Chapter 3
Classical Statistical Mechanics

According to classical mechanics, equations of motion supplemented by initial conditions uniquely determine the subsequent evolution of a given system. For typical systems of our interest, however, the number of mechanical degrees of freedom is of the order of 10^{24}. One cannot possibly write down 10^{24} equations of motion, much less solve them. It is also impossible to specify the initial conditions for such a system with a required accuracy. Moreover, even if we could somehow accomplish all of this, it would be entirely impossible to comprehend the resulting list of coordinates and momenta at any instant. Despite a hopeless scenario this observation might suggest, behavior of a macroscopic system is surprisingly regular as we have seen in thermodynamics. It is as if laws governing behavior of a macroscopic system are quite different from those governing its behavior at a microscopic level. In this chapter, we examine the connection between these two distinct ways of looking at a macroscopic system.

3.1 Macroscopic Measurement

Suppose that we measure the value of a dynamical variable A of some macroscopic body at time t. Is the outcome $A_{\text{expt}}(t)$ equal to the value of A at time t? That is, can we write

$$A_{\text{expt}}(t) = A(q^f(t), p^f(t), t) \ ? \tag{3.1}$$

For example, we might wish to measure the length of an object consisting of N particles (atoms) as in Fig. 3.1. One possible definition for the dynamical variable representing the desired length is

$$l(\boldsymbol{r}^N(t), \boldsymbol{p}^N(t)) = \max_{i,j} \left| x_i(t) - x_j(t) \right| \ . \tag{3.2}$$

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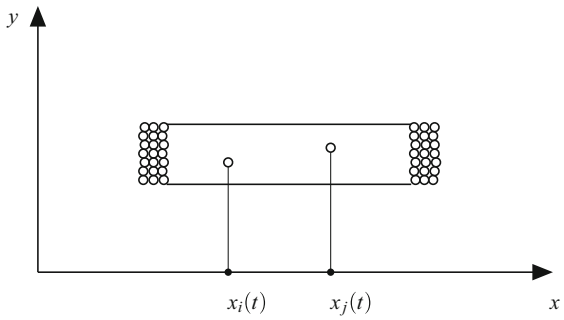


Fig. 3.1 Measurement of the length of a bar.

That is, we define the *instantaneous* length of the object as the maximum difference in the x coordinates of the particles comprising the object. In analogy to the notation q^f and p^f we introduced in Chap. 1, $\boldsymbol{r}^N$ and $\boldsymbol{p}^N$ in (3.2) collectively denote the position vectors and the linear momenta of particles in the system, respectively.

If we observe the time evolution of l, however, we will find that l fluctuates as a result of particles bouncing around in the object. The characteristic time scale for this kind of molecular motion is of the order of 10^{-12} s. See Example 3.1, for example. To measure the length, we can simply place a scale bar next to the object and read the scale with the naked eye. The characteristic time scale for such a measurement is of the order of 10^{-2} s at best. Even if we take a picture to "freeze the motion," the time duration of the measurement will be no shorter than 10^{-4} s or so.

Thus, what we obtain as a result of this measurement is not the instantaneous value $l(t)$ assumed by the dynamical variable, rather it is a time average of $l(t)$. So, a proper expression for $l_{\text{expt}}(t)$ is

$$l_{\text{expt}}(t) = \lim_{\tau\to\infty} \frac{1}{\tau} \int_t^{t+\tau} l(\boldsymbol{r}^N(t'), \boldsymbol{p}^N(t'))\mathrm{d}t' \,, \tag{3.3}$$

where $\tau \to \infty$ simply means that τ, being comparable with the characteristic time scale of a macroscopic measurement, is extremely large compared to the characteristic time scale of molecular motion.

For a general dynamical variable A, therefore, we write

$$A_{\text{expt}}(t) = \lim_{\tau\to\infty} \frac{1}{\tau} \int_t^{t+\tau} A(q^f(t'), p^f(t'), t')\mathrm{d}t' \,, \tag{3.4}$$

Taking an average consolidates a multitude of complexity embodied in the full specification of $q^f(t)$ and $p^f(t)$. The apparent regularity we associate with the behavior of macroscopic bodies is a result of this consolidation.

It is instructive to consider a simple, if somewhat artificial, example. Let

$$A(q^f, p^f, t) = A_0 + \sum_{i=1} A_i \sin\frac{2\pi t}{T_i} \,, \tag{3.5}$$

where A_0, A_i, and T_i are some constants. The second term on the right-hand side is a superposition of sine waves each with the period T_i and amplitude A_i. Because of this term, A will fluctuate with time in a complex manner. (For an extensive quantity pertaining to a macroscopic body, we typically have $|A_i/A_0| \sim 1/\sqrt{N}$ for all $i \geq 1$ as discussed in Sect. 4.1.) Let us calculate the result of measuring this A. From (3.4), we obtain

$$\begin{aligned} A_{\text{expt}}(t) &= \lim_{\tau\to\infty} \frac{1}{\tau} \int_t^{t+\tau} \left(A_0 + \sum_{i=1} A_i \sin \frac{2\pi t'}{T_i} \right) \mathrm{d}t' \\ &= A_0 - \lim_{\tau\to\infty} \frac{1}{\tau} \sum_{i=1} \frac{A_i T_i}{2\pi} \left[\cos \frac{2\pi t'}{T_i} \right]_t^{t+\tau} . \end{aligned} \tag{3.6}$$

Note that the magnitude of $\cos(2\pi t'/T_i)$ is at most 1. Thus, the fluctuating part of A does not contribute to A_{expt} unless T_i is of the order of τ, that is, only extremely slow modes of fluctuation can survive the time averaging implicit in macroscopic measurements and more rapid fluctuations are "hidden" from macroscopic measurements.

Even though these rapid fluctuations are hidden in the sense just indicated, their effect may be felt at a macroscopic level. Heat is a notable mechanism through which such hidden modes of fluctuation manifest themselves at a macroscopic level.

In principle, (3.4) provides a prescription for predicting the value of $A_{\text{expt}}(t)$ for the system of interest "simply" by solving the equations of motion. This is the basic idea behind the molecular dynamics simulation method, in which equations of motion are solved numerically for systems containing a large number of particles interacting through effective potentials that are designed to mimic the actual molecular interactions. One can easily deal with systems containing $10^4 \sim 10^5$ or even larger number of particles. In pursuing this approach, one must first identify appropriate dynamical variables corresponding to various macroscopic quantities of interest. For certain quantities, such as temperature, entropy, free energies, and chemical potentials, however, it is not immediately obvious what they should be. The role of statistical mechanics, in part, is to provide microscopic interpretations and *microscopic expressions* for various quantities we deal with in a macroscopic description of our world.

Example 3.1. Vibration of a monomer in liquid water: To estimate a characteristic time scale of the vibrational motion of molecules, let us focus on liquid water and suppose that a molecule in the liquid phase may be regarded as a rigid spherical particle confined to a rigid spherical cavity of radius $R_l = (3/4\pi n_l)^{1/3}$, where n_l is the number density of molecules. For liquid water at 298.15 K, $R_l = 1.928$ Å. If we approximate the effective radius R_w of a water molecule by the Lennard–Jones radius used in a model potential of water, such as the TIP4P model potential, $R_w \approx 1.577$ Å. The magnitude of the x-component of the velocity, on average, is given by $\sqrt{k_B T/m}$ as seen

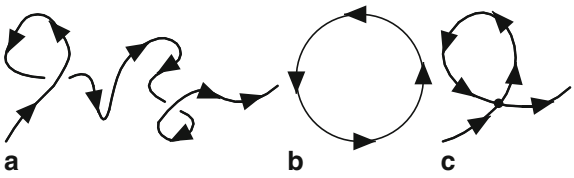


Fig. 3.2 **a** and **b** are examples of possible phase trajectories, while **c** is an impossible phase trajectory.

from (3.170). At 298.15 K, this gives $v_x = 371.0$ (m/s). Assuming that a given molecule is bouncing around between $x = R_l$ and $x = -R_l$ at this velocity, the period of the vibrational motion is $4(R_l - R_w)/v_x = 3.78 \times 10^{-12}$ s.

3.2 Phase Space

The mechanical state of a system is specified by giving numerical values to $2f$ variables, q^f and p^f. If we consider a space spanned by the axis $q_1, \ldots, q_f$ and $p_1, \ldots, p_f$, then the mechanical state of the system will be represented by a point in this $2f$ dimensional space. This space is called the **phase space**, and the point representing the state of the system is called the **phase point**. As the mechanical system evolves with time, $q_1, \ldots, q_f$ and $p_1, \ldots, p_f$ will also change, and the phase point will move along a path, which is referred to as the **phase trajectory**. Trajectories in Fig. 3.2a, b are examples of possible phase trajectories, with the latter representing a periodic motion.[13] However, trajectory in Fig. 3.2c indicates an impossible phase trajectory. According to what we saw in Chap. 1, if the system is at a particular point in the phase space at some instant of time t_0, its position in this space at any other time $t \neq t_0$ is completely determined by the equations of motion. Trajectory c violates this principle.[14]

Example 3.2. Free fall of a particle: Consider a free fall of a particle of mass m from the height h at $t = 0$. Taking the z-axis as vertically upward from the ground and setting the initial velocity to zero, we find

$$z(t) = -\frac{1}{2}gt^2 + h \quad \text{and} \quad \dot{z} = -gt \ . \tag{3.7}$$

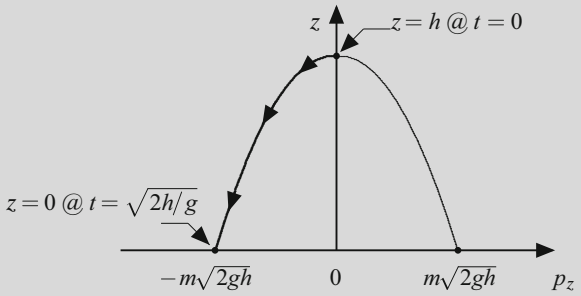
Thus,

$$p_z(t) = m\dot{z} = -mgt \ . \tag{3.8}$$

Eliminating t from the equations for $z(t)$ and $p_z(t)$, we find

$$z = -\frac{1}{2}g\left(-\frac{p_z}{mg}\right)^2 + h = -\frac{{p_z}^2}{2m^2 g} + h\,. \tag{3.9}$$

This is, then, the equation for the phase trajectory. Because the particle is moving toward the negative z-direction, only the portion with $p_z \leq 0$ in the following diagram is relevant.



Setting $z = 0$ in (3.7), we see that the particle hit the ground at $t = \sqrt{2h/g}$. According to (3.8),

$$p_z = -mg\sqrt{\frac{2h}{g}} = -m\sqrt{2gh} \tag{3.10}$$

at this very moment.

Exercise 3.1. A particle is confined to a potential well $\phi(x) = kx^2/2$ $(k > 0)$. Assuming that the particle moves in the x-direction only, draw its phase trajectory. ///

3.3 Ensemble Average

Suppose that we observe a system over a long duration of time that commences at time t and ends at $t + \tau$. During τ, the system evolves according to the equations of motion and passes through various regions in the phase space. As shown in Fig. 3.3 for the case of $f = 1$, we take an infinitesimal volume element $\mathrm{d}q^f \mathrm{d}p^f$ around a phase point (q^f, p^f) and denote by $\Delta t(q^f, p^f, t)$ the total amount of time the system spent in this volume element. Then, we define ρ by

$$\rho(q^f, p^f, t)\mathrm{d}q^f \mathrm{d}p^f := \lim_{\tau\to\infty} \frac{\Delta t(q^f, p^f, t)}{\tau}\,. \tag{3.11}$$

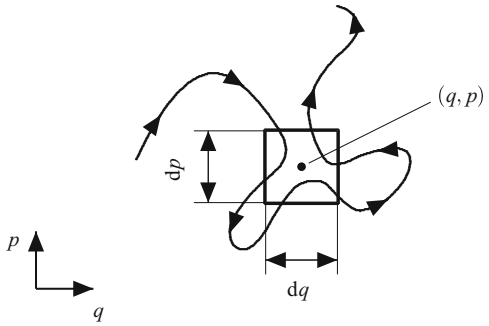


Fig. 3.3 A phase trajectory passing through a volume element $\mathrm{d}q\mathrm{d}p$ centered around a phase point (q,p) in a two-dimensional phase space during a time duration τ.

The quantity $\rho \mathrm{d}q^f \mathrm{d}p^f$ is the probability of finding the system inside the volume element if it is observed at some instant of time t', which we choose arbitrarily with uniform probability between t and $t+\tau$. We can easily see that $\rho \mathrm{d}q^f \mathrm{d}p^f$ satisfies the usual requirements of probability. Firstly, because $\Delta t \geq 0$, we have $\rho \geq 0$ everywhere in the phase space. Secondly, because the system is always found somewhere in the phase space, the summation of Δt for all the volume elements yields τ:

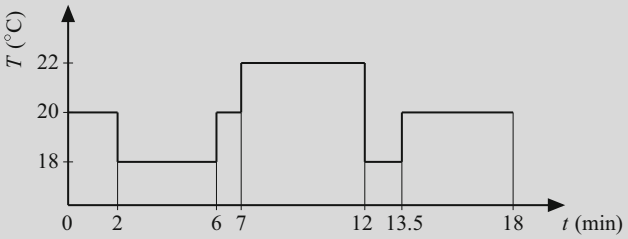
$$\int \rho(q^f, p^f, t) \mathrm{d}q^f \mathrm{d}p^f = 1 \,, \tag{3.12}$$

where the integration is over the *entire phase space*. Because of the probabilistic interpretation of $\rho \mathrm{d}q^f \mathrm{d}p^f$, we may write the long-time average of the dynamical variable $A(q^f, p^f, t)$ as

$$A_{\mathrm{expt}}(t) = \int A(q^f, p^f, t) \rho(q^f, p^f, t) \mathrm{d}q^f \mathrm{d}p^f \,. \tag{3.13}$$

For the reason that becomes clear in Sect. 3.5, the expression on the right is referred to as the **ensemble average**, or the **thermal average**, of the dynamical variable A. To help you convince yourself of the validity of (3.13), consider the following example.

Example 3.3. Temperature of a house as experienced by a moving object: Suppose that you picked up a thermometer and walked around in your house, visiting multiple times three of the rooms, kept at different temperatures. The temperature reading from the thermometer, as a function of time, may look like this:



What is the average temperature T_{expt} you have experienced? Equation (3.4) applied to this problem gives

$$T_{\text{expt}} = \frac{1}{18}\left[(20\times 2)+(18\times 4)+(20\times 1)+(22\times 5)+(18\times 1.5)+(20\times 4.5)\right] . \tag{3.14}$$

Evidently, this expression can be rewritten somewhat more compactly as

$$T_{\text{expt}} = \frac{1}{18}\left[18\times(4+1.5)+20\times(2+1+4.5)+22\times 5\right] . \tag{3.15}$$

To make it look more like (3.13), let T_i and Δt_i denote the temperature of room i and the total amount of time you spent in room i, respectively. From the graph shown above, we can construct the following table:

i	T_i (°C)	Δt_i (min)
1	18	5.5
2	20	7.5
3	22	5

Then, the above equation for T_{expt} becomes

$$T_{\text{expt}} = \frac{1}{\tau}\sum_{i=1}^{3} T_i \Delta t_i = \sum_{i=1}^{3} T_i \rho_i , \tag{3.16}$$

where $\tau = 18(\text{min})$ and $\rho_i := \Delta t_i/\tau$. This expression for T_{expt} should be compared against (3.13).

We note that the value of ρ, at fixed q^f and p^f, can depend on t, because Δt we obtain from our measurement may very well depend on when we commence our measurement. The explicit time dependence of A indicated in (3.13) deserves some comment, however.

Note that the explicit time dependence can arise in a dynamical variable if the system is subject to a time-dependent external field. If the field changes very rapidly during the time interval Δt, then in general, we cannot expect (3.13) to hold. To see this, one might consider a somewhat artificial example in which A is independent of

q^f and p^f but depends explicitly on time as

$$A(q^f, p^f, t') = \begin{cases} 1 \text{ if } t \leq t' < t + \varepsilon \\ 0 \text{ otherwise,} \end{cases} \tag{3.17}$$

where $\varepsilon \ll \tau$. In this case, $A_{\text{expt}}(t) \approx 0$ from (3.4). But according to (3.13), in which the integrand is evaluated at time t, $A_{\text{expt}}(t) = 1$. In writing (3.13), therefore, it is tacitly assumed that the change in A due to its *explicit* time dependence occurs sufficiently slowly during τ. In other words, we are allowing only for external fields that changes very slowly. On the other hand, rapid variations that may be exhibited by A due to its *implicit* dependence, that is, the change in A due to changes in q^f and p^f with t, is captured by the dependence of ρ on q^f and p^f.

3.4 Statistical Equilibrium

So far, all we have done is to rewrite (3.4) using a newly defined quantity ρ. But, to compute ρ from (3.11), we still have to solve the equations of motion. So, why do we even bother with the quantity ρ?

By expressing A_{expt} by means of ρ, we are hoping that we could somehow come up with an educated guess for the functional form of ρ *without ever having to solve the equations of motion*. It will be very difficult to do this for the most general situations. However, if we restrict our attention only to systems in *equilibrium*, maybe we can come up with a sensible guess for ρ without too much difficulty.

Of course, you note that we have converted the problem of evaluating the one-dimensional integral in (3.4) along with the solution of $2f$-coupled first-order differential equations into that of evaluating $2f$-dimensional integral as given by (3.13). How should that make the actual calculation of A_{expt} any easier? For example, this $2f$-dimensional integral is often evaluated numerically by means of Monte Carlo simulation. The required computational effort is comparable to that of molecular dynamics.

However, and this is the point: By introducing the new quantity ρ, we have completely changed the nature of the problem. This, in turn, allows for a completely new set of logical deductions and physical insights to operate, enabling us to introduce reasonable approximations in a manner unimaginable if we insist on solving the equations of motion as required by (3.4). Even more importantly, it is now possible to find explicit expressions for entropy and free energies in terms of functions of q^f and p^f as we shall see.

Because we have decided to limit our considerations to systems in equilibrium, we should first define precisely what is meant by equilibrium. We say that the system is in **statistical equilibrium** if and only if $\mathrm{d}A_{\text{expt}}/\mathrm{d}t = 0$ at any instant of time for *any* dynamical variable A that does *not* depend *explicitly* on time. For such A, the total time derivative of (3.13) can be evaluated as follows. First, we recall the definition

of the derivative:

$$\frac{\mathrm{d}A_{\mathrm{expt}}(t)}{\mathrm{d}t} = \lim_{\Delta t \to 0} \frac{1}{\Delta t} \left[A_{\mathrm{expt}}(t+\Delta t) - A_{\mathrm{expt}}(t) \right] . \tag{3.18}$$

Using (3.13), we find

$$\frac{\mathrm{d}A_{\mathrm{expt}}(t)}{\mathrm{d}t} = \lim_{\Delta t \to 0} \frac{1}{\Delta t} \left[\int A(q^f, p^f) \rho(q^f, p^f, t+\Delta t) \mathrm{d}q^f \mathrm{d}p^f - \int A(q^f, p^f) \rho(q^f, p^f, t) \mathrm{d}q^f \mathrm{d}p^f \right] . \tag{3.19}$$

Since both integrals are taken over the entire phase space, they can be combined to give

$$\frac{\mathrm{d}A_{\mathrm{expt}}(t)}{\mathrm{d}t} = \lim_{\Delta t \to 0} \frac{1}{\Delta t} \int A(q^f, p^f) \left[\rho(q^f, p^f, t+\Delta t) - \rho(q^f, p^f, t) \right] \mathrm{d}q^f \mathrm{d}p^f . \tag{3.20}$$

For a small enough Δt, the change in ρ during the time duration Δt may be written as

$$\rho(q^f, p^f, t+\Delta t) - \rho(q^f, p^f, t) = \frac{\partial \rho(q^f, p^f, t)}{\partial t} \Delta t \tag{3.21}$$

with sufficient accuracy. Introducing this expression in (3.20), we obtain

$$\frac{\mathrm{d}A_{\mathrm{expt}}(t)}{\mathrm{d}t} = \int A(q^f, p^f) \frac{\partial \rho(q^f, p^f, t)}{\partial t} \mathrm{d}q^f \mathrm{d}p^f . \tag{3.22}$$

At equilibrium, this quantity must vanish at any instant of time for *any* choice of A. Thus, the necessary and sufficient condition for statistical equilibrium is that

$$\frac{\partial \rho(q^f, p^f, t)}{\partial t} = 0 \tag{3.23}$$

holds everywhere in the phase space at any instant. In other words, ρ does not depend explicitly on t.

3.5 Statistical Ensemble

Recall that we constructed ρ by observing a single system over a long duration of time starting at time t. This ρ, and hence A_{expt} calculated by means of (3.13), will in general depend on t. When this time dependence is absent for any A_{expt} that corresponds to a dynamical variable A without an explicit time dependence, we say that the system is in statistical equilibrium. While this definition of equilibrium makes good physical sense, (3.23) that followed from it does not appear to offer any useful insight toward an educated guess for the functional form of ρ. For this reason, we introduce the following construction.

First, we create a large number, say $\mathcal{N}$, of copies of the original system. Copies have the identical mechanical construction to the original. If there are time-dependent external fields, their time dependence are common to all copies. In other words, the *functional form* of the Hamiltonian of a copy is identical to that of the original *including* the explicit time dependence. Such a collection of $\mathcal{N}$ copies is called the **statistical ensemble**.

At a given instant t, each copy of the ensemble has a representative point, as specified by $(q^f(t), p^f(t))$, in the phase space. While all copies in the ensemble are characterized by the same functional form of the Hamiltonian, we do not require that their mechanical states, and hence the corresponding phase points in the phase space, at any instant should coincide. Instead, we construct the statistical ensemble so that the number of copies whose mechanical state falls within the infinitesimal volume element $\mathrm{d}q^f \mathrm{d}p^f$ taken around (q^f, p^f) is given by

$$\mathcal{N}\rho(q^f, p^f)\mathrm{d}q^f \mathrm{d}p^f \ . \tag{3.24}$$

That is, the number density of copies in the phase space at (q^f, p^f) is $\mathcal{N}\rho(q^f, p^f)$.

It should be emphasized that a given copy in the ensemble does *not* interact with the other copies in the ensemble. Each copy has its own representative point in the phase space and moves along its own phase trajectory according to the equations of motion pertaining only to that copy.

If we take a fixed control volume in the phase space, the number of copies found in it may change with time as some copies leave the control volume while others enter it. However, once we put $\mathcal{N}$ copies in the phase space and watch what happens to them, no copy will simply disappear from the phase space, nor will a new one appear spontaneously out of nothing. This implies that the number density $\mathcal{N}\rho$ of the copies satisfies the equivalent of mass balance or the equation of continuity from fluid mechanics in the phase space. This observation leads to an important theorem, which guide us in our search for the equilibrium distribution as we shall see next.

3.6 Liouville's Theorem

Let us start by reviewing the equation of continuity from fluid mechanics in ordinary three-dimensional space. (The current derivation is adopted solely for the sake of expediency. For a physically more natural derivation of the equation of continuity, see Chap. 3 of Ref. [6].)

Consider a control volume V fixed in space at all time. The total number of particles within V at a given moment t is given by

$$\int_V \rho(\boldsymbol{r}, t)\mathrm{d}\boldsymbol{r} \ , \tag{3.25}$$

where $\rho(\boldsymbol{r}, t)$ temporarily denotes the number density of particles such as molecules at position $\boldsymbol{r}$ at time t. If we exclude the possibility of chemical reactions, the rate of

change of this integral can be expressed in terms of the flux across the boundary A of V:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_V \rho(\boldsymbol{r},t)\mathrm{d}\boldsymbol{r} = -\oint_A \rho(\boldsymbol{r},t)\boldsymbol{v}(\boldsymbol{r},t)\cdot\boldsymbol{n}(\boldsymbol{r})\mathrm{d}A\,, \tag{3.26}$$

where $\boldsymbol{n}$ is the outward unit normal and $\boldsymbol{v}$ is the average velocity of the particles passing through the surface element $\mathrm{d}A$.

Because our control volume remains fixed at all time, the total time derivative on the left-hand side can be brought inside the integral sign, where it becomes a partial derivative for the integrand is a function of $\boldsymbol{r}$ as well. Furthermore, by means of the divergence theorem, the surface integral in (3.26) may be converted into a volume integral, thus yielding

$$\int_V \left[\frac{\partial\rho}{\partial t} + \nabla\cdot(\rho\boldsymbol{v})\right]\mathrm{d}\boldsymbol{r} = 0\,. \tag{3.27}$$

Because this equation holds for any choice of the control volume V,

$$\frac{\partial\rho}{\partial t} + \nabla\cdot(\rho\boldsymbol{v}) = 0 \tag{3.28}$$

must hold everywhere at any instant. Writing out the divergence term $\nabla\cdot(\rho\boldsymbol{v})$ using a Cartesian coordinate system, we have

$$\frac{\partial\rho}{\partial t} + \frac{\partial(\rho v_x)}{\partial x} + \frac{\partial(\rho v_y)}{\partial y} + \frac{\partial(\rho v_z)}{\partial z} = 0\,. \tag{3.29}$$

where the subscripts label the respective components of $\boldsymbol{v}$.

In the phase space, the coordinates are $q_1, \ldots, q_f$ and $p_1, \ldots, p_f$ instead of x, y, and z. Instead of the components v_x, v_y, and v_z, of the average velocity $\boldsymbol{v}$, we have $\dot{q}_1$, $\ldots$, $\dot{q}_f$ and $\dot{p}_1, \ldots, \dot{p}_f$ for the components of the average velocity of phase points. Finally, $\mathscr{N}\rho$ takes the place of ρ. Thus, by analogy to (3.29), we have

$$\frac{\partial(\mathscr{N}\rho)}{\partial t} + \sum_{i=1}^{f}\left[\frac{\partial(\mathscr{N}\rho\dot{q}_i)}{\partial q_i} + \frac{\partial(\mathscr{N}\rho\dot{p}_i)}{\partial p_i}\right] = 0\,. \tag{3.30}$$

Noting that $\mathscr{N}$ is a constant independent of q^f, p^f, and t, and using Hamilton's equations of motion (1.162), we find

$$\begin{aligned} 0 &= \frac{\partial\rho}{\partial t} + \sum_{i=1}^{f}\left[\frac{\partial}{\partial q_i}\left(\rho\frac{\partial H}{\partial p_i}\right) - \frac{\partial}{\partial p_i}\left(\rho\frac{\partial H}{\partial q_i}\right)\right] \\ &= \frac{\partial\rho}{\partial t} + \sum_{i=1}^{f}\left(\frac{\partial\rho}{\partial q_i}\frac{\partial H}{\partial p_i} + \rho\frac{\partial^2 H}{\partial q_i\partial p_i} - \frac{\partial H}{\partial q_i}\frac{\partial\rho}{\partial p_i} - \rho\frac{\partial^2 H}{\partial p_i\partial q_i}\right)\,. \end{aligned} \tag{3.31}$$

Since the second derivatives are independent of the order of differentiation, we arrive at

$$\frac{\partial \rho}{\partial t} + \sum_{i=1}^{f} \left(\frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial H}{\partial q_i} \frac{\partial \rho}{\partial p_i} \right) = 0 \,. \tag{3.32}$$

Recalling the definition of the Poisson bracket (1.184), we may rewrite (3.32) as

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = \frac{\partial \rho}{\partial t} + \{\rho, H\} = 0 \,, \tag{3.33}$$

where the first equality is an example of (1.185). Equation (3.33) is known as **Liouville's theorem** and indicates that ρ is a constant of motion. (Our usage of this phrase is slightly inappropriate here. Constant of motion usually refers to a dynamical variable pertaining to a single mechanical system rather than to a collection of them.)

According to (3.23), therefore, the necessary and sufficient condition of statistical equilibrium is that ρ be a constant of motion that *does not depend explicitly on time*. For this to be the case, it is sufficient (but not necessary) that ρ is a function of constants of motion that are not, themselves, explicit functions of time. In fact, let $\{A_1, \ldots, A_n\}$ be a set of such constants of motion and suppose that

$$\rho = \rho(A_1, \ldots, A_n). \tag{3.34}$$

Then, because A_i does not depend explicitly on t,

$$\frac{\partial \rho}{\partial t} = \sum_{i=1}^{n} \frac{\partial \rho}{\partial A_i} \frac{\partial A_i}{\partial t} = 0 \tag{3.35}$$

and, because A_i is a constant of motion,

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = \sum_{i=1}^{n} \frac{\partial \rho}{\partial A_i} \frac{\mathrm{d}A_i}{\mathrm{d}t} = 0 \tag{3.36}$$

as required by (3.23) and (3.33), respectively.

As we have seen, Liouville's theorem simply states that the number of copies in a statistical ensemble is conserved. This is a general requirement ρ must satisfy *regardless* of whether the system is in statistical equilibrium or not. Statistical equilibrium imposes an additional requirement (3.23), which is quite distinct from (3.33). Because of (3.33), one often expresses (3.23) as

$$\{\rho, H\} = 0 \,. \tag{3.37}$$

We observe that any set of two equations taken from (3.23), the second equality in (3.33), and (3.37), is equivalent to any other such set.

3.7 Significance of H

Accepting (3.34) as our guiding principle in our search for the equilibrium distribution, we still have to decide on the set of dynamical variables. In the absence of a time-dependent external field, a system of f mechanical degrees of freedom has $2f-1$ independent constants of motion, each without an explicit time dependence. (See the next section.) The mechanical energy E, the total linear momentum $\boldsymbol{P}$, and the total angular momentum $\boldsymbol{M}$ are notable examples of such constants. (See (1.106), (1.138), and (1.145) for definitions.) Functions of these constants are also constants of motion. Among the multitude of constants, how do we choose our dynamical variable in terms of which to express ρ?

In Sect. 1.8, we saw that conservation laws of E, $\boldsymbol{P}$, and $\boldsymbol{M}$ followed from a very general consideration regarding symmetry of space and time. In particular, it was unnecessary to refer to any specific details of the mechanical system. As such, conservation laws of these quantities are of very general character. In our search for a general theory applicable to *all* systems in equilibrium, the claim that they should serve a critical role is extremely compelling.

Typically, we are interested in macroscopic bodies at rest and E is the only relevant dynamical variable. Therefore, using H instead of E to emphasize its dependence on q^f and p^f, we suppose that

$$\rho = \rho(H)\,. \tag{3.38}$$

The justification of this hypothesis ultimately rests on the agreement between predictions of our theory and experimental observations.

3.8 †The Number of Constants of Motion

Let us see how many *independent* constants of motion are associated with a given mechanical system. We assume that the system is subject to no time-dependent external field.

We start by noting that the solution of Hamilton's equations of motion may be written as

$$q_i(t) = \mathscr{F}_{q_i}(t-t_0, a^f, b^f) \quad \text{and} \quad p_i(t) = \mathscr{F}_{p_i}(t-t_0, a^f, b^f)\,, \quad i = 1, \ldots, f\,, \tag{3.39}$$

where we introduced a temporary notation $\mathscr{F}_x$ to indicate functional dependence of the quantity x on the variables listed in the brackets. The first equation indicates, for example, that q_i at time t depends only on the time that has passed since some arbitrary chosen instant t_0 and the values q^f and p^f assumed at t_0, which we denote by a^f and b^f, respectively. In the absence of a time-dependent external field, the time dependence of q^f and p^f occurs only through $t-t_0$.

If the set of $2f$ equations (3.39) is solved for $2f$ variables $a_1, \ldots, a_f, b_1, \ldots, b_{f-1}$, and $t - t_0$, we obtain

$$\begin{aligned} a_i &= \mathscr{F}_{a_i}(q^f, p^f, b_f)\,, \quad i = 1, \ldots, f \\ b_i &= \mathscr{F}_{b_i}(q^f, p^f, b_f)\,, \quad i = 1, \ldots, f-1 \\ t_0 &= t - \mathscr{F}_{t-t_0}(q^f, p^f, b_f)\,. \end{aligned} \tag{3.40}$$

Thus, $a_1, \ldots, a_f, b_1, \ldots, b_{f-1}$, and t_0 are all functions of q^f and p^f that remain constant, that is, they are constants of motion. Excluding t_0, which depends explicitly on t, we are left with $2f-1$ constants of motion with no explicit time dependence. Insofar as their values can be specified independent of each other, $\mathscr{F}_{a_1}, \ldots, \mathscr{F}_{a_f}$ and $\mathscr{F}_{b_1}, \ldots, \mathscr{F}_{b_{f-1}}$ are independent functions.

Example 3.4. Free fall of a particle: Let us see how the above general scheme works for the problem of free-falling particle in Example 3.2. As the initial condition, we suppose that $z = z_0$ and $v_z = v_0$ at $t = t_0$. In terms of the notation adopted above, we have

$$q_1 = z\,, \quad p_1 = p_z\,, \quad a_1 = z_0\,, \quad \text{and} \quad b_1 = v_0\,. \tag{3.41}$$

Since $f = 1$, we expect to find $2 \times 1 - 1 = 1$ constant of motion.

Now, in place of (3.39), we have

$$\begin{aligned} z &= -\frac{1}{2}g(t-t_0)^2 + v_0(t-t_0) + z_0 \\ p_z &= -mg(t-t_0) + mv_0\,. \end{aligned} \tag{3.42}$$

Solving these equations for z_0 and $t - t_0$, we find

$$z_0 = z + \frac{1}{2m^2 g}\left({p_z}^2 - m^2 {v_0}^2\right) \quad \text{and} \quad t - t_0 = \frac{mv_0 - p_z}{mg}\,. \tag{3.43}$$

The first equation gives z_0 as a function of the time-dependent coordinate z and the momentum p_z but displays no explicit time dependence.

Rearranging the equation a little, we arrive at

$$mgz_0 + \frac{1}{2}m{v_0}^2 = mgz + \frac{{p_z}^2}{2m}\,, \tag{3.44}$$

which is recognized as the mechanical energy E. According to this equation, E is also a constant of motion. However, E is given in terms of z_0 and hence is not independent of z_0. So, the number of independent constants of motion with no explicit time dependence is just one as advertised.

3.9 Canonical Ensemble

At this point, we need to come up with an explicit expression for ρ. Let us suppose then that

$$\rho(q^f, p^f) = \frac{1}{C} e^{-\beta H(q^f, p^f)} \tag{3.45}$$

and see where it will take us. In Sect. 3.11, we see that there is actually a compelling reason for choosing this particular form of ρ. Nevertheless, (3.45) is a hypothesis, the ultimate justification of which must be sought through experimental scrutiny. The constant C is determined by the normalization condition of ρ:

$$C = \int e^{-\beta H(q^f, p^f)} \mathrm{d}q^f \mathrm{d}p^f \ , \tag{3.46}$$

where the integration extends over all phase space. For applications we have in mind, there is usually no upper limit to values H can assume while H is bounded from below. (The potential energy of interaction between two atoms takes the minimum possible value when the distance between the atoms is of the order of the atomic diameter. When they are squeezed closer together, the potential energy increases indefinitely.) In order for the integral in (3.46) to exist, therefore, the constant β must be positive. The statistical ensemble characterized by (3.45) is called the **canonical ensemble**.

Note that copies with different values of energy are present in the canonical ensemble. But, ρ was constructed from a phase trajectory along which H is constant. We shall come back to this point in Sect. 3.11. For now, we simply accept the canonical ensemble as given and explore its implications. We start by looking for physical meaning of β and C in this section.

We define the internal energy U of a system by

$$U := \langle H \rangle = \int H(q^f, p^f) \rho(q^f, p^f) \mathrm{d}q^f \mathrm{d}p^f = \frac{1}{C} \int H(q^f, p^f) e^{-\beta H(q^f, p^f)} \mathrm{d}q^f \mathrm{d}p^f \ , \tag{3.47}$$

where we introduced a new notation for the **ensemble average** we encountered earlier:

$$\langle A \rangle := \int A(q^f, p^f) \rho(q^f, p^f) \mathrm{d}q^f \mathrm{d}p^f = \frac{1}{C} \int A(q^f, p^f) e^{-\beta H(q^f, p^f)} \mathrm{d}q^f \mathrm{d}p^f \ . \tag{3.48}$$

Recalling (3.13), we have

$$\langle A \rangle = A_{\text{expt}} \ . \tag{3.49}$$

As with (3.13), this identity is a consequence of our construction of the statistical ensemble.

We recall from thermodynamics that

$$\mathrm{d}U = T \mathrm{d}S + \text{work term.} \tag{3.50}$$

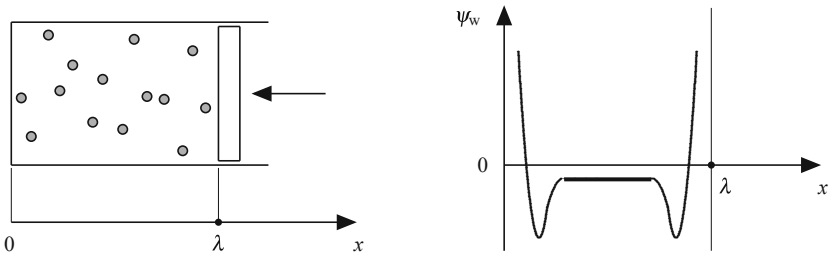


Fig. 3.4 Gas particles confined to a cylinder. Each particle is subject to the external field generated by the walls of the cylinder. The figure on the *right* illustrates the net field ψ_w produced by the vertical wall on the left and the piston on the right.

If we can develop an expression for dU based on (3.47) for a process involving work, we should be able to relate T and S to statistical mechanical quantities such as ρ, β, and C. This forms a basis for exploring a link between thermodynamics and the microscopic description of matter based on mechanics.

First, we introduce a few notations. Let $\Theta = \beta^{-1}$ and rewrite (3.45) as

$$H = -\Theta \ln \rho - \Theta \ln C \,. \tag{3.51}$$

Upon taking the average, we find

$$U = -\Theta \langle \ln \rho \rangle - \Theta \ln C = \Theta \eta + \alpha \,, \tag{3.52}$$

where we used the fact that $\langle A \rangle = A$ if A is independent of q^f and p^f. We also defined

$$\eta := -\langle \ln \rho \rangle \quad \text{and} \quad \alpha := -\Theta \ln C \,. \tag{3.53}$$

From (3.52),

$$dU = \eta \, d\Theta + \Theta d\eta + d\alpha \,. \tag{3.54}$$

Equation (3.54) with three terms on the right cannot be compared directly with (3.50). We also need to relate quantities on the right-hand side of (3.54) with the work. To this end, let us consider the example shown in Fig. 3.4 illustrating N gas particles confined to a cylinder. By moving the piston, we can exert work on the gas. Since we require the ability to control λ at will, we choose the gas particles as our statistical mechanical system and regard *the piston as a movable source of an external field*, which, together with the field generated by the fixed walls, confines the particles to the cylinder. So, the value of λ is common to all members of the statistical ensemble. The Hamiltonian of the system is given by

$$H = \sum_{i=1}^{N} \frac{\|\boldsymbol{p}_i\|^2}{2m} + \phi(\boldsymbol{r}^N) + \psi(\boldsymbol{r}^N, \lambda) \,, \tag{3.55}$$

where ϕ is the potential energy due to mutual interaction among the particles and ψ is the net external field generated by the piston and the other walls of the cylinder.

The point here is that we can perform work on the system by changing λ and that the Hamiltonian is a function of λ.

From (3.46), we see that C is a function of $\Theta = \beta^{-1}$ and λ, and hence

$$\mathrm{d}C = \left(\frac{\partial C}{\partial \Theta}\right)_\lambda \mathrm{d}\Theta + \left(\frac{\partial C}{\partial \lambda}\right)_\Theta \mathrm{d}\lambda \ . \tag{3.56}$$

Now, using (3.53) and (3.56), we find

$$\mathrm{d}\alpha = -\mathrm{d}\Theta \ln C - \frac{\Theta}{C}\mathrm{d}C = \left[\frac{\alpha}{\Theta} - \frac{\Theta}{C}\left(\frac{\partial C}{\partial \Theta}\right)_\lambda\right]\mathrm{d}\Theta - \frac{\Theta}{C}\left(\frac{\partial C}{\partial \lambda}\right)_\Theta \mathrm{d}\lambda \ . \tag{3.57}$$

Using (3.46), we can rewrite the partial derivatives in a little more illuminating form:

$$\frac{1}{C}\left(\frac{\partial C}{\partial \Theta}\right)_\lambda = \frac{1}{C}\frac{\partial}{\partial \Theta}\int e^{-H/\Theta}\mathrm{d}q^f\mathrm{d}p^f \ . \tag{3.58}$$

Since Θ appears only as the denominator in the exponent, $\partial/\partial\Theta$ can be brought inside the integral:

$$\frac{1}{C}\left(\frac{\partial C}{\partial \Theta}\right)_\lambda = \frac{1}{C}\int \frac{\partial}{\partial \Theta} e^{-H/\Theta}\mathrm{d}q^f\mathrm{d}p^f = \frac{1}{C}\int \frac{H}{\Theta^2} e^{-H/\Theta}\mathrm{d}q^f\mathrm{d}p^f = \frac{U}{\Theta^2} \ , \tag{3.59}$$

where we used (3.47). Similarly,

$$\begin{aligned}\frac{1}{C}\left(\frac{\partial C}{\partial \lambda}\right)_\Theta &= \frac{1}{C}\frac{\partial}{\partial \lambda}\int e^{-H/\Theta}\mathrm{d}q^f\mathrm{d}p^f = \frac{1}{C}\int \frac{\partial}{\partial \lambda} e^{-H/\Theta}\mathrm{d}q^f\mathrm{d}p^f \\ &= \frac{1}{C}\int -\frac{1}{\Theta}\frac{\partial H}{\partial \lambda} e^{-H/\Theta}\mathrm{d}q^f\mathrm{d}p^f \ ,\end{aligned} \tag{3.60}$$

where the partial derivative in the integrand is for fixed q^f and p^f. Using (3.48),

$$\frac{1}{C}\left(\frac{\partial C}{\partial \lambda}\right)_\Theta = -\frac{1}{\Theta}\left\langle \frac{\partial H}{\partial \lambda}\right\rangle \ . \tag{3.61}$$

Substituting (3.59) and (3.61) in (3.57) and using (3.52), we obtain

$$\mathrm{d}\alpha = \frac{1}{\Theta}(\alpha - U)\mathrm{d}\Theta + \left\langle \frac{\partial H}{\partial \lambda}\right\rangle \mathrm{d}\lambda = -\eta \mathrm{d}\Theta + \left\langle \frac{\partial H}{\partial \lambda}\right\rangle \mathrm{d}\lambda \ . \tag{3.62}$$

This equation can be brought into (3.54) to yield

$$\mathrm{d}U = \Theta \mathrm{d}\eta + \left\langle \frac{\partial H}{\partial \lambda}\right\rangle \mathrm{d}\lambda \ . \tag{3.63}$$

We identify the term proportional to the displacement, $\mathrm{d}\lambda$, as the work term. Because η depends on λ, a term proportional to $\mathrm{d}\lambda$ is implicit in $\mathrm{d}\eta$. In essence, the work in thermodynamics is *defined* to be $\langle \partial H/\partial\lambda\rangle \mathrm{d}\lambda$. This definition seems very

reasonable since $-\partial H/\partial\lambda$ is the x-component of the force exerted on the piston by the gas molecules. The appearance of thermal average is also natural provided that the characteristic time scale over which the work is performed is considerably larger than that of typical molecular motions.

Upon comparison between (3.50) and (3.63), we finally arrive at

$$\Theta \mathrm{d}\eta = T\mathrm{d}S\,. \tag{3.64}$$

This equation implies that $\Theta \propto T$ and $\mathrm{d}\eta \propto \mathrm{d}S$. The proportionality constant between $\mathrm{d}S$ and $\mathrm{d}\eta$ is quite arbitrary and the most logical choice for the constant perhaps is just unity. However, for a historical reason, we introduce the Boltzmann constant k_B and write (3.64) as

$$\Theta \mathrm{d}\eta = k_B T \mathrm{d}(S/k_B)\,. \tag{3.65}$$

This suggests that we set

$$T = \frac{\Theta}{k_B} \tag{3.66}$$

and

$$S = k_B\eta + \text{const.} = -k_B\langle \ln\rho\rangle + \text{const.} \tag{3.67}$$

Since we are usually interested only in a entropy difference, we set the constant rather arbitrarily to zero. For an in-depth discussion on this choice, see Chap. 3 of Ref. [4]. In any case, we now have

$$S = k_B\eta = -k_B\langle \ln\rho\rangle\,. \tag{3.68}$$

Equations (3.66) and (3.68) are, then, the statistical mechanical expressions for T and S, respectively.

Equation (3.68) is due to Gibbs, and is known as **Gibbs's entropy formula**. From (3.66), we note that changing the choice of the constant k_B in (3.65) simply amounts to changing the scale for measuring the temperature. Since $\Theta = \beta^{-1}$ and k_B are both positive, T must be positive as well. With the identification

$$\beta := \frac{1}{k_B T}\,, \tag{3.69}$$

the expression $e^{-\beta H}$ is called the **Boltzmann factor**.

Equation (3.66) makes it clear that T is *not* an average of some dynamical variable. Instead, it is a parameter characterizing the distribution of the members of the statistical ensemble over states of different energy values. Later, we see that T is proportional to the average kinetic energy per particle. However, this does *not* imply that T is *defined* in terms of the average kinetic energy. The average becomes computable only *after* we specify T.

We note that

$$\alpha = U - \Theta\eta = U - TS \tag{3.70}$$

is the Helmholtz free energy F. Thus, combining (3.53) and (3.66), we finally arrive at

$$F = -k_B T \ln C\,. \tag{3.71}$$

As exciting all these results are, (3.71) turns out to be not quite correct. To see why this is so, however, we have to temporarily accept (3.71) and explore its consequences. It is only by comparing the predictions of (3.71) against other areas of our experience that we are able to uncover the fatal flaw hidden in (3.71). Until Sect. 3.12, where we introduce corrections to both (3.68) and (3.71), we pretend as if everything is fine and press on.

Exercise 3.2.

a. Show that

$$U = -\frac{\partial \ln C}{\partial \beta} \,. \tag{3.72}$$

This is the statistical mechanical version of the **Gibbs–Helmholtz equation** derived in Exercise 2.15.

b. Show that

$$\frac{\partial^2 \ln C}{\partial \beta^2} = \left\langle (H - \langle H \rangle)^2 \right\rangle \,. \tag{3.73}$$

c. Show that

$$\frac{\partial^2 \ln C}{\partial \beta^2} = k_B T^2 C_V \,. \tag{3.74}$$

Combining parts b and c, we see that C_V is related to the characteristic width of fluctuation of H. ///

Exercise 3.3. Using (3.45) and (3.68), derive (3.71). ///

3.10 Simple Applications of Canonical Ensemble

To gain some familiarity with the formalism we have developed so far, we shall consider several simple model systems and compute a few of their thermodynamic properties using the canonical ensemble.

3.10.1 Rectangular Coordinate System

Example 3.5. Particle in a box: Consider a particle of mass m confined to a rectangular box of dimension $L_x \times L_y \times L_z$. The Hamiltonian of the system may be written as

$$H(\boldsymbol{r},\boldsymbol{p}) = \frac{p^2}{2m} + \psi_{\mathrm{w}}(\boldsymbol{r}) \,, \tag{3.75}$$

where $p^2 = \|\boldsymbol{p}\|^2$ and ψ_{w} is the potential energy arising from the interaction between the particle and the wall of the box. In this problem, we assume a

simple form for it:

$$\psi_{\mathrm{w}}(\boldsymbol{r}) = \begin{cases} 0 & \text{if } \boldsymbol{r} \text{ is in the box,} \\ \infty & \text{otherwise.} \end{cases} \tag{3.76}$$

The corresponding Boltzmann factor is given by

$$e^{-\beta H(\boldsymbol{r},\boldsymbol{p})} = \begin{cases} e^{-\beta p^2/2m} & \text{if } \boldsymbol{r} \text{ is in the box,} \\ 0 & \text{otherwise.} \end{cases} \tag{3.77}$$

The normalization constant C is obtained by integrating this expression over all phase space:[15]

$$C = \int e^{-\beta H} \mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{p} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-\beta H} \mathrm{d}x\mathrm{d}y\mathrm{d}z\mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z \,. \tag{3.78}$$

Let us start by considering the innermost integral:

$$\int_{-\infty}^{\infty} e^{-\beta H} \mathrm{d}x \,. \tag{3.79}$$

Since the integrand vanishes outside the box, it is sufficient to integrate from 0 to L_x. Over this interval, the integrand is independent of x. Thus,

$$\int_{-\infty}^{\infty} e^{-\beta H} \mathrm{d}x = L_x e^{-\beta H} \,. \tag{3.80}$$

When this expression is brought back into (3.78) and the integration with respect to y and z are performed in the similar manner, we find that

$$C = V \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-\beta H} \mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z \,, \tag{3.81}$$

where $V := L_x L_y L_z$ is the volume of the box. Next, we note that

$$p^2 = {p_x}^2 + {p_y}^2 + {p_z}^2 \,, \tag{3.82}$$

and hence

$$C = V \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-\beta {p_x}^2/2m} e^{-\beta {p_y}^2/2m} e^{-\beta {p_z}^2/2m} \mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z \,. \tag{3.83}$$

When performing the innermost integral with respect to p_x, we may regard p_y and p_z as constant. Thus,

$$C = V \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-\beta {p_y}^2/2m} e^{-\beta {p_z}^2/2m} \left[\int_{-\infty}^{\infty} e^{-\beta {p_x}^2/2m} \mathrm{d}p_x\right] \mathrm{d}p_y\mathrm{d}p_z \,. \tag{3.84}$$

Since the quantity in the square bracket is independent of p_y and p_z, it can be pulled out of the integrals with respect to p_y and p_z. The remaining two-dimensional integral can be performed similarly to yield

$$C = V\left[\int_{-\infty}^{\infty} e^{-\beta {p_x}^2/2m} \mathrm{d}p_x\right]\left[\int_{-\infty}^{\infty} e^{-\beta {p_y}^2/2m} \mathrm{d}p_y\right]\left[\int_{-\infty}^{\infty} e^{-\beta {p_z}^2/2m} \mathrm{d}p_z\right] . \tag{3.85}$$

Using the formula established in Exercise 3.4 to carry out the integrals, we obtain

$$C = V\left(\frac{2\pi m}{\beta}\right)^{3/2} . \tag{3.86}$$

By means of (3.71), we find

$$F = -k_B T\left[\ln V + \frac{3}{2}\ln\left(\frac{2\pi m}{\beta}\right)\right] . \tag{3.87}$$

This equation gives F as a function of T, V, and $N = 1$, and hence is a fundamental equation of the system. Other thermodynamic properties of the system can be obtained just by taking partial derivatives. For example, the pressure P is given by

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{k_B T}{V} , \tag{3.88}$$

which is recognized as the ideal gas equation of state applied to a system containing only a single particle. The internal energy follows from (3.72):

$$U = -\frac{\partial \ln C}{\partial \beta} = \frac{3}{2\beta} = \frac{3}{2}k_B T . \tag{3.89}$$

From (2.49),

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2}k_B . \tag{3.90}$$

These nontrivial results were obtained straightforwardly once the multidimensional integral in (3.78) was evaluated. It is doubtful that we would be so successful if we insisted on solving the equations of motion of the particle instead.

Exercise 3.4. Derive the following equality:

$$I(a) := \int_0^{\infty} e^{-ax^2} \mathrm{d}x = \frac{1}{2}\sqrt{\frac{\pi}{a}} . \tag{3.91}$$

Using this result, show that

$$\int_0^{\infty} x^2 e^{-ax^2} \mathrm{d}x = \frac{1}{4}\sqrt{\frac{\pi}{a^3}} \quad \text{and} \quad \int_0^{\infty} x^4 e^{-ax^2} \mathrm{d}x = \frac{3}{8}\sqrt{\frac{\pi}{a^5}} . \tag{3.92}$$

///

Example 3.6. Three-dimensional harmonic oscillator: Consider a particle of mass m bound to the origin by a harmonic potential $\psi(\boldsymbol{r}) = kr^2/2$. Using a Cartesian coordinate system, we specify the position of the particle by x, y, and z. The conjugate momenta are just the components of the linear momentum, that is, p_x, p_y, and p_z. Thus, the system Hamiltonian is

$$H(\boldsymbol{r},\boldsymbol{p}) = \frac{1}{2m}\left({p_x}^2 + {p_y}^2 + {p_z}^2\right) + \frac{1}{2}k\left(x^2+y^2+z^2\right) = \frac{p^2}{2m} + \frac{1}{2}kr^2 \,. \quad (3.93)$$

The normalization constant C is given by

$$C = \int e^{-\beta H(\boldsymbol{r},\boldsymbol{p})} \mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{p} = \int e^{-\beta p^2/2m} e^{-\beta k r^2/2} \mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{p} \,. \quad (3.94)$$

Noting that the result of carrying out the integration with respect to $\boldsymbol{r}$ is independent of $\boldsymbol{p}$, we have

$$C = \left[\int e^{-\beta p^2/2m} \mathrm{d}\boldsymbol{p}\right]\left[\int e^{-\beta k r^2/2} \mathrm{d}\boldsymbol{r}\right] \,. \quad (3.95)$$

These integrals can be evaluated using the Cartesian coordinate system as in Example 3.5. However, the numerical values of these integrals should be independent of the choice of the coordinate system we use. It is actually easier to evaluate them using the spherical coordinate system. For example,

$$\int e^{-\beta k r^2/2} \mathrm{d}\boldsymbol{r} = \int_0^\infty e^{-\beta k r^2/2} 4\pi r^2 \mathrm{d}r = \left(\frac{2\pi}{\beta k}\right)^{3/2} . \quad (3.96)$$

The first equality is justified because the integrand depends only on r and the volume of the spherical shell defined by two radii r and $r + \mathrm{d}r$ is, to the first order of $\mathrm{d}r$, given by $4\pi r^2 \mathrm{d}r$. The second equality follows from a formula from Exercise 3.4. Evaluating the second integral in (3.95) similarly, we arrive at

$$C = \left(\frac{2\pi m}{\beta}\right)^{3/2}\left(\frac{2\pi}{\beta k}\right)^{3/2} , \quad (3.97)$$

Since $C \propto \beta^{-3}$, we have $\ln C = -3\ln\beta + \text{const}$. Thus,

$$U = 3k_B T \quad \text{and} \quad C_V = 3k_B \,. \quad (3.98)$$

Exercise 3.5. Suppose that the Hamiltonian H of the system of N particles is given by

$$H(\boldsymbol{r}^N,\boldsymbol{p}^N) = \sum_{i=1}^{N} \frac{\|\boldsymbol{p}_i\|^2}{2m_i} + \phi(\boldsymbol{r}^N) \,. \quad (3.99)$$

Show that the probability $\rho(\boldsymbol{p}_1)\mathrm{d}\boldsymbol{p}_1$ that particle 1 has the linear momentum within the volume element $\mathrm{d}\boldsymbol{p}_1$ taken around $\boldsymbol{p}_1$ is given by

$$\rho(\boldsymbol{p}_1)\mathrm{d}\boldsymbol{p}_1 = \frac{1}{(2\pi m_1 k_B T)^{3/2}} \exp\left(-\frac{\|\boldsymbol{p}_1\|^2}{2m_1 k_B T}\right) \mathrm{d}\boldsymbol{p}_1 \ . \tag{3.100}$$

This is the well-known **Maxwell–Boltzmann distribution**, which is more often expressed as

$$\rho(\boldsymbol{v}_1)\mathrm{d}\boldsymbol{v}_1 = \left(\frac{m_1}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{m_1\|\boldsymbol{v}_1\|^2}{2k_B T}\right) \mathrm{d}\boldsymbol{v}_1 \ , \tag{3.101}$$

where we used $\mathrm{d}\boldsymbol{p}_1 = \mathrm{d}p_{1x}\mathrm{d}p_{1y}\mathrm{d}p_{1z} = {m_1}^3\mathrm{d}v_{1x}\mathrm{d}v_{1y}\mathrm{d}v_{1z} = {m_1}^3\mathrm{d}\boldsymbol{v}_1$. It is worth emphasizing that the Maxwell–Boltzmann distribution holds regardless of the form of the potential energy term $\phi(\boldsymbol{r}^N)$. ///

3.10.2 Equipartition Theorem

Looking back at Examples 3.5 and 3.6, we notice something interesting. In particular, each quadratic term, such as x^2 and ${p_x}^2$, in the Hamiltonian leads to a factor of $\beta^{-1/2}$ in C. In view of (3.72), this means that each quadratic term makes a contribution of $k_B T/2$ and $k_B/2$ to U and C_V, respectively.

This observation can be generalized straightforwardly. Thus, suppose that q_1 occurs in Hamiltonian as a quadratic term and appears nowhere else:

$$H(q^f, p^f) = a{q_1}^2 + h(q_2, \cdots, q_f, p_1, \cdots, p_f) \ . \tag{3.102}$$

If $e^{-\beta H}$ decays sufficiently fast with increasing $|q_1|$, the limits of integration for q_1 that is occurring in (3.46) can be extended to cover from $-\infty$ to ∞. Then, the $a{q_1}^2$ term gives rise to a factor of $(\pi/\beta a)^{1/2}$ in C.

Exercise 3.6. For a system described by the Hamiltonian given by (3.102), show that

$$\langle a{q_1}^2 \rangle = \frac{1}{2} k_B T \ . \tag{3.103}$$

///

More generally, if

$$H(q^f, p^f) = \sum_{i=1}^{f} \left(a_i {q_i}^2 + b_i {p_i}^2\right) \ , \tag{3.104}$$

and the limits of integration can be similarly extended to from $-\infty$ to ∞ for all q^f and p^f, then,

$$U = f k_B T, \quad \text{and} \quad C_V = f k_B \ . \tag{3.105}$$

This is called the **equipartition theorem** or the **principle of equipartition of energy** to indicate that U, on average, is partitioned equally among each mechanical degrees of freedom.

3.10.3 Spherical Coordinate System

In Example 3.6, we wrote down the expression for H using the Cartesian coordinate system and used the spherical coordinate system only in the last step when computing the multidimensional integrals for C. It is instructive to rework the same problem using the spherical coordinate system from the beginning.

Example 3.7. Three-dimensional harmonic oscillator: spherical coordinate system: We start from the Lagrangian:

$$L(\boldsymbol{r},\dot{\boldsymbol{r}}) = \frac{1}{2m}\left(\dot{x}^2+\dot{y}^2+\dot{z}^2\right) - \frac{1}{2}kr^2 \,. \tag{3.106}$$

In a spherical coordinate system,

$$x = r\sin\theta\cos\phi, \quad y = r\sin\theta\sin\phi, \quad z = r\cos\theta \,. \tag{3.107}$$

Taking the time derivative of these expressions, we find

$$\begin{aligned} \dot{x} &= \dot{r}\sin\theta\cos\phi + r\dot{\theta}\cos\theta\cos\phi - r\dot{\phi}\sin\theta\sin\phi \\ \dot{y} &= \dot{r}\sin\theta\sin\phi + r\dot{\theta}\cos\theta\sin\phi + r\dot{\phi}\sin\theta\cos\phi \\ \dot{z} &= \dot{r}\cos\theta - r\dot{\theta}\sin\theta \,. \end{aligned} \tag{3.108}$$

Using these expressions, we find[16]

$$\dot{x}^2+\dot{y}^2+\dot{z}^2 = \dot{r}^2 + r^2\dot{\theta}^2 + r^2\dot{\phi}^2\sin^2\theta \,. \tag{3.109}$$

Thus, in terms of the generalized coordinates r, θ, ϕ, and the corresponding generalized velocities $\dot{r}$, $\dot{\theta}$, and $\dot{\phi}$, the Lagrangian is given by

$$L = \frac{1}{2}m\left(\dot{r}^2 + r^2\dot{\theta}^2 + r^2\dot{\phi}^2\sin^2\theta\right) - \frac{1}{2}kr^2 \,. \tag{3.110}$$

By definition (1.103), the corresponding generalized momenta are

$$p_r = \frac{\partial L}{\partial \dot{r}} = m\dot{r}, \quad p_\theta = \frac{\partial L}{\partial \dot{\theta}} = mr^2\dot{\theta}, \quad p_\phi = \frac{\partial L}{\partial \dot{\phi}} = mr^2\dot{\phi}\sin^2\theta \,. \tag{3.111}$$

The Hamiltonian follows from (1.156) and is given by

$$H = \sum_i p_i \dot{q}_i - L = \frac{{p_r}^2}{2m} + \frac{{p_\theta}^2}{2mr^2} + \frac{{p_\phi}^2}{2mr^2 \sin^2\theta} + \frac{1}{2}kr^2 \,. \tag{3.112}$$

According to (3.46), the normalization constant C is given by

$$C = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} e^{-\beta H} \mathrm{d}\phi \mathrm{d}\theta \mathrm{d}r \mathrm{d}p_\phi \mathrm{d}p_\theta \mathrm{d}p_r \,, \tag{3.113}$$

in which ϕ, θ, and r are the generalized coordinates in this problem with the corresponding generalized momentum given by p_ϕ, p_θ, and p_r, respectively. Carrying out the integrations with respect to p_ϕ, p_θ, and p_r by means of the formula from Exercise 3.4, we find

$$C = \int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} \left(\frac{2\pi m}{\beta}\right)^{1/2} \left(\frac{2\pi mr^2}{\beta}\right)^{1/2} \left(\frac{2\pi mr^2 \sin^2\theta}{\beta}\right)^{1/2} \times e^{-\frac{1}{2}\beta k r^2} \mathrm{d}\phi \mathrm{d}\theta \mathrm{d}r \,. \tag{3.114}$$

But, because $\sin\theta \geq 0$ for $0 \leq \theta \leq \pi$, we have $(\sin^2\theta)^{1/2} = \sin\theta$. Thus,

$$C = \left(\frac{2\pi m}{\beta}\right)^{3/2} \int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} e^{-\frac{1}{2}\beta k r^2} r^2 \sin\theta \mathrm{d}\phi \mathrm{d}\theta \mathrm{d}r \,. \tag{3.115}$$

We observe that the Jacobian $r^2 \sin\theta$ of the coordinate transformation from (x, y, z) to (r, θ, ϕ) appeared naturally *without us having to put it in by hand*. Evaluating the integrals over ϕ, θ, and r in this order, we find

$$C = \left(\frac{2\pi m}{\beta}\right)^{3/2} \left(\frac{2\pi}{\beta k}\right)^{3/2} \tag{3.116}$$

in agreement with the result we found in Example 3.6.

Exercise 3.7. Counting the number of quadratic terms in (3.93), we conclude from the equipartition theorem that $U = 3k_BT$. Doing the same in (3.112), one might conclude that $U = 2k_BT$. Resolve this apparent contradiction. ///

Exercise 3.8. As a model for a diatomic molecule, take a pair of particles of mass m_1 and m_2 connected by a massless rigid rod of length l:

a. Calculate the normalization constant C for the system consisting of a single diatomic molecule confined to a cubic box of volume V. You may assume that $V^{1/3} \gg l$. Why is this assumption convenient?
b. What is the constant volume heat capacity C_V of the system?

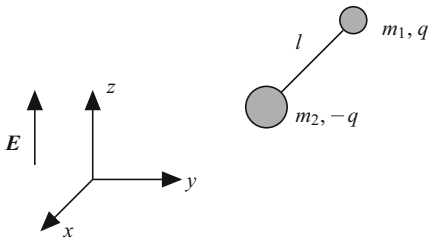


Fig. 3.5 A simple model of a polar molecule.

c. Replace the rigid rod by a harmonic spring of natural length l and spring constant k, and then redo the calculation. To make the computation analytically tractable, assume that $e^{-\beta k l^2/2} \approx 0$. ///

Exercise 3.9. Continuing with the rigid diatomic molecule from Exercise 3.8, suppose that the particles m_1 and m_2 carry electric charges q and $-q$, respectively. (See Fig. 3.5.) In the presence of a static electric field $\boldsymbol{E}$, the additional term $-\boldsymbol{m}_e \cdot \boldsymbol{E}$ is needed in the Hamiltonian of the molecule, where the dipole moment $\boldsymbol{m}_e$ is a vector of length ql pointing from m_2 to m_1:

a. Evaluate C of the molecule confined to a cubic box of volume V.
b. Show that
$$\frac{\partial \ln C}{\partial \boldsymbol{E}} = \beta \langle \boldsymbol{m}_e \rangle \,. \tag{3.117}$$
c. Show that
$$\frac{\partial E}{\partial \boldsymbol{E}} = \frac{\boldsymbol{E}}{E} \,, \tag{3.118}$$
where $E := \|\boldsymbol{E}\|$ should not be confused with energy.
d. Show that
$$\langle \boldsymbol{m}_e \rangle = m_e \mathscr{L}(\beta m_e E)\boldsymbol{e} \,, \tag{3.119}$$
where $\boldsymbol{e}$ is the unit vector pointing in the direction of the field and
$$\mathscr{L}(x) := \coth x - \frac{1}{x} = \frac{\cosh x}{\sinh x} - \frac{1}{x} \tag{3.120}$$
is the **Langevin function**.

In part a, the computation will be considerably easier if you align the z-axis with $\boldsymbol{E}$ as shown in Fig. 3.5. Since our choice of the coordinate system is arbitrary, this leads to no loss of generality. ///

3.10.4 †General Equipartition Theorem

In this section, we consider a more general form of the equipartition theorem. In particular, we establish that

$$\left\langle q_i \frac{\partial H}{\partial q_i} \right\rangle = k_B T \quad \text{and} \quad \left\langle p_i \frac{\partial H}{\partial p_i} \right\rangle = k_B T \,. \tag{3.121}$$

For example, let

$$H = \frac{1}{2m}\left({p_x}^2 + {p_y}^2 + {p_z}^2\right) \,. \tag{3.122}$$

According to (3.121),

$$k_B T = \left\langle p_x \frac{\partial H}{\partial p_x} \right\rangle = \left\langle \frac{{p_x}^2}{m} \right\rangle \tag{3.123}$$

in agreement with the more restricted form of the theorem discussed in Sect. 3.10.2.

To prove (3.121), let us first consider the following partial derivative:

$$\frac{\partial}{\partial q_1}\left(q_1 e^{-\beta H}\right) = e^{-\beta H} - \beta q_1 \frac{\partial H}{\partial q_1} e^{-\beta H} \,. \tag{3.124}$$

Integrating this expression over the entire phase space,

$$\int \left[q_1 e^{-\beta H}\right]_{q_1=-\infty}^{q_1=\infty} \mathrm{d}q_2 \cdots \mathrm{d}q_f \mathrm{d}p^f = C - \beta \int q_1 \frac{\partial H}{\partial q_1} e^{-\beta H} \mathrm{d}q^f \mathrm{d}p^f \,. \tag{3.125}$$

If the Hamiltonian is such that the Boltzmann factor vanishes for sufficiently large values of $|q_1|$, then the left-hand side of this equation is zero, yielding

$$k_B T = \frac{1}{C} \int q_1 \frac{\partial H}{\partial q_1} e^{-\beta H} \mathrm{d}q^f \mathrm{d}p^f = \left\langle q_1 \frac{\partial H}{\partial q_1} \right\rangle \,. \tag{3.126}$$

Likewise for the other q's. Carrying out the similar analysis with p_i, we obtain the second of (3.121).

3.11 Canonical Ensemble and Thermal Contact

In this section, we shall return to the question posed at the beginning of Sect. 3.9. On the one hand, ρ was determined by observing a single system for a long duration of time. During such an observation, the energy of the system should remain constant. On the other hand, the canonical ensemble contains the copies with various values of the energy. Does this mean that the canonical ensemble, despite its apparent success we saw in the previous sections, is purely an artificial construction with no counterpart in the real-world situation?

Let us go back to (3.45). This equation tells us that if we wanted to predict macroscopic behavior of a system by means of a canonical ensemble, we must first specify its temperature. Under an observational situation in which we wish to specify and control temperature, however, we must allow for an exchange of energy between the system and the surroundings. As a result, the energy of the system does not, in general, remain constant. So, the fact that the canonical ensemble contains the copies with various values of the energy does not invalidate this ensemble. Rather, it suggests that the ensemble may be relevant in describing the behavior of a system in *thermal contact* with the surroundings. In fact, under a modest set of assumptions, we can show that the canonical ensemble is the only possible ensemble one can construct for such cases.

First, we need to introduce the notion of a **weak interaction**. Let us consider an isolated system $\mathscr{S}_t$, in which we take a subsystem $\mathscr{S}_s$ enclosed by a rigid wall impermeable to particles. The other part of $\mathscr{S}_t$ will be referred to as the surroundings and denoted by $\mathscr{S}_r$. Quite generally then, the Hamiltonian H_t of $\mathscr{S}_t$ can be written as

$$H_t(q^{m+n}, p^{m+n}) = H_s(q^m, p^m) + H_r(q^n, p^n) + H_{\text{int}}(q^{m+n}, p^{m+n}) \,, \tag{3.127}$$

where m and n denote the numbers of mechanical degrees of freedom of $\mathscr{S}_s$ and $\mathscr{S}_r$, respectively. The last term H_{int} arises from the interaction between $\mathscr{S}_s$ and $\mathscr{S}_r$.

We note that this division of $\mathscr{S}_t$ into $\mathscr{S}_s$ and $\mathscr{S}_r$ would be purely formal and quite useless if H_{int} is of a comparable magnitude to either H_s or H_r. On the other hand, if H_{int} is identically zero, then we might as well imagine $\mathscr{S}_s$ and $\mathscr{S}_r$ as sitting at the opposite ends of a galaxy, and there will be very little motivation for us to study them simultaneously by regarding them as constituting a composite system $\mathscr{S}_t$. The situation we are interested in is somewhere in between.

With this in mind, the interaction between $\mathscr{S}_s$ and $\mathscr{S}_r$ is said to be *weak* if (1) H_{int} is of a negligible magnitude compared to H_s and H_r for typical values of their arguments to justify the approximation,

$$H_t(q^{m+n}, p^{m+n}) \approx H_s(q^m, p^m) + H_r(q^n, p^n) \tag{3.128}$$

but, at the same time, (2) it is still sufficient to ensure exchange of energy between $\mathscr{S}_s$ and $\mathscr{S}_r$ over a long duration of time.

Now, suppose that $\mathscr{S}_s$ consists of subsystems A and B and denote the numbers of mechanical degrees of freedom of these subsystems by m_a and m_b, respectively. Clearly, $m = m_a + m_b$. Furthermore, suppose that the interaction between A and B is also weak in the sense just defined. Then, we may write

$$H_s(q^m, p^m) \approx H_a(q^{m_a}, p^{m_a}) + H_b(q^{m_b}, p^{m_b}) \,, \tag{3.129}$$

where we note that H_a depends only on the generalized coordinates and the conjugate momenta pertaining to the mechanical degrees of freedom of subsystem A. Likewise for H_b. Thus, when Hamilton's equations of motion are obtained from H_s,

we should find out that those equations of motion dictating the time evolution of (q^{m_a}, p^{m_a}) are decoupled from those governing (q^{m_b}, p^{m_b}).

This approximate independence between the two subsystems implies that

$$\rho_s \approx \rho_a \rho_b \,, \tag{3.130}$$

and hence that

$$\ln \rho_s \approx \ln \rho_a + \ln \rho_b \,. \tag{3.131}$$

We recall from Sect. 3.6 that ρ is a function of constants of motion. Here we see that $\ln \rho$ is also additive. These requirements will be met if $\ln \rho$ is a linear function of constants of motion which are themselves additive. We note that energy is such a quantity and that the linear dependence of $\ln \rho$ on energy already indicates the canonical distribution.[17]

To see this more explicitly, let us suppose that ρ is a function of H only. If statistical mechanics is to have any predictive ability at all, this function $\rho(H)$ cannot be specific to each system we happen to choose for our study. Instead, we demand that the form of the function $\rho(H)$ is independent of a particular system under consideration. Thus, letting

$$\rho = a f(H) \,, \tag{3.132}$$

where a is a system-dependent constant that can be determined by the normalization condition of ρ, we write

$$a_s f(H_a + H_b) = a_a f(H_a) a_b f(H_b) \,. \tag{3.133}$$

Differentiating this equation with respect to H_a, we find

$$a_s f'(H_a + H_b) = a_a f'(H_a) a_b f(H_b) \,, \tag{3.134}$$

while differentiation with respect to H_b yields

$$a_s f'(H_a + H_b) = a_a f(H_a) a_b f'(H_b) \,. \tag{3.135}$$

From these two equations,

$$\frac{f'(H_a)}{f(H_a)} = \frac{f'(H_b)}{f(H_b)} \,, \tag{3.136}$$

which must hold regardless of the values of H_a and H_b. Note that the left-hand side depends only on H_a, while the right-hand side depends only on H_b, indicating that they can only be a constant. For example, we may arbitrarily fix H_a at 1J, and then allow H_b to change. Even then the equation must hold true since it holds for *any* values of H_a and H_b. Likewise, we can fix H_b and allow H_a to change. In any event, the expressions in (3.136) are equal to some constant, which we denote by $-\beta$. Upon integration, then we find

$$f(x) = b e^{-\beta x} \,, \tag{3.137}$$

where b is a constant. When this expression is substituted into (3.132) and ab is determined by the normalization condition of ρ, we find that

$$\rho_a = {C_a}^{-1} e^{-\beta H_a} , \quad \rho_b = {C_b}^{-1} e^{-\beta H_b} , \quad \text{and} \quad \rho_s = {C_s}^{-1} e^{-\beta H_s} , \tag{3.138}$$

which is the canonical distribution as advertised.

That β is common to subsystems A and B is quite consistent with our earlier conclusion that $\beta = (k_B T)^{-1}$. At equilibrium, the subsystems A and B both in contact with the same surroundings should have the same temperature. As noted already in Sect. 3.9, β must be positive in order for the integral for C to converge, an observation consistent with β being $(k_B T)^{-1}$.

If we substitute (3.138) into (3.130) and use (3.129), we arrive at the conclusion that

$$C_s = C_a C_b . \tag{3.139}$$

Or, equivalently,

$$\ln C_s = \ln C_a + \ln C_b , \tag{3.140}$$

which in light of (3.71) indicates that the Helmholtz free energy is an additive quantity.

It is significant that the additivity of the free energy relies on the interaction between the two subsystems A and B being sufficiently weak. This is the case if A and B are both macroscopic and the intermolecular potential between the molecules of A and those of B are sufficiently short ranged as to affect only those molecules near the boundary of the subsystems. Then, the interaction amounts to a surface effect, which is usually negligible for a macroscopic body.

If you look back at our derivation of Liouville's theorem in Sect. 3.6, which guided our search for ρ, you might wonder, however. Did we not write down equations of motion for the system assuming that it was isolated? Then, in our search for ρ of a system in thermal contact with the surroundings, why can we still accept the conclusion drawn from Liouville's theorem and limit our search of ρ to the functions of H alone?

But, we recall that the interaction between the system and the surroundings were supposed to be sufficiently weak. So, over a time interval that is not too long, the system behaves like an isolated system to a sufficient degree of accuracy. The equations of motion obtained by ignoring H_{int}, and hence Liouville's theorem, will be sufficiently accurate over such a time interval. If many segments of phase trajectory from many such intervals of time are combined together, we expect to end up with a canonical distribution.

Exercise 3.10. What is the role of the surroundings $\mathscr{S}_r$ in arriving at (3.138)? ///

Exercise 3.11. Show that the entropy as given by Gibbs's entropy formula is additive. ///

3.12 Corrections from Quantum Mechanics

As pointed out at the end of Sect. 3.9, our formula (3.71) for F is not quite correct as it stands. In this section, we see why this is so and then introduce necessary corrections.

3.12.1 A System of Identical Particles

Suppose that we have N noninteracting identical particles in a rectangular box of dimension $L_x \times L_y \times L_z$. The Hamiltonian is given by

$$H(\boldsymbol{r}^N, \boldsymbol{p}^N) = \sum_{i=1}^{N} \frac{\|\boldsymbol{p}_i\|^2}{2m} + \psi_{\mathrm{w}}(\boldsymbol{r}^N) \,, \tag{3.141}$$

where ψ_{w} is the wall potential as in Example 3.5. With $\boldsymbol{p}_i \doteq (p_{ix}, p_{iy}, p_{iz})$, we have $\|\boldsymbol{p}_i\|^2 = {p_{ix}}^2 + {p_{iy}}^2 + {p_{iz}}^2$. Thus,

$$C = \int e^{-\beta H(\boldsymbol{r}^N, \boldsymbol{p}^N)} \mathrm{d}\boldsymbol{r}^N \mathrm{d}\boldsymbol{p}^N = V^N \left(\frac{2\pi m}{\beta} \right)^{3N/2} . \tag{3.142}$$

(If this result is not obvious to you, set $N = 2$ and evaluate C following Example 3.5.) Combining (3.71) and (3.142), we obtain

$$F = -k_B T \left[\frac{3N}{2} \ln(2\pi m k_B T) + N \ln V \right] \tag{3.143}$$

for the Helmholtz free energy of the system. The pressure of the system follows from

$$P = -\left(\frac{\partial F}{\partial V} \right)_{T,N} = \frac{N k_B T}{V} \,, \tag{3.144}$$

which is the ideal gas equation of state.

Our expression for F, however, is not quite correct. To see this, let us rewrite (3.143) as

$$F = a_1(T) N + a_2(T) N \ln V \,, \tag{3.145}$$

where a_1 and a_2 are some functions of T. Now, we recall from (3.140) and also from thermodynamics that F is extensive, that is,

$$F(T, \lambda V, \lambda N) = \lambda F(T, V, N) \,, \tag{3.146}$$

which is in direct conflict with the result just obtained. Equally disturbing is the fact that (3.145) fails to satisfy the Euler relation as you can easily verify by writing the latter as

$$F = -PV + \mu N \,. \tag{3.147}$$

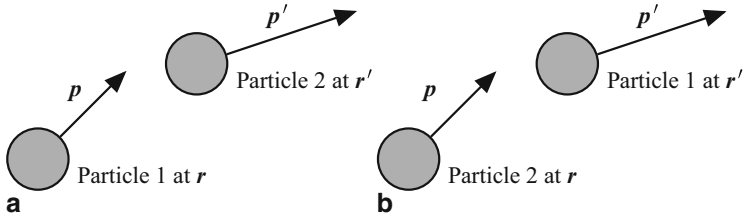


Fig. 3.6 In classical mechanics, **a** and **b** represent two distinct microstates $(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{p}_1,\boldsymbol{p}_2) = (\boldsymbol{r},\boldsymbol{r}',\boldsymbol{p},\boldsymbol{p}')$ and $(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{p}_1,\boldsymbol{p}_2) = (\boldsymbol{r}',\boldsymbol{r},\boldsymbol{p}',\boldsymbol{p})$, respectively. According to quantum mechanics, they represent the same state.

Statistical mechanics as we have developed it so far cannot coexist with thermodynamics!

What went wrong? The problem is *not* with our development of statistical mechanics. Rather, it is with our starting point, that is, classical mechanics. The difficulty lies in the fact that the behavior of molecules is governed not by classical mechanics but by quantum mechanics. To address the difficulty with (3.143), we simply borrow a few relevant facts from quantum mechanics.

In classical mechanics, particles are distinguishable even if they look exactly the same. At $t = 0$, we can mentally label all the molecules in the system and measure their positions and velocities. Then, the equations of motion will tell us precisely which particle is where at any other instant. Thus, for any particle we pick at a later time, we know the label we have given it at the earlier time even if we were not paying any attention to the system in between. According to quantum mechanics, however, this simply cannot be done *even in principle*. In the quantum mechanical world, identical particles are *fundamentally indistinguishable*, that is, neither a computational nor an experimental means of distinguishing them can ever be constructed.

Recall that C was introduced as the normalization constant. By writing

$$C = \int e^{-\beta H(\boldsymbol{r}^N,\boldsymbol{p}^N)} \mathrm{d}\boldsymbol{r}^N \mathrm{d}\boldsymbol{p}^N \,, \tag{3.148}$$

we hoped to sum the unnormalized probability $e^{-\beta H}\mathrm{d}\boldsymbol{r}^N\mathrm{d}\boldsymbol{p}^N$ over all possible states. According to quantum mechanics, however, this amounts to counting each state many times.

To figure out exactly how many times, consider a system of just two particles. In the integral

$$C = \int e^{-\beta H} \mathrm{d}\boldsymbol{r}_1 \mathrm{d}\boldsymbol{r}_2 \mathrm{d}\boldsymbol{p}_1 \mathrm{d}\boldsymbol{p}_2 \,, \tag{3.149}$$

the configurations shown in Fig. 3.6a and b are both included. But, quantum mechanics tells us to count these classical mechanically distinct two states as a single state. Since these two states have the identical value of the Boltzmann factor, they contribute equally to C. The same consideration applies to any other pair of

N	Exact	(3.152)	(3.153)
1	0	−0.8106	−1
2	0.6931	0.6518	−0.6137
3	1.7917	1.7641	0.29584
4	3.1781	3.1573	1.5452
5	4.7875	4.7708	3.0472
10	15.104	15.096	13.026
50	148.48	148.48	145.60
100	363.74	363.74	360.52
1000	5912.1	5912.1	5907.8
10000	82109	82109	82103

Table 3.1 Accuracy of the approximate formulae, (3.152) and (3.153), for computing $\ln N!$.

classical mechanically distinct, but quantum mechanically identical, states. Thus, we should really be writing the normalization constant as

$$C' = \frac{1}{2}\int e^{-\beta H}\mathrm{d}\boldsymbol{r}_1\mathrm{d}\boldsymbol{r}_2\mathrm{d}\boldsymbol{p}_1\mathrm{d}\boldsymbol{p}_2\ . \tag{3.150}$$

What happens if we have three particles? To answer this, we note that Fig. 3.6b was obtained from Fig. 3.6a simply by switching the labels "1" and "2" attached to the two particles, and the number 2 which divides C can be understood as the number of distinct ways of labeling the particles in the system. When we have three particles, there are $3! = 3\cdot 2\cdot 1 = 6$ distinct ways of labeling them. (Using the labels 1, 2, and 3 once and only once.)

Generalizing this result to a system of N identical particles, we conclude that the number of distinct permutations of N particles is $N! := N(N-1)(N-2)\cdots 3\cdot 2\cdot 1$. So, we should have defined the normalization factor by

$$C' = \frac{1}{N!}\int e^{-\beta H(\boldsymbol{r}^N,\boldsymbol{p}^N)}\mathrm{d}\boldsymbol{r}^N\mathrm{d}\boldsymbol{p}^N\ . \tag{3.151}$$

For a sufficiently large N, the following approximate relation, called **Stirling's formula**, holds.

$$\ln N! \approx N\ln N - N + \frac{1}{2}\ln(2\pi N) \tag{3.152}$$

$$\approx N\ln N - N\ . \tag{3.153}$$

The accuracy of these approximate formulae is illustrated in Table 3.1. In statistical mechanics, the typical values of N are in the order of 10^{24} and (3.153) is seen to be quite sufficient.

Using (3.153), we can show that the Helmholtz free energy defined by

$$F := -k_B T\ln C' \tag{3.154}$$

is an extensive quantity for a system of N noninteracting identical particles.

Exercise 3.12. Prove this statement. ///

Exercise 3.13. Provide a plausibility argument to support (3.153). ///

What if N is not large enough to ensure the accuracy of Stirling's formula? In this case, even with the $N!$ factor, the Helmholtz free energy of the system is not extensive. This is not a cause for a concern, though. If two small systems are brought together, the energy of their mutual interaction can be comparable with the energy of either one of them alone. As discussed in Sect. 3.11, there is no reason to expect the free energy to be extensive in such cases.

As of now, we shall officially retire (3.71). You do not need (3.154) beyond this point, either. In its place, we introduce the correct formula for F in (3.167). That is the equation you need to remember and use.

3.12.2 Implication of the Uncertainty Principle

There is another important quantum mechanical effect, which we have ignored up to this point. Contrary to the underlying assumption of classical mechanics, the **Heisenberg uncertainty principle** states that both $\boldsymbol{r}$ and $\boldsymbol{p}$ of a particle cannot be determined simultaneously with absolute precision. Instead, quantum mechanics places a *fundamental limit* on the precision that is achievable in our measurement.

Focusing only on the x-component, let $(\Delta x)_{QM}$ denote the uncertainty[18] associated with the measured value of x. Likewise, $(\Delta p_x)_{QM}$ is the uncertainty associated with the measured value of p_x. Naturally, we would like to make both $(\Delta x)_{QM}$ and $(\Delta p_x)_{QM}$ as small as possible. However, the uncertainty principle demands that, for a *simultaneous* measurement of x and p_x, they satisfy

$$(\Delta x)_{QM}(\Delta p_x)_{QM} \gtrsim h\,, \tag{3.155}$$

where the quantity $h = 6.626 \times 10^{-34}$ (J·s) is the **Planck constant** having the dimension of *action* as in action integral. The similar relations hold for the y- and z- components of $\boldsymbol{r}$ and $\boldsymbol{p}$. Even though h is very small, it is not zero. If we are to determine x with absolute certainty, that is, if $(\Delta x)_{QM} = 0$, then we have absolutely no idea what p_x is at that very moment. We emphasize that this limitation is not due to practical difficulties in manufacturing a measuring device, but that it is a consequence of the principles of quantum mechanics.

To explore the consequence of (3.155), let us consider a system of a single particle confined to a one-dimensional container. In its phase space, suppose we take a box of area h. Classical mechanically, there are infinitely many distinct states in this box, and the integration

$$\int_{p_x-(\Delta p_x)_{QM}/2}^{p_x+(\Delta p_x)_{QM}/2} \int_{x-(\Delta x)_{QM}/2}^{x+(\Delta x)_{QM}/2} e^{-\beta H(x,p_x)} \mathrm{d}x\mathrm{d}p_x \tag{3.156}$$

adds up the Boltzmann factor for all of these states. According to quantum mechanics, however, it is meaningless to try to distinguish these states. Thus, the integration should be replaced by a single Boltzmann factor.

Because the area h of the box is actually quite small, the Boltzmann factor remains essentially constant within the box. (We could of course make $(\Delta x)_{QM}$ extremely small causing $(\Delta p_x)_{QM}$ to be extremely large, and vice versa. Such a choice of a box must be excluded in order for our argument to hold.) So, in place of (3.156), we can simply write

$$e^{-\beta H(x^*, {p_x}^*)} \tag{3.157}$$

without being precise about the values of x^* and p^* except to note that (x^*, p^*) should be somewhere in the box of area h:

$$x - \frac{(\Delta x)_{QM}}{2} \le x^* \le x + \frac{(\Delta x)_{QM}}{2} \quad \text{and} \quad p_x - \frac{(\Delta p_x)_{QM}}{2} \le {p_x}^* \le p_x + \frac{(\Delta p_x)_{QM}}{2} . \tag{3.158}$$

Due to the smallness of h, we can replace (3.157) by its average taken inside the box:

$$\frac{1}{h} \int_{p_x - (\Delta p_x)_{QM}/2}^{p_x + (\Delta p_x)_{QM}/2} \int_{x - (\Delta x)_{QM}/2}^{x + (\Delta x)_{QM}/2} e^{-\beta H(x, p_x)} \mathrm{d}x \mathrm{d}p_x \tag{3.159}$$

without introducing a noticeable change in the end result. Computationally, this is a much easier quantity to handle than (3.157).

The uncertainty relation holds for any pair of a generalized coordinate and its conjugate momentum. Thus, generalizing the above consideration to the case of a mechanical system having f degrees of freedom, we may regard a volume element of size h^f in the phase space as containing a single state, and write the normalization constant as

$$Z = \frac{1}{h^f} \int e^{-\beta H(q^f, p^f)} \mathrm{d}q^f \mathrm{d}p^f . \tag{3.160}$$

As we saw in the previous section, if there are identical particles in the system and the integration over q^f and p^f induces $\mathscr{P}$ distinct permutations of identical particles, we have

$$Z = \frac{1}{h^f \mathscr{P}} \int e^{-\beta H(q^f, p^f)} \mathrm{d}q^f \mathrm{d}p^f . \tag{3.161}$$

The quantity Z is called the **canonical partition function** and is *dimensionless*.

For a system of N identical particles in a three-dimensional space, we have $h^f \mathscr{P} = h^{3N} N!$, and hence the partition function is given by

$$Z = \frac{1}{h^{3N} N!} \int e^{-\beta H(\boldsymbol{r}^N, \boldsymbol{p}^N)} \mathrm{d}\boldsymbol{r}^N \mathrm{d}\boldsymbol{p}^N . \tag{3.162}$$

The actual uncertainty relation reads

$$\langle \Delta x \rangle_{QM} \langle \Delta p_x \rangle_{QM} \ge \frac{h}{4\pi} \tag{3.163}$$

as we shall see in Sect. 8.7.2. However, 4π does not factor in here. The $1/h^{3N}N!$ factor is chosen so that the quantum mechanical partition function agrees with our Z in the so called classical limit. See Sect. 8.16.5 for details.

We emphasize that the correction factor $1/h^f\mathscr{P}$ (or $1/h^{3N}N!$) arises from quantum mechanical considerations and is quite foreign to purely classical mechanical view of the world. This makes an intuitive interpretation of such *hybrid formula* as (3.161) and (3.162) difficult to obtain. In fact, any such attempt, if taken too literally, leads to contradiction with the correct quantum mechanical interpretation. Nevertheless, we find it convenient to interpret $\int$ as "the sum over states" as before and regard

$$e^{-\beta H(q^f,p^f)}\frac{\mathrm{d}q^f\mathrm{d}p^f}{h^f\mathscr{P}}\,, \tag{3.164}$$

as the unnormalized probability of finding the system within the infinitesimal volume element $\mathrm{d}q^f\mathrm{d}p^f$ in the phase space taken around the phase point (q^f,p^f). Dividing (3.164) by the normalization factor Z, we see that

$$\rho(q^f,p^f)\mathrm{d}q^f\mathrm{d}p^f=\frac{1}{Z}e^{-\beta H(q^f,p^f)}\frac{\mathrm{d}q^f\mathrm{d}p^f}{h^f\mathscr{P}} \tag{3.165}$$

is the normalized probability of finding the system within the infinitesimal volume element $\mathrm{d}q^f\mathrm{d}p^f$.

The breakdown of Z into the sum over states and the unnormalized probability is not unique. We note, however, that the probability given by (3.165) is dimensionless while the probability *density* ρ as defined by this equation carries the dimension of $1/(\text{action})^f$. This is what one should expect.

The ensemble average $\langle A\rangle$ of a dynamical variable A is now given by

$$\langle A\rangle=\frac{1}{Z}\int A(q^f,p^f)e^{-\beta H(q^f,p^f)}\frac{\mathrm{d}q^f\mathrm{d}p^f}{h^f\mathscr{P}}\,. \tag{3.166}$$

Since $Z=C/h^f\mathscr{P}$, the correction factor $h^f\mathscr{P}$ drops out when computing the ensemble average and (3.48) requires no modification. However, (3.71) must be corrected. Introducing the correction factor $h^f\mathscr{P}$ into C, we have

$$F=-k_BT\ln Z\,. \tag{3.167}$$

in place of (3.71). As seen from the following exercise, we have

$$S=-k_B\langle\ln(h^f\mathscr{P}\rho)\rangle\,. \tag{3.168}$$

The latter is identical to (3.68) except for the $h^f\mathscr{P}$ factor.

Exercise 3.14. Using (3.165), (3.167), and the definition $F:=U-TS$, show that S is given by (3.168). ///

3.12.3 Applicability of Classical Statistical Mechanics

We introduced the $1/h^{3N}N!$ factor based on quantum mechanical considerations. By simply grafting quantum concepts onto the classical mechanical framework, however, we cannot possibly expect to arrive at a theory that agrees with quantum mechanical predictions on *all* accounts. It is therefore important for us to know when we can expect classical statistical mechanics, with the factor $1/h^{3N}N!$, to be an acceptable mode of description.

First, we define

$$(\Delta p_x)_{SM} := \left\langle (p_x - \langle p_x \rangle)^2 \right\rangle^{1/2} , \tag{3.169}$$

which may be considered as the purely statistical mechanical uncertainty in p_x. For a classical mechanical particle in a box,

$$\frac{1}{2}k_B T = \left\langle \frac{{p_x}^2}{2m} \right\rangle . \tag{3.170}$$

as we saw in Example 3.5. You can also easily convince yourself that $\langle p_x \rangle = 0$ since the probability density ρ is an even function of p_x. Thus,

$$(\Delta p_x)_{SM} = \sqrt{m k_B T} . \tag{3.171}$$

Given that this statistical mechanical uncertainty is always present in systems of our interest, we have no reason to require the quantum mechanical uncertainty $(\Delta p_x)_{QM}$ to be any smaller than this. At the same time, we probably do not want $(\Delta p_x)_{QM}$ to be much larger than $(\Delta p_x)_{SM}$, either. Otherwise, predictions of classical statistical mechanics would be of little use. Demanding, therefore, that they are of comparable magnitude, we may rewrite (3.155) as

$$(\Delta x)_{QM} \approx \frac{h}{\sqrt{m k_B T}} \approx \frac{h}{\sqrt{2\pi m k_B T}} =: \Lambda , \tag{3.172}$$

where the quantity Λ, defined by the expression proceeding it, is known as the **thermal wavelength**.

The classical approach would be acceptable if Λ is much smaller than the diameter of particles in the system since in that case, *for all practical purposes* we know "exactly" where our particles are. Assuming a typical value of 2×10^{-10} m for the diameter of an atom, this requirement translates to $T \gg 2$ K for argon and $T \gg 20$ K for helium.

Exercise 3.15. By making an appropriate change to the normalization constant C you have computed in Exercise 3.8a, compute the partition function Z for the rigid diatomic molecule. ///

Exercise 3.16. As a model for an ideal gas, consider a collection of N noninteracting identical particles confined to a container of volume V:

a. Compute the partition function Z of the ideal gas.
b. Derive expressions for internal energy, pressure, and chemical potential of the ideal gas. ///

Exercise 3.17. A binary ideal gas mixture consisting of $2N$ particles of species A and N particles of species B is confined to a container of volume V made of diathermal, rigid, and impermeable wall, and is maintained at constant T. Find the reversible work required to isothermally separate the mixture into pure A and B occupying $V/3$ and $2V/3$, respectively. ///

3.13 †A Remark on the Statistical Approach

In the traditional approach to statistical mechanics, the notion of statistical ensemble and that of an ensemble average are introduced independent of a long-time average. The equivalence between these two kinds of average,

$$\langle A \rangle = A_{\text{expt}} \,, \tag{3.173}$$

is then adopted as a hypothesis. Any attempt to justifying this hypothesis on the basis of classical mechanics leads to a very difficult problem called the **ergodic problem**.

For us, (3.173) is a consequence of how we constructed our statistical ensemble. This, however, *does not* mean that we have circumvented the ergodic problem. In fact, we have not shown how our observation of a single mechanical system over the time period τ should lead to ρ that is given by (3.45).

We recall that $\tau \to \infty$ in (3.11) only meant that τ is much longer than the characteristic time scale of vibrational molecular motion. The actual value of τ we had in mind is comparable with a duration of a typical measurement, say 10^{-4} s or so. Certainly, this is not sufficiently long for a given molecule, in a glass of water for example, to fully explore all possible positions (and momentum) accessible to it. Diffusive exploration by this molecule throughout the entire glass takes much longer than 10^{-4} s. Nevertheless, the Boltzmann factor $e^{-\beta H}$ is nonzero for all possible positions of this molecule with finite H. Despite this contradiction, our statistical approach is apparently very successful. Why is that?

We can offer at least two qualitative explanations. Firstly, our macroscopic measurement is not fine enough to distinguish two molecules of the same species. Quantum mechanics actually preclude this possibility. Thus, we are concerned only with those dynamical variables that are invariant with respect to permutation of *identical* molecules. The value of a dynamical variable A evaluated at two distinct phase points

$$(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3, \ldots, \boldsymbol{r}_N, \boldsymbol{p}_1, \boldsymbol{p}_2, \boldsymbol{p}_3, \ldots, \boldsymbol{p}_N) \quad \text{and} \quad (\boldsymbol{r}_2, \boldsymbol{r}_1, \boldsymbol{r}_3, \ldots, \boldsymbol{r}_N, \boldsymbol{p}_2, \boldsymbol{p}_1, \boldsymbol{p}_3, \ldots, \boldsymbol{p}_N) \,, \tag{3.174}$$

for example, should be equal.

Secondly, macroscopic measurements are usually not sufficiently sensitive. Thus, even if the phase trajectory is perturbed slightly, our measurement lacks the sensitivity to detect the resulting change in A.

These observations suggest that the appropriate construction of the probability density ρ is not quite what we saw in Sect. 3.3. Instead, we proceed as follows: Given a phase trajectory of a mechanical system, we consider all possible permutations of the coordinates of the identical particles and then "smear out" the trajectories thus obtained to give them a nonzero thickness. Whether our newly constructed ρ leads to (3.45) is still an open question, of course.

We shall take a pragmatic point of view in what follows. We accept (3.45) and (3.173) as the fundamental hypothesis of our theory. The hypothesis should be deemed appropriate if the theory produces predictions in agreement with the outcome of experiments. This is how physical theories are constructed elsewhere.

3.14 ‡Expressions for P and μ

In statistical mechanics, T is a parameter characterizing a statistical ensemble. Nevertheless, it is possible to express T as a thermal average of a dynamical variable. In fact, the equipartition theorem implies that

$$T = \frac{2}{3k_B N} \left\langle \sum_{i=1}^{N} \frac{\|\boldsymbol{p}_i\|^2}{2m} \right\rangle \tag{3.175}$$

for a system of N identical particles confined to a three-dimensional box. In a similar manner, we can express other intensive quantities, P and μ, as thermal averages of some dynamical variables in a canonical ensemble even though they are parameters characterizing statistical ensembles as we shall see in Chap. 4.

In this section, we derive expressions for P and μ for a system of N identical particles with the Hamiltonian

$$H = \sum_{i=1}^{N} \frac{\|\boldsymbol{p}_i\|^2}{2m} + \phi(\boldsymbol{r}^N) \,, \tag{3.176}$$

in which ϕ is the potential energy due to interparticle interactions. The canonical partition function of the system is given by

$$Z = \frac{1}{h^{3N} N!} \int e^{-\beta H(\boldsymbol{r}^N, \boldsymbol{p}^N)} d\boldsymbol{r}^N \mathrm{d}\boldsymbol{p}^N = \frac{1}{\Lambda^{3N} N!} \int e^{-\beta \phi(\boldsymbol{r}^N)} \mathrm{d}\boldsymbol{r}^N \,, \tag{3.177}$$

where we carried out the momentum integration, that is, the integration with respect to $\boldsymbol{p}^N$. The remaining integral

$$\int e^{-\beta \phi(\boldsymbol{r}^N)} \mathrm{d}\boldsymbol{r}^N \tag{3.178}$$

is called the **configurational integral**.

3.14.1 ‡Pressure

Recalling (2.193), we have

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = k_B T \left(\frac{\partial \ln Z}{\partial V}\right)_{T,N} . \tag{3.179}$$

In (3.178), V appears in the limits of integration with respect to $\boldsymbol{r}^N$. To facilitate the computation of the partial derivative, we assume that the system is a cube of side length $L = V^{1/3}$ and introduce a new set of variables by

$$\boldsymbol{r}_i =: L\boldsymbol{s}_i , \quad i = 1, \ldots, N . \tag{3.180}$$

We note that

$$\mathrm{d}\boldsymbol{r}_i = \mathrm{d}x_i \mathrm{d}y_i \mathrm{d}z_i = L^3 \mathrm{d}s_{ix} \mathrm{d}s_{iy} \mathrm{d}s_{iz} = V \mathrm{d}\boldsymbol{s}_i \tag{3.181}$$

with s_{ix} denoting the x-component of $\boldsymbol{s}_i$ and similarly for s_{iy} and s_{iz}. Thus,

$$Z = \frac{V^N}{\Lambda^{3N} N!} \int e^{-\beta\phi(L\boldsymbol{s}_1, \ldots, L\boldsymbol{s}_N)} \mathrm{d}\boldsymbol{s}^N =: \frac{V^N}{\Lambda^{3N} N!} Q_N , \tag{3.182}$$

where the integration is over the unit cube, that is, the cube of side length 1. We see that the V dependence of Z is now made explicit in the factor V^N and in the potential energy ϕ. From (3.179) and (3.182),

$$P = k_B T \left[\frac{N}{V} + \frac{1}{Q_N}\left(\frac{\partial Q_N}{\partial V}\right)_{T,N}\right] = P^{\mathrm{id}} - \left\langle \frac{\partial \phi}{\partial V} \right\rangle , \tag{3.183}$$

where $P^{\mathrm{id}} := k_B T N/V$ is the ideal gas contribution to P and $\partial\phi/\partial V$ is evaluated for fixed $\boldsymbol{s}^N$. Invoking the chain rule, we find

$$\frac{\partial \phi}{\partial V} = \frac{\mathrm{d}L}{\mathrm{d}V}\frac{\partial \phi}{\partial L} = \frac{L}{3V}\sum_{i=1}^{N} \frac{\partial \boldsymbol{r}_i}{\partial L} \cdot \nabla_i \phi(\boldsymbol{r}^N) = \frac{1}{3V}\sum_{i=1}^{N} \boldsymbol{r}_i \cdot \nabla_i \phi(\boldsymbol{r}^N) , \tag{3.184}$$

where

$$\nabla_i \phi \doteq \left(\frac{\partial \phi}{\partial x_i}, \frac{\partial \phi}{\partial y_i}, \frac{\partial \phi}{\partial z_i}\right) \tag{3.185}$$

is the negative of the net force exerted on the ith particle by the other particles in the system. Defining the internal **virial** by

$$\mathscr{V} := -\frac{1}{3}\sum_{i=1}^{N} \boldsymbol{r}_i \cdot \nabla_i \phi , \tag{3.186}$$

we have

$$P = P^{\mathrm{id}} + \frac{\langle \mathscr{V} \rangle}{V} . \tag{3.187}$$

It is convenient and often acceptable to assume the **pairwise additivity** of ϕ. That is, we assume that ϕ may be written as

$$\phi(\boldsymbol{r}^N) = \frac{1}{2}\sum_{j=1}^{N}\sum_{k=1}^{N}{}' v(r_{jk}) \,, \tag{3.188}$$

where v is called the **pair potential** and $'$ on the second summation sign indicates that the $k = j$ term is excluded from the sum. We also defined

$$\boldsymbol{r}_{jk} := \boldsymbol{r}_j - \boldsymbol{r}_k \tag{3.189}$$

and made the usual assumption that the potential energy of interaction between jth and kth particles depends only on the distance $r_{jk} := \|\boldsymbol{r}_{jk}\|$ between them.

In order to compute $\nabla_i \phi$ in the internal virial, we must first isolate $\boldsymbol{r}_i$-dependent terms in (3.188). These are the terms corresponding to either $j = i$ or $k = i$. So, the quantity of our interest is

$$\frac{1}{2}\sum_{k\neq i} v(r_{ik}) + \frac{1}{2}\sum_{j\neq i} v(r_{ji}) \,. \tag{3.190}$$

The first term is obtained by retaining only the $j = i$ term in the summation over j and noting that the condition $k \neq j$ on the second sum translates to $k \neq i$ for this term. Similarly for the second term. Since k in the first term of (3.190) is just a dummy index, it can be replaced by j without affecting its value. We also note that $r_{ji} = r_{ij}$ in the second term. So, we can rewrite (3.190) as

$$\sum_{j\neq i} v(r_{ij}) \,, \tag{3.191}$$

which is just the sum of v for all the pairwise interactions involving the ith particle. This is exactly what the phrase "pairwise additivity" suggests. In any case, we now have

$$\nabla_i \phi(\boldsymbol{r}^N) = \sum_{j\neq i} \nabla_i v(r_{ij}) \,, \tag{3.192}$$

indicating simply that the net force exerted on the ith particle by the rest of the particles in the system is given by the sum of the individual contribution from each particle.

The expression $\nabla_i v(r_{ij})$ can be evaluated as follows. From (3.189) and

$${r_{ij}}^2 = {x_{ij}}^2 + {y_{ij}}^2 + {z_{ij}}^2 \,, \tag{3.193}$$

we see that

$$2r_{ij}\frac{\partial r_{ij}}{\partial x_i} = 2x_{ij}\frac{\partial x_{ij}}{\partial x_i} = 2x_{ij} \,. \tag{3.194}$$

So,

$$\frac{\partial r_{ij}}{\partial x_i} = \frac{x_{ij}}{r_{ij}} \,. \tag{3.195}$$

Noting the similar relations for $\partial r_{ij}/\partial y_i$ and $\partial r_{ij}/\partial z_i$, we have

$$\nabla_i r_{ij} = \frac{\boldsymbol{r}_{ij}}{r_{ij}} \,, \tag{3.196}$$

Thus, by means of the chain rule, we have

$$\nabla_i v(r_{ij}) = \frac{\mathrm{d}v(r_{ij})}{\mathrm{d}r_{ij}} \frac{\boldsymbol{r}_{ij}}{r_{ij}} \,. \tag{3.197}$$

Combining everything,

$$\sum_{i=1}^{N} \boldsymbol{r}_i \cdot \nabla_i \phi = \sum_{i=1}^{N} \sum_{j=1}^{N}{}' \frac{\mathrm{d}v(r_{ij})}{\mathrm{d}r_{ij}} \frac{\boldsymbol{r}_{ij}}{r_{ij}} \cdot \boldsymbol{r}_i = \sum_{i=1}^{N} \sum_{j=1}^{N}{}' \frac{\mathrm{d}v(r_{ji})}{\mathrm{d}r_{ji}} \frac{\boldsymbol{r}_{ji}}{r_{ji}} \cdot \boldsymbol{r}_j \,. \tag{3.198}$$

Adding the last two alternative expressions for the same quantity and noting that $\boldsymbol{r}_{ji} = -\boldsymbol{r}_{ij}$ while $r_{ij} = r_{ji}$, we find

$$\sum_{i=1}^{N} \boldsymbol{r}_i \cdot \nabla_i \phi = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N}{}' \frac{\mathrm{d}v(r_{ij})}{\mathrm{d}r_{ij}} r_{ij} \,. \tag{3.199}$$

So, for a pairwise additive potential, the internal virial is

$$\mathscr{V} = -\frac{1}{6} \sum_{i=1}^{N} \sum_{j=1}^{N}{}' \frac{\mathrm{d}v(r_{ij})}{\mathrm{d}r_{ij}} r_{ij} \tag{3.200}$$

and we finally arrive at the desired expression for P:

$$P = P^{\mathrm{id}} - \frac{1}{6V} \left\langle \sum_{i=1}^{N} \sum_{j=1}^{N}{}' \frac{\mathrm{d}v(r_{ij})}{\mathrm{d}r_{ij}} r_{ij} \right\rangle \,. \tag{3.201}$$

3.14.2 ‡Chemical Potential

According to (2.193),

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V} \,. \tag{3.202}$$

Since the number of molecules can only be a nonnegative integer, the partial derivative with respect to N is not well defined. Since $N \approx 10^{24} \gg 1$, we may write

$$\mu = F(T,V,N+1) - F(T,V,N) = -k_B T \ln \frac{Z_{N+1}}{Z_N} , \tag{3.203}$$

where the subscripts $N+1$ and N refer to the number of molecules in the system. (In Chap. 2, we used N to denote the number of *moles*. In this chapter, the same symbol represents the number of *molecules* in the system. This difference simply translates to the change in units of μ. This is why we have k_B instead of the gas constant R in (3.203).)

To evaluate the ratio Z_{N+1}/Z_N, let

$$\Delta(\boldsymbol{r}^{N+1}) := \phi(\boldsymbol{r}^{N+1}) - \phi(\boldsymbol{r}^N) \tag{3.204}$$

denote the change in the potential energy when the $N+1$th particle is added to the system of N particles at the position $\boldsymbol{r}_{N+1}$. Then,

$$\begin{aligned} \frac{Z_{N+1}}{Z_N} &= \frac{1}{\Lambda^3(N+1)} \frac{\int e^{-\beta\phi(\boldsymbol{r}^{N+1})} \mathrm{d}\boldsymbol{r}^{N+1}}{\int e^{-\beta\phi(\boldsymbol{r}^N)} \mathrm{d}\boldsymbol{r}^N} \\ &= \frac{1}{\Lambda^3(N+1)} \frac{\int e^{-\beta\phi(\boldsymbol{r}^N)} \left[\int e^{-\beta\Delta} \mathrm{d}\boldsymbol{r}_{N+1}\right] \mathrm{d}\boldsymbol{r}^N}{\int e^{-\beta\phi(\boldsymbol{r}^N)} \mathrm{d}\boldsymbol{r}^N} \\ &= \frac{V}{\Lambda^3(N+1)} \left\langle \frac{1}{V} \int e^{-\beta\Delta} \mathrm{d}\boldsymbol{r}_{N+1} \right\rangle , \end{aligned} \tag{3.205}$$

where we suppressed $\boldsymbol{r}^{N+1}$ dependence of Δ, a convention we shall continue to follow throughout the remainder of this section. Using this expression in (3.203), we see that

$$\mu = -k_B T \ln \frac{V}{\Lambda^3(N+1)} - k_B T \ln \left\langle \frac{1}{V} \int e^{-\beta\Delta} \mathrm{d}\boldsymbol{r}_{N+1} \right\rangle , \tag{3.206}$$

in which

$$-k_B T \ln \frac{V}{\Lambda^3(N+1)} \tag{3.207}$$

is the chemical potential of an ideal gas. This expression is obtained by applying (3.203) to the ideal gas and should be compared against

$$\mu^{\mathrm{id}} = -k_B T \ln \frac{V}{\Lambda^3 N} \tag{3.208}$$

which follows from (3.202). (See Exercise 3.16b.) Equation (3.206) is the basis of **Widom's test particle insertion method**, a common approach for estimating the chemical potential in molecular simulation.

We now derive an alternative expression for the chemical potential. For this purpose, let us define

$$\phi(\lambda) := \phi(\boldsymbol{r}^N) + \lambda\Delta \,. \tag{3.209}$$

Clearly,

$$\phi(0) = \phi(\boldsymbol{r}^N) \quad \text{and} \quad \phi(1) = \phi(\boldsymbol{r}^{N+1}) \,. \tag{3.210}$$

If we define

$$Z(\lambda) := \frac{1}{\Lambda^{3N} N!} \int e^{-\beta\phi(\lambda)} \mathrm{d}\boldsymbol{r}^{N+1} \,, \tag{3.211}$$

we see that

$$Z(0) = V Z_N \quad \text{and} \quad Z(1) = \Lambda^3 (N+1) Z_{N+1} \,, \tag{3.212}$$

where we used (3.177). It follows that

$$\ln \frac{Z_{N+1}}{Z_N} = \ln \frac{V}{\Lambda^3 (N+1)} + \ln \frac{Z(1)}{Z(0)} \,. \tag{3.213}$$

But,

$$\ln \frac{Z(1)}{Z(0)} = \ln Z(1) - \ln Z(0) = \int_0^1 \left(\frac{\partial \ln Z(\lambda)}{\partial \lambda} \right)_{\beta,V,N} \mathrm{d}\lambda \tag{3.214}$$

From (3.211),

$$\left(\frac{\partial \ln Z(\lambda)}{\partial \lambda} \right)_{\beta,V,N} = -\beta \langle \Delta \rangle_\lambda \,, \tag{3.215}$$

where $\langle \cdots \rangle_\lambda$ is the thermal average when the interparticle potential energy is $\phi(\lambda)$. Using (3.213) – (3.215) in (3.203), we obtain

$$\mu = -k_B T \ln \frac{V}{\Lambda^3 (N+1)} + \int_0^1 \langle \Delta \rangle_\lambda \, \mathrm{d}\lambda \,. \tag{3.216}$$

This is an example of the **thermodynamic integration method**, in which a thermodynamic quantity is expressed in terms of an integration of some thermal average.

The connection between (3.206) and (3.216) can be made clearer by considering an intermediate approach between them. Thus, let

$$\lambda_i := \frac{i}{k} \,, \quad i = 0, \ldots, k \tag{3.217}$$

so that $\lambda_0 = 0$ and $\lambda_k = 1$. Then,

$$\frac{Z(1)}{Z(0)} = \frac{Z(\lambda_k)}{Z(\lambda_0)} = \frac{Z(\lambda_k)}{Z(\lambda_{k-1})} \frac{Z(\lambda_{k-1})}{Z(\lambda_{k-2})} \cdots \frac{Z(\lambda_{i+1})}{Z(\lambda_i)} \cdots \frac{Z(\lambda_1)}{Z(\lambda_0)} \,. \tag{3.218}$$

But,

$$\frac{Z(\lambda_{i+1})}{Z(\lambda_i)} = \frac{\int e^{-\beta\phi(\lambda_{i+1})} \mathrm{d}\boldsymbol{r}^{N+1}}{\int e^{-\beta\phi(\lambda_i)} \mathrm{d}\boldsymbol{r}^{N+1}} = \langle e^{-\beta\Delta/k} \rangle_{\lambda_i} \,. \tag{3.219}$$

For a sufficiently large k, $e^{-\beta\Delta/k} \approx 1 - \beta\Delta/k$, and hence

$$\frac{Z(\lambda_{i+1})}{Z(\lambda_i)} \approx 1 - \frac{\beta}{k}\langle\Delta\rangle_{\lambda_i} . \tag{3.220}$$

Because $\ln(1-x) \approx -x$ if $|x| \ll 1$, we have

$$\ln\frac{Z(1)}{Z(0)} \approx \sum_{i=0}^{k-1} \ln\left(1 - \frac{\beta}{k}\langle\Delta\rangle_{\lambda_i}\right) \approx -\sum_{i=0}^{k-1}\frac{\beta}{k}\langle\Delta\rangle_{\lambda_i} \approx -\beta\int_0^1 \langle\Delta\rangle_\lambda \mathrm{d}\lambda , \tag{3.221}$$

which is just (3.214) and we recover (3.216). One may say that the test particle insertion method, if broken down to a series of "partial particle insertions," reduces to the thermodynamic integration method.

3.15 †Internal Energy

In Sect. 3.9, we identified the average Hamiltonian $\langle H\rangle$ with the internal energy U. However, U is usually defined as a part of $\langle H\rangle$ reflecting only the internal state of the system. The kinetic energy due to its macroscopic translational motion as a whole and the potential energy due to its position in an external field are excluded in defining U.

Let us examine in details what is involved in this separation. What we have in mind is a collection of N particles that are held together either by intermolecular forces or by a container. In the latter case, we shall regard the particles making up the container as a part of the system. Then, the system as a whole experiences a translational motion under the influence of an external field ψ.

3.15.1 †Equilibrium in Motion?

It might be argued that a system in motion is not in equilibrium. However, a system in motion in one frame of reference is also at rest in another. If there is no time-dependent external field in the second, the system will eventually reach equilibrium. Our goal here is to describe that equilibrium from the first frame of reference with respect to which the system is in macroscopic motion.

Let us choose an inertial frame $\mathscr{O}^a$, with respect to which the system is moving, and write down its Lagrangian L^a as

$$L^a = \sum_{i=1}^N \frac{1}{2}m_i\|\boldsymbol{v}_i^a\|^2 - \sum_{i=1}^N \psi(\boldsymbol{r}_i^a, m_i) - \phi(\boldsymbol{r}_1^a, \ldots, \boldsymbol{r}_N^a) , \tag{3.222}$$

where we use the superscript a to signify that the quantities bearing them are evaluated in $\mathscr{O}^a$. From the outset, we assume that ψ has the following special form

$$\psi(\boldsymbol{r}_i, m_i) = -m_i \boldsymbol{b} \cdot \boldsymbol{r}_i \,, \tag{3.223}$$

where $\boldsymbol{b}$ is a constant. In the case of the gravitational field, $\boldsymbol{b} = \boldsymbol{g}$, for example.

Exercise 3.18. Find equations of motion for the particles. ///

By definition, (1.103), the momentum $\boldsymbol{p}_i^a$ conjugate to $\boldsymbol{r}_i^a$ is given by

$$\boldsymbol{p}_i^a := \frac{\partial L^a}{\partial \boldsymbol{v}_i^a} = m_i \boldsymbol{v}_i^a \,. \tag{3.224}$$

The Hamiltonian follows from (1.156) as

$$H^a := \sum_{i=1}^N \boldsymbol{p}_i^a \cdot \boldsymbol{v}_i^a - L^a = \sum_{i=1}^N \frac{\|\boldsymbol{p}_i^a\|^2}{2m_i} + \sum_{i=1}^N \psi(\boldsymbol{r}_i^a, m_i) + \phi(\boldsymbol{r}_1^a, \ldots, \boldsymbol{r}_N^a) \,. \tag{3.225}$$

Note that the Hamiltonian also bears the superscript a because it is expressed in terms of the position and the momenta of particles as measured in $\mathscr{O}^a$.

If we assume a canonical distribution, can we say that

$$\rho^a = \frac{e^{-\beta H^a}}{Z^a} \,? \tag{3.226}$$

Because of the macroscopic motion with respect to $\mathscr{O}^a$, when our system occupies a certain region in $\mathscr{O}^a$, it does so only once and only for a brief interval of time. From this observation, it might seem that ρ^a vanishes everywhere in the phase space because Δt in (3.11) becomes vanishingly small in comparison to τ. This is not quite correct. We must remember that τ is supposed to be very long only in comparison to the time scale of molecular motion but comparable with the time scale of our measurement. *If* $l/\|\boldsymbol{V}\| \gg \tau$, where l is the characteristic length scale of the system and $\boldsymbol{V}$ is the velocity of the system, the system may be regarded as occupying essentially the same region in $\mathscr{O}^a$ over the duration τ and ρ^a takes nonzero values over the corresponding region of the phase space. However, this region of nonzero ρ^a continues to move in the phase space in accordance with the translational motion of the system in $\mathscr{O}^a$.

The immediate conclusion is that (3.23), or $\partial \rho^a / \partial t \equiv 0$, is not an appropriate definition for statistical equilibrium. How do we define statistical equilibrium of our system then? It is also unsatisfactory that we have to impose an upper limit on the velocity of the macroscopic motion when discussing statistical equilibrium.

We note that the motion we are considering can be eliminated entirely in a suitably chosen frame of reference. So, the difficulty we have just described is only apparent and can be made to disappear by introducing a new coordinate system $\mathscr{O}$ that *moves with the system*. One might say, then, that the system is in statistical equilibrium if there is a frame of reference in which $\partial \rho / \partial t \equiv 0$.

We expect equilibrium to eventually prevail in $\mathscr{O}$ if there is no time-dependent field in $\mathscr{O}$. Assuming that there is a thermal contact between the system and its surroundings, ρ at equilibrium will be given by the canonical distribution. Thus, we will first have to find the Hamiltonian H of the system that is appropriate for $\mathscr{O}$. Then, the only remaining problem is that of translating ρ in $\mathscr{O}$ back to ρ^a in $\mathscr{O}^a$. This is the plan we follow.

3.15.2 †*From a Stationary to a Moving Frame*

We denote the velocity of $\mathscr{O}$ with respect to $\mathscr{O}^a$ by $\boldsymbol{V}(t)$. The time dependence of $\boldsymbol{V}$ is included because the system, in general, experiences acceleration with respect to $\mathscr{O}^a$ in the presence of an external field. This implies that $\mathscr{O}$ is not an inertial frame in general.

In order to find the Lagrangian L and the Hamiltonian H written for $\mathscr{O}$, we need to figure out the relationship between the position $\boldsymbol{r}^a$ and the velocity $\boldsymbol{v}^a$ of a particle in $\mathscr{O}^a$ on the one hand and their counterparts, $\boldsymbol{r}$ and $\boldsymbol{v}$ in $\mathscr{O}$, on the other. Clearly,

$$\boldsymbol{r}^a = \boldsymbol{r} + \boldsymbol{R}\,, \tag{3.227}$$

where $\boldsymbol{R}$ is the position of the origin of $\mathscr{O}$ as measured in $\mathscr{O}^a$. To find the relation between $\boldsymbol{v}^a$ and $\boldsymbol{v}$, suppose that, after a time duration $\mathrm{d}t$, the position of the particle in $\mathscr{O}^a$ is $\boldsymbol{r}^a + \mathrm{d}\boldsymbol{r}^a$. The location of this same particle in $\mathscr{O}$ may be denoted by $\boldsymbol{r} + \mathrm{d}\boldsymbol{r}$. At the same time, however, $\mathscr{O}$ itself has moved by $\boldsymbol{V}\mathrm{d}t$. Thus, applying (3.227) to the varied state,

$$\boldsymbol{r}^a + \mathrm{d}\boldsymbol{r}^a = (\boldsymbol{r} + \mathrm{d}\boldsymbol{r}) + (\boldsymbol{R} + \boldsymbol{V}\mathrm{d}t)\,. \tag{3.228}$$

Subtracting (3.227) from (3.228), and then dividing the resulting equation by $\mathrm{d}t$, we find

$$\boldsymbol{v}^a = \boldsymbol{v} + \boldsymbol{V}\,, \tag{3.229}$$

which could have been obtained simply by taking the time derivative of (3.227). Equation (3.227) and $t^a = t$ taken together is called a **Galilean transformation**.

Substituting (3.227) and (3.229) into (3.222), we find

$$L^a = \sum_{i=1}^{N} \frac{1}{2} m_i \|\boldsymbol{v}_i\|^2 - \sum_{i=1}^{N} \psi(\boldsymbol{r}_i, m_i) - \phi(\boldsymbol{r}^N) + \boldsymbol{V} \cdot \sum_{i=1}^{N} m_i \boldsymbol{v}_i + \frac{1}{2} M \|\boldsymbol{V}\|^2 + M\boldsymbol{b} \cdot \boldsymbol{R}\,, \tag{3.230}$$

where we used (3.223) to rewrite the external field term. As in Sect. 1.4, $M := \sum_i m_i$ is the total mass of the system.

We now *assume* that $\boldsymbol{R}$ and $\boldsymbol{V}$ may be regarded as explicit functions of t only. That is, we suppose that they do not depend on $\boldsymbol{r}_1^a, \ldots, \boldsymbol{v}_N^a$. Whether this actually is the case depends on how we choose $\boldsymbol{R}$ and will be discussed in Sect. 3.15.3. Under this assumption, the right-hand side of (3.230) is a function of t and the variables pertaining only to $\mathscr{O}$, and hence it may be used as the Lagrangian L in $\mathscr{O}$

from which equations of motion appropriate for $\mathscr{O}$ can be derived. These equations should be equivalent to those obtained from L^a for $\mathscr{O}^a$. In fact, since $L^a \equiv L$ for any mechanical state of the system at any instant, the action integral $\mathscr{S}^a$ computed in $\mathscr{O}^a$ is numerically equal to the action integral $\mathscr{S}$ in $\mathscr{O}$. Thus, the stationarity condition of the former coincides with that of the latter.

Exercise 3.19. Verify this statement by deriving equations of motion from (3.230) and comparing your results against what you found in Exercise 3.18. ///

For this choice of L, (1.104) yields

$$\boldsymbol{p}_i = \frac{\partial L}{\partial \boldsymbol{v}_i} = m_i(\boldsymbol{v}_i + \boldsymbol{V}) \,. \tag{3.231}$$

Recalling (1.156), we have

$$H = \sum_{i=1}^{N} \frac{\|\boldsymbol{p}_i\|^2}{2m_i} + \sum_{i=1}^{N} \psi(\boldsymbol{r}_i, m_i) + \phi(\boldsymbol{r}^N) - \boldsymbol{V}\cdot\boldsymbol{P} - M\boldsymbol{b}\cdot\boldsymbol{R} \,, \tag{3.232}$$

where $\boldsymbol{P} := \sum_{i=1}^{N} \boldsymbol{p}_i$ is, by (1.138), the total linear momentum of the system. We observe that unless $\boldsymbol{R}$ is constant and hence $\boldsymbol{V} \equiv \boldsymbol{0}$, this H depends explicitly on time. It is not at all clear if such a system can reach equilibrium even to an observer in $\mathscr{O}$. It is possible, however, to use somewhat different expressions for L and H.

First, we recall that the last two terms of (3.230) are, by our assumption, functions of t only, and hence can be expressed as the total time derivative of some function of t. By Exercise 1.8, they can be dropped without affecting the resulting equations of motion. Next, we rewrite the term linear in $\boldsymbol{V}$ in (3.230) by noting that

$$\boldsymbol{V}\cdot\boldsymbol{v}_i = \frac{\mathrm{d}}{\mathrm{d}t}(\boldsymbol{V}\cdot\boldsymbol{r}_i) - \frac{\mathrm{d}\boldsymbol{V}}{\mathrm{d}t}\cdot\boldsymbol{r}_i \,. \tag{3.233}$$

The first term on the right-hand side can be dropped from the Lagrangian for the same reason. In this way, we see that the Lagrangian L may be redefined as

$$L := \sum_{i=1}^{N} \frac{1}{2} m_i \|\boldsymbol{v}_i\|^2 - \sum_{i=1}^{N} \psi(\boldsymbol{r}_i, m_i) - \phi(\boldsymbol{r}^N) - \frac{\mathrm{d}\boldsymbol{V}}{\mathrm{d}t}\cdot\sum_{i=1}^{N} m_i\boldsymbol{r}_i \,. \tag{3.234}$$

Exercise 3.20. Derive equations of motion using this Lagrangian. ///

With this Lagrangian, we have

$$\boldsymbol{p}_i = \frac{\partial L}{\partial \boldsymbol{v}_i} = m_i\boldsymbol{v}_i \tag{3.235}$$

and

$$H = \sum_{i=1}^{N} \frac{\|\boldsymbol{p}_i\|^2}{2m_i} + \sum_{i=1}^{N} \psi(\boldsymbol{r}_i, m_i) + \phi(\boldsymbol{r}^N) + \frac{\mathrm{d}\boldsymbol{V}}{\mathrm{d}t}\cdot\sum_{i=1}^{N} m_i\boldsymbol{r}_i \,. \tag{3.236}$$

Because of (3.235), the first term of this H is the kinetic energy of the system *as measured in* $\mathscr{O}$. This situation should be contrasted to that in (3.232), for which such an interpretation does not hold due to the presence of $\boldsymbol{V}$ in (3.231).

Up to this point, our choice of $\boldsymbol{R}$ was quite arbitrary. When discussing macroscopic motion of a collection of particles, it is often convenient to place $\mathscr{O}$ at the center of mass of the system. One often points to this choice of the coordinate system when defining the internal energy of a moving system in thermodynamics.

In this case, $\boldsymbol{R}$ is equal to the position of the center of mass as measured in $\mathscr{O}^a$, which we denote by $\boldsymbol{R}_{\mathrm{cm}}$:

$$\boldsymbol{R} \equiv \boldsymbol{R}_{\mathrm{cm}} = \frac{1}{M}\sum_{i=1}^{N} m_i \boldsymbol{r}_i^a = \frac{1}{M}\sum_{i=1}^{N} m_i (\boldsymbol{r}_i + \boldsymbol{R}_{\mathrm{cm}}) \,, \tag{3.237}$$

where we recall that a container, if present, must be included in computing $\boldsymbol{R}_{\mathrm{cm}}$. From this equation, it follows that

$$\sum_{i=1}^{N} m_i \boldsymbol{r}_i \equiv \boldsymbol{0} \tag{3.238}$$

and that

$$\sum_{i=1}^{N} \psi(\boldsymbol{r}_i, m_i) \equiv 0 \,. \tag{3.239}$$

When these results are substituted into (3.234) and (3.236), we find

$$L = \sum_{i=1}^{N} \frac{1}{2} m_i \|\boldsymbol{v}_i\|^2 - \phi(\boldsymbol{r}^N) \quad \text{and} \quad H = \sum_{i=1}^{N} \frac{\|\boldsymbol{p}_i\|^2}{2m_i} + \phi(\boldsymbol{r}^N) \,. \tag{3.240}$$

These equations indicate that the effect of the external field vanishes in a coordinate system that moves with the center of mass of the system. It should be emphasized that we reached this conclusion *only* for the external field having the form of (3.223) and only by making a rather special choice of L in (3.234). Nevertheless, (3.240) represent a very satisfying state of affair. Both L and H are well defined without any reference to the motion of $\mathscr{O}$ relative to some inertial frame $\mathscr{O}^a$ that is external to $\mathscr{O}$.

For a given mechanical state of the system, the value of H^a evaluated by (3.225) and that of H given by (3.240) are, in general, different. This is not surprising and, in fact, is expected on the basis of Exercise 1.9. It is straightforward to show that

$$H^a = H + \frac{1}{2} M \|\boldsymbol{V}_{\mathrm{cm}}\|^2 + \psi(\boldsymbol{R}_{\mathrm{cm}}, M) \,, \tag{3.241}$$

where $\boldsymbol{V}_{\mathrm{cm}} := \mathrm{d}\boldsymbol{R}_{\mathrm{cm}}/\mathrm{d}t$. In this form, we can clearly see the separation of H^a into something "intrinsic" to the system and the remaining terms due to its macroscopic motion.

Exercise 3.21. Verify (3.241). ///

Now that $\mathscr{O}$ moves with $\boldsymbol{R}_{\rm cm}$, the region of nonzero ρ will be stationary in the phase space for $\mathscr{O}$ and the condition of equilibrium may be expressed as $\partial\rho/\partial t \equiv 0$. For a system in thermal contact with the surroundings, we have $\rho \propto e^{-\beta H}$ with H given by (3.240).

In writing the statistical distribution ρ for an observer in $\mathscr{O}$, however, we must remember that the center of mass of the system is fixed at its origin. As a result, $\boldsymbol{r}^N$ must satisfy (3.238), and hence are not all independent. Because the equation holds at all t, it also holds upon taking the time derivative. These constraints are most easily imposed by means of the Dirac δ-function:

$$\rho_{\rm cm}(\boldsymbol{r}^N,\boldsymbol{p}^N) = \delta[\cdots]\frac{1}{Z_{\rm cm}}\frac{e^{-\beta H}}{h^{3(N-1)}\mathscr{P}}\,, \tag{3.242}$$

where we introduced a shorthand notation

$$\delta[\cdots] := \delta\left(\frac{\sum_{i=1}^N m_i\boldsymbol{r}_i}{M}\right)\delta\left(\sum_{i=1}^N \boldsymbol{p}_i\right) \tag{3.243}$$

for the product of two Dirac δ-functions. (See Appendix D.4 for the definition of the three-dimensional δ-function.) As before, $\mathscr{P}$ is the number of distinct permutations of identical particles if there are any and the subscript cm remind us of the constraints on the center of mass. Because of the constraints, the mechanical degrees of freedom of the system is reduced by 3 from the original value of $3N$. This accounts for the factor $h^{3(N-1)}$ in place of now familiar h^{3N}. Finally, the normalization constant is given by

$$Z_{\rm cm} = \frac{1}{h^{3(N-1)}\mathscr{P}}\int \delta[\cdots]e^{-\beta H}\mathrm{d}\boldsymbol{r}^N\mathrm{d}\boldsymbol{p}^N\,. \tag{3.244}$$

3.15.3 †Back to the Stationary Frame

With the expression of $\rho_{\rm cm}$ now in hand, we can determine $\rho^a_{\rm cm}$ as follows. We first note that the quantity

$$\rho_{\rm cm}(\boldsymbol{r}^N,\boldsymbol{p}^N)\mathrm{d}\boldsymbol{r}^N\mathrm{d}\boldsymbol{p}^N \tag{3.245}$$

represents the probability of finding the system within the infinitesimal volume element $\mathrm{d}\boldsymbol{r}^N\mathrm{d}\boldsymbol{p}^N$ taken around the phase point $(\boldsymbol{r}^N,\boldsymbol{p}^N)$ of the phase space for $\mathscr{O}$. But, as seen from (3.224), (3.227), (3.229), and (3.235), the Jacobian of transformation from $(\boldsymbol{r}^a_1,\ldots,\boldsymbol{p}^a_N)$ to $(\boldsymbol{r}^N,\boldsymbol{p}^N)$ is unity, that is, the volume occupied by $\mathrm{d}\boldsymbol{r}^N\mathrm{d}\boldsymbol{p}^N$ in the phase space for $\mathscr{O}$ is equal to the volume occupied by $\mathrm{d}\boldsymbol{r}^a_1\cdots\mathrm{d}\boldsymbol{p}^a_N$ in the phase space for $\mathscr{O}^a$. It follows that the probability (3.245) can also be written as

$$\rho^a_{\rm cm}(\boldsymbol{r}^a_1,\ldots,\boldsymbol{p}^a_N)\mathrm{d}\boldsymbol{r}^a_1\cdots\mathrm{d}\boldsymbol{p}^a_N \tag{3.246}$$

with $\rho^a_{\rm cm}$ given simply by $\rho_{\rm cm}$ expressed in terms of $\boldsymbol{r}^a_1,\ldots,\boldsymbol{p}^a_N$. Thus,

$$\rho^a_{\rm cm}(\boldsymbol{r}^a_1,\ldots,\boldsymbol{p}^a_N)=\delta^a[\cdots]\frac{1}{Z^a_{\rm cm}}\frac{e^{-\beta(H^a-E_{\rm mm})}}{h^{3(N-1)}\mathscr{P}}\,, \tag{3.247}$$

where we defined

$$\delta^a[\cdots]:=\delta\left(\frac{\sum_{i=1}^N m_i\boldsymbol{r}^a_i}{M}-\boldsymbol{R}_{\rm cm}(t)\right)\delta\left(\sum_{i=1}^N\boldsymbol{p}^a_i-\boldsymbol{P}_{\rm cm}(t)\right) \tag{3.248}$$

with $\boldsymbol{P}_{\rm cm}=M\boldsymbol{V}_{\rm cm}$ and

$$E_{\rm mm}=\frac{1}{2}M\|\boldsymbol{V}_{\rm cm}\|^2+\psi(\boldsymbol{R}_{\rm cm},M) \tag{3.249}$$

is the energy due to macroscopic motion as observed in $\mathscr{O}^a$. The normalization of $\rho^a_{\rm cm}$ leads to

$$Z^a_{\rm cm}=\frac{1}{h^{3(N-1)}\mathscr{P}}\int\delta^a[\cdots]e^{-\beta(H^a-E_{\rm mm})}{\rm d}\boldsymbol{r}^a_1\cdots{\rm d}\boldsymbol{p}^a_N\,, \tag{3.250}$$

which is equal to $Z_{\rm cm}$ numerically. The δ-functions ensure that only those phase points consistent with the given functions $\boldsymbol{R}_{\rm cm}(t)$ and $\boldsymbol{P}_{\rm cm}(t)$ are accounted for.

We still have to show that $\boldsymbol{R}_{\rm cm}(t)$ and $\boldsymbol{V}_{\rm cm}(t)$ may be regarded as some prescribed function depending only on t. Using the equations of motion derived in Exercise 3.18, we obtain

$$\boldsymbol{V}_{\rm cm}(t)=\boldsymbol{b}t+\boldsymbol{c}_0\quad\text{and}\quad\boldsymbol{R}_{\rm cm}(t)=\frac{1}{2}\boldsymbol{b}t^2+\boldsymbol{c}_0t+\boldsymbol{c}_1\,, \tag{3.251}$$

where $\boldsymbol{c}_0$ and $\boldsymbol{c}_1$ are constant vectors to be determined by $\boldsymbol{V}_{\rm cm}$ and $\boldsymbol{R}_{\rm cm}$ at time $t=0$. Given these initial conditions, the subsequent evolution of $\boldsymbol{R}_{\rm cm}$ and $\boldsymbol{V}_{\rm cm}$ is given by (3.251), and hence they are explicit functions of t only. This is what we needed to show.

Because of the interaction between the system and the surroundings, the actual time evolution of $\boldsymbol{R}_{\rm cm}$ and $\boldsymbol{V}_{\rm cm}$ deviates from the predictions of (3.251) in a manner that depends on $\boldsymbol{r}^N$ and $\boldsymbol{p}^N$. Strictly speaking, therefore, the assumption we introduced after (3.230) does not hold and the separation of $\langle H\rangle$ into $U_{\rm cm}$ and $E_{\rm mm}$ must be regarded as an approximation.

Exercise 3.22. Derive (3.251). ///

Finally, when the contribution of the macroscopic motion is separated out, we define the internal energy $U_{\rm cm}$ as $\langle H\rangle$ computed with respect to $\rho_{\rm cm}$:

$$U_{\rm cm}=-\frac{\partial\ln Z_{\rm cm}}{\partial\beta}\,. \tag{3.252}$$

Since $\rho_{\rm cm}$ and $\rho^a_{\rm cm}$ are numerically equal, this may also be written as

$$U_{\rm cm} = -\frac{\partial \ln Z^a_{\rm cm}}{\partial \beta} \tag{3.253}$$

We note that $U_{\rm cm}$ reflects the average behavior of $3(N-1)$ mechanical degrees of freedom. The macroscopic motion of the center of mass accounts for the remaining three degrees of freedom.

3.16 †Equilibrium of an Accelerating Body

If we enclose a system of N particles in a rigid container and make the container move in the manner we prescribe, the system will, in general, experience acceleration. Insofar as the acceleration is prescribed, it is common to all members of the ensemble. If we limit our consideration to a *constant* linear acceleration, its effect will be seen to manifest itself as a *time-independent* external field. This allows for a statistical equilibrium to establish. The same holds for a *uniform* rotation as observed in centrifugation. In this section, we shall derive the appropriate expressions for the statistical weight ρ for these cases. We attach a moving coordinate system $\mathscr{O}$ to the container. Because the container is then fixed in $\mathscr{O}$, there is no need to include the container in our definition of the system.

3.16.1 †Linear Translation

We may take (3.236) as our starting point and rewrite it using (3.223):

$$H = H_0 + \sum_{i=1}^{N} \psi(\boldsymbol{r}_i, m_i) + \boldsymbol{A} \cdot \sum_{i=1}^{N} m_i \boldsymbol{r}_i = H_0 + (\boldsymbol{A} - \boldsymbol{b}) \cdot \sum_{i=1}^{N} m_i \boldsymbol{r}_i \,, \tag{3.254}$$

where $\boldsymbol{A} := \mathrm{d}\boldsymbol{V}/\mathrm{d}t$ is the acceleration of the container and

$$H_0 := \sum_{i=1}^{N} \frac{\|\boldsymbol{p}_i\|^2}{2m_i} + \phi\left(\boldsymbol{r}^N\right) \tag{3.255}$$

is the part of the Hamiltonian that appears *intrinsic* to an observer in $\mathscr{O}$ as was pointed out following (3.236).

We see from (3.254) that the effect of the acceleration $\boldsymbol{A}$ of the container manifest itself as an *effective* external field and acts only to modify the existing external field ψ. *If* $\boldsymbol{A}$ does not depend on t, that is, for a constant linear acceleration, H has no explicit time dependence and we expect the system to reach a statistical equilibrium. We note that the coordinate system $\mathscr{O}$ is attached to the container wall and not to

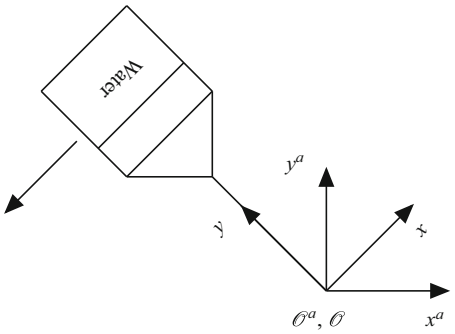


Fig. 3.7 A rotating bucket of water as observed from the inertial frame $\mathscr{O}^a$ and the frame $\mathscr{O}$ that rotates with the bucket.

the center of mass of the particles. This means that the constraint (3.243) is absent here. Instead of (3.242), therefore, we have

$$\rho\left(\boldsymbol{r}^N, \boldsymbol{p}^N\right) = \frac{1}{Z}\frac{e^{-\beta H}}{h^{3N}\mathscr{P}} \quad \text{and} \quad Z = \frac{1}{h^{3N}\mathscr{P}}\int e^{-\beta H}\mathrm{d}\boldsymbol{r}^N\mathrm{d}\boldsymbol{p}^N \tag{3.256}$$

for a system in thermal contact with the surroundings.

3.16.2 †Rotation

Let us consider the case of rotation without any linear translation. Once again, we adopt a frame of reference $\mathscr{O}$ that is attached to the container rotating with respect to the inertial frame $\mathscr{O}^a$. For simplicity, we assume that these two frames share the same origin. Figure 3.7 illustrates the situation.

The frame $\mathscr{O}$ clearly is not an inertial frame: A particle at rest in the rotating frame is accelerating with respect to the inertial frame. In general, the effect of acceleration is felt as **apparent forces**. In the case of rotation, they are the **centrifugal force**, the **Coriolis force**, and the **Euler force** as we shall see in Example 3.8. This last terminology is due to Ref. [2].

It is clear that an external field ψ that is time independent in $\mathscr{O}^a$ *varies with time* in $\mathscr{O}$ in general. In this section, therefore, we assume that the effect of ψ is negligible in comparison to the intermolecular forces *and* the apparent forces.

Again, we need to establish the relationship between the velocity vector of a particle as measured in $\mathscr{O}^a$ and that in $\mathscr{O}$. For this purpose, suppose that the position vector of a particle, as measured in $\mathscr{O}$, changed from $\boldsymbol{r}$ to $\boldsymbol{r}+\mathrm{d}\boldsymbol{r}$ during a time duration $\mathrm{d}t$. If we denote the same vectors as observed in $\mathscr{O}^a$ by $\boldsymbol{r}^a$ and $\boldsymbol{r}^a+\mathrm{d}\boldsymbol{r}^a$, respectively, then,

$$\boldsymbol{r} = \boldsymbol{r}^a \tag{3.257}$$

because both $\boldsymbol{r}$ and $\boldsymbol{r}^a$ refer to the same arrow in space. But the final vector $\boldsymbol{r}+\mathrm{d}\boldsymbol{r}$ is not equal to $\boldsymbol{r}^a+\mathrm{d}\boldsymbol{r}^a$ because of the rotation of $\mathscr{O}$ with respect to $\mathscr{O}^a$. We stress that $\mathrm{d}\boldsymbol{r}^a$ is the change *as observed in* $\mathscr{O}^a$ of the vector $\boldsymbol{r}^a$. This change is brought about by two contributions, one is the change $\mathrm{d}\boldsymbol{r}$ as observed in $\mathscr{O}$ of the vector $\boldsymbol{r}$ and the other is the rotation of $\mathscr{O}$ with respect to $\mathscr{O}^a$. This is why $\mathrm{d}\boldsymbol{r}^a \neq \mathrm{d}\boldsymbol{r}$.

To make things easier, let us first suppose that $\boldsymbol{r}$ remained constant in $\mathscr{O}$. Denoting the rotation of $\mathscr{O}$ with respect to $\mathscr{O}^a$ by $\mathbf{d}\boldsymbol{\phi}$ as we have done in Sect. 1.8.2, we see that

$$\mathrm{d}\boldsymbol{r}^a = \mathbf{d}\boldsymbol{\phi}\times\boldsymbol{r}\,, \tag{3.258}$$

and hence

$$\boldsymbol{r}^a+\mathrm{d}\boldsymbol{r}^a = \boldsymbol{r}+\mathbf{d}\boldsymbol{\phi}\times\boldsymbol{r}\,. \tag{3.259}$$

If $\boldsymbol{r}$ did not remain constant but became $\boldsymbol{r}+\mathrm{d}\boldsymbol{r}$, we have only to replace $\boldsymbol{r}$ by $\boldsymbol{r}+\mathrm{d}\boldsymbol{r}$ and obtain

$$\boldsymbol{r}^a+\mathrm{d}\boldsymbol{r}^a = (\boldsymbol{r}+\mathrm{d}\boldsymbol{r})+\mathbf{d}\boldsymbol{\phi}\times(\boldsymbol{r}+\mathrm{d}\boldsymbol{r})\,. \tag{3.260}$$

Now we cancel $\boldsymbol{r}^a$ and $\boldsymbol{r}$ using (3.257) and divide the resulting expression by $\mathrm{d}t$ to arrive at

$$\boldsymbol{v}^a = \boldsymbol{v}+\boldsymbol{\Omega}\times\boldsymbol{r}\,, \tag{3.261}$$

where we ignored the higher order term $\mathbf{d}\boldsymbol{\phi}\times\mathrm{d}\boldsymbol{r}$. The new vector $\boldsymbol{\Omega}:=\mathbf{d}\boldsymbol{\phi}/\mathrm{d}t$ is called the **angular velocity** of $\mathscr{O}$ with respect to $\mathscr{O}^a$.

Using (3.257) and (3.261) in (3.222) with $\psi\equiv 0$, we find

$$L^a = \sum_{i=1}^{N}\frac{1}{2}m_i\|\boldsymbol{v}_i\|^2-\phi\left(\boldsymbol{r}^N\right)+\sum_{i=1}^{N}m_i\boldsymbol{v}_i\cdot\boldsymbol{\Omega}\times\boldsymbol{r}_i+\sum_{i=1}^{N}\frac{1}{2}m_i\|\boldsymbol{\Omega}\times\boldsymbol{r}_i\|^2\,. \tag{3.262}$$

Example 3.8. Apparent forces: Let $N=1$ in (3.262):

$$L^a = \frac{1}{2}m\|\boldsymbol{v}\|^2+m\boldsymbol{v}\cdot\boldsymbol{\Omega}\times\boldsymbol{r}+\frac{1}{2}m\|\boldsymbol{\Omega}\times\boldsymbol{r}\|^2\,, \tag{3.263}$$

from which we derive Lagrange's equation of motion of the particle in $\mathscr{O}$. This allows us to identify the expressions for the apparent forces.

From (3.263),

$$\frac{\partial L^a}{\partial\boldsymbol{v}} = m\boldsymbol{v}+m\boldsymbol{\Omega}\times\boldsymbol{r}\,. \tag{3.264}$$

To compute $\partial L^a/\partial\boldsymbol{r}$, we make use of (A.32):

$$\frac{\partial}{\partial\boldsymbol{r}}(\boldsymbol{v}\cdot\boldsymbol{\Omega}\times\boldsymbol{r}) = \frac{\partial}{\partial\boldsymbol{r}}(\boldsymbol{r}\cdot\boldsymbol{v}\times\boldsymbol{\Omega}) = \boldsymbol{v}\times\boldsymbol{\Omega}\,. \tag{3.265}$$

We also note that

$$\|\boldsymbol{\Omega}\times\boldsymbol{r}\|^2 = \|\boldsymbol{\Omega}\|^2\|\boldsymbol{r}\|^2\sin^2\theta = \|\boldsymbol{\Omega}\|^2\|\boldsymbol{r}\|^2(1-\cos^2\theta) = \|\boldsymbol{\Omega}\|^2\|\boldsymbol{r}\|^2-(\boldsymbol{\Omega}\cdot\boldsymbol{r})^2\,. \tag{3.266}$$

Thus,

$$\frac{1}{2}\frac{\partial\|\boldsymbol{\Omega}\times\boldsymbol{r}\|^2}{\partial\boldsymbol{r}} = \|\boldsymbol{\Omega}\|^2\boldsymbol{r} - (\boldsymbol{\Omega}\cdot\boldsymbol{r})\boldsymbol{\Omega} = \|\boldsymbol{\Omega}\|^2(\boldsymbol{r}-\boldsymbol{r}_\parallel) = \|\boldsymbol{\Omega}\|^2\boldsymbol{r}_\perp\,, \tag{3.267}$$

where we defined

$$\boldsymbol{r}_\parallel := \frac{\boldsymbol{\Omega}}{\|\boldsymbol{\Omega}\|}\|\boldsymbol{r}\|\cos\theta \quad \text{and} \quad \boldsymbol{r}_\perp := \boldsymbol{r}-\boldsymbol{r}_\parallel\,. \tag{3.268}$$

Geometrically, this decomposes $\boldsymbol{r}$ into a part ($\boldsymbol{r}_\parallel$) that is parallel to $\boldsymbol{\Omega}$ and the other ($\boldsymbol{r}_\perp$) that is perpendicular to $\boldsymbol{\Omega}$ as seen from Fig. 3.8.

From Lagrange's equation of motion, we obtain

$$m\dot{\boldsymbol{v}} + m\dot{\boldsymbol{\Omega}}\times\boldsymbol{r} + m\boldsymbol{\Omega}\times\boldsymbol{v} = m\boldsymbol{v}\times\boldsymbol{\Omega} + m\|\boldsymbol{\Omega}\|^2\boldsymbol{r}_\perp\,. \tag{3.269}$$

Solving for $m\dot{\boldsymbol{v}}$,

$$m\dot{\boldsymbol{v}} = 2m\boldsymbol{v}\times\boldsymbol{\Omega} + m\|\boldsymbol{\Omega}\|^2\boldsymbol{r}_\perp - m\dot{\boldsymbol{\Omega}}\times\boldsymbol{r}\,. \tag{3.270}$$

In this equation, the terms on the right are the apparent forces. From the left, they are the Coriolis force, the centrifugal force, and the Euler force. Being perpendicular to $\boldsymbol{v}$, the Coriolis force does not perform any work on the particle.

Coming back to (3.262), we simply adopt it as the Lagrangian L in $\mathscr{O}$ without further modifications. Thus,

$$\boldsymbol{p}_i := \frac{\partial L}{\partial\boldsymbol{v}_i} = m_i(\boldsymbol{v}_i + \boldsymbol{\Omega}\times\boldsymbol{r}_i) = m_i\boldsymbol{v}_i^a = \boldsymbol{p}_i^a\,, \tag{3.271}$$

and hence

$$H := \sum_{i=1}^N \boldsymbol{p}_i\cdot\boldsymbol{v}_i - L = \sum_{i=1}^N \boldsymbol{p}_i^a\cdot(\boldsymbol{v}_i^a - \boldsymbol{\Omega}\times\boldsymbol{r}_i) - L^a\,. \tag{3.272}$$

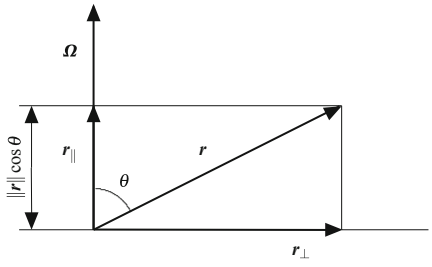


Fig. 3.8 Decomposition of $\boldsymbol{r}$ into $\boldsymbol{r}_\perp$ and $\boldsymbol{r}_\parallel$.

Since the first and the third terms taken together is H^a, it may be replaced by the expression given in (3.225), where we recall that $\psi \equiv 0$ in this section. Noting once again that $\boldsymbol{r}_i^a = \boldsymbol{r}_i$ and $\boldsymbol{p}_i^a = \boldsymbol{p}_i$, we find

$$H = \sum_{i=1}^{N} \frac{\|\boldsymbol{p}_i\|^2}{2m_i} + \phi(\boldsymbol{r}^N) - \sum_{i=1}^{N} \boldsymbol{p}_i \cdot \boldsymbol{\Omega} \times \boldsymbol{r}_i \,. \tag{3.273}$$

Using the vector identity (A.32) and the definition (1.145) of the total angular momentum, we have

$$\sum_{i=1}^{N} \boldsymbol{p}_i \cdot \boldsymbol{\Omega} \times \boldsymbol{r}_i = \boldsymbol{\Omega} \cdot \sum_{i=1}^{N} \boldsymbol{r}_i \times \boldsymbol{p}_i = \boldsymbol{\Omega} \cdot \boldsymbol{M} \,, \tag{3.274}$$

and hence

$$H = \sum_{i=1}^{N} \frac{\|\boldsymbol{p}_i\|^2}{2m_i} + \phi(\boldsymbol{r}^N) - \boldsymbol{\Omega} \cdot \boldsymbol{M} \,. \tag{3.275}$$

When $\boldsymbol{\Omega}$ is independent of time, the rotation is said to be uniform. For a *uniform rotation*, H has no explicit time dependence and the system is expected to reach equilibrium eventually. The statistical distribution is then given by

$$\rho(\boldsymbol{r}^N, \boldsymbol{p}^N) = \frac{1}{Z} \frac{e^{-\beta H}}{h^{3N} \mathscr{P}} \quad \text{and} \quad Z = \frac{1}{h^{3N} \mathscr{P}} \int e^{-\beta H} \mathrm{d}\boldsymbol{r}^N \mathrm{d}\boldsymbol{p}^N \,. \tag{3.276}$$

While $\boldsymbol{p}_i$ is the generalized momentum conjugate to $\boldsymbol{r}_i$, it is *not* the mechanical momentum $m_i \boldsymbol{v}_i$ an observer in $\mathscr{O}$ would compute based on the values of $\boldsymbol{v}^N$ measured in that frame. The situation is entirely analogous to (3.231). To extract from H an energy term this observer would compute, we use (3.271) to eliminate $\boldsymbol{p}_i$ from (3.275) in favor of the **mechanical momentum** defined by $\boldsymbol{\pi}_i := m_i \boldsymbol{v}_i$. This leads to

$$E = \sum_{i=1}^{N} \frac{\|\boldsymbol{\pi}_i\|^2}{2m_i} + \phi(\boldsymbol{r}^N) - \sum_{i=1}^{N} \frac{1}{2} m_i \|\boldsymbol{\Omega} \times \boldsymbol{r}_i\|^2 =: E_0 + \psi_{\mathrm{cp}} \,, \tag{3.277}$$

where

$$E_0 := \sum_{i=1}^{N} \frac{\|\boldsymbol{\pi}_i\|^2}{2m_i} + \phi(\boldsymbol{r}^N) \quad \text{and} \quad \psi_{\mathrm{cp}} := -\sum_{i=1}^{N} \frac{1}{2} m_i \|\boldsymbol{\Omega} \times \boldsymbol{r}_i\|^2 \,. \tag{3.278}$$

The expression (3.277) is numerically equal to H in (3.275) but it is not a Hamiltonian since E is given in terms of the *mechanical* rather than the *generalized* momenta. Nevertheless, the expression is illuminating. In particular, E_0 is the energy an observer in $\mathscr{O}$ would compute based on the values of $\boldsymbol{r}^N$ and $\boldsymbol{\pi}^N$ measured in this frame without any regard to the fact that $\mathscr{O}$ is rotating. Equation (3.277) also makes it clear that the effect of rotation of our coordinate system manifests itself only through the *apparent external field* ψ_{cp} called the **centrifugal potential energy**.

Exercise 3.23. Verify (3.277). ///

Because of its intuitive appeal, it will be desirable to use E rather than H to express the statistical distribution. To find the functional form of this distribution, let

$$\rho'(\boldsymbol{r}^N, \boldsymbol{\pi}^N) \mathrm{d}\boldsymbol{r}^N \mathrm{d}\boldsymbol{\pi}^N \tag{3.279}$$

denote the probability of finding the system of interest within the infinitesimal volume element $\mathrm{d}\boldsymbol{r}^N \mathrm{d}\boldsymbol{\pi}^N$ taken around the point $(\boldsymbol{r}^N, \boldsymbol{\pi}^N)$ in the space spanned by $2N$ vectors $\boldsymbol{r}^N$ and $\boldsymbol{\pi}^N$. From (3.271), we see that the Jacobian of the coordinate transformation from $(\boldsymbol{r}^N, \boldsymbol{p}^N)$ to $(\boldsymbol{r}^N, \boldsymbol{\pi}^N)$ is unity. As in Sect. 3.15.3, this implies that ρ' is simply ρ expressed in terms of $\boldsymbol{r}^N$ and $\boldsymbol{\pi}^N$. From (3.276), we arrive at

$$\rho'(\boldsymbol{r}^N, \boldsymbol{\pi}^N) = \frac{1}{Z'} \frac{e^{-\beta(E_0+\psi_{\mathrm{cp}})}}{h^{3N}\mathscr{P}} \quad \text{and} \quad Z' := \frac{1}{h^{3N}\mathscr{P}} \int e^{-\beta(E_0+\psi_{\mathrm{cp}})} \mathrm{d}\boldsymbol{r}^N \mathrm{d}\boldsymbol{\pi}^N \,. \tag{3.280}$$

3.17 Frequently Used Symbols

$\langle A \rangle$, ensemble average of a dynamical variable A.

f , the number of mechanical degrees of freedom.
h , Planck constant. 6.626×10^{-34} (J·sec).
k_B , Boltzmann constant, 1.3806×10^{-23} J/K.
m_i , mass of the ith particle.
p_i , generalized momentum conjugate to q_i.
p^f , collective notation for $p_1, \ldots, p_f$.
$\boldsymbol{p}_i$, linear momentum of the ith particle.
$\boldsymbol{p}^N$, collective notation for $\boldsymbol{p}_1, \ldots, \boldsymbol{p}_N$.
q_i , the ith generalized coordinate.
q^f , collective notation for $q_1, \ldots, q_f$.
$\boldsymbol{r}_i$, position vector of the ith particle.
$\boldsymbol{r}^N$, collective notation for $\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N$.
t , time.
$\boldsymbol{v}_i$, velocity vector of the ith particle.
$\boldsymbol{v}^N$, collective notation for $\boldsymbol{v}_1, \ldots, \boldsymbol{v}_N$.

A , a generic dynamical variable.
C , normalization constant for ρ.
C_V , constant volume heat capacity.
F , Helmholtz free energy.
H , Hamiltonian.
L , Lagrangian.
M , total mass of a many-particle system.

N , total number of particles in a system.
S , entropy.
T , absolute temperature.
U , internal energy.
V , volume.
Z , canonical partition function.

$\mathscr{N}$, total number of copies in a statistical ensemble.
$\mathscr{P}$, the number of permutations of identical particles.
$\mathscr{V}$, internal virial.

β , $1/k_BT$.
$\delta(x)$, Dirac δ-function.
ρ , statistical weight.
$\boldsymbol{\pi}$, mechanical momentum.
ϕ , potential energy due to interparticle interactions.
ψ , potential energy due to an external field.

Λ , thermal wavelength $h/\sqrt{2\pi mk_BT}$ of a particle of mass m.
$\boldsymbol{\Omega}$, angular velocity.

References and Further Reading

1. Gibbs J W (1981) Elementary principles in statistical mechanics. Ox Bow Press, Connecticut
   Our Sect. 3.9 followed Chap. 4 of the book, where the canonical ensemble was introduced. The same chapter demonstrates the relationship between statistical mechanics and thermodynamics and provides further motivation for the canonical ensemble.
2. Lanczos C (1986) The variational principles of mechanics. Dover, New York
   The phrase "Euler force" is introduced in p. 103.
3. Landau L D, Lifshitz E M (1980) Statistical physics: Part 1, 3rd edn. Pergamon Press, New York
   In developing the basic principles of statistical mechanics, we loosely followed Chap. 1 of the book. Our treatment of a rotating body is based on their treatment of the subject, in particular, Sects. 26 and 34.
4. Schrödinger E (1989) Statistical thermodynamics. Dover, New York
   Chapter 3 of the book provides a detailed discussion on the meaning of setting the constant term in (3.67) to zero. He uses Boltzmann's entropy formula rather than that of Gibbs. But, the former can be derived from the latter as we shall see later.
5. Tolman R C (1979) The principles of statistical mechanics. Dover, New York
   For an extended discussion on the statistical approach and its validity, see Chap. 3. A brief summary is in Sect. 25.
6. Whitaker S (1992) Introduction to fluid mechanics. Krieger Publishing Company, Florida
   It is far more natural and physically compelling to write down laws of physics, such as the conservation of mass, Newton's equation of motion, and the first law of thermodynamics, for a (possibly moving and deforming) body than to do so for a control volume fixed in space. A derivation of the equation of continuity from this more satisfactory stand point is found in Chap. 3.