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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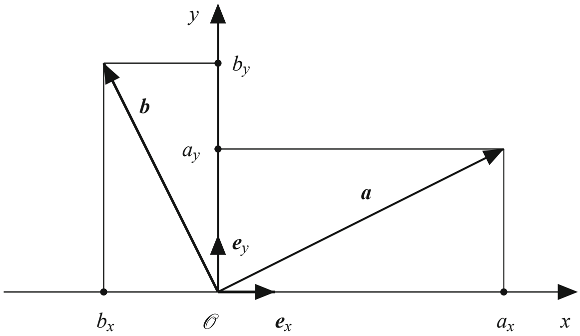

Fig. A.1 Components of two-dimensional vectors $\boldsymbol{a}$ and $\boldsymbol{b}$.

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.

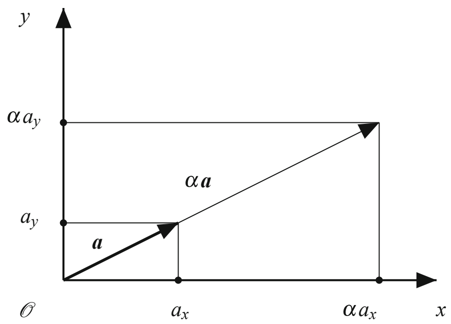

Fig. A.2 Components of $\boldsymbol{a}$ and multiplication of a vector $\boldsymbol{a}$ by a number α.

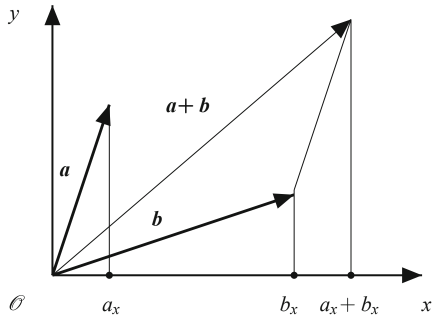

Fig. A.3 Addition of two vectors $\boldsymbol{a}$ and $\boldsymbol{b}$.

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

$$\boldsymbol{a}\cdot\boldsymbol{b} := a_x b_x + a_y b_y + a_z b_z \ . \tag{A.4}$$

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:

$$\cos\theta(\boldsymbol{a},\boldsymbol{b}) = \frac{\boldsymbol{a} \cdot \boldsymbol{b}}{\|\boldsymbol{a}\|\|\boldsymbol{b}\|} \,, \quad \text{where} \quad 0 \le \theta(\boldsymbol{a},\boldsymbol{b}) \le \pi \,. \tag{A.9}$$

Since $-1 \le \cos\theta \le 1$, you can find $\theta(\boldsymbol{a},\boldsymbol{b})$ from this formula if and only if

$$-1 \le \frac{\boldsymbol{a} \cdot \boldsymbol{b}}{\|\boldsymbol{a}\|\|\boldsymbol{b}\|} \le 1 \,. \tag{A.10}$$

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

$$(\boldsymbol{a}\cdot\boldsymbol{b})^2 \le \|\boldsymbol{a}\|^2\|\boldsymbol{b}\|^2 \tag{A.23}$$

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,

$$f(x_0+a) = f(x_0) + \left.\frac{\mathrm{d}f}{\mathrm{d}x}\right|_{x=x_0} a + \frac{1}{2!}\left.\frac{\mathrm{d}^2 f}{\mathrm{d}x^2}\right|_{x=x_0} a^2 + \frac{1}{3!}\left.\frac{\mathrm{d}^3 f}{\mathrm{d}x^3}\right|_{x=x_0} a^3 + \cdots , \quad \text{(B.1)}$$

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

$$f(x) = f(x_0) + \left.\frac{\mathrm{d}f}{\mathrm{d}x}\right|_{x=x_0} (x-x_0) + \frac{1}{2!}\left.\frac{\mathrm{d}^2 f}{\mathrm{d}x^2}\right|_{x=x_0} (x-x_0)^2 + \cdots . \quad \text{(B.2)}$$

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

$$\begin{aligned}&\int_a^b f(x)\ln f(x)\mathrm{d}x - \int_a^b f(x)\ln g(x)\mathrm{d}x \\ &\quad = \int_a^b f(x)\ln\frac{f(x)}{g(x)}\mathrm{d}x = \int_a^b g(x)\left[\frac{f(x)}{g(x)}\ln\frac{f(x)}{g(x)} - \frac{f(x)}{g(x)} + 1\right]\mathrm{d}x \,,\end{aligned} \tag{B.35}$$

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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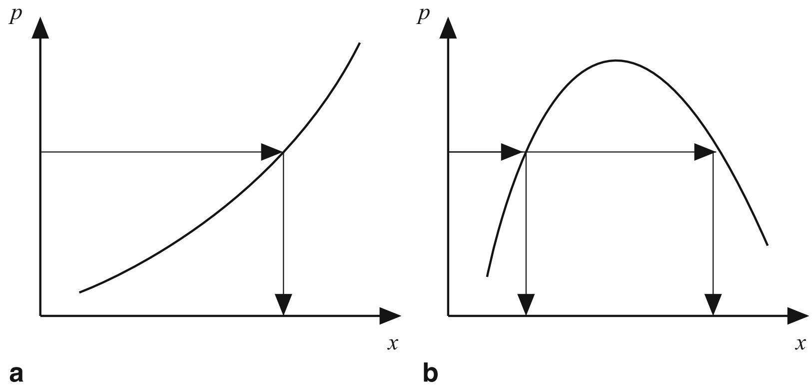

Fig. C.1 The function $p = p(x)$ can be inverted to give $x = x(p)$ if $p = p(x)$ is monotonic as indicated in **a**. If this is not the case, there may be multiple values of x for a given value of p as in **b** and the function $p = p(x)$ cannot be inverted.

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

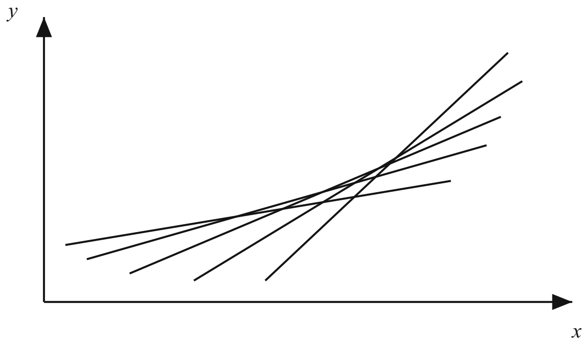

Fig. C.2 A curve emerges from a set of lines.

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 $x = 0$.

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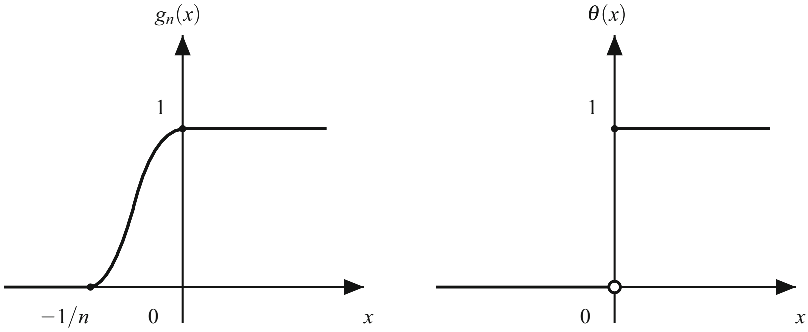

Fig. D.1 Behavior of $g_n(x)$ and $\theta(x) := \lim_{n\to\infty} g_n(x)$.

Let $g_n(x)$ $(n = 1, 2, \ldots)$ 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

$$g_n(x) = \begin{cases} 1 \text{ if } x \geq 0 \\ 0 \text{ if } x \leq -1/n \ , \end{cases} \tag{D.10}$$

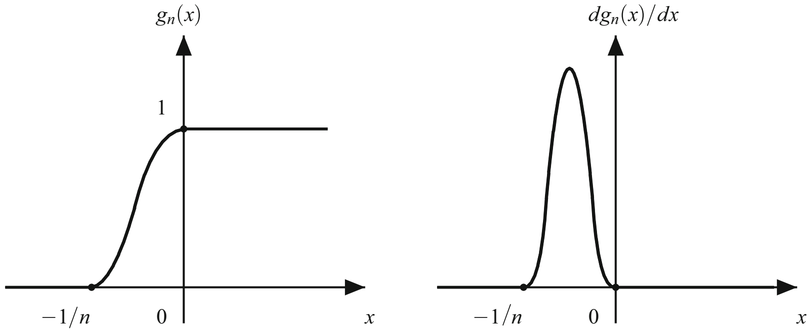

Fig. D.2 Behavior of $g_n(x)$ and $\mathrm{d}g_n(x)/\mathrm{d}x$.

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:

$$\int_{-\infty}^{\infty} f(x)\delta(x)\mathrm{d}x = f(0)\,, \quad \int_{-\infty}^{\infty} f(x)\delta'(x)\mathrm{d}x = -f'(0)\,,$$
$$\int_{-\infty}^{\infty} f(x)\delta''(x)\mathrm{d}x = f''(0)\,, \quad \int_{-\infty}^{\infty} f(x)\delta'''(x)\mathrm{d}x = -f'''(0)\,,\ldots \tag{D.37}$$

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

$$\int_{-\infty}^{0} \frac{dg_n(x)}{dx} dx = 1 \quad \text{and} \quad \int_{0}^{\infty} \frac{dg_n(x)}{dx} dx = 0\,, \tag{D.44}$$

and taking the limit $n \to \infty$,

$$\int_{-\infty}^{0} \delta(x) dx = 1 \quad \text{and} \quad \int_{0}^{\infty} \delta(x) dx = 0\,. \tag{D.45}$$

In contrast, for $h_n(x)$, we have

$$\int_{-\infty}^{0} \frac{dh_n(x)}{dx} dx = \frac{1}{2} \quad \text{and} \quad \int_{0}^{\infty} \frac{dh_n(x)}{dx} dx = \frac{1}{2}\,, \tag{D.46}$$

and hence

$$\int_{-\infty}^{0} \delta(x) dx = \frac{1}{2} \quad \text{and} \quad \int_{0}^{\infty} \delta(x) dx = \frac{1}{2}\,. \tag{D.47}$$

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,

$$\int_V \delta(\boldsymbol{r}) d\boldsymbol{r} = \int\int\int \delta(x)\delta(y)\delta(z) dx dy dz \tag{D.49}$$

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*,
DOI 10.1007/978-3-319-13809-1

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 $\boldsymbol{r}$.

I. Kusaka, *Statistical Mechanics for Engineers*,
DOI 10.1007/978-3-319-13809-1

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 $q_1, \ldots, q_f$ and $p_1, \ldots, p_f$ 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 $q_1, \ldots, q_f$ except for q_i and all of $\dot{q}_1, \ldots, \dot{q}_f$ 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 $\mu_1, \ldots, \mu_c$, 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 $N_1, \ldots, N_c$ 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 $N_1, \ldots, N_c$ 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 $\boldsymbol{p}_2, \ldots, \boldsymbol{p}_N$.

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

$$\int_{-l}^{\infty}(x+l)^2 e^{-\beta kx^2/2}\mathrm{d}x \approx \int_{-\infty}^{\infty}(x+l)^2 e^{-\beta kx^2/2}\mathrm{d}x = \int_{-\infty}^{\infty}(x^2+l^2)e^{-\beta kx^2/2}\mathrm{d}x \,, \tag{G3.5}$$

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 $\partial \boldsymbol{r}_i^a / \partial \boldsymbol{r}_i = \hat{I}$, where $\hat{I}$ 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

$$0 \equiv \phi(\boldsymbol{r}_1^a + \mathrm{d}\boldsymbol{r},\ldots,\boldsymbol{r}_N^a + \mathrm{d}\boldsymbol{r}) - \phi(\boldsymbol{r}_1^a,\ldots,\boldsymbol{r}_N^a) = \sum_{i=1}^{N} \frac{\partial \phi}{\partial \boldsymbol{r}_i^a} \cdot \mathrm{d}\boldsymbol{r} + \text{h.o.} \tag{G3.19}$$

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 dr centered around the origin. Ignoring the higher order terms, the volume dS_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 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. $-k_B T \ln X = 0$.

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 $(i \le m)$ 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

$\widetilde{\text{V}}3$: 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.
$\widetilde{\text{V}}4$: Define $\overline{F} \in \widetilde{V}$ by $\overline{F}(x) := (x, \bar{f})$ 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

$$\frac{1}{2}\frac{\partial^2 S_b}{\partial {E_b}^2}\bigg|_0 {E_a}^2 \quad \text{and} \quad \frac{\partial S_b}{\partial E_b}\bigg|_0 E_a ,$$

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

$$-k_B T\frac{\delta n(\boldsymbol{r})}{\delta u(\boldsymbol{r}')} = -k_B T\frac{\delta^2 \Omega}{\delta u(\boldsymbol{r})\delta u(\boldsymbol{r}')} = \langle \hat{n}(\boldsymbol{r},\boldsymbol{r}^N)\hat{n}(\boldsymbol{r}',\boldsymbol{r}^N)\rangle - \langle \hat{n}(\boldsymbol{r},\boldsymbol{r}^N)\rangle\langle \hat{n}(\boldsymbol{r}',\boldsymbol{r}^N)\rangle ,$$

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

$$\int_V \delta n(\boldsymbol{r})\delta u(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \le 0$$

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 $e^{\mathrm{rep}}(\boldsymbol{r}) = e^{\mathrm{rep}}(r)$,

$$\frac{\delta F_{\mathrm{int}}^{\mathrm{exc}}[n,v^{\mathrm{rep}}]}{\delta e^{\mathrm{rep}}(\boldsymbol{r})} \neq \frac{\delta F_{\mathrm{int}}^{\mathrm{exc}}[n,v^{\mathrm{rep}}]}{\delta e^{\mathrm{rep}}(r)} .$$

In fact,

$$\delta F_{\mathrm{int}}^{\mathrm{exc}}[n,v^{\mathrm{rep}}] = -\frac{k_B T}{2}V\int_0^\infty \frac{n^{(2)}(r)}{e^{\mathrm{rep}}(r)}\delta e^{\mathrm{rep}}(r)4\pi r^2\mathrm{d}r .$$

Thus,

$$\frac{\delta F_{\mathrm{int}}^{\mathrm{exc}}[n,v^{\mathrm{rep}}]}{\delta e^{\mathrm{rep}}(r)} = -\frac{k_B T}{2}V\frac{n^{(2)}(r)}{e^{\mathrm{rep}}(r)}4\pi r^2 = 4\pi r^2\frac{\delta F_{\mathrm{int}}^{\mathrm{exc}}[n,v^{\mathrm{rep}}]}{\delta e^{\mathrm{rep}}(\boldsymbol{r})} .$$

[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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