical degrees of freedom.
h , Planck constant. 6.626×10^{-34}(J·s).
$\hbar$, $h/2\pi$.
k_B , Boltzmann constant, 1.3806×10^{-23} J/K.
m_i , mass of the ith particle.
p_i , generalized momentum conjugate to q_i.
p^f , collective notation for $p_1, \ldots, p_f$.
$\boldsymbol{p}_i$, linear momentum of the ith particle.
$\boldsymbol{p}^N$, collective notation for $\boldsymbol{p}_1, \ldots, \boldsymbol{p}_N$.
q_i , the ith generalized coordinate.
q^f , collective notation for $q_1, \ldots, q_f$.
$\boldsymbol{r}_i$, position vector of the ith particle.
$\boldsymbol{r}^N$, collective notation for $\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N$.
$\boldsymbol{v}_i$, velocity vector of the ith particle.
$\boldsymbol{v}^N$, collective notation for $\boldsymbol{v}_1, \ldots, \boldsymbol{v}_N$.
z , absolute fugacity. $e^{\beta\mu}/\Lambda^3$.

A , a generic dynamical variable.
C_M , microcanonical partition function.
E , energy of the system.
F , Helmholtz free energy.
H , Hamiltonian.
N , total number of particles in a system.
P , pressure.
S , entropy.
T , absolute temperature.
U , internal energy.
V , volume.
Y , isothermal–isobaric partition function.

Z , canonical partition function.

$\mathscr{P}$, the number of permutations of identical particles.
$\mathscr{W}(E)$, the number of microstates with $H \leq E$.

β , $1/k_B T$.
$\delta(x)$, Dirac δ-function.
ρ , statistical weight.
μ , chemical potential.
$\theta(x)$, step function defined by (D.2).

Λ , thermal wavelength $h/\sqrt{2\pi m k_B T}$ of a particle of mass m.
Ξ , grand canonical partition function.
$\overline{\Omega}$, density of states.

References and Further Reading

1. Hill T L (1986) An Introduction to Statistical Thermodynamics. Dover, New York
   See Chap. 8 for a more detailed treatment of diatomic molecules. Chap. 9 is on polyatomic molecules.
2. McQuarrie D A (2000) Statistical Mechanics. University Science Books, Sausalito, California

Chapter 5
Simple Models of Adsorption

As an illustration of canonical and grand canonical ensembles, we discuss a few variants of a simple model of adsorption. Despite their simplicity, these models provide important insights into diverse phenomena ranging from oxygen binding to hemoglobin to vapor–liquid phase coexistence.

5.1 Exact Solutions

Let us first look at simple exactly solvable model. It forms a basis for introducing approximations that become necessary when we deal with more complex model systems.

5.1.1 *Single Site*

Consider a single adsorption site exposed to a gas phase. We assume that the site can accommodate at most a single gas particle. The quantity of our primary interest is the average number $\langle N \rangle$ of gas particles adsorbed at the site. Before proceeding, we note that this quantity is actually the probability p_1 that the site is occupied by a particle since

$$\langle N \rangle = 0 \times (1 - p_1) + 1 \times p_1 = p_1 \ . \tag{5.1}$$

If we define our system as in Fig. 5.1, it is an open system, for which the relevant ensemble is the grand canonical ensemble with the surrounding gas phase setting the temperature T and the chemical potential μ for the system.

We recall from Exercise 4.10 that

$$\langle N \rangle = \left(\frac{\partial \ln \Xi}{\partial \beta\mu} \right)_{\beta,V} \ . \tag{5.2}$$

I. Kusaka, *Statistical Mechanics for Engineers*,
DOI 10.1007/978-3-319-13809-1_5

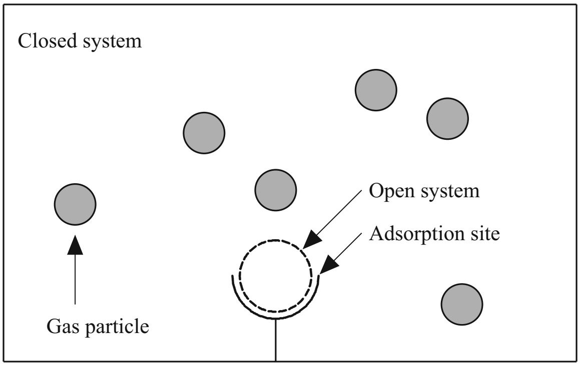


Fig. 5.1 A single adsorption site model.

So, to figure out $\langle N \rangle$, our first task is to compute Ξ, for which we need $\overline{\Omega}(E,N)$.

To simplify our analysis, we suppose that the system can take only two distinct states: the unoccupied state for which $E = 0$ and the occupied state for which $E = -\varepsilon < 0$. We shall refer to ε as the **binding energy** and take a closer look at it in the next subsection. In a meanwhile, the following three cases need to be considered:

a. $N = 0$. In this case, the energy E of the system can only be zero. Thus, there is no state if $E < 0$ or $E > 0$, but there is a single state if $E = 0$, leading to the picture in Fig. 5.2a. Thus,

$$\mathscr{W}(E,0) = \theta(E) \tag{5.3}$$

and hence

$$\overline{\Omega}(E,0) = \frac{\partial \mathscr{W}(E,0)}{\partial E} = \delta(E)\,, \tag{5.4}$$

which is nothing but (4.135).

b. $N = 1$. Now, the energy can only be $-\varepsilon$ and a consideration similar to case a leads to the picture in Fig. 5.2b, from which we obtain

$$\mathscr{W}(E,1) = \theta(E+\varepsilon) \tag{5.5}$$

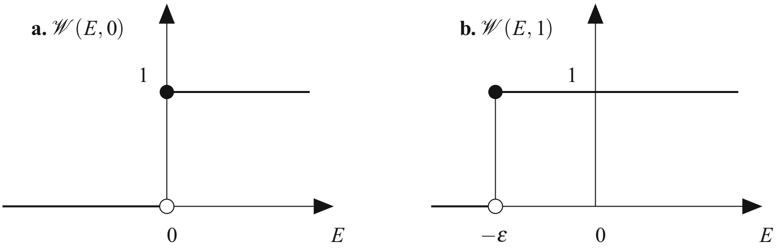


Fig. 5.2 $\mathscr{W}(E,N)$ for $N = 0$ and $N = 1$.

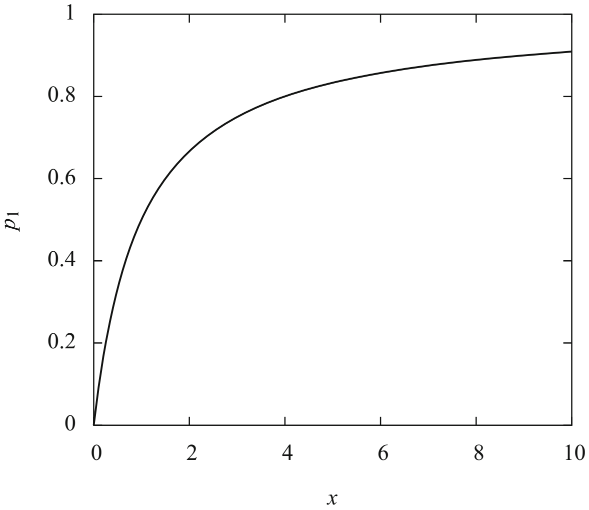


Fig. 5.3 Dependence of p_1 on $x := e^{\beta\mu}e^{\beta\varepsilon}$.

and

$$\overline{\Omega}(E,1) = \frac{\partial \mathscr{W}(E,1)}{\partial E} = \delta(E+\varepsilon)\,. \tag{5.6}$$

c. $N \geq 2$. In this case, $\mathscr{W}(E,N) \equiv 0$ and hence $\overline{\Omega}(E,N) \equiv 0$.

Using these results in (4.128), we find

$$\begin{aligned}\Xi &= e^{\beta\mu 0}\int \delta(E)e^{-\beta E}\mathrm{d}E + e^{\beta\mu 1}\int \delta(E+\varepsilon)e^{-\beta E}\mathrm{d}E + \sum_{N=2}^{\infty} e^{\beta\mu N}\int 0e^{-\beta E}\mathrm{d}E \\ &= 1 + e^{\beta\mu}e^{\beta\varepsilon} = 1 + x\,, \end{aligned} \tag{5.7}$$

where we defined $x := e^{\beta(\mu+\varepsilon)}$. Using (5.2), we arrive at

$$p_1 = \langle N \rangle = \frac{\mathrm{d}\ln\Xi}{\mathrm{d}x}\left(\frac{\partial x}{\partial \beta\mu}\right)_{\beta} = \frac{x}{1+x}\,. \tag{5.8}$$

As shown in Fig. 5.3, $\langle N \rangle$ or the probability p_1 that the site is occupied increases with increasing x and approaches unity as x tends toward infinity. Note that the increase in x can be achieved by either decreasing $T = 1/k_B\beta$ or increasing μ.

5.1.2 †Binding Energy

In the previous subsection, we assumed that the adsorption site can be in either of the two states, empty or occupied. To the latter state, we assigned the binding energy ε. In reality, however, an adsorbed particle can still move around through a vibrational motion. Let us see how this aspect can be incorporated into our model.

This time, we take the entire box shown in Fig. 5.1 as our system. The system is closed and held at a given temperature T. So the relevant partition function to compute is Z. Let V_t denote the volume of the system. The volume of the open system will be indicated by v. We suppose that there are N_t noninteracting identical particles in the system and write

$$Z = \frac{1}{h^{3N_t} N_t!} \int e^{-\beta H(\boldsymbol{r}^{N_t}, \boldsymbol{p}^{N_t})} \mathrm{d}\boldsymbol{r}^{N_t} \mathrm{d}\boldsymbol{p}^{N_t} = \frac{1}{\Lambda^{3N_t} N_t!} \int e^{-\beta \psi(\boldsymbol{r}^{N_t})} \mathrm{d}\boldsymbol{r}^{N_t} , \tag{5.9}$$

where we carried out the integration with respect to $\boldsymbol{p}^{N_t}$, and denoted the potential energy due to the interaction between a particle and the adsorption site by ψ.

We consider the particle to be adsorbed to the site if its center is anywhere in v. The site is otherwise empty. We set ψ to zero if no particle occupies v. If the ith particle occupies the site and no other particle is in v at the same time, we write $\psi = \psi(\boldsymbol{r}_i)$ to allow for the dependence of ψ on the exact position of the adsorbed particle. As before, we do not allow for multiple particles to occupy the site simultaneously, so we set ψ to infinity in that case. Thus,

$$e^{-\beta \psi(\boldsymbol{r}^{N_t})} = \begin{cases} 1 & \text{if } v \text{ is empty,} \\ e^{-\beta \psi(\boldsymbol{r}_i)} & \text{if } v \text{ is occupied by the } i\text{th particle,} \\ 0 & \text{if } v \text{ is occupied by more than one particle.} \end{cases} \tag{5.10}$$

With this much preparations, we can rewrite the integral with respect to $\boldsymbol{r}^{N_t}$ as

$$\int e^{-\beta \psi(\boldsymbol{r}^{N_t})} \mathrm{d}\boldsymbol{r}^{N_t} = \int_{\boldsymbol{r}^{N_t} \in V_t - v} \mathrm{d}\boldsymbol{r}^{N_t} + \sum_{i=1}^{N_t} \int_{\boldsymbol{r}_i \in v, \boldsymbol{r}^{N_t - 1} \in V_t - v} e^{-\beta \psi(\boldsymbol{r}_i)} \mathrm{d}\boldsymbol{r}^{N_t} , \tag{5.11}$$

where the subscripts to $\int$ denote the conditions imposed on the coordinates of particles. The first integral is taken under the condition that all the particles are outside v, resulting in $(V_t - v)^{N_t}$. The integrand in the second term depends only on $\boldsymbol{r}_i$. Thus,

$$\int_{\boldsymbol{r}_i \in v, \boldsymbol{r}^{N_t - 1} \in V_t - v} e^{-\beta \psi(\boldsymbol{r}_i)} \mathrm{d}\boldsymbol{r}^{N_t} = (V_t - v)^{N_t - 1} \int_{\boldsymbol{r}_i \in v} e^{-\beta \psi(\boldsymbol{r}_i)} \mathrm{d}\boldsymbol{r}_i = (V_t - v)^{N_t - 1} A_i , \tag{5.12}$$

where we defined

$$A_i := \int_{\boldsymbol{r}_i \in v} e^{-\beta \psi(\boldsymbol{r}_i)} \mathrm{d}\boldsymbol{r}_i . \tag{5.13}$$

However, since $\psi(\boldsymbol{r})$ is common to all particles, A_i is independent of i. Stated differently, $\boldsymbol{r}_i$ is simply an integration variable in (5.13) and can be replaced by any $\boldsymbol{r}_{j \neq i}$ without affecting the value of A_i. Thus, dropping the subscript i, we obtain

$$Z = \frac{1}{\Lambda^{3N_t} N_t!} \left[(V_t - v)^{N_t} + N_t A (V_t - v)^{N_t - 1} \right] = \frac{(V_t - v)^{N_t}}{\Lambda^{3N_t} N_t!} \left(1 + \frac{N_t}{V_t - v} A \right) . \tag{5.14}$$

In this expression, the term proportional to A, that is,

$$Z_1 := \frac{(V_t - v)^{N_t}}{\Lambda^{3N_t} N_t!} \frac{N_t}{V_t - v} A \tag{5.15}$$

comes from microstates with the single occupancy of the site. Therefore, the probability p_1 that the site is occupied is given by

$$p_1 = \frac{Z_1}{Z} = \frac{\frac{N_t}{V_t - v} A}{1 + \frac{N_t}{V_t - v} A} . \tag{5.16}$$

Ignoring v in comparison to V_t and using the relation

$$\frac{N_t}{V_t} = \frac{e^{\beta\mu}}{\Lambda^3} \tag{5.17}$$

which follows from (4.139) and (4.140) for an ideal gas, we rewrite the above expression for p_1 as

$$p_1 = \frac{e^{\beta\mu} A / \Lambda^3}{1 + e^{\beta\mu} A / \Lambda^3} . \tag{5.18}$$

Comparing this expression with (5.8), we find

$$e^{\beta\varepsilon} = \frac{A}{\Lambda^3} . \tag{5.19}$$

Thus,

$$-\varepsilon = -k_B T \ln \left[\frac{1}{\Lambda^3} \int_{\boldsymbol{r} \in v} e^{-\beta\psi(\boldsymbol{r})} \mathrm{d}\boldsymbol{r} \right] , \tag{5.20}$$

identifying $-\varepsilon$ as the Helmholtz *free energy* of a particle subject to the external field $\psi(\boldsymbol{r})$ generated by the adsorption site.

By incorporating more realism into our model, we did not materially change the behavior of p_1. Instead, we obtained an explicit expression for the binding energy. In principle, this allows us to *predict* $-\varepsilon$ from a detailed molecular level model of particles and the adsorption site.

Exercise 5.1. Analyze the current model using a grand canonical ensemble applied to the open system v. ///

5.1.3 *Multiple Independent Sites*

Let us consider a collection of M independent adsorption sites instead of just one. By the sites being independent, we mean that whether a given site is occupied or not has no impact on any other site being occupied or not. In this case, we expect that the probability p_1 that a given site is occupied still is given by $x/(1+x)$. Now that there are M such sites, we should have $\langle N \rangle = Mx/(1+x)$. Let us try to reach this conclusion through an explicit computation. Along the way, we are reminded of the notion of the binomial coefficients, which we use later.

As in Sect. 5.1.1, we take a small volume around each of the adsorption sites. The collection of M such volumes forms an open system, which can be treated using a grand canonical ensemble. Our starting point still is (4.128), in which we have to give an expression for $\overline{\Omega}(E,N)$. We need to consider the following cases:

a. $N = 0$. In this case E can only take a single value, zero, and hence

$$\mathscr{W}(E,0) = \theta(E) \quad \text{and} \quad \overline{\Omega}(E,0) = \delta(E) . \tag{5.21}$$

b. $N = 1$. In this case, E can only be $-\varepsilon$. But there are M different choices for the site to occupy. Thus,

$$\mathscr{W}(E,1) = M\theta(E+\varepsilon) \quad \text{and} \quad \overline{\Omega}(E,1) = M\delta(E+\varepsilon) . \tag{5.22}$$

c. $N = 2$. Now, E can only be -2ε. The number of different ways of choosing two sites to occupy from the M sites is given by $M(M-1)/2$. To see this, note that there are M different ways of choosing the first site to occupy. For each such choice, there are $M-1$ different choices for the second site to occupy. This gives you $M(M-1)$ options. But, all what matters is which pair of sites is being occupied in the end and not the order in which the two sites were occupied. Reversing the order gives you exactly the same state. So, we need to divide $M(M-1)$ by 2. Therefore,

$$\mathscr{W}(E,2) = \frac{M(M-1)}{2}\theta(E+2\varepsilon) \quad \text{and} \quad \overline{\Omega}(E,1) = \frac{M(M-1)}{2}\delta(E+2\varepsilon) . \tag{5.23}$$

d. Generalizing the above considerations to $N(\leq M)$ occupied sites, we find

$$\overline{\Omega}(E,N) = \frac{M!}{N!(M-N)!}\delta(E+N\varepsilon) \quad (N \leq M) . \tag{5.24}$$

To check the validity of this formula, set $N = 0, 1$, and 2. (Note that $0! = 1$).

e. Needless to say, $\overline{\Omega}(E,N) \equiv 0$ if $N > M$.

Before we continue, we recall the standard notation for the **binomial coefficient**:

$$\binom{M}{N} := \frac{M!}{N!(M-N)!} , \tag{5.25}$$

which gives the number of distinct ways of selecting N objects out of M objects without any regard to the particular order in which the selection was made.

Using (5.24) in (4.128), we find

$$\Xi = \sum_{N=0}^{M} e^{\beta\mu N}\binom{M}{N}\int \delta(E+N\varepsilon)e^{-\beta E}\mathrm{d}E = \sum_{N=0}^{M}\binom{M}{N}e^{\beta(\mu+\varepsilon)N} = \sum_{N=0}^{M}\binom{M}{N}x^N , \tag{5.26}$$

where $x := e^{\beta(\mu+\varepsilon)}$ as before.

To compute the summation explicitly, we recall (B.30) for the binomial expansion. Then, from (5.26),

$$\Xi = \sum_{N=0}^{M} \binom{M}{N} x^N 1^{M-N} = (1+x)^M \,. \tag{5.27}$$

Using (5.2), we obtain the average number $\langle N \rangle$ of particles in the entire system as

$$\langle N \rangle = \left(\frac{\partial \ln \Xi}{\partial \beta\mu} \right)_{\beta,V} = \frac{Mx}{1+x}, \tag{5.28}$$

in which $V := Mv$ is the volume of the system, that is, the collection of M adsorption sites each with the volume v. Thus,

$$p_1 := \frac{\langle N \rangle}{M} = \frac{x}{1+x} \,. \tag{5.29}$$

Exercise 5.2. Derive (5.29) using (5.9) as the starting point. Assume that $N_t \gg M$ meaning there are far more particles in the entire closed system than there are the adsorption sites. Note that we tacitly made this approximation in this subsection by using a grand canonical ensemble. Without this approximation, μ of the gas phase would depend on the number of adsorbed particles. ///

5.1.4 Four Sites with Interaction Among Particles

Consider an array of four adsorption sites placed at the four vertices of a regular tetrahedron as shown in Fig. 5.4. We assume that these sites are distinguishable

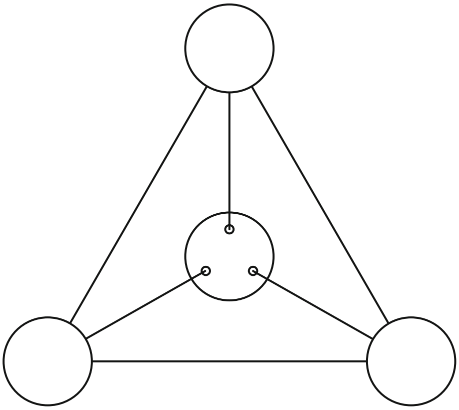


Fig. 5.4 Four adsorption sites on the vertices of a regular tetrahedron.

(That is to say, for example, the state in which only the lower left corner being occupied and the state in which only the middle site being occupied are to be considered as two distinct states.) and that each site can accommodate up to a single particle. The binding energy per site is ε, and the interaction energy between a pair of adjacent particles is $-w$. We immerse this array of adsorption sites in a gas of particles held at constant T and μ. Our goal again is to compute p_1.

We note that there are $2^4 = 16$ states the system can take, which are divided among the following cases:

a. $N = 0$ with energy $E = 0$. As before, we have

$$\overline{\Omega}(E,0) = \delta(E)\ . \tag{5.30}$$

b. $N = 1$, and hence $E = -\varepsilon$. Since there are four distinct states (reflecting the four choices we can make for the occupied site), we have

$$\overline{\Omega}(E,1) = 4\delta(E+\varepsilon)\ . \tag{5.31}$$

c. $N = 2$, in which case, $E = -2\varepsilon - w$ and there are $\binom{4}{2} = 6$ distinct states, leading to

$$\overline{\Omega}(E,2) = 6\delta(E+2\varepsilon+w)\ . \tag{5.32}$$

d. $N = 3$, for which

$$\overline{\Omega}(E,3) = 4\delta(E+3\varepsilon+3w)\ . \tag{5.33}$$

e. $N = 4$, for which

$$\overline{\Omega}(E,4) = \delta(E+4\varepsilon+6w)\ . \tag{5.34}$$

Note that the coefficients of the δ-functions add up to 16 as they should. As before, $\overline{\Omega}(E,N) \equiv 0$ for $N \geq 5$.

The grand canonical partition function follows from the above expressions for $\overline{\Omega}(E,N)$ and (4.128), and is given by

$$\Xi = \sum_{N=0}^{\infty} e^{\beta\mu N} \int \overline{\Omega}(E,N) e^{-\beta E} \mathrm{d}E = 1 + 4x + 6x^2y + 4x^3y^3 + x^4y^6\ , \tag{5.35}$$

where $x := e^{\beta(\mu+\varepsilon)}$ and $y := e^{\beta w}$. Then,

$$p_1 = \frac{\langle N \rangle}{4} = \frac{1}{4}\left(\frac{\partial \ln \Xi}{\partial \beta\mu}\right)_{\beta,V} = \frac{x + 3x^2y + 3x^3y^3 + x^4y^6}{1 + 4x + 6x^2y + 4x^3y^3 + x^4y^6}\ . \tag{5.36}$$

When $\beta w = 0$, the sites behave independent of each other. Noting that $y = 1$ in this case, you can verify that this equation reduces to (5.29).

Figure 5.5 illustrates the dependence of p_1 on x for a few values of w. The plot for $\beta w = 0$ is identical to what was shown in Fig. 5.3. For larger values of w, p_1 is seen to change more rapidly over a much smaller range of x compared to the plot for $w = 0$. This is an example of the **cooperative phenomena**. The presence of

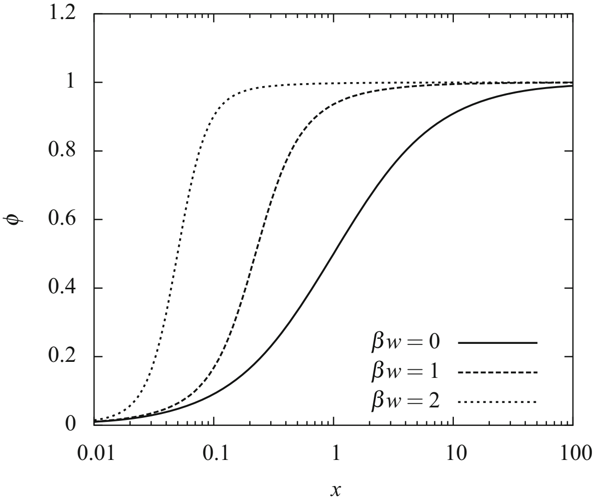


Fig. 5.5 Dependence of p_1 on $x := e^{\beta(\mu+\varepsilon)}$ for a few values of βw.

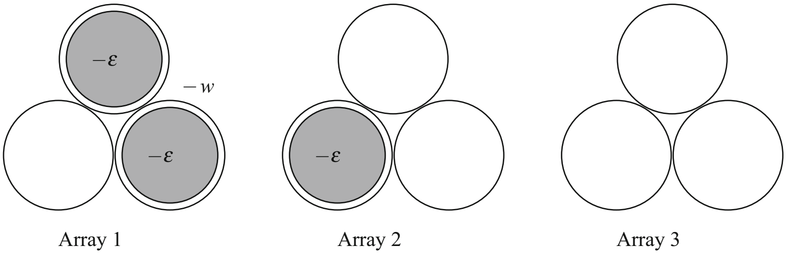


Fig. 5.6 Three triangular arrays of adsorption sites. The *filled circles* represent occupied sites, while the *open circles* are unoccupied. For the configuration shown, we have $E = -3\varepsilon - w$.

adsorbed particles enhance the probability of further adsorption of another, hence the word "cooperative."

The four-site model we just studied is a classical model for hemoglobin. In this context, the cooperative behavior accounts for the sensitivity of a hemoglobin in regulating the O_2 adsorption/desorption in response to a small change in the partial pressure of O_2.

Exercise 5.3. Consider three triangular arrays, each carrying three adsorption sites as shown in Fig. 5.6. Each site can accommodate up to a single particle. The binding energy per site is ε, while the interaction between a pair of adjacent particles, both in the same array, is $-w$. There is no interaction among particles adsorbed on different arrays.

Now suppose that the arrays are placed in a closed system with only three identical particles and held at a constant temperature. While many distinct states are accessible to the system, we focus only on the following two situations:

a. All three particles are adsorbed to a single array.
b. Each array carries exactly one particle.

For what range of temperature is situation a more likely than situation b? For the sake of this problem, assume that the nine adsorption sites are all distinguishable. ///

5.2 Mean-Field Approximation

So far, we have evaluated the partition functions Ξ, Z, and the probability p_1 that a given site is occupied by carrying out the required computations exactly.

However, it is not hard to see that the computation becomes quickly unmanageable with the increasing number of adsorption sites. There will be too many distinct microstates to enumerate, which may or may not have the same energy. In such cases, we are forced to introduce some approximation. In this section, we will look at one very popular approximation scheme known as the **mean-field approximation**.

Note that the complication in carrying out the exact computation arises from the interaction among adsorbed particles. In fact, M independent site model we saw in Sect. 5.1.3 was no more complicated than a single site model of Sect. 5.1.1. But, if there is no interaction ($w = 0$), there is no cooperative behavior either and the model will not be very interesting to study in the first place.

The basic idea of a mean-field approximation is to treat each site as if it is independent of the others while at the same time trying to capture *some* of the effects of the actual interactions among adsorbed particles.

5.2.1 Four Sites with Interaction Among Particles

We have already obtained the exact expression for p_1 for this model. This forms a basis for evaluating our approximation scheme. We will consider a much larger system in Sect. 5.2.2.

A key observation is that a particle on a given site may be considered as "feeling" the presence of particles on the other sites through an effective field they generate. To illustrate the idea, let us focus on the particle at the central site in Fig. 5.4, which we shall refer to as site 1.

There are three peripheral sites to consider. If only one of them is filled, the interaction energy is $-w$. From the perspective of the particle at site 1, this has the same effect as sitting alone but with the *effective* binding energy $\varepsilon_{\text{eff}} = \varepsilon + w$. When two of the peripheral sites are filled, then ε_{eff} felt by the central particle will be

$\varepsilon + 2w$. Finally, if all three sites are occupied, $\varepsilon_{\text{eff}} = \varepsilon + 3w$. To summarize,

$$\varepsilon_{\text{eff}} = \varepsilon + Nw \,, \tag{5.37}$$

where N is the total number of particles adsorbed at the peripheral sites.

So far, everything is exact. The difficulty of continuing with the exact solution lies in the fact that ε_{eff} at site 1 depends on the value of N, and hence on the state of the peripheral sites, which may change with time. A simple approximation to circumvent this difficulty is to replace the exact N-dependent effective field by its average. Noting that the average number of particles in each of the peripheral sites is p_1, we have

$$\varepsilon_{\text{eff}} \approx \langle \varepsilon_{\text{eff}} \rangle = \varepsilon + \langle N \rangle w = \varepsilon + 3p_1 w \,. \tag{5.38}$$

Being a thermal average, this expression is independent of the instantaneous state of the peripheral sites. According to (5.38), site 1 may be regarded as the binding site in the single site model of Sect. 5.1.1 but with the binding energy $\varepsilon + 3p_1 w$.

Under this approximation, we can immediately take over (5.8) and write down the probability that site 1 is occupied as

$$\frac{e^{\beta(\mu+\varepsilon_{\text{eff}})}}{1+e^{\beta(\mu+\varepsilon_{\text{eff}})}} \approx \frac{e^{\beta(\mu+\varepsilon+3wp_1)}}{1+e^{\beta(\mu+\varepsilon+3wp_1)}} = \frac{xy^{3p_1}}{1+xy^{3p_1}} \,. \tag{5.39}$$

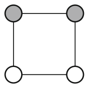
But, this quantity can only be p_1 since all the sites are equivalent and there is nothing in the model that serves to single out site 1. Thus,

$$p_1 = \frac{xy^{3p_1}}{1+xy^{3p_1}} \,. \tag{5.40}$$

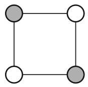
This is, then, the equation for p_1 under the mean-field approximation. The phrase “mean-field” originates from our replacing the actual *fluctuating* field ε_{eff} generated by particles on the peripheral sites by its *average* $\langle \varepsilon_{\text{eff}} \rangle$.

For $w = 0$, we have $y = 1$ and the approximation is, of course, exact. At $\beta w = 1$, the approximation is reasonably good as seen from Fig. 5.7a. With increasing w, however, its prediction starts to deviate from the actual one as indicated by Fig. 5.7b. When $\beta w = 2$, the mean-field approximation incorrectly predicts a sudden jump in p_1, or a phase transition, with increasing x.

Exercise 5.4. Consider an array of four adsorption sites placed at four corners of a square. We assume that these sites are distinguishable and that each site can accommodate up to a single particle. The binding energy per site is ε, and the interaction energy between a pair of particles occupying the nearest neighbor sites is $-w$. There is no interaction across the diagonally separated particles because they are not a nearest neighbor pair. The distance between them is $\sqrt{2}$ times the lattice constant. For example,



$E = -2\varepsilon - w$



$E = -2\varepsilon$

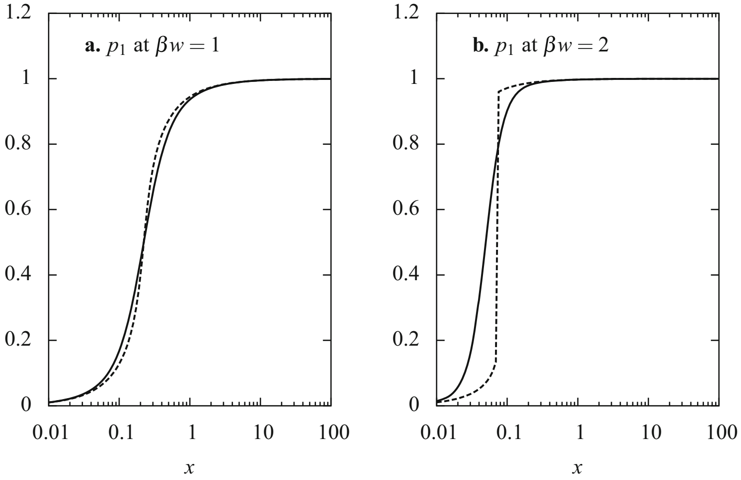


Fig. 5.7 Dependence of p_1 on x in the four interaction site model. Comparison between the exact solution (*solid line*) and the mean-field approximation (*dashed line*).

This array is exposed to a gas phase of particles held at constant T and μ.

a. Let $w = 0$, that is, there is no interaction among adsorbed particles. Find the exact expression for the average number ϕ of adsorbed particles per site.
b. Let $w \neq 0$. Find the exact expression for ϕ.
c. Use the mean-field approximation to derive the equation for ϕ. Rather than computing the partition function, consider the effective field generated by other particles at a given site and then use your answer from part a. ///

5.2.2 Two-Dimensional Lattice

Suppose now that the M adsorption sites are arranged on a two-dimensional square lattice. We continue to assign a binding energy ε per site and the interaction energy of $-w$ between a nearest neighbor pair. The diagrams in Exercise 5.4 illustrate the situation for $M = 4$.

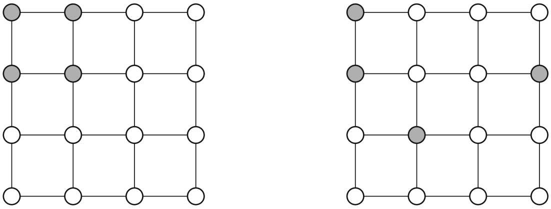
We fix the number of particles $N(\leq M)$ and work with the canonical ensemble. Even before we get started, we see right away that $p_1 = N/M$ in this case. So, what is the point? Why do we even bother with this problem? Well, $p_1 = N/M$ is the probability that a given site is occupied *if the system is, on average, homogeneous throughout*. But, whether the system can remain homogeneous depends on its thermodynamic *stability*. If the phase is unstable or even metastable for a given value of N/M, then the system will eventually separate into two phases, one with p_1 less than N/M and the other with p_1 greater than N/M.

One way to investigate such a possibility is to compute the free energy of the system as a function of p_1 *assuming* that it is homogeneous. The resulting free energy function will tell us about the stability and the eventual fate of any given homogeneous phase.

Now, the relevant partition function is given by (4.72). As we saw in Sect. 5.1.3, there are $\binom{M}{N}$ different ways of putting N particles in M sites. For a given configuration, the energy of the system may be written as

$$E = -\varepsilon N - wN_{n.n.}\ , \tag{5.41}$$

where $N_{n.n.}$ is the number of the nearest neighbor pairs in that particular configurations. Note carefully that $N_{n.n.}$ depends on the configuration under consideration. For example, compare the following two configurations, both with $M = 16$, $N = 4$.



$N_{n.n.} = 4$ $N_{n.n.} = 1$

Now, let $\Gamma(N_{n.n.})$ denote the number of configurations containing exactly $N_{n.n.}$ nearest neighbor pairs. Clearly, Γ satisfies

$$\binom{M}{N} = \sum_{N_{n.n.}} \Gamma(N_{n.n.})\ . \tag{5.42}$$

In terms of Γ, we can write $\overline{\Omega}$ as

$$\overline{\Omega}(E) = \sum_{N_{n.n.}} \Gamma(N_{n.n.})\delta(E + \varepsilon N + wN_{n.n.})\ . \tag{5.43}$$

The canonical partition function is now given by

$$\begin{aligned} Z &= \int \sum_{N_{n.n.}} \Gamma(N_{n.n.})\delta(E + \varepsilon N + wN_{n.n.})e^{-\beta E}\mathrm{d}E \\ &= \sum_{N_{n.n.}} \Gamma(N_{n.n.})e^{\beta\varepsilon N}e^{\beta wN_{n.n.}} = e^{\beta\varepsilon N}\binom{M}{N}\sum_{N_{n.n.}} \frac{\Gamma(N_{n.n.})}{\binom{M}{N}}e^{\beta wN_{n.n.}}\ , \end{aligned} \tag{5.44}$$

in which we identify the ratio $\Gamma(N_{n.n.})/\binom{M}{N}$ as the probability of finding $N_{n.n.}$ nearest neighbor pairs in a configuration if it is chosen randomly with an equal probability from $\binom{M}{N}$ configurations. Denoting the average with respect to this probability by $\langle\cdots\rangle_0$, we obtain

$$Z = e^{\beta\varepsilon N}\binom{M}{N}\left\langle e^{\beta wN_{n.n.}}\right\rangle_0\ . \tag{5.45}$$

Up to this point, everything is exact. But, evaluation of the average in this expression is a difficult task. As a simple approximation, let us replace the average of the exponential by the exponential of the average:

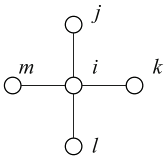
$$Z \approx e^{\beta\varepsilon N}\binom{M}{N}e^{\langle\beta w N_{n.n.}\rangle_0} = e^{\beta\varepsilon N}\binom{M}{N}e^{\beta w\langle N_{n.n.}\rangle_0} . \tag{5.46}$$

This step, as carried out at the level of partition function, implements the **mean-field approximation**. We will soon see why this is so.

Exercise 5.5. In this problem, we investigate how the mean-field approximation affects the predicted free energy of the system:

a. Show that $e^x \geq 1 + x$ for any real number x.
b. Noting that $e^x = e^{\langle x\rangle}e^{x-\langle x\rangle}$ and using the result from part a, show that $\langle e^x\rangle \geq e^{\langle x\rangle}$.
c. What is the implication of the inequality in part b on the free energy of the system estimated using the mean-field approximation? ///

To evaluate $\langle N_{n.n.}\rangle_0$, let us focus on a particular site i and its $z = 4$ nearest neighbor sites as shown below:



These sites (i, j, k, l, and m) may or may not be occupied. The probability that i is occupied in a particular configuration we choose from $\binom{M}{N}$ is simply N/M.[27] The same applies to site j. Thus, the probability that both i and j are occupied, that is, the probability that a nearest neighbor pair exists between sites i and j, is $(N/M)^2$. Similarly for other pairs involving site i. Thus, the average number of the nearest neighbor pairs centered around i is given by $(N/M)^2 z$. There is nothing special about site i and the same consideration applies to other sites as well. This suggests that the average number of the nearest neighbor pairs in the system is

$$\left(\frac{N}{M}\right)^2 zM , \tag{5.47}$$

But, counting the pairs in this manner, we have counted each pair twice. When counting the number of pairs centered around site i, we counted the i–j pair once. Then, when counting the number of pairs centered around site j, we counted this same pair for the second time. Dividing (5.47) by two to correct for the double counting, we have

$$\langle N_{n.n.}\rangle_0 = \frac{zN^2}{2M} . \tag{5.48}$$

So, (5.46) finally becomes

$$Z \approx e^{\beta \varepsilon N} \binom{M}{N} \exp\left(\frac{\beta w z}{2M} N^2\right) . \tag{5.49}$$

Now that we have the partition function, we can compute the Helmholtz free energy of the system:

$$\begin{aligned}\beta F &= -\ln Z = -\beta \varepsilon N - \ln \binom{M}{N} - \frac{\beta z w}{2M} N^2 \\ &\approx N \ln \frac{N}{M} + (M-N) \ln \frac{M-N}{M} - \beta \varepsilon N - \frac{\beta z w}{2M} N^2 ,\end{aligned} \tag{5.50}$$

where we used Stirling's formula (3.153). On per site basis, therefore,

$$f := \frac{\beta F}{M} = \phi \ln \phi + (1-\phi) \ln(1-\phi) - \beta \varepsilon \phi - \frac{1}{2} \beta z w \phi^2 , \tag{5.51}$$

where we defined $\phi := N/M$. We already remarked at the beginning of this section that $p_1 = \phi$ holds only in a *homogeneous phase*. The quantity f is the (nondimensional) free energy per site of this homogeneous phase.

Let us assume for a moment that a homogeneous system is stable and find the relationship between ϕ and the chemical potential μ of the particle. The latter follows from the identity:

$$\begin{aligned}\beta \mu &= \left(\frac{\partial \beta F}{\partial N}\right)_{T,M} = \left(\frac{\partial \beta F/M}{\partial N/M}\right)_{T,M} = \left(\frac{\partial f}{\partial \phi}\right)_T \\ &= \ln \phi - \ln(1-\phi) - \beta \varepsilon - \beta z w \phi ,\end{aligned} \tag{5.52}$$

where we assumed that the lattice constant is held fixed and treated w as a constant. In this case, holding volume constant is equivalent to fixing M. From (5.52), it follows that

$$\frac{\phi}{1-\phi} = e^{\beta(\mu + \varepsilon + w z \phi)} . \tag{5.53}$$

This result should be compared with (5.8), which may be rewritten as

$$\frac{p_1}{1-p_1} = e^{\beta(\mu+\varepsilon)} . \tag{5.54}$$

Our homogeneous system of interacting N particles is seen to be equivalent to a single-site model provided that ε in the latter is replaced by the effective binding energy, or the mean-field, $\varepsilon + w z \phi$.

Let $x := e^{\beta(\mu+\varepsilon)}$ and $y := e^{\beta w}$ as before, and rewrite (5.53) as

$$\phi = \frac{x y^{z\phi}}{1 + x y^{z\phi}} . \tag{5.55}$$

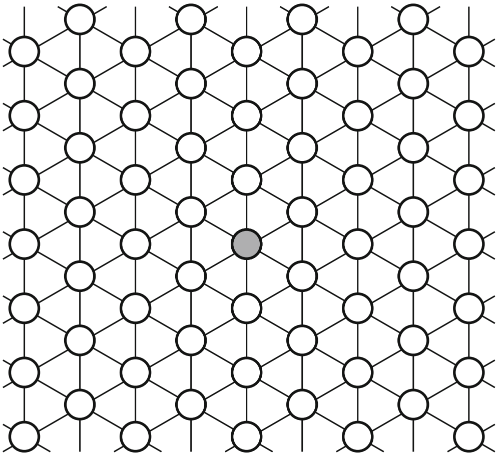


Fig. 5.8 A two-dimensional triangular lattice. A given site *(filled circle)* has six nearest neighbor sites.

This is essentially (5.40) with 3 replaced by z. Thus, under the mean-field approximation, the quantity z, often referred to as the **coordination number** is the only parameter reflecting the lattice structure of the model system. For example, in both two-dimensional triangular lattices (see Fig. 5.8.) and three-dimensional cubic lattices, the mean-field approximation gives (5.55) with $z = 6$. In reality, these two systems behave differently especially near the critical point. For details, see Ref. [1].

Let us now examine the stability of a homogeneous system. The f versus ϕ plot is shown in Fig. 5.9 for a few values of w. For simplicity, we set $\varepsilon = 0$. Note that, as βzw is increased, the graph starts to exhibit two inflection points. Between these points, the graph is concave down and the system is unstable. That is, the free energy of the system can be lowered by splitting into two phases. This mechanism of phase separation is known as the **spinodal decomposition**.

We recall that the inflection points of the curve are determined by

$$\partial^2 f/\partial\phi^2 = 0. \tag{5.56}$$

According to (5.51), this equation has two real solutions in the interval $[0,1]$ if T is sufficiently low. In this case, a homogeneous phase is unstable, metastable, or stable depending on its value of ϕ.

Let us denote the two real solutions of (5.56) by ϕ^a and ϕ^b, where $\phi^a < \phi^b$. Then, a phase with $\phi^a \le \phi \le \phi^b$ is unstable and will separate into two coexisting phases one with p_1^c and the other with p_1^d, where $p_1^c < \phi^a < \phi^b < p_1^d$. If $p_1^c < \phi < \phi^a$ or $\phi^b < \phi < p_1^d$, the phase is metastable and will separate into the two phases (p_1^c and p_1^d) given a sufficient amount of time. Phases with $\phi < p_1^c$ or $\phi > p_1^d$ are stable.

The two solutions ϕ^a and ϕ^b of (5.56) approach each other with increasing T and eventually merge at the **critical temperature** T_c. Above T_c, there is no real solution to (5.56). That is, a homogeneous phase is stable for all values of ϕ and there will be no phase separation.

Exercise 5.6. Show that p_1 values at phase coexistence can be determined by means of the common tangent construction. In this method, one looks for a tangent line to the f versus ϕ plot having two points of contact. If this common tangent exists, then the points of contact give the desired p_1 values. (See Sect. 2.16.2.4 for another example of this graphical method.) ///

Exercise 5.7.

a. For $w > 0$, find the critical temperature below which the system undergoes a phase separation. Note that the result is *independent of* ε.
b. Is there a phase separation if $w < 0$? ///

Can we approach the same problem using a grand canonical ensemble? Combining (4.72) and (4.128), we see that Ξ may be written as

$$\Xi = \sum_{N=0}^{M} e^{\beta\mu N} Z(T,V,N) \,. \tag{5.57}$$

When Z from (5.49) is substituted in this equation, the result is a rather difficult expression to evaluate.

However, based on what we saw in Sect. 4.1, N is expected to be extremely sharply peaked around $\langle N \rangle$ for large enough M. In this case, the summation in (5.57) may be replaced by the maximum term in the summand. Moreover, the value of N

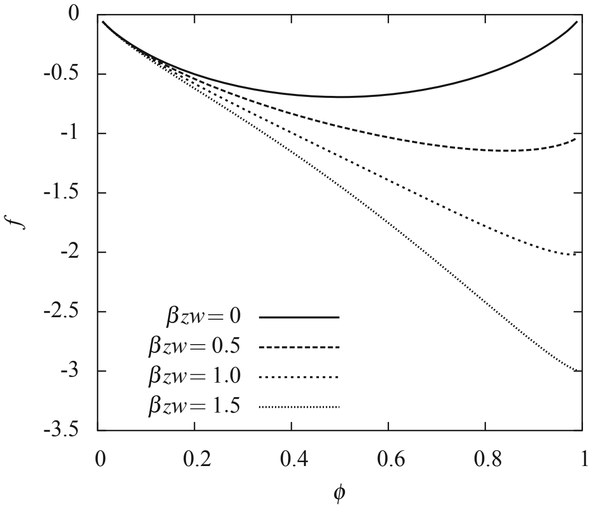


Fig. 5.9 $f := \beta F/M$ versus ϕ when $\varepsilon = 0$.

corresponding to this maximum term may safely be identified with its average $\langle N \rangle$. Thus, we write

$$\Xi \approx e^{\beta\mu N} Z(T,M,N) \tag{5.58}$$

and then maximize Ξ (or minimize $\beta\Omega = -\ln\Xi$) with respect to N. When we identify the optimum value of N with $\langle N \rangle$, the result is (5.52). In fact, from (5.58),

$$\left.\frac{\partial \ln\Xi}{\partial N}\right|_{N=\langle N \rangle} = \beta\mu + \left.\frac{\partial \ln Z}{\partial N}\right|_{N=\langle N \rangle} = 0\,, \tag{5.59}$$

which is just the first equality in (5.52).

Example 5.1. Liquid crystal:[28] Simple liquid crystals are systems consisting of nonspherical, for example, rod-like, molecules. At high temperatures, the orientation of these molecules is random; this is called the isotropic phase. At low temperatures, molecules align parallel to each other; this is called the nematic phase. The simplest lattice model for this transition is a three-state model in which a molecule can take any one of three orthogonal orientations, which we designate as x, y, and z. If two nearest molecules lie parallel to each other, there is an energy gain of $-\varepsilon$, ($\varepsilon > 0$). If they lie perpendicular, the energy gain is zero. Assuming single occupancy on each site and no vacancy, we may define variables $\sigma_x(i)$, $\sigma_y(i)$, and $\sigma_z(i)$, such that $\sigma_x(i) = 1$ if the molecule i lies parallel to the x-axis, $\sigma_x(i) = 0$ otherwise and likewise for other orientations. Of course, $\sigma_x(i) + \sigma_y(i) + \sigma_z(i) = 1$:

a. Construct an energy function for the system.
b. Let

$$\sigma_x := \frac{1}{N}\sum_{i=1}^{N} \sigma_x(i) \tag{5.60}$$

denote the fraction of molecules pointing in the x-direction. What is $\langle \sigma_x \rangle$ in the isotropic phase?
c. Define an order parameter such that it is zero in the isotropic phase, nonzero in the nematic phase and reaches a maximum of 1 at zero temperature.
d. Find the isotropic–nematic transition temperature T_t.

Solution

a. Let

$$\boldsymbol{\sigma}(i) = \sigma_x(i)\boldsymbol{e}_x + \sigma_y(i)\boldsymbol{e}_y + \sigma_z(i)\boldsymbol{e}_z\,. \tag{5.61}$$

If $\boldsymbol{\sigma}(i)$ and $\boldsymbol{\sigma}(j)$ point in the same direction, $\boldsymbol{\sigma}(i)\cdot\boldsymbol{\sigma}(j)=1$. The dot product is zero otherwise. Thus,

$$E=-\frac{1}{2}\varepsilon\sum_i\sum_{j\neq i}\boldsymbol{\sigma}(i)\cdot\boldsymbol{\sigma}(j)\,. \tag{5.62}$$

For given i, the summation over j includes only the nearest neighbors of i. The factor $1/2$ corrects for the double counting of each nearest neighbor pair.

b. In an isotropic phase, each direction is equivalent to any other. Thus, we have $\langle\sigma_x\rangle=\langle\sigma_y\rangle=\langle\sigma_z\rangle$. But, because

$$\langle\sigma_x+\sigma_y+\sigma_z\rangle=\langle\sigma_x\rangle+\langle\sigma_y\rangle+\langle\sigma_z\rangle=1\,, \tag{5.63}$$

we see that

$$\langle\sigma_x\rangle=\langle\sigma_y\rangle=\langle\sigma_z\rangle=\frac{1}{3}\,. \tag{5.64}$$

c. From (5.61)

$$\langle\boldsymbol{\sigma}\rangle=\langle\sigma_x\rangle\boldsymbol{e}_x+\langle\sigma_y\rangle\boldsymbol{e}_y+\langle\sigma_z\rangle\boldsymbol{e}_z. \tag{5.65}$$

Because of (5.63), this graphically is a vector pointing from the origin $\mathscr{O}$ to a point, call it X, on the plane defined by the following three points:

$$\mathrm{A}\doteq(1,0,0)\,,\quad \mathrm{B}\doteq(0,1,0)\,,\quad\text{and}\quad \mathrm{C}\doteq(0,0,1)\,. \tag{5.66}$$

Since components $\langle\sigma_x\rangle$, $\langle\sigma_y\rangle$, and $\langle\sigma_z\rangle$ are all nonnegative, the point X is confined to the triangle ABC. The isotropic phase is represented by the point

$$\mathrm{S}\doteq\left(\frac{1}{3},\frac{1}{3},\frac{1}{3}\right)\,. \tag{5.67}$$

One possible choice of an order parameter η is the distance $|\mathrm{SX}|$ between S and X, or more conveniently,

$$\begin{aligned}|\mathrm{SX}|^2&=\left(\langle\sigma_x\rangle-\frac{1}{3}\right)^2+\left(\langle\sigma_y\rangle-\frac{1}{3}\right)^2+\left(\langle\sigma_z\rangle-\frac{1}{3}\right)^2\\&=\langle\sigma_x\rangle^2+\langle\sigma_y\rangle^2+\langle\sigma_z\rangle^2-\frac{1}{3}\,.\end{aligned} \tag{5.68}$$

(We want to avoid the square root, which is a bit awkward to handle.) For an isotropic phase, this quantity is zero. At zero temperature, the system is in a completely ordered state, corresponding to point A, B, or C, for which

$$|\mathrm{SA}|^2=|\mathrm{SB}|^2=|\mathrm{SC}|^2=\frac{2}{3}\,. \tag{5.69}$$

(This is because the minimum energy state completely dominates the summation in Z given below.) Normalizing $|\mathrm{SX}|^2$ so that it is unity for A, B, and C, we arrive at

$$\eta := \frac{3}{2}\left(\langle\sigma_x\rangle^2+\langle\sigma_y\rangle^2+\langle\sigma_z\rangle^2\right)-\frac{1}{2} \tag{5.70}$$

d. The canonical partition function is given by

$$Z=\sum e^{-\beta E} , \tag{5.71}$$

where the summation is over all possible orientations of all the molecules in the system. To perform this summation, we organize it according to the number N_α of molecules pointing in the α-direction. We note that for given N_α $(\alpha=x,y,z)$, there are

$$W(N_x,N_y,N_z) := \frac{N!}{N_x!N_y!N_z!} \tag{5.72}$$

distinct configurations. But, not all of them has the same energy, since the latter depends on the number $N_{\alpha\alpha}$ of nearest neighbor pairs of molecules *both* pointing in the α-direction.

Let $\Gamma(N_{xx},N_{yy},N_{zz}|N_x,N_y,N_z)$ denote the number of distinct configurations with given values of $N_{\alpha\alpha}$ $(\alpha=x,y,z)$ that are consistent with the given values of N_α. Clearly,

$$W(N_x,N_y,N_z)=\sum_{\{N_{\alpha\alpha}|N_\alpha\}}\Gamma(N_{xx},N_{yy},N_{zz}|N_x,N_y,N_z) , \tag{5.73}$$

where the summation is over all possible values of $N_{\alpha\alpha}$ $(\alpha=x,y,z)$ for given values of N_α. We can also express E in terms of $N_{\alpha\alpha}$ as

$$E=-\varepsilon\left(N_{xx}+N_{yy}+N_{zz}\right) . \tag{5.74}$$

Then,

$$Z=\sum_{\{N_\alpha\}}\sum_{\{N_{\alpha\alpha}|N_\alpha\}}\Gamma(N_{xx},N_{yy},N_{zz}|N_x,N_y,N_z)e^{\beta\varepsilon\left(N_{xx}+N_{yy}+N_{zz}\right)} \tag{5.75}$$

where the first summation is over all possible values of N_α $(\alpha=x,y,z)$. To introduce the mean-field approximation, we rewrite this expression as

$$Z=\sum_{\{N_\alpha\}}W(N_x,N_y,N_z)\sum_{\{N_{\alpha\alpha}|N_\alpha\}}\frac{\Gamma(N_{xx},N_{yy},N_{zz}|N_x,N_y,N_z)}{W(N_x,N_y,N_z)}e^{\beta\varepsilon\left(N_{xx}+N_{yy}+N_{zz}\right)} , \tag{5.76}$$

where the ratio Γ/W is the probability of finding exactly $N_{\alpha\alpha}$ pairs of molecules both pointing in the α-direction if we are to choose randomly with equal probability a single configuration from the total of W configurations. Denoting the average with respect to this probability by $\langle\cdots\rangle_0$, we have

$$\begin{aligned} Z &= \sum_{\{N_\alpha\}} W(N_x,N_y,N_z)\left\langle e^{\beta\varepsilon(N_{xx}+N_{yy}+N_{zz})}\right\rangle_0 \\ &\approx \sum_{\{N_\alpha\}} W(N_x,N_y,N_z)e^{\beta\varepsilon\langle N_{xx}+N_{yy}+N_{zz}\rangle_0} \ . \end{aligned} \tag{5.77}$$

We still have to express $\langle N_{\alpha\alpha}\rangle_0$ in terms of N_α. Noting that the desired average is with respect to the probability Γ/W, which does not take the Boltzmann factor into account, we have

$$\langle N_{\alpha\alpha}\rangle_0 = \frac{1}{2}\times\frac{N_\alpha}{N}\times\frac{N_\alpha}{N}z\times N = \frac{z}{2N}{N_\alpha}^2 \ , \tag{5.78}$$

where z is the coordination number. So, we now have

$$Z \approx \sum_{\{N_\alpha\}} W(N_x,N_y,N_z)e^{\frac{\beta\varepsilon z}{2N}\left({N_x}^2+{N_y}^2+{N_z}^2\right)} =: \sum_{\{N_\alpha\}} q(N_x,N_y,N_z) \ . \tag{5.79}$$

To simplify the computation further, we note that the summand q is proportional to the probability of finding exactly N_α molecules pointing in the α-direction. For a macroscopic system, we expect this probability to be extremely sharply peaked around the average. This observation allows us to replace the summation by the maximum term of the summand:

$$Z \approx \max_{\{N_\alpha\}}\{q(N_x,N_y,N_z)\} \ . \tag{5.80}$$

Using Stirling's formula, we have

$$\ln q = -N(\sigma_x\ln\sigma_x+\sigma_y\ln\sigma_y+\sigma_z\ln\sigma_z)+\frac{1}{2}\beta\varepsilon zN\left({\sigma_x}^2+{\sigma_y}^2+{\sigma_z}^2\right) \ . \tag{5.81}$$

where $\sigma_\alpha := N_\alpha/N$ by (5.60). We need to maximize $\ln q$ under the constraint that

$$\begin{cases} \sigma_x+\sigma_y+\sigma_z = 1 \ , \\ 0\le\sigma_x\le 1 \ , \quad 0\le\sigma_y\le 1 \ , \quad 0\le\sigma_z\le 1 \ . \end{cases} \tag{5.82}$$

This may also be written as

$$\begin{cases} \sigma_z = 1 - (\sigma_x + \sigma_y)\ , \\ 0 \le \sigma_x \le 1\ , \quad 0 \le \sigma_y \le 1\ , \quad 0 \le \sigma_x + \sigma_y \le 1\ . \end{cases} \tag{5.83}$$

That is, the degrees of freedom here is just 2 not 3. So, in order to find the maximum of $\ln q$, we replace σ_z in (5.81) by $1 - \sigma_x - \sigma_y$ and then compute

$$\frac{\partial \ln q}{\partial \sigma_x} = N \ln \frac{1 - \sigma_x - \sigma_y}{\sigma_x} + \beta \varepsilon z N (2\sigma_x + \sigma_y - 1) \tag{5.84}$$

and

$$\frac{\partial \ln q}{\partial \sigma_y} = N \ln \frac{1 - \sigma_x - \sigma_y}{\sigma_y} + \beta \varepsilon z N (\sigma_x + 2\sigma_y - 1)\ . \tag{5.85}$$

(Just as a check, note that the second equation can be obtained by exchanging x and y in the first. This must be so because the expression for $\ln q$ is symmetric with respect to such an exchange.)

The value of σ_α that maximizes $\ln q$ is just $\langle \sigma_\alpha \rangle$ because q is extremely sharply peaked around the average. Thus,

$$\ln \frac{1 - \langle \sigma_x \rangle - \langle \sigma_y \rangle}{\langle \sigma_x \rangle} + \beta \varepsilon z (2\langle \sigma_x \rangle + \langle \sigma_y \rangle - 1) = 0 \tag{5.86}$$

and

$$\ln \frac{1 - \langle \sigma_x \rangle - \langle \sigma_y \rangle}{\langle \sigma_y \rangle} + \beta \varepsilon z (\langle \sigma_x \rangle + 2\langle \sigma_y \rangle - 1) = 0\ . \tag{5.87}$$

We see that the isotropic phase (at point S)

$$(\langle \sigma_x \rangle \langle \sigma_y \rangle, \langle \sigma_z \rangle) \doteq \left(\frac{1}{3}, \frac{1}{3}, \frac{1}{3} \right) \tag{5.88}$$

is always a solution. But, there might be other solutions. Physically, we expect that, when $T > T_t$, the entropy dominates the free energy and $\ln q$ is the maximum (the corresponding free energy $F \approx -k_B T \ln q$ being minimum) for the isotropic phase. In contrast, if $T < T_t$, we expect that the energy dominates the free energy and we have a nematic phase, that is, the maximum of $\ln q$ should occur elsewhere even though $\ln q$ is still extremum at point S.

This suggests that the extremum at S changes from (local) maximum to local minimum at $T = T_t$. To see this transition, we need to expand $\ln q$ into the Taylor series around S and retain at least up to the second-order terms. The first-order term, as we have just seen, is zero. The second derivatives of $\ln q$ at S are:

$$\left.\frac{\partial^2 \ln q}{\partial {\sigma_x}^2}\right|_{\mathrm{S}} = N\left(-\frac{1}{1-\sigma_x-\sigma_y}-\frac{1}{\sigma_x}\right)+2N\beta\varepsilon z\Big|_{\mathrm{S}} = 2N(\beta\varepsilon z-3)\,,$$
$$\left.\frac{\partial^2 \ln q}{\partial {\sigma_y}^2}\right|_{\mathrm{S}} = 2N(\beta\varepsilon z-3)\,, \quad \text{and} \quad \left.\frac{\partial^2 \ln q}{\partial \sigma_x \partial \sigma_y}\right|_{\mathrm{S}} = N(\beta\varepsilon z-3)\,. \quad (5.89)$$

Retaining up to the second-order terms and using (B.17),

$$\ln q \approx \ln q_S + N(\beta\varepsilon z-3)\left[(\Delta\sigma_x)^2+\Delta\sigma_x\Delta\sigma_y+(\Delta\sigma_y)^2\right]\,, \quad (5.90)$$

where q_S is the value of q of the isotropic phase. We also defined

$$\Delta\sigma_x := \sigma_x - \frac{1}{3} \quad \text{and} \quad \Delta\sigma_y := \sigma_y - \frac{1}{3}\,. \quad (5.91)$$

But,

$$(\Delta\sigma_x)^2+\Delta\sigma_x\Delta\sigma_y+(\Delta\sigma_y)^2 = \left(\Delta\sigma_x+\frac{1}{2}\Delta\sigma_y\right)^2+\frac{3}{4}(\Delta\sigma_y)^2 \quad (5.92)$$

is zero only for the isotropic phase and positive otherwise. If $\beta < 3/\varepsilon z$, $\ln q$ is a (local) maximum at S and the isotropic phase prevails. On the other hand, if $\beta > 3/\varepsilon z$, $\ln q$ is a local minimum at S. That is, the isotropic phase is unstable and we have a nematic phase. Thus, the transition temperature T_t is $\varepsilon z/3k_B$.

5.3 Frequently Used Symbols

$\langle A \rangle$, ensemble average of a dynamical variable A.

p_1 , probability that an adsorption site is occupied.
$\boldsymbol{p}_i$, linear momentum of the ith particle.
$\boldsymbol{p}^N$, collective notation for $\boldsymbol{p}_1, \ldots, \boldsymbol{p}_N$.
$\boldsymbol{r}_i$, position vector of the ith particle.
$\boldsymbol{r}^N$, collective notation for $\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N$.
w , interaction energy between two nearest neighbor particles.
z , coordination number.

A , a generic dynamical variable.
E , energy of a system.

F , Helmholtz free energy.
T , absolute temperature.
Z , canonical partition function.

$\mathscr{W}(E)$, the number of microstates with $H \leq E$.

β , $1/k_B T$.
ε , binding energy.
$\delta(x)$, Dirac δ-function.
μ , chemical potential.
$\theta(x)$, step function defined by (D.2).

Λ , thermal wavelength $h/\sqrt{2\pi m k_B T}$ of a particle of mass m.
Ξ , grand canonical partition function.
$\overline{\Omega}$, density of states.

Reference

1. N. Goldenfeld (1992), *Lectures on phase transitions and the renormalization group*, Addison-Wesley, Reading Massachusetts

Chapter 6
Thermodynamics of Interfaces

Fundamental equations of thermodynamics are commonly written for homogeneous systems without explicitly accounting for effects of the container wall. Similarly, we treat a system consisting of multiple coexisting phases as if it is made of homogeneous parts separated by sharp interfaces. This is an acceptable practice provided that the number of molecules in the vicinity of the container wall or the interface is negligibly small compared with the number of the molecules in the bulk. The approach becomes inappropriate for microscopic systems in which the majority of molecules are near a wall or an interface. For example, inhomogeneity extends throughout the entire system of interest when a fluid is confined to a narrow pore of several atomic diameters. In this case, the phase behavior changes dramatically compared to that in the bulk. It is also possible that the phenomena of interest are dictated by the properties of the interface. Examples include formation of microemulsion, wetting of a solid surface, condensation of a vapor phase, and crystallization from a melt or a solution. In this chapter, we examine how thermodynamics can be extended to explicitly account for effects of interfaces.

6.1 Interfacial Region

When studying a system in two-phase coexistence, we usually ignore the microscopic details of the interface separating the phases. Instead, we simply think of the interface as a diathermal and movable wall that is permeable to all species. In Chap. 2, this led to the conditions of equilibrium expressed as

$$T^{\alpha} = T^{\beta} , \quad P^{\alpha} = P^{\beta} , \quad \text{and} \quad \mu_i^{\alpha} = \mu_i^{\beta} , \quad i = 1, \ldots, c , \tag{6.1}$$

where the superscripts α and β label the phases.

However, it is unrealistic to expect that the interface is sharply defined at the atomistic length scale. For example, the interface between liquid water and its saturated vapor is an inhomogeneous transition region over which the density changes

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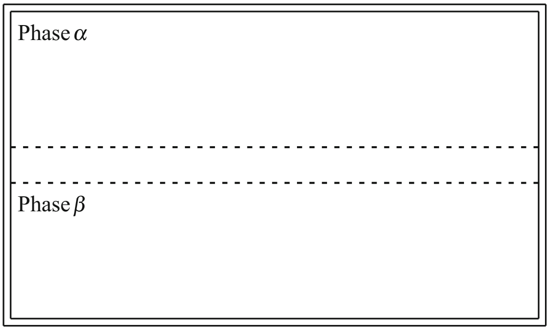

Fig. 6.1 The interfacial region is indicated by a pair of dashed lines and separates two coexisting bulk phases α and β.

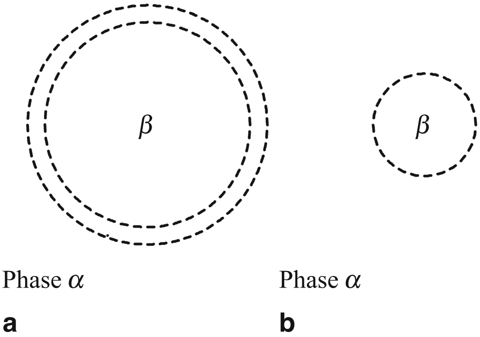

Fig. 6.2 A droplet (β) in equilibrium with a supersaturated vapor α. At a lower degree of supersaturation, the droplet attains bulk-like properties near its center, a situation we indicate with a pair of *dashed circles* in **a**. At a higher degree of supersaturation, however, it becomes inhomogeneous even at its center as indicated by a *single dashed circle* in **b**.

continuously from the bulk liquid value to that of the vapor. Typically, the thickness of this transition region is of the order of several atomic diameters. In the case of a multicomponent system, the density of certain species within the transition region may be significantly higher or lower than its values in the coexisting bulk phases. To emphasize the nonzero thickness of the transition region, we use a pair of dashed lines to indicate an interface between phases as shown in Fig. 6.1.

The equilibrium between two phases may involve a curved interface. A familiar example is meniscus formation where the interface meets the wall. As we shall see, a vapor phase can be compressed beyond its saturation pressure without undergoing a phase transition. This supersaturated vapor can coexist with a liquid droplet. Similarly, a bubble can coexists with superheated liquid phase. In these cases also, we have a transition region of nonzero thickness, which is again indicated by a pair of dashed circles as in Fig. 6.2a.

With the increasing degree of supersaturation, the droplet (in equilibrium with the supersaturated vapor) becomes smaller and eventually loses a bulk-like properties even at its center. The same applies for the bubble with an increasing degree of superheating. This will be indicated as in Fig. 6.2b using a single dashed circle, within which the state of the matter is inhomogeneous.

Following Ref. [12], we develop thermodynamics of interfaces for a system containing a spherical droplet. With the assumed spherical symmetry, our theory remains applicable even for extremely small droplets illustrated in Fig. 6.2b. No satisfactory extension of the theory has been developed to cope with the situation in Fig. 6.2b without the spherical symmetry. Our formulation carries over to the flat interface in Fig. 6.1 simply by increasing the characteristic radius of the interface indefinitely.

6.2 Defining a System

Let us consider an isolated macroscopic body that contains a small inhomogeneous region. For concreteness, we consider a microscopic liquid droplet floating in a supersaturated (metastable) vapor phase. We suppose that the droplet is spherically symmetric. As shown in Fig. 6.3, we take a spherical region of radius R_0 centered around the center of symmetry and mentally divide the body into two parts. The region inside the sphere will be called region I. The region outside the sphere is region II. Then, region I contains the droplet, some portion of the metastable vapor phase, and the interface between them. Region II contains only the remaining portion of the homogeneous vapor phase.

Because region I contains all that is interesting to us, it will be advantageous to take region I as the system,treating region II as the surroundings. But, we must first ask if thermodynamic quantities such as the internal energy U^I, entropy S^I, and the number N_i^I of molecules of species i are well defined for region I. This is because we are interested in effects of interfaces in this chapter and we cannot afford to simply ignore the interaction between I and II, which is mediated by molecules near the boundary at R_0.

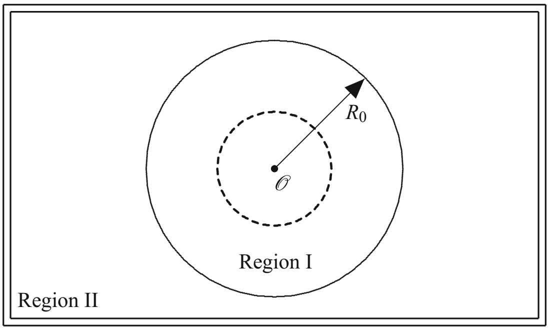

Fig. 6.3 An isolated system containing a metastable vapor phase and a spherical liquid droplet (*dashed line*). The sphere of radius R_0 (*solid line*) separates the isolated system into regions I and II.

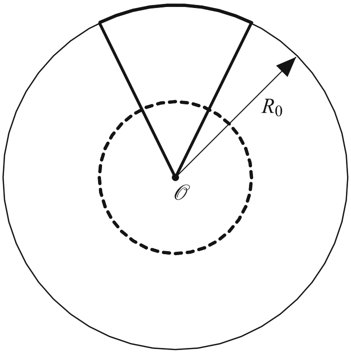

Fig. 6.4 The system defined as the conic region (*thick solid lines*).

To define N_i^I, we adopt the convention that a molecule of species i belongs to region I if its center of mass is inside I.[29] How about U^I? Due to our choice of R_0, the region of inhomogeneity is contained in region I, and region II is homogeneous. Thus, the internal energy density is uniform throughout region II and its internal energy is this energy density multiplied by the volume of region II. Because the macroscopic body is isolated, its internal energy is a well-defined quantity. We obtain U^I as the difference between these energies. The same argument applies to S^I.

Now that region I is shown to have well-defined U^I, S^I, and N_i^I, can we choose it as our system? Not quite. Recall that thermodynamic quantities are classified into either extensive or intensive quantities. This classification plays an essential role in thermodynamics and gives rise to such important identities as the Euler and the Gibbs–Duhem relations. When extending thermodynamics to include effects of interfaces, it is highly desirable that we maintain this classification. To say that U^I is extensive, we must show that the internal energy of a system that is λ times region I is λU^I. But, what is that system when $\lambda = \sqrt{2}$, for example?

Instead of region I, we define our system as a conic region with its apex at $\mathscr{O}$ and a portion of the boundary at R_0 as its base as shown in Fig. 6.4. We use ω to denote the solid angle subtended by the base at $\mathscr{O}$.

The **solid angle** subtended by an object at a point is the area occupied by the object when it is projected onto a unit sphere centered around the point by means of rays of light emanating from or converging onto that point. So, the solid angle of a sphere at its center is 4π, while that of the hemisphere is 2π. The solid angle subtended at the center of a cube by one of its six faces is $4\pi/6 = 2\pi/3$.[30]

Because of the spherical symmetry of region I, the internal energy, entropy, and the number of moles of species i in the system are given by

$$U = \frac{\omega}{4\pi}U^I\,, \quad S = \frac{\omega}{4\pi}S^I\,, \quad \text{and} \quad N_i = \frac{\omega}{4\pi}N_i^I\,, \tag{6.2}$$

respectively. Since U^I, S^I, and N_i^I are all well-defined, so are U, S, and N_i for any ω between 0 and 4π.

6.3 Condition of Equilibrium

To formulate the condition of equilibrium, we will have to consider variations in the state of the system. Here again, a careful analysis is required to account for the interaction across the system boundaries. This is the subject of Sect. 6.3.1. The key conclusion is that, to the first order of variations, we may regard the variations to be affecting the state of the system only, while leaving the surroundings unaffected. This is despite the fact that these two parts are in direct contact with each other. If you wish to omit Sect. 6.3.1, keep this conclusion in mind and head to Sect. 6.3.2.

6.3.1 †Variations in the State of the System

Because the system is inhomogeneous, densities of the internal energy, entropy, and the number of molecules vary across the system, and collectively determine the state of the matter. In what follows, we adopt a generic notation $\xi(\boldsymbol{r})$ for these densities. At the initial state, ξ depends only on the radial distance $r := \|\boldsymbol{r}\|$ from $\mathscr{O}$ and reaches a constant as R_0 is approached from $\mathscr{O}$.

Let us now consider a variation in the state of the system, and denote by $\xi(\boldsymbol{r}) + \delta\xi(\boldsymbol{r})$ the value of ξ in the varied state. Unless the variation is accompanied by a similar change in the surroundings, $\xi(\boldsymbol{r}) + \delta\xi(\boldsymbol{r})$ will not be spherically symmetric over the entire 4π nor is it uniform across R_0. The resulting infinitesimal discrepancy in the state of the matter between the two parts may cause $\delta\xi$ to exhibit a complex $\boldsymbol{r}$ dependence across the system boundaries, which is very difficult to account for. For these more general variations, called **discontinuous variation** for brevity,[31] how do we evaluate the values of δU and δS?

The simplest approach is to ignore the complex behavior of $\delta\xi(\boldsymbol{r})$ across the boundaries. When figuring out U and S of the system in its varied state, we *pretend* that the surroundings have experienced a similar variation to ensure the spherical symmetry of region I over the entire 4π and the uniformity across R_0.[32] This is indicated by the dashed line in Fig. 6.5. *For the same varied state* we are considering, the internal energy and entropy of the surroundings are computed by assuming that the state of the matter in the surroundings continues beyond the boundaries and that the spherical symmetry of region I and the uniformity across R_0 still hold. The same convention can be adopted when considering simultaneous variations involving both the system and the surroundings.

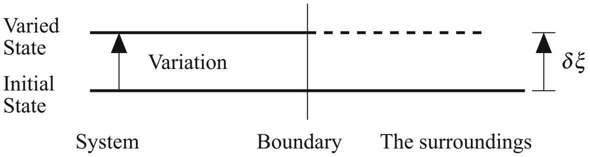

Fig. 6.5 Discontinuous variation of the system.

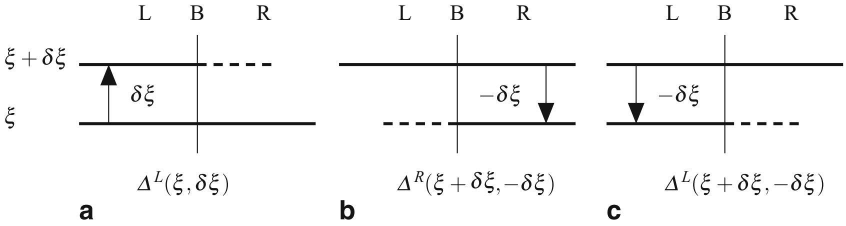

Fig. 6.6 Three distinct discontinuous variations either in the system (*L*) or in the surroundings (*R*). In each diagram, the *long horizontal solid lines* indicates the initial state, while the *shorter horizontal line* continued across the boundary (*B*) in *dashed line* indicates the varied state.

This is how we proceed. As far as the internal energy and entropy of the *entire* isolate system is concerned, the error thus committed is in the higher order terms of the variations, and does not affect our discussion of the condition of equilibrium.

To see this, let us consider the three distinct variations illustrated in Fig. 6.6. In Fig. 6.6a, we consider an infinitesimal variation $\delta\xi$ in the state of the system starting from the initial state specified by ξ. Our method of computing the variation of the internal energy (or the entropy) in the system (L) and the surroundings (R) leads to an error in our estimate of the variation of the internal energy of the composite system, which we denote by $\Delta^L(\xi,\delta\xi)$, where the superscript L indicates that the variation is taken in L. Similarly for the superscript R in the case of variations in R.

But, in the vicinity of the boundary (B), the varied state in Fig. 6.6a is identical to that in Fig. 6.6b. Thus,

$$\Delta^L(\xi,\delta\xi) = \Delta^R(\xi+\delta\xi,-\delta\xi)\,. \tag{6.3}$$

Now, Fig. 6.6b, c share the identical initial state in which the state of the matter is locally symmetric around B. If we focus only on the immediate vicinity of B, their varied states are the mirror images of each other. This implies that

$$\Delta^R(\xi+\delta\xi,-\delta\xi) = \Delta^L(\xi+\delta\xi,-\delta\xi)\,. \tag{6.4}$$

Thus, we have an equality

$$\Delta^L(\xi,\delta\xi) = \Delta^L(\xi+\delta\xi,-\delta\xi)\,. \tag{6.5}$$

Expanding the expression on the left in the Maclaurin series (see Appendix B.1) with respect to the second argument, we have

$$\Delta^L(\xi,\delta\xi) = \Delta^L(\xi,0) + \Delta^L_2(\xi,0)\delta\xi + \text{h.o.} = \Delta^L_2(\xi,0)\delta\xi + \text{h.o.}\,, \tag{6.6}$$

where Δ^L_2 is the partial derivative of Δ^L with respect to its second argument. We also used the fact that $\Delta^L(\xi,0) \equiv 0$ for any ξ. That is, no error is introduced if no variation is taken. Likewise, we have

$$\Delta^L(\xi+\delta\xi,-\delta\xi) = -\Delta_2^L(\xi+\delta\xi,0)\delta\xi + \text{h.o.} = -\Delta_2^L(\xi,0)\delta\xi + \text{h.o.}\,, \tag{6.7}$$

where the last step follows from the Taylor expansion with respect to the first argument. Using (6.6) and (6.7) in (6.5), we see that $\Delta_2(\xi,0)$ can only be zero. Thus,

$$\Delta^L(\xi,\delta\xi) = \text{h.o.} \tag{6.8}$$

For alternative demonstrations of the same idea, see Refs. [4, 11].

We note that the symmetry around B of the initial state of the matter entered as a key ingredient of our analysis. However, because the system boundaries are curved, one side of B is not entirely equivalent to the other if we focus on a larger portion of the boundary. This is why we have taken a "local" view when looking for the symmetry. Because our system is made of atoms, one may argue that $\xi(\boldsymbol{r})$ loses its meaning in an extremely local view. This is not so. In thermodynamics, we are interested in thermally averaged quantities, and $\xi(\boldsymbol{r})$ is well defined at every point in space.

If there should remain any doubt about our analysis, it is with variations taken near the apex $\mathscr{O}$ of the cone. (See Fig. 6.4.) For a sufficiently small ω, a discontinuous variation taken in the system affects only those molecules of the surroundings near $\mathscr{O}$. A similar discontinuous variation taken in the surroundings may affect all the molecules of the system near $\mathscr{O}$. In that case, it seems unreasonable to expect (6.4) to hold.

We can easily circumvent the difficulty indicated here for a nucleus with a homogeneous core. We simply exclude the apex and its vicinity by means of another spherical boundary passing through the homogeneous core. For the situation indicated by Fig. 6.2b, however, this is not possible. Even in such cases, one can insist on the *formal* significance of the theory we develop on the basis of (6.8) provided that various physical quantities behave in a physically sensible manner, for example, a quantity that must be real and positive remains so.

Far more satisfactory will be methods based on the principle of statistical mechanics that apply regardless of the presence or absence of the homogeneous core. Classical density functional theory discussed in Chap. 7 is one such theory. Molecular simulation is another satisfactory approach. The important point is that thermodynamics of interfaces provides a useful framework when trying to interpret the predictions of these statistical mechanical approaches. In fact, no inconsistency has ever been discovered to implicate (6.8).

6.3.2 Fixed System Boundaries

As we have just demonstrated, we may suppose that the state of the system can be varied without affecting the surroundings to the first order of the variation. Thus, if we limit our considerations up to this order, the system can be treated as if it is iso-

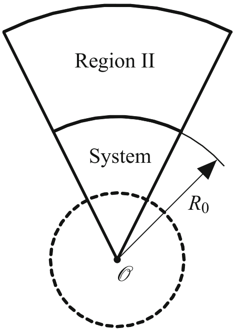

Fig. 6.7 The composite system consisting of the system and a portion of region II.

lated. This being case, the condition of its equilibrium is that S takes the maximum possible value for given U, $N_1,\dots,N_c$, and the fixed system boundaries specified by R_0 and ω. It is important to note that specification of the system volume alone is not sufficient for an inhomogeneous system. We can adjust R_0 and ω without changing the system volume. But this will certainly affect the amount of the interfacial region included in our system.

The condition of equilibrium can be expressed in different ways. For example, we may demand that U be minimum for given S, $N_1,\dots,N_c$, R_0, and ω. But, the most convenient formulation is that of Sect. 2.9.3, according to which the necessary condition of equilibrium is that

$$\delta U = A_0 \delta S + \sum_{i=1}^{c} A_i \delta N_i \ , \quad R_0, \omega \text{ const.} \tag{6.9}$$

holds for any *reversible* variations with fixed system boundaries.[33] Here, A_0 and $A_1,\dots,A_c$ are constants yet to be determined. We recall from Sect. 2.9.3 that a variation δX_i of some additional variable X_i is said to be reversible if it can take both positive and negative values.

To determine the values of A_0 and A_i, which are the temperature and chemical potentials of species i of the system, we consider a composite system consisting of our original system and a portion of region II as shown in Fig. 6.7. The composite system itself may be regarded as isolated in the same way the original system was. Because the boundary between the original system and region II is purely a construct of our imagination, it exerts no physical effect. In other words, it is a diathermal and rigid wall permeable to all species. Thus, provided that S and $N_1,\dots,N_c$ of the system are all capable of reversible variations, the condition of equilibrium of the composite system demands that A_0 be equal to the temperature T of the surroundings and A_i to the chemical potential μ_i of species i of the surroundings. Accordingly, (6.9) now reads

$$\delta U = T \delta S + \sum_{i=1}^{c} \mu_i \delta N_i \ , \quad R_0, \omega \text{ const.} \tag{6.10}$$

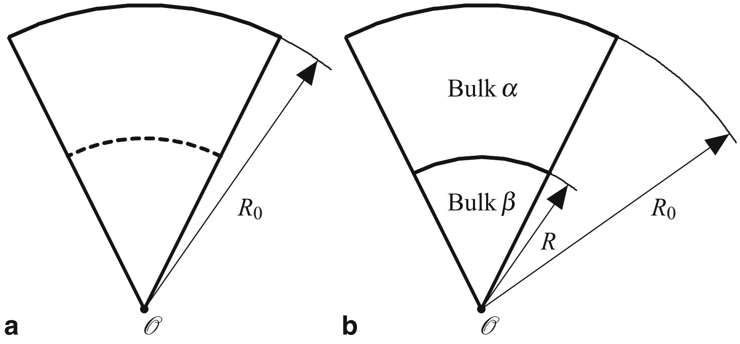

Fig. 6.8 Construction of a reference system. **a** Actual system. **b** Reference system with a dividing surface at R.

6.3.3 Reference System

Before considering the generalization of (6.10) for the case of movable system boundaries in Sect. 6.3.4, it is convenient to introduce the **reference system**, also known as the **hypothetical system**, as illustrated in Fig. 6.8. First, we draw a spherical surface, called the **dividing surface**, of radius R ($< R_0$) according to some arbitrary rule to be decided on later. Then, we fill the space between R and R_0 of the system by bulk phase α. By "bulk phase," we mean that it behaves as if it is a portion of macroscopic and homogeneous phase α. The space between $\mathscr{O}$ and R is filled with bulk phase β *that has the same temperature and chemical potentials* as α phase. This does *not* imply that phase β is identical to phase α. In other words,

$$\mu_i^\alpha(T,P^\alpha,x_1^\alpha,\ldots,x_{c-1}^\alpha) = \mu_i^\beta(T,P^\beta,x_1^\beta,\ldots,x_{c-1}^\beta)\,, \quad i=1,\ldots,c \tag{6.11}$$

where x_i is the mole fraction of species i, has a nontrivial solution with $P^\alpha \neq P^\beta$.

For these bulk phases, we have

$$\delta U^\alpha = T\delta S^\alpha + \sum_{i=1}^{c} \mu_i \delta N_i^\alpha \quad \text{and} \quad \delta U^\beta = T\delta S^\beta + \sum_{i=1}^{c} \mu_i \delta N_i^\beta \tag{6.12}$$

for variations that do not affect the system boundaries. Subtracting (6.12) from (6.10), we find

$$\delta U^s = T\delta S^s + \sum_{i=1}^{c} \mu_i \delta N_i^s\,, \quad R_0, \omega \text{ const.} \tag{6.13}$$

In this equation, the quantities defined by

$$U^s := U - (U^\alpha + U^\beta)\,, \quad S^s := S - (S^\alpha + S^\beta)\,, \quad \text{and} \quad N_i^s := N_i - (N_i^\alpha + N_i^\beta)\,. \tag{6.14}$$

are known as the **surface excess quantities**.

By construction, the reference system has no interface. Thus, any difference between the actual and the reference systems can be attributed to the presence of the interface. We emphasize that the reference system is purely a theoretical construct that cannot be created in practice. The role it plays is entirely analogous to that of various ideal systems, such as ideal gas mixture and ideal mixtures, introduced in order to characterize the behavior of real mixtures.

6.3.4 Movable System Boundaries

Equation (6.10) can be generalized easily for the case of movable system boundaries. Because the system boundary at R_0 is passing through a homogeneous region, its motion introduces a simple work term that may be written as

$$-\omega {R_0}^2 P^\alpha \delta R_0 \,, \tag{6.15}$$

where $\omega {R_0}^2 \delta R_0$ is the volume swept out by the boundary as it moves to the new position $R_0 + \delta R_0$. In contrast, a change in ω involves stretching or compressing of the inhomogeneous region and the associated work term seems difficult to compute. We do know, however, that it should be proportional to $\delta\omega$. That is, since U is a function of $S, N_1, \dots, N_c, R_0$, and ω, the work term in question is $(\partial U/\partial\omega)_{S,N,R_0}\delta\omega$, which we shall denote simply as $\sigma\delta\omega$. Thus,

$$\delta U = T\delta S + \sum_{i=1}^{c} \mu_i \delta N_i - \omega {R_0}^2 P^\alpha \delta R_0 + \sigma\delta\omega \,. \tag{6.16}$$

But, how do we evaluate the value of σ? For our thermodynamic formulation to be of any use, this quantity must be related to something we can measure at least in principle. For this purpose, it proves useful to consider the generalization of (6.13).

We note that δU^s is determined completely if δU, δU^α, and δU^β are given. The latter two quantities refer to the bulk homogeneous phases and are given, respectively, by

$$\delta U^\alpha = T\delta S^\alpha - P^\alpha \delta V^\alpha + \sum_{i=1}^{c} \mu_i \delta N_i^\alpha \tag{6.17}$$

and

$$\delta U^\beta = T\delta S^\beta - P^\beta \delta V^\beta + \sum_{i=1}^{c} \mu_i \delta N_i^\beta \tag{6.18}$$

for movable system boundaries.

A part of δV^α comes from a change in R_0 and makes the identical contribution to δU and δU^α, thus dropping out from δU^s. The remaining part of δV^α, δV^β, and $\delta\omega$ are completely determined once δR and δA are given, where A is the area of the dividing surface, because of the geometric relations

$$A = \omega R^2 \,, \quad V^\alpha = \frac{\omega}{3}\left({R_0}^3 - R^3\right) \,, \quad \text{and} \quad V^\beta = \frac{\omega}{3} R^3 \,. \tag{6.19}$$

The validity of these equations is most readily seen by applying them for the entire spherical region, for which $\omega = 4\pi$. It follows that

$$\delta U^s = T\delta S^s + \sum_{i=1}^{c} \mu_i \delta N_i^s + \gamma\delta A + C\delta R\,. \tag{6.20}$$

Because this result holds for any variation and S^s, $N_1^s, \dots, N_c^s$, A, and R are path-independent state functions, we conclude that

$$U^s = U^s(S^s, N_1^s, \dots, N_c^s, A, R)\,. \tag{6.21}$$

From these two equations, we see that

$$C = \left(\frac{\partial U^s}{\partial R}\right)_{S^s, N^s, A} = C(S^s, N_1^s, \dots, N_c^s, A, R)\,. \tag{6.22}$$

Combining (6.17), (6.18), and (6.20), we obtain

$$\delta U = T\delta S + \sum_{i=1}^{c} \mu_i \delta N_i - P^\alpha \delta V^\alpha - P^\beta \delta V^\beta + \gamma\delta A + C\delta R\,. \tag{6.23}$$

Exercise 6.1. Express σ in terms of γ, P^α, P^β, R and R_0. ///

6.3.5 *Laplace Equation*

As we saw in Sect. 6.3.2, the equilibrium of the system demands that its temperature and chemical potentials be equal to those in the surrounding phase α. In this section, we derive an additional condition of equilibrium.

For variations taken while holding S, $N_1, \dots, N_c$, R_0 and ω constant, we have

$$\begin{aligned} &\delta S = 0\,, \quad \delta N_1 = \cdots = \delta N_c = 0\,, \\ &\delta V^\alpha = -\omega R^2 \delta R\,, \quad \delta V^\beta = \omega R^2 \delta R\,, \quad \text{and} \quad \delta A = 2\omega R\delta R\,. \end{aligned} \tag{6.24}$$

Substituting these relations into (6.23), we find

$$(\delta U)_{S,N,R_0,\omega} = (P^\alpha - P^\beta)\omega R^2 \delta R + 2\gamma\omega R\delta R + C\delta R = \left(P^\alpha - P^\beta + \frac{2\gamma}{R} + c_a\right) A\delta R\,, \tag{6.25}$$

where $c_a := C/A$.

Provided that $R > 0$, δR can be either positive or negative. Recalling (2.97), we conclude that

$$P^\beta - P^\alpha = \frac{2\gamma}{R} + c_a\,. \tag{6.26}$$

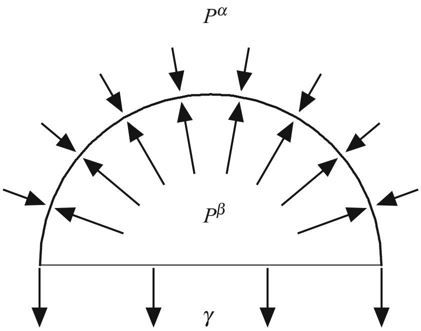

Fig. 6.9 The surrounding fluid pushes the hemisphere of radius R downward with the pressure $\pi R^2 P^\alpha$, and so does the tension γ with the force $2\pi R\gamma$. (From (6.20), we see that γ has the dimension of energy per unit area or force per unit length.) The fluid in the sphere pushes the hemisphere upward with the force $\pi R^2 P^\beta$. The balance of these forces leads to (6.28).

So far, we have left unspecified how we choose the radius R of the dividing surface for a given state of the system. Accordingly, (6.26) holds for any choice for the dividing surface. One common choice is to determine R by

$$C = 0\,. \tag{6.27}$$

For any given state of the system in equilibrium, the quantities S^s, $N_1^s, \dots, N_c^s$, and A in (6.22) all depend only on R. Thus, (6.27) indeed is an equation for R. For a sufficiently large droplet (or bubble) shown in Fig. 6.2a, the thickness of the interfacial region is considerably smaller than its radius of curvature. In this case, the solution of (6.27) exists and the dividing surface so determined is located within the inhomogeneous transition region. An explicit demonstration is found in Ref. [4].

For the choice of the dividing surface just indicated, (6.26) reduces to

$$P^\beta - P^\alpha = \frac{2\gamma}{R}\,. \tag{6.28}$$

This is known as the **Laplace equation**, and is identical to the condition of mechanical equilibrium of a membrane of zero thickness having the tension γ but no rigidity while separating a spherical region at P^β from the surroundings at P^α. This is illustrated in Fig. 6.9. For this reason, the dividing surface defined by (6.27) and γ associated with this dividing surface are called the **surface of tension** and the **surface tension**, respectively. We choose the surface of tension as the dividing surface with the expectation that γ may be measurable by some mechanical measurement technique.

In the $R \to \infty$ limit, a spherical interface becomes a flat interface separating two macroscopic phases in equilibrium. At the same time, (6.28) reduces to $P^\alpha = P^\beta$, which is just the second equation in (6.1). In other words, the presence of an interface does not affect the condition of phase coexistence across a flat interface.

6.4 Euler Relation

Applying (6.20) to an infinitesimal process that takes the system from a state of equilibrium to another,[34] we obtain

$$\mathrm{d}U^s = T\mathrm{d}S^s + \sum_{i=1}^{c} \mu_i \mathrm{d}N_i^s + \gamma \mathrm{d}A + C\mathrm{d}R\,. \tag{6.29}$$

We now integrate (6.29) from $\omega = 0$ to some nonzero ω ($\leq 4\pi$) without changing the intensive state of the system. During such a process, T and $\mu_1, \ldots, \mu_c$ are constant. If we do not vary the condition to determine the radius of the dividing surface, γ and R are also constant. (Because U^s and A are both extensive variables, $\gamma = (\partial U^s/\partial A)_{S^s, \mathbf{N}^s, R}$ should be intensive.) Thus,

$$U^s = TS^s + \sum_{i=1}^{c} \mu_i N_i^s + \gamma A\,, \tag{6.30}$$

which is the Euler relation for the inhomogeneous system.

According to (6.30), γA is *the reversible work required to convert the reference system into the actual system by creating an interface*. (See Fig. 6.10.) To see this, let $[U]$ denote the increase in the internal energy of the system upon the reversible creation of the interface. Because the surroundings can be made arbitrarily large, T and $\mu_1, \ldots, \mu_c$ remain constant during the process. Thus, if we regard the system and its surroundings as forming an isolated system, the increase in the internal energy of the surroundings is given by

$$-T[S] - \sum_{i=1}^{c} \mu_i [N_i]\,, \tag{6.31}$$

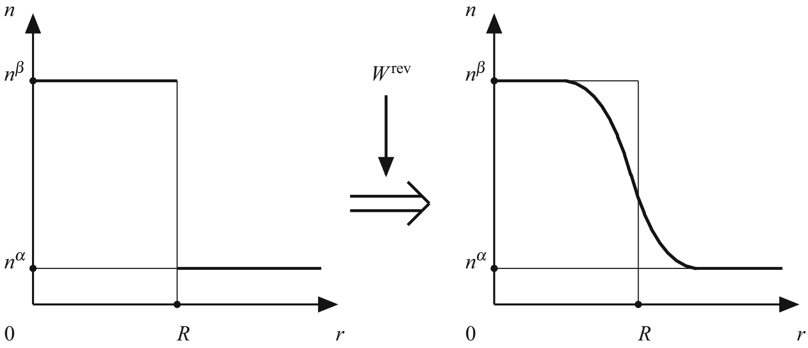

Fig. 6.10 Introduction of an interface into the reference system by means of a reversible work source. The number density of molecules is denoted by n with a *superscript* indicating its values in the bulk reference phases.

where $[S]$ and $[N_i]$ are defined similarly to $[U]$. This expression follows from the fundamental property relation (2.37) applied to the surroundings and the fact that the number of molecules of each species is constant in the isolated system (in the absence of chemical reactions). Its entropy also remains constant for a reversible process.

In the isolated system, any increase in its internal energy must be due to the reversible work source. Recalling that

$$[U] = U - (U^{\alpha} + U^{\beta}) = U^s \,, \quad \text{etc.} \,, \tag{6.32}$$

we obtain the desired reversible work as

$$[U] - T[S] - \sum_{i=1}^{c} \mu_i [N_i] = U^s - TS^s - \sum_{i=1}^{c} \mu_i N_i^s = \gamma A \,. \tag{6.33}$$

We note that γ must be positive in order for the interface to be stable. Otherwise, the system can lower its free energy simply by increasing A.[35]

6.5 Gibbs–Adsorption Equation

Upon differentiation of (6.30), we obtain

$$\mathrm{d}U^s = T\mathrm{d}S^s + \sum_{i=1}^{c} \mu_i \mathrm{d}N_i^s + \gamma \mathrm{d}A + S^s \mathrm{d}T + \sum_{i=1}^{c} N_i^s \mathrm{d}\mu_i + A\mathrm{d}\gamma \,. \tag{6.34}$$

Substituting (6.29) into this expression, we find

$$\mathrm{d}\gamma = -s^s \mathrm{d}T - \sum_{i=1}^{c} \Gamma_i \mathrm{d}\mu_i + c_a \mathrm{d}R \,, \tag{6.35}$$

where

$$s^s := \frac{S^s}{A} \quad \text{and} \quad \Gamma_i := \frac{N_i^s}{A} \tag{6.36}$$

are called the **superficial densities** of the entropy and the number of molecules of species i. We observe from (6.35) that

$$\gamma = \gamma(T, \mu_1, \dots, \mu_c, R) \tag{6.37}$$

and that

$$s^s = -\left(\frac{\partial \gamma}{\partial T}\right)_{\mu,R} \,, \quad \Gamma_i = -\left(\frac{\partial \gamma}{\partial \mu_i}\right)_{T,\mu_{j\neq i},R} \,, \quad \text{and} \quad c_a = \left(\frac{\partial \gamma}{\partial R}\right)_{T,\mu} \,. \tag{6.38}$$

If we fix the condition for locating the dividing surface, R will change in response to changes in T and $\mu_1, \dots, \mu_c$. For example, the radius of the surface of tension, assumed to be finite, is determined by

$$c_a(T,\mu_1,\ldots,\mu_c,R)=0\ . \tag{6.39}$$

The radius R we find by solving this equation, in general, is a function of T and $\mu_1,\ldots,\mu_c$.[36] Thus, the partial derivatives in (6.38) are all taken *while modifying the condition for locating the dividing surface.* For a reformulation of thermodynamics of interfaces emphasizing this perspective, see Ref. [6].

For the surface of tension, the last equation in (6.38) gives

$$c_a=\left(\frac{\partial\gamma}{\partial R}\right)_{T,\mu}=0\ , \tag{6.40}$$

which has the following interpretation. For a given intensive state of the system, γ changes depending on our choice for the dividing surface. But, this dependence is such that γ takes an extremum value for the surface of tension. Using (6.39) in (6.35), we see that

$$\mathrm{d}\gamma=-s^s\mathrm{d}T-\sum_{i=1}^{c}\Gamma_i\mathrm{d}\mu_i\ , \tag{6.41}$$

for this dividing surface. This result is known as the **Gibbs adsorption equation**. Instead of (6.38), we now have

$$s^s=-\left(\frac{\partial\gamma}{\partial T}\right)_{\mu}\qquad\text{and}\quad \Gamma_i=-\left(\frac{\partial\gamma}{\partial\mu_i}\right)_{T,\mu_{j\neq i}}\ . \tag{6.42}$$

In these equations, R is absent from the list of variables that are held fixed. Instead, R is a function of T and $\mu_1,\ldots,\mu_c$, and is allowed to change in response to infinitesimal changes of these variables so as to satisfy (6.40).

6.6 Flat Interface

In contrast to the case of a spherical interface, the value of γ of a flat interface does not depend on the choice of the dividing surface.

To see this,we note that the reversible work required to create a unit area of the interface from a reference system should remain finite even in the $R\rightarrow\infty$ limit for any choice of the dividing surface. In this limit, therefore, (6.26) reduces to

$$\left(\frac{\partial\gamma}{\partial R}\right)_{T,\mu}=c_a=P^\beta-P^\alpha-\frac{2\gamma}{R}\rightarrow 0\quad\text{as}\quad R\rightarrow\infty\ , \tag{6.43}$$

where we recall that P^α and P^β are independent of the choice of the dividing surface and that $P^\alpha=P^\beta$ in the same limit we are considering.

We can reach the same conclusion through a more explicit computation. Let $\gamma_{\infty,1}$ denote the value of γ of a flat interface for the dividing surface at z_1 in Fig. 6.11.

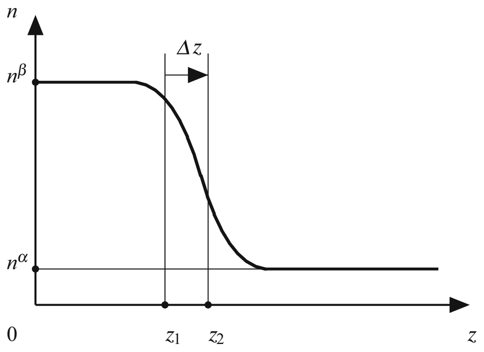

Fig. 6.11 The number density profile $n(z)$ of molecules across a flat interface. Two possible choices are shown for the dividing surface.

Using (6.30),

$$\gamma_{\infty,1}A = U - (U^\alpha + U^\beta) - T[S - (S^\alpha + S^\beta)] - \sum_{i=1}^{c} \mu_i [N_i - (N_i^\alpha + N_i^\beta)] \,. \tag{6.44}$$

When we move the dividing surface to $z_2 := z_1 + \Delta z$ as shown in Fig. 6.11, U^α and U^β in (6.44) must be replaced by

$$U^\alpha - u^\alpha A\Delta z \quad \text{and} \quad U^\beta + u^\beta A\Delta z \,, \tag{6.45}$$

respectively, where u^α is the internal energy density of the bulk α phase. Similarly for u^β. Denoting the entropy density by s and the number density of molecules of species i by n_i, we have

$$\begin{aligned}\gamma_{\infty,2}A &= \gamma_{\infty,1}A + \left[\left(u^\alpha - Ts^\alpha - \sum_{i=1}^{c} \mu_i n_i^\alpha\right) - \left(u^\beta - Ts^\beta - \sum_{i=1}^{c} \mu_i n_i^\beta\right)\right] A\Delta z \\ &= \gamma_{\infty,1}A + (P^\beta - P^\alpha)A\Delta z = \gamma_{\infty,1}A \,,\end{aligned} \tag{6.46}$$

where we used $P^\beta = P^\alpha$ for the flat interface.

6.7 W^{rev} as a Measure of Stability

As an application of thermodynamics of interfaces, let us compute the reversible work W^{rev} required to create a spherical fragment of a new phase β within a metastable phase α. Because our formalism applies only to systems in equilibrium, we shall limit our consideration to a **critical nucleus**, which is in equilibrium with a given metastable phase.

As we shall see, $W^{\text{rev}} > 0$, implying that the equilibrium is unstable. The system containing a critical nucleus can lower its free energy not only by shrinking the nucleus but also by growing it further until a macroscopic portion of a new phase forms. In this sense, formation of a critical nucleus, called **nucleation**, marks the first successful stage of new phase formation, thus the word "critical."

Nucleation is ubiquitous in nature and plays an important role in atmospheric science, biological processes, and chemical and pharmaceutical manufacturing. See Refs. [16, 19] for recent reviews.

According to (2.180), nucleation and the subsequent transition to a new phase become more probable with decreasing W^{rev}. In this sense, W^{rev} serves as a measure of stability of the metastable phase. More quantitatively, the **nucleation rate**, defined as the rate of critical nucleus formation per unit volume of the metastable phase, is proportional to $e^{-\beta W^{\text{rev}}}$. This follows from (2.180) and additional considerations regarding the kinetics of the process. The details can be found in Ref. [15], for example.

We emphasize that the results of this section apply *only to* a critical nucleus, that is, to a single value of R determined by a specific rule for locating the dividing surface for a given intensive state of the metastable phase. A generalization of our results to noncritical nuclei is possible. An interested reader should consult Refs. [1, 2, 3, 8, 13].

6.7.1 Exact Expression

Suppose that a supersaturated multicomponent macroscopic phase α is contained in an adiabatic, rigid, and impermeable wall. We take imaginary boundary B in this isolated system and refer to the region inside B as system I. The remaining part of the isolated system will be referred to as system II.

We suppose that a nucleus forms in system I. If B is taken to enclose a sufficiently large region compared to the physical extent of the nucleus, B can be made to pass through a homogeneous region both before and after the formation of the nucleus.[37]

Let $[U]$ denote the increment of the internal energy of system I upon nucleation. The corresponding quantity in system II is given by

$$-T[S]-\sum_i \mu_i[N_i] \tag{6.47}$$

with $[S]$ and $[N_i]$ defined similarly to $[U]$. Because the system as a whole is isolated, the net increase in its internal energy must be due to the reversible work source. That is,

$$W^{\text{rev}} = [U]-T[S]-\sum_i \mu_i[N_i] \,. \tag{6.48}$$

Initially, system I is filled with uniform bulk phase α. Thus, the number of molecules of species i in system I is

$$n_i^\alpha (V^\alpha + V^\beta) \,, \tag{6.49}$$

where $V^\alpha + V^\beta$ is the volume of system I expressed in terms of those of the bulk reference phases. The number of molecules in the final state may be expressed as

$$n_i^\alpha V^\alpha + n_i^\beta V^\beta + \Gamma_i A \, . \tag{6.50}$$

Thus,

$$[N_i] = n_i^\alpha V^\alpha + n_i^\beta V^\beta + \Gamma_i A - n_i^\alpha (V^\alpha + V^\beta) = (n_i^\beta - n_i^\alpha) V^\beta + \Gamma_i A \, . \tag{6.51}$$

Using (6.51) and other similar expressions in (6.48), we find

$$\begin{aligned} W^{\text{rev}} &= (u^\beta - u^\alpha)V^\beta + u^s A - T[(s^\beta - s^\alpha)V^\beta + s^s A] - \sum_{i=1}^{c} \mu_i [(n_i^\beta - n_i^\alpha)V^\beta + \Gamma_i A] \\ &= -V^\beta (P^\beta - P^\alpha) + \gamma A \, , \end{aligned} \tag{6.52}$$

where we used (2.148) and (6.30).

The term γA is referred to as the surface term and is positive since γ is positive, while $-V^\beta(P^\beta - P^\alpha)$ is called the bulk term and is negative because $P^\beta > P^\alpha$ as seen from (6.28). The balance of these two terms leads to a nonnegative value of W^{rev}. In fact, using (6.28) and noting that the nucleus by our assumption is spherical, we can rewrite (6.52) as

$$W^{\text{rev}} = \frac{1}{3}\gamma A = \frac{1}{2}(P^\beta - P^\alpha)V^\beta = \frac{16\pi\gamma^3}{3(P^\beta - P^\alpha)^2} \, , \tag{6.53}$$

in which each expression is manifestly nonnegative. Thus, nucleation is an unfavorable event. This is the origin of the metastability of phase α.

Exercise 6.2. Because (6.30) holds for an arbitrary dividing surface, so does (6.52). But, W^{rev} has a physical significance, and its value cannot depend on the convention we adopt for the dividing surface. Based on this observation, derive (6.26). (In contrast, (6.53) is a result of combining (6.52) and (6.28), and holds only for the surface of tension.) ///

Because every point in the macroscopic metastable phase is equivalent to any other, a critical nucleus can form anywhere in the system. As pointed out by Lothe and Pound as early as in 1962 [10], it is very unreasonable to expect that these “translational (and rotational) degrees of freedom” are properly reflected in the bulk thermodynamic quantities, such as the pressure and the chemical potentials. The same concern can be raised against γ. This observation casts a shadow of doubts on the validity of (6.52), which appears otherwise exact. For a detailed discussion on this point, see Ref. [7] and references therein.

According to the formalism we developed, we compute W^{rev} as follows:

a. For a given intensive state of a metastable phase, as specified by T, P^α, and $x_1^\alpha,\dots,x_{c-1}^\alpha$, solve

$$\mu_i^\alpha(T,P^\alpha,x_1^\alpha,\dots,x_{c-1}{}^\alpha)=\mu_i^\beta(T,P^\beta,x_1^\beta,\dots,x_{c-1}{}^\beta)\,,\quad i=1,\dots,c\,. \tag{6.54}$$

for P^β and $x_1^\beta,\dots,x_{c-1}^\beta$.

b. Solve (6.28) for R, the radius of the surface of tension.

c. Compute W^{rev} by (6.52) or (6.53).

Step a requires only the equations of state of the bulk phases. According to (6.41),

$$\gamma=\gamma(T,\mu_1,\dots,\mu_c)\,. \tag{6.55}$$

To execute step b, therefore, the explicit form of this function must be known. This is often, if not always, a very difficult requirement to meet, and we are forced to introduce an approximation for γ. In the next subsection, we present one such approximation scheme.

6.7.2 ‡Classical Theory Approximations

In a very popular approximation scheme known as **classical theory approximation**, we simply replace γ by experimentally measurable γ_∞, the value of the surface tension for a flat interface at saturation, and obtain

$$W^{\text{rev}}\approx-V^\beta(P^\beta-P^\alpha)+\gamma_\infty A=\frac{16\pi\gamma_\infty{}^3}{3(P^\beta-P^\alpha)^2}\,. \tag{6.56}$$

If the nucleating phase is incompressible between P^α and P^β, the bulk term $-V^\beta(P^\beta-P^\alpha)$ can be expressed in terms of the chemical potentials. To see this, let us apply the Gibbs–Duhem relation (2.155) to a constant temperature process:

$$V^\beta \mathrm{d}P^\beta=\sum_{i=1}^c N_i^\beta \mathrm{d}\mu_i^\beta\,,\quad T \text{ const.} \tag{6.57}$$

Here, $N_i^\beta=n_i^\beta V^\beta$ is the number of molecules of species i in V^β taken inside a macroscopic reference phase β. Integrating (6.57) from P^α to P^β without changing T or $N_1^\beta,\dots,N_c^\beta$, we find

$$V^\beta(P^\beta-P^\alpha)=\sum_{i=1}^c N_i^\beta\Delta\mu_i\,, \tag{6.58}$$

where

$$\begin{aligned}\Delta\mu_i&:=\mu_i^\beta(T,P^\beta,x_1^\beta,\dots,x_{c-1}^\beta)-\mu_i^\beta(T,P^\alpha,x_1^\beta,\dots,x_{c-1}^\beta)\\&=\mu_i^\alpha(T,P^\alpha,x_1^\alpha,\dots,x_{c-1}^\alpha)-\mu_i^\beta(T,P^\alpha,x_1^\beta,\dots,x_{c-1}^\beta)\,.\end{aligned} \tag{6.59}$$

In the last equality, we used (6.54). Introducing (6.58) into (6.56), we arrive at

$$W^{\text{rev}} \approx -\sum_{i=1}^{c} N_i^\beta \Delta\mu_i + \gamma_\infty A = \frac{16\pi{\gamma_\infty}^3}{3(\sum_{i=1}^{c} n_i^\beta \Delta\mu_i)^2} \,. \tag{6.60}$$

If $P^\beta \gg P^\alpha$, then,

$$P^\beta - P^\alpha = (P^\beta - P_{\text{sat}}) - (P^\alpha - P_{\text{sat}}) \approx P^\beta - P_{\text{sat}} \,, \tag{6.61}$$

where P_{sat} is the pressure at saturation. Under this approximation, (6.59) gives

$$\begin{aligned}\Delta\mu_i &\approx \mu_i^\beta(T, P^\beta, x_1^\beta, \dots, x_{c-1}^\beta) - \mu_i^\beta(T, P_{\text{sat}}, x_1^\beta, \dots, x_{c-1}^\beta) \\ &= \mu_i^\alpha(T, P^\alpha, x_1^\alpha, \dots, x_{c-1}^\alpha) - \mu_i^\alpha(T, P_{\text{sat}}, x_{1,\text{sat}}^\alpha, \dots, x_{c-1,\text{sat}}^\alpha) \,,\end{aligned} \tag{6.62}$$

where we used

$$\mu_i^\beta(T, P_{\text{sat}}, x_1^\beta, \dots, x_{c-1}^\beta) = \mu_i^\alpha(T, P_{\text{sat}}, x_{1,\text{sat}}^\alpha, \dots, x_{c-1,\text{sat}}^\alpha) \,, \quad i = 1, \dots, c \,. \tag{6.63}$$

at the two-phase coexistence. To apply (6.62) for a given intensive state of the metastable phase α, we first find the intensive state of bulk β phase by solving (6.54). Then, we solve (6.63) to find P_{sat} and $x_{1,\text{sat}}, \dots, x_{c,\text{sat}}$.

If bulk phase α may be regarded as an ideal gas mixture, (2.201) applies:

$$\Delta\mu_i = k_B T \ln \frac{x_i^\alpha P^\alpha}{x_{i,\text{sat}}^\alpha P_{\text{sat}}} \,, \quad i = 1, \dots, c \,. \tag{6.64}$$

We replaced the gas constant R in (2.201) by k_B since μ_i in this chapter has the dimension of energy per molecule. For a single component system, (6.64) reduces to

$$\Delta\mu = k_B T \ln \frac{P^\alpha}{P_{\text{sat}}} \,, \tag{6.65}$$

in which $P^\alpha / P_{\text{sat}}$ is commonly called the **supersaturation ratio**. By means of (6.65), (6.60) becomes

$$W^{\text{rev}} \approx -N^\beta k_B T \ln \frac{P^\alpha}{P_{\text{sat}}} + \gamma_\infty A \,. \tag{6.66}$$

6.7.3 †Thermodynamic Degrees of Freedom

In step a of Sect. 6.7.1, we took it for granted that (6.54) has a nontrivial solution ($P^\beta \neq P^\alpha$) for given T, $x_1^\alpha, \dots, x_{c-1}^\alpha$, and for any P^α, which we choose between P_{sat} and the pressure at the onset of instability. According to the Gibbs phase rule we saw in Sect. 2.12, however, the thermodynamic degrees of freedom should be just c for a c component system in two-phase coexistence. So, all degrees of freedom appear to be used up by T and $x_1^\alpha, \dots, x_{c-1}^\alpha$. How is it then that we can specify P^α also?

We must remember that the Gibbs phase rule was derived on the basis of the conditions of equilibrium and the Gibbs–Duhem relations for macroscopic homogeneous phases. Our attempt to provide an explicit account of the interfacial region brought about some modifications to this basic construct. Let us find out how this modification impacts the Gibbs phase rule.

Consider a metastable phase α containing a critical nucleus. As we have seen, thermodynamic behavior of this inhomogeneous system can be described in terms of a composite system consisting of the bulk reference phases and the sharp interface located at the surface of tension with the fundamental equation of the interface given by either (6.20) or (6.21).[38]

At equilibrium, T and $\mu_1, \ldots, \mu_c$ are uniform throughout the system. If the equilibrium is to be maintained after some perturbation, they must remain so. Thus, dT and $\mathrm{d}\mu_1, \ldots, \mathrm{d}\mu_c$ are subject to the Gibbs–Duhem relations for the bulk phases

$$
\begin{aligned}
S^\alpha \mathrm{d}T - V^\alpha \mathrm{d}P^\alpha + \sum_{i=1}^{c} N_i^\alpha \mathrm{d}\mu_i &= 0\,, \\
S^\beta \mathrm{d}T - V^\beta \mathrm{d}P^\beta + \sum_{i=1}^{c} N_i^\beta \mathrm{d}\mu_i &= 0\,,
\end{aligned}
\tag{6.67}
$$

and also to the Gibbs adsorption equation (6.41). In addition, the Laplace equation (6.28), providing the condition of mechanical equilibrium, must hold both before and after the perturbation, thus leading to

$$
\mathrm{d}P^\beta - \mathrm{d}P^\alpha = \frac{2}{R}\mathrm{d}\gamma - \frac{2\gamma}{R^2}\mathrm{d}R\,. \tag{6.68}
$$

In total, therefore, we have four equations among $c+5$ infinitesimal quantities dT, $\mathrm{d}\mu_1, \ldots, \mathrm{d}\mu_c$, $\mathrm{d}P^\alpha$, $\mathrm{d}P^\beta$, $\mathrm{d}\gamma$ and dR. Accordingly, the thermodynamic degrees of freedom is $c+1$ as opposed to just c as might be expected on the basis of the usual Gibbs phase rule.

For given values of dT and $\mathrm{d}\mu_1, \ldots, \mathrm{d}\mu_c$, for example, the values of $\mathrm{d}P^\alpha$, $\mathrm{d}P^\beta$, and $\mathrm{d}\gamma$ are determined uniquely by (6.41) and (6.67). The equilibrium is maintained by adjusting R according to (6.68). This additional degrees of freedom is absent if we limit ourselves to phase coexistence across a flat interface.

6.7.4 *Small Nucleus*

With increasing degree of supersaturation, the metastable phase eventually becomes unstable. At the onset of instability, we expect that $W^{\mathrm{rev}} = 0$. (Recall that W^{rev} is the measure of stability of the supersaturated phase.) Equation (6.53) implies that γ and R must *also* vanish at the onset. This is because $P^\beta - P^\alpha \neq 0$ for P^β determined by (6.54). Otherwise, we would simply have the phase coexistence across a flat interface. In addition, since μ_i^α and μ_i^β are finite, $P^\beta - P^\alpha$ should remain finite at the onset as well.

We expect that γ, R, and W^{rev} vary continuously with the degree of supersaturation. Thus, when the degree of supersaturation is increased, a critical nucleus is expected to become smaller and gradually lose its homogeneous core.

In classical theory approximation, the supersaturation dependence of γ is ignored. Thus, its predictions are likely to worsen with increasing degree of supersaturation. How about the exact expression (6.53)? As we remarked in Sect. 6.1, the formalism we developed remains applicable even in such cases. Nevertheless, its practical utility is severely limited due to our inability to experimentally determine the fundamental equation (6.55) in this regime.

For example, in very small nuclei, such as a liquid water droplet consisting only of a few tens of molecules or less, P^{β} may no longer be equal to the mechanical pressure at the center of the nucleus, and the identification of γ with the mechanical tension becomes questionable at best. Simultaneously, the thickness of the interfacial region becomes comparable with R itself because the majority of molecules are in the interfacial region. This will frustrate any attempt to locate the surface of tension precisely.

Recall that the nucleation rate is proportional to $e^{-\beta W^{\mathrm{rev}}}$ and thus vanishes exponentially fast with increasing W^{rev}. The implication is that nucleation is likely to occur under the condition where classical theory approximation is inadequate *but* the input needed for the exact theory is inaccessible. This is a fundamental challenge in thermodynamics of interfaces that can only be addressed by statistical mechanics. Before we turn to this subject in Chap. 7, we shall discuss an approach that lies between pure thermodynamics we have seen so far and full-fledged statistical mechanics in the following two optional sections. Two equations, (6.92) and (6.98), derived in Sect. 6.9 find their applications in Sect. 7.6.

6.8 †Gibbs–Tolman–Koenig Equation

The form of the function (6.55) cannot be determined either within the framework of thermodynamics itself or by experiments. Starting with the Gibbs adsorption equation, however, we can derive an exact differential equation for this function. The differential equation, known as the **Gibbs–Tolman–Koenig** (GTK) **equation**, was first derived by Tolman for single component systems [18] and was almost immediately generalized to multicomponent systems by Koenig [5]. In this section, we derive the GTK equation for single component systems.

Before we get started, we note that the GTK equation cannot be solved without a detailed knowledge regarding the molecular-level structure of the interfacial region. Nevertheless, the equation forms a basis for improving the classical approximation through the **Tolman correction**, which we discuss toward the end of this section.

Writing down (6.41) and (6.67) for a single component system ($c = 1$) and recalling (6.68), we see that the values of $\mathrm{d}P^{\alpha}$, $\mathrm{d}P^{\beta}$, $\mathrm{d}\gamma$, and $\mathrm{d}\mu$ are completely determined once the values of $\mathrm{d}T$ and $\mathrm{d}R$ are given. Thus, we can use T and the curvature $q := 1/R$ of the surface of tension as the independent variables instead of T and μ.

In fact, the dependence of γ on the degree of supersaturation is usually formulated as its curvature dependence.

For a constant T process, (6.41) reduces to

$$\mathrm{d}\gamma = -\Gamma \mathrm{d}\mu\,, \quad T \text{ const.} \tag{6.69}$$

Dividing both sides by dq,

$$\left(\frac{\partial \gamma}{\partial q}\right)_T = -\Gamma \left(\frac{\partial \mu}{\partial q}\right)_T . \tag{6.70}$$

To rewrite the right-hand side, we recall the Gibbs–Duhem relation for bulk phase α:

$$\mathrm{d}P^\alpha = n^\alpha \mathrm{d}\mu\,, \quad T \text{ const.} \tag{6.71}$$

and obtain

$$\left(\frac{\partial P^\alpha}{\partial q}\right)_T = n^\alpha \left(\frac{\partial \mu}{\partial q}\right)_T . \tag{6.72}$$

Similarly,

$$\left(\frac{\partial P^\beta}{\partial q}\right)_T = n^\beta \left(\frac{\partial \mu}{\partial q}\right)_T . \tag{6.73}$$

From (6.68), we also have

$$\mathrm{d}P^\beta - \mathrm{d}P^\alpha = 2\gamma \mathrm{d}q + 2q\mathrm{d}\gamma\,, \tag{6.74}$$

which holds for any process including the constant T process. Thus,

$$\left(\frac{\partial P^\beta}{\partial q}\right)_T - \left(\frac{\partial P^\alpha}{\partial q}\right)_T = 2\gamma + 2q\left(\frac{\partial \gamma}{\partial q}\right)_T . \tag{6.75}$$

Using (6.72) and (6.73) in (6.75),

$$\left(\frac{\partial \mu}{\partial q}\right)_T = \frac{2}{n^\beta - n^\alpha}\left[\gamma + q\left(\frac{\partial \gamma}{\partial q}\right)_T\right] . \tag{6.76}$$

Substituting this expression into (6.70) and solving the resulting equation for $(\partial\gamma/\partial q)_T$, we find

$$\left(\frac{\partial \ln \gamma}{\partial q}\right)_T = -\frac{2\Gamma}{n^\beta - n^\alpha + 2\Gamma q} . \tag{6.77}$$

This is the desired differential equation. But, one commonly eliminates Γ by introducing an **auxiliary surface**. *For the case of single component systems*, this is the **equimolar dividing surface** defined by

$$\Gamma_e(T,\mu,R_e) = 0\,, \tag{6.78}$$

where the subscript e refers to the quantities pertaining to this dividing surface. The indicated dependence of Γ_e on T, μ, and R_e follows from (6.37) and (6.38).

Corresponding to the two choices for the dividing surface, we now have two reference systems. Using the surface of tension, we can express the number N of molecules in the system as

$$N = \frac{1}{3}\omega R^3 n^\beta + \frac{1}{3}\omega({R_0}^3 - R^3)n^\alpha + \omega R^2 \Gamma \ . \tag{6.79}$$

The same quantity may be expressed for the equimolar dividing surface as

$$N = \frac{1}{3}\omega {R_e}^3 n^\beta + \frac{1}{3}\omega({R_0}^3 - {R_e}^3)n^\alpha \ . \tag{6.80}$$

Subtracting (6.80) from (6.79) and solving the resulting equation for Γ, we obtain

$$\Gamma = (n^\beta - n^\alpha)\delta\left(1 + \delta q + \frac{1}{3}\delta^2 q^2\right) , \tag{6.81}$$

where

$$\delta := R_e - R \ . \tag{6.82}$$

This distance between the surface of tension and the auxiliary surface is known as the **Tolman length**. By means of (6.81), (6.77) finally becomes

$$\left(\frac{\partial \ln \gamma}{\partial q}\right)_T = -\frac{2\delta\left(1 + \delta q + \frac{1}{3}\delta^2 q^2\right)}{1 + 2\delta q\left(1 + \delta q + \frac{1}{3}\delta^2 q^2\right)} , \tag{6.83}$$

which is the GTK equation. Interestingly, the GTK equation retains this basic form when generalized to multicomponent systems. But the proper choice for the auxiliary surface will have to be modified.

The GTK equation can be solved only if we know δ as a function of q. As we shall see in Sect. 6.9, this requires that the (position dependent) free energy density be known across the interface. This is where we must resort to statistical mechanics. Within the framework of pure thermodynamics, the GTK equation simply replaces the difficulty of measuring γ by that of measuring δ.

Nevertheless, recasting of the original problem in the language of GTK equation may suggest a different set of approximations that are inconceivable in its absence. The famous Tolman correction is one such example. At saturation, $q = 0$ and the GTK equation yields

$$\left(\frac{\partial \gamma}{\partial q}\right)_T\bigg|_{q=0} = -\frac{2\gamma\delta\left(1 + \delta q + \frac{1}{3}\delta^2 q^2\right)}{1 + 2\delta q\left(1 + \delta q + \frac{1}{3}\delta^2 q^2\right)}\Bigg|_{q=0} = -2\gamma_\infty\delta_\infty , \tag{6.84}$$

where δ_∞ is the Tolman length in the flat interface. In accordance with (6.82) for a spherical nucleus, δ_∞ is positive if the surface of tension penetrates deeper toward the nucleating phase (β) than does the equimolar dividing surface. Integrat-

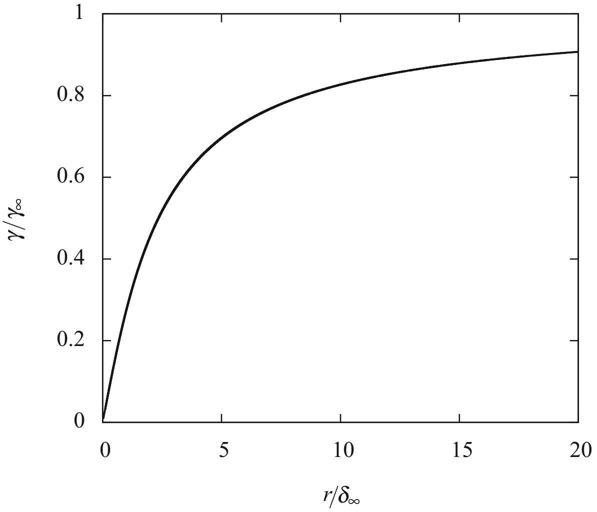

Fig. 6.12 A numerical solution of the GTK equation under the assumption that $\delta = \delta_\infty > 0$. *GTK* Gibbs-Tolman-Koenig.

ing (6.84), we have

$$\gamma \approx \gamma_\infty - 2\gamma_\infty \delta_\infty q \approx \frac{\gamma_\infty}{1+2\delta_\infty q} \tag{6.85}$$

to the first order of q. This result is known as the **Tolman correction**.

If we assume that $\delta \equiv \delta_\infty \neq 0$, (6.83) can be written as

$$\left(\frac{\partial \ln \gamma^*}{\partial x}\right)_T = -\frac{2\left(1+x+\frac{1}{3}x^2\right)}{1+2x\left(1+x+\frac{1}{3}x^2\right)}\,, \tag{6.86}$$

where $\gamma^* := \gamma/\gamma_\infty$ and $x := \delta_\infty q$. For a positive value of δ_∞, x varies from 0 (flat interface) to $+\infty$ (onset of instability). Equation (6.86) can be integrated either numerically or analytically [17] over the entire range of x with the result shown in Fig. 6.12. For a negative value of δ_∞, x varies from 0 to $-\infty$. But, the denominator on the right-hand side of (6.86) becomes zero at $x \approx -1.794$, leading to an unphysical behavior of γ^*. Thus, the assumption of constant δ is untenable if $\delta_\infty < 0$. According to (6.82), however, if $\delta_\infty > 0$ for droplet formation, then $\delta_\infty < 0$ for bubble formation, and vice versa.

As we have remarked already, γ_∞ is often accessible experimentally. In contrast, the prediction of δ_∞ must rely on a statistical mechanical approach. All we can say here is that δ_∞ *for the case of single component systems* is not expected to exceed a typical thickness of the interfacial region, say several atomic diameters. This is because both the surface of tension and the equimolar dividing surface are expected to reside within the interfacial region. For multicomponent systems, the same may not hold because the equimolar dividing surface is not in general the appropriate choice for the auxiliary surface. See Refs. [9, 14], for example.

6.9 †Interfacial Properties

As we shall see in Chap. 7, the grand potential of an inhomogeneous system may be written as the integral of the grand potential density $\chi(\boldsymbol{r})$ over its volume V:

$$\Omega = \int_V \chi(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \,. \tag{6.87}$$

In this section, we shall develop expressions for γ_∞ and δ_∞ assuming that the function $\chi(\boldsymbol{r})$ is known. The method for finding $\chi(\boldsymbol{r})$ will be developed in Chap. 7.

Let us first recall (6.48), which is an exact expression for the reversible work of formation of a spherical critical nucleus inside imaginary boundary B. In Sect. 6.7.1, we obtained (6.48) as the increment upon the nucleus formation of the internal energy of the isolated system that contains B. But, the same expression can also be regarded as the increment of the grand potential inside B. Thus, using a spherical coordinate system whose origin coincides with the center of the nucleus, we have

$$W^{\mathrm{rev}} = 4\pi \int_0^\infty [\chi(r) + P^\alpha] r^2 \mathrm{d}r \,, \tag{6.88}$$

where we recognize $-P^\alpha$ as the grand potential density of the homogeneous α phase. The upper limit ∞ of the integral simply indicates that the integration extends sufficiently deep into the α phase, where the integrand vanishes. This is an acceptable convention provided that the integrand approaches zero sufficiently fast to ensure the convergence of the integral. In what follows, we shall assume this to be the case for all integrals involving $\pm\infty$ in their limits. (If this is not allowed, the effect of container walls must be accounted for explicitly.)

We can separate the integral at the dividing surface at R and rewrite (6.88) as

$$W^{\mathrm{rev}} = 4\pi \int_0^R [\chi(r) + P^\beta] r^2 \mathrm{d}r + 4\pi \int_R^\infty [\chi(r) + P^\alpha] r^2 \mathrm{d}r - \frac{4\pi}{3} R^3 (P^\beta - P^\alpha) \,, \tag{6.89}$$

which may be compared with (6.52) to yield

$$\gamma = \frac{1}{R^2} \left\{ \int_0^R [\chi(r) + P^\beta] r^2 \mathrm{d}r + \int_R^\infty [\chi(r) + P^\alpha] r^2 \mathrm{d}r \right\} \,. \tag{6.90}$$

Exercise 6.3. As we saw in Exercise 6.2, (6.52) holds for an arbitrary dividing surface. The same applies for (6.89) and (6.90). Based on this observation, derive (6.26) from (6.90). ///

The expression for γ_∞ should emerge from (6.90) as its $R \to \infty$ limit is taken without changing the convention for the dividing surface. To evaluate this limit, let us rewrite (6.90) using a new variable $\xi := r - R$:

$$\gamma = \int_{-R}^0 [\chi(\xi + R) + P^\beta] \left(1 + \frac{\xi}{R}\right)^2 \mathrm{d}\xi + \int_0^\infty [\chi(\xi + R) + P^\alpha] \left(1 + \frac{\xi}{R}\right)^2 \mathrm{d}\xi \,. \tag{6.91}$$

For a sufficiently large R, the nucleus has a homogeneous core, implying that $\chi + P^\beta$ vanishes rapidly once $|\xi|$ exceeds a few times the width of the interfacial thickness. The same applies to $\chi + P^\alpha$. In the $R \to \infty$ limit, therefore, $1 + \xi/R$ may safely be replaced by unity without worrying about its large $|\xi|$ behavior. Since $P^\beta \to P^\alpha$ in this limit, (6.91) becomes the integral of $\chi(\xi) + P^\alpha$ over the interval of ξ that fully contains the interfacial region. Thus, writing $\chi(\xi)$ for $\chi(\xi + R)$ so that $\chi(0)$ gives the grand potential density at $r = R$, we have

$$\gamma_\infty = \int_{-\infty}^{\infty} [\chi(\xi) + P^\alpha]\,\mathrm{d}\xi\ , \tag{6.92}$$

which is manifestly independent of the choice of the dividing surface. (See Sect. 6.6.) At the two-phase coexistence, the two bulk reference phases have the same grand potential density $-P^\alpha$. According to (6.92), γ_∞ is the superficial density of the grand potential. This is in agreement with the physical interpretation given to γ in Sect. 6.4.

Using (6.91) in the third equation of (6.38), in which the partial derivative is taken while holding the intensive state of the system constant, we find

$$\begin{aligned} c_a = &-\frac{2}{R^2}\int_{-R}^{0}[\chi(\xi+R)+P^\beta]\xi\left(1+\frac{\xi}{R}\right)\mathrm{d}\xi + \int_{-R}^{\infty}\frac{\mathrm{d}\chi(\xi+R)}{\mathrm{d}R}\left(1+\frac{\xi}{R}\right)^2\mathrm{d}\xi\ . \\ &-\frac{2}{R^2}\int_{0}^{\infty}[\chi(\xi+R)+P^\alpha]\xi\left(1+\frac{\xi}{R}\right)\mathrm{d}\xi \end{aligned} \tag{6.93}$$

The lower limit $-R$ of the first integral in (6.91) does not contribute to c_a because the integrand is zero at $\xi = -R$. (For a sufficiently large R, we may first replace the lower limit by some constant ξ_c $(-R < \xi_c \ll 0)$ without affecting the value of the integral because the integrand will be zero if $\xi \le \xi_c$. Then, we can take the derivative to obtain (6.93).)

The second integral of (6.93) is zero. To see this, we first rewrite it as

$$\lim_{\Delta R\to 0}\frac{1}{\Delta R}\int_{0}^{\infty}[\chi(r+\Delta R)-\chi(r)]\left(\frac{r}{R}\right)^2\mathrm{d}r\ , \tag{6.94}$$

where we used the definition of the derivative:

$$\frac{\mathrm{d}\chi(\xi+R)}{\mathrm{d}R} = \lim_{\Delta R\to 0}\frac{\chi(\xi+R+\Delta R)-\chi(\xi+R)}{\Delta R} \tag{6.95}$$

and reverted to the original variable $r = \xi + R$. But, the quantity $\chi(r+\Delta R) - \chi(r)$ represents the change in $\chi(r)$ that is observed at r when the function $\chi(r)$ is shifted by ΔR in the direction of decreasing r. This same change may also be regarded as being brought about by an infinitesimal variation in the state of the system. But, because the system is in equilibrium initially, the grand potential of the system remains unaffected to the first order of such variations. (See Sect. 7.2.1 for details.) It follows that the integral in (6.94) is at most second order of ΔR. This proves the assertion.

Because of the assumption we made earlier, the remaining integrals in (6.93) converge and c_a vanishes in the $R \to \infty$ limit as demanded by (6.43). To find the location of the surface of tension, we recall that $C = 4\pi R^2 c_a$ and use (6.27), which now reads

$$\int_{-R}^{0} [\chi(\xi+R)+P^\beta]\xi\left(1+\frac{\xi}{R}\right)\mathrm{d}\xi + \int_{0}^{\infty} [\chi(\xi+R)+P^\alpha]\xi\left(1+\frac{\xi}{R}\right)\mathrm{d}\xi = 0\,. \tag{6.96}$$

Provided that $\chi(r)$ is known, this equation can be solved (numerically in most cases) for R, which is then the radius of the surface of tension. The $R \to \infty$ limit of this equation can be evaluated by repeating the same argument we have given to (6.91). In this way, we obtain

$$\int_{-\infty}^{\infty} [\chi(\xi)+P^\alpha]\,\xi\mathrm{d}\xi = 0 \tag{6.97}$$

for a flat interface. We replace the relation $\xi = r - R$ by $\xi = z - z_s$, where the z-axis is perpendicular to the interface and z_s is the location of the surface of tension. Using (6.92), we arrive at

$$z_s = \frac{1}{\gamma_\infty}\int_{-\infty}^{\infty} [\chi(z)+P^\alpha]\,z\mathrm{d}z\,. \tag{6.98}$$

Once again, we note that the integrand is zero as we move sufficiently away from the interfacial region.

The location z_e of the equimolar dividing surface is determined by

$$\int_{-\infty}^{z_e} [n(z)-n^\beta]\mathrm{d}z + \int_{z_e}^{\infty} [n(z)-n^\alpha]\mathrm{d}z = 0\,, \tag{6.99}$$

where $n(z)$ is the density profile, that is, the z-dependent number density of molecules across the system. Then, the Tolman length for the flat interface is given by $\delta_\infty = z_e - z_s$.

Finally, it should be noted that the above elaboration is entirely unnecessary for spherical critical nuclei. Once $\chi(r)$ is known, we can simply compute W^{rev} using (6.88). Then, (6.28) and (6.53) serve as the set of simultaneous equations for γ and R. However, such an approach cannot be applied directly to flat interfaces.

6.10 Frequently Used Symbols

$[\theta]$, increment of an extensive quantity θ during a process under consideration.
θ^s , surface excess quantity of an extensive variable θ.

c , the number of species.
c_a , C/A.
k_B , Boltzmann constant, 1.3806×10^{-23} J/K.
n_i , the number density of species i.

q , curvature $1/R$ of the surface of tension.
s^s , S^s/A.
u^s , U^s/A.
x_i , mole fraction of species i.

A , area of a dividing surface.
C , $(\partial U^s/\partial R)_{S^s,N^s,A}$.
N_i , the number of molecules of species i. We drop the subscript i for a pure system.
P , pressure.
R , radius of the dividing surface.
R_0 , radius of the spherical region containing an inhomogeneous region.
R_e , radius of the equimolar dividing surface.
S , entropy.
T , absolute temperature.
U , internal energy.
V , volume.
W^{rev} , reversible work of critical nucleus formation.

α , label for the bulk metastable phase.
β , label for the bulk nucleating phase.
δ , Tolman length.
δ_∞ , Tolman length of a flat interface.
γ , $(\partial U^s/\partial A)_{S^s,N^s,R}$ for a generic dividing surface and surface tension if the dividing surface is the surface of tension.
γ_∞ , surface tension of a flat interface.
μ_i , chemical potential of species i. We drop the subscript i for a pure system.
χ , grand potential per unit volume.
ω , solid angle.

Γ_i , N_i^s/A.
Ω , grand potential.

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Chapter 7
Statistical Mechanics of Inhomogeneous Fluids

While thermodynamics of interfaces provides a theoretical foundation for understanding various interfacial phenomena, its application depends on the availability of the fundamental equation. That is, the explicit form of the function (6.55) must be known. In the absence of experimental access to this information, this is a task best left to statistical mechanics. In this chapter, we introduce a powerful method from statistical mechanics that allows us to study interfaces and inhomogeneous systems in general based on underlying molecular-level models.

7.1 Functional

The concept of functionals and their derivatives play a central role in what follows. In this section, we introduce the functionals as a generalization of ordinary functions and explore the rules of computing with the functionals.

7.1.1 Definition

Given a function $f(x)$, we often represent it graphically using the horizontal axis for the independent variable x and the vertical axis for the dependent variable f. For a function $f(x,y)$ of two variables, the graph is a surface in a three-dimensional space. For a function of three or more variables, such a graphical representation is not possible.

We can devise a far less ambitious approach, in which we use two diagrams, one showing only the values assumed by the independent variables and the other showing the value of the function corresponding to the given values of the independent variables.

As an example, let us consider a function $f(u_1,u_2,u_3)$. A conventional graphical approach would require a four-dimensional space to plot it. Instead, we show the

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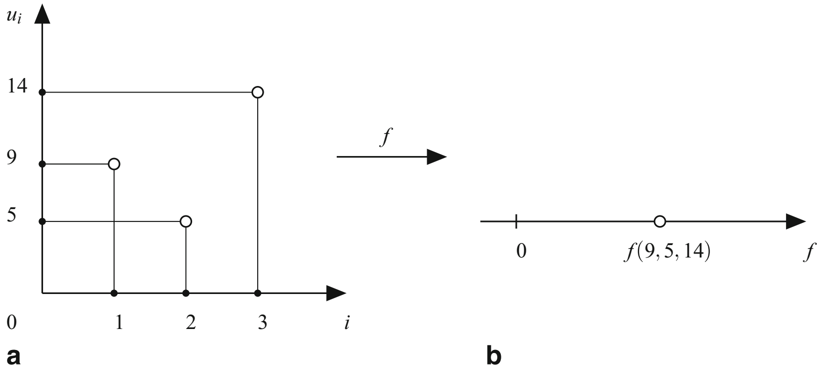

Fig. 7.1 The function $f(u_1,u_2,u_3)$ maps the triplet $(9,5,14)$ on **a** to a real number $f(9,5,14)$ on **b**.

values of u_1, u_2, and u_3 in one diagram as shown in Fig. 7.1a. The value of f corresponding to those specific u_1, u_2, and u_3 is then shown in another diagram, Fig. 7.1b. We can explore the behavior of the function by changing the values of u_1, u_2, and u_3, which amounts to vertical movements of the open circles in Fig. 7.1a, and then observing the corresponding horizontal movement of the open circle in Fig. 7.1b.

Admittedly, this new approach does not convey as much information as the conventional one. But, it has a virtue of being applicable regardless of the number of independent variables. Thus, a function $f(u_1,\dots,u_n)$ of n variables can be expressed in the same manner even if $n = 1000$. In this case, we simply have 1000 open circles in Fig. 7.1a indicating the values of all these independent variables. Figure 7.1b will still contain just one open circle showing the value of f corresponding to those specific values of the independent variables.

Coming back to the case of just three independent variables, we note that nothing in our approach limits the index i on u_i to an integer. We could easily introduce new variables, such as $u_{1.2}$, $u_{\sqrt{2}}$, or $u_{7/3}$, and generate a new function

$$f(u_1,u_{1.2},u_{\sqrt{2}},u_2,u_{7/3},u_3)\ . \tag{7.1}$$

All we have to do is draw more circles at appropriate positions in Fig. 7.1a. Continuing in this manner, we can include more and more circles between $i = 1$ and $i = 3$ until they form a continuous curve on the iu_i-plane in this interval. What we have then is a rule f of assigning a number to a function $u(i)$ defined for all *real numbers* i in the interval $1 \le i \le 3$. Such a rule of assignment is called a **functional**.

More generally, a functional is a rule of assigning a number $\mathscr{F}$ to a function $u(x)$ defined on some interval, such as $a \le x \le b$.[39] The functional dependence of $\mathscr{F}$ on the function $u(x)$ is indicated by a pair of square brackets. So, the functional is denoted by $\mathscr{F}[u]$. One particularly simple example of a functional is

$$\mathscr{F}_1[u] = \int_a^b u(x)\mathrm{d}x\ . \tag{7.2}$$

A slightly less trivial example is

$$\mathscr{F}_2[u] = \int_a^b x e^{u(x)} \mathrm{d}x \, . \tag{7.3}$$

The action integral $\mathscr{S}$ we encountered in Chap. 1 affords yet another example of a functional:

$$\mathscr{S}[q] = \int_{t_1}^{t_2} L(q, \dot{q}, t) \mathrm{d}t \, , \tag{7.4}$$

in which $\dot{q} = \mathrm{d}q/\mathrm{d}t$ is a known function of t once $q(t)$ is specified. Perhaps a little unexpectedly,

$$\mathscr{F}_3[u] = u(x_0) \, , \quad a \leq x_0 \leq b \, , \tag{7.5}$$

is also a functional. In fact, $\mathscr{F}_3$ assigns a number $u(x_0)$ to the function $u(x)$ defined on the interval $a \leq x \leq b$. The point becomes clearer if we rewrite (7.5) as

$$\mathscr{F}_3[u] = \int_a^b \delta(x - x_0) u(x) \mathrm{d}x \, , \quad a \leq x_0 \leq b \tag{7.6}$$

using the Dirac δ-function. (See Appendix D.) In what follows, we shall omit the explicit reference to the limits of integration unless demanded by the situation.

7.1.2 Functional Derivative

Let us consider a functional defined by

$$\mathscr{F}[u] := \int \ln[u(x) + 1] \mathrm{d}x \tag{7.7}$$

and compute the difference

$$\mathscr{F}[u + \delta u] - \mathscr{F}[u] = \int \{\ln[u(x) + \delta u(x) + 1] - \ln[u(x) + 1]\} \mathrm{d}x \, . \tag{7.8}$$

Using (B.6), we note that

$$\ln(x + a) = \ln x + \frac{a}{x} + \text{h.o.} \tag{7.9}$$

Replacing x by $u(x) + 1$ and a by $\delta u(x)$ in this formula, we obtain

$$\ln[u(x) + \delta u(x) + 1] - \ln[u(x) + 1] = \frac{1}{u(x) + 1} \delta u(x) + \text{h.o.} \tag{7.10}$$

So,

$$\mathscr{F}[u + \delta u] - \mathscr{F}[u] = \int \frac{1}{u(x) + 1} \delta u(x) \mathrm{d}x + \text{h.o.} \tag{7.11}$$

The coefficient of $\delta u(x)$ in the integrand, $1/[u(x)+1]$, is called the first functional derivative of $\mathscr{F}[u]$.

More generally, we define the first **functional derivative** $\delta\mathscr{F}/\delta u(x)$ of $\mathscr{F}[u]$ by

$$\mathscr{F}[u+\delta u]-\mathscr{F}[u]=\int\frac{\delta\mathscr{F}}{\delta u(x)}\delta u(x)\mathrm{d}x+\text{h.o.} \tag{7.12}$$

We denote the first term on the right-hand side by $\delta\mathscr{F}$:

$$\delta\mathscr{F}:=\int\frac{\delta\mathscr{F}}{\delta u(x)}\delta u(x)\mathrm{d}x\,. \tag{7.13}$$

These equations generalizes the corresponding relations for ordinary functions,

$$f(u_1+\delta u_1,\ldots,u_n+\delta u_n)-f(u_1,\ldots,u_n)=\sum_{i=1}^{n}\frac{\partial f}{\partial u_i}\delta u_i+\text{h.o.} \tag{7.14}$$

and

$$\mathrm{d}f=\sum_{i=1}^{n}\frac{\partial f}{\partial u_i}\delta u_i\,, \tag{7.15}$$

respectively. When the index i on the variable u_i is replaced by x, which changes continuously, the summation with respect to i is replaced by the integration with respect to x.[40]

Example 7.1. Functional derivative:

a. For the functional $\mathscr{F}_1$ in (7.2),

$$\mathscr{F}_1[u+\delta u]-\mathscr{F}_1[u]=\int\delta u(x)\mathrm{d}x\,, \tag{7.16}$$

and hence

$$\frac{\delta\mathscr{F}_1}{\delta u(x)}=1\,. \tag{7.17}$$

b. For the functional $\mathscr{F}_2$ in (7.3),

$$\mathscr{F}_2[u+\delta u]-\mathscr{F}_2[u]=\int x[e^{u(x)+\delta u(x)}-e^{u(x)}]\mathrm{d}x=\int xe^{u(x)}\delta u(x)\mathrm{d}x+\text{h.o.} \tag{7.18}$$

Thus,

$$\frac{\delta\mathscr{F}_2}{\delta u(x)}=xe^{u(x)}\,. \tag{7.19}$$

c. Noting that (7.5) may be written as (7.6),

$$\mathscr{F}_3[u+\delta u]-\mathscr{F}_3[u]=\int\delta(x-x_0)\delta u(x)\mathrm{d}x\,. \tag{7.20}$$

So,

$$\frac{\delta \mathscr{F}_3}{\delta u(x)} = \frac{\delta u(x_0)}{\delta u(x)} = \delta(x - x_0)\ . \tag{7.21}$$

d. As a somewhat less trivial example, let

$$\mathscr{F}_4[u] = \int\int \phi(x_1, x_2) u(x_1) u(x_2) \mathrm{d}x_1 \mathrm{d}x_2 \tag{7.22}$$

and suppose that the limits of integrations are the same for x_1 and x_2. Noting that

$$\begin{aligned}&[u(x_1) + \delta u(x_1)][u(x_2) + \delta u(x_2)] - u(x_1)u(x_2) \\ &\qquad = u(x_1)\delta u(x_2) + u(x_2)\delta u(x_1) + \text{h.o.}\ ,\end{aligned} \tag{7.23}$$

we find

$$\delta \mathscr{F}_4[u] = \int\int \phi(x_1, x_2)[u(x_1)\delta u(x_2) + u(x_2)\delta u(x_1)] \mathrm{d}x_1 \mathrm{d}x_2\ . \tag{7.24}$$

Since x_1 and x_2 are just integration variables, they can be replaced by anything we like. For example, we can use x_2 for x_1 and x_1 for x_2, respectively. Thus,

$$\int\int \phi(x_1, x_2) u(x_1) \delta u(x_2) \mathrm{d}x_1 \mathrm{d}x_2 = \int\int \phi(x_2, x_1) u(x_2) \delta u(x_1) \mathrm{d}x_1 \mathrm{d}x_2\ . \tag{7.25}$$

Because the limits of integrations are the same for x_1 and x_2, we can now combine the two terms in (7.24) to find

$$\delta \mathscr{F}_4[u] = \int \left\{ \int [\phi(x_2, x_1) + \phi(x_1, x_2)] u(x_2) \mathrm{d}x_2 \right\} \delta u(x_1) \mathrm{d}x_1\ , \tag{7.26}$$

So,

$$\frac{\delta \mathscr{F}_4}{\delta u(x_1)} = \int [\phi(x_2, x_1) + \phi(x_1, x_2)] u(x_2) \mathrm{d}x_2\ . \tag{7.27}$$

If $\phi(x_1, x_2) = \phi(x_2, x_1)$, then,

$$\frac{\delta \mathscr{F}_4}{\delta u(x_1)} = 2 \int \phi(x_1, x_2) u(x_2) \mathrm{d}x_2\ . \tag{7.28}$$

Exercise 7.1. Let

$$\mathscr{F}[u] = \int f(u(x), x) \mathrm{d}x\ . \tag{7.29}$$

Show that

$$\frac{\delta \mathscr{F}}{\delta u(x)} = \frac{\partial}{\partial u(x)} f(u(x),x) \,. \tag{7.30}$$

The functional derivatives of $\mathscr{F}_1$, $\mathscr{F}_2$, and $\mathscr{F}_3$ we considered in Example 7.1 can be found using this formula. ///

Exercise 7.2. Let

$$\mathscr{F}[u] = \int_V f(u(\boldsymbol{r}), \nabla u(\boldsymbol{r}))\mathrm{d}\boldsymbol{r} \,. \tag{7.31}$$

Assuming that $\delta u(\boldsymbol{r}) \equiv 0$ on the surface of V, show that

$$\frac{\delta \mathscr{F}}{\delta u(\boldsymbol{r})} = \frac{\partial f}{\partial u} - \nabla \cdot \frac{\partial f}{\partial \nabla u} \,. \tag{7.32}$$

Equations (7.31) and (7.32) should be compared with (1.59) and the integrand of (1.71), respectively. ///

From Example 7.1, we see that $\delta \mathscr{F}/\delta u(x)$ is either a function of $u(x)$ or a functional of $u(x)$. By (7.6), the former may also be regarded as a functional. Thus, the first functional derivative is not only a function of x but also a functional of $u(x)$. If needed, we can express this fact by writing

$$\mathscr{F}^{(1)}(x,u] := \frac{\delta \mathscr{F}}{\delta u(x)} \,. \tag{7.33}$$

We can now define the second functional derivative $\delta^2 \mathscr{F}/\delta u(x_1)\delta u(x_2)$ of $\mathscr{F}$ by

$$\mathscr{F}^{(1)}(x_1, u+\delta u] - \mathscr{F}^{(1)}(x_1,u] = \int \frac{\delta^2 \mathscr{F}}{\delta u(x_1)\delta u(x_2)}\mathrm{d}x_2 + \mathrm{h.o}\,. \tag{7.34}$$

Example 7.2. Second functional derivative: For $\mathscr{F}_1$ and $\mathscr{F}_3$ we saw in Example 7.1,

$$\frac{\delta^2 \mathscr{F}_1}{\delta u(x_1)\delta u(x_2)} = 0 \quad \text{and} \quad \frac{\delta^2 \mathscr{F}_3}{\delta u(x_1)\delta u(x_2)} = 0 \,. \tag{7.35}$$

Rewriting (7.19) as

$$\frac{\delta \mathscr{F}_2}{\delta u(x_1)} = \int x_2 e^{u(x_2)} \delta(x_2 - x_1)\mathrm{d}x_2 \,, \tag{7.36}$$

we find

$$\frac{\delta^2 \mathscr{F}_2}{\delta u(x_1)\delta u(x_2)} = x_2 e^{u(x_2)} \delta(x_2 - x_1) \,. \tag{7.37}$$

Finally, (7.27) gives

$$\frac{\delta^2 \mathscr{F}_4}{\delta u(x_1)\delta u(x_2)} = \phi(x_2,x_1) + \phi(x_1,x_2) \,, \tag{7.38}$$

which reduces to $2\phi(x_1,x_2)$ if $\phi(x_1,x_2) = \phi(x_2,x_1)$. We can reach the same conclusion if we start from (7.28). So, everything is consistent.

Recall the Taylor series expansion of a function f of multiple variables $u_1,\dots,u_n$:

$$f(u_1+\delta u_1,\dots,u_n+\delta u_n) - f(u_1,\dots,u_n) = \sum_{i=1}^{n} \frac{\partial f}{\partial u_i}\delta u_i + \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n} \frac{\partial^2 f}{\partial u_i \partial u_j}\delta u_i \delta u_j + \text{h.o.} \tag{7.39}$$

Corresponding to this formula is the **functional Taylor series expansion** given by

$$\mathscr{F}[u+\delta u] - \mathscr{F}[u] = \int \frac{\delta \mathscr{F}}{\delta u(x_1)}\delta u(x_1)\mathrm{d}x_1 + \frac{1}{2}\int \frac{\delta^2 \mathscr{F}}{\delta u(x_1)\delta u(x_2)}\delta u(x_1)\delta u(x_2)\mathrm{d}x_1\mathrm{d}x_2 + \text{h.o.} \tag{7.40}$$

Finally, if $u = u(x_1,x_2)$, the first functional derivative of $\mathscr{F}[u]$ is defined by

$$\mathscr{F}[u+\delta u] - \mathscr{F}[u] = \int\int \frac{\delta \mathscr{F}}{\delta u(x_1,x_2)}\delta u(x_1,x_2)\mathrm{d}x_1\mathrm{d}x_2 + \text{h.o.} \tag{7.41}$$

For example, if

$$\mathscr{F}[u] = \int\int\int \phi(x_1,x_2,x_3)u(x_1,x_2)u(x_2,x_3)u(x_3,x_1)\mathrm{d}x_1\mathrm{d}x_2\mathrm{d}x_3\ , \tag{7.42}$$

and ϕ is invariant with respect to any permutation of the arguments, that is, $\phi(x_1,x_2,x_3) = \phi(x_2,x_1,x_3) = \cdots$, then,

$$\frac{\delta \mathscr{F}}{\delta u(x_1,x_2)} = 3\int\int \phi(x_1,x_2,x_3)u(x_2,x_3)u(x_3,x_1)\mathrm{d}x_3\ . \tag{7.43}$$

Exercise 7.3. Derive (7.43). ///

7.2 Density Functional Theory

For simplicity, let us focus on a single component system and consider an open system of volume V. The system may contain an interfacial region or may otherwise be inhomogeneous. As we saw in Sect. 6.3.2, the temperature T and the chemical potential μ will be uniform throughout the system in equilibrium.[41] Their values are imposed by the surroundings serving as a reservoir of heat and molecules. In contrast, the number density n of molecules may vary across the system. How is

n determined as a function of position $\boldsymbol{r}$ in a system in equilibrium? How do we construct a fundamental equation of the system?

7.2.1 Equilibrium Density Profile

Following an analysis similar to what we saw in Sect. 2.13.2, we can deduce the condition of equilibrium of an open system:

> ***Condition of Equilibrium 7*** *For equilibrium of an open system held at a given temperature T, volume V, and chemical potential μ, it is necessary and sufficient that*
>
> $$(\delta\Omega)_{T,V,\mu} \geq 0 \tag{7.44}$$
>
> *holds for any possible variation of the state of the system.*

We recall that variations considered here are brought about through infinitesimal changes in the *unconstrained variables* $X_1,\ldots,X_m$. Thus,

$$(\delta\Omega)_{T,V,\mu} = \sum_{i=1}^{m} \left(\frac{\partial\Omega}{\partial X_i}\right)_{T,V,\mu,X_{j\neq i}} \delta X_i\,. \tag{7.45}$$

Equation (7.44) then determines the equilibrium values of $X_1,\ldots,X_m$.

Instead of $X_1,\ldots,X_m$, we now have a position-dependent function $n(\boldsymbol{r})$. Its value at each $\boldsymbol{r}$ is an unconstrained variable. Since $\boldsymbol{r}$ is capable of continuous variation, the sum over i in (7.45) must be replaced by the integration with respect to $\boldsymbol{r}$. Thus, the condition of equilibrium is that

$$\delta\Omega = \int_V \frac{\delta\Omega}{\delta n(\boldsymbol{r})}\delta n(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \geq 0 \tag{7.46}$$

holds for all possible values of $\delta n(\boldsymbol{r})$, where the integration is over the system volume V and we omitted the subscripts T, V, and μ.

Provided that $n(\boldsymbol{r})$ is positive everywhere, $\delta n(\boldsymbol{r})$ is capable of taking negative as well as positive values. Then, (7.46) leads to

$$\frac{\delta\Omega}{\delta n(\boldsymbol{r})} = 0\,. \tag{7.47}$$

Given an explicit expression for the functional $\Omega[n]$, called a **density functional** or a **free energy functional**, (7.47) leads to an explicit equation for the equilibrium density profile $n^{\mathrm{eq}}(\boldsymbol{r})$. Once $n^{\mathrm{eq}}(\boldsymbol{r})$ is determined, we can compute the free energy $\Omega[n^{\mathrm{eq}}]$ of the system, which is then a fundamental equation of the inhomogeneous system. This method of computing $n^{\mathrm{eq}}(\boldsymbol{r})$ and the grand potential is known as the *statistical mechanical* or *classical* **density functional theory** (DFT), to be distinguished from the quantum mechanical DFT that aims to compute the electron density and the energy of quantum mechanical systems.

7.2.2 Microscopic Definition of Density

Before turning to the problem of finding the explicit form of $\Omega[n]$, we need to be a little more specific about what is meant by the density profile $n(\boldsymbol{r})$.

As we saw in Sect. 3.1, a measurable quantity of our interest is not a dynamical variable itself, but its ensemble average. So, what is the dynamical variable whose ensemble average gives $n(\boldsymbol{r})$?

It is very natural to demand that, for an arbitrary region of volume $\mathscr{R}$,

$$\int_{\mathscr{R}} n(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \tag{7.48}$$

should give the number of particles inside that region. The **density operator** defined by

$$\hat{n}(\boldsymbol{r},\boldsymbol{r}^N) := \sum_{i=1}^{N} \delta(\boldsymbol{r}-\boldsymbol{r}_i) \tag{7.49}$$

satisfies this demand. In fact,

$$\int_{\mathscr{R}} \delta(\boldsymbol{r}-\boldsymbol{r}_i)\mathrm{d}\boldsymbol{r} \tag{7.50}$$

is unity if the ith particle is inside $\mathscr{R}$ and zero otherwise. (See Appendix D.4 on the three-dimensional δ-function.) So, the integral of $\hat{n}$ over $\mathscr{R}$ gives the number of particles in $\mathscr{R}$. Taking the ensemble average, we identify

$$n(\boldsymbol{r}) = \langle \hat{n}(\boldsymbol{r},\boldsymbol{r}^N)\rangle = \left\langle \sum_{i=1}^{N} \delta(\boldsymbol{r}-\boldsymbol{r}_i) \right\rangle \tag{7.51}$$

as the **density profile**.

Given this definition of the density profile, let us see how it can be related to a partition function. For this purpose, consider a system subject to an external field $\psi(\boldsymbol{r})$. Its Hamiltonian is given by

$$H_N(\boldsymbol{r}^N,\boldsymbol{p}^N) = \sum_{i=1}^{N} \frac{\|\boldsymbol{p}_i\|^2}{2m} + \phi(\boldsymbol{r}^N) + \sum_{i=1}^{N} \psi(\boldsymbol{r}_i)\ . \tag{7.52}$$

The grand canonical partition function of this system is given by

$$\Xi = \sum_{N=0}^{\infty} \frac{e^{\beta\mu N}}{\Lambda^{3N}N!} \int e^{-\beta\phi(\boldsymbol{r}^N)} e^{-\beta\sum_{i=1}^{N}\psi(\boldsymbol{r}_i)}\mathrm{d}\boldsymbol{r}^N\ , \tag{7.53}$$

in which we carried out the integration with respect to the momenta.

In order to introduce $\hat{n}$ into our formulation, we rewrite the external field term as follows:

$$\sum_{i=1}^{N} \psi(\boldsymbol{r}_i) = \sum_{i=1}^{N} \int_V \delta(\boldsymbol{r}-\boldsymbol{r}_i)\psi(\boldsymbol{r})\mathrm{d}\boldsymbol{r} = \int_V \hat{n}(\boldsymbol{r},\boldsymbol{r}^N)\psi(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \,. \tag{7.54}$$

Using this expression in (7.53), we see that Ξ is a functional of $\psi(\boldsymbol{r})$. By considering an infinitesimal variation of $\psi(\boldsymbol{r})$, we obtain

$$\frac{\delta \Xi}{\delta \psi(\boldsymbol{r})} = -\beta \sum_{N=0}^{\infty} \frac{e^{\beta\mu N}}{\Lambda^{3N} N!} \int \hat{n}(\boldsymbol{r},\boldsymbol{r}^N) e^{-\beta\phi(\boldsymbol{r}^N)} e^{-\beta\sum_{i=1}^{N}\psi(\boldsymbol{r}_i)} \mathrm{d}\boldsymbol{r}^N \,. \tag{7.55}$$

Thus,

$$\frac{\delta \Omega}{\delta \psi(\boldsymbol{r})} = -k_B T \frac{\delta \ln \Xi}{\delta \psi(\boldsymbol{r})} = n(\boldsymbol{r}) \,. \tag{7.56}$$

Because the ensemble average is taken with respect to the equilibrium distribution, $n(\boldsymbol{r})$ computed by means of (7.56) actually is the equilibrium density profile $n^{\mathrm{eq}}(\boldsymbol{r})$ for given T, V, μ, and the external field $\psi(\boldsymbol{r})$.

Exercise 7.4. Derive (7.55). ///

Exercise 7.5. Consider an ideal gas in equilibrium in the presence of an external field $\psi(\boldsymbol{r})$. Using a grand canonical ensemble, derive the following results:

a.

$$n^{\mathrm{eq}}(\boldsymbol{r}) = \frac{e^{\beta[\mu-\psi(\boldsymbol{r})]}}{\Lambda^3} \,. \tag{7.57}$$

b.

$$\Omega[n^{\mathrm{eq}}] = -k_B T \int_V n^{\mathrm{eq}}(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \,. \tag{7.58}$$

For a homogeneous phase, $\Omega = -PV$ and (7.58) reduces to $PV = k_B T\langle N\rangle$, the ideal gas equation of state. ///

7.2.3 Ω for a Nonequilibrium Density Profile

Recall that the functional derivative $\delta\Omega/\delta n(\boldsymbol{r})$ is defined by the relation

$$\Omega[n+\delta n] - \Omega[n] = \int_V \frac{\delta\Omega}{\delta n(\boldsymbol{r})}\delta n(\boldsymbol{r})\mathrm{d}\boldsymbol{r} + \text{h.o.} \,. \tag{7.59}$$

Thus, in order to apply (7.47), we need to know $\Omega[n]$ not only for the equilibrium density profile $n^{\mathrm{eq}}(\boldsymbol{r})$ but also for an arbitrary density profile $n(\boldsymbol{r})$. The following example illustrates the point.

Example 7.3. Ideal gas: Motivated by (7.58), let us suppose that

$$\Omega[n] = -k_B T \int_V n(\boldsymbol{r}) \mathrm{d}\boldsymbol{r} \,, \tag{7.60}$$

for an arbitrary $n(\boldsymbol{r})$. Then,

$$\frac{\delta \Omega}{\delta n(\boldsymbol{r})} = -k_B T \,. \tag{7.61}$$

According to (7.47), the left-hand side of this equation is zero at equilibrium. But, because the temperature of an ideal gas can be specified as we please, this is a contradiction. What went wrong?

We must remember that (7.58) applies only to the ideal gas in *equilibrium*. Thus, when we perturbed $n(\boldsymbol{r})$ in (7.60), we have also changed the external field so that the varied state is in equilibrium. In contrast, the functional derivative in (7.47) must be taken while holding the external field constant along with T, V, and μ. So, the contradiction is only apparent. But it does illustrate the need to develop an expression for $\Omega[n]$ for an arbitrary $n(\boldsymbol{r})$.

For given T, V, μ, and the external field, Ω of the system in equilibrium is, at least conceptually, a well-defined quantity. Thus, let us suppose in this section that $\Omega[n^{\mathrm{eq}}]$ is known and establish its relation to $\Omega[n]$ for an arbitrary $n(\boldsymbol{r})$.

For clarity, we denote by $n_a(\boldsymbol{r})$ the equilibrium density profile of a system under the influence of an external field $\psi_a(\boldsymbol{r})$. In general, the value of n_a at some point in the system depends on the form of the function $\psi_a(\boldsymbol{r})$ throughout the system. That is, n_a is not only a function of $\boldsymbol{r}$ but also a function*al* of ψ_a. To emphasize this fact, we write

$$n_a(\boldsymbol{r}) = n^{\mathrm{eq}}(\boldsymbol{r}, \psi_a] \,. \tag{7.62}$$

Our goal is to express $\Omega[n_a, \psi_b]$, the grand potential of the system with the density profile $n_a(\boldsymbol{r})$ and the external field $\psi_b(\boldsymbol{r})$, in terms of the known quantity $\Omega[n_a, \psi_a]$. To figure out their difference $\Omega[n_a, \psi_b] - \Omega[n_a, \psi_a]$, we consider the system in equilibrium under ψ_a and imagine suddenly changing the field to ψ_b. At this very moment, that is, before the system starts to respond to the new field, the system is characterized by the density profile n_a and the external field ψ_b. What would the value of Ω be? We recall the definition of the grand potential (2.202) and Gibbs's entropy formula

$$S = -k_B \langle \ln(h^{3N} N! \rho) \rangle \tag{7.63}$$

from Exercise 4.9. Then,

$$\Omega = U - TS - \mu \langle N \rangle = \langle H_N \rangle + k_B T \langle \ln(h^{3N} N! \rho) \rangle - \mu \int_V n(\boldsymbol{r}) \mathrm{d}\boldsymbol{r} \,, \tag{7.64}$$

in which ρ is the statistical weight. If we suppose that ρ has yet to adjust itself to the new field, the only difference between $\Omega[n_a, \psi_a]$ and $\Omega[n_a, \psi_b]$ is in $\langle H_N \rangle$, implying that

$$\Omega[n_a,\psi_b]-\Omega[n_a,\psi_a]=\left\langle\sum_{i=1}^{N}[\psi_b(\boldsymbol{r}_i)-\psi_a(\boldsymbol{r}_i)]\right\rangle=\int_V n_a(\boldsymbol{r})[\psi_b(\boldsymbol{r})-\psi_a(\boldsymbol{r})]\mathrm{d}\boldsymbol{r}\,, \tag{7.65}$$

where the last step follows from (7.54). So,

$$\Omega[n_a,\psi_b]=\Omega[n_a,\psi_a]+\int_V n_a(\boldsymbol{r})[\psi_b(\boldsymbol{r})-\psi_a(\boldsymbol{r})]\mathrm{d}\boldsymbol{r}\,. \tag{7.66}$$

To compute $\Omega[n_a,\psi_b]$, we need to find the field ψ_a that produces n_a as the equilibrium density profile. Theorem 7.3 in Sect. 7.3 guarantees the existence of such ψ_a.

Gibbs's entropy formula was established *only* for systems in equilibrium. By applying (7.63) to the nonequilibrium state, we have actually adopted a particular *definition* of $\Omega[n_a,\psi_b]$ among others that may be equally plausible. What matters here, though, is that (7.66) is compatible with the principle of thermodynamics. That is, $n_a=n_b$ is a solution of (7.47) when Ω is given by (7.66). Exercise 7.6 verifies this statement for the case of an ideal gas. For a more general demonstration, see Exercise 7.8. The issue discussed here has a statistical mechanical counterpart. See paragraph containing (7.94).

Exercise 7.6. Let us build on the Exercise 7.5 and examine the density functional for an ideal gas:

a. Show that

$$\Omega[n_a,\psi_b]=k_BT\int_V n_a(\boldsymbol{r})\left[\ln\frac{n_a(\boldsymbol{r})}{n_b(\boldsymbol{r})}-1\right]\mathrm{d}\boldsymbol{r}\,. \tag{7.67}$$

b. Show that

$$\Omega[n_a,\psi_b]=k_BT\int_V n_a(\boldsymbol{r})[\ln\Lambda^3 n_a(\boldsymbol{r})-1]\mathrm{d}\boldsymbol{r}-\int_V n_a(\boldsymbol{r})[\mu-\psi_b(\boldsymbol{r})]\mathrm{d}\boldsymbol{r}\,. \tag{7.68}$$

c. Use (7.67) in (7.47) to show that $n_a=n_b$ at equilibrium.

d. Use (7.68) in (7.47) to obtain (7.57). ///

7.2.4 †A Few Remarks on $\Omega[n_a,\psi_b]$

Taking the functional derivative of (7.66) with respect to ψ_b while holding n_a fixed, we find

$$\frac{\delta\Omega[n_a,\psi_b]}{\delta\psi_b(\boldsymbol{r})}=n_a(\boldsymbol{r})\,,\quad \text{fixed } n_a\,. \tag{7.69}$$

Similarly, the functional derivative of (7.66) with respect to ψ_a with n_a fixed yields

$$\frac{\delta\Omega[n_a,\psi_a]}{\delta\psi_a(\boldsymbol{r})} = n_a(\boldsymbol{r}) \;, \quad \text{fixed } n_a \;. \tag{7.70}$$

These results appear identical to (7.56). However, (7.56) was obtained without imposing any constraint on the density profile. In fact, our derivation of (7.56) amounts to comparing the values of Ω of the system *in equilibrium* under slightly different external fields.

Therefore, it is of some interest to derive (7.56) directly from (7.66). Given a system in equilibrium under the external field ψ_a, we perturb the field while allowing the system to adjust n_a so as to maintain the equilibrium. We denote the modified field by $\psi_a + \delta\psi$ and the corresponding equilibrium density profile by $n_a + \delta n$. Then,

$$\begin{aligned}&\Omega[n_a+\delta n,\psi_a+\delta\psi]-\Omega[n_a,\psi_a]\\ &\quad=\Omega[n_a+\delta n,\psi_a+\delta\psi]-\Omega[n_a+\delta n,\psi_a]+\Omega[n_a+\delta n,\psi_a]-\Omega[n_a,\psi_a]\;.\end{aligned} \tag{7.71}$$

Using (7.66),

$$\begin{aligned}&\Omega[n_a+\delta n,\psi_a+\delta\psi]-\Omega[n_a+\delta n,\psi_a]\\ &\qquad=\int_V[n_a(\boldsymbol{r})+\delta n(\boldsymbol{r})]\delta\psi(\boldsymbol{r})\mathrm{d}\boldsymbol{r}=\int_V n_a(\boldsymbol{r})\delta\psi(\boldsymbol{r})\mathrm{d}\boldsymbol{r}+\text{h.o.}\;,\end{aligned} \tag{7.72}$$

while

$$\Omega[n_a+\delta n,\psi_a]-\Omega[n_a,\psi_a]=\text{h.o.} \tag{7.73}$$

because n_a is the equilibrium density profile for the field ψ_a. It follows that

$$\delta\Omega=\int_V n_a(\boldsymbol{r})\delta\psi(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \tag{7.74}$$

for the perturbation under consideration. Thus,

$$\frac{\delta\Omega}{\delta\psi_a(\boldsymbol{r})}=n_a(\boldsymbol{r})\;, \tag{7.75}$$

which is (7.56).

Equation (7.66) may be rewritten in a physically more illuminating manner. For this purpose, let us first define what may be referred to as the **intrinsic grand potential** by

$$\Omega_{\text{int}}[n_a,\psi_a]:=\Omega[n_a,\psi_a]-\int_V n_a(\boldsymbol{r})\psi_a(\boldsymbol{r})\mathrm{d}\boldsymbol{r}\;, \tag{7.76}$$

which is the part of the grand potential of the system in equilibrium that excludes the contribution to $\langle H_N\rangle$ from the external field.

We also recall from (7.62) that $n_a(\boldsymbol{r})$ is uniquely determined by $\psi_a(\boldsymbol{r})$. Thus, the explicit reference to n_a in $\Omega_{\mathrm{int}}[n_a, \psi_a]$ is redundant and can be dropped. Moreover, as we shall show in Sect. 7.3, it is also true that $n_a(\boldsymbol{r})$ uniquely determines $\psi_a(\boldsymbol{r})$. That is, $\psi_a(\boldsymbol{r})$ is a functional of $n_a(\boldsymbol{r})$:

$$\psi_a(\boldsymbol{r}) = \psi(\boldsymbol{r}, n_a] \tag{7.77}$$

and the functional dependence on ψ_a may be replaced by that on n_a. In summary, therefore,

$$\Omega_{\mathrm{int}}[n_a, \psi_a] = \Omega_{\mathrm{int}}[\psi_a] = \Omega_{\mathrm{int}}[n_a] \, . \tag{7.78}$$

Using (7.76) and (7.78), we can rewrite (7.66) as

$$\Omega[n_a, \psi_b] = \Omega_{\mathrm{int}}[n_a] + \int_V n_a(\boldsymbol{r})\psi_b(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \, , \tag{7.79}$$

which is the desired expression indicating that $\Omega[n_a, \psi_b]$ is the sum of two contributions. One is the intrinsic part of the grand potential of the system in equilibrium with the density profile n_a. The other is the potential energy due to the external field ψ_b.

Dropping references to ψ_a and n_a, respectively, from Ω_{int} and Ω in (7.76), we obtain

$$\Omega_{\mathrm{int}}[n_a] = \Omega[\psi_a] - \int_V n_a(\boldsymbol{r})\psi_a(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \, . \tag{7.80}$$

In view of (7.75), Ω_{int} is a Legendre transform of Ω.[42] Accordingly, we anticipate that

$$\frac{\delta \Omega_{\mathrm{int}}}{\delta n_a(\boldsymbol{r})} = -\psi_a(\boldsymbol{r}) \, . \tag{7.81}$$

Exercise 7.7. Derive (7.81). ///

Exercise 7.8. Using (7.66), show that $n_b(\boldsymbol{r})$ satisfies (7.47). ///

7.3 Formal Development

In Sect. 7.2.1, we introduced the notion of density functional purely on the basis of thermodynamics. The subsequent development made only a very modest use of the concepts from statistical mechanics. While this may help us develop physical intuitions about DFT, the ultimate goal of the theory is to generate the fundamental equation of an inhomogeneous system starting from the Hamiltonian. That is, DFT is one example among many applications of statistical mechanics, and warrants a purely statistical mechanical formulation.

7.3.1 Definitions

Consider a grand canonical ensemble and let $\rho(\boldsymbol{r}^N,\boldsymbol{p}^N,N)$ denote a probability distribution over all possible microstates. The equilibrium probability distribution

$$\rho^{\mathrm{eq}}(\boldsymbol{r}^N,\boldsymbol{p}^N,N)=\frac{1}{\Xi^{\mathrm{eq}}}\frac{e^{\beta[\mu N-H_N(\boldsymbol{r}^N,\boldsymbol{p}^N)]}}{h^{3N}N!}\ , \tag{7.82}$$

in which Ξ^{eq} is the grand canonical partition function, is an example of ρ. In DFT, however, we consider more general probability distributions. So, the form of the function ρ is arbitrary except that it must satisfy the normalization condition:

$$\mathrm{Tr}^{\mathrm{cl}}\{\rho(\boldsymbol{r}^N,\boldsymbol{p}^N,N)\}=1\ , \tag{7.83}$$

where $\mathrm{Tr}^{\mathrm{cl}}$ is the so-called **classical trace**, and is defined by

$$\mathrm{Tr}^{\mathrm{cl}}\{A(\boldsymbol{r}^N,\boldsymbol{p}^N,N)\}=\sum_{N=0}^{\infty}\int A(\boldsymbol{r}^N,\boldsymbol{p}^N,N)\mathrm{d}\boldsymbol{r}^N\mathrm{d}\boldsymbol{p}^N\ . \tag{7.84}$$

For example,

$$\Xi^{\mathrm{eq}}=\mathrm{Tr}^{\mathrm{cl}}\left\{\frac{e^{\beta(\mu N-H_N)}}{h^{3N}N!}\right\}\ . \tag{7.85}$$

We now define a functional of ρ by

$$\Omega[\rho]:=\mathrm{Tr}^{\mathrm{cl}}\left\{\rho\left[H_N-\mu N+k_BT\ln(h^{3N}N!\rho)\right]\right\}\ . \tag{7.86}$$

7.3.2 Key Properties of the Density Functional

Let us record the following three key properties of the functional $\Omega[\rho]$ as theorems and collect their proofs in Sect. 7.3.3.

Theorem 7.1.

$$\Omega[\rho^{\mathrm{eq}}]=-k_BT\ln\Xi^{\mathrm{eq}}\ , \tag{7.87}$$

which we recognize as the grand potential.

Theorem 7.2.

$$\Omega[\rho]\geq\Omega[\rho^{\mathrm{eq}}]\ , \tag{7.88}$$

where the equality holds if and only if $\rho\equiv\rho^{\mathrm{eq}}$.

Theorem 7.3. *Suppose that* ρ *may be written as*

$$\rho(\boldsymbol{r}^N,\boldsymbol{p}^N,N)=\frac{1}{\Xi}\frac{e^{\beta[\mu N-H_N^0-\sum_{i=1}^N u(\boldsymbol{r}_i)]}}{h^{3N}N!} \tag{7.89}$$

with the constant Ξ *determined by (7.83). Here,*

$$H_N^0 := \sum_{i=1}^{N} \frac{\|\boldsymbol{p}_i\|^2}{2m} + \phi(\boldsymbol{r}^N) \tag{7.90}$$

is the Hamiltonian of the system excluding the external field ψ*. If we limit our consideration to* ρ *that can be expressed as (7.89), there is a one-to-one correspondence between* ρ *and the density profile*

$$n(\boldsymbol{r}) = \mathrm{Tr}^{\mathrm{cl}}\{\rho \hat{n}\} , \tag{7.91}$$

where $\hat{n}$ *is the density operator defined by (7.49).*

The actual system of our interest is subject to the external field $\psi(\boldsymbol{r})$. Thus, ρ defined by (7.89) is not the equilibrium distribution unless $u(\boldsymbol{r}) \equiv \psi(\boldsymbol{r})$. Equation (7.91) gives the equilibrium density profile of the system if it is subject to the external field $u(\boldsymbol{r})$ in place of $\psi(\boldsymbol{r})$.

By virtue of Theorem 7.3, Ω may be expressed as a functional of n:

$$\Omega[\rho] = \Omega[n] . \tag{7.92}$$

(It must be clearly understood that the explicit form of the functional $\Omega[\rho]$ differs from that of $\Omega[n]$.) Theorem 7.2 then reads

$$\Omega[n] \geq \Omega[n^{\mathrm{eq}}] \tag{7.93}$$

with the equality holding if and only if $n \equiv n^{\mathrm{eq}}$. This is a statistical mechanical version of (7.44).

Finally, (7.89) does *not* exhaust all possible forms of ρ. For example,

$$\rho(\boldsymbol{r}^N, \boldsymbol{p}^N, N) \propto \exp\left\{\beta\left[\mu N - H_N^0(\boldsymbol{r}^N, \boldsymbol{p}^N) + f(\boldsymbol{p}^N)\right]\right\} \tag{7.94}$$

cannot be written in the form of (7.89). The same applies if we have $f(\|\boldsymbol{r}_2 - \boldsymbol{r}_1\|)$ in place of $f(\boldsymbol{p}^N)$, for example. The point, however, is that ρ in the form of (7.89) is sufficient to guarantee the existence of the density functional $\Omega[n]$ that is compatible with the principle of thermodynamics embodied in (7.44).

Example 7.4. Statistical mechanical derivation of (7.66): Consider a system with the density profile $n_a(\boldsymbol{r})$ in the presence of the external field $u_b(\boldsymbol{r})$. Given $n_a(\boldsymbol{r})$, Theorem 7.3 guarantees the existence of the corresponding ρ_a (and hence of u_a):

$$\rho_a = \frac{1}{\Xi_a} \frac{e^{\beta[\mu N - H_N^0 - \sum_{i=1}^N u_a(\boldsymbol{r}_i)]}}{h^{3N} N!} . \tag{7.95}$$

Using this expression in (7.86), we obtain

$$\Omega[n_a, u_b] = \mathrm{Tr}^{\mathrm{cl}} \left\{ \rho_a \left[H_N^0 + \sum_{i=1}^{N} u_b(\boldsymbol{r}_i) - \mu N + k_B T \ln(h^{3N} N! \rho_a) \right] \right\} \tag{7.96}$$

Replacing u_b by u_a,

$$\Omega[n_a, u_a] = \mathrm{Tr}^{\mathrm{cl}} \left\{ \rho_a \left[H_N^0 + \sum_{i=1}^{N} u_a(\boldsymbol{r}_i) - \mu N + k_B T \ln(h^{3N} N! \rho_a) \right] \right\} \tag{7.97}$$

Subtracting (7.97) from (7.96), we obtain

$$\Omega[n_a, u_b] - \Omega[n_a, u_a] = \mathrm{Tr}^{\mathrm{cl}} \left\{ \rho_a \sum_{i=1}^{N} [u_b(\boldsymbol{r}_i) - u_a(\boldsymbol{r}_i)] \right\} . \tag{7.98}$$

Using the density operator,

$$\begin{aligned} \mathrm{Tr}^{\mathrm{cl}} \left\{ \rho_a \sum_{i=1}^{N} [u_b(\boldsymbol{r}_i) - u_a(\boldsymbol{r}_i)] \right\} &= \mathrm{Tr}^{\mathrm{cl}} \left\{ \rho_a \int_V \hat{n}(\boldsymbol{r}, \boldsymbol{r}^N) [u_b(\boldsymbol{r}) - u_a(\boldsymbol{r})] \mathrm{d}\boldsymbol{r} \right\} \\ = \int_V \mathrm{Tr}^{\mathrm{cl}} \{\rho_a \hat{n}\} [u_b(\boldsymbol{r}) - u_a(\boldsymbol{r})] \mathrm{d}\boldsymbol{r} &= \int_V n_a(\boldsymbol{r}) [u_b(\boldsymbol{r}) - u_a(\boldsymbol{r})] \mathrm{d}\boldsymbol{r} , \end{aligned} \tag{7.99}$$

where we used (7.91). Thus,

$$\Omega[n_a, u_b] - \Omega[n_a, u_a] = \int_V n_a(\boldsymbol{r}) [u_b(\boldsymbol{r}) - u_a(\boldsymbol{r})] \mathrm{d}\boldsymbol{r} , \tag{7.100}$$

which is (7.66).

7.3.3 †*Proofs of Theorems*

Let us prove the theorems just introduced.

Proof of Theorem 7.1

We have only to replace ρ in (7.86) by ρ^{eq} and substitute (7.82) for the second ρ^{eq}. □

Proof of Theorem 7.2

$$\begin{aligned}\Omega[\rho] &= \mathrm{Tr}^{\mathrm{cl}}\left\{\rho\left[H_N-\mu N+k_BT\ln(h^{3N}N!\rho)\right]\right\} \\ &= \mathrm{Tr}^{\mathrm{cl}}\left\{\rho\left[H_N-\mu N+k_BT\ln(h^{3N}N!\rho^{\mathrm{eq}})\right]\right\}+k_BT\mathrm{Tr}^{\mathrm{cl}}\left\{\rho\left(\ln\rho-\ln\rho^{\mathrm{eq}}\right)\right\} \\ &\geq \mathrm{Tr}^{\mathrm{cl}}\left\{\rho\left[H_N-\mu N+k_BT\ln(h^{3N}N!\rho^{\mathrm{eq}})\right]\right\}\ ,\end{aligned} \tag{7.101}$$

where we used the Gibbs–Bogoliubov inequality discussed in Appendix B.5. The equality in (7.101) holds if and only if $\rho \equiv \rho^{\mathrm{eq}}$.

From (7.82),

$$k_BT\ln(h^{3N}N!\rho^{\mathrm{eq}}) = \mu N - H_N - k_BT\ln\Xi^{\mathrm{eq}} = \mu N - H_N + \Omega[\rho^{\mathrm{eq}}]\ , \tag{7.102}$$

which is now substituted into (7.101) to give

$$\Omega[\rho] \geq \mathrm{Tr}^{\mathrm{cl}}\{\rho\Omega[\rho^{\mathrm{eq}}]\} = \Omega[\rho^{\mathrm{eq}}]\mathrm{Tr}^{\mathrm{cl}}\{\rho\} = \Omega[\rho^{\mathrm{eq}}]\ . \tag{7.103}$$

The second step is justified because $\Omega[\rho^{\mathrm{eq}}]$, being a quantity obtained after the classical trace, does not dependent on $\boldsymbol{r}^N$, $\boldsymbol{p}^N$, or N. The last step follows from the normalization condition (7.83). ☐

Proof of Theorem 7.3

For a given $u(\boldsymbol{r})$, ρ is completely determined by (7.89). The corresponding $n(\boldsymbol{r})$ follows from (7.91). Pictorially, we have

$$u \longrightarrow \rho \longrightarrow n\ . \tag{7.104}$$

The content of Theorem 7.3 is that, if we limit ourselves to ρ written in the form of (7.89), there is always one and only one ρ that corresponds to *any* density $n(\boldsymbol{r})$ we prescribe to the system. In view of (7.104), it is sufficient to prove the existence and the uniqueness of $u(\boldsymbol{r})$ that produces the given $n(\boldsymbol{r})$:

$$n \longrightarrow u\ . \tag{7.105}$$

By (7.91), $n(\boldsymbol{r})$ is the *equilibrium* density profile of the system subject to the field $u(\boldsymbol{r})$ instead of $\psi(\boldsymbol{r})$. Using the notation introduced in (7.62), therefore, we have

$$n(\boldsymbol{r}) = n^{\mathrm{eq}}(\boldsymbol{r},u]\ . \tag{7.106}$$

The claim we wish to prove is that (7.106), regarded as an equation for $u(\boldsymbol{r})$, has a unique solution for any $n(\boldsymbol{r})$. We prove the uniqueness of $u(\boldsymbol{r})$ first and then argue for its existence.

Uniqueness

The proof is by contradiction. Suppose that

$$n(\boldsymbol{r}) = n^{\mathrm{eq}}(\boldsymbol{r}, u_a] = n^{\mathrm{eq}}(\boldsymbol{r}, u_b] \,, \tag{7.107}$$

where u_a and u_b are two *distinct* external fields, for which (7.89) reads

$$\rho_a = \frac{1}{\Xi_a} \frac{e^{\beta[\mu N - H_N^0 - \sum_{i=1}^N u_a(\boldsymbol{r}_i)]}}{h^{3N} N!} \quad \text{and} \quad \rho_b = \frac{1}{\Xi_b} \frac{e^{\beta[\mu N - H_N^0 - \sum_{i=1}^N u_b(\boldsymbol{r}_i)]}}{h^{3N} N!} \,, \tag{7.108}$$

respectively. By (7.86) and Theorem 7.2, we have

$$\begin{aligned} \Omega[\rho_a] &= \mathrm{Tr}^{\mathrm{cl}} \left\{ \rho_a \left[H_N^0 - \mu N + k_B T \ln(h^{3N} N! \rho_a) + \sum_{i=1}^N u_a(\boldsymbol{r}_i) \right] \right\} \\ &< \mathrm{Tr}^{\mathrm{cl}} \left\{ \rho_b \left[H_N^0 - \mu N + k_B T \ln(h^{3N} N! \rho_b) + \sum_{i=1}^N u_a(\boldsymbol{r}_i) \right] \right\} \\ &= \Omega[\rho_b] + \mathrm{Tr}^{\mathrm{cl}} \left\{ \rho_b \sum_{i=1}^N [u_a(\boldsymbol{r}_i) - u_b(\boldsymbol{r}_i)] \right\} \,. \end{aligned} \tag{7.109}$$

Using (7.99), we find

$$\Omega[\rho_a] < \Omega[\rho_b] + \int_V n(\boldsymbol{r})[u_a(\boldsymbol{r}) - u_b(\boldsymbol{r})] \mathrm{d}\boldsymbol{r} \,. \tag{7.110}$$

Similarly,

$$\Omega[\rho_b] < \Omega[\rho_a] + \int_V n(\boldsymbol{r})[u_b(\boldsymbol{r}) - u_a(\boldsymbol{r})] \mathrm{d}\boldsymbol{r} \,. \tag{7.111}$$

Adding these two inequalities, we arrive at the contradiction:

$$\Omega[\rho_a] + \Omega[\rho_b] < \Omega[\rho_a] + \Omega[\rho_b] \,. \tag{7.112}$$

Thus, $u_a \equiv u_b$. □

Existence

Suppose that a system is under the external field $u(\boldsymbol{r})$. Left undisturbed, the system will eventually reach a state of equilibrium, in which

$$n(\boldsymbol{r}) = n^{\mathrm{eq}}(\boldsymbol{r}, u] \,. \tag{7.113}$$

So, at least for this $n(\boldsymbol{r})$, the corresponding external field does exist.

Now we show that the external field exists also for any density profile that is infinitesimally different from $n(\boldsymbol{r})$. For this purpose, we consider an infinitesimal perturbation $\delta u(\boldsymbol{r})$ to the field. According to the definition of the functional derivative, the response is given by

$$\delta n(\boldsymbol{r}) = \int_V \frac{\delta n(\boldsymbol{r})}{\delta u(\boldsymbol{r}')} \delta u(\boldsymbol{r}')\mathrm{d}\boldsymbol{r}' \tag{7.114}$$

to the first order of the variation.

As we have seen, $u(\boldsymbol{r})$ for a given $n(\boldsymbol{r})$ is unique. So, any distinct perturbations $\delta u_1(\boldsymbol{r}')$ and $\delta u_2(\boldsymbol{r}')$ produce distinct responses $\delta n_1(\boldsymbol{r})$ and $\delta n_2(\boldsymbol{r})$, respectively.[43] Conversely, it is clear from (7.89) and (7.91) that distinct responses can result only from distinct perturbations of the field. It follows that (7.114) is invertible and we can write

$$\delta u(\boldsymbol{r}') = \int_V \frac{\delta u(\boldsymbol{r}')}{\delta n(\boldsymbol{r})} \delta n(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \,. \tag{7.115}$$

By means of this equation, we can compute $\delta u(\boldsymbol{r}')$ that produces any response $\delta n(\boldsymbol{r})$ we desire.[44]

What about an arbitrary density profile $n_b(\boldsymbol{r})$ that may differ from the initial equilibrium profile $n_a(\boldsymbol{r}) = n^{\mathrm{eq}}(\boldsymbol{r}, u_a]$ by more than an infinitesimal amount? In this case, we can apply (7.115) repeatedly to a series of infinitesimal variations $\delta n(\boldsymbol{r})$ until we eventually arrive at the desired profile. The corresponding field $u_b(\boldsymbol{r}')$ is the initial field $u_a(\boldsymbol{r}')$ plus the sum of all the infinitesimal variations $\delta u(\boldsymbol{r}')$ evaluated by (7.115) along the way. As an example, consider a particular path specified by

$$n_\lambda(\boldsymbol{r}) = n_a(\boldsymbol{r}) + \lambda[n_b(\boldsymbol{r}) - n_a(\boldsymbol{r})] \,, \quad 0 \le \lambda \le 1 \,. \tag{7.116}$$

The thermodynamic integration method described in the next section leads to

$$u_b(\boldsymbol{r}') = u_a(\boldsymbol{r}') + \int_0^1 \int_V \frac{\delta u_\lambda(\boldsymbol{r}')}{\delta n_\lambda(\boldsymbol{r})} [n_b(\boldsymbol{r}) - n_a(\boldsymbol{r})]\mathrm{d}\boldsymbol{r}\mathrm{d}\lambda \,, \tag{7.117}$$

where $n_\lambda(\boldsymbol{r}) = n^{\mathrm{eq}}(\boldsymbol{r}, u_\lambda]$. ☐

Substituting (7.115) with $\boldsymbol{r}$ replaced by $\boldsymbol{r}''$ into (7.114), we see that

$$\begin{aligned} \delta n(\boldsymbol{r}) &= \int_V \frac{\delta n(\boldsymbol{r})}{\delta u(\boldsymbol{r}')} \left[\int_V \frac{\delta u(\boldsymbol{r}')}{\delta n(\boldsymbol{r}'')} \delta n(\boldsymbol{r}'')\mathrm{d}\boldsymbol{r}'' \right] \mathrm{d}\boldsymbol{r}' \\ &= \int_V \left[\int_V \frac{\delta n(\boldsymbol{r})}{\delta u(\boldsymbol{r}')} \frac{\delta u(\boldsymbol{r}')}{\delta n(\boldsymbol{r}'')} \mathrm{d}\boldsymbol{r}' \right] \delta n(\boldsymbol{r}'')\mathrm{d}\boldsymbol{r}'' \,. \end{aligned} \tag{7.118}$$

It follows that

$$\int_V \frac{\delta n(\boldsymbol{r})}{\delta u(\boldsymbol{r}')} \frac{\delta u(\boldsymbol{r}')}{\delta n(\boldsymbol{r}'')} \mathrm{d}\boldsymbol{r}' = \delta(\boldsymbol{r} - \boldsymbol{r}'') \,. \tag{7.119}$$

The two functional derivatives in the integrand are said to be the **functional inverse** of each other.

7.4 Construction of a Density Functional

Before DFT can be utilized for any practical purposes, we must identify the explicit form of the density functional. The basic tool we use for this purpose is the **thermodynamic integration method**. That is, we first compute $\delta\Omega$ in response to a particular variation either of the external field and/or the intermolecular potential. The resulting expression is then integrated from a reference state for which Ω is known to the actual state of our interest.

Because the functional derivative, to which $\delta\Omega$ is related, and the subsequent integration are the opposite operations, it seems strange to suggest that anything useful should come out of this. Nevertheless, the functional derivative gives rise to quantities which afford direct physical interpretations. This opens up the possibility of developing physically meaningful approximations for them even if they may be difficult to evaluate exactly.

7.4.1 *Variation of the External Field*

Consider a system in equilibrium subject to the external field ψ_a. The quantity of interest is the difference

$$\Omega[n_b, \psi_b] - \Omega[n_a, \psi_a] \,. \tag{7.120}$$

Since the expression involves only the equilibrium density profiles, this is the reversible work required to change the external field from ψ_a to ψ_b. To compute this quantity, we use a reversible work source to generate an external field

$$\lambda[\psi_b(\boldsymbol{r}) - \psi_a(\boldsymbol{r})] \tag{7.121}$$

so that the total external field experienced by the system is

$$\psi_\lambda(\boldsymbol{r}) := \psi_a(\boldsymbol{r}) + \lambda[\psi_b(\boldsymbol{r}) - \psi_a(\boldsymbol{r})] \,. \tag{7.122}$$

Clearly, $\psi_{\lambda=0} = \psi_a$ and $\psi_{\lambda=1} = \psi_b$. If we change λ very slowly from 0 to 1, the system will have a sufficient time to establish the equilibrium density profile

$$n_\lambda(\boldsymbol{r}) := n^{\text{eq}}(\boldsymbol{r}, \psi_\lambda] \tag{7.123}$$

at each value of λ. Such a process is reversible.

Now, recalling the definition of the functional derivative and using (7.56), in which $n(\boldsymbol{r})$ is the equilibrium density profile for a given external field, we have

$$\delta\Omega[\psi_\lambda] = \int_V \frac{\delta\Omega}{\delta\psi_\lambda(\boldsymbol{r})}\delta\psi_\lambda(\boldsymbol{r})\mathrm{d}\boldsymbol{r} = \int_V n_\lambda(\boldsymbol{r})\delta\psi_\lambda(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \,. \tag{7.124}$$

According to (7.122),

$$\delta\psi_\lambda(\boldsymbol{r}) = [\psi_b(\boldsymbol{r}) - \psi_a(\boldsymbol{r})]\delta\lambda \tag{7.125}$$

for an infinitesimal change in λ and (7.124) becomes

$$\delta\Omega[\psi_\lambda] = \int_V n_\lambda(\boldsymbol{r})[\psi_b(\boldsymbol{r}) - \psi_a(\boldsymbol{r})]\delta\lambda \mathrm{d}\boldsymbol{r} . \tag{7.126}$$

Dividing both sides by $\delta\lambda$ and taking the limit of $\delta\lambda \to 0$, we obtain

$$\frac{\partial\Omega}{\partial\lambda} = \int_V n_\lambda(\boldsymbol{r})[\psi_b(\boldsymbol{r}) - \psi_a(\boldsymbol{r})]\mathrm{d}\boldsymbol{r} . \tag{7.127}$$

We now integrate this expression from $\lambda = 0$ to $\lambda = 1$ and obtain

$$\Omega[n_b, \psi_b] = \Omega[n_a, \psi_a] + \int_0^1 \int_V n_\lambda(\boldsymbol{r})[\psi_b(\boldsymbol{r}) - \psi_a(\boldsymbol{r})]\mathrm{d}\boldsymbol{r}\mathrm{d}\lambda . \tag{7.128}$$

7.4.2 Variation of the Intermolecular Potential: Case 1

Consider a system in equilibrium under the external field ψ. This time, the thermodynamic integration involves a continuous change in the intermolecular potential $\phi(\boldsymbol{r}^N)$. But, the external field will be held fixed.

We assume the **pairwise additivity** of the intermolecular potential and write

$$\phi(\boldsymbol{r}^N) = \frac{1}{2}\sum_{i=1}^{N}{\sum_{j=1}^{N}}' v(\boldsymbol{r}_i, \boldsymbol{r}_j) , \tag{7.129}$$

where v is referred to as the **pair potential** and $'$ indicates that the $j = i$ term is excluded from the second sum.

The quantity of our interest is the difference

$$\Omega[n_b, v_b] - \Omega[n_a, v_a] , \tag{7.130}$$

where

$$n_a(\boldsymbol{r}) := n^{\mathrm{eq}}(\boldsymbol{r}, v_a] . \tag{7.131}$$

is the equilibrium density profile when the pair potential is $v_a(\boldsymbol{r})$. Similarly for n_b.

In order to consider the functional derivative of Ω with respect to v, we define

$$\hat{I}(\boldsymbol{r}, \boldsymbol{r}') := \sum_{i=1}^{N}{\sum_{j=1}^{N}}' \delta(\boldsymbol{r} - \boldsymbol{r}_i)\delta(\boldsymbol{r}' - \boldsymbol{r}_j) \tag{7.132}$$

and rewrite (7.129) as

$$\phi(\boldsymbol{r}^N) = \frac{1}{2}\int_V\int_V \hat{I}(\boldsymbol{r}, \boldsymbol{r}')v(\boldsymbol{r}, \boldsymbol{r}')\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}' . \tag{7.133}$$

Using (7.133) in (7.53) and recalling (7.41), we observe that

$$\frac{\delta \Omega}{\delta v(\boldsymbol{r},\boldsymbol{r}')} = \frac{1}{2}\langle \hat{I}(\boldsymbol{r},\boldsymbol{r}',\boldsymbol{r}^N)\rangle =: \frac{1}{2}n^{(2)}(\boldsymbol{r},\boldsymbol{r}') =: \frac{1}{2}n(\boldsymbol{r})n(\boldsymbol{r}')g(\boldsymbol{r},\boldsymbol{r}') \, , \tag{7.134}$$

in which $n^{(2)}(\boldsymbol{r},\boldsymbol{r}')$ and $g(\boldsymbol{r},\boldsymbol{r}')$ are called, respectively, the **pair distribution function** and the **radial distribution function**. Their physical content will be discussed in Sect. 7.4.4. Using g, we can write

$$\delta \Omega = \frac{1}{2}\int_V\int_V n(\boldsymbol{r})n(\boldsymbol{r}')g(\boldsymbol{r},\boldsymbol{r}')\delta v(\boldsymbol{r},\boldsymbol{r}')\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}' \, , \tag{7.135}$$

in which n and g are to be computed for the system in equilibrium before we made an infinitesimal change in the pair potential.

As in the previous subsection, let

$$v_\lambda(\boldsymbol{r},\boldsymbol{r}') := v_a(\boldsymbol{r},\boldsymbol{r}') + \lambda[v_b(\boldsymbol{r},\boldsymbol{r}') - v_a(\boldsymbol{r},\boldsymbol{r}')] \, , \tag{7.136}$$

which is v_a if $\lambda = 0$ and v_b if $\lambda = 1$. For this particular choice of v_λ,

$$\delta v_\lambda(\boldsymbol{r},\boldsymbol{r}') = [v_b(\boldsymbol{r},\boldsymbol{r}') - v_a(\boldsymbol{r},\boldsymbol{r}')]\delta\lambda \, . \tag{7.137}$$

Substituting this expression into (7.135), dividing the resulting equation by $\delta\lambda$, and then taking the $\delta\lambda \to 0$ limit, we obtain

$$\frac{\partial \Omega}{\partial \lambda} = \frac{1}{2}\int_V\int_V n_\lambda(\boldsymbol{r})n_\lambda(\boldsymbol{r}')g_\lambda(\boldsymbol{r},\boldsymbol{r}')[v_b(\boldsymbol{r},\boldsymbol{r}') - v_a(\boldsymbol{r},\boldsymbol{r}')]\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}' \, , \tag{7.138}$$

where g_λ and n_λ are, respectively, the radial distribution function and the equilibrium density profile in the system in which the pair potential is v_λ. Integrating (7.138) with respect to λ, we find

$$\begin{aligned} \Omega[n_b,v_b] &= \Omega[n_a,v_a] \\ &\quad + \frac{1}{2}\int_0^1\int_V\int_V n_\lambda(\boldsymbol{r})n_\lambda(\boldsymbol{r}')g_\lambda(\boldsymbol{r},\boldsymbol{r}')[v_b(\boldsymbol{r},\boldsymbol{r}') - v_a(\boldsymbol{r},\boldsymbol{r}')]\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}'\mathrm{d}\lambda \, . \end{aligned} \tag{7.139}$$

7.4.3 Variation of the Intermolecular Potential: Case 2

In Sect. 7.4.1, we considered the variation of the external field $\psi(\boldsymbol{r})$ without changing the functional form of the pair potential $v(\boldsymbol{r},\boldsymbol{r}')$. In Sect. 7.4.2, the functional form of $\psi(\boldsymbol{r})$ was fixed while $v(\boldsymbol{r},\boldsymbol{r}')$ was varied. In both cases, this meant that the density profile had to change along the integration path.

However, Theorem 7.3 guarantees the existence of $\psi(\boldsymbol{r})$ for *any* equilibrium density profile we prescribe to the system. This means that, as we vary $v(\boldsymbol{r},\boldsymbol{r}')$, we can always adjust $\psi(\boldsymbol{r})$ to maintain the same equilibrium density profile. For the particular variation given by (7.137), we have

$$\delta\Omega = \int_V n(\boldsymbol{r})\delta\psi_\lambda(\boldsymbol{r})\mathrm{d}\boldsymbol{r} + \frac{1}{2}\int_V\int_V n(\boldsymbol{r})n(\boldsymbol{r}')g_\lambda(\boldsymbol{r},\boldsymbol{r}')[v_b(\boldsymbol{r},\boldsymbol{r}') - v_a(\boldsymbol{r},\boldsymbol{r}')]\delta\lambda\,\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}' \,, \tag{7.140}$$

where $\delta\psi_\lambda(\boldsymbol{r})$ is the adjustment that must be made to the external field in order to keep the density profile unchanged when v_λ is varied by an infinitesimal amount. Dividing (7.140) by $\delta\lambda$ and taking the $\delta\lambda \to 0$ limit, we obtain

$$\frac{\partial\Omega}{\partial\lambda} = \int_V n(\boldsymbol{r})\frac{\partial\psi_\lambda(\boldsymbol{r})}{\partial\lambda}\mathrm{d}\boldsymbol{r} + \frac{1}{2}\int_V\int_V n(\boldsymbol{r})n(\boldsymbol{r}')g_\lambda(\boldsymbol{r},\boldsymbol{r}')[v_b(\boldsymbol{r},\boldsymbol{r}') - v_a(\boldsymbol{r},\boldsymbol{r}')]\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}' \,. \tag{7.141}$$

We integrate this equation with respect to λ and obtain

$$\begin{aligned}\Omega[n,v_b] &= \Omega[n,v_a] + \int_V n(\boldsymbol{r})[\psi_b(\boldsymbol{r}) - \psi_a(\boldsymbol{r})]\mathrm{d}\boldsymbol{r} \\ &\quad + \frac{1}{2}\int_0^1\int_V\int_V n(\boldsymbol{r})n(\boldsymbol{r}')g_\lambda(\boldsymbol{r},\boldsymbol{r}')[v_b(\boldsymbol{r},\boldsymbol{r}') - v_a(\boldsymbol{r},\boldsymbol{r}')]\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}'\mathrm{d}\lambda \,,\end{aligned} \tag{7.142}$$

where $\psi_a(\boldsymbol{r})$ is the external field that yield $n(\boldsymbol{r})$ as the equilibrium density profile when the pair potential is $v_a(\boldsymbol{r},\boldsymbol{r}')$. Similarly for $\psi_b(\boldsymbol{r})$. Using (7.76), we rewrite (7.142) as

$$\begin{aligned}\Omega[n,v_b] &= \Omega_{\text{int}}[n,v_a] + \int_V n(\boldsymbol{r})\psi_b(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \\ &\quad + \frac{1}{2}\int_0^1\int_V\int_V n(\boldsymbol{r})n(\boldsymbol{r}')g_\lambda(\boldsymbol{r},\boldsymbol{r}')[v_b(\boldsymbol{r},\boldsymbol{r}') - v_a(\boldsymbol{r},\boldsymbol{r}')]\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}'\mathrm{d}\lambda \,.\end{aligned} \tag{7.143}$$

We now recall the relation $F = \Omega + \mu N$ and define the **intrinsic Helmholtz free energy** by

$$F_{\text{int}}[n,v_a] := \Omega_{\text{int}}[n,v_a] + \mu\int_V n(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \,. \tag{7.144}$$

Then, we can rewrite (7.143) as

$$\begin{aligned}\Omega[n,v_b] &= F_{\text{int}}[n,v_a] - \int_V n(\boldsymbol{r})[\mu - \psi_b(\boldsymbol{r})]\mathrm{d}\boldsymbol{r} \\ &\quad + \frac{1}{2}\int_0^1\int_V\int_V n(\boldsymbol{r})n(\boldsymbol{r}')g_\lambda(\boldsymbol{r},\boldsymbol{r}')[v_b(\boldsymbol{r},\boldsymbol{r}') - v_a(\boldsymbol{r},\boldsymbol{r}')]\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}'\mathrm{d}\lambda \,,\end{aligned} \tag{7.145}$$

which relates the grand potential of the system of our interest (with v_b) to the intrinsic Helmholtz free energy of the reference system (with v_a).

Combining (7.68), (7.79), and (7.144), we find

$$F_{\text{int}}^{\text{id}}[n] = k_BT\int_V n(\boldsymbol{r})[\ln\Lambda^3 n(\boldsymbol{r}) - 1]\mathrm{d}\boldsymbol{r} \tag{7.146}$$

for an ideal gas. As with (7.68), this result is exact. We now define the intrinsic **excess Helmholtz free energy** by

$$F^{\mathrm{exc}}_{\mathrm{int}}[n,v_a] := F_{\mathrm{int}}[n,v_a] - F^{\mathrm{id}}_{\mathrm{int}}[n] \tag{7.147}$$

and rewrite (7.145) as

$$\begin{aligned}\Omega[n,v_b] &= k_BT\int_V n(\boldsymbol{r})[\ln\Lambda^3 n(\boldsymbol{r})-1]\mathrm{d}\boldsymbol{r} + F^{\mathrm{exc}}_{\mathrm{int}}[n,v_a] - \int_V n(\boldsymbol{r})[\mu-\psi_b(\boldsymbol{r})]\mathrm{d}\boldsymbol{r}\\ &\quad+\frac{1}{2}\int_0^1\int_V\int_V n(\boldsymbol{r})n(\boldsymbol{r}')g_\lambda(\boldsymbol{r},\boldsymbol{r}')[v_b(\boldsymbol{r},\boldsymbol{r}')-v_a(\boldsymbol{r},\boldsymbol{r}')]\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}'\mathrm{d}\lambda\ .\end{aligned} \tag{7.148}$$

This is the desired expression. Of course, we still have to choose the reference pair potential v_a, determine the explicit form of the functional $F^{\mathrm{exe}}_{\mathrm{int}}[n,v_a]$, and then evaluate $g_\lambda(\boldsymbol{r},\boldsymbol{r}')$ for $0\le\lambda\le 1$.

7.4.4 Pair Distribution Function

In this section, we make a few key observations about g of homogeneous systems. This will guide our choice for the reference potential v_a.

We start by seeking for the physical content of $n^{(2)}$. For this purpose, it is actually easier to work with a canonical ensemble. Thus, we define the **density profile** and the **pair distribution function** by

$$n_N(\boldsymbol{r}) := \langle\hat{n}(\boldsymbol{r},\boldsymbol{r}^N)\rangle_N \tag{7.149}$$

and

$$n^{(2)}_N(\boldsymbol{r},\boldsymbol{r}') := \langle\hat{I}(\boldsymbol{r},\boldsymbol{r}',\boldsymbol{r}^N)\rangle_N\ , \tag{7.150}$$

respectively, where the subscript N reminds us of the canonical ensemble in which N is fixed. For the Hamiltonian given by (7.52), we have

$$\begin{aligned}&\langle\delta(\boldsymbol{r}-\boldsymbol{r}_1)\rangle_N\\ &\quad=\frac{1}{Z}\frac{1}{\Lambda^{3N}N!}\int\delta(\boldsymbol{r}-\boldsymbol{r}_1)e^{-\beta\phi(\boldsymbol{r}^N)}e^{-\beta\sum_{i=1}^N\psi(\boldsymbol{r}_i)}\mathrm{d}\boldsymbol{r}^N\\ &\quad=\frac{1}{Z}\frac{1}{\Lambda^{3N}N!}\int e^{-\beta\phi(\boldsymbol{r},\boldsymbol{r}_2,\dots,\boldsymbol{r}_N)}e^{-\beta\psi(\boldsymbol{r})}e^{-\beta\sum_{i=2}^N\psi(\boldsymbol{r}_i)}\mathrm{d}\boldsymbol{r}_2\cdots\mathrm{d}\boldsymbol{r}_N\ .\end{aligned} \tag{7.151}$$

This is a function of $\boldsymbol{r}$ and represents the probability density of finding particle 1 at $\boldsymbol{r}$. Because particle 1 is no different from any other in the system, we have

$$\langle\delta(\boldsymbol{r}-\boldsymbol{r}_1)\rangle_N = \langle\delta(\boldsymbol{r}-\boldsymbol{r}_i)\rangle_N\ ,\quad \text{for } i=2,\dots,N\ , \tag{7.152}$$

and (7.149) becomes

$$n_N(\boldsymbol{r}) = N\langle\delta(\boldsymbol{r}-\boldsymbol{r}_1)\rangle_N\ . \tag{7.153}$$

Similarly, we have

$$
\begin{aligned}
&\langle \delta(\boldsymbol{r}-\boldsymbol{r}_1)\delta(\boldsymbol{r}'-\boldsymbol{r}_2)\rangle_N \\
&\quad = \frac{1}{Z}\frac{1}{\Lambda^{3N}N!}\int \delta(\boldsymbol{r}-\boldsymbol{r}_1)\delta(\boldsymbol{r}'-\boldsymbol{r}_2)e^{-\beta\phi(\boldsymbol{r}^N)}e^{-\beta\sum_{i=1}^N\psi(\boldsymbol{r}_i)}\mathrm{d}\boldsymbol{r}^N \\
&\quad = \frac{1}{Z}\frac{1}{\Lambda^{3N}N!}\int e^{-\beta\phi(\boldsymbol{r},\boldsymbol{r}',\boldsymbol{r}_3,\ldots,\boldsymbol{r}_N)}e^{-\beta[\psi(\boldsymbol{r})+\psi(\boldsymbol{r}')]}e^{-\beta\sum_{i=3}^N\psi(\boldsymbol{r}_i)}\mathrm{d}\boldsymbol{r}_3\cdots\mathrm{d}\boldsymbol{r}_N\,, \qquad (7.154)
\end{aligned}
$$

which is the probability density of finding particle 1 at $\boldsymbol{r}$ *and* particle 2 at $\boldsymbol{r}'$ regardless of the coordinates of other particles. Since the pair of particles 1 and 2 is no different from any other pair, (7.150) gives

$$
n_N^{(2)}(\boldsymbol{r},\boldsymbol{r}') = N(N-1)\langle \delta(\boldsymbol{r}-\boldsymbol{r}_1)\delta(\boldsymbol{r}'-\boldsymbol{r}_2)\rangle_N\,. \qquad (7.155)
$$

Given the physical content of (7.151) and (7.154), we see that the ratio

$$
\frac{\langle \delta(\boldsymbol{r}-\boldsymbol{r}_1)\delta(\boldsymbol{r}'-\boldsymbol{r}_2)\rangle_N\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}'}{\langle \delta(\boldsymbol{r}-\boldsymbol{r}_1)\rangle_N\mathrm{d}\boldsymbol{r}} \qquad (7.156)
$$

is the conditional probability that particle 2 is within the volume element $\mathrm{d}\boldsymbol{r}'$ taken around $\boldsymbol{r}'$ given that particle 1 is inside $\mathrm{d}\boldsymbol{r}$ taken around $\boldsymbol{r}$. Because particles are identical, this probability is no different for any other particle (particle 3 through particle N in place of particle 2). Thus, on average, the number of particles within $\mathrm{d}\boldsymbol{r}'$ is given by

$$
(N-1)\frac{\langle \delta(\boldsymbol{r}-\boldsymbol{r}_1)\delta(\boldsymbol{r}'-\boldsymbol{r}_2)\rangle_N\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}'}{\langle \delta(\boldsymbol{r}-\boldsymbol{r}_1)\rangle_N\mathrm{d}\boldsymbol{r}} = \frac{n_N^{(2)}(\boldsymbol{r},\boldsymbol{r}')}{n_N(\boldsymbol{r})}\mathrm{d}\boldsymbol{r}'\,. \qquad (7.157)
$$

In other words, $n_N^{(2)}(\boldsymbol{r},\boldsymbol{r}')/n_N(\boldsymbol{r})$ is the number density of particles at $\boldsymbol{r}'$ when there is a particle at $\boldsymbol{r}$. This is the physical content of $n_N^{(2)}$ we seek. We have the factor $N-1$ instead of N because the particle fixed at $\boldsymbol{r}$ is not available to occupy $\boldsymbol{r}'$.

If the condition that a particle must be at $\boldsymbol{r}$ is disregarded, then the density at $\boldsymbol{r}'$ is simply $n_N(\boldsymbol{r}')$. Dividing (7.157) by $n_N(\boldsymbol{r}')$, therefore, we isolate the effect of the particle at $\boldsymbol{r}$ on the density at $\boldsymbol{r}'$:

$$
g_N(\boldsymbol{r},\boldsymbol{r}') := \frac{n_N^{(2)}(\boldsymbol{r},\boldsymbol{r}')}{n_N(\boldsymbol{r})n_N(\boldsymbol{r}')}\,. \qquad (7.158)
$$

This definition of the **radial distribution function** $g_N(\boldsymbol{r},\boldsymbol{r}')$ should be compared with (7.134) for the grand canonical ensemble. (Our definition of $g_N(\boldsymbol{r},\boldsymbol{r}')$ follows the convention adopted in Ref. [9]. The choice is not unique, however. For example, g_N in Ref. [8] is $(N-1)/N$ times our g_N. The latter definition is perhaps more convenient for a *homogeneous* system, but it leads to a somewhat different interpretation of g_N.)

Let us now consider a qualitative behavior of g_N in a homogeneous system in the absence of any external field. In this case,

$$n_N(\boldsymbol{r}) = n_N(\boldsymbol{r}') = \frac{N}{V} =: n \tag{7.159}$$

is a constant. Since every point in the system is equivalent to any other, we have

$$g_N(\boldsymbol{r},\boldsymbol{r}') = g_N(\boldsymbol{0},\boldsymbol{r}'-\boldsymbol{r}) = g_N(\boldsymbol{r}'-\boldsymbol{r}) \,, \tag{7.160}$$

where we dropped the explicit reference to $\boldsymbol{0}$. We shall also assume that the system is isotropic so that g_N and $n_N^{(2)} = n^2 g_N$ depend only on $r := \|\boldsymbol{r}'-\boldsymbol{r}\|$. (Notice that $r \neq \|\boldsymbol{r}\|$ here. Fortunately, we do not have to consider $\|\boldsymbol{r}\|$ in the remainder of this section.)

For an ideal gas, the presence of a particle at $\boldsymbol{r}$ does not affect the probability density of finding another at $\boldsymbol{r}'$, which is therefore $(N-1)/V$ with -1 accounting for the particle fixed at $\boldsymbol{r}$ and hence cannot simultaneously occupy $\boldsymbol{r}'$. Division by n yields

$$g_N(r) = 1 - \frac{1}{N} \,, \tag{7.161}$$

which is essentially unity for a macroscopic system. Alternatively, we notice that

$$\langle \delta(\boldsymbol{r}-\boldsymbol{r}_1)\delta(\boldsymbol{r}'-\boldsymbol{r}_2)\rangle_N = \langle \delta(\boldsymbol{r}-\boldsymbol{r}_1)\rangle_N \langle \delta(\boldsymbol{r}'-\boldsymbol{r}_2)\rangle_N \tag{7.162}$$

for an ideal gas. Thus, (7.157) reduces to

$$\frac{n_N^{(2)}(\boldsymbol{r},\boldsymbol{r}')}{n_N(\boldsymbol{r})} = (N-1)\langle \delta(\boldsymbol{r}'-\boldsymbol{r}_2)\rangle_N = \left(1 - \frac{1}{N}\right) n_N(\boldsymbol{r}') \,, \tag{7.163}$$

from which we obtain (7.161).

In the case of a low-density gas, it is rare for a given particle to have another nearby, and having two particles nearby is extremely rare. Thus, a particle fixed at $\boldsymbol{r}$ serves as the sole source of an external field $v(\boldsymbol{r}'-\boldsymbol{r})$ for another at $\boldsymbol{r}'$, implying that

$$\frac{n_N^{(2)}(r)}{n_N} \propto e^{-\beta v(r)} \,, \tag{7.164}$$

where we assumed that v depends only on the distance r between the two particles. Typically, $v(r)$ vanishes with increasing r. At the same time, g_N should approach the value for an ideal gas. This is sufficient to fix the proportionality constant in (7.164) and leads to

$$g_N(r) = \left(1 - \frac{1}{N}\right) e^{-\beta v(r)} \,. \tag{7.165}$$

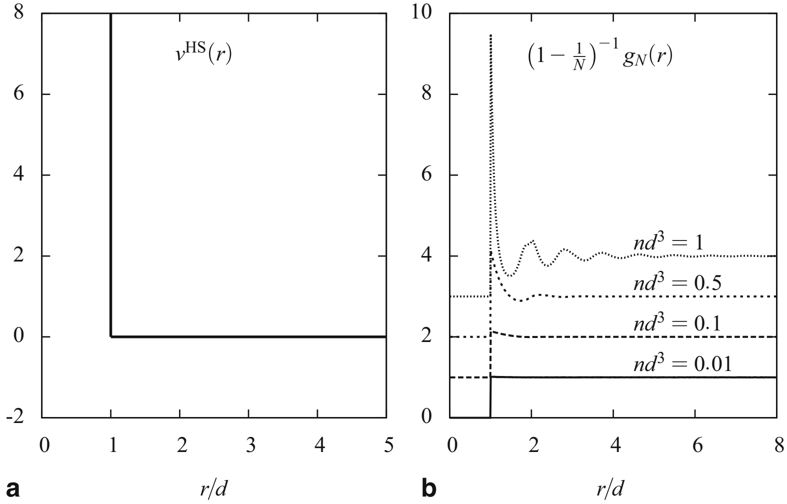

Fig. 7.2 **a** Hard-sphere potential and **b** its radial distribution functions g_N from Monte Carlo simulations at different densities $nd^3 = 0.01$, $nd^3 = 0.1$, $nd^3 = 0.5$, and $nd^3 = 1$. In view of (7.161), g_N is multiplied by $(1-1/N)^{-1}$. For clarity, the plots for $nd^3 = 0.1$, $nd^3 = 0.5$, and $nd^3 = 1$ are shifted upward by 1, 2, and 3, respectively. Note that g_N of a hard-sphere fluid does not have any temperature dependence since $v^{\mathrm{HS}}(r)/k_BT$ is independent of T. The system was taken as a cubic box of volume $8000d^3$ under periodic boundary conditions.

As an example, consider the **hard-sphere potential** defined by

$$v^{\mathrm{HS}}(r) = \begin{cases} \infty & \text{if } r < d \\ 0 & \text{otherwise,} \end{cases} \tag{7.166}$$

where the parameter d is called the **hard-sphere diameter**. Equation (7.165) then is the step function:

$$g_N(r) = \left(1 - \frac{1}{N}\right)\theta(r-d) := \begin{cases} 0 & \text{if } r < d \\ 1 - \frac{1}{N} & \text{otherwise.} \end{cases} \tag{7.167}$$

That $g_N(r) = 0$ for $r < d$ makes perfect sense because the hard-sphere potential prohibits a pair of particles to get any closer than d. Figure 7.2 shows the pair potential along with the radial distribution function obtained by Monte Carlo simulations at a few values of n. At the lowest density considered, (7.167) indeed is an excellent approximation. At the highest density shown in the figure, g_N exhibits a considerable oscillatory behavior. What is causing this?

As the density is increased, a hard-sphere particle at $\boldsymbol{r}$ starts to get surrounded by other hard-spheres that are all pushed toward the particle at $\boldsymbol{r}$. But their centers cannot enter the spherical region of diameter d around $\boldsymbol{r}$, thus leading to formation of a layer as illustrated in Fig. 7.3. This explains the first peak of $g_N(r)$ observed in

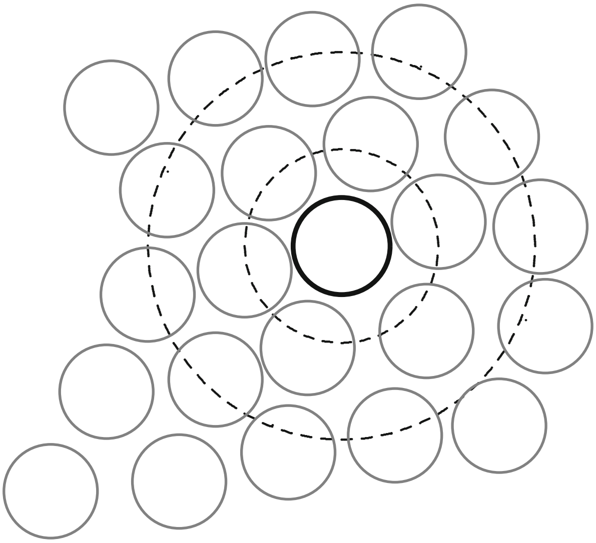

Fig. 7.3 Formation of coordination shells (*gray circles*) around a particle at $\mathbf{r}$ (*black circle*). Radii of the *dashed circles* are d and $2d$.

Fig. 7.2b. These spheres in what we might call the "first coordination shell," in turn, exclude other particles from their cores, leading to formation of the "second coordination shell" and hence to the second peak of $g_N(r)$. Continuing in this way, $g_N(r)$ exhibits an oscillatory behavior with the amplitude of oscillation gradually decreasing with increasing r. For sufficiently large r, (7.162) holds and $g_N(r)$ asymptotes toward $1-1/N$. The important thing to remember is that even a homogeneous fluid has a structure when observed from the perspective of a given particle.

Essentially, the same behavior is observed for other pair potentials having a less harsh but still short-ranged repulsive core.

As an example, let us take the **Lennard–Jones potential**:

$$v^{\mathrm{LJ}}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], \tag{7.168}$$

where the energy parameter ε is positive and σ is called the **Lennard–Jones diameter**. Figure 7.4a illustrates the form of this potential. We note that $v^{\mathrm{LJ}}(\sigma) = 0$ and that v^{LJ} takes its minimum value $-\varepsilon$ at the distance $r_{\min} := 2^{1/6}\sigma$.

It is often more convenient to work with the **truncated and shifted Lennard–Jones potential** defined by

$$v^{\mathrm{tsLJ}}(r) = \begin{cases} v^{\mathrm{LJ}}(r) - v^{\mathrm{LJ}}(r_c) & \text{if } r < r_c \\ 0 & \text{otherwise.} \end{cases} \tag{7.169}$$

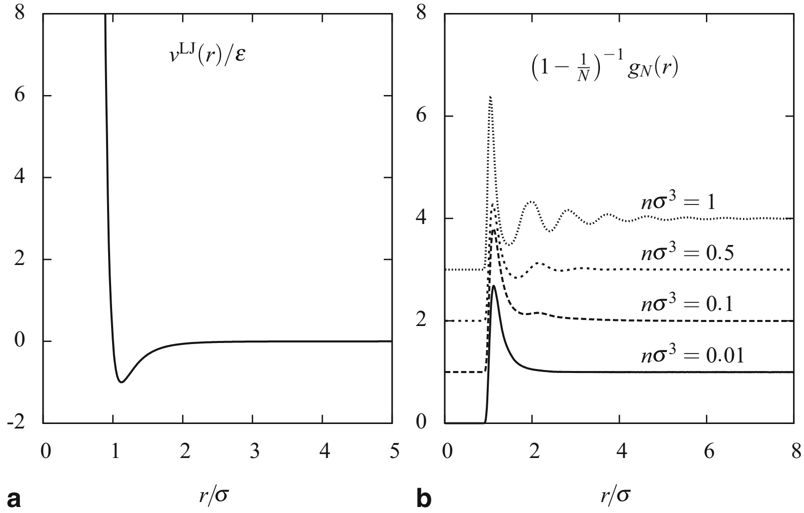

Fig. 7.4 **a** Lennard–Jones potential and **b** the radial distribution functions for its truncated and shifted version ($r_c = 2.5\sigma$) from Monte Carlo simulations at four different densities $n\sigma^3 = 0.01$, $n\sigma^3 = 0.1$, $n\sigma^3 = 0.5$, and $n\sigma^3 = 1$. For clarity, the plots for $n\sigma^3 = 0.1$, $n\sigma^3 = 0.5$, and $n\sigma^3 = 1$ are shifted upward by 1, 2, and 3, respectively. The system temperature was $T = \varepsilon/k_B$. The system was taken as a cubic box of volume $8000\sigma^3$ under periodic boundary conditions.

The radial distribution function for $v^{\mathrm{tsLJ}}(r)$ with $r_c = 2.5\sigma$ is shown in Fig. 7.4b for a few values of density. Equation (7.165) is very accurate for the lowest density value shown in the figure. We can also see the development of the oscillatory behavior with increasing density.

We note that $g_N(r)$ of a hard-sphere fluid captures essential features of $g_N(r)$ of other fluids having a short-ranged repulsive core. This is illustrated in Fig. 7.5, in which we compare $g_N(r)$ of a hard-sphere fluid against that of a Lennard–Jones fluid. At the densities indicated, they look fairly similar with the higher density results showing closer resemblance.

For an open system, fixing a particle at $\boldsymbol{r}$ does not affect the number of particles available at $\boldsymbol{r}'$. Thus, we can simply drop the $1 - 1/N$ factor from (7.161), (7.165), and (7.167) to obtain the corresponding radial distribution function $g(r)$ for open systems.

Before we conclude this section, we note that $g(r)$ is related to the Fourier transform of the so-called static structure factor, which is directly measurable by means of neutron or X-ray scattering experiments. Approximate theories for $g(r)$ can also be developed (For details of these topics, see Chap. 4 of Ref. [8] or Chap. 5 of Ref. [9], for example.) As we shall see in Sect. 7.7, a direct link exists between $g(r)$ and equations of state.

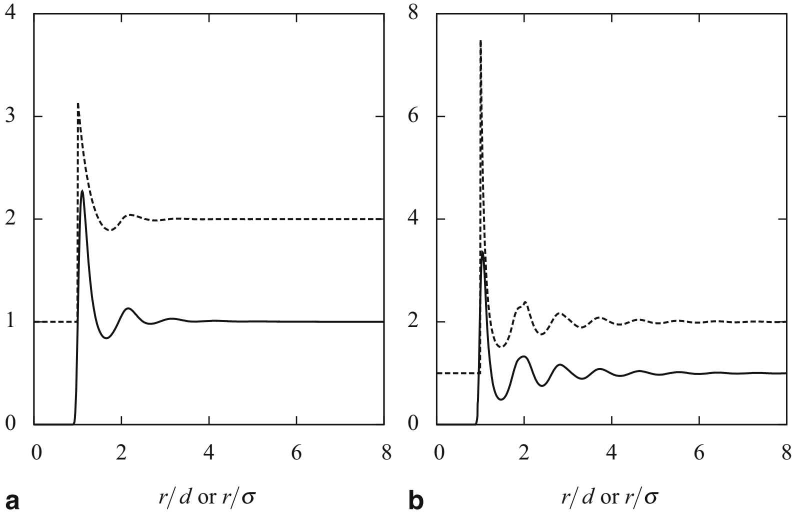

Fig. 7.5 Comparison of the radial distribution functions of the hard-sphere fluid (*dashed line*) and the truncated and shifted Lennard–Jones fluid (*solid line*) at $T = \varepsilon/k_B$. **a** $nd^3 = n\sigma^3 = 0.5$. **b** $nd^3 = n\sigma^3 = 1$. For clarity, the plots for the hard-sphere fluid are shifted upward by one.

7.4.5 Repulsive Potential

To construct the density functional by means of (7.148) for a system, in which the pair potential is $v(r)$, we must first choose a reference pair potential. How should we proceed here?

As we have seen in the previous subsection, $g(r)$ is determined primarily by the short-ranged repulsive part of the pair potential $v(r)$. This suggest that the λ dependence of $g_\lambda(r)$ in (7.148) will be small if we take the repulsive part of $v(r)$ as the reference potential.

But, how do we separate $v(r)$ into the repulsive part $v^{\text{rep}}(r)$ and the rest, which we refer to as the attractive tail $v^{\text{att}}(r)$? There is no unique answer to this question, and merits of each method must be judged by the accuracy of the predictions it produces. Here, we mention one particularly useful scheme known as the **Weeks-Chandler-Andersen** (WCA) **separation** [12]. Taking $v^{\text{LJ}}(r)$ as the example, this scheme separates the potential into

$$v^{\text{rep}}(r) = \begin{cases} v^{\text{LJ}}(r) + \varepsilon & \text{if } r \le r_{\text{min}} \\ 0 & \text{otherwise} \end{cases} \quad \text{and} \quad v^{\text{att}}(r) = \begin{cases} -\varepsilon & \text{if } r \le r_{\text{min}} \\ v^{\text{LJ}}(r) & \text{otherwise,} \end{cases} \tag{7.170}$$

leading to the graphs in Fig. 7.6.

Having settled on the reference potential, we move on to the evaluation of the excess Helmholtz free energy $F_{\text{int}}^{\text{exc}}[n, v^{\text{rep}}]$ of the reference system. A common approach for an inhomogeneous system consists of two parts. First, we seek for

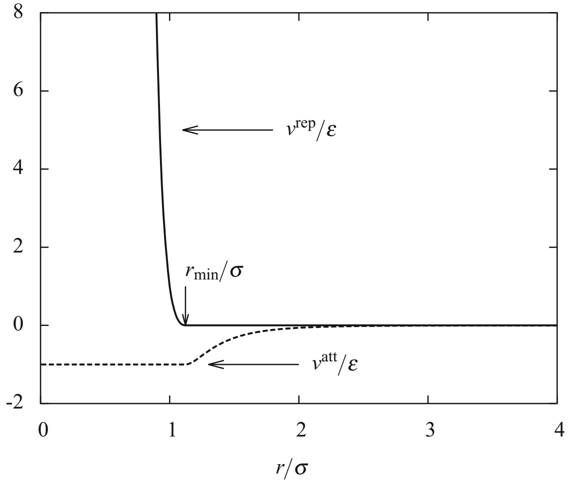

Fig. 7.6 WCA separation of the Lennard–Jones pair potential. *WCA* Weeks–Chandler–Andersen.

a "mapping" from a *homogeneous* reference system to a *homogeneous* hard-sphere (hHS) fluid. This is because properties of a hHS fluid have been studied extensively, and a very accurate formula is available for the excess Helmholtz free energy of a hard-sphere fluid. Second, we devise a method for incorporating the effect of inhomogeneity.

The most general mapping from the reference system to a hard-sphere fluid would involve two parameters, the hard-sphere diameter d and the density n^{eff} of the hard-sphere fluid. However, one commonly set $n = n^{\text{eff}}$ and determine the optimum value of d so as to minimize the error involved in the approximation

$$F^{\text{exc}}_{\text{int}}[n, v^{\text{rep}}] \approx F^{\text{exc}}_{\text{int}}[n, v^{\text{HS}}] \,. \tag{7.171}$$

The optimum value of d is then a function of T and n in general. However, an approximate solution to this optimization problem leads to the expression

$$d = \int_0^\infty \left[1 - e^{-\beta v^{\text{rep}}(r)}\right] \mathrm{d}r \,, \tag{7.172}$$

which is a function of T only. Equation (7.172) is known as the **Barker–Henderson scheme** [1, 12] and is derived in Sect. 7.4.7.

As an illustration, let us consider the truncated and shifted Lennard–Jones potential with $r_c = 2.5\sigma$. After v^{rep} is determined by the WCA separation, we can compute d using (7.172). The result is summarized in Fig. 7.7. The $T \to 0$ limit of d is given by $r_{\text{min}} = 2^{1/6}\sigma$. This makes perfect physical sense because βv^{rep} reduces to the hard-sphere potential with $d = r_{\text{min}}$ in this limit. The observed decrease in d with increasing T is also very reasonable physically since βv^{rep} becomes less harsh for higher temperatures.

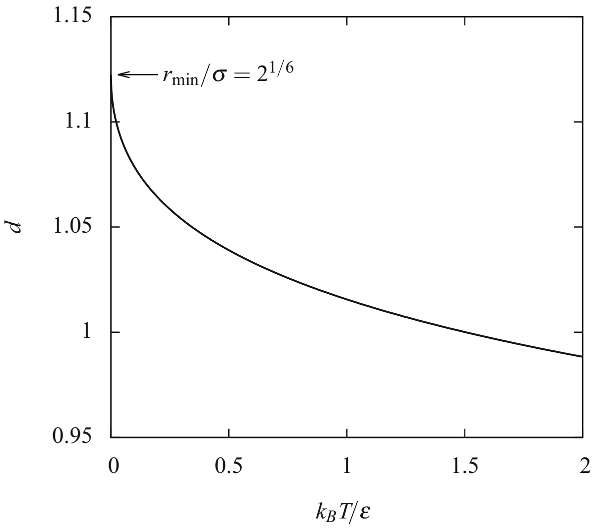

Fig. 7.7 Temperature dependence of the hard-sphere diameter as determined by the Barker–Henderson scheme for the truncated and shifted Lennard–Jones potential ($r_c = 2.5\sigma$).

The simplest approximation to cope with the inhomogeneity is the **local density approximation** (LDA), in which an inhomogeneous system is regarded as a collection of infinitesimally small homogeneous systems. Within LDA, therefore, we write

$$F^{\text{exc}}_{\text{int}}[n, v^{\text{HS}}] \approx \int_V f^{\text{exc}}_{\text{hHS}}(n(\boldsymbol{r}))\mathrm{d}\boldsymbol{r} , \tag{7.173}$$

where $f^{\text{exc}}_{\text{hHS}}(n)$ is the excess Helmholtz free energy per unit volume of a hHS fluid of density n.

If the density changes slowly over many particle diameters, LDA is expected to perform well. For a system exhibiting more rapid spatial variation of density, however, the underlying assumption of LDA does not apply. A common approximation scheme is to replace the local density $n(\boldsymbol{r})$ in (7.173) by the weighted density $\overline{n}(\boldsymbol{r})$ defined by

$$\overline{n}(\boldsymbol{r}) := \int_V w(\boldsymbol{r}, \boldsymbol{r}')n(\boldsymbol{r}')\mathrm{d}\boldsymbol{r}' , \tag{7.174}$$

where $w(\boldsymbol{r}, \boldsymbol{r}')$ is a properly normalized weighting function:

$$\int_V w(\boldsymbol{r}, \boldsymbol{r}')\mathrm{d}\boldsymbol{r}' = 1 . \tag{7.175}$$

Various choices for the weighting function are possible, but the resulting approximation schemes are collectively called the **weighted density approximation** (WDA). For fluids, w is often chosen as

$$w(\|\boldsymbol{r}' - \boldsymbol{r}\|) = \begin{cases} \frac{3}{\pi d^4}(d - \|\boldsymbol{r}' - \boldsymbol{r}\|) & \text{if } \|\boldsymbol{r}' - \boldsymbol{r}\| \leq d \\ 0 \quad \text{otherwise.} \end{cases} \tag{7.176}$$

WDA can be developed even for a crystal, which is regarded as a highly inhomogeneous fluid, and provides an accurate estimate for the melting density of hard-sphere crystals [4, 5].

The explicit form of $f_{\text{hHS}}^{\text{exe}}$ can be deduced from an equation of state. The **Carnahan–Starling formula** [2, 3] is one famous example of highly accurate equations of state of hard-sphere fluids. According to this formula,

$$\frac{\beta P_{\text{hHS}}}{n} = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3} , \tag{7.177}$$

where

$$\eta := \frac{\pi}{6} d^3 n \tag{7.178}$$

is called the **packing fraction**. Because $\pi d^3/6$ is the volume of a hard-sphere, η represents the volume occupied by the spheres per unit volume of the fluid. Spheres cannot be packed without leaving any gap among them. So, the maximum packing fraction $\eta_{\max}$ is less than unity and is given by

$$\eta_{\max} = \frac{\pi}{3\sqrt{2}} , \tag{7.179}$$

which is realized when the spheres are packed into the face-centered-cubic (fcc) structure.

Exercise 7.9. Confirm (7.179). ///

To find the expression for the excess free energy of a hard-sphere fluids, we recall the Gibbs–Duhem relation for a constant T process:

$$\mathrm{d}P_{\text{hHS}} = n\mathrm{d}\mu_{\text{hHS}} , \quad T \text{ const.} \tag{7.180}$$

Subtracting off the same equation applied to an ideal gas at the same density, we find

$$\mathrm{d}P_{\text{hHS}}^{\text{exc}} = n\mathrm{d}\mu_{\text{hHS}}^{\text{exc}} , \quad T \text{ const.} \tag{7.181}$$

Dividing this equation by dn,

$$\left(\frac{\partial \beta \mu_{\text{hHS}}^{\text{exc}}}{\partial n}\right)_T = \frac{1}{n}\left(\frac{\partial \beta P_{\text{hHS}}^{\text{exc}}}{\partial n}\right)_T . \tag{7.182}$$

Now we integrate this equation from some reference state density n_0 to the density of interest:

$$\beta\mu^{\mathrm{exc}}_{\mathrm{hHS}}(n) - \beta\mu^{\mathrm{exc}}_{\mathrm{hHS}}(n_0) = \int_{n_0}^{n} \frac{1}{n}\left(\frac{\partial \beta P^{\mathrm{exc}}_{\mathrm{hHS}}}{\partial n}\right)_T \mathrm{d}n = \int_{\eta_0}^{\eta} \frac{1}{\eta}\left(\frac{\partial \beta P^{\mathrm{exc}}_{\mathrm{hHS}}}{\partial n}\right)_T \mathrm{d}\eta\ . \tag{7.183}$$

Using the ideal gas equation of state ($\beta P^{\mathrm{id}} = n$) and (7.177),

$$\beta P^{\mathrm{exc}}_{\mathrm{hHS}} = \beta P_{\mathrm{hHS}} - n = n\frac{4\eta - 2\eta^2}{(1-\eta)^3}\ . \tag{7.184}$$

So,

$$\left(\frac{\partial \beta P^{\mathrm{exc}}_{\mathrm{hHS}}}{\partial n}\right)_T = \frac{4\eta - 2\eta^2}{(1-\eta)^3} + \eta\frac{\mathrm{d}}{\mathrm{d}\eta}\left[\frac{4\eta - 2\eta^2}{(1-\eta)^3}\right]\ . \tag{7.185}$$

We can now carry out the integration in (7.183) and obtain

$$\beta\mu^{\mathrm{exc}}_{\mathrm{hHS}}(n) - \beta\mu^{\mathrm{exc}}_{\mathrm{hHS}}(n_0) = \left[\frac{2}{1-\eta} + \frac{1}{(1-\eta)^2} + \frac{4\eta - 2\eta^2}{(1-\eta)^3}\right]_{\eta_0}^{\eta}\ . \tag{7.186}$$

In the limit of $\eta_0 \to 0$, the fluid approaches the ideal gas and hence $\mu^{\mathrm{exc}}_{\mathrm{hHS}}(n_0) \to 0$. Thus,

$$\beta\mu^{\mathrm{exc}}_{\mathrm{hHS}}(n) = \frac{2}{1-\eta} + \frac{1}{(1-\eta)^2} + \frac{4\eta - 2\eta^2}{(1-\eta)^3} - 3 = \frac{\eta(3\eta^2 - 9\eta + 8)}{(1-\eta)^3}\ . \tag{7.187}$$

Recalling that $F := U - TS = -PV + \mu N$, we finally arrive at

$$\beta f^{\mathrm{exc}}_{\mathrm{hHS}}(n) := \frac{\beta F^{\mathrm{exc}}_{\mathrm{hHS}}}{V} = n\frac{\eta(4-3\eta)}{(1-\eta)^2}\ . \tag{7.188}$$

Even though we introduced a mapping from v^{rep} to the hard-sphere potential, this is only for the purpose of computing $F^{\mathrm{exc}}_{\mathrm{int}}$. Thus, we emphasize that the pair potential of our reference system is still v^{rep} and $v_b - v_a$ in (7.148) is v^{att}, not $v - v^{\mathrm{HS}}$. In various theories of homogeneous fluids with mapping onto hard-spheres, v^{rep} still plays an important role, for example, in approximating the radial distribution function $g_\lambda(r)$.

7.4.6 Radial Distribution Function

The radial distribution function $g(\boldsymbol{r},\boldsymbol{r}')$ of an inhomogeneous system is not very well known even for a hard-sphere fluid. This is not surprising since $g(\boldsymbol{r},\boldsymbol{r}')$ depends on three spatial variables even in the simplest case of a flat interface. Consequently, we must adopt a rather drastic approximation for $g_\lambda(\boldsymbol{r},\boldsymbol{r}')$.

For example, we can take over (7.167), without the $1 - 1/N$ factor for an open system, and write

$$g_\lambda(\boldsymbol{r},\boldsymbol{r}') \approx \theta(\|\boldsymbol{r}' - \boldsymbol{r}\| - d) \ . \tag{7.189}$$

with d determined by the Barker–Henderson scheme. Alternative approximation is based on (7.165) and is given by

$$g_\lambda(\boldsymbol{r},\boldsymbol{r}') \approx e^{-\beta v^{\mathrm{rep}}(\|\boldsymbol{r}'-\boldsymbol{r}\|)} \ , \tag{7.190}$$

where we recall $v^{\mathrm{rep}} = v_{\lambda=0}$ is the pair potential of the reference system. The simplest approximation is

$$g_\lambda(\boldsymbol{r},\boldsymbol{r}') \approx 1 \ , \tag{7.191}$$

which is exact only for an ideal gas.

We are now in position to write down approximate density functionals. The simplest density functional is based on LDA and (7.191), and is given by

$$\begin{aligned}\Omega[n] = k_BT\int_V n(\boldsymbol{r})[\ln\Lambda^3 n(\boldsymbol{r}) - 1]\mathrm{d}\boldsymbol{r} + \int_V f^{\mathrm{exc}}_{\mathrm{hHS}}(n(\boldsymbol{r}))\mathrm{d}\boldsymbol{r} - \int_V n(\boldsymbol{r})[\mu - \psi(\boldsymbol{r})]\mathrm{d}\boldsymbol{r} \\ + \frac{1}{2}\int_V\int_V n(\boldsymbol{r})n(\boldsymbol{r}')v^{\mathrm{att}}(\|\boldsymbol{r}'-\boldsymbol{r}\|)\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}' \ ,\end{aligned} \tag{7.192}$$

where we dropped the reference to the pair potential v from $\Omega[n,v]$.

Equation (7.192) motivates the following definition for the grand potential density:

$$\begin{aligned}\chi(\boldsymbol{r},n] := k_BTn(\boldsymbol{r})[\ln\Lambda^3 n(\boldsymbol{r}) - 1] + f^{\mathrm{exc}}_{\mathrm{hHS}}(n(\boldsymbol{r})) - n(\boldsymbol{r})[\mu - \psi(\boldsymbol{r})] \\ + \frac{1}{2}n(\boldsymbol{r})\int_V n(\boldsymbol{r}')v^{\mathrm{att}}(\|\boldsymbol{r}'-\boldsymbol{r}\|)\mathrm{d}\boldsymbol{r}' \ ,\end{aligned} \tag{7.193}$$

in terms of which we may write

$$\Omega[n] = \int_V \chi(\boldsymbol{r},n]\mathrm{d}\boldsymbol{r} \ . \tag{7.194}$$

We have already made use of (7.194) in Sect. 6.9. A few illustrative applications of (7.192) will be given in Sects. 7.5 and 7.6.

7.4.7 †*Barker–Henderson Scheme*

The only difference between $F^{\mathrm{exc}}_{\mathrm{int}}[n,v^{\mathrm{rep}}]$ and $F^{\mathrm{exc}}_{\mathrm{int}}[n,v^{\mathrm{HS}}]$ is in the pair potentials. Thus, one possible approach for minimizing the error associated with (7.171) may be to expand $F^{\mathrm{exc}}_{\mathrm{int}}[n,v^{\mathrm{rep}}]$ into the functional Taylor series around $v^{\mathrm{rep}} = v^{\mathrm{HS}}$ and then choose d so that the first-order term becomes identically zero. If this can be done, the error will be in the higher order terms. Glancing at Fig. 7.6, we see immediately that v^{rep} and v^{HS} are very different regardless of how we choose d. In fact, for $r < d$,

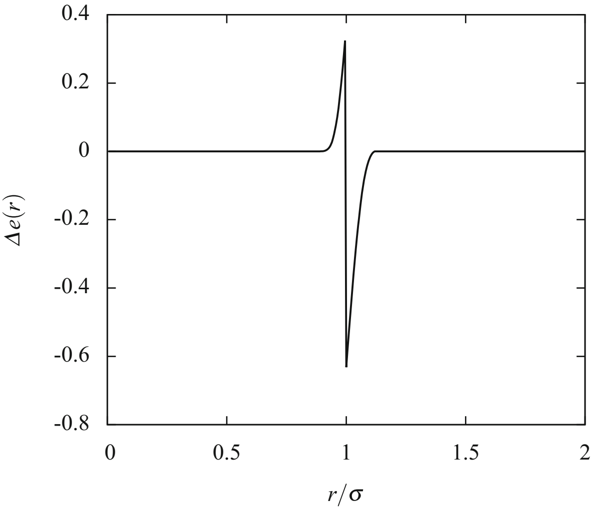

Fig. 7.8 The blip function. We set $\sigma = d$ and $T = \varepsilon/k_B$.

their difference is infinitely large. This implies that the higher order terms probably cannot be neglected.

What we need is a better way to characterize the difference between v^{rep} and v^{HS}. For this purpose, we define

$$e(r) := e^{-\beta v(r)} . \tag{7.195}$$

For the pair potentials at hand,

$$e^{\mathrm{rep}}(r) = e^{-\beta v^{\mathrm{rep}}(r)} \quad \text{and} \quad e^{\mathrm{HS}}(r) = e^{-\beta v^{\mathrm{HS}}(r)} . \tag{7.196}$$

The difference between them

$$\Delta e(r) := e^{\mathrm{rep}}(r) - e^{\mathrm{HS}}(r) \tag{7.197}$$

is known as the **blip function**. The origin of this term is revealed in Fig. 7.8. Unlike $v^{\mathrm{rep}} - v^{\mathrm{HS}}$, Δe remains finite for all values of r.

Now, we proceed to evaluate the functional derivative of $F^{\mathrm{exc}}_{\mathrm{int}}[n, v^{\mathrm{rep}}]$ with respect to e^{rep}. Since $F^{\mathrm{id}}_{\mathrm{int}}$ is independent of $v^{\mathrm{rep}}(r)$,

$$\frac{\delta F^{\mathrm{exc}}_{\mathrm{int}}[n, v^{\mathrm{rep}}]}{\delta v^{\mathrm{rep}}(\boldsymbol{r}, \boldsymbol{r}')} = \frac{\delta F_{\mathrm{int}}[n, v^{\mathrm{rep}}]}{\delta v^{\mathrm{rep}}(\boldsymbol{r}, \boldsymbol{r}')} . \tag{7.198}$$

From (7.76) and (7.144), we observe that

$$F_{\mathrm{int}}[n, v] = \Omega[n, v] + \int_V [\mu - \psi(\boldsymbol{r})]\, n(\boldsymbol{r}) \mathrm{d}\boldsymbol{r} . \tag{7.199}$$

Recalling (7.134), we find

$$\frac{\delta F^{\text{exc}}_{\text{int}}[n, v^{\text{rep}}]}{\delta v^{\text{rep}}(\boldsymbol{r},\boldsymbol{r}')} = \frac{1}{2} n^{(2)}(\boldsymbol{r},\boldsymbol{r}') \,, \tag{7.200}$$

Note that we replaced the distance r between a pair of particles by their coordinates $\boldsymbol{r}$ and $\boldsymbol{r}'$. It follows from (7.41) that

$$\delta F^{\text{exc}}_{\text{int}}[n, v^{\text{rep}}] = \frac{1}{2}\int_V \int_V n^{(2)}(\boldsymbol{r},\boldsymbol{r}')\delta v^{\text{rep}}(\boldsymbol{r},\boldsymbol{r}')\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}' \,. \tag{7.201}$$

From (7.196), we have

$$v^{\text{rep}}(\boldsymbol{r},\boldsymbol{r}') = -k_B T \ln e^{\text{rep}}(\boldsymbol{r},\boldsymbol{r}') \,, \tag{7.202}$$

and hence

$$\delta v^{\text{rep}}(\boldsymbol{r},\boldsymbol{r}') = -\frac{k_B T}{e^{\text{rep}}(\boldsymbol{r},\boldsymbol{r}')}\delta e^{\text{rep}}(\boldsymbol{r},\boldsymbol{r}') \,. \tag{7.203}$$

Using this expression in (7.201), we have

$$\delta F^{\text{exc}}_{\text{int}}[n, v^{\text{rep}}] = -\frac{k_B T}{2}\int_V \int_V \frac{n^{(2)}(\boldsymbol{r},\boldsymbol{r}')}{e^{\text{rep}}(\boldsymbol{r},\boldsymbol{r}')}\delta e^{\text{rep}}(\boldsymbol{r},\boldsymbol{r}')\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}' \,. \tag{7.204}$$

We now change the variables from $(\boldsymbol{r},\boldsymbol{r}')$ to $(\boldsymbol{r},\boldsymbol{R})$, where $\boldsymbol{R} := \boldsymbol{r}' - \boldsymbol{r}$. The pair potential, by assumption, is a function of $R := \|\boldsymbol{R}\|$. For a *homogeneous and isotropic* system, the same applies to $n^{(2)}$ as well. Thus,

$$\begin{aligned}\delta F^{\text{exc}}_{\text{int}}[n, v^{\text{rep}}] &= -\frac{k_B T}{2}\int_V \int_V \frac{n^{(2)}(R)}{e^{\text{rep}}(R)}\delta e^{\text{rep}}(R)\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{R} \\ &= -\frac{k_B T}{2} V \int_V \frac{n^{(2)}(R)}{e^{\text{rep}}(R)}\delta e^{\text{rep}}(R)\mathrm{d}\boldsymbol{R} \,,\end{aligned} \tag{7.205}$$

where we note that the determinant of the Jacobian matrix for the change of variables from $(\boldsymbol{r},\boldsymbol{r}')$ to $(\boldsymbol{r},\boldsymbol{R})$ is unity. Using $\boldsymbol{r}$ in place of $\boldsymbol{R}$, we arrive at[45]

$$\frac{\delta F^{\text{exc}}_{\text{int}}[n, v^{\text{rep}}]}{\delta e^{\text{rep}}(\boldsymbol{r})} = -\frac{k_B T}{2} V \frac{n^{(2)}(r)}{e^{\text{rep}}(r)} = -\frac{k_B T}{2} n^2 V \frac{g^{\text{rep}}(r)}{e^{\text{rep}}(r)} \,. \tag{7.206}$$

Evaluating this expression for $e^{\text{rep}}(r) \equiv e^{\text{HS}}(r)$,

$$\left.\frac{\delta F^{\text{exc}}_{\text{int}}[n, v^{\text{rep}}]}{\delta e^{\text{rep}}(\boldsymbol{r})}\right|_{v^{\text{rep}}=v^{\text{HS}}} = -\frac{k_B T}{2} n^2 V y^{\text{HS}}(r) \,, \tag{7.207}$$

where we defined

$$y(r) := \frac{g(r)}{e(r)} \,. \tag{7.208}$$

We observe that $y(r)$ may be regarded as the correction factor to the low-density approximation (7.165) without the $1-1/N$ factor. Thus, the functional Taylor series expansion of $F_{\text{int}}^{\text{exc}}[n, v^{\text{rep}}]$ around $e^{\text{rep}}(r) \equiv e^{\text{HS}}(r)$ is given by

$$F_{\text{int}}^{\text{exc}}[n, v^{\text{rep}}] = F_{\text{int}}^{\text{exc}}[n, v^{\text{HS}}] - \frac{1}{2} k_B T n^2 V \int_V y^{\text{HS}}(r) \Delta e(r) \mathrm{d}\boldsymbol{r} + \text{h.o.} \tag{7.209}$$

The desired equation for d is therefore,

$$\int_V y^{\text{HS}}(r) \Delta e(r) \mathrm{d}\boldsymbol{r} = 4\pi \int_0^\infty y^{\text{HS}}(r) \Delta e(r) r^2 \mathrm{d}r = 0\,. \tag{7.210}$$

From Fig. 7.8, we see that the blip function is nonzero only around $r = d$, suggesting that $r^2 y^{\text{HS}}(r)$ in (7.210) may be replaced by $d^2 y^{\text{HS}}(d)$ without significantly affecting the value of the integral. (We note that $y(r)$ is a continuous function of r even for a discontinuous $v(r)$, such as the hard-sphere pair potential. For an explicit demonstration of this fact, see Sect. 5.3 of Ref. [9].) With this approximation, (7.210) reduces to

$$\int_0^\infty \Delta e(r) \mathrm{d}r = \int_0^\infty \left[e^{\text{rep}}(r) - e^{\text{HS}}(r) \right] \mathrm{d}r = 0\,, \tag{7.211}$$

which may be rewritten as

$$\int_0^\infty \left[e^{\text{rep}}(r) - 1 \right] \mathrm{d}r = \int_0^\infty \left[e^{\text{HS}}(r) - 1 \right] \mathrm{d}r = -d\,. \tag{7.212}$$

But, this is just (7.172).

7.5 Hard-Sphere Fluid Under Gravity

As the first example illustrating the use of (7.192), let us look at something simple: a hard-sphere fluid in a container under gravity. In this case, we have

$$v^{\text{att}}(\boldsymbol{r}) \equiv 0\,. \tag{7.213}$$

Taking the z-axis vertically upward from the bottom of the container, the external field due to gravity is given by

$$\psi(\boldsymbol{r}) = m_w g z\,, \tag{7.214}$$

where m_w and g are the mass of a hard-sphere and the gravitational acceleration, respectively.

Using these expressions in (7.192), we see that

$$\Omega[n] = k_B T \int_V n(\boldsymbol{r}) \left[\ln \Lambda^3 n(\boldsymbol{r}) - 1\right] \mathrm{d}\boldsymbol{r} + \int_V f^{\mathrm{exc}}_{\mathrm{hHS}}(n(\boldsymbol{r}))\mathrm{d}\boldsymbol{r} + \int_V n(\boldsymbol{r})(m_w g z - \mu)\mathrm{d}\boldsymbol{r} \,. \tag{7.215}$$

The equilibrium density profile is determined by (7.47), which now reads

$$\frac{\delta \Omega}{\delta n(\boldsymbol{r})} = k_B T \ln \Lambda^3 n(\boldsymbol{r}) + \mu^{\mathrm{exc}}_{\mathrm{hHS}}(n(\boldsymbol{r})) + (m_w g z - \mu) = 0 \,. \tag{7.216}$$

Since $k_B T \ln \Lambda^3 n(z)$ is the ideal gas contribution to the chemical potential, this equation may be rewritten as

$$\mu = k_B T \ln \Lambda^3 n(\boldsymbol{r}) + \mu^{\mathrm{exe}}_{\mathrm{hHS}}(n(\boldsymbol{r})) + m_w g z = \mu_{\mathrm{hHS}}(n(\boldsymbol{r})) + m_w g z \,, \tag{7.217}$$

indicating that the intrinsic part of the chemical potential and the external field, added together, must be constant throughout the system in equilibrium.

Equation (7.216) indicates that $n(\boldsymbol{r})$ depends only on z. We can readily solve the equation for z (but not for $n(z)$):

$$z = \frac{1}{m_w g}\left[\mu - \mu^{\mathrm{exc}}_{\mathrm{hHS}}(n(z)) - k_B T \ln \Lambda^3 n(z)\right] \,. \tag{7.218}$$

If we denote the density at $z = 0$ by n_0,

$$0 = \frac{1}{m_w g}\left[\mu - \mu^{\mathrm{exc}}_{\mathrm{hHS}}(n_0) - k_B T \ln \Lambda^3 n_0\right] \,, \tag{7.219}$$

which can be subtracted from (7.218) to give

$$z = \frac{1}{m_w g}\left[\mu^{\mathrm{exc}}_{\mathrm{hHS}}(n_0) - \mu^{\mathrm{exc}}_{\mathrm{hHS}}(n(z)) + k_B T \ln \frac{n_0}{n(z)}\right] \,. \tag{7.220}$$

With n_0 set to the maximum possible value of $\sqrt{2}/d^3$, which corresponds to the hard-spheres packed into the fcc structure, (7.220) leads to the density profile shown in Fig. 7.9. Despite its appearance, Fig. 7.9 does *not* imply vapor–liquid coexistence for the hard-sphere fluid. The attractive part of the pair potential is needed for such a phase behavior.

7.6 Vapor–Liquid Coexistence

As a less trivial example, let us examine vapor–liquid equilibrium in a truncated and shifted Lennard–Jones fluid. For simplicity, we set the external field to zero in (7.192). For this potential, WCA separation gives

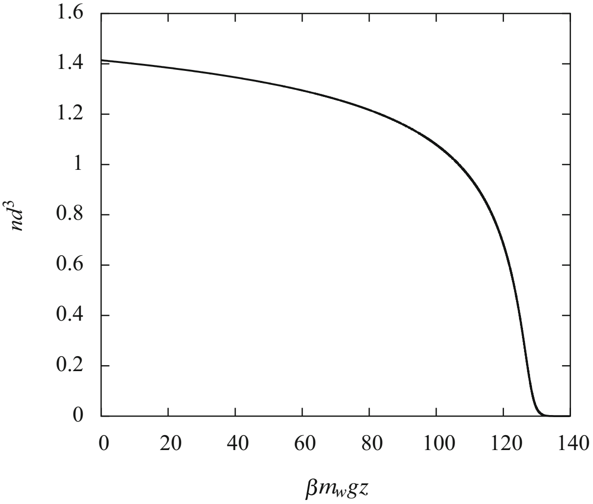

Fig. 7.9 Equilibrium density profile of hard-sphere fluids under gravity. The graph was obtained by assuming maximum packing fraction at $z = 0$.

$$v^{\text{att}}(r) = \begin{cases} -\varepsilon - v^{\text{LJ}}(r_c) & \text{if } r \le r_{\min} \\ v^{\text{LJ}}(r) - v^{\text{LJ}}(r_c) & \text{if } r_{\min} < r \le r_c \\ 0 \quad \text{otherwise.} \end{cases} \tag{7.221}$$

The repulsive potential $v^{\text{rep}}(r)$ is still given by (7.170). In fact, $v^{\text{rep}}(r)$ for $r \le r_{\min}$ is $v^{\text{tsLJ}}(r)$ minus its minimum value at $r_{\min} = 2^{1/6}\sigma$, both of which received the same upward shift by $v^{\text{LJ}}(r_c)$ when defining $v^{\text{tsLJ}}(r)$ in terms of $v^{\text{LJ}}(r)$. In our numerical computation below, we set $r_c = 2.5\sigma$.

7.6.1 Phase Diagram

It is convenient to work with the Helmholtz free energy. Since $F = \Omega + \mu N$ and $\psi(\boldsymbol{r}) \equiv 0$, (7.192) gives

$$F[n] = k_B T \int_V n(\boldsymbol{r})[\ln \Lambda^3 n(\boldsymbol{r}) - 1]\mathrm{d}\boldsymbol{r} + \int_V f^{\text{exc}}_{\text{hHS}}(n(\boldsymbol{r}))\mathrm{d}\boldsymbol{r} \\ + \frac{1}{2}\int_V \int_V n(\boldsymbol{r})n(\boldsymbol{r}')v^{\text{att}}(\|\boldsymbol{r}' - \boldsymbol{r}\|)\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}' \,. \tag{7.222}$$

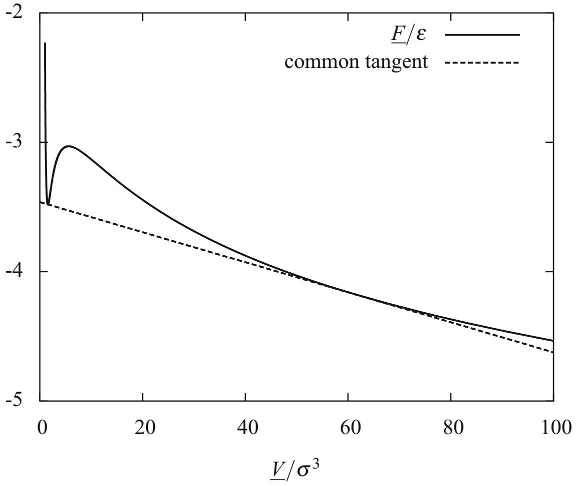

Fig. 7.10 $\underline{F}$ versus $\underline{V}$ plot at $T = 0.8\varepsilon/k_B$.

The Helmholtz free energy of a homogeneous phase follows from (7.222) simply by setting $n(\boldsymbol{r})$ to a constant n:

$$f := \frac{F}{V} = k_B T n[\ln \Lambda^3 n - 1] + f_{\text{hHS}}^{\text{exc}}(n) + \frac{1}{2}\alpha^{\text{att}} n^2 , \tag{7.223}$$

which is then a fundamental equation of the homogeneous fluid. Here, α^{att} is a constant defined by

$$\alpha^{\text{att}} := \frac{1}{V}\int_V \int_V v^{\text{att}}(\|\boldsymbol{r}' - \boldsymbol{r}\|)\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}' = \frac{1}{V}\int_V \int_V v^{\text{att}}(R)\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{R} = \int_V v^{\text{att}}(R)\mathrm{d}\boldsymbol{R} , \tag{7.224}$$

where we defined $\boldsymbol{R} := \boldsymbol{r}' - \boldsymbol{r}$ and $R := \|\boldsymbol{R}\|$. We also made use of the fact that the determinant of the Jacobian matrix for the change of variables from $(\boldsymbol{r}, \boldsymbol{r}')$ to $(\boldsymbol{r}, \boldsymbol{R})$ is unity. Given the fundamental equation (7.223), we can obtain expressions for P and μ:

$$P = k_B T n + P_{\text{hHS}}^{\text{exc}} + \frac{1}{2}\alpha^{\text{att}} n^2 \tag{7.225}$$

and

$$\mu = k_B T \ln \Lambda^3 n + \mu_{\text{hHS}}^{\text{exc}} + \alpha^{\text{att}} n . \tag{7.226}$$

Exercise 7.10. Verify (7.225) and (7.226). ///

Figure 7.10 shows the dependence of $\underline{F} := F/N$ on $\underline{V} := V/N$ at $T = 0.8\varepsilon/k_B$. At this temperature, a portion of the $\underline{F}$ versus $\underline{V}$ plot is concave down and the curve has a common tangent. We recall from Sect. 2.16.1 that we can read off P and μ of a fluid by drawing a tangent line to the $\underline{F}$ versus $\underline{V}$ plot. In particular, its slope and the intercept on the $\underline{F}$-axis are, respectively, $-P$ and μ of the fluid at the point of tangent.

Therefore, the existence of a common tangent implies the equilibrium between two phases, vapor and liquid in this case. The precise values for the densities of the coexisting phases are found as the nontrivial solution (for which $n^l \neq v^v$) of the coupled equations:

$$P(T,n^v) = P(T,n^l) \quad \text{and} \quad \mu(T,n^v) = \mu(T,n^l), \tag{7.227}$$

where the superscripts v and l refer to vapor and liquid phases, respectively. The locus of the coexisting bulk phase densities (traced by varying T) is called a **binodal line**.

The onset of instability is determined by

$$\left(\frac{\partial P}{\partial n}\right)_T = 0\,, \tag{7.228}$$

the locus of which defines the spinodal line. A bulk phase inside the region enclosed by this line is unstable with respect to an infinitesimal density fluctuation and undergoes phase separation by a mechanism called **spinodal decomposition**. (See 5.2.2.) Metastable phases reside in the regions between the binodal and spinodal lines with the lower density part corresponding to supersaturated vapor and the higher density part to superheated (or stretched) liquid. The mechanism of phase separation of a metastable phase is **nucleation**.

Finally, (7.228) and

$$\left(\frac{\partial^2 P}{\partial n^2}\right)_T = 0 \tag{7.229}$$

determine the critical point.

Results of these computations are shown in Fig. 7.11 and are compared against the results of the Gibbs ensemble simulations [11]. We see that our theory predicts qualitatively correct behavior, though it fails at a quantitative level especially for the liquid phase densities. A further refinement is expected to be possible by using a more accurate mapping scheme between the reference system (with v^{rep}) and hard-sphere fluids as well as a better approximation for $g_\lambda(r)$.

The critical point is not particularly well predicted by DFT. This is a generic feature of DFT, which does not adequately account for the effect of fluctuations that become increasingly important near the critical point. In fact, we see shortly that DFT is a form of a mean-field approximation discussed in Sect. 5.2.

7.6.2 Interfacial Properties

For our choice of the density functional, (7.47) leads to

$$\mu = k_B T \ln \Lambda^3 n(\boldsymbol{r}) + \mu_{\text{hHS}}^{\text{exc}}(n(\boldsymbol{r})) + \int_V n(\boldsymbol{r}')v^{\text{att}}(\|\boldsymbol{r}' - \boldsymbol{r}\|)\mathrm{d}\boldsymbol{r}'\,. \tag{7.230}$$

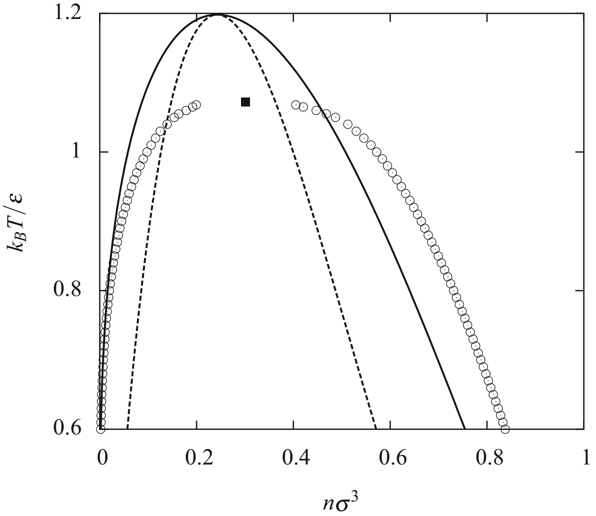

Fig. 7.11 Phase diagram of the truncated and shifted Lennard–Jones fluid ($r_c = 2.5\sigma$). The binodal (*solid line*) and the spinodal (*dashed line*) lines, both from the density functional theory. The coexisting densities (⊙) and the critical point (■), both from Gibbs ensemble simulation involving the total of 1000 particles.

For given T and μ, this equation determines the equilibrium density profile $n^{\text{eq}}(\boldsymbol{r})$. Comparing (7.217) and (7.230), we see that the last term of (7.230) represents the effective field at $\boldsymbol{r}$ that is being generated by the particles in the system. Thus, the density functional we constructed, in essence, is a fluid-phase version of the **mean-field approximation** we saw in Sect. 5.2.

Figure 7.12 exhibits equilibrium density profiles at the vapor–liquid coexistence for a few values of T. Using this information, we computed the surface tension γ_∞ for a range of temperatures using (7.193) and (6.92). The results are shown in Fig. 7.13 and is compared against the predictions of Monte Carlo simulations. Despite the failure of DFT in accurately predicting the critical point and the liquid phase densities at coexistence, the DFT predictions of γ_∞ are in reasonably good agreement with the simulation results. In both cases, γ_∞ decreases monotonically and eventually vanishes at the critical point where the distinction between the vapor and the liquid phases disappears.

The location of the surface of tension is determined by (6.98) and is shown by the curve labeled as z_s in Fig. 7.12. The intersection between the curve and the density profile at a given temperature gives z_s at that T. Similarly for other curves labeled as z_{95} and z_{05}. The former denotes the position at which the density $n^{\text{eq}}(z)$ decreases from its bulk liquid value n^l by 5% of $n^l - n^v$. Likewise, z_{05} is the position at which $n^{\text{eq}}(z)$ decreases to $n^v + 0.05(n^l - n^v)$.

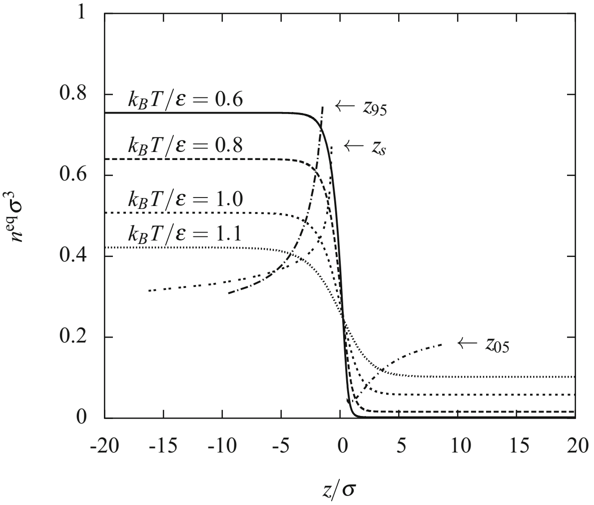

Fig. 7.12 Density profiles across flat interfaces for the truncated and shifted Lennard–Jones fluid ($r_c = 2.5\sigma$).

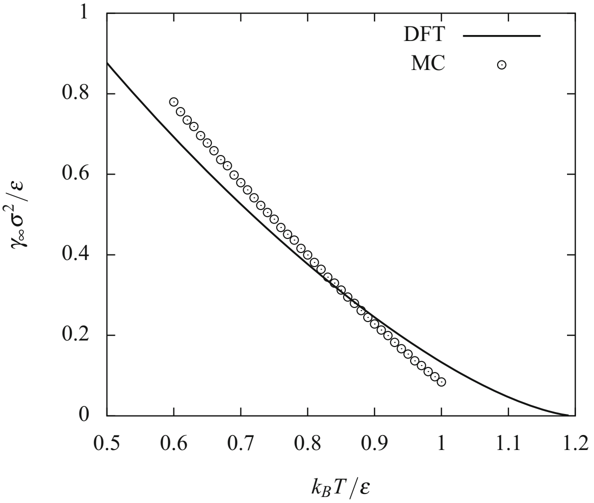

Fig. 7.13 Surface tension versus temperature for the truncated and shifted Lennard–Jones fluid ($r_c = 2.5\sigma$). Monte Carlo (*MC*) simulation employed 8000 particles in a rectangular box (dimension $20\sigma \times 20\sigma \times 80\sigma$) under periodic boundary conditions.

The thickness of the interfacial region may be conveniently characterized by $z_{05} - z_{95}$. Our DFT prediction indicates that $z_{05} - z_{95} = 2.11\sigma$ at $k_BT/\varepsilon = 0.5$. The interface becomes more diffuse with increasing temperature. For example, $z_{05} - z_{95} = 5.22\sigma$ at $k_BT/\varepsilon = 1.0$.

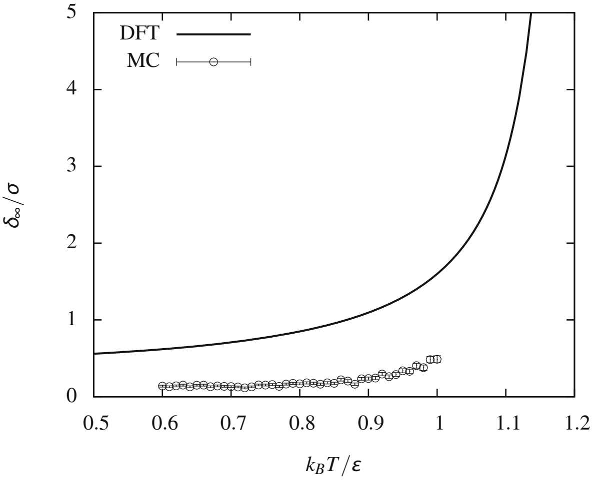

Fig. 7.14 Tolman length versus temperature for the truncated and shifted Lennard–Jones fluid ($r_c = 2.5\sigma$). Monte Carlo (*MC*) simulation employed 8000 particles in a rectangular box (dimension $20\sigma \times 20\sigma \times 80\sigma$) under periodic boundary conditions.

At low temperatures, $z_{95} < z_s < z_{05}$ in agreement with Gibbs's conclusion that the surface of tension should be located within the interfacial region. At temperatures very close to the critical temperature, the interface becomes very diffuse and the arbitrary cut-off at z_{95} does not mark the end of the interfacial region. At $k_BT/\varepsilon \gtrsim 1.14$, for example, $z_s < z_{95}$.

According to DFT, the Tolman length δ_∞ is 0.56σ at $k_BT/\varepsilon = 0.5$ and increases with increasing T. At $k_BT/\varepsilon = 1$ for example, $\delta_\infty = 1.6\sigma$. As shown in Fig. 7.14, the same trend is observed also in Monte Carlo simulations. However, the DFT predictions are considerably larger than the results from the simulations. In this regard, we note that a recent very-large-scale molecular dynamics study casts some doubts on the ability of DFT and small-scale simulations, such as the one included in Fig. 7.14, to accurately predict δ_∞ [10].

7.7 ‡Equations of State from the Radial Distribution Function

In this section, we shall establish a connection between thermodynamic properties of a homogeneous system and the radial distribution function. Since we are interested only in homogeneous systems, the external field is set to zero.

7.7.1 ‡Compressibility Equation of State

Upon integration over the volume V of the system, (7.51) yields

$$\int_V n(\boldsymbol{r})\mathrm{d}\boldsymbol{r} = \left\langle \sum_{i=1}^N \int_V \delta(\boldsymbol{r}-\boldsymbol{r}_i)\mathrm{d}\boldsymbol{r} \right\rangle = \left\langle \sum_{i=1}^N 1 \right\rangle = \langle N \rangle \ . \tag{7.231}$$

Similarly, integration of $n^{(2)}$ defined by (7.134) gives

$$\int_V \int_V n^{(2)}(\boldsymbol{r},\boldsymbol{r}')\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}' = \left\langle \sum_{i=1}^N {\sum_{j=1}^N}' \int_V \int_V \delta(\boldsymbol{r}-\boldsymbol{r}_i)\delta(\boldsymbol{r}'-\boldsymbol{r}_j)\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}' \right\rangle = \langle N(N-1) \rangle \ . \tag{7.232}$$

Combining these two equations,

$$\int_V \int_V [n^{(2)}(\boldsymbol{r},\boldsymbol{r}') - n(\boldsymbol{r})n(\boldsymbol{r}')]\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}' = \langle N^2 \rangle - \langle N \rangle - \langle N \rangle^2 \ . \tag{7.233}$$

In a homogeneous system, $n(\boldsymbol{r}) = n(\boldsymbol{r}') =: n$ is a constant. In addition, our choice for the origin of the coordinate system should be immaterial, leading to

$$n^{(2)}(\boldsymbol{r},\boldsymbol{r}') = n^{(2)}(\boldsymbol{0},\boldsymbol{R}) = n^2 g(\boldsymbol{0},\boldsymbol{R}) = n^2 g(\boldsymbol{R}) \ , \tag{7.234}$$

where $\boldsymbol{R} := \boldsymbol{r}' - \boldsymbol{r}$ and we dropped the explicit reference to $\boldsymbol{0}$. Using $\boldsymbol{r}$ and $\boldsymbol{R}$ as the new integration variables, we rewrite the left-hand side of (7.233) as

$$n^2 \int_V \int_V [g(\boldsymbol{R}) - 1]\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{R} = n^2 V \int_V [g(\boldsymbol{R}) - 1]\mathrm{d}\boldsymbol{R} \ . \tag{7.235}$$

On the other hand, (4.155) gives

$$\langle N^2 \rangle - \langle N \rangle - \langle N \rangle^2 = \langle N \rangle (k_B T n \kappa_T - 1) \ . \tag{7.236}$$

Thus, noting that $\langle N \rangle = nV$, we arrive at

$$k_B T n \kappa_T = 1 + n \int_V [g(\boldsymbol{r}) - 1]\mathrm{d}\boldsymbol{r} \ , \tag{7.237}$$

which is known as the **compressibility equation of state**. For an isotropic system, $g(\boldsymbol{r}) = g(r)$. For an ideal gas, $g(r) = 1$. Thus,

$$k_B T n \kappa_T = 1 \ , \tag{7.238}$$

the validity of which can easily be checked using the ideal gas equation of state.

7.7.2 ‡Virial Equation of State

Under the assumption of pairwise additivity of the intermolecular potential, we obtained a statistical mechanical expression for pressure in a canonical ensemble in Sect. 3.14.1. It is possible to rewrite our result (3.201) in terms of g_N.

For this purpose, we note that

$$\left\langle \sum_{i=1}^{N} \sum_{j=1}^{N}{}' \frac{\mathrm{d}v(r_{ij})}{\mathrm{d}r_{ij}} r_{ij} \right\rangle_N = N(N-1) \left\langle \frac{\mathrm{d}v(r_{12})}{\mathrm{d}r_{12}} r_{12} \right\rangle_N , \tag{7.239}$$

where we introduced the subscript N to indicate ensemble averages in the canonical ensemble. But, in the expression

$$\left\langle \frac{\mathrm{d}v(r_{12})}{\mathrm{d}r_{12}} r_{12} \right\rangle_N = \frac{1}{Z} \frac{1}{\Lambda^{3N} N!} \int \frac{\mathrm{d}v(r_{12})}{\mathrm{d}r_{12}} r_{12} \left[\int e^{-\beta\phi(\boldsymbol{r}^N)} \mathrm{d}\boldsymbol{r}_3, \ldots, \mathrm{d}\boldsymbol{r}_N \right] \mathrm{d}\boldsymbol{r}_1 \mathrm{d}\boldsymbol{r}_2 , \tag{7.240}$$

$\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ are just the integration variables that can be replaced, respectively, by $\boldsymbol{r}$ and $\boldsymbol{r}'$ without affecting the value of the integral. When the resulting expression is compared against (7.154) with ψ set to zero, we find

$$\left\langle \frac{\mathrm{d}v(r_{12})}{\mathrm{d}r_{12}} r_{12} \right\rangle_N = \int_V \int_V \frac{\mathrm{d}v(R)}{\mathrm{d}R} R \langle \delta(\boldsymbol{r}-\boldsymbol{r}_1)\delta(\boldsymbol{r}'-\boldsymbol{r}_2) \rangle_N \mathrm{d}\boldsymbol{r} \mathrm{d}\boldsymbol{r}' . \tag{7.241}$$

Recalling (7.155) and (7.158) with $n_N(\boldsymbol{r}) = n_N(\boldsymbol{r}')$ replaced by $n = N/V$, we obtain

$$\begin{aligned} N(N-1) \left\langle \frac{\mathrm{d}v(r_{12})}{\mathrm{d}r_{12}} r_{12} \right\rangle_N &= n^2 \int_V \int_V \frac{\mathrm{d}v(R)}{\mathrm{d}R} R g_N(\boldsymbol{r}, \boldsymbol{r}') \mathrm{d}\boldsymbol{r} \mathrm{d}\boldsymbol{r}' \\ &= n^2 V \int_V \frac{\mathrm{d}v(R)}{\mathrm{d}R} R g_N(\boldsymbol{R}) \mathrm{d}\boldsymbol{R} . \end{aligned} \tag{7.242}$$

With this expression, (3.201) becomes

$$P = P^{\mathrm{id}} - \frac{1}{6} n^2 \int_V \frac{\mathrm{d}v(r)}{\mathrm{d}r} r g_N(\boldsymbol{r}) \mathrm{d}\boldsymbol{r} , \tag{7.243}$$

which is referred to as the **virial equation of state**. If $v(r) \equiv 0$, this equation reduces to the ideal gas equation of state.

7.8 Frequently Used Symbols

$\mathscr{F}[u]$, a functional $\mathscr{F}$ of a function $u(x)$.
$\delta\mathscr{F}/\delta u(x)$, functional derivative.
$\mathrm{Tr}^{\mathrm{cl}}$, classical trace.

d , hard-sphere diameter.
f , F/V.
$g(\boldsymbol{r},\boldsymbol{r}')$, radial distribution function in a grand canonical ensemble.
$g_N(\boldsymbol{r},\boldsymbol{r}')$, radial distribution function in a canonical ensemble.
k_B , Boltzmann constant, 1.3806×10^{-23} J/K.
$n(\boldsymbol{r})$ density profile in a grand canonical ensemble.
$n_N(\boldsymbol{r})$ density profile in a canonical ensemble.
$n^{\text{eq}}(\boldsymbol{r})$, equilibrium density profile.
$n^{(2)}(\boldsymbol{r},\boldsymbol{r}')$, pair distribution function in a grand canonical ensemble.
$n_N^{(2)}(\boldsymbol{r},\boldsymbol{r}')$, pair distribution function in a canonical ensemble.
$\hat{n}(\boldsymbol{r},\boldsymbol{r}^N)$, density operator.
$\boldsymbol{p}_i$, linear momentum of the ith particle.
r_c , cut-off radius for the truncated and shifted Lennard–Jones potential.
$r_{\min}$, $2^{1/6}\sigma$, the distance at which $v^{\text{LJ}}(r)$ takes its minimum value $-\varepsilon$.
$\boldsymbol{r}_i$, position vector of the ith particle.
$v(\boldsymbol{r},\boldsymbol{r}')$, pair potential, that is, the potential energy due to interaction between two particles, one at $\boldsymbol{r}$ and the other at $\boldsymbol{r}'$.
$v^{\text{att}}(r)$, attractive part of $v(r)$.
$v^{\text{rep}}(r)$, repulsive part of $v(r)$.
$v^{\text{HS}}(r)$, hard-sphere potential.
$v^{\text{LJ}}(r)$, Lennard–Jones potential.
$v^{\text{tsLJ}}(r)$, truncated and shifted Lennard–Jones potential.

F_{int} , intrinsic Helmholtz free energy.
$F_{\text{int}}^{\text{exc}}$, intrinsic excess Helmholtz free energy.
$F_{\text{int}}^{\text{id}}$, intrinsic Helmholtz free energy of an ideal gas.
N , the number of particles.
P , pressure.
P_{hHS} , pressure of a homogeneous hard-sphere fluid.
$P_{\text{hHS}}^{\text{exc}}$, excess pressure of a homogeneous hard-sphere fluid.
T , absolute temperature.
V , volume.
X_i , the ith additional variable needed to specify the state of a system that is not in equilibrium.

β , $1/k_BT$.
ε , energy parameter of the Lennard–Jones potential.
η , packing fraction.
μ , chemical potential.
μ_{hHS} , chemical potential of a homogeneous hard-sphere fluid.
$\mu_{\text{hHS}}^{\text{exc}}$, excess chemical potential of a homogeneous hard-sphere fluid.
ρ , statistical weight.
ρ^{eq} , statistical weight at equilibrium.
σ , Lennard–Jones diameter.
$\phi(\boldsymbol{r}^N)$, potential energy due to intermolecular interaction.
$\psi(\boldsymbol{r})$, external field.

$\Delta e(r)$, blip function.
Λ , thermal wavelength.
Ξ , grand canonical partition function.
Ω , grand potential.
Ω_{int} , intrinsic grand potential.

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Chapter 8
Quantum Formulation

In this chapter, we present the mathematical formalism used in quantum mechanics first and then derive expressions for canonical and microcanonical partition functions for quantum mechanical systems. This will help you develop familiarity with the basic ideas of quantum mechanics and the bra–ket notation you may encounter when consulting more advanced textbooks on statistical mechanics.

The important conclusion of this chapter is that (4.24) and (4.72) we obtained by means of classical statistical mechanics remain applicable in quantum statistical mechanics as well. Thus, the distinction between classical and quantum mechanical versions of statistical mechanics stems from the explicit expressions for $\overline{\Omega}(E)$ these mechanics predict and from the manner in which a given system populates the microstates accessible to it.

Many optional sections are included to provide explicit derivations of several key results from quantum mechanics we have already used in earlier chapters, but should probably be omitted upon the first reading. Keeping with our most immediate goals, we will not concern ourselves with experimental findings that forced the radical departure from classical mechanics and the eventual formulation of quantum mechanics in the early twentieth century. Interested readers can find these accounts in Refs. [7, 9] as well as in earlier chapters of many textbooks on quantum mechanics.

8.1 Vector Space

In classical mechanics, a microstate of a system with f mechanical degrees of freedom is specified by $2f$ variables (q^f, p^f). In quantum mechanics, a microstate of a system is specified by a vector in a complex vector space. In this section, we spend some time familiarizing ourselves with the basic properties of a vector space.

Before proceeding with the abstract vector space, it may be helpful for you to review the materials in Appendix A, in which vectors in the ordinary three-

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dimensional space is discussed. This provides a useful analogy as we talk about abstract vector space in a more general term.

8.1.1 Definition

Let $\mathbb{K}$ denote either the set $\mathbb{C}$ of all complex numbers or the set $\mathbb{R}$ of all real numbers. We shall take for granted the rules for addition and multiplication of two numbers in $\mathbb{K}$. On this basis, we construct a vector space as follows. Let V be a set of objects and suppose that:

a. There is an operation called *addition* that assigns for each $x \in V$ and for each $y \in V$ another element in V, which we denote by $x+y$.
b. There is an operation called *multiplication by a number* that assigns for each number $\alpha \in \mathbb{K}$ and each $x \in V$ another element in V, which we denote by αx.

When the following properties are satisfied, the set V is said to be a **vector space**:

V1: $x+y=y+x$ for all $x,y \in V$.
V2: $x+(y+z)=(x+y)+z$ for all $x,y,z \in V$.
V3: There is an element $\theta \in V$ such that $x+\theta=x$ for all $x \in V$.
V4: To each $x \in V$, there corresponds an element $\overline{x} \in V$ such that $x+\overline{x}=\theta$.
V5: $\alpha(x+y)=\alpha x+\alpha y$ for all $x,y \in V$ and for all $\alpha \in \mathbb{K}$.
V6: $(\alpha+\beta)x=\alpha x+\beta x$ for all $\alpha,\beta \in \mathbb{K}$ and for all $x \in V$.
V7: $\alpha(\beta x)=(\alpha\beta)x$ for all $\alpha,\beta \in \mathbb{K}$ and for all $x \in V$.
V8: $1x=x$ for all $x \in V$, in which 1 is a number.

An element of V is called a **vector** and θ is called the **zero vector**. If $\mathbb{K}=\mathbb{R}$, V is a **real vector space**. If $\mathbb{K}=\mathbb{C}$ instead, V is a **complex vector space**.

We note that the standard notation for $\overline{x}$ appearing in V4 is $-x$. Thus, $x+\overline{y}=x+(-y)$, which is more commonly written as $x-y$. We note that $-x$ is a vector that gives θ when added to another vector x. In contrast, $(-1)x$ is a vector obtained by multiplying x by a number called -1. Thus, they are conceptually distinct objects. It is in order to stress this distinction that we use $\overline{x}$ for $-x$, even though they *turn out to be* the same vector as you can convince yourself in Exercise 8.1d.

Example 8.1. A real vector space: The set V of all pairs of real numbers, that is, $V=\{(x,y)|x,y \in \mathbb{R}\}$, is a real vector space with the addition defined by

$$(x_1,y_1)+(x_2,y_2)=(x_1+x_2,y_1+y_2) \tag{8.1}$$

and the multiplication by a number defined by

$$\alpha(x,y)=(\alpha x,\alpha y) \text{ for each } \alpha \in \mathbb{R}\,. \tag{8.2}$$

As a slightly less trivial example, let us consider a set of functions.

Example 8.2. A real vector space: The set V of all real-valued functions defined on the interval $[a,b] \subset \mathbb{R}$ is a vector space with the addition defined by

$$(f+g)(x) := f(x)+g(x) \text{ for each } f,g \in V \tag{8.3}$$

and the multiplication by a number defined by

$$(\alpha f)(x) := \alpha f(x) \text{ for each } f \in V \text{ and each } \alpha \in \mathbb{R}\,. \tag{8.4}$$

It is important to recognize the meaning of (8.3), in which $f+g$ is the name of a function in V. Being a function, there has to be a rule of assigning a real number to each $x \in \mathbb{R}$. This rule is given by (8.3) in terms of the rule for adding two real numbers and the rules that assign real numbers $f(x)$ and $g(x)$ to each $x \in \mathbb{R}$. Likewise, αf on the left-hand side of (8.4) is the name of a function in V. The rule of assigning a number to each $x \in \mathbb{R}$ is given in terms of the rule for multiplying two numbers, α and $f(x)$, and the rule of assignment for the function f.

Finally, if we replace $\alpha \in \mathbb{R}$ in (8.4) by $\alpha \in \mathbb{C}$ while insisting that V is still a set of all real-valued functions only, then V is no longer a vector space since $\alpha f \notin V$ if $\alpha \notin \mathbb{R}$.

An example of a complex vector space can be generated easily with a slight modification to the previous one.

Example 8.3. A complex vector space: The set V of all complex-valued functions defined on the interval $[a,b] \subset \mathbb{R}$ is a vector space with the addition defined by

$$(f+g)(x) := f(x)+g(x) \text{ for each } f,g \in V \tag{8.5}$$

and the multiplication by a number defined by

$$(\alpha f)(x) := \alpha f(x) \text{ for each } f \in V \text{ and each } \alpha \in \mathbb{C}\,. \tag{8.6}$$

Even if we limit ourselves to $\alpha \in \mathbb{R}$, V still is a vector space. According to our definition, however, V now becomes a real vector space.

Using the properties of a vector space enumerated above, we can prove various useful facts about it.

Example 8.4. Zero vector is unique: Take property V3, for example. This property demands that there must be a zero vector in a vector space. But, it does not say how many zero vectors a particular vector space might contain. Nevertheless, we can show that, in any vector space V, there is only one zero vector. To see this, let both θ_1 and θ_2 be zero vectors of V. From V3, we have

$$x+\theta_1 = x \text{ for any } x \in V \tag{8.7}$$

and

$$x+\theta_2 = x \text{ for any } x \in V\ . \tag{8.8}$$

Since (8.7) holds for *any* $x \in V$, it holds for $\theta_2 \in V$ as well:

$$\theta_2+\theta_1 = \theta_2\ . \tag{8.9}$$

Using the property V1 of a vector space, we may rewrite this as

$$\theta_1+\theta_2 = \theta_2\ . \tag{8.10}$$

From (8.8) with $x = \theta_1 \in V$,

$$\theta_1+\theta_2 = \theta_1\ , \tag{8.11}$$

Comparing the last two equations, we find that $\theta_1 = \theta_2$.

Exercise 8.1. Let V be a vector space:

a. Suppose that θ' satisfies $x+\theta' = x$ for a *particular* $x \in V$. Show that θ' is a zero vector of V.
b. Show that $0x = \theta$.
c. Show that, if $x+y = \theta$, then $y = \overline{x}$.
d. Show that $(-1)x = \overline{x}$.
e. Show that $\alpha\overline{x} = (-\alpha)x$ for any $\alpha \in \mathbb{K}$.
f. Show that $\alpha\theta = \theta$ for any $\alpha \in \mathbb{K}$.
g. Show that $\alpha\overline{x} = \overline{\alpha x}$ for any $\alpha \in \mathbb{K}$.
h. Show that

$$\alpha(x-y) = \alpha x - \alpha y \text{ for any } \alpha \in \mathbb{K} \tag{8.12}$$

and that

$$(\alpha-\beta)x = \alpha x - \beta x \text{ for any } \alpha, \beta \in \mathbb{K}. \tag{8.13}$$

Note that we interpret $\alpha x - \alpha y$ as $\alpha x + \overline{\alpha y}$ and $\alpha x - \beta x$ as $\alpha x + \overline{\beta x}$. ///

8.1.2 Linear Independence

For vectors $x_1,\dots,x_m \in V$ and the numbers $c_1,\dots,c_m \in \mathbb{K}$, the sum

$$c_1x_1 + \cdots + c_mx_m \tag{8.14}$$

is called a **linear combination** of $x_1, \dots, x_m$. The set U of *all* possible linear combinations of $x_1, \dots, x_m$ is a vector space called the **span** of the set $\{x_1,\dots,x_m\}$, which is denoted by

$$\operatorname{span}(\{x_1,\dots,x_m\})\ . \tag{8.15}$$

We say that the vectors $x_1, \dots, x_m$ **span** this vector space. In the ordinary three-dimensional space, for example, two vectors $\boldsymbol{a}$ and $\boldsymbol{b}$, neither of which is a scalar multiple of the other, span a two-dimensional vector space, whose elements are vectors on the plane containing $\boldsymbol{a}$ and $\boldsymbol{b}$.

Vectors $x_1, \dots, x_m$ are said to be **linearly independent** if

$$c_1x_1 + \cdots + c_mx_m = \theta \tag{8.16}$$

requires

$$c_i = 0 \text{ for all } i = 1,\dots,m\ . \tag{8.17}$$

Equation (8.17) is clearly sufficient for (8.16) and is referred to as the **trivial solution** of (8.16). The vectors are **linearly dependent** if there is a nontrivial solution of (8.16), for which not every c_i is zero.

Example 8.5. Linear independence:

a. Two vectors $\boldsymbol{a}$ and $\boldsymbol{b}$ in the ordinary three-dimensional space are linearly dependent if one of them is a scalar multiple of the other:

$$\boldsymbol{a} = c\boldsymbol{b} \text{ for some } c \in \mathbb{R}. \tag{8.18}$$

On the other hand, if neither is a scalar multiple of the other, then they are linearly independent.

b. The zero vector, taken by itself, is linearly dependent since

$$c\theta = \theta \text{ for any } c \in \mathbb{K}. \tag{8.19}$$

c. Vectors $\theta, x_1, \dots, x_m$ are linearly dependent since

$$c_0\theta + c_1x_1 + \cdots + c_mx_m = \theta \tag{8.20}$$

is satisfied for any value of $c_0 \in \mathbb{K}$ if $c_1 = \cdots = c_m = 0$.

8.1.3 Basis

A set of vectors

$$\{\phi_1,\dots,\phi_r\}\ , \tag{8.21}$$

where $\phi_i \in V$ for $i=1,\dots,r$, is said to be a **basis** of V if *any* $x \in V$ can be expressed as a linear combination of ϕ_1, ..., ϕ_r in one and only one way. A member of the basis is referred to as a **basis vector**.

A vector space V may have multiple bases. However, the number of basis vectors is the same for all of them. It is therefore an *intrinsic property* of V and is called the **dimension** of V. In other words, if the dimension of V is r, a set of m vectors cannot be a basis if $m > r$ or $m < r$. This is established by the following two theorems, the proofs of which are provided in the next optional subsection.

Theorem 8.1. *A set of vectors* $\mathscr{B} := \{\phi_1,\dots,\phi_r\}$ *is a basis of* V *if and only if* $\operatorname{span}(\mathscr{B}) = V$ *and* ϕ_1, ..., ϕ_r *are linearly independent.*

Theorem 8.2. *Suppose that* $\mathscr{B} := \{\phi_1,\dots,\phi_r\}$ *is a basis of* V.

a. Vectors ψ_1, ..., ψ_m *are not linearly independent if* $m > r$.
b. Vectors ψ_1, ..., ψ_m *does not span* V *if* $m < r$.

8.1.4 †Proofs of Theorems

For completeness, we prove of the theorems just introduced.

Proof of Theorem 8.1

Let us suppose that $\mathscr{B}$ is a basis and establish the "only if" part of the theorem. We first show that $\operatorname{span}(\mathscr{B}) = V$. If $x \in V$, x may be expressed as a linear combination of ϕ_1, ..., ϕ_r, and hence $x \in \operatorname{span}(\mathscr{B})$. On the other hand, if $x \in \operatorname{span}(\mathscr{B})$, then $x \in V$. Thus, the membership of $\operatorname{span}(\mathscr{B})$ is identical to that of V. So, we have $\operatorname{span}(\mathscr{B}) = V$. To establish that ϕ_1, ..., ϕ_r are linearly independent, suppose that

$$c_1\phi_1 + \cdots + c_r\phi_r = \theta\ . \tag{8.22}$$

We note that θ can also be written as

$$\theta = 0\phi_1 + \cdots + 0\phi_r\ . \tag{8.23}$$

But, each vector in V, including θ, has a unique expression when written as a linear combination of the basis vectors in $\mathscr{B}$. Thus, comparing (8.22) and (8.23), we conclude that $c_i = 0$ for all $i = 1,\dots,r$.

Conversely, suppose that $\mathrm{span}(\mathscr{B}) = V$ and that the members of $\mathscr{B}$ are linearly independent. Then, any member x of V belongs to $\mathrm{span}(\mathscr{B})$. This guarantees that x may be expressed as a linear combination of $\phi_1, \ldots, \phi_r$. If we suppose

$$x = c_1\phi_1 + \cdots + c_r\phi_r = d_1\phi_1 + \cdots + d_r\phi_r \,, \tag{8.24}$$

then,

$$(c_1 - d_1)\phi_1 + \cdots + (c_r - d_r)\phi_r = \theta \,. \tag{8.25}$$

Since $\phi_1, \ldots, \phi_r$ are linearly independent, only the trivial solution is possible, that is, $c_i = d_i$ for all $i = 1, \ldots, r$. That is, there is only one way to express x as a linear combination of $\phi_1, \ldots, \phi_r$. □

Proof of Theorem 8.2

We prove each part of the theorem by contradiction. That is, we assume that the claim is false and then show that this assumption leads to a contradiction:

a. Let us suppose that $\psi_1, \ldots, \psi_m$ $(m > r)$ are linearly independent. Since $\mathscr{B}$ is a basis,

$$\psi_1 = c_1\phi_1 + \cdots + c_r\phi_r \,, \tag{8.26}$$

in which at least one of $c_1, \ldots, c_r$ is nonzero. To be concrete, we suppose that c_1 is nonzero and solve (8.26) for ϕ_1:

$$\phi_1 = \frac{1}{c_1}\psi_1 - \frac{c_2}{c_1}\phi_2 - \cdots - \frac{c_r}{c_1}\phi_r \,. \tag{8.27}$$

There is no loss of generality here since we can always relabel ϕ_i's if necessary. By means of Theorem 8.1, we now show that

$$\mathscr{B}_1 := \{\psi_1, \phi_2, \ldots, \phi_r\} \tag{8.28}$$

is a basis. Since $\mathscr{B}$ is a basis, for any $x \in V$, we have

$$x = d_1\phi_1 + \cdots + d_r\phi_r = \frac{d_1}{c_1}\psi_1 + \left(d_2 - \frac{d_1 c_2}{c_1}\right)\phi_2 + \cdots + \left(d_r - \frac{d_1 c_r}{c_1}\right)\phi_r \,, \tag{8.29}$$

where we used (8.27). So, any $x \in V$ can be written as a linear combination of $\psi_1, \phi_2, \ldots, \phi_r$. To see that these vectors are linearly independent, let us consider the equation:

$$e_1\psi_1 + e_2\phi_2 + \cdots + e_r\phi_r = \theta \,. \tag{8.30}$$

If $e_1 \neq 0$, then ψ_1 is a linear combination of $\phi_2, \ldots, \phi_r$. This is contrary to the supposition that $c_1 \neq 0$ in (8.26). Since by definition of basis, the expression (8.26) is unique. So, $e_1 = 0$ and (8.30) reduces to

$$e_2\phi_2 + \cdots + e_r\phi_r = \theta \,. \tag{8.31}$$

But, since $\phi_2, \ldots, \phi_r$ are linearly independent, the only possible solution is that $e_2 = \cdots = e_r = 0$. Thus, only the trivial solution can satisfy (8.30).
Now that $\mathscr{B}_1$ is shown to be a basis, we can write

$$\psi_2 = f_1\psi_1 + f_2\phi_2 + \cdots + f_r\phi_r \, . \tag{8.32}$$

We observe that at least one of $f_2, \ldots, f_r$ is nonzero. Otherwise, we have $\psi_2 = f_1\psi_1$, which is in odds with our supposition that $\psi_1, \ldots, \psi_m$ are linearly independent. For concreteness, we assume that $f_2 \neq 0$ and write

$$\phi_2 = -\frac{f_1}{f_2}\psi_1 + \frac{1}{f_2}\psi_2 - \frac{f_3}{f_2}\phi_3 - \cdots - \frac{f_r}{f_2}\phi_r \, . \tag{8.33}$$

As before, we can show that

$$\mathscr{B}_2 := \{\psi_1, \psi_2, \phi_3, \ldots, \phi_r\} \tag{8.34}$$

is a basis. In fact, by means of (8.33), any linear combination of $\psi_1, \phi_2, \ldots, \phi_r$ may be expressed as a linear combination of $\psi_1, \psi_2, \phi_3, \ldots, \phi_r$. Let

$$g_1\psi_1 + g_2\psi_2 + g_3\phi_3 + \cdots + g_r\phi_r = \theta \, , \tag{8.35}$$

If $g_2 \neq 0$, this equation can be solved to express ψ_2 as a linear combination of $\psi_1, \phi_3, \ldots, \phi_r$, which is in odds with (8.32) with $f_2 \neq 0$. So, $g_2 = 0$. It follows that $g_1, g_3, \ldots, g_r$ are all zero since $\psi_1, \phi_3, \ldots, \phi_r$ are linearly independent as we have already established below (8.30).
Proceeding in this manner, we may establish that

$$\mathscr{B}_r := \{\psi_1, \ldots, \psi_r\} \tag{8.36}$$

is a basis. Thus, $\psi_{r+1}, \ldots, \psi_m$ can be expressed as linear combinations of $\psi_1, \ldots, \psi_r$, which contradicts our assumption that $\psi_1, \ldots, \psi_m$ are linearly independent. □

b. This time, we suppose that $m < r$ but that

$$V = \operatorname{span}(\{\psi_1, \ldots, \psi_m\}) \, . \tag{8.37}$$

If $\psi_1, \ldots, \psi_m$ are linearly independent, then by definition, $\{\psi_1, \ldots, \psi_m\}$ is a basis of V. But, then according to part a of the current theorem, $\phi_1, \ldots, \phi_r$ with $r > m$ cannot be linearly independent, contrary to the supposition that $\mathscr{B}$ is a basis. If $\psi_1, \ldots, \psi_m$ are linearly dependent, then

$$c_1\psi_1 + \cdots + c_m\psi_m = \theta \tag{8.38}$$

and at least one of $c_1, \ldots, c_m$ is nonzero. To be concrete, suppose that $c_1 \neq 0$. Then,

$$\psi_1 = -\frac{c_2}{c_1}\psi_2 - \cdots - \frac{c_m}{c_1}\psi_m \, , \tag{8.39}$$

in terms of which any $x \in V$ may be expressed as a linear combination of $\psi_2, \ldots, \psi_m$:

$$x = d_1 \psi_1 + \cdots + d_m \psi_m = \left(d_2 - \frac{d_1 c_2}{c_1} \right) \psi_2 + \cdots + \left(d_m - \frac{d_1 c_m}{c_1} \right) \psi_m \,. \quad (8.40)$$

In this way, we can remove ψ_i's one by one until the remaining ψ_i's are linearly independent. But, the span of the set consisting of the remaining ψ_i's is still V. As we saw above, this leads to a contradiction. □

8.1.5 Scalar Product Space

Let V be a complex vector space. If there is a rule that assigns a *number* $(x,y) \in \mathbb{C}$ for each pair of $x, y \in V$ and if the rule satisfies the following properties, then we call (x,y) the **scalar product** of x and y and the vector space V a **scalar product space**:

S1: $(x+y,z) = (x,z) + (y,z)$ for all $x,y,z \in V$.
S2: $(y,x) = (x,y)^*$ for all $x,y \in V$, where * denotes the complex conjugation.
S3: $(\alpha x, y) = \alpha (x,y)$ for all $x,y \in V$ and for all $\alpha \in \mathbb{C}$.
S4: $(x,x) \geq 0$ for all $x \in V$.
S5: $(x,x) = 0$ if and only if $x = \theta$.

According to S2, (x,x) is a real number. Because of S4, it is also nonnegative. Thus, $\|x\| := \sqrt{(x,x)}$, called the **norm** of the vector x, is a real number. We say that $x \neq \theta$ and $y \neq \theta$ are **orthogonal** if $(x,y) = 0$. If V is a real vector space, we demand that $(x,y) \in \mathbb{R}$ instead and replace S2 and S3 as follows:

S2′ $(y,x) = (x,y)$ for all $x,y \in V$.
S3′ $(\alpha x, y) = \alpha (x,y)$ for all $x,y \in V$ and for all $\alpha \in \mathbb{R}$.

Example 8.6. Three-dimensional vectors: The vector space V of ordinary three-dimensional vectors is a scalar product space if

$$(\boldsymbol{a}, \boldsymbol{b}) := \boldsymbol{a} \cdot \boldsymbol{b} \,. \quad (8.41)$$

With this definition, the norm of $\boldsymbol{a}$ is just the length of $\boldsymbol{a}$, which we have been denoting by $\|\boldsymbol{a}\|$.

The following example illustrates a scalar product defined on a complex vector space.

Example 8.7. Complex-valued functions: Let V be a complex vector space of complex-valued functions defined on the interval $[a,b] \subset \mathbb{R}$. If the membership of V is such that the integral

$$(f,g) := \int_a^b g^*(x) f(x) \mathrm{d}x \tag{8.42}$$

exists for all $f,g \in V$, then V is a scalar product space.

Exercise 8.2. Let V be a scalar product space. Show that

a.
$$(x, \alpha y) = \alpha^* (x,y) \text{ for any } \alpha \in \mathbb{C}. \tag{8.43}$$

b.
$$(x, \theta) = (\theta, x) = 0 \, . \tag{8.44}$$

c.
$$(x, y+z) = (x,y) + (x,z) \, . \tag{8.45}$$

///

From (8.43) and (8.45), it follows that

$$(x, \alpha y + \beta z) = \alpha^* (x,y) + \beta^* (x,z) \, . \tag{8.46}$$

We refer to this result by saying that the scalar product is **anti-linear** in the second argument.

8.1.6 Orthonormal Basis

A basis $\{b_1, \ldots, b_r\}$ is said to form an **orthonormal basis** if

$$(b_i, b_j) = \delta_{ij} \text{ for all } i,j = 1, \ldots, r \, , \tag{8.47}$$

where δ_{ij} is the Kronecker delta.

Provided that r is finite, an orthonormal basis can be constructed from any basis. Given an arbitrary basis $\{\phi_1, \ldots, \phi_r\}$, we proceed as

$$\begin{aligned}
b_1 &:= \phi_1 / \|\phi_1\| \, , \\
b_2 &:= b_2' / \|b_2'\| \, , \; b_2' := \phi_2 - (\phi_2, b_1) b_1 \, , \\
b_3 &:= b_3' / \|b_3'\| \, , \; b_3' := \phi_3 - (\phi_3, b_1) b_1 - (\phi_3, b_2) b_2 \, , \\
&\cdots \\
b_r &:= b_r' / \|b_r'\| \, , \; b_r' := \phi_r - \sum_{j=1}^{r-1} (\phi_r, b_j) b_j \, .
\end{aligned} \tag{8.48}$$

The newly constructed basis vectors clearly have the unit norm. This construction is know as the **Gram–Schmidt orthogonalization**.

Exercise 8.3. Check the orthogonality of the basis $\{b_1, \ldots, b_r\}$. ///

8.1.7 Functions

A complex vector space plays an essential role in quantum mechanics. Accordingly, we shall restrict ourselves to such spaces in what follows.

Consider two sets V and W. A rule that assigns for each $x \in V$ precisely one element $y \in W$ is called a function. That F is such a function is indicated by the symbol $F : V \longrightarrow W$. The element in W assigned to $x \in V$ by F is denoted by $F(x)$. Now, let $F : V \longrightarrow W$ and $G : V \longrightarrow W$. If $F(x) = G(x)$ for each $x \in V$, then F and G refer to one and the same rule of assignment. The functions F and G are said to be identical.

8.1.8 Linear Functional

The function $F : V \longrightarrow \mathbb{C}$ on a vector space V is a **linear functional** if it satisfies:

F1: $F(x+y) = F(x) + F(y)$
F2: $F(\alpha x) = \alpha F(x)$

for all $x, y \in V$ and all $\alpha \in \mathbb{C}$. A linear functional is determined completely once the value of $F(x)$ is given for each $x \in V$. Because any x can be expressed in terms of an orthonormal basis $\{b_1, \ldots, b_r\}$ of V as[46]

$$x = c_1 b_1 + \cdots + c_r b_r \, , \tag{8.49}$$

we have

$$F(x) = c_1 F(b_1) + \cdots + c_r F(b_r) \, . \tag{8.50}$$

Thus, F is completely determined by specifying r complex numbers $F(b_1), \ldots, F(b_r)$.

A scalar product is an example of a linear functional. Let us pick a particular $f \in V$ and define F by

$$F(x) := (x, f) \text{ for all } x \in V \, . \tag{8.51}$$

Clearly, $F(x)$ satisfies the properties F1 and F2, and hence is a linear functional. It follows that any vector in V defines a linear functional.

The converse is also true. That is, to any linear functional F, there corresponds a *unique* vector $f \in V$ such that $F(x) = (x, f)$ for all $x \in V$. In fact, consider

$$f = F(b_1)^* b_1 + \cdots + F(b_r)^* b_r \, . \tag{8.52}$$

That is, given F, we first compute r complex numbers $F(b_1), \ldots, F(b_r)$. We then take their complex conjugate and construct f according to (8.52). The resulting vector f satisfies $(x, f) = F(x)$ for all $x \in V$.

Exercise 8.4. Verify this assertion. ///

Exercise 8.5. Given a linear functional $F(x)$, show that there is only one vector $f \in V$ that satisfies (8.51). ///

We have just seen that there is a one-to-one correspondence between a vector in V and a linear functional on V. Let $\widetilde{V}$ denote a set of all linear functionals on V and define the addition of two linear functionals and the multiplication of a linear functional by a number as follows:

D1: $(F+G)(x) := F(x) + G(x)$ for all $F, G \in \widetilde{V}$.
D2: $(\alpha F)(x) := \alpha F(x)$ for all $F \in \widetilde{V}$ and for all $\alpha \in \mathbb{C}$.

Then, $\widetilde{V}$ is called the **dual space** of V. We now show that $\widetilde{V}$ is a vector space. First, we need to ensure that the following two properties are satisfied by our definitions of the addition (D1) and the multiplication by a number (D2):

a. $F + G \in \widetilde{V}$. That is, $F + G$ is a linear functional, and hence

$$(F+G)(x+y) = (F+G)(x) + (F+G)(y) \tag{8.53}$$

and

$$(F+G)(\alpha x) = \alpha (F+G)(x) \tag{8.54}$$

hold for any $x, y \in V$ and $\alpha \in \mathbb{C}$.

b. $\alpha F \in \widetilde{V}$. That is, αF is a linear functional, and hence

$$(\alpha F)(x+y) = (\alpha F)(x) + (\alpha F)(y) \tag{8.55}$$

and

$$(\alpha F)(\beta x) = \beta (\alpha F)(x) \tag{8.56}$$

hold for any $x, y \in V$ and $\beta \in \mathbb{C}$.

The content of (8.54), which may seem a little obscure at first sight, is that applying $F + G$ on αx produces the same result as applying $F + G$ on x first and then multiplying the result by α. Equation (8.56) indicates that applying the function αF on βx gives the same result as applying αF on x first and then multiplying the result by β.

Exercise 8.6. Prove (8.53) and (8.54) from D1 and (8.55) and (8.56) from D2. ///

Now we have to show that D1 and D2 are compatible with V1–V8. For this purpose, let f and g in V correspond to F and G in $\widetilde{V}$, respectively. As we have just established, $F + G$ and αF are elements of $\widetilde{V}$. What are their corresponding vectors in V? From D1 and (8.51), we see that

$$(F+G)(x) = F(x) + G(x) = (x, f) + (x, g) = (x, f+g) , \tag{8.57}$$

where the last step follows from (8.45). Thus, $F+G \in \widetilde{V}$ corresponds $f+g \in V$. Similarly, using D2 and (8.51),

$$(\alpha F)(x) = \alpha F(x) = \alpha(x,f) = (x,\alpha^* f) \,, \tag{8.58}$$

where the last step follows from (8.43). So, $\alpha F \in \widetilde{V}$ corresponds $\alpha^* f \in V$. It is worth emphasizing that the corresponding vector is $\alpha^* f$ and *not* αf.

Exercise 8.7. Show that the dual space is a vector space. ///

8.1.9 Linear Operator

Let both V and W be vector spaces. The function $T : V \longrightarrow W$ is a **linear operator** if T satisfies:

L1: $T(x+y) = T(x) + T(y)$ for all $x, y \in V$.
L2: $T(\alpha x) = \alpha T(x)$ for all $\alpha \in \mathbb{C}$ and for all $x \in V$.

We often write $T(x)$ as Tx.

Example 8.8. Linear operators: The function $f(x) = ax$, where $a, x \in \mathbb{C}$, is a linear operator from $\mathbb{C}$ to $\mathbb{C}$. In contrast, $g(x) = ax + b$, where $b \neq 0$, is not.

Let V be a set of continuously differentiable functions. That is, if $f \in V$, then $\mathrm{d}f/\mathrm{d}x$ exists and $\mathrm{d}f/\mathrm{d}x$ is continuous. If W is the set of all continuous functions, then the derivative $\mathrm{d}/\mathrm{d}x$ is a linear operator from V to W.

Exercise 8.8. Let $T : V \longrightarrow W$ be a linear operator. Show that

a. $T(\theta_V) = \theta_W$, where θ_V is the zero vector in V and θ_W is the zero vector in W.
b. $T(x-y) = T(x) - T(y)$. ///

8.2 Kets, Bras, and Operators

In classical mechanics, a microstate of a system is specified by (q^f, p^f). In quantum mechanics, a microstate is specified by a **ket**, a vector in a complex vector space called a **ket space** V_k. As in Sect. 8.1.8, we can construct a dual space of V_k through the scalar product defined on V_k. The dual space $V_b = \widetilde{V}_k$ so constructed is referred to as a **bra space**, a member of which is a **bra**. These vectors and the spaces they belong to constitute a fundamental construct of quantum mechanics. In this section, we develop rules of computing with bras and kets.

8.2.1 Bra–Ket

A ket is denoted by a symbol $|\cdots\rangle$ replacing "$\cdots$" by an appropriate label. For a given $|f\rangle \in V_k$,

$$F(|x\rangle) := (|x\rangle, |f\rangle) \text{ for all } |x\rangle \in V_k \tag{8.59}$$

defines a linear functional F. When this is done for all $|f\rangle \in V_k$, we have a set V_b of linear functionals. A member of V_b is called a bra and is denoted by $\langle\cdots|$ with "$\cdots$" replaced by an appropriate label. In this notation, the linear functional F derived from $|f\rangle$ is simply written as $\langle f|$. Thus, in place of (8.59), we write

$$\langle f|x\rangle := (|x\rangle, |f\rangle) \text{ for all } |x\rangle \in V_k. \tag{8.60}$$

As we saw in Sect. 8.1.8, this establishes the one-to-one correspondence between $|f\rangle \in V_k$ and $\langle f| \in V_b$. Pictorially, we write

$$|f\rangle \in V_k \overset{\text{DC}}{\longleftrightarrow} \langle f| \in V_b\,, \tag{8.61}$$

where "DC" stands for "dual-correspondence."

Now that the correspondence between kets in V_k and bras in V_b is established, we can turn V_b into a vector space by defining the addition of two bras and the multiplication of a bra by a number in accordance with D1 and D2 from Sect. 8.1.8. (See Exercise 8.7.) In terms of the bra–ket notation, they are given by

$$(\langle f| + \langle g|)|x\rangle = \langle f|x\rangle + \langle g|x\rangle \text{ for all } \langle f|\,, \langle g| \in V_b, \tag{8.62}$$

and

$$(c\langle f|)|x\rangle = c\langle f|x\rangle \text{ for all } \langle f| \in V_b \text{ and for all } c \in \mathbb{C}, \tag{8.63}$$

respectively. Equation (8.57) now reads

$$(\langle f| + \langle g|)|x\rangle = (|x\rangle, |f\rangle + |g\rangle)\,, \tag{8.64}$$

from which we conclude

$$|f\rangle + |g\rangle \in V_k \overset{\text{DC}}{\longleftrightarrow} \langle f| + \langle g| \in V_b\,. \tag{8.65}$$

Similarly, we see from (8.58) that

$$(c\langle f|)|x\rangle = (|x\rangle, c^*|f\rangle)\,, \tag{8.66}$$

and hence

$$c^*|f\rangle \in V_k \overset{\text{DC}}{\longleftrightarrow} c\langle f| \in V_b\,. \tag{8.67}$$

It is often helpful to think of V_b as some sort of a mirror image of V_k with the rule of finding a mirror image of a particular object in V_k given by (8.61), (8.65), and (8.67). Additional rules will be derived in what follows.

Exercise 8.9. Let $|\theta\rangle$ be the zero vector in a ket space V_k. Show that the corresponding bra $\langle\theta|$ is the zero vector in the corresponding bra space V_b. ///

Because $\langle x|y\rangle$ is a scalar product, it satisfies the properties S1–S5. In the current notation, they are:

S1$_{\mathrm{bk}}$: $\langle z|(|x\rangle+|y\rangle)=\langle z|x\rangle+\langle z|y\rangle$.
S2$_{\mathrm{bk}}$: $\langle x|y\rangle=\langle y|x\rangle^*$.
S3$_{\mathrm{bk}}$: $\langle y|(c|x\rangle)=c\langle y|x\rangle$ for all $c\in\mathbb{C}$.
S4$_{\mathrm{bk}}$: $\langle x|x\rangle\geq 0$.
S5$_{\mathrm{bk}}$: $\langle x|x\rangle=0$ if and only if $|x\rangle=|\theta\rangle$.

As with any scalar product space, two kets $|x\rangle\neq|\theta\rangle$ and $|y\rangle\neq|\theta\rangle$ in V_k are said to be **orthogonal** if $\langle x|y\rangle=0$. The quantity $\sqrt{\langle x|x\rangle}$ is the **norm** of $|x\rangle$:

$$\||x\rangle\|:=\sqrt{\langle x|x\rangle}\,. \tag{8.68}$$

At this point, our terminology “bra” and “ket” should appear appropriate:

$$\underset{\text{bra(c)ket}}{\langle x \;|\; y\rangle}\,. \tag{8.69}$$

This “bra–ket” notation is due to P. A. M. Dirac and allows us to manipulate various quantities arising in quantum mechanics rather mechanically.

Exercise 8.10. Let $c\in\mathbb{C}$. Show that

$$\langle y|(c|x\rangle)=(\langle y|c)|x\rangle\,, \tag{8.70}$$

which indicates that brackets are unnecessary and we shall write the product simply as $\langle y|c|x\rangle$. ///

Equations (8.62), (8.63), and those occurring S1$_{\mathrm{bk}}$–S5$_{\mathrm{bk}}$ are simply a matter of definitions. However, (8.62) and S1$_{\mathrm{bk}}$ taken together indicates that multiplication between a ket and a bra is *distributive* over addition. According to (8.70), the multiplication of a bra, a number, and a ket, written in this order, is *associative*. S3$_{\mathrm{bk}}$ then allows us to pull out the complex number placed between a bra and a ket, leaving an uninterrupted bra–ket. Without the benefit of the bra–ket notation, we have to express this fact as

$$(c|x\rangle,|y\rangle)=(|x\rangle,c^*|y\rangle)=c(|x\rangle,|y\rangle)\,. \tag{8.71}$$

Dirac’s bra–ket notation expresses various definitions and properties pertaining to a scalar product space and its dual space through intuitively transparent distributive and associative laws. We shall encounter a few more such instances that illustrates the power of his notation.

8.2.2 Operator and Adjoint

Let $\hat{X}$ denote a linear operator from V_k to V_k. Then, we may write

$$|\beta\rangle = \hat{X}|\alpha\rangle \ . \tag{8.72}$$

to express the fact that, when the operator $\hat{X}$ acts on $|\alpha\rangle$, it produces another ket $|\beta\rangle$. Even though $\hat{X}$ is a linear operator on V_k, it is actually possible to define its action on a bra and hence think of $\hat{X}$ as a linear operator from V_b to V_b.

By convention, an operator acting on a bra is written to the right of the bra as in $\langle\alpha|\hat{X}$. This is a new construct, to which we have complete freedom to assign any meaning we wish. Taking advantage of this freedom, we declare that $\langle\alpha|\hat{X}$ be a functional on V_k, that is, it acts on a ket in V_k and produces a complex number. But, a functional is defined completely once its action on every $|\beta\rangle \in V_k$ is specified. Accordingly, we *define* $\langle\alpha|\hat{X}$ by

$$(\langle\alpha|\hat{X})|\beta\rangle := \langle\alpha|(\hat{X}|\beta\rangle) \text{ for all } |\beta\rangle \in V_k \ . \tag{8.73}$$

Since $\hat{X}$, when regarded as acting on V_k, is a linear operator, this definition implies that the functional $\langle\alpha|\hat{X}$ is linear. In fact,

$$\begin{aligned}(\langle\alpha|\hat{X})(|\beta\rangle+|\gamma\rangle) &= \langle\alpha|[\hat{X}(|\beta\rangle+|\gamma\rangle)] = \langle\alpha|(\hat{X}|\beta\rangle+\hat{X}|\gamma\rangle) \\ &= \langle\alpha|(\hat{X}|\beta\rangle)+\langle\alpha|(\hat{X}|\gamma\rangle) = (\langle\alpha|\hat{X})|\beta\rangle+(\langle\alpha|\hat{X})|\gamma\rangle \ ,\end{aligned} \tag{8.74}$$

where the third equality follows from $\mathrm{S1_{bk}}$. Also,

$$(\langle\alpha|\hat{X})(c|\beta\rangle) = \langle\alpha|[\hat{X}(c|\beta\rangle)] = \langle\alpha|(c\hat{X}|\beta\rangle) = c\langle\alpha|(\hat{X}|\beta\rangle) = c(\langle\alpha|\hat{X})|\beta\rangle \ , \tag{8.75}$$

where we used $\mathrm{S3_{bk}}$ in the third equality.

Since $\langle\alpha|\hat{X}$ is a linear functional on V_k, it is nothing but a bra in V_b. So, we are justified in writing

$$\langle\alpha|\hat{X} = \langle\gamma_\alpha| \in V_b \ , \tag{8.76}$$

where we use the subscript α to indicate the $\langle\alpha|$ dependence of the resulting bra. That is, $\hat{X}$ acts on a particular bra $\langle\alpha|$ and produces yet another bra $\langle\gamma_\alpha|$, which in turn is completely specified by means of (8.73). If $\langle\alpha|\hat{X}$ is defined for all $\langle\alpha| \in V_b$ by (8.73), the end result is a function $\hat{X}$ on V_b.

We note that $\hat{X}$ acting on V_b is a linear operator, that is,

$$(\langle\alpha|+\langle\beta|)\hat{X} = \langle\alpha|\hat{X}+\langle\beta|\hat{X} \ , \tag{8.77}$$

and

$$(c\langle\alpha|)\hat{X} = c(\langle\alpha|\hat{X}) \text{ for all } c \in \mathbb{C}. \tag{8.78}$$

Exercise 8.11. Prove (8.77) and (8.78). ///

We recall from Sect. 8.1.8 that, for each bra in V_b, there corresponds a ket in V_k. We denote the ket corresponding to $\langle\alpha|\hat{X}$ by $\hat{X}^\dagger|\alpha\rangle$:

$$\langle\alpha|\hat{X} \overset{\text{DC}}{\longleftrightarrow} \hat{X}^\dagger|\alpha\rangle\ . \tag{8.79}$$

As a consequence of (8.77) and (8.78), $\hat{X}^\dagger$ acting on V_k is a linear operator. To see this, let $|\gamma\rangle = |\alpha\rangle + |\beta\rangle$. Then,

$$\hat{X}^\dagger(|\alpha\rangle + |\beta\rangle) = \hat{X}^\dagger|\gamma\rangle \overset{\text{DC}}{\longleftrightarrow} \langle\gamma|\hat{X} = (\langle\alpha| + \langle\beta|)\hat{X}\ , \tag{8.80}$$

where we used (8.65) in the last step. On the other hand, (8.77) gives

$$(\langle\alpha| + \langle\beta|)\hat{X} = \langle\alpha|\hat{X} + \langle\beta|\hat{X} \overset{\text{DC}}{\longleftrightarrow} \hat{X}^\dagger|\alpha\rangle + \hat{X}^\dagger|\beta\rangle\ , \tag{8.81}$$

where the last step also follows from (8.65). Since dual correspondence is one-to-one, we conclude that

$$\hat{X}^\dagger(|\alpha\rangle + |\beta\rangle) = \hat{X}^\dagger|\alpha\rangle + \hat{X}^\dagger|\beta\rangle\ . \tag{8.82}$$

Exercise 8.12. Show that

$$\hat{X}^\dagger(c|\alpha\rangle) = c(\hat{X}^\dagger|\alpha\rangle) \text{ for all } c \in \mathbb{C}, \tag{8.83}$$

thus completing the demonstration that $\hat{X}^\dagger$ on V_k is linear. We have already seen how the linearity of $\hat{X}$ on V_k implied that of $\hat{X}$ on V_b. It follows that $\hat{X}^\dagger$ on V_b is also linear. ///

In view of (8.73), the multiplication of a bra, an operator, and a ket, written in this order, is associative. Thus, the brackets are unnecessary and we may simply write $\langle\alpha|\hat{X}|\beta\rangle$ for the product. The content of (8.73) is far from trivial. Written by means of the earlier notation for a scalar product, it reads

$$(|\beta\rangle, \hat{X}^\dagger|\alpha\rangle) = (\hat{X}|\beta\rangle, |\alpha\rangle)\ . \tag{8.84}$$

Dirac's notation allows us to perform complex operations such as this one effortlessly and is extremely useful for computation.

We now show that

$$\langle\alpha|\hat{X}^\dagger|\beta\rangle = \langle\beta|\hat{X}|\alpha\rangle^*\ . \tag{8.85}$$

From what was just said about (8.73),

$$\langle\alpha|\hat{X}^\dagger|\beta\rangle = \langle\alpha|(\hat{X}^\dagger|\beta\rangle)\ . \tag{8.86}$$

Using (8.60) and S2,

$$\langle\alpha|(\hat{X}^{\dagger}|\beta\rangle) = (\hat{X}^{\dagger}|\beta\rangle, |\alpha\rangle) = (|\alpha\rangle, \hat{X}^{\dagger}|\beta\rangle)^* \ . \tag{8.87}$$

But, since the bra corresponding to the ket $\hat{X}^{\dagger}|\beta\rangle$ is just $\langle\beta|\hat{X}$, we have

$$(|\alpha\rangle, \hat{X}^{\dagger}|\beta\rangle) = (\langle\beta|\hat{X})|\alpha\rangle = \langle\beta|\hat{X}|\alpha\rangle \ . \tag{8.88}$$

Combining everything, we arrive at (8.85).

Exercise 8.13. Show that

$$(\hat{X}^{\dagger})^{\dagger} = \hat{X} \ . \tag{8.89}$$

///

Exercise 8.14. Show that

$$(c\hat{X})^{\dagger} = c^*\hat{X}^{\dagger} \ , \tag{8.90}$$

where

$$(c\hat{X})|\alpha\rangle := c(\hat{X}|\alpha\rangle) \text{ for all } c \in \mathbb{C}. \tag{8.91}$$

///

The linear operator $\hat{X}^{\dagger}$ is called the **adjoint** of $\hat{X}$. In general,

$$\hat{X}^{\dagger}|\alpha\rangle \neq \hat{X}|\alpha\rangle \ , \tag{8.92}$$

and hence $\hat{X}^{\dagger} \neq \hat{X}$. *If* $\hat{X}^{\dagger} = \hat{X}$, then the operator $\hat{X}$ is said to be **Hermitian**.

8.2.3 Addition and Multiplication of Operators

Addition of two operators is defined by

$$(\hat{X} + \hat{Y})|\alpha\rangle := \hat{X}|\alpha\rangle + \hat{Y}|\alpha\rangle \text{ for all } |\alpha\rangle \in V_k, \tag{8.93}$$

while multiplication of two operators is defined by

$$(\hat{X}\hat{Y})|\alpha\rangle := \hat{X}(\hat{Y}|\alpha\rangle) \text{ for all } |\alpha\rangle \in V_k. \tag{8.94}$$

Repeated application of (8.73) combined with (8.94) yields

$$\langle\beta|(\hat{X}\hat{Y}) = (\langle\beta|\hat{X})\hat{Y} \ . \tag{8.95}$$

In fact, for any $|\alpha\rangle \in V_k$,

$$[\langle\beta|(\hat{X}\hat{Y})]|\alpha\rangle = \langle\beta|[(\hat{X}\hat{Y})|\alpha\rangle] = \langle\beta|[\hat{X}(\hat{Y}|\alpha\rangle)] = (\langle\beta|\hat{X})(\hat{Y}|\alpha\rangle) = [(\langle\beta|\hat{X})\hat{Y}]|\alpha\rangle \ . \tag{8.96}$$

Since this holds for any $|\alpha\rangle$, we arrive at (8.95).

Exercise 8.15. Prove the following relations:

a.
$$\hat{X}(\hat{Y}+\hat{Z}) = \hat{X}\hat{Y}+\hat{Y}\hat{Z}\,. \tag{8.97}$$

b.
$$(\hat{X}\hat{Y})\hat{Z} = \hat{X}(\hat{Y}\hat{Z})\,, \tag{8.98}$$

c.
$$(\hat{X}\hat{Y})^\dagger = \hat{Y}^\dagger\hat{X}^\dagger\,. \tag{8.99}$$

///

Equation (8.98) indicates that a multiplication of operators is associative, and hence the product may be written simply as $\hat{X}\hat{Y}\hat{Z}$. Multiplication, however, is not necessarily commutative:

$$\hat{X}\hat{Y} \neq \hat{Y}\hat{X}. \tag{8.100}$$

The difference between these two products defines a **commutator** between $\hat{X}$ and $\hat{Y}$:

$$[\hat{X},\hat{Y}] := \hat{X}\hat{Y} - \hat{Y}\hat{X}\,, \tag{8.101}$$

which is another operator. The following set of identities can be verified easily:

$$[\hat{X},\hat{X}] = 0\,, \tag{8.102}$$
$$[c,\hat{X}] = 0\,, \quad c\in\mathbb{C} \tag{8.103}$$
$$[\hat{X},\hat{Y}+\hat{Z}] = [\hat{X},\hat{Y}]+[\hat{X},\hat{Z}]\,, \tag{8.104}$$
$$[\hat{X},\hat{Y}\hat{Z}] = \hat{Y}[\hat{X},\hat{Z}]+[\hat{X},\hat{Y}]\hat{Z}\,, \tag{8.105}$$

and

$$[\hat{X},[\hat{Y},\hat{Z}]]+[\hat{Y},[\hat{Z},\hat{X}]]+[\hat{Z},[\hat{X},\hat{Y}]] = 0\,. \tag{8.106}$$

The last equation is the quantum mechanical version of **Jacobi's identity** to be compared with (1.196).

8.2.4 Unitary Operator

Let $\hat{I}$ denote the **unit operator** defined by

$$\hat{I}|\alpha\rangle = |\alpha\rangle \text{ for all } |\alpha\rangle \in V_k\,. \tag{8.107}$$

An operator $\hat{U}$ satisfying

$$\hat{U}\hat{U}^\dagger = \hat{U}^\dagger\hat{U} = \hat{I} \tag{8.108}$$

is called a **unitary operator**.

Since $(\hat{U}^\dagger)^\dagger = \hat{U}$, (8.108) indicates that $\hat{V} = \hat{U}^\dagger$ is unitary if $\hat{U}$ is. Unitary operators do not affect the norm of a ket:

$$\|\hat{U}|\alpha\rangle\| = \||\alpha\rangle\| \,. \tag{8.109}$$

This follows immediately from (8.108):

$$\|\hat{U}|\alpha\rangle\| = \sqrt{\langle\alpha|\hat{U}^\dagger\hat{U}|\alpha\rangle} = \sqrt{\langle\alpha|\hat{I}|\alpha\rangle} = \sqrt{\langle\alpha|\alpha\rangle} \,. \tag{8.110}$$

Exercise 8.16. Show that $\hat{X}\hat{I} = \hat{I}\hat{X} = \hat{X}$. ///

8.2.5 Outer Product

As we have seen, the scalar product $\langle\alpha|\beta\rangle$ is a complex number. Here, we define the so-called **outer product** of $|\alpha\rangle$ and $\langle\beta|$ by the equation

$$(|\alpha\rangle\langle\beta|)|\gamma\rangle := |\alpha\rangle(\langle\beta|\gamma\rangle) \text{ for all } |\gamma\rangle \in V_k \,. \tag{8.111}$$

On the right-hand side, we have a complex number multiplying a ket, the result being another ket in V_k. That is, the outer product $|\alpha\rangle\langle\beta|$ acting on a ket produces a new ket proportional to $|\alpha\rangle$. Because of the linearity of the scalar product, the outer product is a linear operator. As shown in Exercise 8.17, however, the outer product $|\alpha\rangle\langle\beta|$ is *not* a Hermitian operator unless $|\alpha\rangle = |\beta\rangle$. Finally, (8.111) indicates that the multiplication of a ket, a bra, and a ket, written in this order, is associative. Thus, the brackets are unnecessary and we shall write the product simply as $|\alpha\rangle\langle\beta|\gamma\rangle$.

Exercise 8.17.

a. Let $\hat{X}$=$|\alpha\rangle\langle\beta|$. Show that $\hat{X}^\dagger = |\beta\rangle\langle\alpha|$.
b. Let $\hat{Y} = -i|\alpha\rangle\langle\beta|$ and find $\hat{Y}^\dagger$. ///

If a given pair of expressions, each including bras, kets, operators, or complex numbers, are in dual correspondence with each other, they are said to be the **adjoint** of each other. Table 8.2.5 summarizes useful rules and formulae for finding the adjoint of a given expression.

8.3 Eigenkets and Eigenvalues

Eigenvalues of operators and their corresponding kets play a crucial role in quantum mechanics. Accordingly, we shall summarize their properties in this section.

Dual correspondence	Equation	Identity	Equation
$\vert f\rangle \overset{\text{DC}}{\longleftrightarrow} \langle f\vert$	(8.61)	$\langle\alpha\vert\hat{X}^\dagger\vert\beta\rangle = \langle\beta\vert\hat{X}\vert\alpha\rangle^*$	(8.85)
$\vert f\rangle + \vert g\rangle \overset{\text{DC}}{\longleftrightarrow} \langle f\vert + \langle g\vert$	(8.65)	$(\hat{X}^\dagger)^\dagger = \hat{X}$	(8.89)
$c^*\vert f\rangle \overset{\text{DC}}{\longleftrightarrow} c\langle f\vert$	(8.67)	$(c\hat{X})^\dagger = c^*\hat{X}^\dagger$	(8.90)
$\hat{X}^\dagger\vert f\rangle \overset{\text{DC}}{\longleftrightarrow} \langle f\vert\hat{X}$	(8.79)	$(\hat{X}\hat{Y})^\dagger = \hat{Y}^\dagger\hat{X}^\dagger$	(8.99)
$c\vert\alpha\rangle\langle\beta\vert \overset{\text{DC}}{\longleftrightarrow} c^*\vert\beta\rangle\langle\alpha\vert$	Exercise 8.17		

Table 8.1 A list of useful rules and formulae for finding the adjoint of a given expression.

8.3.1 Definition

In general, an operator $\hat{X}$ acting on a ket produces another ket different from the original one. However, there may be a ket $|\alpha\rangle$ for which

$$\hat{X}|\alpha\rangle = \lambda|\alpha\rangle \ , \ \lambda \in \mathbb{C} \tag{8.112}$$

holds. If this happens, λ and $|\alpha\rangle$ are called, respectively, an **eigenvalue** of $\hat{X}$ and the **eigenket** corresponding (or belonging) to λ. The set of all eigenvalues is called the **spectrum** of $\hat{X}$.

In view of Exercise 8.8a,

$$\hat{X}|\theta\rangle = |\theta\rangle = \lambda|\theta\rangle \text{ for any } \lambda \in \mathbb{C} \tag{8.113}$$

for any linear operator $\hat{X}$. That is, $|\theta\rangle$ satisfies (8.112) for arbitrary $\lambda \in \mathbb{C}$. By convention, however, the zero vector is not an eigenket. According to the definition, if $|\alpha\rangle$ is an eigenket, so is $c|\alpha\rangle$, where c is a nonzero complex number.

For a given eigenvalue, there may be multiple corresponding *linearly independent* eigenkets. Such an eigenvalue is said to be **degenerate**. If the number of linearly independent eigenkets corresponding to this eigenvalue is s, we say that the eigenvalue is s-fold degenerate or that its **degeneracy** is s.

Suppose that the eigenvalue λ of $\hat{X}$ is s-fold degenerate and denotes the corresponding s linearly independent eigenkets by $|\alpha_1\rangle$, ..., $|\alpha_s\rangle$. Then, their linear combination

$$|\phi\rangle := \sum_{k=1}^{s} c_k|\alpha_k\rangle \tag{8.114}$$

is also an eigenket of $\hat{X}$ corresponding to λ. In fact,

$$\hat{X}|\phi\rangle = \sum_{k=1}^{s} c_k\hat{X}|\alpha_k\rangle = \lambda\sum_{k=1}^{s} c_k|\alpha_k\rangle = \lambda|\phi\rangle \ . \tag{8.115}$$

The set of vectors $\{|\alpha_1\rangle,\ldots,|\alpha_s\rangle\}$ spans a s-dimensional vector space, called the **eigensubspace** of the eigenvalue λ.

Example 8.9. Rotation: If we take an ordinary three-dimensional vector $\boldsymbol{a}$ and rotate it around a given axis by an angle θ $(0 < \theta < 2\pi)$, the result is another vector $\boldsymbol{b}$. The rotation is a linear operator, which we denote by $\hat{R}_\theta$. While $\boldsymbol{b} \neq \boldsymbol{a}$ in general,

$$\hat{R}_\theta \boldsymbol{a} = \lambda \boldsymbol{a} \ , \ \lambda \in \mathbb{R} \tag{8.116}$$

holds with $\lambda = 1$ for vectors that are either parallel or antiparallel to the axis of rotation. Then, $\lambda = 1$ is a nondegenerate eigenvalue of $\hat{R}_\theta$ with the said vectors all belonging to this eigenvalue. Geometrically, it is clear that there is no other eigenvalue for a general value of θ. However, $\hat{R}_\pi$ has another eigenvalue $\lambda = -1$. The vectors perpendicular to the axis of rotation are the corresponding eigenvectors. Because these vectors lie on a plane, the degeneracy of $\lambda = -1$ is two.

8.3.2 Closure relation

A Hermitian operator $\hat{X}$ defined on a ket space V_k is said to be an **observable** if a set of all linearly independent eigenkets of $\hat{X}$ forms a basis of V_k. It can be shown that a Hermitian operator always is an observable if the dimension of V_k is finite. In what follows, we denote generic observables by the symbols $\hat{A}$, $\hat{B}$, $\hat{C}$, and so on to distinguish them clearly from more general linear operators, which we continue to indicate by $\hat{X}$, $\hat{Y}$, $\hat{Z}$, etc.

Let $\hat{A}$ be an observable and denote its eigenvalues by $a_1, \ldots, a_r$. We label an eigenket by the eigenvalue to which it belongs. For example,

$$\hat{A}|a_1\rangle = a_1|a_1\rangle \ , \ldots, \ \hat{A}|a_r\rangle = a_r|a_r\rangle \ . \tag{8.117}$$

If there is a degenerate eigenvalue, some of a_i's are equal. For example, if $a_1 = 5$ is twofold degenerate, $a_1 = a_2 = 5$ and both $|a_1\rangle$ and $|a_2\rangle$ would become $|5\rangle$, requiring additional label to distinguish them. This may be the case especially during a solution of a concrete numerical problem. However, since we do not need to refer to actual numerical values of a_i's in what follows, the notation we have just adopted will be sufficient.

Theorem 8.3. *Let $\hat{A}$ be an observable. Then,*

a. The eigenvalues of $\hat{A}$ are real.
b. The eigenkets of $\hat{A}$ corresponding to different eigenvalues are orthogonal.

Proof. Let

$$\hat{A}|a_i\rangle = a_i|a_i\rangle \quad \text{and} \quad \hat{A}|a_j\rangle = a_j|a_j\rangle \ . \tag{8.118}$$

Multiplying the first equation by $\langle a_j|$ from the left,

$$\langle a_j|\hat{A}|a_i\rangle = a_i\langle a_j|a_i\rangle \ . \tag{8.119}$$

Taking the adjoint of the second equation and multiplying the resulting equation by $|a_i\rangle$ from the right,

$$\langle a_j|\hat{A}|a_i\rangle = a_j{}^*\langle a_j|a_i\rangle \ , \tag{8.120}$$

where we note that $\hat{A}^\dagger = \hat{A}$. Subtracting (8.120) from (8.119),

$$(a_i - a_j{}^*)\langle a_j|a_i\rangle = 0 \ . \tag{8.121}$$

Let $a_i = a_j$. Since $|a_i\rangle \neq |\theta\rangle$ by convention, (8.121) implies that $a_i = a_i{}^*$. This proves a. Because of a, (8.121) becomes

$$(a_i - a_j)\langle a_j|a_i\rangle = 0 \ . \tag{8.122}$$

If $a_i \neq a_j$, then $\langle a_j|a_i\rangle = 0$, thus establishing b. □

What happens if an eigenvalue is s-fold degenerate? According to this theorem, these s eigenkets are certainly orthogonal to eigenkets belonging to *other* eigenvalues. However, the theorem does not tell us if they are orthogonal among themselves. Fortunately, the Gram–Schmidt orthogonalization we saw in Sect. 8.1.6 allows us to construct s mutually orthogonal eigenkets as linear combinations of the original eigenkets. With a proper normalization, therefore, a set of all linearly independent eigenkets of $\hat{A}$ can be made orthonormal:

$$\langle a_i|a_j\rangle = \delta_{ij} \ . \tag{8.123}$$

In what follows, we shall assume that this is done.

Using an orthonormal basis $\{|a_1\rangle, \ldots, |a_r\rangle\}$ so constructed, we may write any ket $|\alpha\rangle \in V_k$ as

$$|\alpha\rangle = \sum_{i=1}^{r} C_{a_i}|a_i\rangle \ . \tag{8.124}$$

Multiplying (8.124) by $\langle a_j|$, we find

$$\langle a_j|\alpha\rangle = \sum_{i=1}^{r} C_{a_i}\langle a_j|a_i\rangle = \sum_{i=1}^{r} C_{a_i}\delta_{ji} = C_{a_j} \ . \tag{8.125}$$

When this is substituted back into (8.124), we obtain

$$|\alpha\rangle = \sum_{i=1}^{r}\left(\langle a_i|\alpha\rangle\right)|a_i\rangle = \sum_{i=1}^{r}|a_i\rangle\left(\langle a_i|\alpha\rangle\right) = \sum_{i=1}^{r}\left(|a_i\rangle\langle a_i|\right)|\alpha\rangle = \left[\sum_{i=1}^{r}|a_i\rangle\langle a_i|\right]|\alpha\rangle \ . \tag{8.126}$$

Since this holds for any $|\alpha\rangle \in V_k$, we conclude that

$$\sum_{i=1}^{r}|a_i\rangle\langle a_i| = \hat{I} \ , \tag{8.127}$$

which is to be compared with (A.21). Equation (8.127) is known as the **closure relation** and will be in frequent use in what follows.

Exercise 8.18. Rewrite (8.52) using the bra–ket notation. ///

Exercise 8.19. Show that

$$\hat{A} = \sum_{i=1}^{r} |a_i\rangle a_i \langle a_i| \, . \tag{8.128}$$

///

A function $f(\hat{A})$ of the operator $\hat{A}$ is a yet another operator and is defined by its Maclaurin expansion. (See Sect. B.1.) That is,

$$f(\hat{A}) = f(0)\hat{I} + f'(0)\hat{A} + \frac{1}{2}f''(0)\hat{A}^2 + \frac{1}{3}f'''(0)\hat{A}^3 + \cdots \, . \tag{8.129}$$

Exercise 8.20. Prove the following relations:

a.

$$f(\hat{A})|a_i\rangle = f(a_i)|a_i\rangle \, . \tag{8.130}$$

b.

$$f(\hat{A}) = \sum_{i=1}^{r} |a_i\rangle f(a_i) \langle a_i| \, . \tag{8.131}$$

///

For certain functions, (8.129) fails to define $f(\hat{A})$. For example, $\sqrt{x}$ does not have the Maclaurin expansion and $\sqrt{\hat{A}}$ cannot be defined by means of (8.129). More generally, we can define a function of an operator by (8.130). In fact, for any $|\alpha\rangle \in V_k$, (8.130) assigns a unique ket in V_k:

$$f(\hat{A})|\alpha\rangle = \sum_{i=1}^{r} f(\hat{A})|a_i\rangle\langle a_i|\alpha\rangle = \sum_{i=1}^{r} f(a_i)|a_i\rangle\langle a_i|\alpha\rangle \, , \tag{8.132}$$

where we used the closure relation in the first equality.

8.3.3 Matrix Representation

Using the closure relation twice, we have

$$\hat{X} = \sum_{i}\sum_{j} |a_i\rangle\langle a_i|\hat{X}|a_j\rangle\langle a_j| \, , \tag{8.133}$$

where $\langle a_i|\hat{X}|a_j\rangle$ is called a **matrix element** of $\hat{X}$ in the A-representation with A referring to the fact that we have used the set of all eigenkets $\{|a_1\rangle, \ldots, |a_r\rangle\}$ of

$\hat{A}$ as the basis. Evidently, numerical values of the matrix elements depend on the representation, that is, the choice of the basis kets.

Let's consider the product $\hat{Z} = \hat{X}\hat{Y}$:

$$\langle a_i|\hat{Z}|a_j\rangle = \langle a_i|\hat{X}\hat{Y}|a_j\rangle = \sum_k \langle a_i|\hat{X}|a_k\rangle\langle a_k|\hat{Y}|a_j\rangle \,. \tag{8.134}$$

With an abbreviation $X_{ij} := \langle a_i|\hat{X}|a_j\rangle$, this equation may be written as

$$Z_{ij} = \sum_k X_{ik}Y_{kj} \,, \tag{8.135}$$

or more explicitly,

$$\begin{pmatrix} Z_{11} & Z_{12} & \cdots \\ Z_{21} & Z_{22} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} = \begin{pmatrix} X_{11} & X_{12} & \cdots \\ X_{21} & X_{22} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} Y_{11} & Y_{12} & \cdots \\ Y_{21} & Y_{22} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} . \tag{8.136}$$

The term "matrix element" is seen to be quite appropriate.

We now turn to the equation:

$$|\beta\rangle = \hat{X}|\alpha\rangle \,. \tag{8.137}$$

Multiplying this equation by $\langle a_i|$ from the left, we find

$$\langle a_i|\beta\rangle = \langle a_i|\hat{X}|\alpha\rangle = \sum_{j=1}^{r} \langle a_i|\hat{X}|a_j\rangle\langle a_j|\alpha\rangle \,, \quad i = 1,\dots,r \,, \tag{8.138}$$

which may be written as

$$\begin{pmatrix} \langle a_1|\beta\rangle \\ \langle a_2|\beta\rangle \\ \vdots \end{pmatrix} = \begin{pmatrix} X_{11} & X_{12} & \cdots \\ X_{21} & X_{22} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} \langle a_1|\alpha\rangle \\ \langle a_2|\alpha\rangle \\ \vdots \end{pmatrix} . \tag{8.139}$$

So, $|\alpha\rangle$ can be represented by a column matrix:

$$|\alpha\rangle \doteq \begin{pmatrix} \langle a_1|\alpha\rangle \\ \langle a_2|\alpha\rangle \\ \vdots \end{pmatrix} . \tag{8.140}$$

Let us see what happens with

$$\langle\beta| = \langle\alpha|\hat{X} \,. \tag{8.141}$$

Multiplying this equation by $|a_i\rangle$ from the right, we find

$$\langle\beta|a_i\rangle = \langle\alpha|\hat{X}|a_i\rangle = \sum_{j=1}^{r} \langle\alpha|a_j\rangle\langle a_j|\hat{X}|a_i\rangle \,, \quad i = 1,\dots,r. \tag{8.142}$$

This may be written as

$$\left(\langle\beta|a_1\rangle \ \langle\beta|a_2\rangle \ \cdots \right) = \left(\langle\alpha|a_1\rangle \ \langle\alpha|a_2\rangle \ \cdots \right) \begin{pmatrix} X_{11} & X_{12} & \cdots \\ X_{21} & X_{22} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} , \tag{8.143}$$

indicating that $\langle\alpha|$ can be represented by a row matrix:

$$\langle\alpha| \doteq \left(\langle\alpha|a_1\rangle \quad \langle\alpha|a_2\rangle \cdots \right) = \left(\langle a_1|\alpha\rangle^* \quad \langle a_2|\alpha\rangle^* \cdots \right) . \tag{8.144}$$

Exercise 8.21. Express $\langle\alpha|\beta\rangle$ using matrices. ///

The **trace** of an operator $\hat{A}$ is defined as the sum of all diagonal elements of the matrix that represents $\hat{A}$:

$$\mathrm{Tr}\{\hat{A}\} := \sum_{i=1}^{r} \langle a_i|\hat{A}|a_i\rangle . \tag{8.145}$$

$\mathrm{Tr}\{\hat{A}\}$ is independent of the basis. To see this, let $\{|a_1\rangle, \ldots, |a_r\rangle\}$ and $\{|a'_1\rangle, \ldots, |a'_r\rangle\}$ be distinct bases. Then,

$$\mathrm{Tr}\{\hat{A}\} = \sum_i \langle a_i|\hat{A}|a_i\rangle = \sum_{i,j} \langle a_i|a'_j\rangle\langle a'_j|\hat{A}|a_i\rangle = \sum_{i,j} \langle a'_j|\hat{A}|a_i\rangle\langle a_i|a'_j\rangle = \sum_j \langle a'_j|\hat{A}|a'_j\rangle . \tag{8.146}$$

Exercise 8.22. Show that

$$\mathrm{Tr}\{\hat{A}\hat{B}\} = \mathrm{Tr}\{\hat{B}\hat{A}\} . \tag{8.147}$$

///

8.3.4 Commuting Observables

An observable $\hat{A}$ is *diagonal* in the A-representation. That is,

$$\langle a_i|\hat{A}|a_j\rangle = \langle a_i|a_j|a_j\rangle = a_j\langle a_i|a_j\rangle = a_j\delta_{ij} , \tag{8.148}$$

where the last step follows from (8.123). Because the basis $\{|a_1\rangle, \ldots, |a_r\rangle\}$ is orthonormal by construction, this equation holds even if some of the eigenvalues are degenerate. What can we say about the A-representation of some other observable $\hat{B}$ that acts in V_k? The following theorem provides a partial answer to this question.

Theorem 8.4. *Let $\hat{A}$ and $\hat{B}$ be observables and suppose that none of the eigenvalues of $\hat{A}$ is degenerate. If $\hat{A}$ and $\hat{B}$ commute, that is, if $[\hat{A},\hat{B}] = 0$, $\hat{B}$ is diagonal in the A-representation*

Proof.

$$0 = \langle a_i|[\hat{A},\hat{B}]|a_j\rangle = \langle a_i|(\hat{A}\hat{B} - \hat{B}\hat{A})|a_j\rangle = \langle a_i|\hat{A}\hat{B}|a_j\rangle - \langle a_i|\hat{B}\hat{A}|a_j\rangle . \tag{8.149}$$

We recall that $|a_i\rangle$ is an eigenket of $\hat{A}$ corresponding to the eigenvalue a_i:

$$\hat{A}|a_i\rangle = a_i|a_i\rangle \ , \tag{8.150}$$

the adjoint of which reads

$$\langle a_i|\hat{A} = a_i\langle a_i| \ , \tag{8.151}$$

where we used the fact that $\hat{A}$ is Hermitian and that a_j is a real number. It follows that

$$0 = \langle a_i|[\hat{A},\hat{B}]|a_j\rangle = a_i\langle a_i|\hat{B}|a_j\rangle - \langle a_i|\hat{B}|a_j\rangle a_j = (a_i - a_j)\langle a_i|\hat{B}|a_j\rangle \ . \tag{8.152}$$

Because the eigenvalues of $\hat{A}$ are nondegenerate by assumption, $i \neq j$ implies $a_i \neq a_j$ and hence $\langle a_i|\hat{B}|a_j\rangle = 0$. □

But, if $\hat{B}$ is diagonal in the A-representation, the effect of $\hat{B}$ on a basis ket $|a_i\rangle$ should be just a multiplication by a number, and hence we have the following theorem:

Theorem 8.5. *Let $\hat{A}$ and $\hat{B}$ be observables satisfying $[\hat{A},\hat{B}] = 0$ and suppose that the eigenvalues of $\hat{A}$ are all nondegenerate. Then, $|a_i\rangle$ is also an eigenket of $\hat{B}$.*

Proof. Using the closure relation,

$$\hat{B}|a_i\rangle = \sum_j |a_j\rangle\langle a_j|\hat{B}|a_i\rangle \ . \tag{8.153}$$

Since the eigenvalues of $\hat{A}$ are nondegenerate, Theorem 8.4 applies and we obtain

$$\hat{B}|a_i\rangle = |a_i\rangle\langle a_i|\hat{B}|a_i\rangle \ . \tag{8.154}$$

That is, $|a_i\rangle$ is an eigenket of $\hat{B}$ corresponding to the eigenvalue $\langle a_i|\hat{B}|a_i\rangle$. □

Let us summarize the content of Theorems 8.3–8.5 here. *In quantum mechanics, we are interested in an observable whose eigenkets span the vector space in which it acts. The eigenkets may be made orthonormal using Gram–Schmidt orthogonalization scheme if necessary.* If *none of the eigenvalues of $\hat{A}$ are degenerate, the basis kets so constructed are simultaneous eigenkets of $\hat{A}$ and all other operators that commute with $\hat{A}$. These operators, including $\hat{A}$, are diagonal in the A-representation.*

What happens to this very nice result if there is a degeneracy? Even then, by means of what is called a **complete set of commuting observables**, the simultaneous eigenkets can still be found and the orthonormal basis can still be constructed using them. The observable in the set are all diagonal in this basis. This is the topic of next optional subsection. No harm will come from omitting it if you choose to accept the claim just made.

8.3.5 †Degenerate Eigenvalues

Now, suppose that $\hat{A}$ has an s-fold degenerate eigenvalue a_1 and that other eigenvalues $a_{s+1}, \dots, a_r$ are nondegenerate. A generalization to cases with multiple degenerate eigenvalues will be trivial. If $[\hat{A}, \hat{B}] = 0$, how does the matrix of $\hat{B}$ look like in the A-representation? We label the eigenkets corresponding to a_1 as $|a^1\rangle, \dots, |a^s\rangle$ and those corresponding to $a_{s+1}, \dots, a_r$ as $|a_{s+1}\rangle, \dots, |a_r\rangle$. We suppose that these kets are, *by construction*, orthonormal. Looking at the last step in the proof of Theorem 8.4, we see that

$$\langle a_i|\hat{B}|a_j\rangle = 0 \text{ if } i \neq j \;, \; \langle a_i|\hat{B}|a^j\rangle = 0 \;, \text{ and } \langle a^i|\hat{B}|a_j\rangle = 0 \;. \tag{8.155}$$

However, the theorem is silent about $\langle a^i|\hat{B}|a^j\rangle$.

For various computations, it would be very convenient if $\hat{B}$ is fully diagonal in the A-representation. Can we somehow accomplish this by properly choosing an orthonormal basis? We would still like to keep using the eigenkets of $\hat{A}$ as the basis kets, of course, since at least $\hat{A}$ is diagonal then.

We observe that (8.155) still holds even if we replace $|a^1\rangle, \dots, |a^s\rangle$ by any of their linear combinations. By Theorem 8.3b, $|a_j\rangle$ is orthogonal to any linear combination of $|a^1\rangle, \dots, |a^s\rangle$. If we choose appropriate linear combinations and use them with $|a_{s+1}\rangle, \dots, |a_r\rangle$ as the basis kets, $\hat{B}$ might become fully diagonal.

To examine this possibility, we confine our attention to the eigensubspace V_{1k} of a_1, that is, the vector space spanned by eigenkets $|a^1\rangle, \dots, |a^s\rangle$ corresponding to the eigenvalue a_1. We recall that, by construction, the set $\{|a^1\rangle, \dots, |a^s\rangle\}$ is an orthonormal basis in V_{k1}. As we just saw, we are free to choose any other orthonormal basis without affecting (8.155). Let us denote this new orthonormal basis in V_{k1} by $\{|a_1\rangle, \dots, |a_s\rangle\}$. Our goal is to construct this new basis from the old. But, this can be accomplished by a linear operator $\hat{U}$ acting in V_{k1}:

$$\hat{U} := \sum_{k=1}^{s} |a_k\rangle\langle a^k| \;. \tag{8.156}$$

In fact,

$$\hat{U}|a^i\rangle = \sum_{k=1}^{s} |a_k\rangle\langle a^k|a^i\rangle = \sum_{k=1}^{s} |a_k\rangle\delta_{ki} = |a_i\rangle \tag{8.157}$$

as desired.

Because we insist that new and old bases are both orthonormal, $\hat{U}$ satisfies (8.108), and hence is a unitary operator. We can easily confirm this:

$$\hat{U}\hat{U}^{\dagger} = \sum_{i,j=1}^{s} |a_i\rangle\langle a^i|a^j\rangle\langle a_j| = \sum_{i,j=1}^{s} |a_i\rangle\delta_{ij}\langle a_j| = \sum_{i=1}^{s} |a_i\rangle\langle a_i| = \hat{I} \;, \tag{8.158}$$

where we used the closure relation in V_{k1}. Similarly for $\hat{U}^{\dagger}\hat{U} = \hat{I}$.

Of course, $|a_k\rangle$ occurring in the definition for $\hat{U}$ *is* the very unknown we are trying to find. So, (8.156) is not an explicit prescription for finding $\hat{U}$.

How do we find $\hat{U}$ then? What we wish to accomplish with this $\hat{U}$ is to find the new basis in which $\hat{B}$ is diagonal:

$$\langle a_i|\hat{B}|a_j\rangle = \lambda\delta_{ij} = \lambda\langle a_i|a_j\rangle\ , \quad i,j=1,\dots,s\ . \tag{8.159}$$

in which λ is also unknown at this point. Because this equation must hold for any $\langle a_i|$, our goal is equivalent to ensuring

$$\hat{B}|a_j\rangle = \lambda|a_j\rangle\ . \tag{8.160}$$

That is, the new basis kets we seek are all eigenvectors of $\hat{B}$.

The method for finding eigenvalues and the corresponding eigenkets are as follows. We multiply (8.160) by $\langle a^i|$ from the left and rewrite the resulting equation using the closure relations:

$$\sum_{k=1}^{s}\langle a^i|\hat{B}|a^k\rangle\langle a^k|a_j\rangle = \lambda\langle a^i|a_j\rangle\ . \tag{8.161}$$

Written in terms of matrices, this reads

$$\begin{pmatrix} B_{11} & \cdots & B_{1s} \\ \vdots & \ddots & \vdots \\ B_{s1} & \cdots & B_{ss} \end{pmatrix} \begin{pmatrix} \langle a^1|a_j\rangle \\ \vdots \\ \langle a^s|a_j\rangle \end{pmatrix} = \lambda \begin{pmatrix} \langle a^1|a_j\rangle \\ \vdots \\ \langle a^s|a_j\rangle \end{pmatrix}\ . \tag{8.162}$$

So that this equation has the nontrivial solutions, that is, for the solutions other than $\langle a^i|a_j\rangle = 0$ for all i to exist, the determinant of the operator $\hat{B}-\lambda\hat{I}$ must vanish:

$$\begin{vmatrix} B_{11}-\lambda & \cdots & B_{1s} \\ \vdots & \ddots & \vdots \\ B_{s1} & \cdots & B_{ss}-\lambda \end{vmatrix} = 0\ . \tag{8.163}$$

The determinant is the sth order polynomial of λ, from which we find s roots $\lambda = b_1,\dots,b_s$. For each $\lambda = b_j$ so determined, we solve (8.162) to find the eigenvector

$$\begin{pmatrix} \langle a^1|a_j\rangle \\ \vdots \\ \langle a^s|a_j\rangle \end{pmatrix}\ . \tag{8.164}$$

When this is completed for each b_j ($j=1,\dots,s$), we have the matrix representation of $\hat{U}$:

$$\langle a^i|\hat{U}|a^j\rangle = \sum_{k=1}^{s}\langle a^i|a_k\rangle\langle a^k|a^j\rangle\ . \tag{8.165}$$

We recall that the newly determined basis vectors span V_{k1} and they are all eigenvectors of $\hat{A}$ corresponding to a_1. Now, by construction, $|a_j\rangle \in V_{k1}$ is also an eigenvector of $\hat{B}$ corresponding to b_j. If s solutions of (8.163) are all distinct, then $|a_1\rangle$, $\dots$, $|a_s\rangle$ are orthogonal by Theorem 8.3b applied to $\hat{B}$. Under the same condition, the pair of numbers a_1 and b_j, taken together, specifies the eigenket completely, which is then denoted by $|a_1 b_j\rangle$. We say that $\hat{B}$ *resolves* the s-fold degeneracy of $\hat{A}$ completely.

The eigenkets $|a_{s+1}\rangle$, $\dots$, $|a_r\rangle$ are also eigenkets of $\hat{B}$ by Theorem 8.5 and may be denoted in the same manner, even though the label b_j $(j = s+1, \dots, r)$ will be redundant for them. Thus, when s-fold degeneracy of $\hat{A}$ is completely resolved by $\hat{B}$, we have the orthonormal basis

$$\{|a_1 b_1\rangle, \dots, |a_1 b_s\rangle, |a_{s+1} b_{s+1}\rangle, \dots, |a_r b_r\rangle\} \tag{8.166}$$

of the original vector space V_k that consists of the simultaneous eigenkets of $\hat{A}$ and $\hat{B}$.

If not all of s solutions of (8.163) are distinct, then there will be multiple eigenkets corresponding to a given pair of numbers, a_1 and one of $b_1, \dots, b_s$. In this case, we can introduce additional operators that commute with both $\hat{A}$, $\hat{B}$, and with each other to further resolve the degeneracy. When all degeneracy is resolved in this manner, we have what is called a **complete set of commuting observables** $\hat{A}_1, \dots, \hat{A}_c$, for which $[\hat{A}_i, \hat{A}_j] = 0$ for *all* pairs of $i, j = 1, \dots, c$, and their simultaneous eigenkets form an orthonormal basis of V_k.

8.4 Postulates of Quantum Mechanics

Now we are *finally* ready to state the fundamental postulates of quantum mechanics.

Postulate 1: The state of the system is represented by the "direction" of a ket, that is, $|\phi\rangle$ and $c|\phi\rangle$ $(c \neq 0)$ represent the same state.

Postulate 2: A dynamical variable A, such as energy, position, and momentum, is *represented* by an observable $\hat{A}$.

Postulate 3: A measurement of A yields one of the eigenvalues a_1, a_2, $\cdots$, a_n, of $\hat{A}$. Equation (8.130) implies that, if a measurement of A yields a_i, then the measurement of $f(A)$ yields $f(a_i)$, which is a very natural thing to demand of our theory.

Postulate 4: If the system is in a state $|\phi\rangle$, the probability of obtaining the value a_i upon measuring A is given by

$$p(a_i) = |\langle a_i|\phi\rangle|^2 \tag{8.167}$$

provided that a_i is nondegenerate and $|\phi\rangle$ is normalized. If $|\phi\rangle$ is not normalized, this expression must be replaced by

$$p(a_i) = \frac{|\langle a_i|\phi\rangle|^2}{\langle\phi|\phi\rangle} . \tag{8.168}$$

Note that the value of $p(a_i)$ is independent of whether $|\phi\rangle$ is normalized or not, as is demanded by Postulate 1. In what follows, state kets are assumed to be normalized.

If a_i is s-fold degenerate, then

$$p(a_i) = \sum_{k=1}^{s} |\langle a_i, k|\phi\rangle|^2 \ , \tag{8.169}$$

where $|a_i, k\rangle$ is the kth eigenket corresponding to a_i.

Example 8.10. Eigenstate and the outcome of a measurement: Suppose that the system is in state $|\phi\rangle$. A measurement of a dynamical variable A of the system yields a_i with certainty *if and only if* $|\phi\rangle = |a_i\rangle$.

To see this, let us suppose first that $|\phi\rangle = |a_i\rangle$ in (8.167). Then,

$$p(a_i) = |\langle a_i|a_i\rangle|^2 = 1 \tag{8.170}$$

since the eigenkets are normalized. On the other hand, if $|\phi\rangle \neq |a_i\rangle$, then

$$|\phi\rangle = C_i|a_i\rangle + \sum_{j\neq i} C_j|a_j\rangle \ , \tag{8.171}$$

where $C_j \neq 0$ for at least one $C_{j\neq i}$. Since $|\phi\rangle$ is normalized,

$$\langle\phi|\phi\rangle = |C_i|^2 + \sum_{j\neq i} |C_j|^2 = 1 \ . \tag{8.172}$$

Thus,

$$p(a_i) = |C_i|^2 = 1 - \sum_{j\neq i} |C_j|^2 < 1 \ . \tag{8.173}$$

This proves the assertion.

Now, let us suppose we measured A of a system in state $|\phi\rangle$ and found the value a_j. If we wait around too long, the state of the system may evolve with time. But, if we measure A *immediately* after the first measurement, the system has no time to evolve. In this case, it seems natural to expect that we should obtain the same result a_j *with certainty*. It follows from Example 8.10 that the state of the system immediately after the measurement which yielded a_j must be $|a_j\rangle$. One may say that the state of the system has changed *abruptly* from $|\phi\rangle$ to $|a_j\rangle$ by the very act of measuring A. This is the so-called collapse postulate of quantum mechanics. For alternative views, see Refs. [1, 8].

Exercise 8.23. Suppose that we measure A right after preparing the system in the state $|\phi\rangle$. If we repeat this procedure many times, including the preparation of the system in the state $|\phi\rangle$, we can find the average value of our many measurements, which we denote by $\langle A\rangle_{\mathrm{QM}}$. Show that

$$\langle A\rangle_{\mathrm{QM}} = \langle\phi|\hat{A}|\phi\rangle \,, \tag{8.174}$$

where $|\phi\rangle$ is normalized. ///

8.5 ‡Uncertainty Principle

Let us consider two observables $\hat{A}$ and $\hat{C}$. We assume that $\hat{A}$ and $\hat{C}$ commute, that is, $[\hat{A},\hat{C}] = 0$ and that $\hat{A}$ is nondegenerate. As we saw in Sect. 8.3.4, $\hat{A}$ and $\hat{C}$ has the simultaneous eigenkets that form an orthonormal basis $\{|a_1c_1\rangle,\dots,|a_rc_r\rangle\}$ of the vector space V_k.

The state ket $|\phi\rangle \in V_k$ of the system can be written using this basis as

$$|\phi\rangle = \sum_{i=1}^{r} \lambda_i |a_ic_i\rangle. \tag{8.175}$$

What would the outcome be of a measurement of the dynamical variable A? According to the postulate of quantum mechanics, the outcome is one of a_i $(i = 1,\dots,r)$ with probability $|\lambda_i|^2$. The state ket right after the measurement that gave a_i is $|a_ic_i\rangle$. Thus, if we measure C now, the outcome is c_i with certainty and the state ket after this second measurement again is $|a_ic_i\rangle$. The subsequent measurements of $\hat{A}$ and $\hat{C}$ in any order will give a_i and c_i with certainty, provided that all measurements are done in rapid succession before the state ket has a time to evolve. We may say that the values of A and C can be determined simultaneously.

The situation is quite different if we consider the measurements of A and B when $[\hat{A},\hat{B}] \neq 0$. In this case, the measurement of A gives a_i and the state ket right after this measurement is still $|a_ic_i\rangle$ as before. If we measure A again, we are certain to get a_i. However, $|a_ic_i\rangle$ is *not* an eigenket of $\hat{B}$. Denoting the orthonormal basis consisting of the eigenkets of $\hat{B}$ by $\{|b_1\rangle,\dots,|b_r\rangle\}$, we write

$$|a_ic_i\rangle = \sum_{i=1}^{r} \lambda_i' |b_i\rangle \,. \tag{8.176}$$

Thus, the subsequent measurement will give one of b_i $(i = 1,\dots,r)$ with probability $|\lambda_i'|^2$. Still, the resulting ket $|b_i\rangle$, though an eigenket of $\hat{B}$, is *not* an eigenket of $\hat{A}$:

$$|b_i\rangle = \sum_{i=1}^{r} \lambda_i'' |a_ic_i\rangle \tag{8.177}$$

and we are no longer certain of the outcome of the future measurement of A. Thus, if $[\hat{A},\hat{B}] \neq 0$, no amount of repeated measurements of A and B will ever give us any certainty regarding the future measurements of *both* of these quantities. That is, values of A and B cannot be determined simultaneously.

The measurements of A and C are said to be **compatible**, while those of A and B are **incompatible**. From many repeated measurements of A and those of B, all done on the identically prepared state $|\phi\rangle$, however, we can still compute the average values, $\langle A\rangle_{\mathrm{QM}}$ and $\langle B\rangle_{\mathrm{QM}}$, and the probability distributions of all possible outcomes around these averages.

To characterize the widths of these distributions, let us take $\hat{A}$ and define

$$\hat{A}_\Delta := \hat{A} - \langle A\rangle_{\mathrm{QM}}\hat{I}\,. \tag{8.178}$$

Then,

$$\hat{A}_\Delta^2 = \hat{A}^2 - 2\langle A\rangle_{\mathrm{QM}}\hat{A} + \langle A\rangle_{\mathrm{QM}}{}^2\hat{I}\,, \tag{8.179}$$

and hence

$$\langle A_\Delta{}^2\rangle_{\mathrm{QM}} = \langle\phi|\hat{A}_\Delta{}^2|\phi\rangle = \langle A^2\rangle_{\mathrm{QM}} - \langle A\rangle_{\mathrm{QM}}{}^2\,. \tag{8.180}$$

This quantity is called the **dispersion** of A and serves as a measure for the width of the distribution for A. Similarly for $\hat{B}$.

The dispersions of noncommuting observables are subject to a fundamental limitation imposed by the **Heisenberg uncertainty principle**:

$$\langle A_\Delta{}^2\rangle_{\mathrm{QM}}\langle B_\Delta{}^2\rangle_{\mathrm{QM}} \geq \frac{1}{4}|\langle[\hat{A},\hat{B}]\rangle_{\mathrm{QM}}|^2\,. \tag{8.181}$$

Equation (3.155) responsible for the $1/h^{3N}$ factor for a classical statistical mechanical partition function stems from this principle as we shall see in Sect. 8.7.2.

The proof of the uncertainty principle requires three ingredients:

a. The Schwarz inequality

$$|\langle\alpha|\beta\rangle|^2 \leq \langle\alpha|\alpha\rangle\langle\beta|\beta\rangle\,, \tag{8.182}$$

the proof of which is similar to that given in Appendix A.5 for the case of ordinary vectors in three-dimensional space. In particular, let $|\gamma\rangle := |\alpha\rangle + \lambda|\beta\rangle$ and note that

$$\langle\gamma|\gamma\rangle = \langle\alpha|\alpha\rangle + \lambda\langle\alpha|\beta\rangle + \lambda^*\langle\beta|\alpha\rangle + \lambda\lambda^*\langle\beta|\beta\rangle \geq 0 \tag{8.183}$$

for any $\lambda \in \mathbb{C}$. Setting $\lambda = -\langle\beta|\alpha\rangle/\langle\beta|\beta\rangle$ we obtain the inequality in question.

b. The average of a Hermitian operator $\hat{A}$ is a real number as is obvious from Theorem 8.3.

c. An operator satisfying $\hat{X}^\dagger = -\hat{X}$ is said to be **anti-Hermitian**. The average of an anti-Hermitian operator is purely imaginary. In fact, using (8.85),

$$\langle\phi|\hat{X}|\phi\rangle^* = \langle\phi|\hat{X}^\dagger|\phi\rangle = -\langle\phi|\hat{X}|\phi\rangle\,. \tag{8.184}$$

Let $\alpha = \hat{A}_\Delta|\phi\rangle$ and $\beta = \hat{B}_\Delta|\phi\rangle$ in the Schwarz inequality. This gives

$$\langle A_\Delta{}^2\rangle_{\text{QM}}\langle B_\Delta{}^2\rangle_{\text{QM}} \geq \left|\langle\phi|\hat{A}_\Delta\hat{B}_\Delta|\phi\rangle\right|^2 . \tag{8.185}$$

To transform the right-hand side, we write

$$\hat{A}_\Delta\hat{B}_\Delta = \frac{1}{2}[\hat{A}_\Delta,\hat{B}_\Delta]_- + \frac{1}{2}[\hat{A}_\Delta,\hat{B}_\Delta]_+ , \tag{8.186}$$

where

$$[\hat{X},\hat{Y}]_\pm := \hat{X}\hat{Y} \pm \hat{Y}\hat{X} . \tag{8.187}$$

The subscript "−" temporarily denotes the now familiar commutator, while the subscript "+" defines the so-called **anti-commutator**.

It is straightforward to show that $[\hat{A}_\Delta,\hat{B}_\Delta]_- = [\hat{A},\hat{B}]_-$ is anti-Hermitian, while $[\hat{A}_\Delta,\hat{B}_\Delta]_+$ is Hermitian. In view of the items b and c above, we conclude that

$$\begin{aligned}\langle A_\Delta{}^2\rangle_{\text{QM}}\langle B_\Delta{}^2\rangle_{\text{QM}} &\geq \frac{1}{4}\left|\langle\phi|[\hat{A},\hat{B}]_-|\phi\rangle\right|^2 + \frac{1}{4}\left|\langle\phi|[\hat{A}_\Delta,\hat{B}_\Delta]_+|\phi\rangle\right|^2 \\ &\geq \frac{1}{4}\left|\langle\phi|[\hat{A},\hat{B}]_-|\phi\rangle\right|^2 ,\end{aligned} \tag{8.188}$$

which is just (8.181).

8.6 ‡Operator with Continuous Spectrum

Certain quantities, such as the position and the momentum of a particle, are expected to be capable of continuous variation. In accordance with the postulates of quantum mechanics, the observables corresponding to these quantities must possess continuous spectrum of eigenvalues. Let $\hat{\xi}$ denote such an observable. Then,

$$\hat{\xi}|\xi\rangle = \xi|\xi\rangle , \tag{8.189}$$

where ξ is the eigenvalue of $\hat{\xi}$ and $|\xi\rangle$ is the corresponding eigenket. As it turns out, the norm of $|\xi\rangle$ is infinite if ξ belongs to a continuous spectrum, and hence $|\xi\rangle$ cannot be normalized. Instead of now familiar

$$\langle a_i|a_j\rangle = \delta_{ij} \tag{8.190}$$

we had for eigenkets belonging to eigenvalues of discrete spectrum, the orthonormality condition becomes

$$\langle\xi'|\xi''\rangle = \delta(\xi' - \xi'') , \tag{8.191}$$

where δ is the Dirac δ-function. The closure relation must be replaced by

$$\int |\xi\rangle\langle\xi| \mathrm{d}\xi = \hat{I} \,. \tag{8.192}$$

In this book, we shall take these results for granted. See Ref. [1] for a brief discussion of a more satisfactory treatment.

Using (8.192), we see immediately that

$$|\alpha\rangle = \int |\xi\rangle\langle\xi|\alpha\rangle \mathrm{d}\xi \,, \tag{8.193}$$

and that

$$\langle\alpha|\beta\rangle = \langle\alpha| \left[\int |\xi\rangle\langle\xi| d\xi \right] |\beta\rangle = \int \langle\alpha|\xi\rangle\langle\xi|\beta\rangle \mathrm{d}\xi \,. \tag{8.194}$$

From (8.189) and (8.191), we have

$$\langle\xi'|\hat{\xi}|\xi''\rangle = \xi''\delta(\xi' - \xi'') \,. \tag{8.195}$$

In place of (8.167), we have

$$|\langle\xi|\phi\rangle|^2 \mathrm{d}\xi \tag{8.196}$$

as the probability that the measurement of ξ yields the value between ξ and $\xi + \mathrm{d}\xi$.

8.6.1 ‡Position Operator and Position Eigenkets

Consider a particle confined to a one-dimensional space and place the x-axis along this space. In accordance with the postulates of quantum mechanics, the position is represented by an observable, which we call a **position operator** $\hat{x}$. If the particle is exactly at x, the measurement of its position should give us x. Thus,

$$\hat{x}|x\rangle = x|x\rangle \,. \tag{8.197}$$

This concept of position operator and its eigenkets may be extended to a three-dimensional space. In doing so, we assume the existence of a *simultaneous* eigenket $|xyz\rangle$ of position operators $\hat{x}$, $\hat{y}$, and $\hat{z}$ so that three components of the position vector of the particle can be determined simultaneously. (See Sect. 8.5.)

In what follows, it proves convenient to use x_1, x_2, x_3 in place of more familiar x, y, z. In this new notation, we have

$$[\hat{x}_i, \hat{x}_j] = 0 \quad i,j = 1,2,3 \tag{8.198}$$

and

$$\hat{x}_1|x_1x_2x_3\rangle = x_1|x_1x_2x_3\rangle \,, \hat{x}_2|x_1x_2x_3\rangle = x_2|x_1x_2x_3\rangle \,, \hat{x}_3|x_1x_2x_3\rangle = x_3|x_1x_2x_3\rangle \,. \tag{8.199}$$

These three equations may be written more compactly as

$$\hat{\boldsymbol{x}}|\boldsymbol{x}\rangle = \boldsymbol{x}|\boldsymbol{x}\rangle \ . \tag{8.200}$$

Because $\hat{\boldsymbol{x}}$ is assumed to be an observable, $\{|\boldsymbol{x}\rangle\}$ forms a basis and hence the closure relation

$$\int |\boldsymbol{x}\rangle\langle\boldsymbol{x}|\mathrm{d}x = \hat{I} \tag{8.201}$$

holds. As a result, any state ket can be expressed as a linear combination of $|\boldsymbol{x}\rangle$:

$$|\alpha\rangle = \int |\boldsymbol{x}\rangle\langle\boldsymbol{x}|\alpha\rangle\mathrm{d}\boldsymbol{x} \ , \tag{8.202}$$

in which the complex-valued function $\phi_\alpha(\boldsymbol{x}) := \langle\boldsymbol{x}|\alpha\rangle$ of $\boldsymbol{x}$ is called the **wave function**. A scalar product between two kets is now expressed as

$$\langle\beta|\alpha\rangle = \int \langle\beta|\boldsymbol{x}\rangle\langle\boldsymbol{x}|\alpha\rangle\mathrm{d}\boldsymbol{x} = \int \phi_\beta^*(\boldsymbol{x})\phi_\alpha(\boldsymbol{x})\mathrm{d}\boldsymbol{x} \ . \tag{8.203}$$

This is the scalar product between two complex-valued function we saw in Example 8.7.

8.7 †Linear Translation

Suppose that a system is in the state represented by $|\alpha\rangle \in V_k$. The system may be just a particle, for example. If we take this system and move it by $\Delta\boldsymbol{x}$ as a whole, the resulting ket, let us call it $|\alpha'\rangle \in V_k$, in general will be different from the original one. Insofar as we may perform such operation for any $|\alpha\rangle \in V_k$, there should be an operator $\hat{T}_{\Delta\boldsymbol{x}}$ representing this linear translation. Thus,

$$|\alpha'\rangle = \hat{T}_{\Delta\boldsymbol{x}}|\alpha\rangle \ . \tag{8.204}$$

We call $\hat{T}_{\Delta\boldsymbol{x}}$ the **translation operator** and demand that it is linear. In this section, we seek for the explicit expression for this operator and study its connection to $\hat{\boldsymbol{x}}$.

8.7.1 †*Properties of Linear Translation*

On physical grounds, we expect $\hat{T}_{\Delta\boldsymbol{x}}$ to satisfy the following conditions:

a. $\hat{T}_{\Delta\boldsymbol{x}}$ preserves the norm of $|\alpha\rangle$. Thus,

$$\langle\alpha'|\alpha'\rangle = \langle\alpha|\hat{T}^\dagger_{\Delta\boldsymbol{x}}\hat{T}_{\Delta\boldsymbol{x}}|\alpha\rangle = \langle\alpha|\alpha\rangle \ , \tag{8.205}$$

for which it is sufficient that

$$\hat{T}^{\dagger}_{\Delta \boldsymbol{x}} \hat{T}_{\Delta \boldsymbol{x}} = \hat{I} \, . \tag{8.206}$$

To understand the reason for demanding this property, recall that

$$\langle \alpha | \alpha \rangle = \sum_{i=1}^{r} \langle \alpha | a_i \rangle \langle a_i | \alpha \rangle = \sum_{i=1}^{r} |\langle a_i | \alpha \rangle|^2 \tag{8.207}$$

is the probability that the measurement of some dynamical variable A gives any of its possible values as an outcome. This probability has to be one and should not change upon linear translation of the system.

b. Two successive linear translations, $\Delta \boldsymbol{x}_1$ followed by $\Delta \boldsymbol{x}_2$, should produce a state identical to the one produced by a single linear translation by $\Delta \boldsymbol{x}_1 + \Delta \boldsymbol{x}_2$. Thus,

$$\hat{T}_{\Delta \boldsymbol{x}_2} \hat{T}_{\Delta \boldsymbol{x}_1} = \hat{T}_{\Delta \boldsymbol{x}_1 + \Delta \boldsymbol{x}_2} \, . \tag{8.208}$$

c. The state of the system will not change at all if no translation is performed. We also do not expect any discontinuity to be present at $\Delta \boldsymbol{x} = \boldsymbol{0}$. Thus,

$$\lim_{\Delta \boldsymbol{x} \to \boldsymbol{0}} \hat{T}_{\Delta \boldsymbol{x}} = \hat{T}_{\Delta \boldsymbol{x} = \boldsymbol{0}} = \hat{I} \, . \tag{8.209}$$

Let us explore some immediate consequence of these requirements. Since $\Delta \boldsymbol{x}_1 + \Delta \boldsymbol{x}_2 = \Delta \boldsymbol{x}_2 + \Delta \boldsymbol{x}_1$, (8.208) implies that

$$\hat{T}_{\Delta \boldsymbol{x}_2} \hat{T}_{\Delta \boldsymbol{x}_1} = \hat{T}_{\Delta \boldsymbol{x}_1} \hat{T}_{\Delta \boldsymbol{x}_2} \, , \tag{8.210}$$

that is,

$$[\hat{T}_{\Delta \boldsymbol{x}_1}, \hat{T}_{\Delta \boldsymbol{x}_2}] = 0 \, . \tag{8.211}$$

Let $\Delta \boldsymbol{x}_2 = \Delta \boldsymbol{x}$ and $\Delta \boldsymbol{x}_1 = -\Delta \boldsymbol{x}$ in (8.208), and apply (8.209). We find

$$\hat{T}_{\Delta \boldsymbol{x}} \hat{T}_{-\Delta \boldsymbol{x}} = \hat{I} \, . \tag{8.212}$$

Multiplying this equation by $\hat{T}^{\dagger}_{\Delta \boldsymbol{x}}$ from the left and using (8.206), we arrive at

$$\hat{T}_{-\Delta \boldsymbol{x}} = \hat{T}^{\dagger}_{\Delta \boldsymbol{x}} \, . \tag{8.213}$$

These properties of $\hat{T}_{\Delta \boldsymbol{x}}$ guide us in our search for a reasonable guess on its form.

To avoid unnecessary complications, let us confine our attention to an infinitesimal linear translation by $\delta \boldsymbol{x}$ so that higher order terms in $\delta \boldsymbol{x}$ can be safely ignored. Then, all of the properties we listed for the linear translation operator are satisfied by the following form of $\hat{T}_{\delta \boldsymbol{x}}$:

$$\hat{T}_{\delta \boldsymbol{x}} = \hat{I} - i \hat{\boldsymbol{K}} \cdot \delta \boldsymbol{x} \, , \tag{8.214}$$

where $\hat{\boldsymbol{K}}$ is a Hermitian operator and

$$\hat{\boldsymbol{K}} \cdot \delta \boldsymbol{x} := \hat{K}_1 \delta x_1 + \hat{K}_2 \delta x_2 + \hat{K}_3 \delta x_3 \, . \tag{8.215}$$

We note that $\hat{T}_{\delta x}$ should not change the dimension of a ket it is acting on. Consequently, $\hat{\boldsymbol{K}}$ has the dimension of inverse length.

Exercise 8.24. Prove that (8.214) satisfies (8.206), (8.208), and (8.209) to the first order of $\delta \boldsymbol{x}$. ///

8.7.2 †Commutation Relations

What effect would the linear translation have on the position eigenket $|\boldsymbol{x}\rangle$? By answering this question, we will be lead to discover the commutation relation between the position operator $\hat{\boldsymbol{x}}$ and $\hat{\boldsymbol{K}}$. Let $|\alpha'\rangle$ denote the state ket obtained by linearly translating $|\alpha\rangle$ by $\delta \boldsymbol{x}$. According to the definition given in Sect. 8.6.1, the corresponding wave functions are given by

$$\phi_\alpha(\boldsymbol{x}) = \langle \boldsymbol{x}|\alpha\rangle \quad \text{and} \quad \phi_{\alpha'}(\boldsymbol{x}) = \langle \boldsymbol{x}|\alpha'\rangle = \langle \boldsymbol{x}|\hat{T}_{\delta \boldsymbol{x}}|\alpha\rangle \,, \tag{8.216}$$

respectively. Because the two states, $|\alpha\rangle$ and $|\alpha'\rangle$, are related by the displacement $\delta \boldsymbol{x}$, it seems utterly natural to expect that their corresponding wave functions should also be so related. That is, the value of $\phi_{\alpha'}$ at $\boldsymbol{x}$ is equal to that of ϕ_α at $\boldsymbol{x} - \delta \boldsymbol{x}$:

$$\phi_{\alpha'}(\boldsymbol{x}) = \phi_\alpha(\boldsymbol{x} - \delta \boldsymbol{x}) \,. \tag{8.217}$$

Using (8.216), we rewrite this equation as

$$\langle \boldsymbol{x}|\hat{T}_{\delta \boldsymbol{x}}|\alpha\rangle = \langle \boldsymbol{x} - \delta \boldsymbol{x}|\alpha\rangle \,. \tag{8.218}$$

Since $|\alpha\rangle \in V_k$ is arbitrary, we conclude that

$$\langle \boldsymbol{x}|\hat{T}_{\delta \boldsymbol{x}} = \langle \boldsymbol{x} - \delta \boldsymbol{x}| \,. \tag{8.219}$$

Taking the adjoint,

$$\hat{T}^\dagger_{\delta \boldsymbol{x}}|\boldsymbol{x}\rangle = |\boldsymbol{x} - \delta \boldsymbol{x}\rangle \,. \tag{8.220}$$

Recalling (8.213),

$$\hat{T}_{-\delta \boldsymbol{x}}|\boldsymbol{x}\rangle = |\boldsymbol{x} - \delta \boldsymbol{x}\rangle \,. \tag{8.221}$$

But because this equality holds for any $\delta \boldsymbol{x}$, it should hold when we replace $\delta \boldsymbol{x}$ by $-\delta \boldsymbol{x}$:

$$\hat{T}_{\delta \boldsymbol{x}}|\boldsymbol{x}\rangle = |\boldsymbol{x} + \delta \boldsymbol{x}\rangle \,, \tag{8.222}$$

Multiplying both sides of this equation by $\hat{\boldsymbol{x}}$, we find

$$\hat{\boldsymbol{x}}\hat{T}_{\delta \boldsymbol{x}}|\boldsymbol{x}\rangle = \hat{\boldsymbol{x}}|\boldsymbol{x} + \delta \boldsymbol{x}\rangle = (\boldsymbol{x} + \delta \boldsymbol{x})|\boldsymbol{x} + \delta \boldsymbol{x}\rangle \,, \tag{8.223}$$

where we used (8.200). On the other hand,

$$\hat{T}_{\delta \boldsymbol{x}}\hat{\boldsymbol{x}}|\boldsymbol{x}\rangle = \hat{T}_{\delta \boldsymbol{x}}\boldsymbol{x}|\boldsymbol{x}\rangle = \boldsymbol{x}\hat{T}_{\delta \boldsymbol{x}}|\boldsymbol{x}\rangle = \boldsymbol{x}|\boldsymbol{x} + \delta \boldsymbol{x}\rangle \,. \tag{8.224}$$

The second equality holds because $\boldsymbol{x}$ is simply a vector having real numbers as its components. The last step follows from (8.222). The last two equations indicate

$$[\hat{\boldsymbol{x}}, \hat{T}_{\delta\boldsymbol{x}}]|\boldsymbol{x}\rangle = \delta\boldsymbol{x}|\boldsymbol{x}+\delta\boldsymbol{x}\rangle \ . \tag{8.225}$$

Expanding $|\boldsymbol{x}+\delta\boldsymbol{x}\rangle$ around $\delta\boldsymbol{x}=\boldsymbol{0}$, and retaining the leading term only, we find

$$[\hat{\boldsymbol{x}}, \hat{T}_{\delta\boldsymbol{x}}]|\boldsymbol{x}\rangle = \delta\boldsymbol{x}|\boldsymbol{x}\rangle \ . \tag{8.226}$$

If a Taylor series expansion of a ket leaves you uncomfortable, we can proceed as follows:

$$\langle\phi|[\hat{\boldsymbol{x}}, \hat{T}_{\delta\boldsymbol{x}}]|\boldsymbol{x}\rangle = \langle\phi|\delta\boldsymbol{x}|\boldsymbol{x}+\delta\boldsymbol{x}\rangle = \delta\boldsymbol{x}\phi(\boldsymbol{x}+\delta\boldsymbol{x}) \approx \delta\boldsymbol{x}\phi(\boldsymbol{x}) = \delta\boldsymbol{x}\langle\phi|\boldsymbol{x}\rangle \ . \tag{8.227}$$

But since ϕ in this equation is arbitrary, this result implies (8.226). Furthermore, since $\{|\boldsymbol{x}\rangle\}$ forms a basis, (8.226) holds even if $|\boldsymbol{x}\rangle$ is replaced by an arbitrary ket. So, we conclude that

$$[\hat{\boldsymbol{x}}, \hat{T}_{\delta\boldsymbol{x}}] = \delta\boldsymbol{x} \ . \tag{8.228}$$

Using (8.214), we transform this equation as follows:

$$\begin{aligned} \hat{\boldsymbol{x}}(\hat{I} - i\hat{\boldsymbol{K}}\cdot\delta\boldsymbol{x}) - (\hat{I} - i\hat{\boldsymbol{K}}\cdot\delta\boldsymbol{x})\hat{\boldsymbol{x}} &= \delta\boldsymbol{x} \\ -i\hat{\boldsymbol{x}}(\hat{\boldsymbol{K}}\cdot\delta\boldsymbol{x}) + i(\hat{\boldsymbol{K}}\cdot\delta\boldsymbol{x})\hat{\boldsymbol{x}} &= \delta\boldsymbol{x} \\ \hat{\boldsymbol{x}}(\hat{\boldsymbol{K}}\cdot\delta\boldsymbol{x}) - (\hat{\boldsymbol{K}}\cdot\delta\boldsymbol{x})\hat{\boldsymbol{x}} &= i\delta\boldsymbol{x} \ . \end{aligned} \tag{8.229}$$

The first (or the x_1-) component of this equation reads

$$\hat{x}_1(\hat{K}_1\delta x_1 + \hat{K}_2\delta x_2 + \hat{K}_3\delta x_3) - (\hat{K}_1\delta x_1 + \hat{K}_2\delta x_2 + \hat{K}_3\delta x_3)\hat{x}_1 = i\delta x_1 \ . \tag{8.230}$$

Since $\delta\boldsymbol{x}$ is arbitrary, we conclude that

$$\hat{x}_1\hat{K}_1 - \hat{K}_1\hat{x}_1 = i \ , \quad \hat{x}_1\hat{K}_2 - \hat{K}_2\hat{x}_1 = 0 \ , \quad \text{and} \quad \hat{x}_1\hat{K}_3 - \hat{K}_3\hat{x}_1 = 0 \ . \tag{8.231}$$

Six additional equations follow from the other components of (8.229). The resulting (total of nine) equations can be summarized compactly as

$$[\hat{x}_i, \hat{K}_j] = i\delta_{ij} \ . \tag{8.232}$$

We introduce a Hermitian operator defined by

$$\hat{\boldsymbol{p}} = \hbar\hat{\boldsymbol{K}} \tag{8.233}$$

and call it the **momentum operator**, whose eigenvalue, by *definition*, is the **momentum**.

Justification of this seemingly arbitrary definition of momentum must be sought among the physical attributes of the eigenvalues predicted by the theory. See Sect. 8.15, for example. Here, we simply remark that $\hat{\boldsymbol{p}}$ does have the correct dimension of momentum because of the factor $\hbar := h/2\pi$, in which h is the Planck constant.

Now, we rewrite (8.232) in terms of the momentum operator as

$$[\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij} \, . \tag{8.234}$$

The appearance of δ_{ij} is quite reasonable on physical grounds if we note that $\hat{\boldsymbol{p}}$ is a part of the linear translation operator. When you measure the x_i coordinate of a particle, it certainly matters whether or not you move the particle in the x_i-direction prior to the measurement, while moving it in the x_j-direction ($i \neq j$) should not have any effect. Substituting (8.234) into (8.181), we arrive at

$$\sqrt{\langle {x_{i\Delta}}^2 \rangle_{\mathrm{QM}} \langle {p_{j\Delta}}^2 \rangle_{\mathrm{QM}}} \geq \frac{\hbar}{2}\delta_{ij} \, , \tag{8.235}$$

which is essentially (3.155).

The commutation relations among $\hat{p}$'s are obtained from (8.211) and (8.214):

$$[\hat{p}_i, \hat{p}_j] = 0 \, . \tag{8.236}$$

Equations (8.198), (8.234), and (8.236) should be contrasted against their classical counterparts given in Exercise 1.17.

8.7.3 †*Momentum Eigenket*

Combining (8.214), (8.216), (8.233), we find

$$\phi_{\alpha'}(\boldsymbol{x}) = \left\langle \boldsymbol{x} \middle| \hat{I} - \frac{i}{\hbar}\hat{\boldsymbol{p}} \cdot \delta\boldsymbol{x} \middle| \alpha \right\rangle = \phi_\alpha(\boldsymbol{x}) - \frac{i}{\hbar}\delta\boldsymbol{x} \cdot \langle \boldsymbol{x}|\hat{\boldsymbol{p}}|\alpha\rangle \, . \tag{8.237}$$

Recall that we kept only up to the first order terms of $\delta\boldsymbol{x}$ in arriving at this equation. Under the same approximation, (8.217) gives

$$\phi_{\alpha'}(\boldsymbol{x}) = \phi_\alpha(\boldsymbol{x}) - \delta\boldsymbol{x} \cdot \nabla\phi_\alpha(\boldsymbol{x}) \, . \tag{8.238}$$

Comparing these two equations, and noting that $\delta\boldsymbol{x}$ is arbitrary, we find that

$$\langle \boldsymbol{x}|\hat{\boldsymbol{p}}|\alpha\rangle = -i\hbar\nabla\langle \boldsymbol{x}|\alpha\rangle \, . \tag{8.239}$$

On the right-hand side, $\langle \boldsymbol{x}|\alpha\rangle$ is the wave function for state $|\alpha\rangle$. On the left, we have the wave function corresponding to the ket $\hat{\boldsymbol{p}}|\alpha\rangle$, that is, the state $|\alpha\rangle$ after it is modified by the operator $\hat{\boldsymbol{p}}$. Equation (8.239) indicates that the effect of the momentum operator $\hat{\boldsymbol{p}}$ in the $\boldsymbol{x}$-representation is to take the derivative of the wave function. More pictorially,

$$\hat{\boldsymbol{p}} : \phi_\alpha(\boldsymbol{x}) \longrightarrow -i\hbar\nabla\phi_\alpha(\boldsymbol{x}) \, . \tag{8.240}$$

Using (8.239), we have

$$\langle \beta|\hat{\boldsymbol{p}}|\alpha\rangle = \int \langle \beta|\boldsymbol{x}\rangle\langle \boldsymbol{x}|\hat{\boldsymbol{p}}|\alpha\rangle \mathrm{d}\boldsymbol{x} = \int \phi_\beta^*(\boldsymbol{x})(-i\hbar\nabla)\phi_\alpha(\boldsymbol{x})\mathrm{d}\boldsymbol{x} \;, \tag{8.241}$$

which is one of the key equations in quantum mechanics.

Other useful results follow from (8.239). Because $|\alpha\rangle$ is arbitrary, we can substitute any ket in its place. In particular, let us use $|\boldsymbol{p}\rangle$, a momentum eigenket corresponding to the eigenvalue $\boldsymbol{p}$:

$$\hat{\boldsymbol{p}}|\boldsymbol{p}\rangle = \boldsymbol{p}|\boldsymbol{p}\rangle \;. \tag{8.242}$$

This gives

$$\boldsymbol{p}\langle \boldsymbol{x}|\boldsymbol{p}\rangle = -i\hbar\nabla\langle \boldsymbol{x}|\boldsymbol{p}\rangle \;. \tag{8.243}$$

But, this is just a differential equation for $\langle \boldsymbol{x}|\boldsymbol{p}\rangle$, with the solution

$$\langle \boldsymbol{x}|\boldsymbol{p}\rangle = c e^{\frac{i}{\hbar}\boldsymbol{p}\cdot\boldsymbol{x}} \;. \tag{8.244}$$

So, the momentum eigenket in the $\boldsymbol{x}$-representation is a plane wave.

Exercise 8.25. Verify that (8.244) satisfies (8.243). ///

How do we determine the constant c? As with $\hat{\boldsymbol{x}}$, we assume that $\hat{\boldsymbol{p}}$ is an observable and hence $\{|\boldsymbol{p}\rangle\}$ forms a basis, that is,

$$|\alpha\rangle = \int |\boldsymbol{p}\rangle\langle \boldsymbol{p}|\alpha\rangle \mathrm{d}\boldsymbol{p} \tag{8.245}$$

for any $|\alpha\rangle$. From (D.53), we see that

$$\int e^{i\boldsymbol{k}\cdot\boldsymbol{x}}\mathrm{d}\boldsymbol{x} = (2\pi)^3\delta(\boldsymbol{k}) \;, \tag{8.246}$$

where $\delta(\boldsymbol{k}) := \delta(k_1)\delta(k_2)\delta(k_3)$ by definition. By means of this identity, we find

$$\delta(\boldsymbol{x}-\boldsymbol{x}') = \langle \boldsymbol{x}|\boldsymbol{x}'\rangle = \int \langle \boldsymbol{x}|\boldsymbol{p}\rangle\langle \boldsymbol{p}|\boldsymbol{x}'\rangle \mathrm{d}\boldsymbol{p} = |c|^2(2\pi\hbar)^3\delta(\boldsymbol{x}-\boldsymbol{x}') \;. \tag{8.247}$$

While c can be any complex number satisfying this equation, the convention dictates that we take the real positive root. Thus,

$$c = \frac{1}{(2\pi\hbar)^{3/2}} \;. \tag{8.248}$$

Now that we have a complete expression for $\langle \boldsymbol{x}|\boldsymbol{p}\rangle$, we can immediately deduce the following relationship between the **coordinate-space wave function** $\phi_\alpha(\boldsymbol{x}) = \langle \boldsymbol{x}|\alpha\rangle$ and the **momentum–space wave function** $\phi_\alpha(\boldsymbol{p}) := \langle \boldsymbol{p}|\alpha\rangle$:

$$\phi_\alpha(\boldsymbol{x}) = \langle \boldsymbol{x}|\alpha\rangle = \int \langle \boldsymbol{x}|\boldsymbol{p}\rangle\langle \boldsymbol{p}|\alpha\rangle \mathrm{d}\boldsymbol{p} = \frac{1}{(2\pi\hbar)^{3/2}}\int \phi_\alpha(\boldsymbol{p})e^{\frac{i}{\hbar}\boldsymbol{p}\cdot\boldsymbol{x}}\mathrm{d}\boldsymbol{p} \tag{8.249}$$

and

$$\phi_\alpha(\boldsymbol{p}) = \langle \boldsymbol{p}|\alpha\rangle = \int \langle \boldsymbol{p}|\boldsymbol{x}\rangle\langle \boldsymbol{x}|\alpha\rangle \mathrm{d}\boldsymbol{x} = \frac{1}{(2\pi\hbar)^{3/2}} \int \phi_\alpha(\boldsymbol{x}) e^{-\frac{i}{\hbar}\boldsymbol{p}\cdot\boldsymbol{x}} \mathrm{d}\boldsymbol{x} \,. \tag{8.250}$$

In other words, $\phi_\alpha(\boldsymbol{x})$ and $\phi_\alpha(\boldsymbol{p})$ are the Fourier transform of each other.

Finally, by setting $|\alpha\rangle = |\boldsymbol{x}'\rangle$ in (8.239), we obtain

$$\langle \boldsymbol{x}|\hat{\boldsymbol{p}}|\boldsymbol{x}'\rangle = -i\hbar\nabla\langle \boldsymbol{x}|\boldsymbol{x}'\rangle = -i\hbar\nabla\delta(\boldsymbol{x}-\boldsymbol{x}') \,, \tag{8.251}$$

where we note that the derivative is with respect to $\boldsymbol{x}$ and not $\boldsymbol{x}'$. This is the matrix element of $\hat{\boldsymbol{p}}$ in the $\boldsymbol{x}$-representation.

Exercise 8.26. Show that

$$\hat{x}|p\rangle = -i\hbar\frac{\mathrm{d}|p\rangle}{\mathrm{d}p} \tag{8.252}$$

for a particle in a one-dimensional space. ///

8.8 †Time Evolution Operator

Now, we have to figure out how the state of a given system evolves with time. What we need is a linear operator that acts on a state ket $|\phi,t\rangle$ at time t and converts it to a new one $|\phi,t+\delta t\rangle$ at a later time $t+\delta t$. As with the linear translation, it is sufficient to consider an infinitesimally small interval of time. That is, we wish to find the **time evolution operator** $\hat{U}_{\delta t}(t)$ satisfying

$$|\phi,t+\delta t\rangle = \hat{U}_{\delta t}(t)|\phi,t\rangle \,, \tag{8.253}$$

where we allowed for the explicit dependence of $\hat{U}_{\delta t}(t)$ on t. As in the case of the linear translation, we list a few reasonable demands to be imposed on $\hat{U}_{\delta t}(t)$:

a. $\hat{U}_{\delta t}(t)$ preserves the norm of $|\phi,t\rangle$:

$$\langle\phi,t+\delta t|\phi,t+\delta t\rangle = \langle\phi,t|\hat{U}_{\delta t}(t)^\dagger\hat{U}_{\delta t}(t)|\phi,t\rangle = \langle\phi,t|\phi,t\rangle \,, \tag{8.254}$$

for which it is sufficient that

$$\hat{U}_{\delta t}(t)^\dagger\hat{U}_{\delta t}(t) = \hat{I} \,. \tag{8.255}$$

b. Two successive time translations, δt_1 followed by another δt_2, should produce a state identical to that produced by a single time translation by $\delta t_1+\delta t_2$. Thus,

$$\hat{U}_{\delta t_2}(t+\delta t_1)\hat{U}_{\delta t_1}(t) = \hat{U}_{\delta t_1+\delta t_2}(t) \,. \tag{8.256}$$

c. The state of the system will not change at all if no time has passed. We also do not expect any discontinuity to be present at $\delta t = 0$. Thus,

$$\lim_{\delta t \to 0} \hat{U}_{\delta t} = \hat{U}_{\delta t = 0} = \hat{I} \, . \tag{8.257}$$

Except for the use of δt in place of $\Delta \boldsymbol{x}$, these demands are identical to what we saw in Sect. 8.7.1. So, we can immediately write down the desired expression for $\hat{U}_{\delta t}$:

$$\hat{U}_{\delta t}(t) = \hat{I} - \frac{i}{\hbar} \hat{H}(t) \delta t \, , \tag{8.258}$$

in which $\hat{H}$, by definition, is called **Hamiltonian operator** and its eigenvalues are called **energy** of the system.

It is straightforward to verify that (8.258) is compatible with the demands we have listed. Unlike $\boldsymbol{x}$, there is no operator corresponding to t. As in classical mechanics, t is a label indicating when things are happening. So, there is no commutation relation to speak of here.

From here, the celebrated Schrödinger equation is just a stone's through away. Using (8.258) in (8.253),

$$|\phi, t + \delta t\rangle = \left[\hat{I} - \frac{i}{\hbar} \hat{H}(t) \delta t \right] |\phi, t\rangle \, . \tag{8.259}$$

Moving $\hat{I}|\phi,t\rangle = |\phi,t\rangle$ to the left and dividing the resulting expression by δt,

$$\frac{|\phi, t + \delta t\rangle - |\phi, t\rangle}{\delta t} = -\frac{i}{\hbar} \hat{H}(t) |\phi, t\rangle \, . \tag{8.260}$$

Taking the $\delta t \to 0$ limit, we find

$$i\hbar \frac{\mathrm{d}|\phi, t\rangle}{\mathrm{d}t} = \hat{H}(t) |\phi, t\rangle \, , \tag{8.261}$$

which is the **Schrödinger equation** written for a state ket. The form this equation takes in $\boldsymbol{r}$-representation is given in Sect. 8.13.

8.9 $\dagger\hat{U}_t$ is Unitary

From (8.258), we see immediately that the infinitesimal time evolution operator $\hat{U}_{\delta t}(t)$ is unitary:

$$\hat{U}^{\dagger}_{\delta t}(t) \hat{U}_{\delta t}(t) = \hat{U}_{\delta t}(t) \hat{U}^{\dagger}_{\delta t}(t) = \hat{I} \, . \tag{8.262}$$

Since any finite duration of time can be divided into many infinitesimal time intervals, (8.262) can be used to establish

$$\hat{U}_t^\dagger \hat{U}_t = \hat{U}_t \hat{U}_t^\dagger = \hat{I} \, , \tag{8.263}$$

where $\hat{U}_t := \hat{U}_t(0)$ is the time evolution operator that converts the state ket at $t = 0$ to that at time t. To see this more explicitly, let

$$\Delta t := \frac{t}{n} \quad \text{and} \quad t_i := i\Delta t \, , \quad i = 0, \ldots, n-1 \tag{8.264}$$

and write

$$\hat{U}_t = \hat{U}_{\Delta t}(t_{n-1}) \hat{U}_{\Delta t}(t_{n-2}) \cdots \hat{U}_{\Delta t}(t_1) \hat{U}_{\Delta t}(t_0) \, . \tag{8.265}$$

Taking the adjoint of this equation, we obtain

$$\hat{U}_t^\dagger = \hat{U}_{\Delta t}^\dagger(t_0) \, , \hat{U}_{\Delta t}^\dagger(t_1) \cdots \hat{U}_{\Delta t}^\dagger(t_{n-2}) \hat{U}_{\Delta t}^\dagger(t_{n-1}) \, , \tag{8.266}$$

In the limit of $n \to \infty$, Δt becomes infinitesimally small and (8.262) applies:

$$\hat{U}_{\Delta t}^\dagger(t_i) \hat{U}_{\Delta t}(t_i) = \hat{U}_{\Delta t}(t_i) \hat{U}_{\Delta t}^\dagger(t_i) = \hat{I} \, , \quad i = 0, \ldots, n-1 \, . \tag{8.267}$$

Combining (8.265), (8.266), and (8.267), we arrive at (8.263).

8.10 ‡Formal Solution of the Schrödinger Equation

In a purely formal manner, (8.261) can be solved for a general Hamiltonian $\hat{H}$. We say that the solution is only *formal* in the sense that it may be very difficult to evaluate the resulting expression for $|\phi, t\rangle$. Nevertheless, the formal solution is often very useful as it allows us to expresses $|\phi, t\rangle$ very compactly.

8.10.1 ‡Time-Independent $\hat{H}$

Let us first assume that $\hat{H}$ is independent of t. To find the formal solution of (8.261), we first expand $|\phi, t\rangle$ into the Taylor series around $t = 0$:

$$|\phi, t\rangle = |\phi, 0\rangle + \left. \frac{\mathrm{d}}{\mathrm{d}t} |\phi, t\rangle \right|_{t=0} t + \frac{1}{2} \left. \frac{\mathrm{d}^2}{\mathrm{d}t^2} |\phi, t\rangle \right|_{t=0} t^2 + \cdots \, . \tag{8.268}$$

From (8.261),

$$\frac{\mathrm{d}}{\mathrm{d}t} |\phi, t\rangle = -\frac{i}{\hbar} \hat{H} |\phi, t\rangle . \tag{8.269}$$

Applying this formula to $\mathrm{d}|\phi,t\rangle/\mathrm{d}t$, which is just a ket, we find

$$\frac{\mathrm{d}^2}{\mathrm{d}t^2}|\phi,t\rangle = -\frac{i}{\hbar}\hat{H}\left[\frac{\mathrm{d}}{\mathrm{d}t}|\phi,t\rangle\right] = -\frac{i}{\hbar}\hat{H}\left[-\frac{i}{\hbar}\hat{H}|\phi,t\rangle\right] = \left(-\frac{i}{\hbar}\hat{H}\right)^2|\phi,t\rangle\,. \tag{8.270}$$

Continuing in this manner, we see that

$$\frac{\mathrm{d}^n}{\mathrm{d}t^n}|\phi,t\rangle = \left(-\frac{i}{\hbar}\hat{H}\right)^n|\phi,t\rangle\,, \quad n = 1,2,\dots \tag{8.271}$$

Setting $t = 0$ in this equation and using the resulting expression in (8.268), we have

$$|\phi,t\rangle = \left[\sum_{n=0}^{\infty}\frac{1}{n!}\left(-\frac{i}{\hbar}\hat{H}t\right)^n\right]|\phi,0\rangle\,, \tag{8.272}$$

which is the desired formal solution. This equation shows that

$$\hat{U}_t := \hat{U}_t(0) = \sum_{n=0}^{\infty}\frac{1}{n!}\left(-\frac{i}{\hbar}\hat{H}t\right)^n \tag{8.273}$$

for a time-independent $\hat{H}$. Using this result, it is straightforward to show that

$$\frac{\mathrm{d}\hat{U}_t}{\mathrm{d}t} = -\frac{i}{\hbar}\hat{H}\hat{U}_t\,, \tag{8.274}$$

which is the Schrödinger equation written for $\hat{U}_t$. Multiplying both sides of (8.274) from the right by $|\phi,0\rangle$ and noting that this ket is independent of t, we recover (8.261).

Exercise 8.27. Derive (8.274) from (8.273). ///

As we saw in Sect. 8.3.2, a function of an operator is defined in terms of the Maclaurin expansion of the function. Recalling (B.5), we see that

$$\hat{U}_t = e^{-\frac{i}{\hbar}\hat{H}t}\,, \tag{8.275}$$

and hence

$$|\phi,t\rangle = e^{-\frac{i}{\hbar}\hat{H}t}|\phi,0\rangle\,. \tag{8.276}$$

8.10.2 †*Time-Dependent $\hat{H}$*

Equation (8.276) cannot be true if $\hat{H}$ depends on t. This becomes immediately clear if we ask ourselves at which instant $\hat{H}$ in the exponent should be evaluated. We must also allow for the possibility that $\hat{H}$ evaluated at different instances may not even commute.

To make a progress, we first integrate (8.261) from $t = 0$ to t:

$$|\phi, t\rangle = |\phi, 0\rangle - \frac{i}{\hbar}\int_0^t \hat{H}(t_1)|\phi, t_1\rangle \mathrm{d}t_1 \ . \tag{8.277}$$

This is not a particularly useful form of expressing $|\phi, t\rangle$ since the right-hand side still contains the unknown ket $|\phi, t_1\rangle$. But, the ket can be expressed using (8.277) as

$$|\phi, t_1\rangle = |\phi, 0\rangle - \frac{i}{\hbar}\int_0^{t_1} \hat{H}(t_2)|\phi, t_2\rangle \mathrm{d}t_2 \ . \tag{8.278}$$

Substituting this expression into (8.277), we obtain

$$|\phi, t\rangle = |\phi, 0\rangle + \left[-\frac{i}{\hbar}\int_0^t \hat{H}(t_1)\mathrm{d}t_1\right]|\phi, 0\rangle + \left(-\frac{i}{\hbar}\right)^2 \int_0^t \int_0^{t_1} \hat{H}(t_1)\hat{H}(t_2)|\phi, t_2\rangle \mathrm{d}t_2\mathrm{d}t_1 \ , \tag{8.279}$$

where we pulled $|\phi, 0\rangle$ out of the integral sign because it is independent of t. Now, we can use (8.277) once again to express $|\phi, t_2\rangle$ as in (8.278). Continuing in this manner, we see that the time evolution operator for a time-dependent $\hat{H}$ is given by

$$\hat{U}_t = \sum_{n=0}^{\infty}\left(-\frac{i}{\hbar}\right)^n \int_0^t \int_0^{t_1} \cdots \int_0^{t_{n-1}} \hat{H}(t_1)\hat{H}(t_2)\cdots\hat{H}(t_n)\mathrm{d}t_n\cdots\mathrm{d}t_2\mathrm{d}t_1 \ , \tag{8.280}$$

in which $n = 0$ term in the summation is the identity operator $\hat{I}$. This result is known as the **Neumann series**.

Iterated integrals in which a limit of an integral depends on the values of the other integration variables is rather tedious to handle. However, we can circumvent this difficulty through a clever trick. To this end, let us consider the integrals for the $n = 2$ term:

$$I_2 := \int_0^t \int_0^{t_1} \hat{H}(t_1)\hat{H}(t_2)\mathrm{d}t_2\mathrm{d}t_1 \ . \tag{8.281}$$

Because t_1 and t_2 are simply the integration variables, we have

$$I_2 = \int_0^t \int_0^{t_2} \hat{H}(t_2)\hat{H}(t_1)\mathrm{d}t_1\mathrm{d}t_2 \ . \tag{8.282}$$

In (8.281), the integral over t_2 runs from 0 to t_1. Thus, $0 \le t_2 \le t_1$. On the other hand, we have $0 \le t_1 \le t_2$ in (8.282).

Let us now define the **time-ordering operator** $\hat{\mathscr{T}}_>$ which acts on a *product of time-dependent operators* and rearranges them so that the time decreases from left to right. Thus, if $t_a < t_b$, we have

$$\hat{\mathscr{T}}_>\left[\hat{A}(t_a)\hat{B}(t_b)\right] = \hat{\mathscr{T}}_>\left[\hat{B}(t_b)\hat{A}(t_a)\right] = \hat{B}(t_b)\hat{A}(t_a) \ . \tag{8.283}$$

Similarly if we have a product of more than two time-dependent operators. By means of $\hat{\mathscr{T}}_>$, we can rewrite (8.281) and (8.282) as

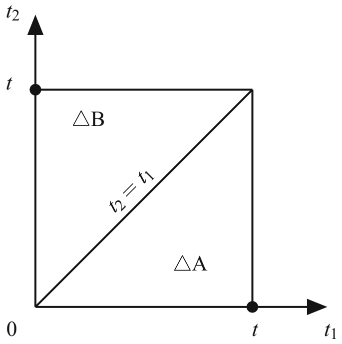

Fig. 8.1 The integral (8.284) is carried out over the *lower triangle* (△A) while (8.285) is over the *upper triangle* (△B). Taken together, they cover the square.

$$I_2 = \int_0^t \int_0^{t_1} \hat{\mathscr{T}}_> \left[\hat{H}(t_1)\hat{H}(t_2)\right] \mathrm{d}t_2 \mathrm{d}t_1 \tag{8.284}$$

and

$$I_2 = \int_0^t \int_0^{t_2} \hat{\mathscr{T}}_> \left[\hat{H}(t_1)\hat{H}(t_2)\right] \mathrm{d}t_1 \mathrm{d}t_2 \, , \tag{8.285}$$

respectively. These two integrals share the same integrand. From Fig. 8.1, we see that these two integrals, taken together, cover the square region defined by $0 \le t_1 \le t$ and $0 \le t_2 \le t$. Thus, adding (8.284) and (8.285), we arrive at

$$I_2 = \frac{1}{2} \int_0^t \int_0^t \hat{\mathscr{T}}_> \left[\hat{H}(t_1)\hat{H}(t_2)\right] \mathrm{d}t_1 \mathrm{d}t_2 \, . \tag{8.286}$$

In a similar manner, it is possible to show that the n-dimensional integral in (8.280) can be written as

$$I_n = \frac{1}{n!} \int_0^t \cdots \int_0^t \hat{\mathscr{T}}_> \left[\hat{H}(t_1) \cdots \hat{H}(t_n)\right] \mathrm{d}t_1 \cdots \mathrm{d}t_n \, . \tag{8.287}$$

In this way, we arrive at

$$\hat{U}_t = \sum_{n=0}^{\infty} \frac{1}{n!} \left(-\frac{i}{\hbar}\right)^n \int_0^t \cdots \int_0^t \hat{\mathscr{T}}_> \left[\hat{H}(t_1) \cdots \hat{H}(t_n)\right] \mathrm{d}t_1 \cdots \mathrm{d}t_n \, , \tag{8.288}$$

which is known as the **Dyson series**. As a short-hand notation, it is common to express this result in terms of the **time-ordered exponential** as

$$\hat{U}_t = \hat{\mathscr{T}}_> \exp\left[-\frac{i}{\hbar} \int_0^t \hat{H}(t')\mathrm{d}t'\right] \, . \tag{8.289}$$

Exercise 8.28. Show that $\hat{U}_t$ given by (8.288) satisfies the Schrödinger equation:

$$\frac{\mathrm{d}\hat{U}_t}{\mathrm{d}t} = -\frac{i}{\hbar}\hat{H}(t)\hat{U}_t \tag{8.290}$$

for the time evolution operator $\hat{U}_t$. ///

If $\hat{H}(t_a)$ and $\hat{H}(t_b)$ commutes for *any* t_a and t_b in the interval $[0,t]$, that is, if

$$\hat{H}(t_a)\hat{H}(t_b) = \hat{H}(t_b)\hat{H}(t_a) \quad \text{for any } t_1, t_2 \in [0,t] \tag{8.291}$$

then we have

$$\hat{\mathscr{T}}_> \left[\hat{H}(t_1)\cdots\hat{H}(t_n)\right] = \hat{H}(t_1)\cdots\hat{H}(t_n)\ , \tag{8.292}$$

that is, a product of $\hat{H}$'s evaluated at different instances defines an unique operator regardless of the order in which $\hat{H}$'s are multiplied. In this case, (8.287) reduces to

$$I_n = \frac{1}{n!}\int_0^t \cdots \int_0^t \hat{H}(t_1)\cdots\hat{H}(t_n)\mathrm{d}t_1\cdots\mathrm{d}t_n = \frac{1}{n!}\left[\int_0^t \hat{H}(t')\mathrm{d}t'\right]^n \tag{8.293}$$

and we now have

$$\hat{U}_t = \exp\left[-\frac{i}{\hbar}\int_0^t \hat{H}(t')\mathrm{d}t'\right]\ . \tag{8.294}$$

in place of (8.289). If $\hat{H}$ is actually independent of t, this expression reduces to (8.275).

8.11 ‡Heisenberg's Equation of Motion

Thus far, we have taken a point of view that the state of a quantum mechanical system is represented by a state ket $|\phi,t\rangle$ with its time evolution dictated by the Schrödinger equation. The time dependence of the average value $\langle A\rangle_{\mathrm{QM}}(t)$ of a dynamical variable A is a result of this time evolution and a possible *explicit* time dependence of $\hat{A}$. This view point is called the **Schrödinger picture**.

An alternative view point emerges through the use of the time evolution operator $\hat{U}_t$:

$$\langle A\rangle_{\mathrm{QM}}(t) = \langle\phi,t|\hat{A}|\phi,t\rangle = \langle\phi,0|\hat{U}_t^\dagger\hat{A}\hat{U}_t|\phi,0\rangle\ , \tag{8.295}$$

where we used the formal solution,

$$|\phi,t\rangle = \hat{U}_t|\phi,0\rangle\ , \tag{8.296}$$

of the Schrödinger equation from Sect. 8.10 and and its adjoint:

$$\langle\phi,t| = \langle\phi,0|\hat{U}_t^\dagger\ . \tag{8.297}$$

We now interpret (8.295) as indicating that the time dependence of $\langle A\rangle_{\mathrm{QM}}(t)$ arises *entirely* from that of the *time-dependent* operator

$$\hat{A}_H(t) := \hat{U}_t^\dagger \hat{A}\hat{U}_t \,, \tag{8.298}$$

while the *state ket* $|\phi,0\rangle$ remains frozen in the ket space. This point of view is called the **Heisenberg picture**. By construction, both pictures lead to the same prediction for $\langle A\rangle_{\mathrm{QM}}(t)$.

Because $\hat{U}_{t=0} = \hat{I}$, the newly defined operator $\hat{A}_H(t)$ satisfies the initial condition that

$$\hat{A}_H(0) = \hat{A} \,. \tag{8.299}$$

What is the differential equation governing its time evolution? To find out, let us take the time derivative of (8.298):

$$\frac{\mathrm{d}\hat{A}_H}{\mathrm{d}t} = \frac{\mathrm{d}\hat{U}_t^\dagger}{\mathrm{d}t}\hat{A}\hat{U}_t + \hat{U}_t^\dagger \hat{A}\frac{\mathrm{d}\hat{U}_t}{\mathrm{d}t} + \hat{U}_t^\dagger \frac{\partial \hat{A}}{\partial t}\hat{U}_t \,. \tag{8.300}$$

As we shall see below, the right-hand side can be rewritten to highlight the formal similarity between this equation from quantum mechanics and the equation of motion (1.185) from classical mechanics.

8.11.1 ‡Time-Independent $\hat{H}$

For time-independent Hamiltonian, (8.274) and its adjoint

$$\frac{\mathrm{d}\hat{U}_t^\dagger}{\mathrm{d}t} = \frac{i}{\hbar}\hat{U}_t^\dagger \hat{H} \tag{8.301}$$

give

$$\frac{\mathrm{d}\hat{A}_H}{\mathrm{d}t} = \frac{i}{\hbar}\hat{U}_t^\dagger \hat{H}\hat{A}\hat{U}_t - \frac{i}{\hbar}\hat{U}_t^\dagger \hat{A}\hat{H}\hat{U}_t + \hat{U}_t^\dagger \frac{\partial \hat{A}}{\partial t}\hat{U}_t \,. \tag{8.302}$$

Following (8.298), we write

$$\left(\frac{\partial \hat{A}}{\partial t}\right)_H := \hat{U}_t^\dagger \frac{\partial \hat{A}}{\partial t}\hat{U}_t \,. \tag{8.303}$$

Since $\hat{U}_t$ and $\hat{U}_t^\dagger$ are both functions of $\hat{H}$ and $\hat{H}$ is independent of time, we have

$$[\hat{H},\hat{U}_t] = 0 \quad \text{and} \quad [\hat{H},\hat{U}_t^\dagger] = 0 \,. \tag{8.304}$$

This allows us to rewrite (8.302) as

$$\frac{\mathrm{d}\hat{A}_H}{\mathrm{d}t} = \frac{i}{\hbar}\hat{H}\hat{A}_H(t) - \frac{i}{\hbar}\hat{A}_H(t)\hat{H} + \left(\frac{\partial \hat{A}}{\partial t}\right)_H = \frac{1}{i\hbar}[\hat{A}_H(t), \hat{H}] + \left(\frac{\partial \hat{A}}{\partial t}\right)_H . \tag{8.305}$$

This is **Heisenberg's equation of motion** to be contrasted against (1.185).

8.11.2 †Time-Dependent $\hat{H}$

Let us turn to a time-dependent $\hat{H}$ next. In this case, we must use (8.290) and its adjoint in place of (8.274) and (8.301). This gives (8.302) with $\hat{H}$ replaced by $\hat{H}(t)$. However, (8.304) can be used *only if* (8.291) holds. What do we do if it does not?

This more general situations can be handled by means of (8.263), which allows us to rewrite (8.302), with $\hat{H}$ replaced by $\hat{H}(t)$, as

$$\begin{aligned}\frac{\mathrm{d}\hat{A}_H}{\mathrm{d}t} &= \frac{i}{\hbar}\hat{U}_t^\dagger \hat{H}(t)\hat{U}_t\hat{U}_t^\dagger \hat{A}\hat{U}_t - \frac{i}{\hbar}\hat{U}_t^\dagger \hat{A}\hat{U}_t\hat{U}_t^\dagger \hat{H}(t)\hat{U}_t + \left(\frac{\partial \hat{A}}{\partial t}\right)_H \\ &= \frac{i}{\hbar}\hat{H}_H(t)\hat{A}_H(t) - \frac{i}{\hbar}\hat{A}_H(t)\hat{H}_H(t) + \left(\frac{\partial \hat{A}}{\partial t}\right)_H \\ &= \frac{1}{i\hbar}[\hat{A}_H(t), \hat{H}_H(t)] + \left(\frac{\partial \hat{A}}{\partial t}\right)_H ,\end{aligned} \tag{8.306}$$

where, following (8.298), we defined

$$\hat{H}_H(t) := \hat{U}_t^\dagger \hat{H}(t)\hat{U}_t . \tag{8.307}$$

If (8.291) holds, then so does (8.304) and we obtain

$$\hat{H}_H(t) = \hat{H}(t)\hat{U}_t^\dagger \hat{U}_t = \hat{H}(t) . \tag{8.308}$$

In this case, (8.306) becomes

$$\frac{\mathrm{d}\hat{A}_H}{\mathrm{d}t} = \frac{1}{i\hbar}[\hat{A}_H(t), \hat{H}(t)] + \left(\frac{\partial \hat{A}}{\partial t}\right)_H , \tag{8.309}$$

which reduces to (8.305) *if* $\hat{H}(t)$ is actually independent of time.

8.12 Eigenstates of $\hat{H}$

As shown in Sect. 8.8, the time evolution of a state ket is determined by the Schrödinger equation (8.261), in which $\hat{H}$ is the Hamiltonian operator. An eigenvalue of the Hamiltonian and the corresponding eigenket are called, respectively, the **energy eigenvalue** and the **energy eigenket**. The entire collection of eigenvalues may form either a continuum spectrum, a discrete spectrum, or a combination thereof. However, for a system of particles confined to a finite region of space, the spectrum is discrete. (See Example 8.13 and Sect. 8.14.) This is the case for systems of our primary interest and we shall pretend that the spectrum is discrete in what follows. Thus, let E_n and $|n\rangle$ denote an energy eigenvalue and the corresponding eigenket:

$$\hat{H}|n\rangle = E_n|n\rangle\ , \quad n = 0, 1, \cdots \tag{8.310}$$

with the label n distinguishing one eigenvalue (or eigenket) from others.

For our purposes, it is sufficient to consider a time-independent $\hat{H}$. Then, $|n\rangle$ is also independent of time. In this case, (8.276) applies and we have

$$|\phi,t\rangle = e^{-\frac{i}{\hbar}\hat{H}t}|\phi,0\rangle = \sum_n e^{-\frac{i}{\hbar}\hat{H}t}|n\rangle\langle n|\phi,0\rangle = \sum_n C_n e^{-\frac{i}{\hbar}E_n t}|n\rangle\ , \tag{8.311}$$

in which

$$C_n := \langle n|\phi,0\rangle \tag{8.312}$$

is a constant determined by initial conditions. Equation (8.311) expresses the time dependent $|\phi,t\rangle$ as a linear combination of energy eigenkets. It follows that the time evolution of the state ket $|\phi,t\rangle$ is completely determined by the solution to the eigenvalue problem (8.310) and initial conditions.

Exercise 8.29. Suppose that the state ket $|\phi,t\rangle$ coincided with one of the energy eigenkets, say $|m\rangle$ at $t = 0$. Being an eigenket of a time-independent $\hat{H}$, $|m\rangle$ remains constant. But, $|\phi,t\rangle$ evolves with time. Show that the expectation value $\langle A\rangle_{\text{QM}}$ of an observable $\hat{A}$ remains constant. For this reason, the energy eigenkets are called **stationary states**. Carry out the similar calculation for more general case, in which $|\phi\rangle$ is given by (8.311). Under what condition is $\langle A\rangle_{\text{QM}}$ constant? ///

Exercise 8.30. Suppose that $\hat{H}$ of the system is time independent. By means of a direct calculation, show that the expectation value of the system energy $\langle\phi,t|\hat{H}|\phi,t\rangle$ remains constant despite the fact that the state of the system $|\phi,t\rangle$ evolves with time. ///

Example 8.11. Two state system: Let

$$\hat{H} = c[|\phi_1\rangle\langle\phi_2| + |\phi_2\rangle\langle\phi_1|]\ , \tag{8.313}$$

where c is a real nonzero constant having the dimension of energy and $\{|\phi_1\rangle, |\phi_2\rangle\}$ is an orthonormal basis. Let us find

a. The eigenvalues of $\hat{H}$.
b. The corresponding eigenkets.
c. The time evolution of a stateket $|\phi,t\rangle$ if $|\phi,0\rangle = |\phi_1\rangle$.

a. Let $\hat{H}|\alpha\rangle = \lambda|\alpha\rangle$. Using the closure relation,

$$\sum_j \hat{H}|\phi_j\rangle\langle\phi_j|\alpha\rangle = \lambda|\alpha\rangle . \tag{8.314}$$

Multiplying this equation by $\langle\phi_i|$, we find

$$\sum_j \langle\phi_i|\hat{H}|\phi_j\rangle\langle\phi_j|\alpha\rangle = \lambda\langle\phi_i|\alpha\rangle . \tag{8.315}$$

For $\hat{H}$ given by (8.313), we have

$$\langle\phi_1|\hat{H}|\phi_1\rangle = \langle\phi_2|\hat{H}|\phi_2\rangle = 0 \quad \text{and} \quad \langle\phi_1|\hat{H}|\phi_2\rangle = \langle\phi_2|\hat{H}|\phi_1\rangle = c . \tag{8.316}$$

Thus, (8.315) may be written more explicitly as

$$\begin{pmatrix} 0 & c \\ c & 0 \end{pmatrix}\begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix} = \lambda\begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix} , \tag{8.317}$$

or,

$$\begin{pmatrix} -\lambda & c \\ c & -\lambda \end{pmatrix}\begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} , \tag{8.318}$$

where

$$\alpha_i := \langle\phi_i|\alpha\rangle . \tag{8.319}$$

Equation (8.318) has a nontrivial solution if and only if

$$\begin{vmatrix} -\lambda & c \\ c & -\lambda \end{vmatrix} = 0 , \tag{8.320}$$

that is, $\lambda^2 - c^2 = 0$. So, the eigenvalues are $\lambda = \pm c$.

b. Let $\lambda = c$. Then, (8.318) becomes

$$\begin{pmatrix} -c & c \\ c & -c \end{pmatrix}\begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} , \tag{8.321}$$

from which we find $\alpha_1 = \alpha_2$. So,

$$|c\rangle = \sum_i |\phi_i\rangle\langle\phi_i|c\rangle = \alpha_1[|\phi_1\rangle + |\phi_2\rangle] . \tag{8.322}$$

Upon normalization, we find

$$|c\rangle = \frac{1}{\sqrt{2}}[|\phi_1\rangle + |\phi_2\rangle] . \tag{8.323}$$

Similarly, the eigenket corresponding to the eigenvalue $-c$ is found to be

$$|-c\rangle = \frac{1}{\sqrt{2}}[|\phi_1\rangle - |\phi_2\rangle] . \tag{8.324}$$

c. According to (8.311), the general solution of the Schrödinger equation is the linear combination of $|c\rangle$ and $|-c\rangle$:

$$|\phi,t\rangle = C_1 e^{-\frac{i}{\hbar}ct}|c\rangle + C_2 e^{\frac{i}{\hbar}ct}|-c\rangle . \tag{8.325}$$

From the initial condition, we have

$$|\phi,0\rangle = C_1|c\rangle + C_2|-c\rangle = |\phi_1\rangle . \tag{8.326}$$

Multiplying this equation by $\langle\phi_1|$ from the left, we find

$$\frac{1}{\sqrt{2}}(C_1 + C_2) = 1 . \tag{8.327}$$

Multiplying by $\langle\phi_2|$ from the left, we have

$$\frac{1}{\sqrt{2}}(C_1 - C_2) = 0 . \tag{8.328}$$

Thus, $C_1 = C_2 = 1/\sqrt{2}$ and

$$|\phi,t\rangle = \frac{1}{\sqrt{2}}\left[e^{-\frac{i}{\hbar}ct}|c\rangle + e^{\frac{i}{\hbar}ct}|-c\rangle\right] . \tag{8.329}$$

Exercise 8.31. Let

$$\hat{H} = a\,[|\phi_1\rangle\langle\phi_1| + i|\phi_1\rangle\langle\phi_2| + i|\phi_2\rangle\langle\phi_1| + |\phi_2\rangle\langle\phi_2|] , \tag{8.330}$$

where a is a real nonzero constant having a dimension of energy. Can this be the Hamiltonian of some two-state system? Why or why not? ///

8.13 ‡Schrödinger Wave Equation

Given a physical system of interest, how do we find its Hamiltonian? As an example, let us consider a particle moving in a one-dimensional space.

Classical mechanically, the Hamiltonian of such a system is

$$H = \frac{p^2}{2m} + \psi(x) , \tag{8.331}$$

where m is the mass of the particle and ψ is an external field. In quantum mechanics, we simply adopt this Hamiltonian and replace p and x by the corresponding Hermitian operators:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \psi(\hat{x}) \,. \tag{8.332}$$

Accordingly, the Schrödinger equation (8.261) becomes

$$i\hbar \frac{\mathrm{d}|\phi,t\rangle}{\mathrm{d}t} = \left[\frac{\hat{p}^2}{2m} + \psi(\hat{x})\right]|\phi,t\rangle \,. \tag{8.333}$$

Let us multiply this equation by $\langle x|$ from the left and consider what happens to each terms. The end result is a differential equation for the wave function $\phi(x,t) := \langle x|\phi,t\rangle$.

Because $\langle x|$ is a *basis bra* in the $\boldsymbol{x}$-representation, it does not depend on time and hence

$$\left\langle x \left| i\hbar \frac{\mathrm{d}}{\mathrm{d}t} \right| \phi,t \right\rangle = i\hbar \frac{\partial}{\partial t}\langle x|\phi,t\rangle = i\hbar \frac{\partial \phi(x,t)}{\partial t} \,. \tag{8.334}$$

Note that we replaced the total time derivative by the partial derivative since the wave function is a function of both x and t. Using (8.130), we find

$$\psi(\hat{x})|x\rangle = \psi(x)|x\rangle \,. \tag{8.335}$$

Since $\hat{H}$ is Hermitian, so is $\psi(\hat{x})$. Thus, the adjoint of this equation reads

$$\langle x|\psi(\hat{x}) = \langle x|\psi(x) \,, \tag{8.336}$$

and we arrive at

$$\langle x|\psi(\hat{x})|\phi,t\rangle = \langle x|\psi(x)|\phi,t\rangle = \psi(x)\langle x|\phi,t\rangle = \psi(x)\phi(x,t) \,. \tag{8.337}$$

The remaining term takes a little more effort. Using the closure relation (8.201) written for the one-dimensional case, we write

$$\langle x|\hat{p}^2|\phi,t\rangle = \int \langle x|\hat{p}|x'\rangle\langle x'|\hat{p}|\phi,t\rangle \mathrm{d}x' \,. \tag{8.338}$$

Using (8.239) and (8.251),

$$\langle x|\hat{p}^2|\phi,t\rangle = (-i\hbar)^2 \int \frac{\partial}{\partial x}\delta(x-x')\frac{\partial}{\partial x'}\phi(x',t)\mathrm{d}x' \,. \tag{8.339}$$

Since the integration is with respect to x', $\partial/\partial x$ can be pulled out of the integral sign, thus leading to

$$\langle x|\hat{p}^2|\phi,t\rangle = -\hbar^2 \frac{\partial}{\partial x}\int \delta(x-x')\frac{\partial}{\partial x'}\phi(x',t)\mathrm{d}x' = -\hbar^2 \frac{\partial^2}{\partial x^2}\phi(x,t) \,. \tag{8.340}$$

Combining everything, we arrive at

$$i\hbar\frac{\partial}{\partial t}\phi(x,t) = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \psi(x)\right]\phi(x,t)\ , \tag{8.341}$$

which is the famous **time-dependent Schrödinger wave equation** applied to the one-dimensional system.

As we have seen in Sect. 8.12, the problem of finding $|\phi,t\rangle$ reduces to that of solving the eigenvalue problem (8.310). Its $\boldsymbol{x}$-representation for the present problem is

$$\left[-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \psi(x)\right]u_n(x) = E_n u_n(x)\ , \tag{8.342}$$

where $u_n(x) := \langle x|n\rangle$ is the **energy eigenfunction** corresponding to the energy eigenvalue E_n. Equation (8.342) is the **time-independent Schrödinger wave equation**. The general solution of (8.341) is obtained by simply expressing (8.311) in the $\boldsymbol{x}$-representation:

$$\phi(x,t) = \sum_n C_n e^{-\frac{i}{\hbar}E_n t}u_n(x)\ . \tag{8.343}$$

As in Sect. 8.12, the solution to the eigenvalue problem (8.342) and initial conditions completely determine the time evolution of the wave function $\phi(x,t)$. One can also obtain (8.342) and (8.343) directly from (8.341) by means of separation of variables, in which one assumes that the solution is of the form of $\phi(x,t) = \theta(t)u(x)$.

In accordance with the postulates of quantum mechanics,

$$|\langle x|\phi,t\rangle|^2\mathrm{d}x = \phi^*(x,t)\phi(x,t)\mathrm{d}x \tag{8.344}$$

is the probability of finding the particle within the interval dx taken around the point x. Because of this probabilistic interpretation, $\phi(x,t)$ cannot diverge. We also expect $\phi(x,t)$ to be a continuous function. If the particle is confined to a finite region of space, these conditions demand that the energy eigenvalues form a discrete spectrum. For a general discussion on this point, see Chap. 3 of Ref. [6]. Specific examples are given in Example 8.13 and Sect. 8.14.

Example 8.12. Free particle: For a free particle moving in a one-dimensional space,

$$\hat{H} = \frac{\hat{p}^2}{2m}\ , \tag{8.345}$$

whose energy eigenfunction is the one-dimensional version of (8.244):

$$\langle x|p\rangle = Ce^{\frac{i}{\hbar}px}\ . \tag{8.346}$$

To see this, we note that

$$\frac{\mathrm{d}}{\mathrm{d}x}\langle x|p\rangle = \frac{i}{\hbar}pCe^{\frac{i}{\hbar}px} = \frac{i}{\hbar}p\langle x|p\rangle \tag{8.347}$$

and

$$\frac{\mathrm{d}^2}{\mathrm{d}x^2}\langle x|p\rangle = \left(\frac{i}{\hbar}p\right)^2\langle x|p\rangle = -\left(\frac{p}{\hbar}\right)^2\langle x|p\rangle\ . \tag{8.348}$$

Thus,

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\langle x|p\rangle = \frac{p^2}{2m}\langle x|p\rangle\ . \tag{8.349}$$

This is just (8.342) written for the free particle, for which $\psi(x)\equiv 0$. That is, $\langle x|p\rangle$ is an eigenfunction of the Hamiltonian (8.345) and belongs to the eigenvalue $p^2/2m$.

Insofar as we have called (though rather arbitrarily) the eigenvalue of $\hat{p}$ momentum in Sect. 8.7, it is quite appropriate that we have identified an eigenvalue E of $\hat{H}$ as the energy in Sect. 8.8. Finally, we note that (8.349) holds for any real number p. In the absence of an external field that confines the particle to a finite region of space, the energy of the system forms a continuous spectrum.

It is straightforward to generalize (8.341) and (8.342) for a system of N particles in a three-dimensional space. The results are

$$i\hbar\frac{\partial}{\partial t}\phi(\boldsymbol{r}^N,t) = \left[\sum_{i=1}^{N}-\frac{\hbar^2}{2m_i}\nabla_i{}^2+\psi(\boldsymbol{r}^N)\right]\phi(\boldsymbol{r}^N,t)\ , \tag{8.350}$$

where ∇_i acts only on the coordinates of the ith particle, and

$$\left[\sum_{i=1}^{N}-\frac{\hbar^2}{2m_i}\nabla_i{}^2+\psi(\boldsymbol{r}^N)\right]\phi(\boldsymbol{r}^N,t) = E\phi(\boldsymbol{r}^N,t)\ , \tag{8.351}$$

respectively.

Example 8.13. Particle in a box: Consider a particle of mass m confined to a rectangular box of dimension $L_x\times L_y\times L_z$. The classical mechanical Hamiltonian of the particle is given by (3.75), in which $\psi_w(\boldsymbol{r})$ is the wall potential specified by (3.76). The corresponding time-independent Schrödinger wave equation reads

$$-\frac{\hbar^2}{2m}\left[\frac{\partial^2u(\boldsymbol{r})}{\partial x^2}+\frac{\partial^2u(\boldsymbol{r})}{\partial y^2}+\frac{\partial^2u(\boldsymbol{r})}{\partial z^2}\right]+\psi_w(\boldsymbol{r})u(\boldsymbol{r}) = Eu(\boldsymbol{r})\ . \tag{8.352}$$

Outside the box, ψ_w is ∞. Provided that E, u, and its second partial derivatives are all finite, we have $u = 0$ outside the box. So, let us focus on the region inside the box, in which $\psi_w(\boldsymbol{r}) = 0$, and hence

$$-\frac{\hbar^2}{2m}\left[\frac{\partial^2 u(\boldsymbol{r})}{\partial x^2}+\frac{\partial^2 u(\boldsymbol{r})}{\partial y^2}+\frac{\partial^2 u(\boldsymbol{r})}{\partial z^2}\right] = Eu(\boldsymbol{r})\,. \tag{8.353}$$

Suppose that $u(\boldsymbol{r}) = X(x)Y(y)Z(z)$. Substituting this expression into (8.353) and dividing the resulting equation by u, we find

$$\frac{1}{X}\frac{\mathrm{d}^2X}{\mathrm{d}x^2}+\frac{1}{Y}\frac{\mathrm{d}^2Y}{\mathrm{d}y^2}+\frac{1}{Z}\frac{\mathrm{d}^2Z}{\mathrm{d}z^2} = -\frac{2mE}{\hbar^2}\,. \tag{8.354}$$

By rewriting this as

$$\frac{1}{X}\frac{\mathrm{d}^2X}{\mathrm{d}x^2} = -\frac{2mE}{\hbar^2}-\frac{1}{Y}\frac{\mathrm{d}^2Y}{\mathrm{d}y^2}-\frac{1}{Z}\frac{\mathrm{d}^2Z}{\mathrm{d}z^2} \tag{8.355}$$

we see that the left-hand side is a function only of x, while the right-hand side is a function only of y and z. Because the equality holds for any x, y, and z, they must equal a constant, which we call $-{k_x}^2$.[47] This gives

$$\frac{\mathrm{d}^2X}{\mathrm{d}x^2}+{k_x}^2X = 0 \quad \text{and} \quad \frac{1}{Y}\frac{\mathrm{d}^2Y}{\mathrm{d}y^2} = -\frac{2mE}{\hbar^2}-\frac{1}{Z}\frac{\mathrm{d}^2Z}{\mathrm{d}z^2}+{k_x}^2\,. \tag{8.356}$$

Again, we see that the left-hand side of the second equation must be a constant, which we denote by $-{k_y}^2$ and obtain

$$\frac{\mathrm{d}^2Y}{\mathrm{d}y^2}+{k_y}^2Y = 0 \quad \text{and} \quad \frac{\mathrm{d}^2Z}{\mathrm{d}z^2}+{k_z}^2Z = 0\,, \tag{8.357}$$

where we defined k_z by

$${k_x}^2+{k_y}^2+{k_z}^2 = \frac{2mE}{\hbar^2}\,. \tag{8.358}$$

So far, we have not placed any restriction on k_x, k_y, or k_z. They may even be a complex number. The ordinary differential equation for X in (8.356) has the following solution:

$$X(x) = A_x\cos k_x x + B_x\sin k_x x\,, \tag{8.359}$$

where A_x and B_x are constants to be determined by the boundary conditions. Because $u(\boldsymbol{r})$ is zero outside the box, $u(\boldsymbol{r}) = 0$ if $x < 0$ or $x > L_x$. But, we also expect that $u(\boldsymbol{r})$ is continuous at the walls of the box. This means that

$X(0) = X(L_x) = 0$. The first equality gives $A_x = 0$, while the second one gives $B_x \sin k_x L_x = 0$. If $B_x = 0$, then $u(\boldsymbol{r}) \equiv 0$, which is not a solution we seek. So, $\sin k_x L_x = 0$, indicating that

$$k_x = \frac{n_x \pi}{L_x} , \quad n_x = 1, 2, 3, \ldots \tag{8.360}$$

We exclude $n_x = 0$, for which $u(\boldsymbol{r}) \equiv 0$. The negative integers ($n_x = -1, -2, -3, \ldots$) does not generate any new solution because $B_x \sin(-k_x x) = -B_x \sin(k_x x)$. A similar procedure leads to

$$Y(y) = B_y \sin k_y y \,, k_y = \frac{n_y \pi}{L_y} , \quad n_y = 1, 2, 3, \ldots \tag{8.361}$$

and

$$Z(z) = B_z \sin k_z z \,, k_z = \frac{n_z \pi}{L_z} , \quad n_z = 1, 2, 3, \ldots \tag{8.362}$$

From (8.358), we see that the energy eigenvalue E is determined by

$$\frac{8mE}{h^2} = \left(\frac{n_x}{L_x}\right)^2 + \left(\frac{n_y}{L_y}\right)^2 + \left(\frac{n_z}{L_z}\right)^2 , \tag{8.363}$$

in which n_x, n_y, and n_z are positive integers and we used $h = 2\pi\hbar$. In contrast to the case of a free particle, energy spectrum is discrete. The corresponding energy eigenfunction is now labeled by three indices n_x, n_y, and n_z:

$$u_{n_x,n_y,n_z}(\boldsymbol{r}) = B \sin\left(\frac{\pi n_x}{L_x} x\right) \sin\left(\frac{\pi n_y}{L_y} y\right) \sin\left(\frac{\pi n_z}{L_z} z\right) . \tag{8.364}$$

The remaining constant B may be determined by the normalization condition. Recalling that $\sin^2\theta = (1 - \cos 2\theta)/2$, we find

$$\int_0^{L_x} \sin^2\left(\frac{\pi n_x}{L_x} x\right) \mathrm{d}x = \frac{L_x}{\pi n_x} \int_0^{\pi n_x} \sin^2\theta \,\mathrm{d}\theta = \frac{L_x}{2} . \tag{8.365}$$

Similarly for the other factors in (8.364). Thus,

$$u_{n_x,n_y,n_z}(\boldsymbol{r}) = \sqrt{\frac{8}{V}} \sin\left(\frac{\pi n_x}{L_x} x\right) \sin\left(\frac{\pi n_y}{L_y} y\right) \sin\left(\frac{\pi n_z}{L_z} z\right) , \tag{8.366}$$

where $V = L_x L_y L_z$ and we chose B to be a real positive number.

8.14 ‡Harmonic Oscillator

For a one-dimensional harmonic oscillator, the Hamiltonian is given by

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}k\hat{x}^2 . \tag{8.367}$$

The primary goal of this section is to find the expression for the energy eigenvalues for this Hamiltonian. We have already made use of the result in Example 4.2.

With $\hat{H}$ given by (8.367), the time-independent Schrödinger wave equation (8.342) reads

$$\left[-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{1}{2}kx^2\right]u_n(x) = E_n u_n(x) , \tag{8.368}$$

which can be solved directly to yield both E_n and $u_n(x)$. See Ref. [6] for details. As an alternative, we shall follow an elegant operator method.

8.14.1 ‡*Operator Method*

Let $\omega := \sqrt{k/m}$ and rewrite (8.367) as

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2}{2}\hat{x}^2 = \frac{m\omega^2}{2}\left(\hat{x}^2 + \frac{\hat{p}^2}{m^2\omega^2}\right) . \tag{8.369}$$

Because $\hat{x}$ and $\hat{p}$ do not commute, we *cannot* just factorize this as

$$\hbar\omega\sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} + \frac{i\hat{p}}{m\omega}\right)\sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} - \frac{i\hat{p}}{m\omega}\right) = \hbar\omega\hat{a}\hat{a}^\dagger , \tag{8.370}$$

where we defined

$$\hat{a} := \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} + \frac{i\hat{p}}{m\omega}\right) \tag{8.371}$$

and hence

$$\hat{a}^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} - \frac{i\hat{p}}{m\omega}\right) . \tag{8.372}$$

By means of direct computations, however, we obtain

$$\hat{a}\hat{a}^\dagger = \frac{m\omega}{2\hbar}\left(\hat{x}^2 - \frac{i}{m\omega}\hat{x}\hat{p} + \frac{i}{m\omega}\hat{p}\hat{x} + \frac{\hat{p}^2}{m^2\omega^2}\right) \tag{8.373}$$

and

$$\hat{a}^\dagger\hat{a} = \frac{m\omega}{2\hbar}\left(\hat{x}^2 + \frac{i}{m\omega}\hat{x}\hat{p} - \frac{i}{m\omega}\hat{p}\hat{x} + \frac{\hat{p}^2}{m^2\omega^2}\right) . \tag{8.374}$$

It follows that

$$[\hat{a}, \hat{a}^\dagger] = -\frac{i}{\hbar}[\hat{x}, \hat{p}] = 1 \tag{8.375}$$

where the last equality follows from (8.234). In contrast,

$$\hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a} = \frac{m\omega}{\hbar}\left(\hat{x}^2 + \frac{\hat{p}^2}{m^2\omega^2}\right) = \frac{2}{\hbar\omega}\hat{H} \,. \tag{8.376}$$

Eliminating $\hat{a}\hat{a}^\dagger$ in (8.376) by means of (8.375), we obtain

$$\hat{H} = \hbar\omega\left(\hat{N} + \frac{1}{2}\right) , \tag{8.377}$$

where

$$\hat{N} := \hat{a}^\dagger\hat{a} \tag{8.378}$$

is known as the **number operator**.

Let n denote the eigenvalue of $\hat{N}$ and write the corresponding eigenket as $|n\rangle$:

$$\hat{N}|n\rangle = n|n\rangle \,. \tag{8.379}$$

From (8.377), it is clear that

$$[\hat{H}, \hat{N}] = 0 \,. \tag{8.380}$$

By Theorem 8.5, the eigenkets of $\hat{N}$ are also energy eigenkets. But,

$$\hat{H}|n\rangle = \hbar\omega\left(\hat{N} + \frac{1}{2}\right)|n\rangle = \hbar\omega\left(n + \frac{1}{2}\right)|n\rangle \,. \tag{8.381}$$

So, $|n\rangle$ belongs to the energy eigenvalue $\hbar\omega(n + 1/2)$.

It might appear that (4.75) follows directly from (8.381). But, we have yet to show that n can only be a nonnegative integer. Since $\hat{N}$ is Hermitian, we know at least that n must be a real number. In addition, n must be nonnegative. This is because the norm of a ket cannot be negative:

$$0 \leq \|(\hat{a}|n\rangle)\|^2 = \langle n|\hat{a}^\dagger\hat{a}|n\rangle = n\langle n|n\rangle \,. \tag{8.382}$$

But, $|n\rangle$ is not a zero ket due to the convention mentioned in Sect. 8.3.1. So, $\langle n|n\rangle > 0$ and we conclude that $n \geq 0$.

In order to further narrow down the possible values n can take, we evaluate

$$\hat{N}\hat{a}|n\rangle = (\hat{a}^\dagger\hat{a})\hat{a}|n\rangle = (\hat{a}\hat{a}^\dagger - 1)\hat{a}|n\rangle = \hat{a}(\hat{a}^\dagger\hat{a} - 1)|n\rangle = (n-1)\hat{a}|n\rangle \,, \tag{8.383}$$

where we used (8.375) to transform the second expression to the third. Equation (8.383) indicates that $\hat{a}|n\rangle$ is an eigenket of $\hat{N}$ corresponding to the eigenvalue $n-1$. That is,

$$\hat{a}|n\rangle = c|n-1\rangle \,. \tag{8.384}$$

The constant c may be determined by demanding the normalization of the energy eigenkets. Noting that

$$|c|^2\langle n-1|n-1\rangle = \langle n|\hat{a}^\dagger\hat{a}|n\rangle = n\langle n|n\rangle = n\,, \tag{8.385}$$

we have $|c|^2 = n$. By convention, we choose a real positive root for c, that is

$$c = \sqrt{n}\,. \tag{8.386}$$

and write (8.384) as

$$\hat{a}|n\rangle = \sqrt{n}|n-1\rangle\,. \tag{8.387}$$

The operator $\hat{a}$, when acting on $|n\rangle$, reduces the value of n by one. Since this corresponds to the decrease in the energy eigenvalue by one quantum unit of energy $\hbar\omega$, $\hat{a}$ is known as the **annihilation operator**.

Repeated applications of $\hat{a}$ on $|n\rangle$ give the following sequence of kets:

$$\begin{aligned}\hat{a}|n\rangle &= \sqrt{n}|n-1\rangle\,,\\ \hat{a}^2|n\rangle &= \sqrt{n(n-1)}|n-2\rangle\,,\\ \hat{a}^3|n\rangle &= \sqrt{n(n-1)(n-2)}|n-3\rangle\,,\cdots\end{aligned} \tag{8.388}$$

As we have seen above, however, $n-m \geq 0$ for any eigenket $|n-m\rangle$ of $\hat{N}$. This means that the sequence (8.388) must terminate before $n-m$ becomes negative. This happens if n is a nonnegative integer because

$$\hat{a}^n|n\rangle = \sqrt{n(n-1)(n-2)\cdots 1}|0\rangle \tag{8.389}$$

and an additional application of $\hat{a}$ produces the zero ket $|\theta\rangle$, which will remain unchanged upon further applications of $\hat{a}$. (See Exercises 8.1b and 8.8a.) Thus, the energy eigenvalues form a discrete set:

$$E_n = \hbar\omega\left(n+\frac{1}{2}\right)\,, \quad n = 0,1,2\ldots\,, \tag{8.390}$$

which is (4.75) we encountered before.

It is important to distinguish $|\theta\rangle$ and $|0\rangle$. The former is the zero ket, the norm of which is zero. The latter, in contrast, is a simultaneous eigenket of $\hat{N}$ and $\hat{H}$ corresponding to the lowest possible energy $\hbar\omega/2$ the harmonic oscillator can take. In other words, $|0\rangle$ is the state ket of the so-called **ground state**. Classical mechanically, the lowest energy occurs when $(x,p)=(0,0)$. Quantum mechanically, such a state is in violation of the Heisenberg uncertainty principle as we saw in Sect. 8.5.

Given the ground state ket $|0\rangle$, $\hat{a}^\dagger$ allows us to systematically generate the other eigenstates of $\hat{N}$. To see this, we evaluate

$$\hat{N}\hat{a}^\dagger|n\rangle = \hat{a}^\dagger(\hat{a}\hat{a}^\dagger)|n\rangle = \hat{a}^\dagger(\hat{a}^\dagger\hat{a}+1)|n\rangle = \hat{a}^\dagger(n+1)|n\rangle = (n+1)\hat{a}^\dagger|n\rangle\,, \tag{8.391}$$

where we used (8.375). According to (8.391), $\hat{a}^\dagger|n\rangle$ is an eigenket of $\hat{N}$ corresponding to the eigenvalue $n+1$:

$$\hat{a}^\dagger|n\rangle = c|n+1\rangle \,, \tag{8.392}$$

where c is a constant. The effect of $\hat{a}^\dagger$ on $|n\rangle$ is to increase the value of n by one and hence the energy eigenvalue by one quantum unit of energy $\hbar\omega$. So, the operator $\hat{a}^\dagger$ is referred to as the **creation operator**.

Because the effect of $\hat{a}$ on $|n\rangle$ is known and $\hat{a}^\dagger$ is the adjoint of $\hat{a}$, the formalism we have developed so far should be sufficient to determine the value of c. In fact, multiplying (8.392) by $\hat{a}$ from the left, we find

$$\begin{aligned}
\hat{a}\hat{a}^\dagger|n\rangle &= c\hat{a}|n+1\rangle \\
\left(\hat{a}^\dagger\hat{a}+1\right)|n\rangle &= c\sqrt{n+1}|n\rangle \\
(n+1)|n\rangle &= c\sqrt{n+1}|n\rangle \,.
\end{aligned} \tag{8.393}$$

Multiplying both sides by $\langle n|$ from the left, we obtain $c=\sqrt{n+1}$. Thus,

$$\hat{a}^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle \,. \tag{8.394}$$

Repeated applications of $\hat{a}^\dagger$ on $|0\rangle$ give

$$\begin{aligned}
\hat{a}^\dagger|0\rangle &= |1\rangle \\
(\hat{a}^\dagger)^2|0\rangle &= \hat{a}^\dagger|1\rangle = \sqrt{2}|2\rangle \\
(\hat{a}^\dagger)^3|0\rangle &= \hat{a}^\dagger\sqrt{2}|2\rangle = \sqrt{3\cdot 2}|3\rangle \\
(\hat{a}^\dagger)^4|0\rangle &= \hat{a}^\dagger\sqrt{3\cdot 2}|3\rangle = \sqrt{4\cdot 3\cdot 2}|4\rangle \,.
\end{aligned} \tag{8.395}$$

Proceeding in this manner, we find

$$|n\rangle = \frac{(\hat{a}^\dagger)^n}{\sqrt{n!}}|0\rangle \,. \tag{8.396}$$

8.14.2 ‡*Energy Eigenfunctions*

It is now straightforward to find the wave function $u_n(x) := \langle x|n\rangle$. We start from

$$\hat{a}|0\rangle = |\theta\rangle \,, \tag{8.397}$$

and hence

$$\langle x|\hat{a}|0\rangle = \langle x|\theta\rangle = 0 \,. \tag{8.398}$$

Using (8.371) and recalling (8.239), we have

$$\left(x+\frac{\hbar}{m\omega}\frac{\mathrm{d}}{\mathrm{d}x}\right)u_0 = 0 \,, \tag{8.399}$$

which can be solved to give

$$u_0(x) = ce^{-\frac{1}{2}\alpha x^2} , \tag{8.400}$$

where $\alpha = m\omega/\hbar$. Upon normalization under the convention that c be a real positive number, we have

$$u_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} . \tag{8.401}$$

Substituting this result into (8.368), we find that $E_0 = \hbar\omega/2$, which is in agreement with (8.390).

From (8.396),

$$u_n(x) = \frac{1}{\sqrt{n!}} \left\langle x \middle| (\hat{a}^\dagger)^n \middle| 0 \right\rangle . \tag{8.402}$$

Once again, we use (8.372) and (8.239) and find

$$\begin{aligned} u_n(x) &= \frac{1}{\sqrt{n!}} \left(\frac{\alpha}{2}\right)^{n/2} \left(x - \frac{1}{\alpha}\frac{\mathrm{d}}{\mathrm{d}x}\right)^n u_0(x) \\ &= \frac{1}{\sqrt{2^n n!}} \left(\sqrt{\alpha}x - \frac{1}{\sqrt{\alpha}}\frac{\mathrm{d}}{\mathrm{d}x}\right)^n \left(\frac{\alpha}{\pi}\right)^{1/4} \exp\left[-\frac{1}{2}\left(\sqrt{\alpha}x\right)^2\right] \\ &=: N_n \left(\xi - \frac{\mathrm{d}}{\mathrm{d}\xi}\right)^n e^{-\xi^2/2} , \end{aligned} \tag{8.403}$$

where $\xi := \sqrt{\alpha}x$ and

$$N_n := \frac{1}{\sqrt{2^n n!}} \left(\frac{\alpha}{\pi}\right)^{1/4} . \tag{8.404}$$

More explicitly, the energy eigenfunctions are given by

$$\begin{aligned} u_0(\xi) &= N_0 e^{-\xi^2/2} , \\ u_1(\xi) &= N_1(2\xi)e^{-\xi^2/2} , \\ u_2(\xi) &= N_2(4\xi^2 - 2)e^{-\xi^2/2} , \\ u_3(\xi) &= N_3(8\xi^3 - 12\xi)e^{-\xi^2/2} , \\ u_4(\xi) &= N_4(16\xi^4 - 48\xi^2 + 12)e^{-\xi^2/2} , \\ u_5(\xi) &= N_5(32\xi^5 - 160\xi^3 + 120\xi)e^{-\xi^2/2} , \cdots . \end{aligned} \tag{8.405}$$

The polynomials in these equations, that is,

$$\begin{aligned} H_0(\xi) &= 1 , \\ H_1(\xi) &= 2\xi , \\ H_2(\xi) &= 4\xi^2 - 2 , \\ H_3(\xi) &= 8\xi^3 - 12\xi , \\ H_4(\xi) &= 16\xi^4 - 48\xi^2 + 12 , \\ H_5(\xi) &= 32\xi^5 - 160\xi^3 + 120\xi , \cdots . \end{aligned} \tag{8.406}$$

are known as the **Hermit polynomials**. For various properties of this mathematical object, see Ref. [6].

Classical mechanically, the energy E of the one-dimensional harmonic oscillator is given by

$$E = \frac{p^2}{2m} + \frac{1}{2}kx^2 = \frac{p^2}{2m} + \frac{1}{2}\hbar\omega\xi^2 \, . \tag{8.407}$$

Thus,

$$\frac{1}{2}\hbar\omega\xi^2 = E - \frac{p^2}{2m} \leq E \, , \tag{8.408}$$

and the motion of the particle is confined to the region defined by

$$|\xi| \leq \sqrt{\frac{2E}{\hbar\omega}} \, . \tag{8.409}$$

$$|\xi| \leq \sqrt{2n+1} \, , \quad n = 0, 1, 2, \dots \tag{8.410}$$

Equation (8.405) indicates, however, that the probability, $u_n^*(x)u_n(x)\mathrm{d}x$, of finding a particle in the classical mechanically forbidden region ($|\xi| > \sqrt{2n+1}$) is nonzero. This is illustrated in Fig. 8.2 for several values of n.

8.15 †Ehrenfest's Theorem

In Sect. 8.11, we derived Heisenberg's equation of motion, which may be regarded as the quantum mechanical counterpart of (1.185) in classical mechanics. Insofar as (1.185) contains Hamilton's and therefore Newton's equations of motion, it is natural to ask if their quantum mechanical counterparts can be derived from Heisenberg's equation of motion. This is indeed the case as we shall see in this section.

For simplicity, we restrict ourselves to a one-dimensional system described by the Hamiltonian:

$$\hat{H}(t) = \frac{\hat{p}^2}{2m} + \psi(\hat{x}, t) \, . \tag{8.411}$$

Applying (8.306) to $\hat{x}_H(t)$ and noting that $\hat{x}$ (an operator in the Schrödinger picture) is independent of time,

$$\frac{\mathrm{d}\hat{x}_H}{\mathrm{d}t} = \frac{1}{i\hbar}[\hat{x}_H(t), \hat{H}_H(t)] = \frac{1}{i\hbar}\hat{U}_t^\dagger[\hat{x}, \hat{H}(t)]\hat{U}_t \, , \tag{8.412}$$

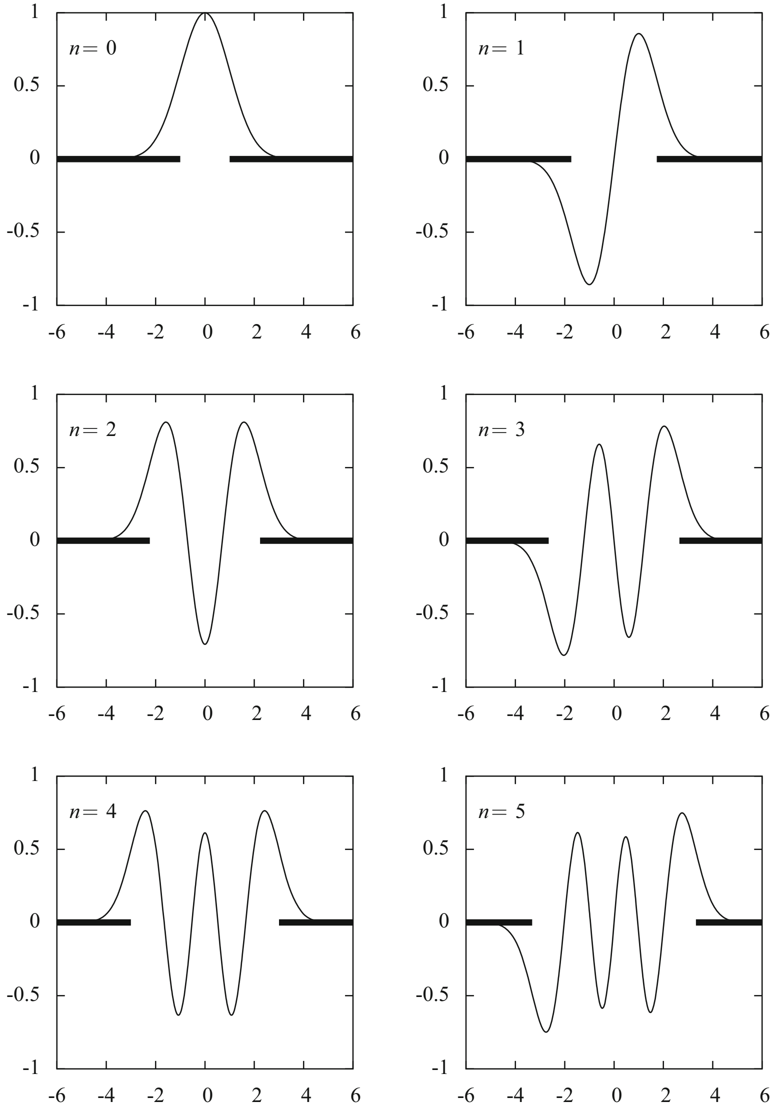

Fig. 8.2 Energy eigenfunctions $(\alpha/\pi)^{-1/4}u_n(\xi)$ (*solid line*) and classically forbidden regions (*thick horizontal lines*) for several values of n. The horizontal axis is ξ.

where we used (8.298) in the last step. But,

$$[\hat{x},\hat{H}(t)] = \left[\hat{x},\frac{\hat{p}^2}{2m}+\psi(\hat{x},t)\right] = \frac{1}{2m}[\hat{x},\hat{p}^2]\,. \tag{8.413}$$

Using (8.105) and (8.234),

$$[\hat{x},\hat{p}^2] = \hat{p}[\hat{x},\hat{p}] + [\hat{x},\hat{p}]\hat{p} = 2i\hbar\hat{p}\,. \tag{8.414}$$

Thus,

$$\frac{\mathrm{d}\hat{x}_H}{\mathrm{d}t} = \frac{1}{m}\hat{U}_t^\dagger\hat{p}\hat{U}_t = \frac{\hat{p}_H(t)}{m}\,. \tag{8.415}$$

This is to be contrasted with one of Hamilton's equations of motion:

$$\dot{x} = \frac{\partial H}{\partial p}\,. \tag{8.416}$$

For the classical mechanical Hamiltonian corresponding to (8.411), this gives

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{p}{m}\,. \tag{8.417}$$

In view of (8.415) and (8.417), the name momentum operator we have given to $\hat{p}$ is quite appropriate.

In a similar manner,

$$\frac{\mathrm{d}\hat{p}_H}{\mathrm{d}t} = \frac{1}{i\hbar}[\hat{p}_H(t),\hat{H}_H(t)] = \frac{1}{i\hbar}\hat{U}_t^\dagger[\hat{p},\hat{H}(t)]\hat{U}_t = \frac{1}{i\hbar}\hat{U}_t^\dagger[\hat{p},\psi(\hat{x},t)]\hat{U}_t\,. \tag{8.418}$$

If $\psi(x,t)$ has the Maclaurin expansion, the operator $\psi(\hat{x},t)$ is given by

$$\psi(\hat{x},t) = \psi(0,t) + \psi'(0,t)\hat{x} + \frac{1}{2}\psi''(0,t)\hat{x}^2 + \frac{1}{3!}\psi'''(0,t)\hat{x}^3 + \cdots\,, \tag{8.419}$$

where $'$ indicates the *partial* derivative with respect to x. With repeated applications of (8.105) and (8.234), we find

$$[\hat{p},1] = 0\,,\quad [\hat{p},\hat{x}] = -i\hbar\,,\quad [\hat{p},\hat{x}^2] = \hat{x}[\hat{p},\hat{x}] + [\hat{p},\hat{x}]\hat{x} = -2i\hbar\hat{x}\,, \tag{8.420}$$

and

$$[\hat{p},\hat{x}^3] = \hat{x}[\hat{p},\hat{x}^2] + [\hat{p},\hat{x}]\hat{x}^2 = -2i\hbar\hat{x}^2 - i\hbar\hat{x}^2 = -3i\hbar\hat{x}^2\,. \tag{8.421}$$

Proceeding in this manner, we obtain

$$[\hat{p},\hat{x}^n] = -i\hbar n\hat{x}^{n-1}\,,\quad n = 1,2,\ldots \tag{8.422}$$

Thus,

$$[\hat{p},\psi(\hat{x},t)] = -i\hbar\psi'(\hat{x},t)\,, \tag{8.423}$$

and hence

$$\frac{\mathrm{d}\hat{p}_H}{\mathrm{d}t} = -\hat{U}_t^\dagger\psi'(\hat{x},t)\hat{U}_t\,. \tag{8.424}$$

Noting that

$$\hat{U}_t^\dagger\hat{x}^n\hat{U}_t = [\hat{x}_H(t)]^n\,, \tag{8.425}$$

as can be seen by inserting $\hat{U}_t\hat{U}_t^\dagger = 1$ between $\hat{x}$'s, we arrive at

$$\frac{\mathrm{d}\hat{p}_H}{\mathrm{d}t} = -\psi'(\hat{x}_H(t),t) \,. \tag{8.426}$$

This result should be compared with its classical mechanical counterpart:

$$\frac{\mathrm{d}p}{\mathrm{d}t} = -\psi'(x,t) \,, \tag{8.427}$$

which follows from the remaining half of Hamilton's equations of motion:

$$\dot{p} = -\frac{\partial H}{\partial x} \,. \tag{8.428}$$

Combining (8.415) and (8.426), we find

$$m\frac{\mathrm{d}^2\hat{x}_H}{\mathrm{d}t^2} = -\psi'(\hat{x}_H(t),t) \,. \tag{8.429}$$

This is the quantum mechanical counterpart of Newton's equation of motion.

As seen from (8.295) and (8.298), the expectation value of an operator in the Heisenberg picture, such as $\hat{x}_H$ and $\hat{p}_H$, must be evaluated using the state ket at $t = 0$. With (8.415), this leads to

$$\frac{\mathrm{d}\langle x\rangle_{\mathrm{QM}}}{\mathrm{d}t} = \frac{\langle p\rangle_{\mathrm{QM}}}{m} \,. \tag{8.430}$$

For the other half of the equations of motion, it is easier to work with (8.424) than with (8.426). The result is

$$\frac{\mathrm{d}\langle p\rangle_{\mathrm{QM}}}{\mathrm{d}t} = -\langle\psi'(\hat{x},t)\rangle_{\mathrm{QM}} \,, \tag{8.431}$$

If the particle is well localized, the approximate relation:

$$\langle\psi'(\hat{x},t)\rangle_{\mathrm{QM}} \approx \psi'(\langle x\rangle_{\mathrm{QM}},t) \tag{8.432}$$

holds. In fact, following Exercise 8.23, we have

$$\begin{aligned}\langle\psi'(\hat{x},t)\rangle_{\mathrm{QM}} &= \langle\phi|\psi'(\hat{x})|\phi\rangle = \int\langle\phi|\psi'(\hat{x})|x\rangle\langle x|\phi\rangle\mathrm{d}x = \int\psi'(x)\langle\phi|x\rangle\langle x|\phi\rangle\mathrm{d}x \\ &= \int\psi'(x)|\langle x|\phi\rangle|^2\mathrm{d}x \,,\end{aligned} \tag{8.433}$$

in which $|\langle x|\phi\rangle|^2\mathrm{d}x$ is the probability that the particle is found between x and $x+\mathrm{d}x$ as seen from (8.344). If this probability is sharply peaked around the average $\langle x\rangle_{\mathrm{QM}}$, then

$$\langle \psi'(\hat{x},t)\rangle_{\mathrm{QM}} \approx \psi'(\langle x\rangle_{\mathrm{QM}}) \int |\langle x|\phi\rangle|^2\mathrm{d}x = \psi'(\langle x\rangle_{\mathrm{QM}})\,. \tag{8.434}$$

Within this approximation,

$$\frac{\mathrm{d}\langle p\rangle_{\mathrm{QM}}}{\mathrm{d}t} = -\psi'(\langle x\rangle_{\mathrm{QM}},t)\,. \tag{8.435}$$

Equations (8.430) and (8.435) are known as **Ehrenfest's theorem**.

Some functions, such as $\psi(x,t)=x^n$ $(n<1)$, do not have the Maclaurin expansion. Even then, (8.423) still holds provided that $\psi'(x,t)$ exists. One way to see this is to expand $\psi(\hat{x},t)$ into a Taylor series around $x=a\neq 0$ and note that a, being a number, commutes with $\hat{p}$. Alternatively, we start by writing

$$\begin{aligned}[\hat{p},\psi(\hat{x})] &= \hat{p}\psi(\hat{x})-\psi(\hat{x})\hat{p} = \int_{-\infty}^{\infty}[\hat{p}|x\rangle\langle x|\psi(\hat{x})-\psi(\hat{x})|x\rangle\langle x|\hat{p}]\mathrm{d}x \\ &= \int_{-\infty}^{\infty}[\hat{p}|x\rangle\psi(x)\langle x|-|x\rangle\psi(x)\langle x|\hat{p}]\mathrm{d}x\,,\end{aligned} \tag{8.436}$$

where we used the closure relation and (8.130). Using the closure relation one more time,

$$\hat{p}|x\rangle = \int_{-\infty}^{\infty}|x_1\rangle\langle x_1|\hat{p}|x\rangle\mathrm{d}x_1 = \int_{-\infty}^{\infty}|x_1\rangle(-i\hbar)\frac{\mathrm{d}}{\mathrm{d}x_1}\delta(x-x_1)\mathrm{d}x_1\,, \tag{8.437}$$

where we made use of (8.251). Let $X := x-x_1$ and use the chain rule:

$$\frac{\mathrm{d}}{\mathrm{d}x_1}\delta(x-x_1) = \frac{\mathrm{d}X}{\mathrm{d}x_1}\frac{\mathrm{d}}{\mathrm{d}X}\delta(X) = -\frac{\mathrm{d}}{\mathrm{d}X}\delta(X) = -\frac{\mathrm{d}}{\mathrm{d}x}\delta(x-x_1)\,, \tag{8.438}$$

Because x is not the integration variable, we have

$$\hat{p}|x\rangle = i\hbar\frac{\mathrm{d}}{\mathrm{d}x}\int|x_1\rangle\delta(x-x_1)\mathrm{d}x_1 = i\hbar\frac{\mathrm{d}|x\rangle}{\mathrm{d}x}\,. \tag{8.439}$$

By means of this equation and its adjoint, we may rewrite (8.436) as

$$\begin{aligned}[\hat{p},\psi(\hat{x})] &= i\hbar\int_{-\infty}^{\infty}\left[\frac{\mathrm{d}|x\rangle}{\mathrm{d}x}\psi(x)\langle x|+|x\rangle\psi(x)\frac{\mathrm{d}\langle x|}{\mathrm{d}x}\right]\mathrm{d}x \\ &= i\hbar\int_{-\infty}^{\infty}\left\{\frac{\mathrm{d}}{\mathrm{d}x}[|x\rangle\psi(x)\langle x|]-|x\rangle\psi'(x)\langle x|\right\}\mathrm{d}x\,,\end{aligned} \tag{8.440}$$

When we compute the expectation value of this expression with respect to the state ket $|\phi,t\rangle$, the first term in the integrand can be dropped provided that $\psi(x)$ becomes much larger than the system energy in the $|x|\to\infty$ limit. This is because $\langle\phi,t|x\rangle$ vanishes rapidly as $|x|\to\infty$ for such $\psi(x)$. (See Fig. 8.2 for example.) More explicitly,

$$
\begin{aligned}
\langle\phi,t|\left\{\int_{-\infty}^{\infty}\frac{\mathrm{d}}{\mathrm{d}x}[|x\rangle\psi(x)\langle x|]\mathrm{d}x\right\}|\phi,t\rangle &= \int_{-\infty}^{\infty}\frac{\mathrm{d}}{\mathrm{d}x}[\langle\phi,t|x\rangle\psi(x)\langle x|\phi,t\rangle]\mathrm{d}x \\
&= \langle\phi,t|x\rangle\psi(x)\langle x|\phi,t\rangle|_{-\infty}^{\infty}=0\,. \quad (8.441)
\end{aligned}
$$

As far as the expectation value is concerned, therefore, we may write

$$[\hat{p},\psi(\hat{x})]=-i\hbar\int_{-\infty}^{\infty}|x\rangle\psi'(x)\langle x|\mathrm{d}x=-i\hbar\psi'(\hat{x})\,, \quad (8.442)$$

where the last step follows from (8.131).

Finally, exchanging the role of $\hat{p}$ and $\hat{x}$ in (8.423) and noting that $[\hat{x},\hat{p}]=-[\hat{p},\hat{x}]=i\hbar$, we find

$$[\hat{x},f(\hat{p})]=i\hbar f'(\hat{p})\,. \quad (8.443)$$

This formula, too, can be extended for f that does not have the Maclaurin expansion.

Exercise 8.32. Using (8.252), show that (8.443) holds even for a function that does not have the Maclaurin expansion. Assume that

$$\lim_{p\to\pm\infty}\langle\phi,t|p\rangle f(p)\langle p|\phi,t\rangle=0\,. \quad (8.444)$$

///

8.16 Quantum Statistical Mechanics

In this final section, we build on the key concepts of quantum mechanics we have reviewed so far and formulate statistical mechanics using the language of quantum mechanics.

8.16.1 Density Matrix

In classical mechanics, we considered the ensemble average given by (3.48):

$$\langle A\rangle=\int A(q^f,p^f)\rho(q^f,p^f)\mathrm{d}q^f\mathrm{d}p^f\,, \quad (8.445)$$

which was identified with the result of a measurement of some dynamical variable A. We suppose that an analogous relation holds for quantum mechanical systems and write

$$\langle A\rangle=\sum_{\alpha}\omega_{\alpha}\langle\phi_{\alpha}|\hat{A}|\phi_{\alpha}\rangle\,, \quad (8.446)$$

where $\langle\phi_\alpha|\hat{A}|\phi_\alpha\rangle$ is the expectation value for the outcome of the measurement of A when the system is in the microstate α for which the state ket is $|\phi_\alpha\rangle$. Note that this averaging is a part of the postulate of quantum mechanics and that it was absent in classical mechanics. The coefficient ω_α is the quantum counterpart of $\rho(q^f, p^f)$ in classical statistical mechanics and is the probability that the system is in the microstate α. Being a probability, ω_α must satisfy the normalization condition:

$$\sum_\alpha \omega_\alpha = 1\,. \tag{8.447}$$

We emphasize that $|\phi_\alpha\rangle$ $(\alpha = 1, 2, \dots)$ do not necessarily form a basis, nor are they orthogonal. In what follows, however, we assume that they are normalized. Using (8.128), we can rewrite (8.446) as

$$\begin{aligned}\langle A\rangle &= \sum_{\alpha,i}\omega_\alpha\langle\phi_\alpha|a_i\rangle a_i\langle a_i|\phi_\alpha\rangle = \sum_{\alpha,i}\langle a_i|\phi_\alpha\rangle\omega_\alpha\langle\phi_\alpha|a_i\rangle a_i = \sum_{\alpha,i}\langle a_i|\phi_\alpha\rangle\omega_\alpha\langle\phi_\alpha|\hat{A}|a_i\rangle\\ &= \sum_i\langle a_i|\left[\sum_\alpha|\phi_\alpha\rangle\omega_\alpha\langle\phi_\alpha|\right]\hat{A}|a_i\rangle =: \sum_i\langle a_i|\hat{\rho}_t\hat{A}|a_i\rangle = \mathrm{Tr}\{\hat{\rho}_t\hat{A}\}\,,\end{aligned} \tag{8.448}$$

where we defined the **density operator** $\hat{\rho}_t$ by

$$\hat{\rho}_t := \sum_\alpha|\phi_\alpha\rangle\omega_\alpha\langle\phi_\alpha|\,. \tag{8.449}$$

In terms of the density operator, (8.447) is written as

$$\mathrm{Tr}\{\hat{\rho}_t\} = 1\,. \tag{8.450}$$

In fact,

$$\mathrm{Tr}\{\hat{\rho}_t\} = \sum_{i,\alpha}\langle a_i|\phi_\alpha\rangle\omega_\alpha\langle\phi_\alpha|a_i\rangle = \sum_{i,\alpha}\omega_\alpha\langle\phi_\alpha|a_i\rangle\langle a_i|\phi_\alpha\rangle = \sum_\alpha\omega_\alpha\langle\phi_\alpha|\phi_\alpha\rangle = \sum_\alpha\omega_\alpha\,, \tag{8.451}$$

where we used the closure relation and the fact that $|\phi_\alpha\rangle$ is normalized.

8.16.2 Statistical Equilibrium

As is the case with classical mechanics, we first define statistical equilibrium by demanding that

$$\frac{\mathrm{d}\langle A\rangle}{\mathrm{d}t} \equiv 0 \tag{8.452}$$

hold for any observable $\hat{A}$ that is independent of time. To express this in a more informative fashion, let us first rewrite the trace using some *time-independent basis*

$\{|b_1\rangle, \dots, |b_r\rangle\}$:

$$\langle A\rangle = \mathrm{Tr}\{\hat{\rho}_t\hat{A}\} = \sum_{i,j}\langle b_i|\hat{\rho}_t|b_j\rangle\langle b_j|\hat{A}|b_i\rangle\ . \tag{8.453}$$

Because $\hat{A}$ is time independent, the matrix element $\langle b_j|\hat{A}|b_i\rangle$ is independent of time and the only time dependence of $\langle A\rangle$ is in $\hat{\rho}_t$. Thus,

$$\frac{\mathrm{d}\langle A\rangle}{\mathrm{d}t} = \sum_{i,j}\left\langle b_i\left|\frac{\mathrm{d}\hat{\rho}_t}{\mathrm{d}t}\right|b_j\right\rangle\langle b_j|\hat{A}|b_i\rangle\ . \tag{8.454}$$

We see shortly that this expression vanishes for arbitrary $\hat{A}$ if and only if *all* the matrix elements of $\mathrm{d}\hat{\rho}_t/\mathrm{d}t$ vanish in the B-representation:

$$\left\langle b_i\left|\frac{\mathrm{d}\hat{\rho}_t}{\mathrm{d}t}\right|b_j\right\rangle \equiv 0 \tag{8.455}$$

which is true if and only if

$$\frac{\mathrm{d}\hat{\rho}_t}{\mathrm{d}t} \equiv 0\ . \tag{8.456}$$

This is then the necessary and sufficient condition for statistical equilibrium.

Equation (8.455) is evidently sufficient for (8.452). To see its necessity, suppose that

$$\langle b_\beta|\hat{A}|b_\alpha\rangle \neq 0\ . \tag{8.457}$$

Because $\hat{A}$ is Hermitian,

$$\langle b_\alpha|\hat{A}|b_\beta\rangle = \langle b_\beta|\hat{A}|b_\alpha\rangle^* \neq 0\ . \tag{8.458}$$

If these are the *only* nonzero matrix elements of $\hat{A}$ in the B-representation, (8.454) becomes

$$\frac{\mathrm{d}\langle A\rangle}{\mathrm{d}t} = \left\langle b_\alpha\left|\frac{\mathrm{d}\hat{\rho}_t}{\mathrm{d}t}\right|b_\beta\right\rangle\langle b_\beta|\hat{A}|b_\alpha\rangle + \left\langle b_\beta\left|\frac{\mathrm{d}\hat{\rho}_t}{\mathrm{d}t}\right|b_\alpha\right\rangle\langle b_\alpha|\hat{A}|b_\beta\rangle\ . \tag{8.459}$$

Because ω_α in (8.449) is a real number, we see that $\hat{\rho}_t$ is a Hermitian at all time. Thus,

$$\frac{\mathrm{d}\hat{\rho}_t}{\mathrm{d}t} = \lim_{\Delta t\to 0}\frac{\hat{\rho}_{t+\Delta t} - \hat{\rho}_t}{\Delta t} \tag{8.460}$$

is also a Hermitian and we can write

$$\frac{\mathrm{d}\langle A\rangle}{\mathrm{d}t} = \left\langle b_\alpha\left|\frac{\mathrm{d}\hat{\rho}_t}{\mathrm{d}t}\right|b_\beta\right\rangle\langle b_\alpha|\hat{A}|b_\beta\rangle^* + \left\langle b_\alpha\left|\frac{\mathrm{d}\hat{\rho}_t}{\mathrm{d}t}\right|b_\beta\right\rangle^*\langle b_\alpha|\hat{A}|b_\beta\rangle\ . \tag{8.461}$$

which is twice the real part of the expression

$$\left\langle b_\alpha\left|\frac{\mathrm{d}\hat{\rho}_t}{\mathrm{d}t}\right|b_\beta\right\rangle\langle b_\alpha|\hat{A}|b_\beta\rangle^*\ . \tag{8.462}$$

Equation (8.452) thus demands that the expression (8.462) be purely imaginary. But, since $\hat{A}$ is arbitrary, and hence $\langle b_\alpha|\hat{A}|b_\beta\rangle$ is a complex number in general, this will be the case only if

$$\left\langle b_\alpha \left| \frac{\mathrm{d}\hat{\rho}_t}{\mathrm{d}t} \right| b_\beta \right\rangle = 0\,. \tag{8.463}$$

8.16.3 *Liouville's Theorem*

Equation (8.456) can be transformed into a more revealing form by means of the quantum mechanical version of Liouville's theorem. The situation parallels what we saw in classical statistical mechanics.

Before proceeding to the proof of the theorem, we must point out that the ket $|\phi_\alpha\rangle$ in $\hat{\rho}_t$, in general, evolves with time. There is nothing in our definition of $\hat{\rho}_t$ to exclude the possibility that the ket evolves to become yet another ket already included in the summation over α or otherwise become something that was not in that summation initially. So, we need to be a little more precise about what is meant by the sum over α in (8.449). The density matrix is constructed at some fixed point in time, say at $t=0$, using the *state kets* $|\phi_1,0\rangle$, $|\phi_2,0\rangle$,.... These kets may evolve with time and, at a later time t, become $|\phi_1,t\rangle$, $|\phi_2,t\rangle$,..., respectively. Then, at time t, our $\hat{\rho}_t$ will be given by

$$\hat{\rho}_t = \sum_\alpha |\phi_\alpha,t\rangle\omega_\alpha\langle\phi_\alpha,t|\,. \tag{8.464}$$

That is, ω_α does not change with time because this refers to the fraction of copies in microstate $|\phi_\alpha\rangle$ at time $t=0$ in the statistical ensemble that was created at that time.

We now proceed to evaluate $\mathrm{d}\hat{\rho}_t/\mathrm{d}t$. Taking the time derivative of (8.464), we have

$$\frac{\mathrm{d}\hat{\rho}_t}{\mathrm{d}t} = \sum_\alpha \left[\frac{\mathrm{d}|\phi_\alpha,t\rangle}{\mathrm{d}t}\omega_\alpha\langle\phi_\alpha,t| + |\phi_\alpha,t\rangle\omega_\alpha\frac{\mathrm{d}\langle\phi_\alpha,t|}{\mathrm{d}t}\right]\,. \tag{8.465}$$

Recall the Schrödinger equation (8.261) and take its adjoint:

$$\frac{\mathrm{d}|\phi_\alpha,t\rangle}{\mathrm{d}t} = \frac{\hat{H}(t)}{i\hbar}|\phi_\alpha,t\rangle \quad \text{and} \quad \frac{\mathrm{d}\langle\phi_\alpha,t|}{\mathrm{d}t} = -\langle\phi_\alpha,t|\frac{\hat{H}(t)}{i\hbar}\,, \tag{8.466}$$

where we allowed for the time dependence of $\hat{H}$ for now. Using these equations in (8.465), we arrive at the quantum mechanical version of **Liouville's theorem**:

$$\frac{\mathrm{d}\hat{\rho}_t}{\mathrm{d}t} + \frac{1}{i\hbar}[\hat{\rho}_t,\hat{H}(t)] = 0\,. \tag{8.467}$$

It should be emphasized that (8.467) is a condition any density operator must satisfy *regardless* of whether the system is in statistical equilibrium or not. This is quite analogous to what was said about (3.33) in classical statistical mechanics.

So, the necessary and sufficient condition of statistical equilibrium is that *both* (8.456) and (8.467) hold. But, this is equivalent to demanding both (8.456) and

$$[\hat{\rho}_t, \hat{H}(t)] = 0 \,. \tag{8.468}$$

This equation is the quantum mechanical version of (3.37) and, in view of Theorem 8.4, implies that $\hat{\rho}_t$ is diagonal in the H-representation. For this to be the case, it is sufficient that $\hat{\rho}_t$ be a function of $\hat{H}$ only:

$$\hat{\rho}_t = f(\hat{H}(t)) \,. \tag{8.469}$$

Equation (8.456) then demands that $\hat{H}$ be independent of time.

Exercise 8.33. If you have read Sects. 8.10 and 8.11, this exercise provides an alternative derivation of (8.467) and (8.468).

a. Show that

$$\hat{\rho}_t = \hat{U}_t \hat{\rho}_0 \hat{U}_t^\dagger \,. \tag{8.470}$$

b. Using (8.290) and (8.470), derive (8.467).

c. Recall (8.298) and show that

$$\mathrm{Tr}\{\hat{\rho}_t \hat{A}\} = \mathrm{Tr}\{\hat{\rho}_0 \hat{A}_H(t)\} \,. \tag{8.471}$$

d. Using (8.306), show that

$$\frac{\mathrm{d}\langle A\rangle}{\mathrm{d}t} = \mathrm{Tr}\{[\hat{H}(t), \hat{\rho}_t]\hat{A}\} \,, \tag{8.472}$$

where $\hat{A}$ is a Hermitian operator that is independent of time. Demanding that (8.452) holds for any $\hat{A}$, we arrive at (8.468). ///

8.16.4 Canonical Ensemble

Restricting ourselves for systems with time-independent $\hat{H}$, we define quantum mechanical **canonical ensemble** by

$$\hat{\rho} = \frac{1}{Z} e^{-\beta \hat{H}} \,, \tag{8.473}$$

where we dropped the subscript t. Since any function of $\hat{H}$ commutes with $\hat{H}$, this expression clearly satisfies (8.468) and is an example of (8.469).

Using the orthonormal basis of energy eigenkets, that is, the H-representation, and recalling (8.131), we can express $\hat{\rho}$ as

$$\hat{\rho} = \frac{1}{Z} \sum_n |n\rangle e^{-\beta E_n} \langle n| \,. \tag{8.474}$$

Comparing this expression with (8.449), we see that the probability in this ensemble that a given copy is in the energy eigenstate $|n\rangle$ belonging to the eigenvalue E_n is $e^{-\beta E_n}/Z$.

The normalization constant Z is the **canonical partition function** and is given by

$$Z = \mathrm{Tr}\{e^{-\beta \hat{H}}\} . \tag{8.475}$$

In the H-representation, this reads

$$Z = \sum_n \langle n|e^{-\beta \hat{H}}|n\rangle = \sum_n e^{-\beta E_n} , \tag{8.476}$$

where the sum is over all energy eigenstates labeled by n. We can also write Z as

$$Z = \sum_{E_n} g(E_n) e^{-\beta E_n} , \tag{8.477}$$

where the sum is now over all distinct energy eigen*values* and $g(E_n)$ is the degeneracy of the eigenvalue E_n, that is, the number of linearly independent eigenkets corresponding to E_n.

Using the Dirac δ-function, we can rewrite (8.477) as

$$Z = \sum_{E_n} g(E_n) \int \delta(E - E_n) e^{-\beta E} \mathrm{d}E = \int \sum_{E_n} g(E_n) \delta(E - E_n) e^{-\beta E} \mathrm{d}E . \tag{8.478}$$

As we have seen in Chaps. 4 and 5,

$$\overline{\Omega}(E) := \sum_{E_n} g(E_n) \delta(E - E_n) \tag{8.479}$$

is nothing but the **density of states** when the possible values of the system energy E form a discrete spectrum. This observation allows us to write (8.477) as

$$Z = \int \overline{\Omega}(E) e^{-\beta E} \mathrm{d}E , \tag{8.480}$$

in agreement with our earlier result of classical statistical mechanics. See (4.72) in particular.

Exercise 8.34. The Hamiltonian of a two-state system is given by

$$\hat{H} = ia \left[|\phi_1\rangle\langle\phi_2| - |\phi_2\rangle\langle\phi_1| \right] , \tag{8.481}$$

where $\langle \phi_i | \phi_j \rangle = \delta_{ij}$ and a is a positive constant having the dimension of energy:

a. Find the energy eigenvalues and the corresponding eigenkets as linear combinations of $|\phi_1\rangle$ and $|\phi_2\rangle$.
b. Suppose that you have an ensemble of the identical systems. At some instant, 30 % of them are in the state $|\phi_1\rangle$ and the rest is in the state $|\phi_2\rangle$. Construct the density matrix and calculate the average energy for the ensemble at that instant.

c. Find the matrix representation of $\hat{\rho}$ in the H-representation.

d. The system is brought to contact with a thermal bath at temperature T, thereby changing $\hat{\rho}$. After a sufficient time has passed, the system has reached statistical equilibrium. Find the Helmholtz free energy and the internal energy of the system. ///

8.16.5 Ideal Gas and Classical Limit

Let us compute the canonical partition function for a particle of mass m confined to a rectangular box of dimension $L_x \times L_y \times L_z$. As shown in Example 8.13, the energy eigenvalues are determined by (8.363).

For a given value of E, (8.363) defines an ellipsoid with semi-principal axes of length $\sqrt{8mE/h^2}L_x$, $\sqrt{8mE/h^2}L_y$, and $\sqrt{8mE/h^2}L_z$ in the three-dimensional space defined by n_x-, n_y-, n_z-axes. (If $L_x = L_y = L_z = L$, the ellipsoid becomes a sphere of radius $\sqrt{8mE/h^2}L$.) Now, each point in the $n_x n_y n_z$-space *whose coordinates are positive integers* represents a distinct energy eigenstate. The number of such points on or inside the ellipsoid gives the number $\mathscr{W}(E)$ of distinct energy eigenstates whose energy is equal to or less than E. But, because each point occupies a unit volume, $\mathscr{W}(E)$ is approximately 1/8 of the volume of the ellipsoid. In the factor $1/8 = (1/2)^3$, the first factor of $1/2$ removes the half of the ellipsoid, which corresponds to $n_x \leq 0$. The second $1/2$ removes the half of the remaining portion of the ellipsoid, for which $n_y \leq 0$, and so on.

We note that the ellipsoid with semi-principal axes of length a, b, and c is obtained from the unit sphere by stretching it by factors of a, b, and c in x-, y-, and z-directions, respectively. So, the volume of the ellipsoid is $4\pi abc/3$. This leads to

$$\mathscr{W}(E) \approx \frac{\pi}{6}\left(\frac{8mE}{h^2}\right)^{3/2} L_x L_y L_z = \frac{\pi}{6}\left(\frac{8mE}{h^2}\right)^{3/2} V \,, \tag{8.482}$$

where $V = L_x L_y L_z$ is the volume of the box. We can now compute the density of states as

$$\overline{\Omega}(E) = \frac{\partial \mathscr{W}}{\partial E} \approx \frac{\pi}{4}\left(\frac{8m}{h^2}\right)^{3/2} V E^{1/2} \,. \tag{8.483}$$

Using this expression in (8.480) and recalling the formula (3.92), we arrive at

$$Z = \frac{V}{\Lambda^3} \tag{8.484}$$

in agreement with the prediction of the classical statistical mechanics, that is, (3.86) with the correction factor h^{-3}.

Suppose now that we have N noninteracting identical particles in the box. In this case, (8.363) is replaced by

$$\frac{8mE}{h^2} = \sum_{i=1}^{N} \left[\left(\frac{n_{xi}}{L_x} \right)^2 + \left(\frac{n_{yi}}{L_y} \right)^2 + \left(\frac{n_{zi}}{L_z} \right)^2 \right] \tag{8.485}$$

with subscript i labeling a particle. This equation defines an ellipsoid in a $3N$-dimensional space. Recalling (4.47), which gives the volume of a n-dimensional unit sphere, we find

$$\mathscr{W}(E) = \frac{1}{8^N N!} \frac{\pi^{3N/2}}{\Gamma(3N/2+1)} \left(\frac{8mE}{h^2} \right)^{3N/2} V^N \tag{8.486}$$

in place of (8.482). Here, the $1/8^N$ factor selects out the portion of the ellipsoid corresponding to the positive values of $n_{x1}, \ldots, n_{zN}$ and the $1/N!$ factor arises from the indistinguishability of identical particles. Thus,

$$\overline{\Omega}(E) = \frac{1}{8N!} \frac{\pi^{3N/2}}{\Gamma(3N/2+1)} \left(\frac{8m}{h^2} \right)^{3N/2} V^N \frac{3N}{2} E^{3N/2-1} . \tag{8.487}$$

With the aid of (4.42) and (4.43), this leads to

$$Z = \frac{V^N}{\Lambda^{3N} N!} \tag{8.488}$$

in agreement with what you saw in Exercise 3.16 for the classical mechanical system.

According to quantum mechanics, a particle is either a **fermion** following a **Fermi–Dirac statistics** or a **boson** following a **Bose–Einstein statistics**. No more than one fermion can occupy the same quantum state (specified by the triplet of numbers n_x, n_y, and n_z for the ideal gas under consideration) at any instant. No such restriction applies to bosons. Yet, (8.488) fails for bosons at high densities. This is because the $1/N!$ factor can no longer properly account for the indistinguishability of identical particles if more than one particle occupies a given quantum state. These are the results of the so-called **exchange effect**, which is present even if the Hamiltonian has no potential energy term due to interaction among particles, and lead to net repulsion among fermions and net attraction among bosons.

If the system is sufficiently dilute, the exchange effect can safely be ignored since there will be far more quantum states than there are particles and the probability that any given quantum state is occupied is very small. This is called the **classical limit**. Because our treatment of the ideal gas ignores the exchange effect, (8.488) is applicable only in this limit. Further details on Fermi–Dirac and Bose–Einstein statistics can be found in Refs. [2, 3, 5].

8.16.6 Microcanonical Ensemble

Following the approach we took in Chap. 4, we introduce a microcanonical ensemble as an approximation to a canonical ensemble when the system under consideration is macroscopic.

In a macroscopic system, the difference between two consecutive energy eigenvalues is very small. This being the case, it makes sense to lump together the densely distributed δ-functions in (8.479) and regard $\overline{\Omega}(E)$ as a continuous function of E. More explicitly, (8.479) may be replaced by the approximate expression

$$\overline{\Omega}(E) \approx \frac{1}{\delta E}\int_{E-\delta E}^{E} \sum_{E_n} g(E_n)\delta(E-E_n)\mathrm{d}E\ , \tag{8.489}$$

without incurring any sensible loss of accuracy in (8.480), where δE is a small interval of energy that is nevertheless much larger than the difference in two consecutive energy eigenvalues.

This modified density of states is usually a very rapidly increasing function of E. When such a function is multiplied by the very rapidly decreasing function $e^{-\beta E}$, where $\beta > 0$, the result is often a very sharply peaked function of E.[48] If this happens, we can take an small interval $(E-\Delta E, E]$ that contains the sharp peak and safely assume that essentially all of the copies in the canonical ensemble belongs to this narrow interval of the energy. For sufficiently small ΔE, all states in the interval $E-\Delta E < E_n \leq E$ may be regarded as equally probable. This then defines our **microcanonical ensemble**. In the H-representation, therefore,

$$\hat{\rho} = \frac{1}{C_M}\sum_n |n\rangle f(E_n)\langle n|\ , \tag{8.490}$$

where

$$f(E_n) = \begin{cases} 1 & \text{if } E-\Delta E < E_n \leq E \\ 0 & \text{otherwise.} \end{cases} \tag{8.491}$$

The quantity C_M is the normalization constant and is determined by the normalization condition (8.450), which now yields the **microcanonical partition function**

$$C_M = \sum_n f(E_n)\ , \tag{8.492}$$

where the summation is over all energy eigenstates. Because of (8.491), C_M is the total number of energy eigenstates corresponding to the energy eigenvalues that fall into the interval $E-\Delta E < E_n \leq E$. Thus, using ΔE for δE in (8.489),

$$C_M = \int_{E-\Delta E}^{E} \sum_{E_n} g(E_n)\delta(E-E_n)\mathrm{d}E = \overline{\Omega}(E)\Delta E\ , \tag{8.493}$$

which is nothing but (4.24).

As we saw in Chap. 4, other statistical ensembles can be derived from (8.493) and the physical interpretation given to $\overline{\Omega}(E)\Delta E$. Our derivation in that chapter made no reference to the underlying mechanics except in the case of the isothermal–isobaric ensemble.[49] Any difference between the classical and the quantum mechanical formulations of statistical mechanics is thus seen to arise in part from the form of $\overline{\Omega}(E)$ prescribed by the underlying mechanics. We have already encountered a profound implication of this difference in Example 4.2. The other difference stems from the exchange effect that impacts how a quantum mechanical system populates those microstates enumerated by $\overline{\Omega}(E)$. This is then a logical place for us to end this brief excursion into quantum mechanics and its application in formulating statistical mechanics.

8.17 Frequently Used Symbols

$\dagger$, adjoint.
c^* , complex conjugate of c.
$\langle A \rangle$, ensemble average of a dynamical variable A.
$\langle A \rangle_{\mathrm{QM}}$, quantum mechanical average of A.
$|n\rangle$, energy eigenket corresponding to the $n$the energy eigenvalue E_n.
$|\boldsymbol{p}\rangle$, momentum eigenket.
$|\boldsymbol{x}\rangle$, position eigenket.
$[\hat{X},\hat{Y}]$, commutator defined by $\hat{X}\hat{Y}-\hat{Y}\hat{X}$.
$[\hat{X},\hat{Y}]_+$, anti-commutator defined by $\hat{X}\hat{Y}+\hat{Y}\hat{X}$.
$\mathrm{Tr}\{\hat{A}\}$, trace of $\hat{A}$.

$\hat{a}$, annihilation operator.
$\hat{a}^\dagger$, creation operator.
$g(E_n)$, degeneracy of the energy eigenvalue E_n.
$\hbar$, $h/2\pi$, where $h = 6.626 \times 10^{-34}$ (J·s) is the Planck constant.
i , imaginary unit $\sqrt{-1}$.
m , mass of a particle.
$\hat{\boldsymbol{p}}$, momentum operator.
r , dimension of a ket space V_k.
s , degeneracy of an eigenvalue.
$\hat{\boldsymbol{x}}$, position operator.

$\hat{A}$, $\hat{B}$,..., observables.
C_M , microcanonical partition function.
E_n , the nth energy eigenvalue.
$\hat{H}$, Hamiltonian operator.
$\hat{I}$, identity operator.
$\hat{N}$, number operator.

$\hat{U}_t$, time evolution operator that advances the state ket from $t = 0$ to t.
$\hat{X}$, $\hat{Y}$,. . . , generic linear operator.
Z , canonical partition function.

$\delta(x)$, the Dirac δ-function.
$\hat{\rho}_t$, density operator at time t.
$\underline{\Omega}$, density of states.

References and Further Reading

1. Ballentine L E (1998) Quantum Mechanics: A Modern Development. World Scientific, River Edge, New Jersey
   For a more careful discussion of infinite dimensional vector space and operators with a continuous spectrum, see Sects. 1.3 and 1.4.
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   Chapter 2 provides a highly readable account of Fermi–Dirac and Bose–Einstein statistics.
3. Landau L D, Lifshitz E M (1980) Statistical physics: Part 1, 3rd edn. Pergamon Press, New York
   A detailed treatment of Fermi–Dirac and Bose–Einstein statistics is found in Chap. 5.
4. Macdonald A (2011) Linear and Geometric Algebra. Printed by CreateSpace
   The first four chapters offer a very compact and highly accessible introduction to linear algebra in just 70 pages.
5. Pathria R K (1972) Statistical Mechanics. Pergamon, Elmsford, New York
   For a detailed consideration of classical limit, see Sect. 5.5.
6. Pauling L, Wilson, Jr. E B (1985) Introduction to Quantum Mechanics with Applications to Chemistry. Dover, New York
   A very lucid and detailed treatment of the one-dimensional harmonic oscillator is found in Chap. 3.
7. Sakurai J J (1985) Modern Quantum Mechanics. Addison-Wesley, Reading, Massachusetts
   The need for defining a quantum mechanical state as a vector in a complex vector space is demonstrated using the Stern-Garlach experiment at the very beginning of the book. Our own outline of quantum mechanics followed the first two chapters of the book, but focusing only on those topics essential for our purpose. The density matrix is treated in some detail in Sect. 3.4 of the book.
8. Schlosshauer M (2007) Decoherence and the Quantum-to-Classical Transition. Springer-Verlag, Heidelberg
9. Tolman R C (1979) The principles of statistical mechanics. Dover, New York
   Chapters 7 and 8 provides a very thorough introduction to quantum mechanics. For a summary of relevant experimental discoveries that lead to quantum mechanics, see Sect. 52.

Appendix A
Vectors in Three-Dimensional Space

In this appendix, we review a few key facts about the algebra of ordinary three-dimensional vectors. In doing so, we recall a few frequently used identities and obtain a useful analogy that will help us in our exploration of a more general vector space in Chap. 8.

A.1 Arrow in Space

A vector $\boldsymbol{a}$, as we were told in our first encounter with it, is an arrow. As an arrow, it has the length and the direction it points to. However, we assign no significance to the absolute location of $\boldsymbol{a}$ in space. Thus, $\boldsymbol{a}$ and $\boldsymbol{a}'$, the latter being obtained by translating $\boldsymbol{a}$ without changing its length or direction, are actually the same vector.

Given a positive number α, we may construct another vector that points to the same direction as $\boldsymbol{a}$ but with its length given by α times that of $\boldsymbol{a}$. This vector is denoted by $\alpha\boldsymbol{a}$. When $\alpha < 0$, we agree to denote by $\alpha\boldsymbol{a}$ a vector pointing to the opposite direction with its length $-\alpha(> 0)$ times that of $\boldsymbol{a}$. If $\alpha = 0$, we say that $\alpha\boldsymbol{a}$ is the **zero vector** and denote it by $\boldsymbol{0}$. The length of $\boldsymbol{0}$ is zero. We do not associate with $\boldsymbol{0}$ any direction as we have no need to do so. Addition of two vectors $\boldsymbol{a}$ and $\boldsymbol{b}$ is defined by means of the parallelogram construction.

A.2 Components of a Vector

It becomes quite tedious, however, to draw arrows and parallelograms each time we refer to vectors and their additions. We need a more efficient way of handling vectors. This is accomplished by representing a vector with the help of a coordinate system.

Given a vector $\boldsymbol{a}$, its components can be found as follows. For simplicity, let us first suppose that the vector is on the *xy*-plane. Figure A.1 illustrates the process.

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DOI 10.1007/978-3-319-13809-1

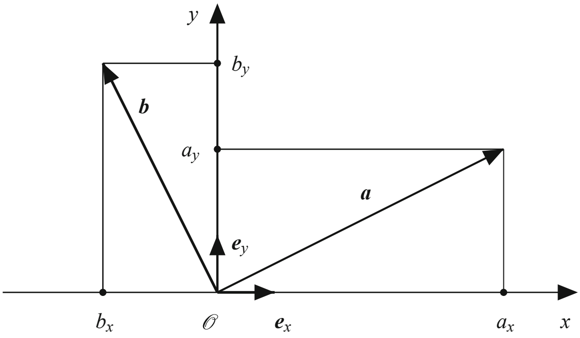

Fig. A.1 Components of two-dimensional vectors $\boldsymbol{a}$ and $\boldsymbol{b}$.

We move the vector, without changing its length or direction, so that the arrow starts from the origin. Then, the x-coordinate of the tip of the arrow, denoted by a_x in Fig. A.1, is the x-component of $\boldsymbol{a}$. Likewise, the y-coordinate of the tip is the y-component of $\boldsymbol{a}$. As is the case with $\boldsymbol{b}$, a component of a vector can be a negative number.

Let $\boldsymbol{e}_x$ be the vector whose x- and y- components are 1 and 0, respectively. Similarly, we denote by $\boldsymbol{e}_y$ the vector whose x- and y- components are, respectively, 0 and 1. Then, from what has been said about the multiplication of a vector $\boldsymbol{a}$ by a number α, we see that $a_x\boldsymbol{e}_x$ is a vector represented by an arrow starting from the origin and ending at the point $(a_x, 0)$ on the x-axis. Likewise, $a_y\boldsymbol{e}_y$ is a vector represented by an arrow from the origin to the point $(0, a_y)$ on the y-axis. By the parallelogram construction for adding two vectors, we see that

$$\boldsymbol{a} = a_x\boldsymbol{e}_x + a_y\boldsymbol{e}_y \,, \tag{A.1}$$

which represents the vector $\boldsymbol{a}$ in terms of its components. (See Fig. A.1.)

Equation (A.1) generalizes naturally to three-dimensional space:

$$\boldsymbol{a} = a_x\boldsymbol{e}_x + a_y\boldsymbol{e}_y + a_z\boldsymbol{e}_z \,. \tag{A.2}$$

We shall often express this relation by

$$\boldsymbol{a} \doteq (a_x, a_y, a_z) \,. \tag{A.3}$$

The symbol "$\doteq$" is used here instead of "$=$" since the quantity on the left is a vector, while the expression on the right is a list of its components. These two things are conceptually different. In fact, $\boldsymbol{a}$, being an arrow in three-dimensional space, does not depend on how the coordinate system is set up, while its components do.

We observe from Fig. A.2 that the x-component of a vector $\alpha\boldsymbol{a}$ is αa_x while Fig. A.3 indicates that the x-component of $\boldsymbol{a}+\boldsymbol{b}$ is $a_x + b_x$. Similarly for their y-components.

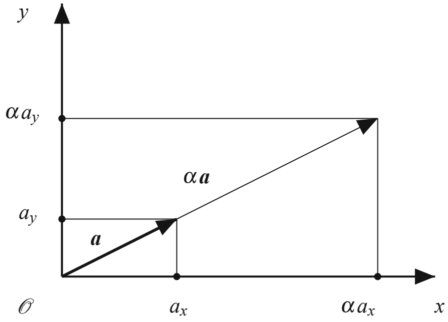

Fig. A.2 Components of $\boldsymbol{a}$ and multiplication of a vector $\boldsymbol{a}$ by a number α.

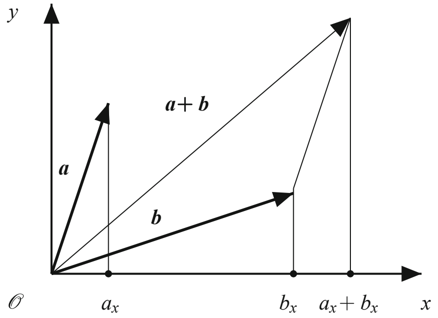

Fig. A.3 Addition of two vectors $\boldsymbol{a}$ and $\boldsymbol{b}$.

A.3 Dot Product

Let $\boldsymbol{a}$ be a vector and denote its x-, y-, and z-components by a_x, a_y, and a_z, respectively. Likewise for $\boldsymbol{b}$. The **dot product** between these two vectors is defined by

$$\boldsymbol{a}\cdot\boldsymbol{b} := a_xb_x + a_yb_y + a_zb_z \ . \tag{A.4}$$

Example A.1. Simple identities involving dot product between $\mathbf{e}_i$*'s*: We first note that

$$\boldsymbol{e}_x \doteq (1,0,0) \ , \quad \boldsymbol{e}_y \doteq (0,1,0) \ , \quad \text{and} \quad \boldsymbol{e}_z \doteq (0,0,1) \ . \tag{A.5}$$

Then,

$$\boldsymbol{e}_x\cdot\boldsymbol{e}_y = 1\times 0 + 0\times 1 + 0\times 0 = 0 \ . \tag{A.6}$$

Likewise, $\boldsymbol{e}_y \cdot \boldsymbol{e}_z = \boldsymbol{e}_z \cdot \boldsymbol{e}_x = 0$. Now,

$$\boldsymbol{e}_x \cdot \boldsymbol{e}_x = 1 \times 1 + 0 \times 0 + 0 \times 0 = 1 \ . \tag{A.7}$$

Likewise, $\boldsymbol{e}_y \cdot \boldsymbol{e}_y = \boldsymbol{e}_z \cdot \boldsymbol{e}_z = 1$.

The length of the vector $\boldsymbol{a}$ is denoted by $\|\boldsymbol{a}\|$ and is defined by

$$\|\boldsymbol{a}\| := \sqrt{\boldsymbol{a} \cdot \boldsymbol{a}} = \sqrt{{a_x}^2 + {a_y}^2 + {a_z}^2} \ . \tag{A.8}$$

To lighten the notation, we often use a for $\|\boldsymbol{a}\|$.

The above definitions allow us to define the angle $\theta(\boldsymbol{a},\boldsymbol{b})$ between the two vectors $\boldsymbol{a}$ and $\boldsymbol{b}$ by the following relations:

$$\cos\theta(\boldsymbol{a},\boldsymbol{b}) = \frac{\boldsymbol{a} \cdot \boldsymbol{b}}{\|\boldsymbol{a}\|\|\boldsymbol{b}\|} \ , \quad \text{where} \quad 0 \leq \theta(\boldsymbol{a},\boldsymbol{b}) \leq \pi \ . \tag{A.9}$$

Since $-1 \leq \cos\theta \leq 1$, you can find $\theta(\boldsymbol{a},\boldsymbol{b})$ from this formula if and only if

$$-1 \leq \frac{\boldsymbol{a} \cdot \boldsymbol{b}}{\|\boldsymbol{a}\|\|\boldsymbol{b}\|} \leq 1 \ . \tag{A.10}$$

That this is always the case follows from the Schwartz inequality proved in Sect. A.5. Note also that the angle is undefined if either $\|\boldsymbol{a}\|$ or $\|\boldsymbol{b}\|$ is zero. This is to be expected since the zero vector does not have a direction associated with it.

Example A.2. Angle between two vectors:

a.

$$\cos\theta(\boldsymbol{e}_x,\boldsymbol{e}_y) = \frac{\boldsymbol{e}_x \cdot \boldsymbol{e}_y}{\|\boldsymbol{e}_x\|\|\boldsymbol{e}_y\|} = 0 \ . \tag{A.11}$$

Thus,

$$\theta(\boldsymbol{e}_x,\boldsymbol{e}_y) = \frac{\pi}{2} \ . \tag{A.12}$$

b. Let $\boldsymbol{a} = a_x\boldsymbol{e}_x + a_y\boldsymbol{e}_y$ so that $\boldsymbol{a} \doteq (a_x, a_y, 0)$. Then,

$$\cos\theta(\boldsymbol{a},\boldsymbol{e}_x) = \frac{\boldsymbol{a} \cdot \boldsymbol{e}_x}{\|\boldsymbol{a}\|\|\boldsymbol{e}_x\|} = \frac{a_x}{\sqrt{{a_x}^2 + {a_y}^2}} \ . \tag{A.13}$$

These two examples indicate that $\theta(\boldsymbol{a},\boldsymbol{b})$ defined by (A.9) agrees with what we expect on the basis of geometry.

A.4 Unit Operator

From (A.2), we see that

$$\boldsymbol{a}\cdot\boldsymbol{e}_x = a_x\ ,\quad \boldsymbol{a}\cdot\boldsymbol{e}_y = a_y\ ,\quad \text{and}\quad \boldsymbol{a}\cdot\boldsymbol{e}_z = a_z\ . \tag{A.14}$$

Substituting these equations back to (A.2), we find

$$\boldsymbol{a} = (\boldsymbol{a}\cdot\boldsymbol{e}_x)\boldsymbol{e}_x + (\boldsymbol{a}\cdot\boldsymbol{e}_y)\boldsymbol{e}_y + (\boldsymbol{a}\cdot\boldsymbol{e}_z)\boldsymbol{e}_z\ . \tag{A.15}$$

Note that $(\boldsymbol{a}\cdot\boldsymbol{b})\boldsymbol{c}$, being a scalar $(\boldsymbol{a}\cdot\boldsymbol{b})$ times a vector $(\boldsymbol{c})$ is a vector. If we agree to define

$$\boldsymbol{a}\cdot(\boldsymbol{b}\boldsymbol{c}) := (\boldsymbol{a}\cdot\boldsymbol{b})\boldsymbol{c}\ , \tag{A.16}$$

we may rewrite (A.15) as

$$\boldsymbol{a} = \boldsymbol{a}\cdot(\boldsymbol{e}_x\boldsymbol{e}_x) + \boldsymbol{a}\cdot(\boldsymbol{e}_y\boldsymbol{e}_y) + \boldsymbol{a}\cdot(\boldsymbol{e}_z\boldsymbol{e}_z) = \boldsymbol{a}\cdot(\boldsymbol{e}_x\boldsymbol{e}_x + \boldsymbol{e}_y\boldsymbol{e}_y + \boldsymbol{e}_z\boldsymbol{e}_z)\ . \tag{A.17}$$

Since $\alpha\boldsymbol{a} = \boldsymbol{a}\alpha$ and $\boldsymbol{a}\cdot\boldsymbol{b} = \boldsymbol{b}\cdot\boldsymbol{a}$, (A.15) can also be written as

$$\boldsymbol{a} = \boldsymbol{e}_x(\boldsymbol{e}_x\cdot\boldsymbol{a}) + \boldsymbol{e}_y(\boldsymbol{e}_y\cdot\boldsymbol{a}) + \boldsymbol{e}_z(\boldsymbol{e}_z\cdot\boldsymbol{a})\ . \tag{A.18}$$

With the definition

$$(\boldsymbol{a}\boldsymbol{b})\cdot\boldsymbol{c} := \boldsymbol{a}(\boldsymbol{b}\cdot\boldsymbol{c})\ , \tag{A.19}$$

we can write

$$\boldsymbol{a} = (\boldsymbol{e}_x\boldsymbol{e}_x)\cdot\boldsymbol{a} + (\boldsymbol{e}_y\boldsymbol{e}_y)\cdot\boldsymbol{a} + (\boldsymbol{e}_z\boldsymbol{e}_z)\cdot\boldsymbol{a} = (\boldsymbol{e}_x\boldsymbol{e}_x + \boldsymbol{e}_y\boldsymbol{e}_y + \boldsymbol{e}_z\boldsymbol{e}_z)\cdot\boldsymbol{a}\ . \tag{A.20}$$

Equations (A.17) and (A.20) indicate that

$$\hat{I} := \boldsymbol{e}_x\boldsymbol{e}_x + \boldsymbol{e}_y\boldsymbol{e}_y + \boldsymbol{e}_z\boldsymbol{e}_z \tag{A.21}$$

is a **unit operator** in the sense that

$$\boldsymbol{a}\cdot\hat{I} = \hat{I}\cdot\boldsymbol{a} = \boldsymbol{a} \tag{A.22}$$

for any vector $\boldsymbol{a}$.

A.5 †Schwarz Inequality

This inequality states that

$$(\boldsymbol{a}\cdot\boldsymbol{b})^2 \leq \|\boldsymbol{a}\|^2\|\boldsymbol{b}\|^2 \tag{A.23}$$

for any $\boldsymbol{a}$ and $\boldsymbol{b}$. To prove it, let $\boldsymbol{c} = \boldsymbol{a} + \lambda \boldsymbol{b}$, where λ is a real number. Since $\|\boldsymbol{c}\|^2 = {c_x}^2 + {c_y}^2 + {c_z}^2$, we have

$$\|\boldsymbol{c}\|^2 \geq 0 \tag{A.24}$$

for any λ. We compute $\|\boldsymbol{c}\|$ as follows:

$$\begin{aligned} \|\boldsymbol{c}\|^2 &= \boldsymbol{c} \cdot \boldsymbol{c} = (\boldsymbol{a} + \lambda \boldsymbol{b}) \cdot (\boldsymbol{a} + \lambda \boldsymbol{b}) = \boldsymbol{a} \cdot \boldsymbol{a} + \lambda \boldsymbol{a} \cdot \boldsymbol{b} + \lambda \boldsymbol{b} \cdot \boldsymbol{a} + \lambda^2 \boldsymbol{b} \cdot \boldsymbol{b} \\ &= \|\boldsymbol{a}\|^2 + 2\lambda \boldsymbol{a} \cdot \boldsymbol{b} + \lambda^2 \|\boldsymbol{b}\|^2 \,. \end{aligned} \tag{A.25}$$

So, we have

$$\|\boldsymbol{a}\|^2 + 2\lambda \boldsymbol{a} \cdot \boldsymbol{b} + \lambda^2 \|\boldsymbol{b}\|^2 \geq 0 \,. \tag{A.26}$$

As indicated above, this inequality holds for any real number λ. In particular, it will hold if we happen to choose λ as

$$\lambda = -\frac{\boldsymbol{a} \cdot \boldsymbol{b}}{\|\boldsymbol{b}\|^2} \,, \tag{A.27}$$

which, of course, is a real number. With this choice of λ, (A.26) becomes

$$\|\boldsymbol{a}\|^2 \geq \frac{(\boldsymbol{a} \cdot \boldsymbol{b})^2}{\|\boldsymbol{b}\|^2} \,. \tag{A.28}$$

Since $\|\boldsymbol{b}\|^2$ is a positive number, this is equivalent to (A.23) and the proof is complete.

A.6 Cross Product

Consider two (nonzero) vectors $\boldsymbol{b}$ and $\boldsymbol{c}$. If neither is a scalar multiple of the other, then, these two vectors are not parallel to each other and hence define a plane. We define the **cross product** $\boldsymbol{b} \times \boldsymbol{c}$ between two vectors $\boldsymbol{b}$ and $\boldsymbol{c}$ as a vector perpendicular to the plane defined by $\boldsymbol{b}$ and $\boldsymbol{c}$. By definition, $\boldsymbol{b} \times \boldsymbol{c}$ points toward the direction a right-handed screw advances if it is rotated to bring $\boldsymbol{b}$ toward $\boldsymbol{c}$ by closing the angle θ $(0 < \theta < \pi)$ between them. Moreover,

$$\|\boldsymbol{b} \times \boldsymbol{c}\| := \|\boldsymbol{b}\| \|\boldsymbol{c}\| \sin\theta \,. \tag{A.29}$$

Since $\sin 0 = \sin \pi = 0$, no ambiguity arises in the above definition regarding the direction of $\boldsymbol{b} \times \boldsymbol{c}$ even if $\theta = 0$ or π, for which $\boldsymbol{b} \times \boldsymbol{c} = \boldsymbol{0}$.

Let us now introduce another vector $\boldsymbol{a}$ and consider the expression

$$\boldsymbol{a} \cdot \boldsymbol{b} \times \boldsymbol{c} \,. \tag{A.30}$$

Since $\boldsymbol{a} \cdot \boldsymbol{b}$ is a scalar, the cross product sign in this expression makes sense only if we interpret this expression as $\boldsymbol{a} \cdot (\boldsymbol{b} \times \boldsymbol{c})$.

If the set of three vectors $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$ *taken in this order* forms a right-handed system as in the x-, y-, and z-axes in a right-handed coordinate system, the expression (A.30) is the volume V of the parallelepiped whose edges are defined by these vectors. In fact, if we denote by ϕ the angle between the two vectors $\boldsymbol{a}$ and $\boldsymbol{b} \times \boldsymbol{c}$, we have

$$\boldsymbol{a} \cdot \boldsymbol{b} \times \boldsymbol{c} = \|\boldsymbol{a}\| \|\boldsymbol{b} \times \boldsymbol{c}\| \cos\phi = \|\boldsymbol{a}\| \|\boldsymbol{b}\| \|\boldsymbol{c}\| \sin\theta \cos\phi \ , \tag{A.31}$$

in which $\|\boldsymbol{b}\| \|\boldsymbol{c}\| \sin\theta$ is the area of the base of the parallelepiped defined by $\boldsymbol{b}$ and $\boldsymbol{c}$, while $\|\boldsymbol{a}\| \cos\phi$ is the height of the parallelepiped.

We are certainly free to consider $\boldsymbol{c}$ and $\boldsymbol{a}$ (or $\boldsymbol{a}$ and $\boldsymbol{b}$) as a pair of vectors defining the base of the parallelepiped, leading to a different way of computing the same volume V of the parallelepiped. In this way, we arrive at the identity

$$\boldsymbol{a} \cdot \boldsymbol{b} \times \boldsymbol{c} = \boldsymbol{b} \cdot \boldsymbol{c} \times \boldsymbol{a} = \boldsymbol{c} \cdot \boldsymbol{a} \times \boldsymbol{b} \ . \tag{A.32}$$

Appendix B
Useful Formulae

This appendix is meant to serve as a duct-tape to hold your prior knowledge on calculus. Other useful computational tools needed in the book are included for convenience.

B.1 Taylor Series Expansion

In the main body of this book, we frequently use Taylor series expansion. Accordingly, we summarize a few key formulae here.

B.1.1 Function of a Single Variable

Let $f(x)$ be a function of a single variable x and suppose that $f(x)$ is differentiable at x_0 however many times we need. Then,

$$f(x_0+a) = f(x_0) + \left.\frac{\mathrm{d}f}{\mathrm{d}x}\right|_{x=x_0} a + \frac{1}{2!}\left.\frac{\mathrm{d}^2 f}{\mathrm{d}x^2}\right|_{x=x_0} a^2 + \frac{1}{3!}\left.\frac{\mathrm{d}^3 f}{\mathrm{d}x^3}\right|_{x=x_0} a^3 + \cdots\,, \qquad \text{(B.1)}$$

where the symbol $\mathrm{d}^n f/\mathrm{d}x^n|_{x=x_0}$ $(n = 1,2,3\ldots)$ indicates that the value of the function $\mathrm{d}^n f/\mathrm{d}x^n$ of x is to be evaluated at $x = x_0$. Let $x = x_0 + a$ and rewrite (B.1) as

$$f(x) = f(x_0) + \left.\frac{\mathrm{d}f}{\mathrm{d}x}\right|_{x=x_0} (x-x_0) + \frac{1}{2!}\left.\frac{\mathrm{d}^2 f}{\mathrm{d}x^2}\right|_{x=x_0} (x-x_0)^2 + \cdots\,. \qquad \text{(B.2)}$$

The expression on the right-hand side of this equation is called the **Taylor series expansion** of $f(x)$ around $x = x_0$. If $x_0 = 0$, the series is also referred to as the **Maclaurin series**.

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Example B.1. Exponential function: One famous example of the Maclaurin series that shows up from time to time is

$$e^x = 1 + x + \frac{1}{2!}x^2 + \frac{1}{3!}x^3 + \cdots . \tag{B.3}$$

In order to arrive at this result, we recalled that

$$\left.\frac{\mathrm{d}^n e^x}{\mathrm{d}x^n}\right|_{x=0} = e^x|_{x=0} = 1 . \tag{B.4}$$

Since $0! = 1$ by definition, (B.3) can be written more compactly as

$$e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!} . \tag{B.5}$$

Note that (B.1) holds for any value of x_0 provided that $f(x)$ is differentiable at x_0 as many times as we desire. This means that the application of (B.1) need not be restricted to a particular value of x_0, and hence we may rewrite it more simply as

$$f(x+a) = f(x) + \frac{\mathrm{d}f}{\mathrm{d}x}a + \frac{1}{2!}\frac{\mathrm{d}^2 f}{\mathrm{d}x^2}a^2 + \frac{1}{3!}\frac{\mathrm{d}^3 f}{\mathrm{d}x^3}a^3 + \cdots . \tag{B.6}$$

When a is replaced by an infinitesimal quantity $\mathrm{d}x$, the second term on the right-hand side of (B.6) is often written as

$$\mathrm{d}f := \frac{\mathrm{d}f}{\mathrm{d}x}\mathrm{d}x . \tag{B.7}$$

The motivation behind this notation becomes clearer if we rewrite this as

$$\mathrm{d}f = \left(\mathrm{d}x\frac{\mathrm{d}}{\mathrm{d}x}\right) f . \tag{B.8}$$

That is, we may regard $\mathrm{d} := \mathrm{d}x(\mathrm{d}/\mathrm{d}x)$ as a differential *operator* acting on f. By analogy, we write

$$\mathrm{d}^2 f = \frac{\mathrm{d}^2 f}{\mathrm{d}x^2}(\mathrm{d}x)^2 = \left(\mathrm{d}x\frac{\mathrm{d}}{\mathrm{d}x}\right)^2 f , \quad \mathrm{d}^3 f = \frac{\mathrm{d}^3 f}{\mathrm{d}x^3}(\mathrm{d}x)^3 = \left(\mathrm{d}x\frac{\mathrm{d}}{\mathrm{d}x}\right)^3 f , \ldots . \tag{B.9}$$

With this notation, we can write

$$\Delta f := f(x+\mathrm{d}x) - f(x) = \mathrm{d}f + \frac{1}{2!}\mathrm{d}^2 f + \frac{1}{3!}\mathrm{d}^3 f + \cdots . \tag{B.10}$$

The nth term on the right is referred to as the nth order term. Note that, unless $\mathrm{d}^n f \equiv 0$ for all $n \geq 2$, $\Delta f \neq \mathrm{d}f$ in general.

More often than not, we are interested only in the most significant contribution ($\mathrm{d}f$) to Δf. In such a situation, we suppress $\mathrm{d}^2 f/2!$, $\mathrm{d}^3 f/3!, \ldots$, and write

$$\Delta f = \mathrm{d}f + \text{h.o.} \tag{B.11}$$

We say that Δf is given by $\mathrm{d}f$ *to the first order of* $\mathrm{d}x$. The symbol h.o. stands for the **higher order terms**.

It is somewhat amusing to note that (B.10) can be rewritten, in a purely formal manner, as follows:

$$f(x+\mathrm{d}x) = \left(1 + \mathrm{d} + \frac{1}{2!}\mathrm{d}^2 + \frac{1}{3!}\mathrm{d}^3 + \cdots\right) f(x) = e^{\mathrm{d}} f(x) , \tag{B.12}$$

indicating that the effect of the operator e^{d} is to "advance" x by $\mathrm{d}x$, thus converting $f(x)$ into $f(x+\mathrm{d}x)$. If we were to define $\mathrm{d}^n f$ by $(n!)^{-1}\mathrm{d}^n f/\mathrm{d}x^n$, this expression would not follow. It should also be noted that, in writing this equation, we have assumed that f is differentiable as many times as we desire.

Suppose that $f(x)$ is continuously differentiable, that is $\mathrm{d}f/\mathrm{d}x$ exists and is continuous. Then, for $f(x)$ to take an extremum value at $x = x_0$, it is necessary and sufficient that

$$\mathrm{d}f = \left.\frac{\mathrm{d}f}{\mathrm{d}x}\right|_{x=x_0} \mathrm{d}x = 0 \tag{B.13}$$

for any $\mathrm{d}x$. We often express this fact by saying that "$f(x_0+\mathrm{d}x) - f(x_0)$ is zero *to the first order of* $\mathrm{d}x$." Because $\mathrm{d}x$ is arbitrary, this is equivalent to

$$\left.\frac{\mathrm{d}f}{\mathrm{d}x}\right|_{x=x_0} = 0 . \tag{B.14}$$

Since $\mathrm{d}f/\mathrm{d}x$ is a function of x, this is an equation for x_0.

B.1.2 Function of Multiple Variables

The similar results hold when f is a scalar-valued function of multiple variables. For example, (B.10) remains valid for $f = f(x,y)$ if the differential operator d is defined by

$$\mathrm{d} := \mathrm{d}x\frac{\partial}{\partial x} + \mathrm{d}y\frac{\partial}{\partial y} . \tag{B.15}$$

In particular, (B.8) generalizes to

$$\mathrm{d}f = \left(\mathrm{d}x\frac{\partial}{\partial x} + \mathrm{d}y\frac{\partial}{\partial y}\right) f = \frac{\partial f}{\partial x}\mathrm{d}x + \frac{\partial f}{\partial y}\mathrm{d}y , \tag{B.16}$$

while

$$\mathrm{d}^2 f = \left(\mathrm{d}x\frac{\partial}{\partial x} + \mathrm{d}y\frac{\partial}{\partial y}\right)^2 f = \frac{\partial^2 f}{\partial x^2}(\mathrm{d}x)^2 + 2\frac{\partial^2 f}{\partial x \partial y}\mathrm{d}x\mathrm{d}y + \frac{\partial^2 f}{\partial y^2}(\mathrm{d}y)^2 \,. \tag{B.17}$$

The condition that $f(x,y)$ takes an extremum value at $(x,y) = (x_0, y_0)$ is a simple generalization of (B.14) and is given by

$$\left.\frac{\partial f}{\partial x}\right|_{(x,y)=(x_0,y_0)} = 0 \quad \text{and} \quad \left.\frac{\partial f}{\partial y}\right|_{(x,y)=(x_0,y_0)} = 0\,, \tag{B.18}$$

from which we can determine x_0 and y_0.

B.2 Exponential

By definition,

$$e = \lim_{n\to\infty}\left(1 + \frac{1}{n}\right)^n \,. \tag{B.19}$$

This relation holds with n replaced by a real number x. In fact,

$$\lim_{x\to\infty}\left(1 \pm \frac{1}{x}\right)^x = e^{\pm 1} \,. \tag{B.20}$$

The simplest way to verify this identity perhaps is to use the Taylor series expansion of $\ln(1+x)$:

$$\ln(1+x) = x - \frac{1}{2}x^2 + \frac{1}{3}x^3 + \cdots \,. \tag{B.21}$$

Now, let

$$f(x) := \left(1 \pm \frac{1}{x}\right)^x \,. \tag{B.22}$$

Using (B.21), we find

$$\ln f(x) = x\ln\left(1 \pm \frac{1}{x}\right) \approx x\left(\pm\frac{1}{x} - \frac{1}{2x^2} \pm \frac{1}{3x^3} - \cdots\right) \,. \tag{B.23}$$

Since this expression approaches ±1 in the $x \to \infty$ limit, we have established (B.20). It follows that

$$\lim_{x\to\infty}\left(1 \pm \frac{a}{x}\right)^x = \lim_{y\to\infty}\left[\left(1 \pm \frac{1}{y}\right)^y\right]^a = e^{\pm a}\,, \tag{B.24}$$

where $y := x/a$.

B.3 Summation of a Geometric Series

The following result may be familiar to you:

$$\sum_{i=1}^{\infty} r^i = \frac{1}{1-r} \quad \text{if } |r| < 1 \,. \tag{B.25}$$

To see why this is so, let

$$S_n := 1 + r + r^2 + \cdots + r^n \,. \tag{B.26}$$

Then,

$$rS_n = r + r^2 + \cdots + r^n + r^{n+1} \,. \tag{B.27}$$

Subtracting (B.27) from (B.26), we find

$$(1-r)S_n = 1 - r^{n+1} \,, \tag{B.28}$$

and hence

$$S_n = \frac{1-r^{n+1}}{1-r} \,. \tag{B.29}$$

If $|r| < 1$, $\lim_{n\to\infty} r^n = 0$. This gives (B.25).

B.4 Binomial Expansion

The following identity holds:

$$(a+b)^M = \sum_{N=0}^{M} \binom{M}{N} a^N b^{M-N} \,, \tag{B.30}$$

in which

$$\binom{M}{N} := \frac{M!}{N!(M-N)!} \tag{B.31}$$

is the **binomial coefficient**. To see this, let us imagine computing $(a+b)^M$ by writing out M factors of $(a+b)$:

$$(a+b) \times (a+b) \times \cdots \times (a+b) \,. \tag{B.32}$$

We choose from each pair of brackets, either a or b, and form their product. Each distinct set of choices we make for the brackets yields a product that will show up in the expansion of $(a+b)^M$. There are 2^M distinct set of choices we can make, and we get 2^M products. But, not all of them have different values.

For example, if we always pick a from each pair of brackets, then, we get a^M. There is only one way to do this. So the coefficient of a^M is just one. If we choose

b only once and a for the remaining $M-1$ times, then, their product is $a^{M-1}b$. But, since there are M distinct ways of choosing the pair of brackets from which to pick b, the coefficient of $a^{M-1}b$ is M, and so on. The coefficient $\binom{M}{N}$ of $a^N b^{M-N}$ is the number of distinct ways of choosing N pairs of brackets from which we pick a when there are M pairs of brackets in total.

B.5 Gibbs–Bogoliubov Inequality

Let $f(x)$ and $g(x)$ be integrable positive functions satisfying

$$\int_a^b f(x)\mathrm{d}x = \int_a^b g(x)\mathrm{d}x \,. \tag{B.33}$$

Then,

$$\int_a^b f(x)\ln f(x)\mathrm{d}x \geq \int_a^b f(x)\ln g(x)\mathrm{d}x \,, \tag{B.34}$$

where the equality holds only when $f(x) \equiv g(x)$. This result is known as the **Gibbs–Bogoliubov inequality**.

To prove the inequality, we first compute

$$\begin{aligned}&\int_a^b f(x)\ln f(x)\mathrm{d}x - \int_a^b f(x)\ln g(x)\mathrm{d}x \\ &\qquad = \int_a^b f(x)\ln\frac{f(x)}{g(x)}\mathrm{d}x = \int_a^b g(x)\left[\frac{f(x)}{g(x)}\ln\frac{f(x)}{g(x)} - \frac{f(x)}{g(x)} + 1\right]\mathrm{d}x \,,\end{aligned} \tag{B.35}$$

where the last equality follows from (B.33). Now, we note that

$$h(x) := x\ln x + 1 - x \geq 0 \tag{B.36}$$

for all $x > 0$ with the equality holding only at $x = 1$. The validity of this inequality can be easily established graphically. In fact,

$$\frac{\mathrm{d}h}{\mathrm{d}x} = \ln x \,, \tag{B.37}$$

which is negative if $0 < x < 1$, zero at $x = 1$, and positive if $x > 1$. Thus, the minimum value of $h(x)$ occurs at $x = 1$ and it is zero. Replacing x by $f(x)/g(x)$, we see from (B.35) that

$$\int_a^b f(x)\ln f(x)\mathrm{d}x - \int_a^b f(x)\ln g(x)\mathrm{d}x \geq 0 \,, \tag{B.38}$$

where the equality holds if and only if $f(x)/g(x) \equiv 1$.

Appendix C
Legendre Transformation

This appendix presents a basic idea of Legendre transformation used in Chaps. 1 and 2.

C.1 Legendre Transformation

The problem we wish to answer is the following: Given a function

$$y = y(x) \,, \tag{C.1}$$

how do we construct a function

$$w = w(p) \tag{C.2}$$

containing just as much information as (C.1), where

$$p := \frac{\mathrm{d}y}{\mathrm{d}x}\ ? \tag{C.3}$$

By saying "(C.1) and (C.2) *contain the same information*," we mean that, given (C.1) *alone*, we can find (C.2) *and also* that we can find (C.1) using (C.2) *alone*.

Let us first take a very simple-minded approach. As we shall see shortly, this leads to a failure. However, an approach very similar to this one will work. So, our effort will not be wasted.

a. Given (C.1), take the derivative, which will give us p as a function of x:

$$p = \frac{\mathrm{d}y}{\mathrm{d}x} = p(x) \,. \tag{C.4}$$

b. Invert this equation to express x as a function of p. Note that this is always possible *provided that* $p = \mathrm{d}y/\mathrm{d}x$ is a monotonic function of x, that is, $\mathrm{d}^2y/\mathrm{d}x^2$ does not change its sign. See Fig. C.1 to understand this point.

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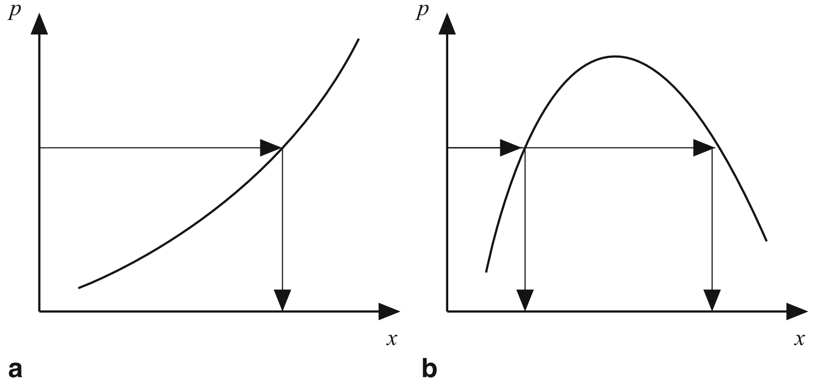

Fig. C.1 The function $p = p(x)$ can be inverted to give $x = x(p)$ if $p = p(x)$ is monotonic as indicated in **a**. If this is not the case, there may be multiple values of x for a given value of p as in **b** and the function $p = p(x)$ cannot be inverted.

c. Substitute this function $x = x(p)$ into (C.1). The end result is y expressed as a function of p. Identify the function so obtained as w in (C.2).

As an example of this approach, let us take $y_0 = x^2$, for which $p = 2x$, and hence $x = p/2$. So, $w_0 = p^2/4$. This approach, however, has a serious flaw. To see this, let us take another function $y_a = (x-a)^2$, where a is a constant. If you go through the same procedure, you will find that $w_a = p^2/4$. So, two different functions y_0 and y_a both give you the same function for w. Thus, the proposed transformation has no unique inverse.

C.1.1 Representation of a Curve

Let us step back a little and take a little more graphical look at the problem.

By writing down an explicit expression for a function $y = y(x)$, such as $y = x^2$ above, we are actually specifying, in a very compact way, a set

$$\{(x_i, y_i) | y_i = y(x_i)\} \ , \tag{C.5}$$

that is, the set of all pairs of numbers (x_i, y_i) for which $y_i = y(x_i)$ holds. Now, you are certainly familiar with a practice of showing a pair of numbers, say (x_1, y_1) as a point on a piece of paper. If this is done for all the members of the set, the resulting collection of points is a curve representing the function $y = y(x)$.

Now, there is an interesting way to draw a curve. You might have tried this back in your elementary school days, perhaps out of boredom during a class. Draw a number of lines as shown in Fig. C.2. What do you see? Do you see a curve emerging from the set of lines? These lines are a set of tangent lines to that curve. So, a curve can

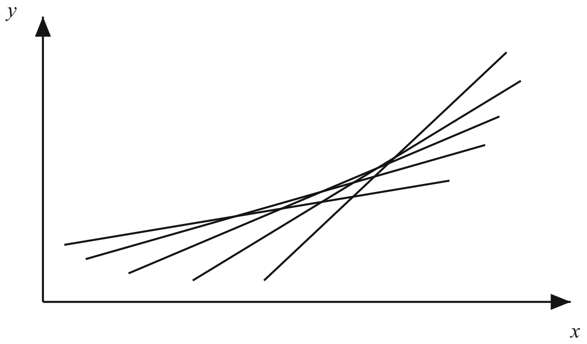

Fig. C.2 A curve emerges from a set of lines.

be specified by a set of tangent lines. But, each line is determined by its slope p and the intercept w on the y-axis. Finally, specifying a set of pairs of numbers (p, w) is equivalent to specifying a function $w = w(p)$. (Provided, of course, that for a given value of p, there is a unique value of w, that is, if (p_1, w_1) and (p_1, w_2) are both in the set, then $w_1 = w_2$. This demands that $\mathrm{d}p/\mathrm{d}x = \mathrm{d}^2y/\mathrm{d}x^2$ be of a definite sign.)

Given a pair of numbers (x_i, y_i) on a curve $y = y(x)$, it is a simple matter to find the corresponding pair (p_i, w_i) for the tangent line of $y = y(x)$ at $x = x_i$:

$$p_i = \left.\frac{\mathrm{d}y}{\mathrm{d}x}\right|_{x=x_i} \quad \text{and} \quad w_i = y(x_i) - p_i x_i \,. \tag{C.6}$$

In this way, a point (x_i, y_i) on the curve on the xy-plane is mapped to a point (p_i, w_i) on the pw-plane. By repeating this process for each point in the set (C.5), we end up with a function $w = w(p)$, which is then an alternative representation of the original function $y = y(x)$, but now the independent variable is p instead of x.

C.1.2 Legendre Transformation

The above consideration leads to the following procedure called the **Legendre transformation**:

a. Given (C.1), compute p as

$$p = \frac{\mathrm{d}y}{\mathrm{d}x} \,, \tag{C.7}$$

which is a function of x.

b. Solve (C.7) to express x in terms of p.

$$x = x(p) \,, \tag{C.8}$$

c. Substitute (C.8) into the relation

$$w = y(x) - px \,, \tag{C.9}$$

which is now expressed in terms of p. The resulting function $w = w(p)$ is called the **Legendre transform** of y.

Going back to the earlier example, let $y_0 = x^2$, for which $p = 2x$ and hence $x = p/2$. Then, $w_0 = y_0 - px = -p^2/4$. On the other hand, if $y_a = (x-a)^2$, then $p = 2(x-a)$ and $x = p/2 + a$, from which you find $w_a = y_a - px = -p^2/4 - ap$. Unlike the earlier approach, $w_0 \neq w_a$.

At this point, you might wonder why the earlier approach failed. There, we expressed y as a function of p and called the resulting function w. This latter function can therefore be written as $y = w(\mathrm{d}y/\mathrm{d}x)$. But, this is a differential equation for y, and hence cannot determine y uniquely without specifying a boundary condition, that is, a pair of numbers such as (x_1, y_1) through which the curve must pass. But, what we wanted was a new equation that is equivalent to the original one. In constructing this new function, we do not wish to carry around the extra piece of information that $y_1 = y(x_1)$, which pertains to the old one.

C.1.3 Inverse Legendre Transformation

The remaining question now is whether we can start from the function w_0 (or w_a) and recover the original function y_0 (or y_a). If we can, then y and w are both satisfactory representation of the same information. Now, given $w = w(p)$, how do we reconstruct $y = y(x)$? From (C.9), we have

$$y = w(p) + px \,. \tag{C.10}$$

In order to obtain $y(x)$, all we need to do is to express p as a function of x. Again from (C.9),

$$\mathrm{d}w = \mathrm{d}y - p\mathrm{d}x - x\mathrm{d}p \,. \tag{C.11}$$

But, since $p = \mathrm{d}y/\mathrm{d}x$, we have $\mathrm{d}y = p\mathrm{d}x$. So, we conclude that

$$\mathrm{d}w = -x\mathrm{d}p \,, \tag{C.12}$$

and hence

$$x = -\frac{\mathrm{d}w}{\mathrm{d}p} \,. \tag{C.13}$$

Thus, we can proceed as follows:

a. Given $w = w(p)$, compute the negative of its derivative. This gives x as a function of p.
b. Solve this equation to express p as a function of x.
c. Substitute the result into (C.10) to obtain y as a function of x.

From (C.10) and (C.13), we see that the procedure is just the Legendre transformation of $w = w(p)$.

Let us see how this goes for $w_0 = -p^2/4$, for which $x = -\mathrm{d}w/\mathrm{d}p = p/2$. So $p = 2x$, and hence $y_0 = w_0 + px = -(2x)^2/4 + 2x \times x = x^2$.

Exercise C.1. Repeat the same process for $w_a = -p^2/4 - ap$ to reconstruct y_a. ///

Exercise C.2. Given a function

$$y = x \ln x \,, \tag{C.14}$$

a. Perform its Legendre transformation to obtain the function $w = w(p)$.
b. Perform the inverse Legendre transformation to recover the function $y = y(x)$. ///

Exercise C.3. Given a function

$$z = x^2 e^y \,, \tag{C.15}$$

a. Perform its Legendre transformation to obtain the function $w = w(x, p)$, where $p := \partial z/\partial y$.
b. Perform the inverse Legendre transformation to recover the function $z = z(x, y)$.

In this problem, treat x as if it is a constant. ///

Appendix D
Dirac δ-Function

Dirac originally defined the δ-function that bears his name through the following properties[2]:

$$\int_{-\infty}^{\infty} \delta(x)dx = 1 \quad \text{and} \quad \delta(x) = 0 \quad \text{for } x \neq 0\,. \tag{D.1}$$

No ordinary function we know from our calculus courses satisfies these properties. Nevertheless, the δ-function permeates our mathematical description of the physical world. We have also made use of this function in Sect. 3.15 and, more extensively, in Chap. 4. This appendix summarizes important facts about the **Dirac δ-function**.

D.1 Definition of $\delta(x)$

Let $\theta(x)$ denote a step function:

$$\theta(x) = \begin{cases} 1 \text{ if } x \geq 0 \\ 0 \text{ if } x < 0\,. \end{cases} \tag{D.2}$$

Because $\theta(x)$ is discontinuous at $x = 0$, it is *not* differentiable there. If we denote its derivative by $\delta(x)$:

$$\delta(x) := \frac{\mathrm{d}\theta(x)}{\mathrm{d}x}\,, \tag{D.3}$$

it is not well-defined at $x = 0$. Nevertheless, it is possible to assign a meaning to a definite integral

$$\int_{-\infty}^{\infty} f(x)\delta(x)\mathrm{d}x\,, \tag{D.4}$$

which contains the dangerous point $x = 0$.

I. Kusaka, *Statistical Mechanics for Engineers*,
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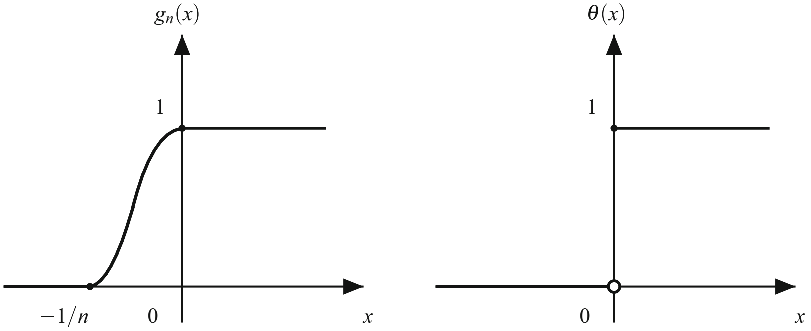

Fig. D.1 Behavior of $g_n(x)$ and $\theta(x) := \lim_{n\to\infty} g_n(x)$.

Let $g_n(x)$ $(n = 1, 2, \dots)$ denote a sequence of sufficiently smooth functions that approaches $\theta(x)$ as n tends toward infinity:

$$\lim_{n\to\infty} g_n(x) = \theta(x) . \tag{D.5}$$

Since $g_n(x)$ is sufficiently smooth, the integral

$$\int_{-\infty}^{\infty} f(x) \frac{\mathrm{d}g_n(x)}{\mathrm{d}x} \mathrm{d}x \tag{D.6}$$

exists for all n provided that $f(x)$ behaves nicely enough. If the limit

$$\lim_{n\to\infty} \int_{-\infty}^{\infty} f(x) \frac{\mathrm{d}g_n(x)}{\mathrm{d}x} \mathrm{d}x \tag{D.7}$$

exists also, then, we adopt

$$\int_{-\infty}^{\infty} f(x)\delta(x)\mathrm{d}x \quad \text{or} \quad \int_{-\infty}^{\infty} f(x) \frac{\mathrm{d}\theta(x)}{\mathrm{d}x} \mathrm{d}x \tag{D.8}$$

as a *compact notation* for that limit. Equation (D.7) should be contrasted against the mathematically ill-defined expression

$$\int_{-\infty}^{\infty} f(x) \frac{\mathrm{d}}{\mathrm{d}x} \left[\lim_{n\to\infty} g_n(x)\right] \mathrm{d}x , \tag{D.9}$$

which is suggested by a more literal interpretation of (D.4).

As an example of $g_n(x)$, let us consider the function depicted in Fig. D.1. More precisely, we set

$$g_n(x) = \begin{cases} 1 \text{ if } x \geq 0 \\ 0 \text{ if } x \leq -1/n , \end{cases} \tag{D.10}$$

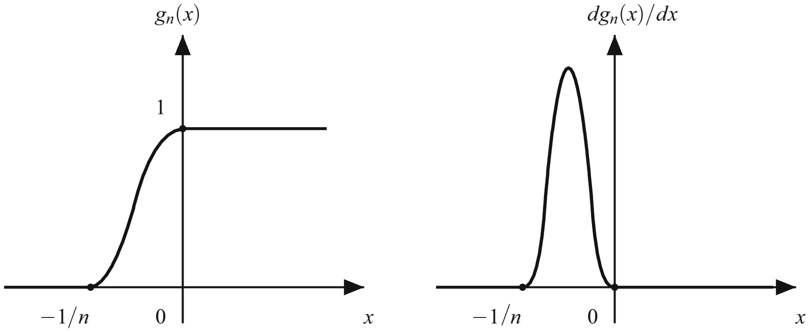

Fig. D.2 Behavior of $g_n(x)$ and $\mathrm{d}g_n(x)/\mathrm{d}x$.

in which n is a positive constant. In between $x = -1/n$ and $x = 0$, we demand that $g_n(x)$ is sufficiently smooth and monotonic. For convenience, we also suppose that the inflection point, at which $\mathrm{d}^2 g_n(x)/\mathrm{d}x^2 = 0$, occurs only once at $x = -1/2n$. For such $g_n(x)$, the derivative $\mathrm{d}g_n(x)/\mathrm{d}x$ is nonzero only for $-1/n < x < 0$ and it takes the maximum value only once at $x = -1/2n$. This is shown in Fig. D.2. As a result, we can rewrite the integral in (D.6) as

$$\int_{-\infty}^{\infty} f(x) \frac{\mathrm{d}g_n(x)}{\mathrm{d}x} \mathrm{d}x = \int_{-1/n}^{0} f(x) \frac{\mathrm{d}g_n(x)}{\mathrm{d}x} \mathrm{d}x \,. \tag{D.11}$$

Integrating by parts, we obtain

$$\begin{aligned}\int_{-1/n}^{0} f(x) \frac{\mathrm{d}g_n(x)}{\mathrm{d}x} \mathrm{d}x &= [f(x) g_n(x)]_{-1/n}^{0} - \int_{-1/n}^{0} \frac{\mathrm{d}f(x)}{\mathrm{d}x} g_n(x) \mathrm{d}x \\ &= f(0) - \int_{-1/n}^{0} \frac{\mathrm{d}f(x)}{\mathrm{d}x} g_n(x) \mathrm{d}x \,.\end{aligned} \tag{D.12}$$

But, the last term of this equation becomes vanishingly small with increasing n. So,

$$\lim_{n \to \infty} \int_{-\infty}^{\infty} f(x) \frac{\mathrm{d}g_n(x)}{\mathrm{d}x} \mathrm{d}x = f(0) \,. \tag{D.13}$$

In terms of the compact notation we introduced, this may be written as

$$\int_{-\infty}^{\infty} f(x) \delta(x) \mathrm{d}x = f(0) \,, \tag{D.14}$$

which is the desired result.

Exercise D.1. Show that

$$\int_{-\infty}^{\infty} f(x) \delta(x - a) \mathrm{d}x = f(a) \,. \tag{D.15}$$

///

It is certainly nice not having to write $\lim_{n\to\infty}$ all the time. But, does our notation make good sense at all? By concealing the limiting process, which we used to get rid of the last term in (D.12), do we not run a risk of making some serious mistakes? So, let us see what happens if we ignore the fact that $\delta(x) = \mathrm{d}\theta(x)/\mathrm{d}x$ does not exist at $x = 0$ and proceed with (D.8). Since $\theta(x) = 0$ for $x < 0$,

$$\begin{aligned}\int_{-\infty}^{\infty} f(x)\delta(x)\mathrm{d}x &= \int_{-\infty}^{+\infty} f(x)\frac{\mathrm{d}\theta(x)}{\mathrm{d}x}\mathrm{d}x = [f(x)\theta(x)]_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty} \frac{\mathrm{d}f(x)}{\mathrm{d}x}\theta(x)\mathrm{d}x \\ &= f(+\infty) - \int_{0}^{+\infty} \frac{\mathrm{d}f(x)}{\mathrm{d}x}\mathrm{d}x = f(+\infty) - f(+\infty) + f(0) = f(0)\end{aligned} \tag{D.16}$$

in agreement with (D.14). This demonstrates that our compact notation, in which (D.7) is written as (D.8), is perfectly acceptable.

It is instructive to seek for an alternative and more intuitive justification of (D.14). To begin with, we see immediately that

$$\int_{-\infty}^{\infty} \frac{\mathrm{d}g_n(x)}{\mathrm{d}x}\mathrm{d}x = [g_n(x)]_{-\infty}^{\infty} = 1 - 0 = 1\ . \tag{D.17}$$

This relation holds for any n. Thus, going to the large n limit, we find

$$\int_{-\infty}^{\infty} \delta(x)\mathrm{d}x = 1\ . \tag{D.18}$$

According to (D.18),

$$\int_{-\infty}^{\infty} f(x)\delta(x)\mathrm{d}x \tag{D.19}$$

may be considered as a weighted average of $f(x)$ with $\delta(x)$ playing the role of the weighting function. If we regard $\delta(x)$ as $\mathrm{d}g_n(x)/\mathrm{d}x$ in the limit of $n \to \infty$, then, $\delta(x)$ is seen to be extremely sharply peaked near $x = 0$. If $f(x)$ is continuous and varies slowly in this critical region, then, $f(x)$ under the integral sign may be replaced by $f(0)$ and taken outside:

$$\int_{-\infty}^{\infty} f(x)\delta(x)\mathrm{d}x = f(0)\int_{-\infty}^{\infty} \delta(x)\mathrm{d}x = f(0)\ , \tag{D.20}$$

where the last equality follows from (D.18).

To summarize, *the Dirac δ-function arises whenever we differentiate a discontinuous function such as $\theta(x)$*. Even though a function is not differentiable at the point of discontinuity, we can ignore this inconvenient fact and carry out the computation consistently *provided that $\delta(x)$ occurs only inside the integral.*

In essence, we pretend that any discontinuity we encounter in our theoretical description of the physical world, such as $\theta(x)$, is an idealization of what is really a continuous transition as described by $g_n(x)$. The alternative approach of not differentiating any function at its point of discontinuity is too restrictive for many of our purposes.

D.2 Basic Properties of the δ-Function

The δ-function satisfies a number of useful identities. Here, we list several famous examples:

a.

$$\delta(-x) = \delta(x) \, . \tag{D.21}$$

b.

$$x\delta(x) = 0 \, . \tag{D.22}$$

c.

$$\delta(\pm ax) = \frac{1}{a}\delta(x) \quad (a > 0) \, , \tag{D.23}$$

which is often expressed as

$$\delta(ax) = \frac{1}{|a|}\delta(x) \quad (a \neq 0) \, . \tag{D.24}$$

d.

$$\delta(x^2 - a^2) = \frac{1}{2|a|}\left[\delta(x-a) + \delta(x+a)\right] \, . \tag{D.25}$$

e.

$$\int_{-\infty}^{\infty} \delta(a-x)\delta(b-x)\mathrm{d}x = \delta(a-b) \, . \tag{D.26}$$

f.

$$f(x)\delta(x-a) = f(a)\delta(x-a) \, . \tag{D.27}$$

g.

$$\delta(g(x)) = \sum_i \frac{\delta(x-a_i)}{|g'(a_i)|} \, , \tag{D.28}$$

where a_i is the ith root of $g(x)$. It is assumed that there are no coincident roots, that is, $g'(a_i) \neq 0$.

Equation (D.21) might appear surprising in view of the graph for $\mathrm{d}g_n(x)/\mathrm{d}x$ shown in Fig. D.2. We must remember, however, that $\delta(x)$ is defined only in terms of an integration in which $\delta(x)$ occurs as a factor in the integrand. Thus, (D.21) should really be interpreted as

$$\int_{-\infty}^{\infty} f(x)\delta(x)\mathrm{d}x = \int_{-\infty}^{\infty} f(x)\delta(-x)\mathrm{d}x \, . \tag{D.29}$$

The same remark applies to other identities.

Exercise D.2. Prove (D.21) – (D.28). ///

Despite the wild variation of $\delta(x)$ at $x = 0$, it is still meaningful to talk about its derivative $\delta'(x)$ provided that it occurs only inside an integral. As with $\delta(x)$, the key is in the proper definition of such integrals. By definition then,

$$\int_{-\infty}^{\infty} f(x)\delta'(x)\mathrm{d}x := \lim_{n\to\infty}\int_{-\infty}^{\infty} f(x)\frac{\mathrm{d}^2 g_n(x)}{\mathrm{d}x^2}\mathrm{d}x\,. \tag{D.30}$$

By applying integration by parts, either to the expression on the left or to that on the right, it is straightforward to show that

$$\int_{-\infty}^{\infty} f(x)\delta'(x)\mathrm{d}x = -f'(0)\,, \tag{D.31}$$

where $f'(x) = \mathrm{d}f(x)/\mathrm{d}x$.

Exercise D.3. Prove (D.31). ///

Exercise D.4. Prove the following identities

a.

$$x\delta'(x) = -\delta(x)\,. \tag{D.32}$$

b.

$$\delta'(x-y) = -\delta'(y-x)\,. \tag{D.33}$$

The second identity implies that $\delta'(x)$ is an odd function. This is what we expect since $\delta(x)$ is an even function as indicated in (D.21). (Recall $\cos\theta$ and $\sin\theta$.) ///

Higher derivatives of the δ-function can be defined analogously. Thus,

$$\begin{aligned}\int_{-\infty}^{\infty} f(x)\delta''(x)\mathrm{d}x &:= \lim_{n\to\infty}\int_{-\infty}^{\infty} f(x)\frac{\mathrm{d}^3 g_n(x)}{\mathrm{d}x^3}\mathrm{d}x\,,\\ \int_{-\infty}^{\infty} f(x)\delta'''(x)\mathrm{d}x &:= \lim_{n\to\infty}\int_{-\infty}^{\infty} f(x)\frac{\mathrm{d}^4 g_n(x)}{\mathrm{d}x^4}\mathrm{d}x\,,\end{aligned} \tag{D.34}$$

and so on. Combined with (B.6), this leads to the following Taylor series expansion of the δ-function:

$$\delta(x+a) = \delta(x) + \delta'(x)a + \frac{1}{2!}\delta''(x)a^2 + \frac{1}{3!}\delta'''(x)a^3 + \cdots\,. \tag{D.35}$$

At first sight, the formula seems incorrect because $\delta(x+a) = 0$ for all $x \neq -a$ and the right-hand side is zero except at $x = 0$. However, identities involving the δ-function and its derivatives must be understood under the integral sign. The limits of integration is to some extent arbitrary, but it must include all the critical points of the integrand, which are $x = -a$ and $x = 0$ in this case. On the left-hand side, we have

$$\int_{-\infty}^{\infty} f(x)\delta(x+a)\mathrm{d}x = f(-a)\,. \tag{D.36}$$

On the right, we have several terms:

$$\int_{-\infty}^{\infty} f(x)\delta(x)\mathrm{d}x = f(0) , \quad \int_{-\infty}^{\infty} f(x)\delta'(x)\mathrm{d}x = -f'(0) ,$$
$$\int_{-\infty}^{\infty} f(x)\delta''(x)\mathrm{d}x = f''(0) , \quad \int_{-\infty}^{\infty} f(x)\delta'''(x)\mathrm{d}x = -f'''(0) ,\dots \tag{D.37}$$

where the last two equalities can be established by integration by parts. Thus,

$$\int_{-\infty}^{\infty} f(x)[\text{R.H.S.}]\mathrm{d}x = f(0) - af'(0) + \frac{1}{2!}a^2 f''(0) - \frac{1}{3!}a^3 f'''(0) + \cdots . \tag{D.38}$$

But, this is just the Taylor series expansion of $f(-a)$. In other words,

$$\int_{-\infty}^{\infty} f(x)[\text{R.H.S.}]\mathrm{d}x = f(-a) \tag{D.39}$$

Comparing (D.36) and (D.39), we see that (D.35) is valid.

D.3 Weak Versus Strong Definitions of the δ-Function

Dirac himself defined the δ-function by means of (D.1). The δ-function we constructed by means of $g_n(x)$ is consistent with this definition.[50] However, there are other ways of constructing a function that satisfies these defining properties.

As an illustration, let us consider the following step function:

$$\eta(x) = \begin{cases} 1 & \text{if } x > 0 \\ \frac{1}{2} & \text{if } x = 0 \\ 0 & \text{if } x < 0 , \end{cases} \tag{D.40}$$

which may be regarded as the large n limit of a smooth and monotonically increasing function $h_n(x)$ satisfying

$$h_n(x) = \begin{cases} 1 & \text{if } x > 1/2n \\ \frac{1}{2} & \text{if } x = 0 \\ 0 & \text{if } x < -1/2n . \end{cases} \tag{D.41}$$

Because

$$\int_{-\infty}^{\infty} \frac{\mathrm{d}h_n(x)}{\mathrm{d}x}\mathrm{d}x = 1 , \tag{D.42}$$

we see that $\delta(x) := \mathrm{d}\eta/\mathrm{d}x$ satisfies (D.18). It is also clear that this $\delta(x)$ is zero except at $x = 0$. So, this $\delta(x)$ is consistent with (D.1). Moreover, an analysis similar to what followed (D.11) indicates that

$$\lim_{n\to\infty} \int_{-\infty}^{\infty} f(x)\frac{\mathrm{d}h_n(x)}{\mathrm{d}x}\mathrm{d}x = f(0) . \tag{D.43}$$

We emphasize that the two versions of δ-function we considered are nonetheless not entirely identical. To see this, we note that

$$\int_{-\infty}^{0} \frac{\mathrm{d}g_n(x)}{\mathrm{d}x}\mathrm{d}x = 1 \quad \text{and} \quad \int_{0}^{\infty} \frac{\mathrm{d}g_n(x)}{\mathrm{d}x}\mathrm{d}x = 0\,, \tag{D.44}$$

and taking the limit $n \to \infty$,

$$\int_{-\infty}^{0} \delta(x)\mathrm{d}x = 1 \quad \text{and} \quad \int_{0}^{\infty} \delta(x)\mathrm{d}x = 0\,. \tag{D.45}$$

In contrast, for $h_n(x)$, we have

$$\int_{-\infty}^{0} \frac{\mathrm{d}h_n(x)}{\mathrm{d}x}\mathrm{d}x = \frac{1}{2} \quad \text{and} \quad \int_{0}^{\infty} \frac{\mathrm{d}h_n(x)}{\mathrm{d}x}\mathrm{d}x = \frac{1}{2}\,, \tag{D.46}$$

and hence

$$\int_{-\infty}^{0} \delta(x)\mathrm{d}x = \frac{1}{2} \quad \text{and} \quad \int_{0}^{\infty} \delta(x)\mathrm{d}x = \frac{1}{2}\,. \tag{D.47}$$

Neither (D.45) nor (D.47) is a part of the defining properties of $\delta(x)$. The original definition due to Dirac is called the **weak definition** of $\delta(x)$. When it is supplemented by (D.45), (D.47), or any other such relations, the definition is said to be **strong**. For our particular purposes, we find it more convenient to work with $\theta(x)$ as the step function rather than $\eta(x)$. Consequently, our δ-function satisfies (D.45) but not (D.47).

D.4 Three-Dimensional δ-Function

Let $\boldsymbol{r}$ be a position vector and (x,y,z) denote its components in a Cartesian coordinate system. Then, $\delta(\boldsymbol{r})$ is a short-hand notation expressing the following product of three one-dimensional δ-functions.

$$\delta(\boldsymbol{r}) := \delta(x)\delta(y)\delta(z)\,. \tag{D.48}$$

Evidently,

$$\int_V \delta(\boldsymbol{r})\mathrm{d}\boldsymbol{r} = \int\int\int \delta(x)\delta(y)\delta(z)\mathrm{d}x\mathrm{d}y\mathrm{d}z \tag{D.49}$$

is unity if the origin ($\boldsymbol{r} = \boldsymbol{0}$) is inside V and zero if it is outside V. If the origin is on the boundary of V, the value of this integral depends on the strong definition being adopted for the one-dimensional δ-function. Insofar as (D.49) is dimensionless, $\delta(\boldsymbol{r})$ has the dimension of the reciprocal volume.

D.5 †Representation of the δ-Function

Let us consider a function given by

$$h_n(x) = \sqrt{\frac{n}{\pi}}e^{-nx^2} \,. \tag{D.50}$$

Using (3.91), we see that

$$\int_{-\infty}^{\infty} h_n(x)\mathrm{d}x = 1 \quad \text{and} \quad \int_{-\infty}^{0} h_n(x)\mathrm{d}x = \int_{0}^{\infty} h_n(x)\mathrm{d}x = \frac{1}{2} \tag{D.51}$$

for any n. Moreover,

$$\lim_{n\to\infty} h_n(x) = 0 \quad \text{if } x \neq 0 \,. \tag{D.52}$$

Thus, the sequence of functions $h_n(x)$ defines the Dirac δ-function that is compatible with (D.47).

Another frequently encountered representation of the δ-function is given by

$$\delta(x) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{ikx}\mathrm{d}k \,, \tag{D.53}$$

where $i := \sqrt{-1}$ is the imaginary unit. To see this, let

$$f_n(x) := \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-\frac{k^2}{4n}+ikx}\mathrm{d}k \,. \tag{D.54}$$

In the limit of $n \to \infty$, the right-hand side approaches the integral in (D.53). On the other hand, $f_n(x)$ can be evaluated explicitly as follows. We first rewrite the exponent as

$$-\frac{k^2}{4n} + ikx = -\frac{1}{4}\left(\frac{k}{\sqrt{n}} - 2i\sqrt{n}x\right)^2 - nx^2 \,. \tag{D.55}$$

Using a new variable $s := (k/\sqrt{n} - 2i\sqrt{n}x)/2$, we find[51]

$$f_n(x) = \frac{\sqrt{n}}{\pi}\int_{-\infty}^{\infty} e^{-s^2}e^{-nx^2}\mathrm{d}s = \sqrt{\frac{n}{\pi}}e^{-nx^2} \to \delta(x) \quad \text{as } n \to \infty \,. \tag{D.56}$$

References and Further Reading

1. Barton B (1989) Elements of Green's Functions and Propagation: Potentials, Diffusion and Waves. Oxford University Press, New York
   A thorough, yet highly accessible, account of the δ-function is in Chap. 1.
2. Dirac P A M (1958) The Principles of Quantum Mechanics, 4th edn. Oxford University Press, New York
   It is still *very* instructive to see how Dirac himself explained his δ-function. See Sect. 15 of the book.

Appendix E
Where to Go from Here

Most of the following textbooks will be accessible to you by now, and should be consulted according to your interests and needs. I have only included textbooks I know reasonably well and feel comfortable recommending to students who have mastered the content of this book.

Statistical Mechanics in General

Chandler D (1987) Introduction to Modern Statistical Mechanics. Oxford, New York
A very concise yet extremely insightful account of statistical mechanics. Some familiarity with quantum mechanics will be useful in parts of the book.

Hill T L (1986) An Introduction to Statistical Thermodynamics. Dover, New York
Relatively accessible textbook on statistical mechanics with various applications.

Hill T L (1986) Statistical Mechanics, Principles and Selected Applications. Dover, New York
More advanced textbook by the same author and publisher as above.

Computer Simulation

Allen M P and Tildesley D J (1987) Computer Simulation of Liquids. Oxford, New York
Short overview of statistical mechanics followed by an in-depth exposition of the inner working of molecular level simulation. If you plan to do any kind of molecular simulation, this will be the best place to start.

Frenkel D and Smit B (2001) Understanding Molecular Simulation, 2nd edn. Academic Press, San Diego

I. Kusaka, *Statistical Mechanics for Engineers*,
DOI 10.1007/978-3-319-13809-1

Discussion on statistical mechanics is *very* short, but covers various advanced algorithm developed in recent years. My recommendation is that you'd read this after Allen & Tildesley.

Tuckerman M E (2010) Statistical Mechanics: Theory and Molecular Simulation. Oxford University Press, New York

Geared towards those with physics background. Nevertheless, chapters on molecular dynamics, free energy calculations, time-dependent phenomena will be accessible and may be of interest to you.

Theory of Liquids, Density Functional Theory

Goodstein D L (1985) States of Matter. Dover, New York

Chapter 4 provides a very nice introduction to integral equation theories of simple liquids.

Evans R (1979) The nature of the liquid-vapor interface and other topics in the statistical mechanics of non-uniform, classical fluids. Adv. Phys. 28:143–200

This isn't a book. But, it is probably the most cited article on the subject of statistical mechanical density functional theory.

Hansen J-P and McDonald I R (1986) Theory of Simple Liquids, 2nd edn. Academic Press, San Diego

Theories of liquids are treated in great depth.

Mean-Field Theory

Goldenfeld N (1992) Lectures on Phase Transitions and the Renormalization Group. Addison-Wesley, Reading, Massachusetts

Highly accessible book on phase transition. Though the focus is on critical phenomena, that is, phase behavior near the critical point, the first several chapters provide a systematic treatment of the mean-field theory.

Appendix F
List of Greek Letters

Greek letters are frequently used in this book, and are listed here for convenience.

Name	Uppercase	Lowercase	Name	Uppercase	Lowercase
alpha	A	α	nu	N	ν
beta	B	β	xi	Ξ	ξ
gamma	Γ	γ	omicron	O	o
delta	Δ	δ	pi	Π	π
epsilon	E	ε	rho	P	ρ
zeta	Z	ζ	sigma	Σ	σ
eta	H	η	tau	T	τ
theta	Θ	θ	upsilon	Υ	υ
iota	I	ι	phi	Φ	ϕ
kappa	K	κ	chi	X	χ
lambda	Λ	λ	psi	Ψ	ψ
mu	M	μ	omega	Ω	ω

I. Kusaka, *Statistical Mechanics for Engineers*,
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Appendix G
Hints to Selected Exercises

Chapter 1

1.1 Since the work required to bring a particle from $\boldsymbol{r}_A$ to $\boldsymbol{r}_{A'}$ is independent of the path taken, we have

$$\psi(\boldsymbol{r}_A,\boldsymbol{r}_{A'}) = \psi(\boldsymbol{r}_A,\boldsymbol{r}) + \psi(\boldsymbol{r},\boldsymbol{r}_{A'}) = \psi(\boldsymbol{r}_A,\boldsymbol{r}) - \psi(\boldsymbol{r}_{A'},\boldsymbol{r}) \,. \tag{G1.1}$$

1.3 Note that

$$\sum_i m_i \boldsymbol{v}_i{}' = \frac{\mathrm{d}}{\mathrm{d}t}\sum_i m_i \boldsymbol{r}_i{}' = \frac{\mathrm{d}}{\mathrm{d}t}\sum_i m_i(\boldsymbol{r}_i - \boldsymbol{R}) = \boldsymbol{0} \,. \tag{G1.2}$$

1.5 Eliminating T from (1.85), we find

$$m(\ddot{x}\cos\theta + \ddot{y}\sin\theta) = -mg\sin\theta \,. \tag{G1.3}$$

But, $\ddot{x}$ and $\ddot{y}$ can be computed by taking the time derivative of (1.76).

1.6

a. The work required to stretch (or compress) the spring from its natural length l_0 to r is given by

$$W = -\int_{l_0}^{r} \boldsymbol{F}\cdot\mathrm{d}\boldsymbol{r} \,, \tag{G1.4}$$

in which $\mathrm{d}\boldsymbol{r} = \mathrm{d}r\boldsymbol{e}_r$ for both stretching and compression. This work is stored in the harmonic spring as its potential energy.

b.

$$L = \frac{1}{2}m[\dot{r}^2 + (r\dot{\theta})^2] + mgr\cos\theta - \frac{1}{2}k(r-l_0)^2 \,. \tag{G1.5}$$

1.7 Start from

$$L = \frac{1}{2}m_1\dot{\boldsymbol{r}}_1{}^2 + \frac{1}{2}m_2\dot{\boldsymbol{r}}_2{}^2 - \phi(\boldsymbol{r}_1 - \boldsymbol{r}_2) \tag{G1.6}$$

and use the definitions for $\boldsymbol{R}$ and $\boldsymbol{r}$ to express $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ in terms of $\boldsymbol{R}$ and $\boldsymbol{r}$.

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Derive Lagrange's equations of motion to see why using $\boldsymbol{R}$ and $\boldsymbol{r}$ is more advantageous than using $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$.

1.8 Since F is a function of q_i's and t only,

$$\frac{\mathrm{d}F}{\mathrm{d}t} = \sum_{j=1}^{f} \frac{\partial F}{\partial q_j}\dot{q}_j + \frac{\partial F}{\partial t} , \tag{G1.7}$$

from which we obtain

$$\frac{\partial}{\partial \dot{q}_i}\frac{\mathrm{d}F}{\mathrm{d}t} = \frac{\partial F}{\partial q_i} \tag{G1.8}$$

and

$$\frac{\partial}{\partial q_i}\frac{\mathrm{d}F}{\mathrm{d}t} = \sum_{j=1}^{f} \frac{\partial^2 F}{\partial q_i \partial q_j}\dot{q}_j + \frac{\partial^2 F}{\partial q_i \partial t} . \tag{G1.9}$$

1.10 Take the origin to coincide with the source of the field and note that $\boldsymbol{M} := \boldsymbol{r}\times\boldsymbol{p}$ is perpendicular to $\boldsymbol{r}$.

1.13 From (1.156),

$$\left(\frac{\partial H}{\partial t}\right)_{q,p} = \sum_i p_i \left(\frac{\partial \dot{q}_i}{\partial t}\right)_{q,p} - \left(\frac{\partial L}{\partial t}\right)_{q,p} , \tag{G1.10}$$

where the subscripts q, p indicate that all of $q_1, \dots, q_f$ and $p_1, \dots, p_f$ are held fixed when evaluating the partial derivatives. Evaluate $(\partial L/\partial t)_{q,p}$ from

$$\mathrm{d}L = \sum_i \left[\left(\frac{\partial L}{\partial q_i}\right)_{q_{j\neq i},\dot{q}} \mathrm{d}q_i + \left(\frac{\partial L}{\partial \dot{q}_i}\right)_{q,\dot{q}_{j\neq i}} \mathrm{d}\dot{q}_i\right] + \left(\frac{\partial L}{\partial t}\right)_{q,\dot{q}} \mathrm{d}t , \tag{G1.11}$$

where the subscripts $q_{j\neq i}, \dot{q}$ indicates that all of $q_1, \dots, q_f$ except for q_i and all of $\dot{q}_1, \dots, \dot{q}_f$ are held fixed.

1.18 Since $\{A, B\}$ is a dynamical variable, (1.185) applies:

$$\frac{\mathrm{d}}{\mathrm{d}t}\{A,B\} = \{\{A,B\},H\} + \frac{\partial}{\partial t}\{A,B\} . \tag{G1.12}$$

Chapter 2

2.1

c. For an adiabatic reversible expansion, $\mathrm{d}S = 0$.
d. For the process under consideration, both S and N remain constant. From (2.39), we see that

$$U_2{}^{3/2} V_2 = U_1{}^{3/2} V_1 , \tag{G2.1}$$

which may be solved for U_2. Alternatively,

$$U_2 - U_1 = W = -\int_{V_1}^{V_2} P\mathrm{d}V \;, \tag{G2.2}$$

in which P may be expressed as a function of V by means of (2.42).

2.2

a. Note that S, U, V, and N are all extensive quantities. When U, V, N are doubled, S must double as well.

2.3

a. For a constant V and $N_1, \ldots, N_c$ process,

$$đQ = \mathrm{d}U = T\mathrm{d}S \;. \tag{G2.3}$$

2.5 For the process under consideration, $\mathrm{d}S = 0$ and hence

$$\mathrm{d}U = -P\mathrm{d}V = \frac{C_V}{NR}(P\mathrm{d}V + V\mathrm{d}P) \;. \tag{G2.4}$$

2.7

a. The fundamental equation of pure i is obtained by setting $N_{j\neq i}$ to zero:

$$S = aN_i + N_iR\left(\frac{3}{2}\ln U + \ln V - \frac{5}{2}\ln N_i\right) \;. \tag{G2.5}$$

After equilibrium is established,

$$T_f^a = T_f^b . \tag{G2.6}$$

In view of (2.26) and (G2.5), this is an equation for U_f^a and U_f^b, the final values of the internal energy in compartments A and B, respectively. We need one more equation for these two unknowns. But, since the composite system is isolated,

$$U_f^a + U_f^b = U_0^a + U_0^b \;, \tag{G2.7}$$

where the subscript 0 refers to the initial state. From (G2.6) and (G2.7), we find that the final temperature is 328.6 K.

b. In addition to (G2.6) and (G2.7), we have

$$\mu_{1f}^a = \mu_{1f}^b \;, \tag{G2.8}$$

and

$$N_{1f}^a + N_{1f}^b = N_1 = 10\;(\mathrm{mol}). \tag{G2.9}$$

These four equations lead to $N_{1f}^a = N_{1f}^b = 5$ mol and 328.6 K for the final temperature.

2.10

a. Because the system is isolated, N_i can change only through the chemical reaction. From the stoichiometry of the reaction, we have

$$\delta N_1 = -\frac{c_1}{c_3}\delta N_3 \quad \text{and} \quad \delta N_2 = -\frac{c_2}{c_3}\delta N_3 \,. \tag{G2.10}$$

Use these relations in the expression for δS.

2.11 Show that

$$s_f = s_1 + \frac{s_2 - s_1}{u_2 - u_1}(u_0 - u_1) \tag{G2.11}$$

and interpret this equation graphically. Note also that

$$s_f V = s_1 V_1 + s_2 V_2 \quad \text{and} \quad u_0 V = u_1 V_1 + u_2 V_2 \,, \tag{G2.12}$$

where V_i denotes the volume of the part having the internal energy density u_i.

2.14 Recall that the molar internal energy $\underline{U} := U/N$ of an ideal gas is a function only of T and hence remains constant for an isothermal process. In addition, from (2.146), P is constant for processes in which T and μ are both constant as in steps a and c. (This holds true for a single component system in general as we shall see in Sect. 2.11.)

You will also have to choose a convention for the definition of heat. Adopting the Convention 2 in Sect. 2.6.5, we have the following results for each step, where ΔU, W, and Q are, respectively, the change in the internal energy of the working fluid, work done *on* the working fluid, and the heat received *by* the fluid:

a. $\Delta U = \underline{U}\Delta N$, $W = -RT\Delta N$, and $Q = (\underline{U} + RT)\Delta N$.
b. $\Delta U = 0$, $W = -(N + \Delta N)(\mu_h - \mu_l)$, and $Q = (N + \Delta N)(\mu_h - \mu_l)$.
c. $\Delta U = -\underline{U}\Delta N$, $W = RT\Delta N$, and $Q = -(\underline{U} + RT)\Delta N$.
d. $\Delta U = 0$, $W = N(\mu_h - \mu_l)$, and $Q = -N(\mu_h - \mu_l)$.

2.17

a. 2 mol.
b. 3 mol. In part c, you will see that this corresponds to the minimum of G even though $\mu_1^a \neq \mu_1^b$.

2.20 At given T and $\mu_1, \dots, \mu_c$, Ω of a homogeneous system is a *linear* function of V.

2.21

a. Looking at the variables with respect to which derivatives are computed and the list of variables being fixed, we see that T, V, and $N_1, \dots, N_c$ are used as the independent variables in this problem. The Helmholtz free energy F becomes a fundamental equation when expressed in terms of these variables. So, you can probably do something with F.

2.22 The number of Maxwell relations we have is

$$\frac{(c+2)(c+1)}{2}(2^{c+2}-1)\,. \tag{G2.13}$$

For $c=1$, this amounts to 21. For $c=2$, the number of Maxwell relations is 90. Of course, not all of them are of any use. This little computation also tells you that you should *never* attempt to memorize Maxwell relations. Knowing how to derive one when needed is more important.

2.23 Note that $\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V$ holds for *any* process in which $N_1,\dots,N_c$ are held fixed. In particular, it holds for a process in which T is also fixed.

Chapter 3

3.2

a. Note that

$$\frac{\partial C}{\partial\beta} = \int \frac{\partial}{\partial\beta} e^{-\beta H(q^f,p^f)}\mathrm{d}q^f\mathrm{d}p^f = \int (-H)e^{-\beta H(q^f,p^f)}\mathrm{d}q^f\mathrm{d}p^f\,. \tag{G3.1}$$

b. Note that

$$\begin{aligned}\left\langle (H-\langle H\rangle)^2\right\rangle &= \left\langle H^2 - 2H\langle H\rangle + \langle H\rangle^2\right\rangle = \langle H^2\rangle - 2\langle H\rangle\langle H\rangle + \langle H\rangle^2\\ &= \langle H^2\rangle - \langle H\rangle^2\,.\end{aligned} \tag{G3.2}$$

c. In evaluating the partial derivative of C, the limits of integrals and the number of mechanical degrees of freedom f are both treated as constant. This implies that the system volume and the number of particles in it are both fixed.

3.4 Evaluate

$$[I(a)]^2 = \left[\int_0^\infty e^{-ax^2}\mathrm{d}x\right] \times \left[\int_0^\infty e^{-ay^2}\mathrm{d}y\right] \tag{G3.3}$$

using polar coordinates. To do this, replace $\mathrm{d}x\mathrm{d}y$ by $r\mathrm{d}\theta\mathrm{d}r$. Other equations are obtained by repeatedly differentiating $I(a)$ with respect to a.

3.5 The probability we seek is the integration of $e^{-\beta H}\mathrm{d}\boldsymbol{r}^N\mathrm{d}\boldsymbol{p}^N/C$ with respect to $\boldsymbol{r}^N$ and $\boldsymbol{p}_2,\dots,\boldsymbol{p}_N$.

3.8

a. We need to find the Hamiltonian first. Recall Exercise 1.7, where we considered the Lagrangian of two particles interacting through the interparticle potential $\phi(\boldsymbol{r})$. Here, $\boldsymbol{r} := \boldsymbol{r}_1 - \boldsymbol{r}_2$ is the vector pointing from m_2 to m_1. Now, ϕ is usually a function only of $\|\boldsymbol{r}\|$. In this part of the problem, $\|\boldsymbol{r}\| = l$ is constant and ϕ can be dropped from the Lagrangian. Thus,

$$L = \frac{1}{2}M\|\dot{\boldsymbol{R}}\|^2 + \frac{1}{2}\mu\|\dot{\boldsymbol{r}}\|^2 \, . \tag{G3.4}$$

Note that, even though $\|\boldsymbol{r}\|$ is constant, $\dot{\boldsymbol{r}}$ is not necessarily zero since $\boldsymbol{r}$ can still change its orientation.

b. $C_V = 5k_B/2$.

c. $C_V = 7k_B/2$. Note that

$$\int_{-l}^{\infty}(x+l)^2 e^{-\beta k x^2/2}\mathrm{d}x \approx \int_{-\infty}^{\infty}(x+l)^2 e^{-\beta k x^2/2}\mathrm{d}x = \int_{-\infty}^{\infty}(x^2+l^2)e^{-\beta k x^2/2}\mathrm{d}x \, , \tag{G3.5}$$

where $x := r - l$.

3.9

b. When considering $\partial H/\partial \boldsymbol{E}$, recall that

$$\frac{\partial H}{\partial \boldsymbol{E}} \doteq \left(\frac{\partial H}{\partial E_x}, \frac{\partial H}{\partial E_y}, \frac{\partial H}{\partial E_z}\right) \tag{G3.6}$$

and that

$$\boldsymbol{m}_e \cdot \boldsymbol{E} = m_{ex}E_x + m_{ey}E_y + m_{ez}E_z \, . \tag{G3.7}$$

c. Take appropriate partial derivatives of $E^2 = {E_x}^2 + {E_y}^2 + {E_z}^2$.

3.10 Which step of the derivation breaks down in the absence of the surroundings?

3.11 Consider a system AB consisting of two subsystems A and B. Assuming that the interaction between A and B is sufficiently weak, show that

$$-S_{ab}/k_B = \langle \ln \rho_{ab} \rangle_{ab} = \langle \ln \rho_a \rangle_a + \langle \ln \rho_b \rangle_b \, , \tag{G3.8}$$

where, the thermal average $\langle X \rangle_{ab}$ is defined by

$$\langle X \rangle_{ab} := \frac{\int X e^{-\beta H_{ab}}\mathrm{d}q^m \mathrm{d}p^m \mathrm{d}q^n \mathrm{d}p^n}{\int e^{-\beta H_{ab}}\mathrm{d}q^m \mathrm{d}p^m \mathrm{d}q^n \mathrm{d}p^n} \tag{G3.9}$$

for any dynamical variable X, where (q^m, p^m) denotes the generalized coordinates and momenta of subsystem A, while (q^n, p^n) denotes those of subsystem B. Similarly,

$$\langle Y \rangle_a := \frac{\int Y e^{-\beta H_a}\mathrm{d}q^m \mathrm{d}p^m}{\int e^{-\beta H_a}\mathrm{d}q^m \mathrm{d}p^m} \tag{G3.10}$$

and likewise for the thermal averages for subsystem B.

3.12 Compute C' and show that F/N is independent of the size of the system using (3.153).

3.13 Draw a graph for $\ln x$. Then, note that

$$\ln N! = \sum_{i=1}^{N} \ln i \tag{G3.11}$$

and interpret the right-hand side graphically.

3.15 Recall that the number of mechanical degrees of freedom is the number of variables we need to specify in order to uniquely determine the configuration of the system. This number is 5.

For example, we can give the Cartesian coordinates (x_2, y_2, z_2) of the particle of mass m_2 and then specify the orientation of the bond connecting the two particles by giving two polar angles θ and ϕ. The former can be replaced by (X, Y, Z), the coordinates of the center of mass of the molecule. But, the degrees of freedom still is 5.

Alternatively, we can argue as follows. The positions of particles can be specified by 6 variables (x_1, y_1, z_1) and (x_2, y_2, z_2). However, these variables are not all independent. Instead, they are subject to the constraint that

$$(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2 = l^2 \,. \tag{G3.12}$$

Thus, the number of independent variables, or the number of variables we need to specify, is $6 - 1 = 5$.

3.16

a.

$$Z = \frac{V^N}{\Lambda^{3N} N!} \,, \tag{G3.13}$$

where $\Lambda := h/\sqrt{2\pi m k_B T}$.

3.17 From (2.174), $W^{\text{rev}} = F_f - F_i = k_B T \ln Z_i / Z_f$ for an isothermal process, where subscripts i and f refer to the initial and final state, respectively.

3.18

$$m_i \frac{\mathrm{d}^2 \boldsymbol{r}_i^a}{\mathrm{d}t^2} = m_i \boldsymbol{b} - \frac{\partial \phi}{\partial \boldsymbol{r}_i^a} \,. \tag{G3.14}$$

3.19 Lagrange's equations of motion lead to

$$m_i \frac{\mathrm{d}}{\mathrm{d}t}(\boldsymbol{v}_i + \boldsymbol{V}) = m_i \boldsymbol{b} - \frac{\partial \phi}{\partial \boldsymbol{r}_i} \,. \tag{G3.15}$$

To see that this reduces to (G3.14), recall (3.229) and note that

$$\phi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) = \phi(\boldsymbol{r}_1 + \boldsymbol{R}, \ldots, \boldsymbol{r}_N + \boldsymbol{R}) = \phi(\boldsymbol{r}_1^a, \ldots, \boldsymbol{r}_N^a) \tag{G3.16}$$

since ϕ is a function only of the relative position of the particles. Using $\partial \boldsymbol{r}_i^a / \partial \boldsymbol{r}_i = \hat{\boldsymbol{I}}$, where $\hat{\boldsymbol{I}}$ is the unit matrix, we have

$$\frac{\partial \phi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)}{\partial \boldsymbol{r}_i} = \frac{\partial \phi(\boldsymbol{r}_1^a, \ldots, \boldsymbol{r}_N^a)}{\partial \boldsymbol{r}_i^a} \,. \tag{G3.17}$$

3.20 From Lagrange's equations of motion, we find

$$m_i \frac{\mathrm{d}\boldsymbol{v}_i}{\mathrm{d}t} = m_i \left(\boldsymbol{b} - \frac{\mathrm{d}\boldsymbol{V}}{\mathrm{d}t} \right) - \frac{\partial \phi}{\partial \boldsymbol{r}_i} \,. \tag{G3.18}$$

Moving the $m_i \mathrm{d}\boldsymbol{V}/\mathrm{d}t$ term to the left, we see that this is noting but (G3.15). We also see that the force exerted on the ith particle by the external field is modified by $-\mathrm{d}\boldsymbol{V}/\mathrm{d}t$. In particular, if $\mathrm{d}\boldsymbol{V}/\mathrm{d}t = \boldsymbol{b}$, then, the particle "feels" no external field at all. If this seems surprising, recall how your body feels lighter when an elevator starts to go down. Extrapolate that feeling to a free fall, for which $\mathrm{d}\boldsymbol{V}/\mathrm{d}t = \boldsymbol{g}$.

3.22 Use (G3.14). Since ϕ depends only on the relative position of particles, we have

$$0 \equiv \phi(\boldsymbol{r}_1^a + \mathrm{d}\boldsymbol{r}, \ldots, \boldsymbol{r}_N^a + \mathrm{d}\boldsymbol{r}) - \phi(\boldsymbol{r}_1^a, \ldots, \boldsymbol{r}_N^a) = \sum_{i=1}^N \frac{\partial \phi}{\partial \boldsymbol{r}_i^a} \cdot \mathrm{d}\boldsymbol{r} + \mathrm{h.o.} \tag{G3.19}$$

for any $\mathrm{d}\boldsymbol{r}$, implying that

$$\sum_{i=1}^N \frac{\partial \phi}{\partial \boldsymbol{r}_i^a} \equiv \boldsymbol{0} \,. \tag{G3.20}$$

3.23 In (3.274),

$$\boldsymbol{p}_i \cdot \boldsymbol{\Omega} \times \boldsymbol{r}_i = \boldsymbol{\pi}_i \cdot (\boldsymbol{\Omega} \times \boldsymbol{r}_i) + m_i \|\boldsymbol{\Omega} \times \boldsymbol{r}_i\|^2 \,. \tag{G3.21}$$

Chapter 4

4.1 If A and B are distinct species, then,

$$S^f - S^i = k_B \ln C_M^f - k_B \ln C_M^i = 2N k_B \ln 2 \,. \tag{G4.1}$$

If A and B are identical species, then,

$$S^f - S^i = k_B \ln \left[2^{2N} \frac{(N!)^2}{(2N)!} \right] \,. \tag{G4.2}$$

Using (3.153),

$$S^f - S^i \approx 0 \tag{G4.3}$$

for a large enough N. Using (3.152) instead, we see that

$$\frac{S^f - S^i}{k_B N} \approx \frac{1}{2N} \ln(\pi N) , \tag{G4.4}$$

which vanishes with increasing N. This is what one expects since, macroscopically, the initial and the final states are identical.

What about small N? For $N = 3$, for example, $(S_f - S_i)/k_B = \ln(16/5)$, which is not negligible. This should not be a surprise, though. With the partition now removed, the system can explore a much larger number of microstates, such as those in which all the particles occupy the same half of the total available volume $2V$. Such states were not accessible when the partition was in place. As N increases, however, microstates are completely dominated by those with equal (or nearly equal) partitioning of particles between the two compartments.

4.2

b. $\Gamma(1) = 1$.
c. $\Gamma(1/2) = \sqrt{\pi}$.

4.3

b. We divide the n-dimensional space into concentric spherical shells of width $\mathrm{d}r$ centered around the origin. Ignoring the higher order terms, the volume $\mathrm{d}S_n$ of the spherical shell can be written as

$$\mathrm{d}S_n = S_n(r + \mathrm{d}r) - S_n(r) = \frac{\mathrm{d}S_n}{\mathrm{d}r}\mathrm{d}r , \tag{G4.5}$$

where $S_n(r) := U_n r^n$. Thus,

$$\mathrm{d}S_n = nU_n r^{n-1}\mathrm{d}r \tag{G4.6}$$

and I_n may be written as

$$I_n = \int_0^\infty nU_n r^{n-1} e^{-r^2} \mathrm{d}r . \tag{G4.7}$$

d. Change variables by

$$\boldsymbol{s}_i := \frac{\boldsymbol{p}_i}{\sqrt{2mE}} . \tag{G4.8}$$

Note that this is a vector equation and that $\mathrm{d}\boldsymbol{s}_i$, for example, represents a volume element in three-dimensional space. Thus,

$$\mathrm{d}\boldsymbol{s}_i = \mathrm{d}s_{ix}\mathrm{d}s_{iy}\mathrm{d}s_{iz} = \frac{\mathrm{d}p_{ix}\mathrm{d}p_{iy}\mathrm{d}p_{iz}}{(2mE)^{3/2}} = \frac{\mathrm{d}\boldsymbol{p}_i}{(2mE)^{3/2}} . \tag{G4.9}$$

Also,

$$H = E\sum_{i=1}^{N} \|\boldsymbol{s}_i\|^2 \tag{G4.10}$$

4.5

$$S = -k_B \langle \ln(p/\overline{\Omega}) \rangle \, . \tag{G4.11}$$

We note that $p(E)\mathrm{d}E$ is the probability of finding the system in the energy interval $(E - \mathrm{d}E, E]$. The number of microstates within this interval is given by $\overline{\Omega}(E)\mathrm{d}E$. Thus, $p/\overline{\Omega}$ is the probability of find the system at a particular microstate. If microstates can be counted as in quantum mechanical systems, then, (G4.11) may be written as

$$S = -k_B \sum_i p_i \ln p_i \, , \tag{G4.12}$$

where the summation is over all microstates that are accessible to the system.

4.6

$$S = -k_B \langle \ln(A_w \Lambda_w p/\overline{\Omega}) \rangle \, . \tag{G4.13}$$

The expression in the natural logarithm can be interpreted as follows. Let us first rewrite it as

$$\frac{A_w \Lambda_w p(E,V)}{\overline{\Omega}(E,V)} = \frac{p(E,V)\mathrm{d}E\mathrm{d}V}{\overline{\Omega}(E,V)\mathrm{d}E \times \frac{\mathrm{d}V}{A_w \Lambda_w}} \, . \tag{G4.14}$$

In this expression, $p(E,V)\mathrm{d}E\mathrm{d}V$ is the probability that the system is found with its energy and volume in their respective intervals $(E - \mathrm{d}E, E]$ and $(V, V + \mathrm{d}V]$. The factor $\overline{\Omega}(E,V)\mathrm{d}E$ is the number of microstates consistent with the given interval of E when the system volume is *exactly* equal to V. From the discussion below (4.105), $\mathrm{d}V/A_w\Lambda_w$ may be regarded as “the number of states” accessible to the piston when the system volume is allowed to be anywhere in $(V, V + \mathrm{d}V]$. The denominator is then the number of microstates accessible to the system+piston consistent with the above intervals for E and V. Note that we may safely ignore here the change in $\overline{\Omega}$ due to the infinitesimal change in V as it leads a higher order term in the denominator of (G4.14). It follows that (G4.14) gives the probability of finding the system at a *particular* microstate.

4.7

$$Y = \frac{1}{\Lambda^{3N}} \left(\frac{k_B T}{P} \right)^{N+1} \, . \tag{G4.15}$$

4.10

c. You will need to prove two identities:

$$\left(\frac{\partial \mu}{\partial N} \right)_{T,V} = \frac{1}{N} \left(\frac{\partial P}{\partial n_v} \right)_T \quad \text{and} \quad \left(\frac{\partial n_v}{\partial P} \right)_T = \frac{\kappa_T}{\underline{V}} \, . \tag{G4.16}$$

The first one follows from the Gibbs–Duhem relation.

4.11

$$k_B T = \frac{2U}{3N} \, , \quad P = \frac{N k_B T}{V} \, , \quad \text{and} \quad \frac{e^{\beta\mu}}{\Lambda^3} = \frac{N}{V} \, . \tag{G4.17}$$

4.12

b. $-k_BT\ln X = 0$.

c.

$$X = \int_0^\infty e^{-\beta PV}\Xi \mathrm{d}V = \int_0^\infty \mathrm{d}V \neq 1\,. \tag{G4.18}$$

Chapter 5

5.2 The integral

$$\int e^{-\beta\psi(\boldsymbol{r}^{N_t})}\mathrm{d}\boldsymbol{r}^{N_t} \tag{G5.1}$$

in (5.9) may be separated into terms depending on the number N of adsorbed particles. Denoting by I_N the value of the integral obtained under the constraint that there are N adsorbed particles, we have

$$I_N = (V-v)^{N_t-N}\binom{M}{N}\frac{N_t!}{(N_t-N)!}A^N\,, \tag{G5.2}$$

where A is defined by (5.13). The coefficient $\binom{M}{N}$ is the number of distinct ways of choosing N sites among M sites. Then, $N_t!/(N_t-N)!$ gives the number of distinct ways of occupying these sites with N *distinguishable* particles chosen from the total of N_t particles. Note that the correction due to indistinguishability of identical particles is dealt with by the $N_t!$ factor in the partition function Z and plays no role at this stage. Here, we are simply trying to evaluate the integral given above. Suppose, for example, that $N=1$. As we allow each of $\boldsymbol{r}_1,\ldots,\boldsymbol{r}_{N_t}$ to move through the entire system under the constraint that $N=1$, each of them will be found inside a given adsorption site.

5.3 $T < 3w/(k_B\ln 9)$.

5.4

a. $\phi = x/(1+x)$, where $x := e^{\beta(\mu+\varepsilon)}$.

b.

$$\phi = \frac{\langle N\rangle}{4} = \frac{x+x^2+2x^2y+3x^3y^2+x^4y^4}{1+4x+2x^2+4x^2y+4x^3y^2+x^4y^4}\,, \tag{G5.3}$$

where $y := e^{\beta w}$.

c. $\phi = xy^{2\phi}/(1+xy^{2\phi})$.

5.5

a. Compare graphs for e^x and $1+x$.

b. $e^x = e^{\langle x\rangle}e^{x-\langle x\rangle}$.

c. $F_{\text{exact}} \leq F$. So, the free energy obtained under the mean-field approximation is an upper bound to the exact free energy.

5.6 Note that $\beta\mu = (\partial f/\partial\phi)_T$ as we saw in (5.52). Also, show that the intercept (at $\phi = 0$) of the tangent line is proportional to the pressure P of the two phases.

5.7

a. $T_c = zw/4k_B$.

Chapter 6

6.1 Using (6.19), find the expressions for δA, δV^α, and δV^β. Use them in (6.23).

Chapter 7

7.2 Recall the vector identity

$$\nabla \cdot [\boldsymbol{a}(\boldsymbol{x}) f(\boldsymbol{x})] = f(\boldsymbol{x}) \nabla \cdot \boldsymbol{a}(\boldsymbol{x}) + \boldsymbol{a}(\boldsymbol{x}) \cdot \nabla f(\boldsymbol{x}) \tag{G6.1}$$

where $\boldsymbol{a}$ is a vector-valued function of $\boldsymbol{x}$ while f is a scalar-valued function of $\boldsymbol{x}$. You will also need to use the divergence theorem:

$$\int_V \nabla \cdot \boldsymbol{a}(\boldsymbol{x}) \mathrm{d}\boldsymbol{r} = \int_A \boldsymbol{n} \cdot \boldsymbol{a}(\boldsymbol{x}) \mathrm{d}A \,, \tag{G6.2}$$

where A is the surface of V and $\boldsymbol{n}$ is the outward unit normal on A.

7.5 Show that

$$\Xi = \exp\left[\frac{e^{\beta\mu}}{\Lambda^3} \int_V e^{-\beta\psi(\boldsymbol{r})} \mathrm{d}\boldsymbol{r}\right] . \tag{G6.3}$$

7.6

a. Using (7.57), show that $n_a(\boldsymbol{r}) = n_b(\boldsymbol{r}) e^{\beta(\psi_b - \psi_a)}$, where we suppressed the $\boldsymbol{r}$ dependence of ψ's in the exponent.

7.7 Subtract (7.76) from the same equation applied to the perturbed state, in which the external field is $\psi_a + \delta\psi$ and the corresponding equilibrium density profile is $n_a + \delta n$.

7.8 Compute $\Omega[n_b + \delta n, \psi_b] - \Omega[n_b, \psi_b]$.

7.10 Note that

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = \left(\frac{\partial f}{\partial n}\right)_T \quad \text{and} \quad P = -f + \mu n \,. \tag{G6.4}$$

Chapter 8

8.1

a. Adding $\bar{x}$ to the both sides of $x+\theta' = x$, you get $\bar{x}+(x+\theta') = \bar{x}+x$. Then, use V2, V1, V4, V1, and V3 in this order to show that $\theta' = \theta$.
b. For the particular element x that is appearing in $0x$, show that $x+0x = x$ and then use part a.
c. Adding $\bar{x}$ on both sides of $x+y = \theta$, you get $\bar{x} = \bar{x}+(x+y)$. Using V2, V1, V4, V1, and V3 in this order, show that the right-hand side is y.
d. Show that $x+(-1)x = 0x$ and use parts b and c.
e. Using part d, $\alpha\bar{x} = \alpha[(-1)x]$.
f. Let $x \in V$. Then, for a particular vector $\alpha x \in V$, show that $\alpha x + \alpha\theta = \alpha x$ and use part a.
g. Show that $\alpha x + \alpha\bar{x} = \alpha\theta = \theta$ and use part c.

8.2

b. Set $\alpha = 0$ in (8.43) and notice that $0y = \theta$ from Exercise 8.1b.

8.3 Use induction. That is, first establish the orthogonality of b_1 and b_2 by directly computing (b_1, b'_2). Then, assuming that the vectors in the set $\{b_1, \ldots, b_m\}$ $(m < r)$ are orthogonal to each other, consider the scalar product between b_i $(i \leq m)$ and b'_{m+1}.

8.4 Since $\{b_1, \ldots, b_r\}$ forms a basis of V, we may write $x = \alpha_1 b_1 + \cdots + \alpha_r b_r$, where, from S1 and the orthonormality of the basis, $\alpha_i = (x, b_i)$.

8.5 Suppose that $F(x) = (x, f) = (x, g)$ for al $x \in V$ and deduce $f = g$.

8.6

(8.53): Use D1, F1, and D1 in this order.
(8.54): Use D1, F2, and D1 in this order.

8.7

$\widetilde{\mathrm{V}}3$: Show that a linear function Θ defined by $\Theta(x) := (x, \theta)$ serves as the zero vector in $\widetilde{V}$, where θ is the zero vector in V.
$\widetilde{\mathrm{V}}4$: Define $\overline{F} \in \widetilde{V}$ by $\overline{F}(x) := (x, \overline{f})$ for all $x \in V$ and show that $(F+\overline{F})(x) = \Theta(x)$.

8.8

a. Show that $T(x) + T(\theta_V) = T(x)$ for $x \in V$.

8.9 Show that $\langle\gamma| + \langle\theta| = \langle\gamma|$ for $\langle\gamma| \in V_k$.

8.11 Use (8.62), (8.63), and (8.73).

8.12 Let $|\gamma\rangle := c|\alpha\rangle$ and consider the adjoint of $\hat{X}^\dagger|\gamma\rangle$. You will need (8.67) and (8.79).

8.13 Use (8.85) twice to compute $\langle\alpha|(\hat{X}^\dagger)^\dagger|\beta\rangle$.

8.17

c. Show that $\langle\delta|\hat{X}^\dagger|\gamma\rangle = \langle\gamma|\hat{X}|\delta\rangle^* = \langle\delta|\beta\rangle\langle\alpha|\gamma\rangle$.

8.23 Start from $\langle\phi|\hat{A}|\phi\rangle$ and use a closure relation.

8.26 Using the closure relation,

$$\hat{x}|p\rangle = \int \hat{x}|x\rangle\langle x|p\rangle \mathrm{d}x = \int x|x\rangle\langle x|p\rangle \mathrm{d}x \,. \tag{G8.1}$$

8.29 The time dependence drops out if $\hat{A}$ is diagonal in the energy representation or equivalently, $[\hat{A},\hat{H}] = 0$.

8.33

a. Note that $\hat{U}_t^\dagger|\phi_\alpha,t\rangle = \hat{U}_t^\dagger\hat{U}_t|\phi_\alpha,0\rangle = |\phi_\alpha,0\rangle$.
c. Recall (8.147).

Appendix D

D.2

a. Let $y = -x$.
c. From part a, $\delta(-ax) = \delta(ax)$. Thus, it is sufficient to show that $\delta(ax) = \delta(x)/a$. Let $y = ax$.
d. Let $s = x^2 - a^2$. Then, $x = \sqrt{s+a^2}$ if $x > 0$ and $x = -\sqrt{s+a^2}$ if $x < 0$.
g. In the vicinity of $x = a_i$, we can write $g(x) = g'(a_i)(x-a_i)$.

D.4

b. Apply integration by parts. In doing so, note that $\delta(x-y)$ is zero as $x \to \pm\infty$ for any fixed value of y. For the integral involving $\delta'(y-x)$, use the chain rule:

$$\frac{\mathrm{d}}{\mathrm{d}x}\delta(y-x) = -\delta'(y-x) \,. \tag{GD.1}$$

Notes

[1] Lanczos C (1997) Linear Differential Operators. Dover, New York.

[2] The statement does not hold if $\boldsymbol{F}$ depends on the third or higher time derivatives of $\boldsymbol{r}$.

[3] If a particle of mass 1 kg is accelerated by 1 m/s^2, the magnitude of the force acting on it is 1 N, where N is a unit of force called Newton.

[4] The symbol "$\doteq$" stands for "has the components given by." Note that $m\boldsymbol{g}$ is a vector, while $(0,0,-mg)$ is its representation in terms of components. These two things are conceptually different. In fact, $\boldsymbol{g}$, being an arrow with a certain length, exists independently of the choice of the coordinate system, while its components do not. To emphasize this distinction, we used "$\doteq$" instead of "=."

[5] More precisely, $\boldsymbol{F} = -\boldsymbol{F}_c + \boldsymbol{\epsilon}$. For a reversed path considered just above (1.21), $\boldsymbol{F} = -\boldsymbol{F}_c - \boldsymbol{\epsilon}$. Since W is linear in $\boldsymbol{F}$, however, the contribution from $\boldsymbol{\epsilon}$ drops out in the limit of $\|\boldsymbol{\epsilon}\| \to 0$.

[6] If this expectation turned out to be false, we would have to believe, at least within the framework of classical mechanics, that the mechanical degrees of freedom is greater than f, requiring more variables than those in the set ($q_1, \ldots, q_f, \dot{q}_1, \ldots, \dot{q}_f$) for the complete specification of the mechanical state of the system.

[7] This problem is motivated by Problem 2.8-1 of Ref. [1] of Chap. 2.

[8] This brings forward a close analogy between thermodynamics and the analysis of mechanical systems at rest. A mechanical system is in equilibrium if its potential energy is stationary with respect to "virtual displacements" of its various constituent parts. As in variations considered in thermodynamics, the virtual displacements must satisfy any mechanical constraints imposed on the system. A generalization of this principle to mechanical systems in motion leads to Hamilton's principle. In all cases, perturbations are denoted by the same symbol δ.

[9] If this sounds too abstract, go to the produce section during your next visit to a grocery store and look for a fine plastic net containing either garlic bulbs or onions. That net makes a fairly accurate representation of the partition considered here.

[10] One such example is found in the footnote straddling pages 257 and 258 of Ref. [3] of Chap. 2.

[11] This formulation of the second law is due to Nishioka, who attributed it to Gibbs.

[12] To appreciate the necessity of the condition just indicated, recall the definition of the partial derivative of $f(x,y)$ with respect to x:

$$\frac{\partial f}{\partial x} = \lim_{\varepsilon \to 0} \frac{f(x+\varepsilon, y) - f(x,y)}{\varepsilon}.$$

Thus, $\partial f/\partial x = \partial g/\partial x$ holds only if $f(x,y) = g(x,y)$ within an interval containing the x value at which the derivative is evaluated.

[13] Allow for the three-dimensional perspective in Fig. 3.2a, even though the dimension of a phase space is an even number.

[14] That is, if there is no *time-dependent* external field. If such a field is present, then we cannot predict the future or the past of a given mechanical system based solely on the knowledge of q^f and p^f at some instant. We also need to know the exact time dependence of the external field.

[15] It might be argued that there is a more sensible choice for the bounds on the components of momentum. According to the special theory of relativity, the speed of an object v cannot exceed that of the light c. Moreover, as v approaches c, our formula for H is no longer valid. However, for common systems of our interest, the values of $\beta = (k_B T)^{-1}$ and m are such that the Boltzmann factor becomes negligible well before the relativistic effects become significant. This being the case, what bounds we place on the components of momentum or whether we replace H by its relativistic counterpart has no bearing on our results.

[16] Alternatively, we note that

$$v^2 = \left(\frac{\mathrm{d}l}{\mathrm{d}t}\right)^2 = \frac{(\mathrm{d}l)^2}{(\mathrm{d}t)^2} ,$$

where $\mathrm{d}l$ is the magnitude of an infinitesimal displacement during the infinitesimal time interval $\mathrm{d}t$. Since the r-, θ- and ϕ- axes are locally orthogonal to each other, the Pythagorean theorem applies, leading to

$$(\mathrm{d}l)^2 = (\mathrm{d}r)^2 + (r\mathrm{d}\theta)^2 + (r\sin\theta\mathrm{d}\phi)^2 ,$$

which yields the same result upon division by $(\mathrm{d}t)^2$.

[17] In addition, the total linear momentum $\boldsymbol{P}$ and the total angular momentum $\boldsymbol{M}$ are such quantities.

[18] More precisely, this is the standard deviation of the x values obtained through repeated measurements performed on a system prepared in an identical quantum mechanical state. See Sects. 8.5 and 8.7.2 for details.

[19] For a homogeneous system, the contribution from the interaction between the adjacent pair of parts, say i and j, can be regarded as being shared equally between these parts. One can then regard g_i and g_j as including this contribution. However, the subsequent argument will not hold unless one assumes the statistical independence between the different parts, which requires that the interaction between them be sufficiently weak.

[20] Let $y = 1/x$. Then, $x\ln x = -(\ln y)/y \to 0$ as $y \to +\infty$.

[21] Because H has the explicit λ dependence, the statistical weight of a given microstate changes with time. We can safely ignore this time dependence because $\Delta\lambda$ is infinitesimally small.

[22] To see this more explicitly, we consider the ratio between

$$\frac{1}{2}\left.\frac{\partial^2 S_b}{\partial {E_b}^2}\right|_0 {E_a}^2 \quad \text{and} \quad \left.\frac{\partial S_b}{\partial E_b}\right|_0 E_a ,$$

which is given by

$$-\frac{E_a}{2T}\left.\frac{\partial T}{\partial E_b}\right|_0 .$$

The quantity $-E_a\partial T/\partial E_b|_0$ is the change in T of system B when its energy changes from E_{ab} to $E_{ab}-E_a$. Provided that $f_a \ll f_b$, this should be negligibly small compared to T itself.

[23] According to (4.72), Z is the Laplace transform of $\overline{\Omega}(E)$.

[24] The number of microstates accessible to system B is given by (4.62) irrespective of the precise value H assumes within the interval $(E-\mathrm{d}E,E]$.

[25] This is a simplified version of the problem discussed in p.132 of Kubo R (1965), Statistical Mechanics. North-Holland Personal Library, Amsterdam.

[26] If there are more than one species present in the system, this should be the semi-grand potential as the system we are considering is open only to one of the species. The corresponding ensemble is the semi-grand canonical ensemble.

[27] Let us see this through an explicit computation. Suppose that none of the M sites is initially occupied and we place N particles one by one. The probability that the first particle is placed on the ith site is $1/M$. The probability that the second particle is placed on the site is

$$\frac{M-1}{M}\times\frac{1}{M-1}=\frac{1}{M}$$

with $(M-1)/M$ representing the probability that the first particle is placed on a site other than the ith one while $1/(M-1)$ is the probability that the second particle is placed on the ith site. Similarly, the probability that the nth particle is placed on the ith site is

$$\frac{M-1}{M}\times\frac{M-2}{M-1}\times\cdots\times\frac{M-n+1}{M-n+2}\times\frac{1}{M-n+1}=\frac{1}{M},$$

which is independent of n. The probability that the ith site is occupied at some point in the process of placing N particles on M sites is obtained by adding these probabilities from $n=1$ to N. This gives N/M.

[28] Courtesy of Professor Zhen-Gang Wang.

[29] More precisely, N_i^I is the long-time average of the instantaneous number of molecules in region I. Even then, N_i^I is well defined when the instantaneous value is defined by this convention.

[30] A solid angle is measured by steradians, sr for short. We shall omit sr in what follows.

[31] Because molecules interact at least over a distance of a few atomic diameters, the energy and entropy densities are expected to change continuously across the boundaries. In contrast, the number density can be made to vary discontinuously. The point is that $\delta\xi(\boldsymbol{r})$ in the varied state exhibits the $\boldsymbol{r}$ dependence that is difficult to predict.

[32] This implies that the *actual* variation of the system under consideration is such that $\xi(\boldsymbol{r})+\delta\xi(\boldsymbol{r})$ is spherically symmetric within the solid angle ω except

for the region right next to the boundaries, where the effect of the surroundings in an infinitesimally different state of the matter cannot be ignored.

[33] The condition is necessary but not sufficient because we have considered reversible variations only. In other words, if there are additional variables incapable of a reversible variation, they are held fixed when computing δU. The system may not remain in equilibrium if we allow these variables to change as well.

[34] In Sect. 2.8.1, we called such a process differentiation.

[35] In making this claim, we are ignoring the effect on γ of bending the interface. This is acceptable for flat or nearly flat interfaces.

[36] If R is infinite as is the case for flat interfaces, we have to go back to the original definition (6.27) instead of (6.39). The latter is always satisfied as seen from (6.43).

[37] Even though we have no prior knowledge on where the nucleus might form, we can always make a proper choice for B after the fact. This is permissible since B is purely a theoretical construct introduced entirely for the convenience of computation.

[38] This is often taken as the starting assumption when developing thermodynamics of interfaces. As we have seen, however, this is *one of the consequences* of thermodynamics of interfaces. The distinction is of paramount importance.

[39] Open or half-open intervals, i.e., $a < x < b$, $a < x \leq b$, or $a \leq x < b$ are also possible.

[40] The partial derivative of f with respect to u_i is defined by

$$\frac{\partial f}{\partial u_i} = \lim_{\varepsilon \to 0} \frac{f(u_1, \ldots, u_{i-1}, u_i + \varepsilon, u_{i+1}, \ldots, u_n) - f(u_1, \ldots, u_n)}{\varepsilon} .$$

This suggests that we define the functional derivative of $\mathscr{F}$ with respect to $u(x)$ as

$$\frac{\delta \mathscr{F}}{\delta u(x)} = \lim_{\varepsilon \to 0} \frac{\mathscr{F}[u(x') + \varepsilon \delta(x' - x)] - \mathscr{F}[u(x')]}{\varepsilon} .$$

This alternative definition is consistent with the one we adopted. In fact, applying (7.12) to the numerator on the right with $\delta u(x)$ replaced by $\varepsilon \delta(x' - x)$, we find

$$\mathscr{F}[u(x') + \varepsilon \delta(x' - x)] - \mathscr{F}[u(x')] = \int \frac{\delta \mathscr{F}}{\delta u(x')} \varepsilon \delta(x' - x) \mathrm{d}x' + \text{h.o.} = \varepsilon \frac{\delta \mathscr{F}}{\delta u(x)} + \text{h.o.}$$

When this expression is substituted into the above definition, we obtain an equality between $\delta \mathscr{F} / \delta u(x)$ computed according to the two definitions.

[41] Strictly speaking, we have only shown that a scalar A_i, to be interpreted as the chemical potential of species i of the interfacial region, is equal to the chemical potential of the same species in the surroundings. This itself does not imply uniformity of the chemical potential across the interfacial region. The same applies to the temperature. These remarks do not affect the development of our theory, however.

[42] As far as known to me, this observation is due to Ref. [6] of Chap. 7, which refers to Ω_{int} as the density functional and Ω as the grand potential.

[43] Is it possible that the difference between $n^{\mathrm{eq}}(\boldsymbol{r},u]$ and $n^{\mathrm{eq}}(\boldsymbol{r},u+\delta u]$ is entirely in the higher order terms and thus $\delta n(\boldsymbol{r}) \equiv 0$ for all $\boldsymbol{r}$? To see how this might happen, consider the integral

$$\int_V \delta n(\boldsymbol{r})\delta u(\boldsymbol{r})\mathrm{d}\boldsymbol{r} = \int_V\int_V \frac{\delta n(\boldsymbol{r})}{\delta u(\boldsymbol{r}')}\delta u(\boldsymbol{r})\delta u(\boldsymbol{r}')\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}' \,.$$

Using (7.55) and (7.56), we can show that

$$-k_BT\frac{\delta n(\boldsymbol{r})}{\delta u(\boldsymbol{r}')} = -k_BT\frac{\delta^2\Omega}{\delta u(\boldsymbol{r})\delta u(\boldsymbol{r}')} = \langle \hat{n}(\boldsymbol{r},\boldsymbol{r}^N)\hat{n}(\boldsymbol{r}',\boldsymbol{r}^N)\rangle - \langle \hat{n}(\boldsymbol{r},\boldsymbol{r}^N)\rangle\langle \hat{n}(\boldsymbol{r}',\boldsymbol{r}^N)\rangle \,,$$

which is a covariance matrix and hence is positive semi-definite. (To see a matrix here, imagine dividing up V into many tiny volume elements and labeling each of them. If $\boldsymbol{r}$ and $\boldsymbol{r}'$ are in the ith and jth volume elements, respectively, $\delta^2\Omega/\delta u(\boldsymbol{r})\delta u(\boldsymbol{r}')$ may be regarded as the ijth element of the matrix. In this picture, an integration over V becomes the sum over one of the indices on the matrix.) It follows that

$$\int_V \delta n(\boldsymbol{r})\delta u(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \leq 0$$

for *any* $\delta u(\boldsymbol{r})$. If $\delta u(\boldsymbol{r})$ is not identically zero, the equality holds only in the absence of any fluctuation of $\hat{n}$. Excluding this situation, therefore, $\delta n(\boldsymbol{r})$ is no-zero at least for some $\boldsymbol{r}$.

[44] We note that δn in (7.114) is limited to only those variations that can be produced by some perturbation δu and we have argued for the invertibility of (7.114) only for such δn. Could there be δn that cannot be produced by any δu? The assumption is that there is none. That is, when δu exhausts all possible scalar-valued functions on V, so does the corresponding δn given by (7.114). This will be the case if we divide up the volume V into many tiny volume elements and replace $\delta n(\boldsymbol{r})$ and $\delta u(\boldsymbol{r})$ by $(\delta n_1,\ldots,\delta n_M)$ and $(\delta u_1,\ldots,\delta u_M)$, respectively. Here M is the number of the volume elements and a quantity bearing the subscript i is to be evaluated inside the ith volume element.

[45] Even though $e^{\mathrm{rep}}(\boldsymbol{r}) = e^{\mathrm{rep}}(r)$,

$$\frac{\delta F^{\mathrm{exc}}_{\mathrm{int}}[n,v^{\mathrm{rep}}]}{\delta e^{\mathrm{rep}}(\boldsymbol{r})} \neq \frac{\delta F^{\mathrm{exc}}_{\mathrm{int}}[n,v^{\mathrm{rep}}]}{\delta e^{\mathrm{rep}}(r)} \,.$$

In fact,

$$\delta F^{\mathrm{exc}}_{\mathrm{int}}[n,v^{\mathrm{rep}}] = -\frac{k_BT}{2}V\int_0^\infty \frac{n^{(2)}(r)}{e^{\mathrm{rep}}(r)}\delta e^{\mathrm{rep}}(r)4\pi r^2\mathrm{d}r \,.$$

Thus,

$$\frac{\delta F^{\mathrm{exc}}_{\mathrm{int}}[n,v^{\mathrm{rep}}]}{\delta e^{\mathrm{rep}}(r)} = -\frac{k_BT}{2}V\frac{n^{(2)}(r)}{e^{\mathrm{rep}}(r)}4\pi r^2 = 4\pi r^2\frac{\delta F^{\mathrm{exc}}_{\mathrm{int}}[n,v^{\mathrm{rep}}]}{\delta e^{\mathrm{rep}}(\boldsymbol{r})} \,.$$

[46] We assume that r is finite in order to avoid the question of convergence of the sum.

[47] Taking a partial derivative of the equation with respect to x, we find

$$\frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{1}{X}\frac{\mathrm{d}^2X}{\mathrm{d}x^2}\right)=0\,,$$

which indicates that the quantity in the brackets is a constant.

[48] As an example, plot $x^n e^{-x}$ $(n=1,2,3,\ldots)$ for increasingly larger values of n for $x>0$. However, the statement is by no means universally true. For example, the product between a rapidly increasing function e^x and a rapidly decreasing function e^{-x} is a constant.

[49] Based on the physical interpretation we have given to (4.99), it is tempting to believe that the equation holds even for quantum mechanical systems provided only that the piston can be regarded as a classical mechanical object. Because the piston is usually a macroscopic object, no significant error is expected to arise from such a treatment.

[50] Technically $\mathrm{d}g_n(x)/\mathrm{d}x$ will be zero at $x=0$ since we demanded smoothness of $g_n(x)$. This does not affect our practical use of $\delta(x)$ because $\mathrm{d}g_n(x)/\mathrm{d}x$ is nonzero only in the immediate left of $x=0$ and we are only concerned with nice enough $f(x)$.

[51] Since s is now a complex variable, we are abusing (3.91). The procedure can be justified by using a contour integration in the complex plane.

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