

# Chapter 3

## The Foundations of Statistical Mechanics

### 3.1 INTRODUCTION

This chapter will be devoted to a presentation of the general principle of statistical mechanics and to its logical justification. The calculational principle will be a generalization, to systems that may include interparticle forces, of the assumption of equal a priori probability. The justification of that assumption will be based, in a fundamental way, on the fact that any macroscopic system contains a vast number of particles. The argument will be closely related to the Law of Large Numbers and the Central Limit Theorem, but it will require an extension of those ideas to variables that are statistically correlated.

The physical systems that are discussed in this chapter will be assumed to satisfy the laws of classical mechanics, rather than quantum mechanics. Actually, a certain improvement in logical elegance can be achieved by starting with a quantum-mechanical formulation and then deriving the corresponding classical mechanical rules by taking the limit  $\hbar \rightarrow 0$ . However, there is a danger that that logical elegance would be gained only at the cost of a clear picture of the meaning of the arguments. Therefore, the quantum-mechanical treatment will be postponed to a later chapter. Because it is convenient to use a Hamiltonian formulation of classical mechanics, the chapter will begin with a brief review of Hamilton's equations. It will then be necessary to introduce a certain amount of formalism, involving observables, statistical ensembles, and density functions, in preparation for treating the central topics of the chapter.

### 3.2 HAMILTON'S EQUATIONS

The dynamical state of a system of  $N$  point particles is completely determined by the values of  $2N$  vector variables that give the positions of the particles and their momenta,  $\mathbf{r}_1, \dots, \mathbf{r}_N$  and  $\mathbf{p}_1, \dots, \mathbf{p}_N$ . We define  $2K$  scalar variables  $(x_1, \dots, x_K)$  and  $(p_1, \dots, p_K)$ , where  $K = 3N$ , by the identifications

$$(x_1, \dots, x_K) = (x_1, y_1, z_1, \dots, x_N, y_N, z_N) \quad (3.1)$$

and

$$(p_1, \dots, p_K) = (p_{1x}, p_{1y}, p_{1z}, p_{2x}, p_{2y}, p_{2z}, \dots) \quad (3.2)$$

The energy of the system, written in terms of these variables, is called the *Hamiltonian function*.

$$E = H(x_1, \dots, x_K, p_1, \dots, p_K) = H(x, p) \quad (3.3)$$

where  $(x, p)$  is a compact symbol for the set of  $2K$  variables. For a physical system composed of  $N$  identical point particles, each of mass  $m$ , in an external potential field  $U(\mathbf{r})$ , and with interparticle forces derivable

from an interaction potential  $\phi(|\mathbf{r}_i - \mathbf{r}_j|)$ , the Hamiltonian function is

$$H(x, p) = \sum_{k=1}^K \frac{p_k^2}{2m} + \sum_{i=1}^N U(\mathbf{r}_i) + \sum_{i < j}^N \phi(|\mathbf{r}_i - \mathbf{r}_j|) \quad (3.4)$$

The time dependence of the  $2K$  dynamical variables  $(x, p)$  is given by Hamilton's equations

$$\dot{x}_k(t) = \frac{\partial H(x, p)}{\partial p_k} \quad (3.5)$$

and

$$\dot{p}_k = -\frac{\partial H(x, p)}{\partial x_k} \quad (3.6)$$

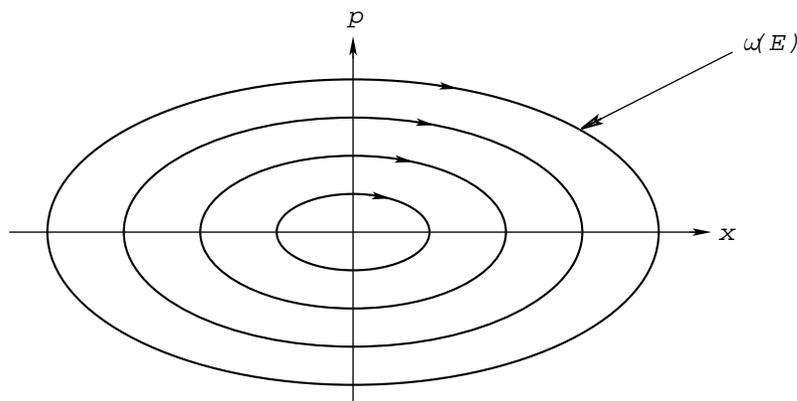
where  $k$  runs from 1 to  $K$ .

### 3.3 PHASE SPACE

The  $2K$  variables  $(x, p)$  may be interpreted as coordinates in a  $2K$ -dimensional space, called the *phase space* of the system. The  $2K$ -dimensional point  $(x, p)$  that represents the dynamical state of the system will be referred to as the *system point*. The time dependence of the complete set of  $2K$  variables that describes the motions of all the particles in the system may then be pictured as the continuous motion of the single system point in the large-dimensional phase space.

The conservation of energy is a simple consequence of Hamilton's equations. If  $x(t)$  and  $p(t)$  is a solution of Hamilton's equations, then, by Eqs. (3.5) and (3.6),

$$\begin{aligned} \frac{dE}{dt} &= \frac{dH(x(t), p(t))}{dt} \\ &= \sum_{k=1}^K \left( \frac{\partial H}{\partial x_k} \dot{x}_k + \frac{\partial H}{\partial p_k} \dot{p}_k \right) \\ &= \sum_{k=1}^K \left( \frac{\partial H}{\partial x_k} \frac{\partial H}{\partial p_k} - \frac{\partial H}{\partial p_k} \frac{\partial H}{\partial x_k} \right) = 0 \end{aligned} \quad (3.7)$$



**Fig. 3.1** For a simple harmonic oscillator,  $H = p^2/2m + kx^2/2$ . Therefore the set of points in phase space defined by  $H = E$  is an ellipse. Because of energy conservation, the system point moves repeatedly around the ellipse defined by its initial energy. For a system with more than one coordinate, the phase space is more than two-dimensional and the set of points defined by  $H = E$  is a many-dimensional surface.

### 3.4 THE ENERGY SURFACE

For any fixed value of  $E$ , the set of points in phase space that satisfy the equation  $H(x, p) = E$  is called the *energy surface*, and will be denoted by the symbol  $\omega(E)$ . Since the phase space has  $2K$  dimensions and the energy surface is defined by a single scalar equation,  $\omega(E)$  is, except for special values of  $E$ , a  $(2K-1)$ -dimensional set. The reader should keep in mind the fact that, although our pictures will show  $\omega(E)$  as a one-dimensional surface in two-dimensional space, it is, for the macroscopic systems in which we are interested, usually an unimaginably convoluted surface in an unimaginably high dimensional space. Because of energy conservation, a system point that begins on the surface  $\omega(E)$  is constrained to remain on that energy surface forever.

### 3.5 OBSERVABLES

A *physical observable* is any quantity that is determined by the dynamical state of the system, such as the system's kinetic energy or angular momentum. Therefore, a physical observable is simply any function  $A(x, p)$  defined on the phase space. Two classes of observables are particularly important, in that they account for almost all observables that actually occur in physical measurements and calculations. They are *one-body* observables and *two-body* observables.

A one-body observable is a function  $A(x, p)$  of the special form

$$A(x, p) = \sum_{i=1}^N a(\mathbf{r}_i, \mathbf{p}_i) \quad (3.8)$$

where  $a(\mathbf{r}, \mathbf{p})$  is any function of  $\mathbf{r}$  and  $\mathbf{p}$ . Two obvious cases of one-body observables are the kinetic energy, for which  $a(\mathbf{r}, \mathbf{p}) = p^2/2m$ , and the external potential energy, for which  $a(\mathbf{r}, \mathbf{p}) = U(\mathbf{r})$ . Another example is any component of the system's total angular momentum

$$\mathbf{L} = \sum_{i=1}^N \mathbf{r}_i \times \mathbf{p}_i \quad (3.9)$$

A two-body observable is a quantity that depends on the simultaneous state of a pair of particles, summed over all distinct pairs in the system. It is an observable of the general form

$$A(x, p) = \sum_{i \neq j} a(\mathbf{r}_i, \mathbf{p}_i, \mathbf{r}_j, \mathbf{p}_j) \quad (3.10)$$

where  $a(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}')$  is an arbitrary function of  $\mathbf{r}$ ,  $\mathbf{p}$ ,  $\mathbf{r}'$ , and  $\mathbf{p}'$ . The most important example of a two-body observable is the interaction potential energy of the system.

$$V_{\text{int}} = \sum_{i < j} \phi(|\mathbf{r}_i - \mathbf{r}_j|) = \frac{1}{2} \sum_{i \neq j} \phi(|\mathbf{r}_i - \mathbf{r}_j|) \quad (3.11)$$

in which case  $a(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}') = \frac{1}{2} \phi(|\mathbf{r} - \mathbf{r}'|)$ . Notice that two-body observables are defined by a sum that excludes the terms with  $i = j$ .

### 3.6 THE MICROSTATE PROBABILITY

The central problem in the foundations of statistical mechanics is to devise some rational method of assigning a fundamental microstate probability function  $P(x, p)$  to the set of possible dynamical states of a complex macroscopic system. Once we have decided upon the fundamental microstate probability, we can, by the general rules of probability theory, make statistical predictions about any observable of the system.

Since a Hamiltonian system is a completely deterministic system, an apparently simple and reasonable solution to this problem is to assign a probability one to the *actual* dynamical state of the system and a probability zero to any other dynamical state. For a system of a few particles, such as the solar system, this *is* a reasonable solution. However, for one mole of gas, the experimental determination of the dynamical state would require the precise and simultaneous measurement of  $3.6 \times 10^{24}$  scalar variables. Such an experimental

operation is completely without practical meaning. Thus “determining the initial state of the system” is a string of words to which no real experimental operation corresponds. We must find some other solution. The fact that the known calculational methods of statistical mechanics can be used reliably to predict the equilibrium properties of large systems shows that a practical solution of the problem exists.

A *microstate probability density* will be taken to mean any function defined on the phase space that has the two properties that

$$P(x, p) \geq 0 \quad (3.12)$$

and

$$\int_{\Omega} P(x, p) d^K x d^K p = 1 \quad (3.13)$$

In Eq. (3.13) we have introduced the symbol  $\Omega$  for the phase space of the system.

Before trying to justify the use of any definite probability function, we will look at the properties of two simple and important particular cases. Because of the possible interpretation of probability density functions in terms of statistical ensembles, it has become the practice to refer to the various important density functions as particular, named, *ensembles*.

### 3.7 THE UNIFORM ENSEMBLE

The uniform ensemble is the probability density function one obtains if a constant probability density is assigned to all states with energy less than or equal to  $E$  (Fig. 3.2). It is of the form

$$P(x, p) = C^{-1} \theta(E - H(x, p)) \quad (3.14)$$

where the unit step function  $\theta(t)$  is defined by

$$\theta(t) = \begin{cases} 0, & t < 0 \\ 1, & t \geq 0 \end{cases} \quad (3.15)$$

and  $C(E)$  is a constant, determined by the normalization condition, Eq. (3.13). The value of  $C(E)$ , which is given by the integral

$$C(E) = \int_{\Omega} \theta(E - H(x, p)) d^K x d^K p, \quad (3.16)$$

can obviously be interpreted as the *volume* enclosed by the energy surface,  $\omega(E)$ .

### 3.8 C(E) FOR AN IDEAL GAS

In order to develop some feeling for these ideas, let us evaluate the normalization constant for a simple many-particle system, namely the ideal gas. We will later find many uses for the results of this calculation. For an ideal gas in a container of volume  $V$ ,

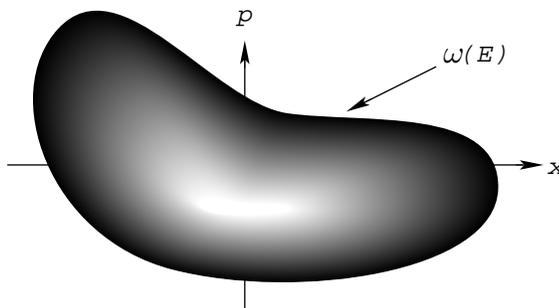
$$H = \frac{1}{2m} \sum_{k=1}^K p_k^2 \quad (3.17)$$

where  $K = 3N$ , and the variables,  $\mathbf{r}_1, \dots, \mathbf{r}_N$  are each restricted to the inside of the container. The integral over the spatial variables gives a factor of  $V^N$ . Therefore,

$$C(E) = V^N \int \theta \left( E - \sum p_k^2 / 2m \right) d^K p \quad (3.18)$$

Defining  $K$  variables,  $q_1, q_2, \dots, q_K$ , by  $q_k = p_k / \sqrt{2m}$ , we can calculate the integral for  $C(E)$  as follows:

$$C(E) = V^N (2m)^{3N/2} \int \theta \left( E - \sum_k q_k^2 \right) d^K q \quad (3.19)$$



**Fig. 3.2** The set of points defined by the inequality,  $H \leq E$ , is the  $2K$ -dimensional interior of the energy surface,  $\omega(E)$ . It has a volume,  $C(E)$ .

where  $R = \sqrt{E}$ . The integral is equal to the volume of a  $K$ -dimensional sphere of radius  $R$ . It is evaluated in the Mathematical Appendix, with the result that

$$C(E) = \frac{V^N (2\pi m E)^{3N/2}}{(3N/2)!} \quad (3.20)$$

Since  $3N/2$  is not necessarily an integer,  $(3N/2)!$  must be defined in terms of the gamma function (again, see the Mathematical Appendix) by the relation

$$x! \equiv \Gamma(x + 1) \quad (3.21)$$

The following calculation will reveal one of the bizarre geometrical properties of high-dimensional spaces. The uniform ensemble for an ideal gas describes a system that has a finite probability of being found with any energy between 0 and  $E$ . Let us now calculate the probability of finding the system with an energy less than  $xE$ , where  $0 < x < 1$ . This is easily seen to be the probability that a point, chosen at random within a  $3N$ -dimensional sphere of radius  $R = \sqrt{E}$ , will fall within the smaller sphere of radius  $R = \sqrt{xE}$ . It is equal to the ratio of the volume of a sphere of radius  $\sqrt{x}R$  to that of a sphere of radius  $R$ .

$$\mathbf{P}[\text{energy} < xE] = x^{3N/2} \quad (3.22)$$

For  $x = 0.999999$  and  $N = N_A$  this is

$$\begin{aligned} \mathbf{P}[\text{energy} < 0.999999E] &= (1 - 10^{-6})^{3N/2} \\ &\approx e^{-9 \times 10^{17}} \end{aligned} \quad (3.23)$$

The last line was obtained by noting that  $\log \mathbf{P} = \frac{3}{2}N \log(1 - 10^{-6})$  and using the approximation,  $\log(1+x) \approx x$ , that is valid for small  $x$ . Since we know that the energy must lie between 0 and  $E$ , this means that

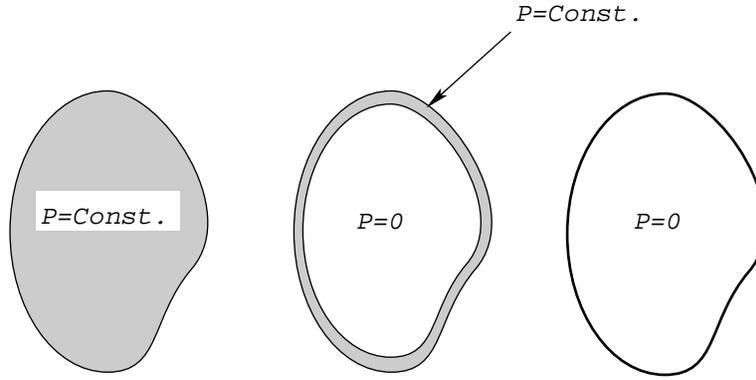
$$\mathbf{P}[0.999999E \leq \text{energy} \leq E] = 1 - e^{-9 \times 10^{17}} \quad (3.24)$$

The uniform ensemble, although it appears to describe a system with a wide range of possible energies, actually describes a system with energy  $E$  with completely negligible uncertainty (see Fig. 3.3). Therefore, in practice, it is equivalent to a probability distribution that concentrates all the probability on the surface of the sphere. That probability distribution is called a *microcanonical ensemble*.

### 3.9 THE MICROCANONICAL ENSEMBLE

The density function that assigns equal probability to all microstates with energies in some narrow range from  $E$  to  $E + \epsilon$  is of the form

$$P(x, p) = \frac{\theta(E + \epsilon - H) - \theta(E - H)}{C(E + \epsilon) - C(E)} \quad (3.25)$$



**Fig. 3.3** In the uniform ensemble, the ensemble points are uniformly distributed within the volume enclosed by the energy surface. From a probability theory point of view, this means that the probability density function is constant throughout that volume and zero outside it. The intermediate ensemble (which was not given a name) has a uniform probability density between two energy surfaces. The extreme case of this is the microcanonical ensemble, in which all of the ensemble points are distributed over a single energy surface.

By integrating  $P(x, p)$  over the phase space, it is easy to check that  $C(E + \epsilon) - C(E)$  is the correct normalization constant. With this density function  $P(x, p)$  is a positive constant if  $E < H(x, p) < E + \epsilon$  and  $P(x, p) = 0$  if  $H(x, p)$  does not fall in that range. The limit of such a density function as  $\epsilon$  goes to zero is called the *microcanonical probability density*. Using the fact that  $d\theta(x)/dx = \delta(x)$ , the Dirac delta function, and defining a function,  $Q(E) = dC(E)/dE$ , the microcanonical density can be written as

$$\begin{aligned}
 P(x, p) &= \lim_{\epsilon \rightarrow 0} \frac{\theta(E + \epsilon - H) - \theta(E - H)}{C(E + \epsilon) - C(E)} \\
 &= \frac{\lim(\theta(E + \epsilon - H) - \theta(E - H))/\epsilon}{\lim(C(E + \epsilon) - C(E))/\epsilon} \\
 &= \frac{\delta(E - H(x, p))}{Q(E)}
 \end{aligned} \tag{3.26}$$

$Q(E)$  can also be defined directly in terms of the microcanonical density function by

$$Q(E) = \int_{\Omega} \delta(E - H(x, p)) d^K x d^K p \tag{3.27}$$

Let us repeat that, in spite of the fact that the uniform and microcanonical density functions appear to be quite different, they always make experimentally indistinguishable predictions for large systems.

### 3.10 AVERAGE VALUES OF OBSERVABLES

Given any fundamental microstate density function  $P(x, p)$ , the average value (or expectation value) of any observable  $A(x, p)$  is given by Eq. (1.52) of probability theory.

$$\bar{A} \equiv \langle A \rangle = \int_{\Omega} P(x, p) A(x, p) d^K x d^K p \tag{3.28}$$

For example, the average value of the external potential energy is given by

$$\langle U \rangle = \int_{\Omega} P(x, p) \sum_{i=1}^N U(\mathbf{r}_i) d^K x d^K p \tag{3.29}$$

But, if we define a particle density function  $n(\mathbf{r})$  by saying that  $n(\mathbf{r}) d^3\mathbf{r}$  is equal to the probability of finding a particle in the volume element  $d^3\mathbf{r}$ , then  $\langle U \rangle$  could also be given as

$$\langle U \rangle = \int_{\mathbf{V}} n(\mathbf{r}) U(\mathbf{r}) d^3\mathbf{r} \tag{3.30}$$

where  $\mathbf{V}$  is the three-dimensional region containing the  $N$ -particle system. (We will write the geometrical region in boldface to distinguish it from the numerical volume of the region, which will be written as  $V$ .)

Clearly, there must be some way of obtaining  $n(\mathbf{r})$  from  $P(x, p)$  that will make Eq. (3.29) identical with Eq. (3.30). It is easy to confirm that the following identification will do exactly that.

$$n(\mathbf{r}) = \int_{\Omega} P(x, p) \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) d^K x d^K p \quad (3.31)$$

where  $\delta(\mathbf{r})$  is the three-dimensional Dirac delta function. Putting this into the right-hand side of Eq. (3.30), we get Eq. (3.29).

$$\begin{aligned} \langle U \rangle &= \int_{\Omega} P(x, p) \sum_{i=1}^N \int_{\mathbf{V}} \delta(\mathbf{r} - \mathbf{r}_i) U(\mathbf{r}) d^3 \mathbf{r} d^K x d^K p \\ &= \int_{\Omega} P(x, p) \sum_{i=1}^N U(\mathbf{r}_i) d^K x d^K p \end{aligned} \quad (3.32)$$

A more complicated example of a one-body operator is the angular momentum, whose expectation value is given by

$$\langle \mathbf{L} \rangle = \int_{\Omega} P(x, p) \sum_{i=1}^N (\mathbf{r}_i \times \mathbf{p}_i) d^K x d^K p \quad (3.33)$$

This also can be given in terms of a density function  $F_1(\mathbf{r}, \mathbf{p})$ , where  $F_1(\mathbf{r}, \mathbf{p}) d^3 \mathbf{r} d^3 \mathbf{p}$  is defined as the probability of finding a particle in the volume element  $d^3 \mathbf{r}$  with momentum in the range  $d^3 \mathbf{p}$ . If, in analogy with Eq. (3.31), we define  $F_1(\mathbf{r}, \mathbf{p})$  by

$$F_1(\mathbf{r}, \mathbf{p}) = \int_{\Omega} P(x, p) \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{p} - \mathbf{p}_i) d^K x d^K p \quad (3.34)$$

then  $\langle \mathbf{L} \rangle$  is given by

$$\langle \mathbf{L} \rangle = \int F_1(\mathbf{r}, \mathbf{p}) (\mathbf{r} \times \mathbf{p}) d^3 \mathbf{r} d^3 \mathbf{p} \quad (3.35)$$

$F_1(\mathbf{r}, \mathbf{p})$  is called the one-particle phase-space density.\* Given  $F_1(\mathbf{r}, \mathbf{p})$ , it is possible to calculate the average value of any one-body observable by a formula similar to Eq. (3.35).

The calculation of the average value of a two-body observable is slightly more complicated. If we define a two-particle phase-space density function  $F_2(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}')$  by

$$\begin{aligned} F_2(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}') &= \int_{\Omega} P(x, p) \sum_{i \neq j}^N \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{p} - \mathbf{p}_i) \\ &\quad \delta(\mathbf{r}' - \mathbf{r}_j) \delta(\mathbf{p}' - \mathbf{p}_j) d^K x d^K p \end{aligned} \quad (3.36)$$

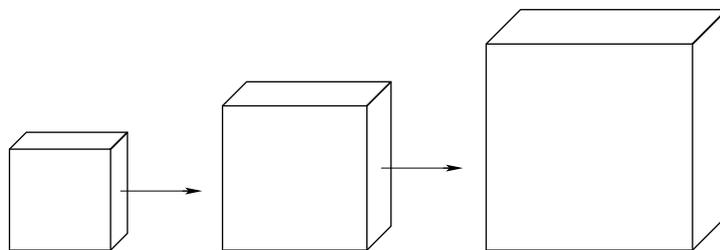
then the average value of the two-body observable  $A = \sum a(\mathbf{r}_i, \mathbf{p}_i, \mathbf{r}_j, \mathbf{p}_j)$  is given in terms of  $F_2$  by

$$\langle A \rangle = \int F_2(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}') a(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}') d^3 \mathbf{r} d^3 \mathbf{p} d^3 \mathbf{r}' d^3 \mathbf{p}' \quad (3.37)$$

The physical interpretation of  $F_2(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}')$  is that  $F_2(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}') d^3 \mathbf{r} d^3 \mathbf{p} d^3 \mathbf{r}' d^3 \mathbf{p}'$  is the probability of finding a particle in  $d^3 \mathbf{r}$  with momentum in  $d^3 \mathbf{p}$  and simultaneously finding a different particle in  $d^3 \mathbf{r}'$  with momentum in  $d^3 \mathbf{p}'$ . From the defining equations of  $F_1$  and  $F_2$ , it is easy to see that they satisfy the following normalization conditions:

$$\int F_1(\mathbf{r}, \mathbf{p}) d^3 \mathbf{r} d^3 \mathbf{p} = N \quad (3.38)$$

\* The term *phase space* is commonly used for both the  $2K$ -dimensional states of the complete system and the six-dimensional  $(\mathbf{r}, \mathbf{p})$  states of a single particle.



**Fig. 3.4** The thermodynamic limit is defined by taking a sequence of systems whose volumes become larger and larger but whose particle density and energy density remain constant.

and

$$\int F_2(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}') d^3\mathbf{r} d^3\mathbf{p} d^3\mathbf{r}' d^3\mathbf{p}' = N(N-1) \quad (3.39)$$

### 3.11 THE THERMODYNAMIC LIMIT

The physical phenomena that are the chief topics of study in statistical mechanics; namely, the approach of a system to a time-independent equilibrium state and the physical properties of that state are characteristics that are peculiar to systems containing very large numbers of particles. Systems such as planetary systems with only a few degrees of freedom show no signs, after very long periods of time, of approaching a uniform, time-independent, “equilibrium” state. In contrast, a liquid, composed of a vast number of individual molecules, if isolated from outside influences, soon reaches a quiescent state and remains that way. Of course, there are systems such as star clusters with fifty or so “particles” that seem to be intermediate between a small system, for which any statistical analysis is inappropriate and of little value, and a system of Avagadro’s number of particles, for which statistical methods offer the only hope of making progress. For these intermediate systems statistical methods give some useful but unreliable information. These systems do seem to settle down to fairly steady states for long periods of time, but will then exhibit large spontaneous fluctuations from the steady state. The exact times of the fluctuations are not predictable by statistical methods. The approach to a time-independent equilibrium state only becomes completely predictable and unambiguous in the limit of very large particle number. Also, the theoretical methods used become more powerful and reliable as  $N$  becomes larger. Clearly, the reasonable way to proceed is to study the physical characteristics of systems in the limit  $N \rightarrow \infty$ . Fortunately, the values of  $N$  encountered in real thermodynamic systems are so large that it is safe to assume that anything that would happen in the limit of infinite  $N$  has already happened for such systems to a high degree of approximation.

We cannot simply let  $N \rightarrow \infty$ , holding all other parameters fixed. If we are studying water, and we double the amount of water, then we have to double the size of the container in order to hold the density constant. We also have to double the system energy, in order to keep a constant energy per particle. We will see that, when these two corrections have been made, we then get reasonable limiting behavior as  $N \rightarrow \infty$ . This is the *thermodynamic limit*. It is defined more precisely in the following.

We begin with a system of  $N_o$  particles with a Hamiltonian function

$$H = \sum_{i=1}^{N_o} p_i^2/2m + \frac{1}{2} \sum_{i \neq j}^{N_o} \phi(r_{ij}) \quad (3.40)$$

where  $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ . The variables  $\mathbf{r}_i$  are restricted to a connected region  $\mathbf{V}_o$ , whose volume is  $V_o$ . We assume that the system has an energy  $E_o$ . Since our aim is to study the limiting properties of a system as  $N$  goes to infinity, we cannot consider only a single system, but must introduce a sequence of larger and larger systems. We do this as follows.

The system defined is considered as a *starting system* for the sequence. For each integer  $N \geq N_o$ , we consider an  $N$ -particle system with a Hamiltonian identical to that given in Eq. (3.40) but with  $N_o$  replaced by  $N$ . The particles of the  $N$ -particle system are restricted to a region  $\mathbf{V}$  that is a uniformly expanded copy of the region  $\mathbf{V}_o$ . If we choose a *scale factor*  $s$  by  $s^3 = N/N_o$  and scale up all dimensions of  $\mathbf{V}_o$  by  $s$ , then

$N/V$  will be equal to  $N_o/V_o$ .  $\mathbf{V}$  is then defined by

$$s\mathbf{r} \in \mathbf{V} \quad \text{if and only if} \quad \mathbf{r} \in \mathbf{V}_o \quad (3.41)$$

The energy of the  $N$ -particle system is chosen to be  $E = s^3 E_o$ . This guarantees that the energy per particle is independent of  $s$ . We can express these relations in a uniform way by the three equations

$$\begin{aligned} N &\equiv s^3 N_o, \\ V &\equiv s^3 V_o, \\ \text{and} \quad E &\equiv s^3 E_o \end{aligned} \quad (3.42)$$

### 3.12 FLUCTUATIONS IN THE THERMODYNAMIC LIMIT

The logical foundation of statistical mechanics is based on a generalization of the Law of Large Numbers. In order to achieve the needed generalization, it is necessary to determine the behavior of the fluctuations (or statistical uncertainties) in macroscopic observables in the thermodynamic limit (Fig. 3.4). That will require that we precisely define the concept of a macroscopic observable, a task that will be postponed until later. At this point, two special classes of macroscopic observables will be introduced. The first class, called *uniform extensive* observables are of the form

$$A = \sum_{i=1}^N a(\mathbf{p}_i) \quad (3.43)$$

The word *uniform* refers to the fact that they are independent of position. The word *extensive* means that  $\langle A \rangle$  is proportional to the size of the system in the thermodynamic limit. The most obvious example of such an observable is the kinetic energy, for which  $a(\mathbf{p}) = p^2/2m$ . The fact that  $\langle A \rangle$  goes to infinity along with  $N$  is inconvenient when studying the thermodynamic limit. That problem is eliminated in the definition of the second class of observables, called uniform *intensive* observables. A uniform intensive observable is either of the form

$$A = \frac{1}{N} \sum_{i=1}^N a(p_i) \quad (3.44)$$

or of the form

$$A = \frac{1}{V} \sum_{i=1}^N a(p_i) \quad (3.45)$$

Since  $V$  is exactly proportional to  $N$  in the thermodynamic sequence, the two forms are really equivalent. Again, the most obvious examples are the kinetic energy per particle and the kinetic energy per unit volume. In general, a uniform intensive observable is the value per particle or per unit volume of some function of momentum. The average value of any uniform intensive observable has a finite limit as  $N$ ,  $V$ , and  $E$  go to infinity.

We now want to look at the expectation values and uncertainties of intensive observables in the thermodynamic limit. Although our aim will be to justify the use of the microcanonical ensemble, we will actually use the microcanonical ensemble density function in our analysis. Of course, it will then be necessary to guard against the use of circular reasoning. Let  $A$  be any uniform intensive observable. Because  $A$  is a one-body observable, the expectation value of  $A$  is given in terms of the one-particle phase-space density function.

$$\langle A \rangle = \frac{1}{N} \int d^3\mathbf{p} \int_{\mathbf{V}} d^3\mathbf{r} F_1(\mathbf{r}, \mathbf{p}) a(\mathbf{p}) \quad (3.46)$$

$\Delta A$ , the uncertainty in  $A$ , is defined by

$$(\Delta A)^2 = \langle (A - \langle A \rangle)^2 \rangle = \langle A^2 \rangle - \langle A \rangle^2 \quad (3.47)$$

The observable  $A^2$  consists of a one-body part plus a two-body part.

$$A^2 = \frac{1}{N^2} \sum_{i=1}^N a^2(\mathbf{p}_i) + \frac{1}{N^2} \sum_{i \neq j}^N a(\mathbf{p}_i) a(\mathbf{p}_j) \quad (3.48)$$

Because the one-body part of  $A^2$  has a factor of  $1/N^2$ , rather than  $1/N$ , preceding it, its expectation value will approach zero in the thermodynamic limit. It will therefore be dropped.  $\langle A^2 \rangle$  can then be written in terms of the two-particle phase-space density.

$$\langle A^2 \rangle = \frac{1}{N^2} \int d^3\mathbf{p} d^3\mathbf{p}' \int_{\mathbf{V}} d^3\mathbf{r} d^3\mathbf{r}' F_2(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}') a(\mathbf{p}) a(\mathbf{p}') \quad (3.49)$$

Combining Eqs. (3.46) and (3.49), we get

$$\begin{aligned} (\Delta A)^2 &= \frac{1}{N^2} \int d^3\mathbf{p} d^3\mathbf{p}' a(\mathbf{p}) a(\mathbf{p}') \\ &\quad \times \int_{\mathbf{V}} d^3\mathbf{r} d^3\mathbf{r}' [F_2(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}') - F_1(\mathbf{r}, \mathbf{p}) F_1(\mathbf{r}', \mathbf{p}')] \end{aligned} \quad (3.50)$$

Recall now that  $F_2(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}') d^3\mathbf{r} d^3\mathbf{p} d^3\mathbf{r}' d^3\mathbf{p}'$  is the probability of simultaneously finding a particle in the phase-space element  $d^3\mathbf{r} d^3\mathbf{p}$  and another particle in the phase-space element  $d^3\mathbf{r}' d^3\mathbf{p}'$ . In almost all cases that we will consider, the force that one particle exerts on another has an effective range of only a few angstroms. Beyond that distance it goes rapidly to zero. Therefore, if we choose two positions,  $\mathbf{r}$  and  $\mathbf{r}'$ , that have a separation much greater than the range of interparticle interactions, one might expect very little statistical correlation between the distribution of particles at  $\mathbf{r}$  and that at  $\mathbf{r}'$ . The statement that the particle distributions at  $\mathbf{r}$  and  $\mathbf{r}'$  are uncorrelated takes the mathematical form that  $F_2(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}') = F_1(\mathbf{r}, \mathbf{p}) F_1(\mathbf{r}', \mathbf{p}')$ . When this is true we say that the two-particle density *factors* into products of one-particle densities. For any finite value of  $|\mathbf{r} - \mathbf{r}'|$  one would not expect the factorization to be exact. However, it certainly seems reasonable to assume that  $F_2(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}') \rightarrow F_1(\mathbf{r}, \mathbf{p}) F_1(\mathbf{r}', \mathbf{p}')$  as  $|\mathbf{r} - \mathbf{r}'| \rightarrow \infty$ . This property is called *asymptotic factorization*. It will be seen that the existence or nonexistence of asymptotic factorization will crucially affect the validity and reliability of our calculational methods. Although the assumption of asymptotic factorization seems very reasonable for particles with short-range interactions, it is not always correct, even for particles with strictly finite-range interactions [that is, particles for which  $\phi(r_{ij}) = 0$  when  $r_{ij} > R$  for some finite distance  $R$ ]. We will return to the question of the validity of this assumption later in this chapter.

There is a technical problem that appears at this point. For any finite value of  $N$  and any finite domain  $\mathbf{V}$  we cannot let  $|\mathbf{r} - \mathbf{r}'|$  approach infinity without having at least one of the two points move outside the system. It is only in the thermodynamic limit that infinite distances become available within the system. Therefore, the property of asymptotic factorization must be defined by coupling the limit  $|\mathbf{r} - \mathbf{r}'| \rightarrow \infty$  and the thermodynamic limit (Fig. 3.5). We do so in the following way.

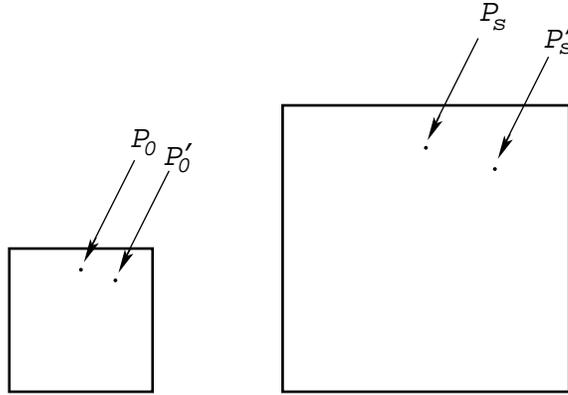
A thermodynamic limit sequence has been defined in terms of a size parameter,  $s$ . If we choose two points,  $\mathbf{r}$  and  $\mathbf{r}'$  ( $\mathbf{r} \neq \mathbf{r}'$ ), both within the starting domain  $\mathbf{V}_o$  then the points  $s\mathbf{r}$  and  $s\mathbf{r}'$  will both be in  $\mathbf{V}$ . We say that a system has the property of asymptotic factorization if the one-particle and two-particle phase-space density functions, calculated using the microcanonical ensemble, satisfy the condition that

$$\lim_{s \rightarrow \infty} [F_2(s\mathbf{r}, \mathbf{p}, s\mathbf{r}', \mathbf{p}') - F_1(s\mathbf{r}, \mathbf{p}) F_1(s\mathbf{r}', \mathbf{p}')] = 0 \quad (3.51)$$

for all  $\mathbf{r}, \mathbf{r}' \in \mathbf{V}_o$  with  $\mathbf{r} \neq \mathbf{r}'$ . The point of defining the property of asymptotic factorization is the following theorem, which will be called the *Zero Fluctuation Theorem*.

**Theorem** If the system has the property of asymptotic factorization, then, in the thermodynamic limit,  $\Delta A \rightarrow 0$  for any uniform intensive observable.

**Proof** The proof is quite simple. In Eq. (3.50) we make the transformation of variables,  $\mathbf{r} = s\mathbf{x}$  and  $\mathbf{r}' = s\mathbf{x}'$ . Then  $d^3\mathbf{r} d^3\mathbf{r}' = s^6 d^3\mathbf{x} d^3\mathbf{x}'$ . The domain of integration of the variables  $\mathbf{x}$  and  $\mathbf{x}'$  is  $\mathbf{V}_o$ . Using the fact that



**Fig. 3.5** As we go further and further in the thermodynamic sequence, the pair of “corresponding” points,  $P$  and  $P'$ , become separated by larger and larger distances. The property of asymptotic factorization is that the physical properties at the two points become statistically uncorrelated.

$s^6/N^2 = 1/N_o^2$ , we obtain the formula

$$(\Delta A)^2 = \frac{1}{N_o^2} \int d^3\mathbf{p} d^3\mathbf{p}' a(\mathbf{p})a(\mathbf{p}') \int_{\mathbf{V}_o} d^3\mathbf{x} d^3\mathbf{x}' [F_2(s\mathbf{x}, \mathbf{p}, s\mathbf{x}', \mathbf{p}') - F_1(s\mathbf{x}, \mathbf{p})F_1(s\mathbf{x}', \mathbf{p}')] \quad (3.52)$$

In the limit  $s \rightarrow \infty$  the right hand side clearly approaches zero.

A nice geometrical interpretation of this theorem can be obtained by using Chebyshev’s inequality in the following way. For any  $\epsilon > 0$  and any point  $(x, p)$  in the system phase-space  $\Omega$ , we define the function  $F_\epsilon(x, p)$  by

$$F_\epsilon(x, p) = \begin{cases} 1, & \text{if } |A(x, p) - \langle A \rangle| > \epsilon \\ 0, & \text{otherwise} \end{cases} \quad (3.53)$$

That is,  $F_\epsilon(x, p)$  is equal to one if and only if the value of observable  $A$  at the point  $(x, p)$  differs from its microcanonical average  $\langle A \rangle$  by more than  $\epsilon$ . Let us call the points at which this is true *exceptional points*, although, for very small  $\epsilon$ , they may not seem at all exceptional. Given the microcanonical probability density  $P(x, p)$  the probability that  $A$  differs from  $\langle A \rangle$  by more than  $\epsilon$  is

$$\begin{aligned} \mathbf{P}[|A - \langle A \rangle| > \epsilon] &= \int_{\Omega} F_\epsilon(x, p) P(x, p) d^K x d^K p \\ &= \frac{\int_{\Omega} F_\epsilon(x, p) \delta(E - H(x, p)) d^K x d^K p}{\int_{\Omega} \delta(E - H(x, p)) d^K x d^K p} \end{aligned} \quad (3.54)$$

The second expression clearly defines the *fraction* of the points on the energy surface that are exceptional. But, by Chebyshev’s inequality,

$$\mathbf{P}[|A - \langle A \rangle| > \epsilon] \leq \frac{(\Delta A)^2}{\epsilon^2} \rightarrow 0 \text{ as } s \rightarrow \infty \quad (3.55)$$

No matter how small we make  $\epsilon$ , in the thermodynamic limit, almost all the microstates on the energy surface  $\omega(E)$  have values of the observable  $A$  that differ from the mean value by less than  $\epsilon$ . In other words, the function  $A(x, p)$  that we are averaging has the constant value  $\langle A \rangle$  for almost all states on the energy surface. An obvious consequence of this fact is that any probability distribution that was restricted to the energy surface and did not, in the thermodynamic limit, become concentrated on the vanishing fraction of exceptional points would give the same average for any uniform intensive observable as is given by the microcanonical ensemble. If all probability distributions give the same result, then we are justified in using whichever one is the most convenient. That one is the microcanonical ensemble density.

Another way of justifying the use of the microcanonical ensemble is as follows. Imagine a macroscopic system that is initially in an exceptional state of energy  $E$ . As time progresses, the system point will move on the energy surface according to Hamilton's equations. Since only a very tiny fraction of the states on the energy surface are exceptional points, it is overwhelmingly probable that the system point will leave the small set of exceptional points and almost never return to them. In other words, it is overwhelmingly probable that the instantaneous value of any uniform intensive observable will smoothly move from its initial, exceptional, value to the microcanonical average value and then remain there. But that is exactly the behavior described as a movement to equilibrium in a macroscopic system. This will be our justification for identifying the microcanonical average value of an observable with the value of that observable in the thermodynamic equilibrium state.

Notice that we are not saying that the unexceptional points (the points that exhibit the average values of macroscopic observables) are, in any way, favored over the exceptional points. There are simply many many more of them. Thus a macroscopic system is driven to equilibrium, not by any dynamical principle that pushes the system into the unexceptional states, but by a purely statistical effect.

### 3.13 INFINITE-RANGE CORRELATIONS

Since it will form the logical foundation for almost everything that follows, it is worth our while to review carefully what has been proved in the last section and to display the faults and shortcomings of the analysis. Basically, we have shown that *if* the microcanonical two-particle density exhibits the property of asymptotic factorization, then the expectation values of *uniform intensive observables* become, in the thermodynamic limit, more or less independent of our choice of a fundamental microstate probability density. We have not proven that any particular system actually has the property of asymptotic factorization, nor have we proven anything at all about arbitrary physical observables.

The problem of extending the theorem to a sufficiently large class of physical observables will be taken up shortly. We will first consider the more important question of the general validity of asymptotic factorization.

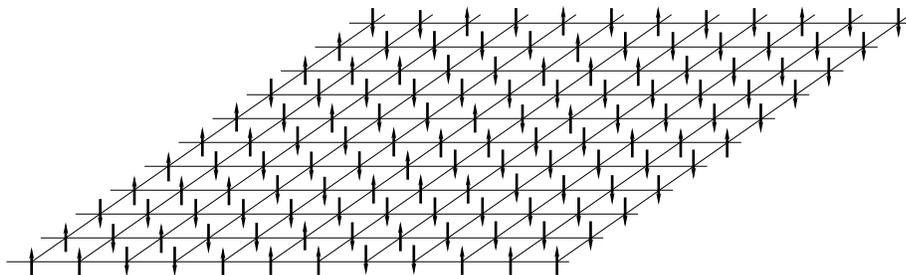
Certainly it seems extremely reasonable that the local physical properties at two widely separated points in a system with strictly short-range interactions will be statistically uncorrelated. However, in spite of its apparent reasonableness, this property is not a universal characteristic of such systems. It is not at all impossible for systems with strictly short-range interactions to develop infinite-range correlations in the thermodynamic limit. For such systems, the values of macroscopic observables calculated with the microcanonical probability density are *unreliable* and, in general, disagree with the experimental values of the same observables.

In order to develop an understanding of the phenomenon of infinite-range correlation in systems with short-range forces, we will consider a simple system that exhibits it.\*

The three-dimensional *Ising model* (cf. Fig. 3.6) is a cubic lattice containing a particle at each lattice site. All mechanical degrees of freedom of the particles are ignored. However, each particle is assumed to have a spin degree of freedom that can have two possible values, which we will call *spin up* and *spin down*. We can interpret the two-valued spin variable as describing the state of a quantized magnetic moment that can point parallel or antiparallel to the  $z$  axis. Certain strongly anisotropic magnetic crystals are reasonably described by the model. We number the particles with an index  $i$ , running from 1 to  $N$ . We introduce  $N$  spin variables,  $\sigma_1, \sigma_2, \dots, \sigma_N$ , that can take the values  $\sigma_i = +1$  (for spin up) and  $\sigma = -1$  (for spin down). Since there are no other degrees of freedom, the configuration of the complete system is described by the set of values of  $\sigma_1, \sigma_2, \dots, \sigma_N$ . A given spin is assumed to interact only with its six *nearest neighbors*. The interaction energy of a pair of neighboring particles, with spin values  $\sigma_1$  and  $\sigma_2$ , called  $U(\sigma_1, \sigma_2)$ , is assumed to have the form

$$U(+1, +1) = U(-1, -1) = -V \quad \text{and} \quad U(+1, -1) = U(-1, +1) = V \quad (3.56)$$

\*This footnote is only for sophisticated readers. In the theory of critical phenomena, one says that a system has infinite-range correlations if the correlation functions do not approach zero exponentially fast at large distances. In the terminology being used here, infinite-range correlation means that the correlation function does not approach zero *at all* for large distances. Thus a system at its critical point does *not* have infinite-range correlations in our terminology.



**Fig. 3.6** The two-dimensional version of the Ising model, pictured here, is a very simple model of a two-dimensional magnetic solid. It is composed of a square lattice of particles. The state of each particle is completely specified by a spin variable that can have only two values, which are called *up* and *down*. Below a certain critical temperature it also exhibits infinite range correlations.

This can be written as

$$U(\sigma_1, \sigma_2) = -V\sigma_1\sigma_2 \quad (3.57)$$

The energy associated with any given configuration of the system  $(\sigma_1, \sigma_2, \dots, \sigma_n)$  is

$$E = -V \sum_{\text{NN}} \sigma_i \sigma_j \quad (3.58)$$

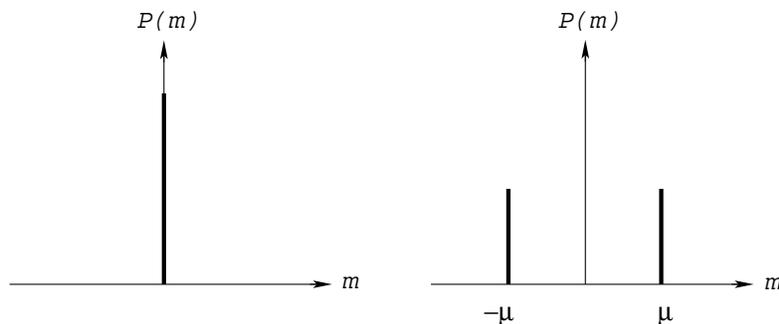
where the sum contains one term for each nearest-neighbor (NN) pair of spins. The system has overall up-down symmetry. That is, the energy is unchanged if all the spins in a configuration are simultaneously flipped from up to down and vice versa.

We will assume that  $V$  is positive, so that a pair of nearest-neighbor spins has a lower energy if they are parallel than if they are antiparallel. Then the interaction would tend to align neighboring spins to be in the same direction. The lowest-energy configurations would be the two configurations in which all spins were up or all spins were down. In general, the more agreement there was between nearest-neighbor spins in a given configuration, the lower would be the energy for that configuration. An Ising model with positive  $V$  is called a *ferromagnetic* Ising model. It is the simplest possible model of a real ferromagnetic material. For any configuration of the system we define the *mean magnetization* associated with that configuration as

$$m = \frac{1}{N} \sum_{i=1}^N \sigma_i \quad (3.59)$$

Let us consider a three-dimensional Ising model that has the form of a very large cube. For example, we might take a cube of dimension  $10^6$  lattice spacings in each direction. Such a cube would contain  $N = 10^{18}$  spins. The total number of possible configurations of the system would be the incredibly large number  $2^N$ . For any given temperature  $T$ , there is a corresponding microcanonical ensemble with an energy  $E(T)$ . The calculation of the function  $E(T)$  is a difficult problem that will be considered in later chapters. As the temperature ranges from zero to infinity, the corresponding energy ranges from  $-3NV$  to 0 (see Problem 3.17). The reason why the Ising model has been introduced at this point is that it can be proved to have the following interesting characteristics.

1. For any energy, the microcanonical average value of the mean magnetization is zero. This is an obvious consequence of the up-down symmetry of the system. (For each configuration of mean magnetization  $m$ , there is another configuration, obtained by reversing all spins, that has the same energy but has mean magnetization equal to  $-m$ .)
2. If the temperature is greater than a certain critical value  $T_c$ , then, for very large  $N$ , almost all configurations in the corresponding microcanonical ensemble have mean magnetization  $m \approx 0$ .
3. If the temperature is less than  $T_c$ , then approximately half the configurations in the corresponding microcanonical ensemble have  $m = +\mu$  while the other half have  $m = -\mu$ , where  $\mu$ , called the *spontaneous magnetization*, is a function of  $T$  that is positive for  $T < T_c$  and goes to zero at  $T = T_c$ .



**Fig. 3.7** If the temperature of the system is greater than  $T_c$  then the probability density for the average magnetization is strongly peaked at  $m = 0$ . At temperatures below  $T_c$ , there is almost zero probability of finding the system with  $m = 0$ , even though that is the ensemble average of  $m$ . Because of the nearest neighbor interactions, the spins tend to line up, either mostly up or mostly down, with equal probabilities for the two cases.

(Fig. 3.7). To be more precise, in the limit  $N \rightarrow \infty$ , the probability density associated with the random variable  $m$  approaches

$$P(m) = \begin{cases} \delta(m) & \text{if } T > T_c \\ \frac{1}{2}[\delta(m - \mu) + \delta(m + \mu)] & \text{if } T < T_c \end{cases} \quad (3.60)$$

What is happening is that, as we lower the temperature, and therefore the energy, we are demanding a greater and greater degree of correlation between the spin states of neighboring particles. We are not demanding that the spins have any preferred orientation, either up or down, but only that neighboring spins should tend to have the *same* orientation. If  $\sigma_b$  is a neighbor of  $\sigma_a$  and  $\sigma_c$  is a neighbor of  $\sigma_b$  (but not of  $\sigma_a$ ), then the correlation between  $\sigma_a$  and  $\sigma_b$  and that between  $\sigma_b$  and  $\sigma_c$  imply some degree of correlation between  $\sigma_a$  and  $\sigma_c$ , even though they do not interact directly. For small degrees of direct nearest-neighbor correlation, this induced correlation between more distant pairs of spins diminishes rapidly with distance. However, larger degrees of correlation between nearest neighbors can be achieved only by statistically coupling all the spins in the lattice. Those degrees of correlation can only be obtained with configurations in which more than half of the spins point in the same direction. The extreme case of this is the microcanonical ensemble for  $E$  equal to the lowest possible energy, namely  $-3NV$ . Then only two states of the system are possible, the state with all spins up or the state with all spins down. They have equal probability.

### 3.14 FLUCTUATIONS AND PHASE TRANSITIONS

Let us now relate this to our analysis of fluctuations in macroscopic observables. The mean magnetization,  $m$ , is clearly a macroscopic observable in the common sense of that phrase. That is, it is a large-scale observable feature of the system. Because of the up-down symmetry of the system, the microcanonical average of  $m$  is zero. But, according to the probability distribution illustrated in Fig. 3.7, if  $T < T_c$ , there is a negligible probability of ever actually observing the system with zero mean magnetization. It can also be shown that the zero microcanonical average does not, in any useful sense, represent the time average of the observed magnetization. Whether the magnetization has the value  $+\mu$  or  $-\mu$  is analogous to whether a coin is heads or tails. The coin has equal probability of having either face showing, but a real coin does not, every now and then, spontaneously flip over from one state to the other. What prevents any gradual drift in the state of a coin is that almost all of the intermediate states have much larger energy and are therefore unavailable. In the same way, almost all of the intermediate magnetization states of an Ising ferromagnet also have larger energy than the states with  $m = \pm\mu$  and are therefore not observed if the system energy is too low.

Using the probability function given in Eq. (3.60), one can see that, for  $T < T_c$ ,  $\Delta m = \mu$ . Thus, the fluctuation in the macroscopic observable,  $m$ , does not approach zero in the thermodynamic limit. Our theorem, relating fluctuations to infinite-range correlations, which could be easily modified to treat variables of the type  $m$ , therefore indicates that, for  $T < T_c$ , the corresponding microcanonical ensemble should exhibit infinite-range correlation. It is easy to see that it does. Suppose we choose an arbitrary configuration from the ensemble and look at the value of a particular spin,  $\sigma_i$ , in that configuration. If we find that  $\sigma_i = +1$ ,

then it is more likely that we have chosen one of the configurations with  $m = +\mu$  than one of those with  $m = -\mu$ . But this information would then affect our estimate of the probability that some other spin in the configuration, say  $\sigma_j$ , is also  $+1$ , even if  $\sigma_j$  is at a great distance from  $\sigma_i$ . The phenomenon of spontaneous magnetization thus introduces statistical correlations between distant spins.

As we lower the temperature from above to below  $T_c$ , the change that occurs is called a *ferromagnetic phase transition*. Other types of phase transitions, such as liquefaction of a gas or solidification of a liquid, can also introduce infinite-range correlations and fluctuations in macroscopic observables into the microcanonical ensemble. For example, consider a system composed of water molecules. We assume that the water is in a container that is coated with hydrophobic material, such as Teflon, so that there is no tendency for the water to adhere to the surface of the container. We also assume that there is no gravitational field present. (The container is floating around in interstellar space.) Certainly there are values for the particle number, volume, and energy for which the state of the system would be part liquid and part vapor. Because of the effects of surface tension, it turns out that the equilibrium states of such systems are states in which the liquid component is in the form of one or a few large-sized pieces. We will call them blobs. However, the energy of the system is completely indifferent to the exact location of the blobs within the volume. (If we had not coated the container with Teflon, this would not be true. The liquid would then be attached to the walls.) Thus, the microcanonical ensemble will contain a collection of states in which the blobs are in all possible positions within the container. An average of the particle density at some fixed location, using that ensemble, will give a value that is intermediate between the liquid density and the vapor density. But, in any real system of this type, the blobs will exist in some particular places. As macroscopic objects, they will not make spontaneous transitions among all the locations they might conceivably have occupied. The local density of a real system will be quite nonuniform, in contrast with the uniform average density predicted by the microcanonical ensemble.

As might be expected, this fluctuation in the microcanonical average of the macroscopic density is associated with infinite-range correlation in the microcanonical ensemble. To see this, let us imagine that we choose some configuration in a microcanonical ensemble for this system. With the chosen configuration we see whether there is a particle in the volume element  $d^3\mathbf{r}_1$ . Remember that any configuration in the microcanonical ensemble will be composed of a few large blobs of liquid in some particular places. (Different configurations will have the blobs in different places.) Because the particle density in the liquid is much larger than that in the vapor, if we find a particle in  $d^3\mathbf{r}_1$ , then  $d^3\mathbf{r}_1$  probably lies within one of the blobs. If we now consider a second volume element,  $d^3\mathbf{r}_2$ , at a macroscopic distance, such as one centimeter, from  $d^3\mathbf{r}_1$ , because the liquid blobs are of very large size, there will be a high probability of finding another particle in  $d^3\mathbf{r}_2$ . That this long-range correlation becomes of infinite range in the thermodynamic limit can only be proved by a more detailed analysis, but it is true.

This phenomenon, in which the expectation values of certain macroscopic variables obtained using the microcanonical ensemble are subject to large uncertainties, is associated with all known phase transitions. Since the study of phase transitions is one of the most important topics in statistical mechanics, the foregoing analysis seems to make any use of the microcanonical ensemble very suspect and unwise.

In fact, the problem of fluctuations in microcanonical averages of macroscopic observables has a very simple and general solution. Consider the liquid–vapor system. If, instead of assuming that the gravitational field is exactly zero, we assume that a very weak, but finite, gravitational field exists within the container, then the disagreement between the physically observed states and the predictions of the microcanonical ensemble disappears completely. The gravitational field will define a direction called *down*. In the physical system the liquid will all move as far as possible in that direction, which will uniquely determine its configuration. On the theoretical side, when the weak gravitational potential is added to the Hamiltonian, this redefines the energy surface,  $\omega(E)$ , and therefore the set of states in the microcanonical ensemble. It can be shown that, in the new microcanonical ensemble, virtually all the states exhibit liquid at the bottom of the container and vapor above it. The introduction of this weak *symmetry-breaking field* (so called because it breaks the exact translational symmetry of the original Hamiltonian) eliminates entirely the fluctuations in the microcanonical ensemble and, with them, the disagreement between the predictions of the microcanonical ensemble and physical observations. For the ferromagnetic Ising model the same thing could be accomplished by introducing an external magnetic field, no matter how weak, that would create an energy difference between the up-magnetized state and the down-magnetized state. With such a modification the microcanonical ensemble will predict only the lower-energy state with negligible uncertainty. For both systems, the introduction of a weak

symmetry-breaking field eliminates the infinite-range correlations that lead to uncertainty in macroscopic observables.

### 3.15 THE STANDARD CALCULATIONAL PROCEDURE

One can therefore define the following standard calculational procedure.

1. Introduce a model Hamiltonian,  $H$ , to describe the physical system of interest. Using the microcanonical ensemble defined by the model Hamiltonian, calculate all the macroscopic properties of the system as a function of the total energy.
2. Check whether the correlation functions defined by the model Hamiltonian have the property of asymptotic factorization. If, for a particular range of  $E$ , they do have that property, then, within that energy range, almost all states of a given energy will exhibit the microcanonical average values for all macroscopic observables and we can safely expect any real system to exhibit those values of the same observables at equilibrium.
3. If, within a certain energy range, the microcanonical ensemble exhibits infinite-range correlations, then introduce a weak symmetry-breaking field to eliminate that phenomenon when making calculations within that energy range.

### 3.16 THE ERGODIC THEOREM

There is still another effect that can, and sometimes does, prevent the measured values of macroscopic observables from agreeing with their microcanonical averages. It is the existence of unexpected conservation laws. If, in addition to the energy, some other observable,  $A(x, p)$ , is exactly conserved, then the system point is restricted to move on the intersection of the energy surface and the surface defined by the equation,  $A(x, p) = A_o$ , where  $A_o$  is the initial value of the conserved quantity. This intersection constitutes a negligible fraction of the total energy surface, and thus there is nothing to guarantee that it is not composed primarily of exceptional points. In fact, if  $A$  is a macroscopic observable, then the average value of  $A$  on the intersection will be  $A_o$ , which might very well disagree with the microcanonical average of  $A(x, p)$ . In that case, the intersection would be composed entirely of exceptional points.

A simple, but not realistic, example of a system with extra conserved quantities (any conserved quantity in addition to the energy will be here called an *extra* conserved quantity) is a collection of interacting particles within a spherically symmetric three-dimensional harmonic oscillator potential. The Hamiltonian for the system is

$$H(x, p) = \sum p_n^2/2m + \sum_{i < j} v(r_{ij}) + \frac{1}{2}k \sum r_n^2 \quad (3.61)$$

In addition to the energy, the total angular momentum of the system is conserved. Therefore, if we happen to start the system with some nonzero angular momentum vector, then it will eventually approach a time-independent equilibrium state in which the mass of particles will rotate like a rigid body (see Problem 3.16). But the average over the energy surface of the angular momentum is zero, and, in fact, for a large system, almost all of the states on the energy surface have approximately zero angular momentum. Thus, for this system, the properties of the observed equilibrium state may not agree with those of the microcanonical average. This is an unrealistic model because the slightest deviation from spherical symmetry will introduce a coupling between the internal energy, associated with the complicated individual particle motions, and the rigid-body rotational energy that will act as a frictional force and eventually dissipate the macroscopic rotational motion.

There is a theorem, due to G. Birkhoff and called the *ergodic theorem*, that relates the time average of any observable to its microcanonical average. For an observable  $A(x, p)$  and any initial point  $(x_o, p_o)$  the time average of  $A$  is defined as

$$\langle A \rangle_{x_o p_o} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T A(x(t), p(t)) dt$$

where  $(x(t), p(t))$  is the solution of Hamilton's equations that started out, at  $t = 0$ , at  $(x_o, p_o)$ . Birkhoff's theorem says that, in the absence of extra conserved quantities, the time average of any observable over the phase-space trajectory of a system point that starts anywhere on the energy surface will be equal to the microcanonical average of the same observable. (There are really some technical mathematical restrictions

on the theorem, but they do not seriously weaken it.) Birkhoff's theorem is very nice. It guarantees that, in the absence of extra conservation laws, a system point that starts in an exceptional state will not just move around within a tiny island of exceptional states, but will eventually move to, and stay in, the much larger ocean of equilibrium states.

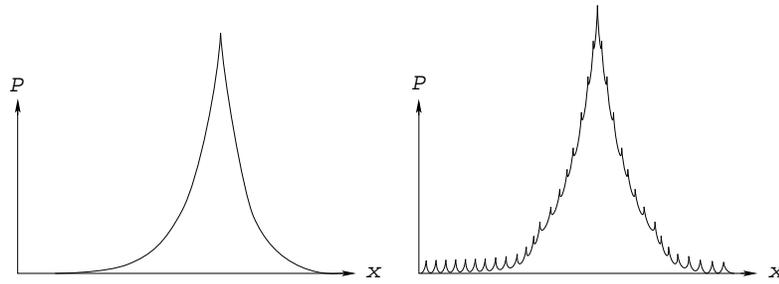
A system that does not have extra conservation laws is called an *ergodic* system. It seems to be almost impossible rigorously to prove that any realistic large system of interacting particles is ergodic. The only significant case of such a proof is a theorem, due to the Russian mathematician Ya. G. Sinai, that a system of billiard-ball particles is ergodic. While it is generally believed that most macroscopic classical systems do not have extra conservation laws, the possible existence of nonergodic systems is a serious problem in the foundations of statistical mechanics. The traditional conservation laws are associated with obvious and simple symmetries. The invariance of physical laws under translation in time leads to the conservation of energy. Invariance under spatial translation yields conservation of linear momentum, while rotational invariance implies the conservation of angular momentum. Such conserved quantities are relatively easy to predict from the nature of the system under study. However, during the 1960s it was discovered that systems that satisfy certain nonlinear wave equations conserve large numbers of other quantities that do not have such simple physical interpretations and whose definitions depend on the detailed nature of the wave equation. Also, all this discussion has been restricted to classical systems. When we consider macroscopic quantum-mechanical systems, the situation changes in an important way. It is not that the ergodic theorem is affected; there exists a quantum-mechanical version of the theorem that is essentially equivalent to the classical one. What changes is that there are many macroscopic quantum-mechanical systems that are known to have extra conserved quantities. The best example is a superconductor.

The magnetic flux encircled by a superconducting loop is strictly conserved as long as the loop is maintained in its superconducting state. This means that the total current flowing in the superconducting loop is also conserved. This is a robust conservation law that does not depend on maintaining some artificial perfect symmetry, as did the case of the system in a spherical potential. As in all cases of extra conservation laws, the observed equilibrium state of the system depends on its past history. In particular, the amount of magnetic flux that is trapped in the loop is equal to the amount of flux that was passing through the loop when it became superconducting. Identical systems at the same temperature can exhibit different time-independent equilibrium states. Only one of the possible equilibrium states is the microcanonical average equilibrium state. Therefore, the microcanonical average is not a reliable predictor of the observed equilibrium properties of such systems. This does not mean that we cannot use statistical mechanics to analyze superconductors. Actually, it is the only thing that we *can* use to understand them. It means only that we have to use it more carefully and intelligently. We must construct an ensemble of states with a given energy *and* a given value for the trapped flux. Once this extra conserved quantity is taken into account, the predictions of all other macroscopic observables becomes completely reliable. The difficulties involving superconductors and their resolution has obvious similarities to those involving spontaneous symmetry breakdown. It is an example of the fact that, in the real world, there is no cookbook procedure that can be reliably used without some thought.

### 3.17 GLASSES

If a system does not have infinite-range correlations and does not have extra conservation laws, then it should eventually approach an equilibrium state that exhibits the macroscopic features predicted by the microcanonical ensemble. However, "eventually" may be a very long time. Ordinary glass is the best example of a material that will remain essentially forever in a nonequilibrium state. In fact, pieces of ancient glass that have not been chemically weathered by rainwater or groundwater show no discernible signs of coming to equilibrium. Typical glasses are made by adding chemical impurities, particularly boron and oxygen, to molten silicon and then rapidly cooling the mixture. If, instead of rapid cooling, the material is subjected to very gradual cooling from the molten state, then, at a certain temperature that depends on the details of the mixture, crystals of silicon begin to form and grow. This behavior clearly indicates that the homogeneous, glassy state is not the true equilibrium state of the system at room temperature. What happens when the material is cooled rapidly is that the system gets caught in a state that is a local equilibrium state but is not the true global equilibrium state.

In Fig. 3.8 the probability of various values of some macroscopic variable  $x$  for two different imaginary systems is shown. The probability is proportional to the number of microstates that have that value of  $x$ ,



**Fig. 3.8** For any given ensemble, the probability density for some macroscopic observable  $x$  is defined by saying that  $P(x) dx$  is the fraction of ensemble members that have  $x$  within the range  $dx$ . *A* and *B* show the structure of  $P(x)$  for some unspecified observable, such as the mass density or the potential energy, in the case of a *normal* system, in which  $P(x)$  is a fairly smooth function with one extremely sharp maximum at the equilibrium value for  $x$ , and in case of a *complex* system, in which  $P(x)$  still has a very large maximum at the equilibrium value but has a very rough structure containing many local maxima of various heights. It may take a very long time for such a system to make transitions from one local maximum to another. If the valleys between the local maxima are deep enough, it can take such a system an absurdly long time to come to true equilibrium.

and therefore the graphs can be interpreted as the number of microstates of the two systems in terms of the parameter  $x$ . Graph *A* describes a normal system. If such a system is started in an improbable nonequilibrium state, its constant transitions from one microstate to another would soon cause its macroscopic features, such as the value of  $x$ , to move to their overwhelmingly more probable equilibrium values. Graph *B* describes what is called a *complex system*. Glasses are the most common examples of complex systems. In a complex system, the function  $P(x)$  has a large global maximum, corresponding to the equilibrium value of  $x$ , but it also has a very rough structure with many local maxima. Typically the graph has a fractal structure in which the roughness persists at all levels of magnification. Such a system, started in a nonequilibrium state, will most likely go to a nearby state of local equilibrium [a state in which  $P(x)$  has a local maximum]. At any given temperature the thermal fluctuations in  $x$  will allow the system to jump from one local equilibrium state to another so long as the valleys between the two maxima are not too low. At higher temperatures larger jumps are possible. At very low temperature the system simply moves to the nearest local equilibrium state and stays there for an extremely long time until a very improbable fluctuation allows it to jump across the valley to a better local equilibrium state.

For a glass, the local equilibrium states describe configurations in which, on a very local scale, the atoms of the material are in energetically advantageous positions and have advantageous chemical bonding patterns. However, they are only local equilibrium states because, by breaking some of the bonds and doing some rearranging, one could find a still better configuration for the system. These rearrangements could be done at many different length scales but the larger the length scale the larger is the barrier to such a rearrangement and thus the more improbable is it that such a rearrangement will take place spontaneously. When the glass is heated to a liquid state the rough structure of the graph disappears entirely. For a normal liquid (in contrast to the supercooled glassy liquid) transitions from one macrostate to another are smooth and easy. Thus the molten glass would go to its true equilibrium state. If the glass is cooled very slowly, then, as the rough structure begins to develop, the system will always have enough energy to jump the valleys and remain in its globally most probable state. Thus, beginning with pure molten quartz ( $\text{SiO}_2$ ), rapid cooling (called quenching) will produce silica glass, a microscopically amorphous material, but very slow cooling (called annealing) will produce a single quartz crystal.

The theoretical analysis of complex systems is a difficult problem that is still under development. It will not be treated any further in this book.

**3.18 NONUNIFORM MACRO. OBSERVABLES\*** The standard calculational procedure is based upon the zero-fluctuation theorem. The most glaring deficiency in that theorem is the limited set of

\* A star indicates an optional section that may be skipped without a serious loss of continuity.

observables to which it applies. In this and the next section, the theorem will be extended to nonuniform one-body and two-body macroscopic observables. The reader who is willing to accept, without detailed proof, that the no-fluctuation theorem can be extended to anything that, in common parlance, would be called a macroscopic variable, can skip to Section 3.20.

In trying to define nonuniform macroscopic observables, it is best to begin with a very specific case and then to generalize the procedure used there. As a starting system, we consider an ideal gas of  $N_o$  particles in a cubic box of volume  $V_o = L_o^3$ , subject to a uniform gravitational field, described by the potential  $U_o(\mathbf{r}) = mgz$ . The Hamiltonian for such a system is

$$H = \sum_{i=1}^{N_o} p_i^2/2m + \sum_{i=1}^{N_o} U_o(\mathbf{r}_i) \quad (3.62)$$

$H$  is composed of two one-body observables. The kinetic energy is a uniform observable and is therefore of no use to us in our task of extending the set of macroscopic observables. The gravitational potential is not a uniform observable. The question to be considered is: "When we scale the system from  $(N_o, V_o, E_o)$  to  $(N, V, E)$ , what potential energy function should be used in the larger system"? There are two natural possibilities. They are:

1. Keep the gravitational field,  $\mathbf{g} = -g\hat{\mathbf{z}}$ , fixed and uniform for the sequence of larger and larger systems. That is, use the same potential function for the scaled system as for the starting system. In that case,  $U_s(\mathbf{r}) = U_o(\mathbf{r})$ .
2. Scale the gravitational potential function so that the potential at a point in the scaled system is equal to the potential in the starting system at the "corresponding" point. To do so, one must modify the potential function by the transformation  $U_s(\mathbf{r}) = U_o(\mathbf{r}/s)$ . The gravitational field strength will then get weaker as the system size increases.

In Problem 3.18 the reader is asked to show that the first alternative, keeping a fixed gravitational field, leads to unphysical results in the thermodynamic limit. As the system size increases, the density and pressure at the bottom of the container approach infinity. In contrast, the second alternative, scaling the potential function, produces a density profile that is independent of the scale size. It is the expected exponential density function, derived in Section 2.6. This is not intended to show that, in real systems, the gravitational field is infinitely weak; of course, it is not. The thermodynamic limit is a mathematical device that is useful in studying the properties of systems that are actually finite but very large. This analysis shows how to apply that mathematical device to nonuniform systems.

The appropriate Hamiltonian function for the scaled system is

$$H = \sum_{i=1}^N p_i^2/2m + \sum_{i=1}^N U_s(\mathbf{r}_i) \quad (3.63)$$

where  $U_s(\mathbf{r}) = U_o(\mathbf{r}/s)$ . In general, we will define an one-body *extensive* observable by choosing an arbitrary one-body observable,  $A = \sum a_o(\mathbf{r}_i, \mathbf{p}_i)$ , in the starting system and extending it to the larger systems in the thermodynamic limit sequence by the rule

$$A = \sum_{i=1}^N a_s(\mathbf{r}_i, \mathbf{p}_i) \quad (3.64)$$

where  $a_s(\mathbf{r}, \mathbf{p}) = a_o(\mathbf{r}/s, \mathbf{p})$ .

A general way of defining corresponding one-body *intensive* observables is to begin with some arbitrary one-body observable in the starting system but extend it to the scaled system by the rule

$$A = \frac{1}{N} \sum_{i=1}^N a_s(\mathbf{r}_i, \mathbf{p}_i) \quad (3.65)$$

The factor of  $1/N$  guarantees that  $\langle A \rangle$  approaches a finite limit as  $N$ ,  $V$ , and  $E$  go to infinity. It is left as a problem to prove that the zero-fluctuation theorem is valid for all one-body intensive observables. Notice

that uniform intensive observables are now just a special case of one-body intensive observables in which the function  $a_o$  does not depend on  $\mathbf{r}$ .

Although the fluctuation in an *extensive* observable does not go to zero in the thermodynamic limit, it can be shown to become negligible in comparison with the average value of the observable. (See Problem 3.20.)

### 3.19 TWO-BODY MACROSCOPIC OBSERVABLES\*

Two-body macroscopic observables can be defined in a way that closely parallels that used for one-body observables. A uniform extensive two-body observable is an observable of the form

$$A = \sum_{i \neq j}^N a(\mathbf{r}_{ij}, \mathbf{p}_i, \mathbf{p}_j) \quad (3.66)$$

where  $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ . The most important example is the interaction potential energy, for which  $a(\mathbf{r}, \mathbf{p}, \mathbf{p}') = \frac{1}{2}\phi(|\mathbf{r}|)$ . Again, the word *uniform* refers to the fact that  $a$  depends only on relative coordinates and is therefore unchanged in a simultaneous translation of the coordinates of all the particles. A corresponding uniform intensive observable can be obtained by dividing the extensive observable by any extensive parameter, such as  $N$  or  $V$ . For example, the density of pairs of particles with relative position vector  $\mathbf{q}$  is the average value of the observable

$$A = \frac{1}{V} \sum_{i \neq j}^N \delta(\mathbf{r}_{ij} - \mathbf{q}) \quad (3.67)$$

A nonuniform two-body observable is defined by choosing an arbitrary two-body observable in the starting system, written in terms of center-of-mass and relative coordinates.

$$A_o = \sum_{i \neq j}^{N_o} a_o(\mathbf{R}_{ij}, \mathbf{r}_{ij}, \mathbf{p}_i, \mathbf{p}_j) \quad (3.68)$$

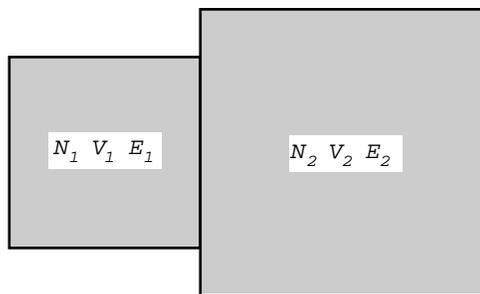
where  $\mathbf{R}_{ij} = \frac{1}{2}(\mathbf{r}_i + \mathbf{r}_j)$  and  $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ . In transporting the observable to further members of the thermodynamic limit sequence, only the center-of-mass coordinate is scaled. For the scaled system,  $A_s$  is defined as

$$A_s = \sum_{i \neq j}^N a_s(\mathbf{R}_{ij}, \mathbf{r}_{ij}, \mathbf{p}_i, \mathbf{p}_j) \quad (3.69)$$

with  $a_s(\mathbf{R}, \mathbf{r}, \mathbf{p}, \mathbf{p}') = a_o(\mathbf{R}/s, \mathbf{r}, \mathbf{p}, \mathbf{p}')$ . Higher order (three-body, etc.) macroscopic observables may also be defined, but the analysis becomes rather technical and is inappropriate for an introductory text. A zero fluctuation theorem can be proven for arbitrary intensive two-body macroscopic observables. It requires that the four-body phase-space density function,  $F_4(1, 2, 3, 4)$  [where  $1 \equiv (\mathbf{r}_1, \mathbf{p}_1)$ , etc.] has an asymptotic factorization property of the form  $F_4(1, 2, 3, 4) \rightarrow F_2(1, 2)F_2(3, 4)$  when the distance between the pair of variables  $(\mathbf{r}_1, \mathbf{r}_2)$  and the pair of variables  $(\mathbf{r}_3, \mathbf{r}_4)$  approaches infinity.

### 3.20 THERMODYNAMIC OBSERVABLES

The standard calculational procedure now seems to be broadly satisfactory. It permits one to calculate the equilibrium value of any macroscopic observable with a reasonable expectation that the value of the corresponding observable in a real system will approach the calculated value. However, it still has the following major deficiency. There is an important class of clearly macroscopic observables about which the standard calculational procedure gives no information whatever. They are what will be called *thermodynamic* observables, as opposed to mechanical observables. A mechanical observable is what we have been calling simply an observable. That is, it is any quantity for which there is a corresponding phase-space function,  $A(x, p)$ . The class of thermodynamic observables may be illustrated by considering its most important member, namely, the *entropy*. For a system of point particles, what function of their positions and momenta is their entropy? A system of a few particles simply does not have an entropy. Entropy is a concept that is only defined for macroscopic systems. This can be seen by considering the role played in thermodynamics



**Fig. 3.9** The two systems can transfer energy by heat conduction. The equilibrium distribution of energy will maximize the total entropy of the system.

by the entropy. We will now do so for a system composed of two components. The subject will be taken up again in a later chapter on thermodynamics, where it will be treated in much more detail.

The total entropy of a system of two components, such as that shown in Fig. 3.9, is the sum of the entropies of its parts. The entropy of each component is a function of that component's particle number, volume, and energy. Thus the total entropy  $S_T = S_1(N_1, V_1, E_1) + S_2(N_2, V_2, E_2)$ . If the systems are allowed to interact (for example, if they are put into thermal contact so that they may exchange energy), and the interaction is maintained for a long period of time, the system will come to an equilibrium state. The equilibrium state will be that state which maximizes the total entropy, taking into account the fundamental conservation laws of energy and particles and the constraints of the allowed interaction (that is, thermal contact allows only energy exchange but a channel between the two systems would allow both energy and particles to be exchanged). For example, if the two components shown in Fig. 3.9 are brought into thermal contact, then the condition that  $S_T$  be maximized, with the constraint that  $E_1 + E_2 = E_T$ , where  $E_T$  is the fixed total system energy, leads to the equilibrium condition

$$\frac{\partial S_1(N_1, V_1, E_1)}{\partial E_1} = \frac{\partial S_2(N_2, V_2, E_2)}{\partial E_2} \quad (3.70)$$

This Entropy Maximization Principle is the defining characteristic of the entropy. But, since its definition involves the concept of thermal equilibrium, the entropy can have no meaning for small systems, which never approach an equilibrium state. Entropy is an observable that emerges, along with the idea of equilibrium states, only in the thermodynamic limit, that is, only for systems of sufficient complexity. All other thermodynamic observables, such as free energy or enthalpy, involve the entropy or its derivatives in their definition and could thus be calculated if one had a statistical mechanical rule for calculating the entropy.

The fact that no phase-space function exists that represents the entropy will not mean that it cannot be calculated by statistical mechanics. The meaning of the entropy in statistical mechanics can be discovered by solving physical problems, using the rules of statistical mechanics, that can also be solved by thermodynamics, and then comparing the solutions obtained by the two methods. The first problem to be considered is the thermal equilibrium problem that, by thermodynamics, led to Eq. (3.70).

The collection of phase-space variables that describe subsystem 1 will be denoted as  $(x_1, p_1)$  and those for subsystem 2 as  $(x_2, p_2)$ . The total system has energy  $E_T$ . The Hamiltonian is an expression that gives the energy in terms of the positions and momenta of the particles. If the interaction between the subsystems is very weak, then the total energy is just the energy of subsystem 1, which depends on its particles, plus the energy of subsystem 2, which depends only on its particles. In that case, which we assume is true, the Hamiltonian function for the complete system can be approximated as

$$H_T = H_1(x_1, p_1) + H_2(x_2, p_2) \quad (3.71)$$

The microcanonical probability density for the complete system is

$$P(x_1, p_1, x_2, p_2) = \frac{\delta(E_T - H_1 - H_2)}{Q_T(E_T)} \quad (3.72)$$

The question to be considered is: "What is the energy of subsystem 1 at equilibrium"? This is equivalent to asking for the equilibrium value of  $\langle H_1 \rangle$ .  $H_1$  is a random variable in the sense of Section 1.10. The general

rule for calculating the probability that a random variable  $A(x)$  will have a value  $a$ , given the microstate probability density  $P(x)$ , is that

$$P_A(a) = \int_{\Omega} \delta(a - A(x))P(x) d^N x \quad (3.73)$$

Therefore, the probability that  $H_1(x_1, p_1) = E_1$  is given by

$$\begin{aligned} P_1(E_1) &= [Q_T(E_T)]^{-1} \int \delta(E_1 - H_1)\delta(E_T - H_1 - H_2) d^{K_1}x_1 d^{K_1}p_1 d^{K_2}x_2 d^{K_2}p_2 \\ &= [Q_T(E_T)]^{-1} \int \delta(E_1 - H_1)\delta(E_T - E_1 - H_2) d^{K_1}x_1 d^{K_1}p_1 d^{K_2}x_2 d^{K_2}p_2 \\ &= \frac{Q_1(E_1)Q_2(E_2)}{Q_T(E_T)} \end{aligned} \quad (3.74)$$

where  $E_2 = E_T - E_1$ . Certainly  $H_1$  is a macroscopic observable, and thus its measured value at equilibrium will almost surely be its most probable value. That value is determined by setting  $\partial P_1(E_1)/\partial E_1 = 0$ , which gives

$$Q'_1(E_1)Q_2(E_2) - Q_1(E_1)Q'_2(E_2) = 0 \quad (3.75)$$

or

$$\frac{Q'_1(E_1)}{Q_1(E_1)} = \frac{Q'_2(E_2)}{Q_2(E_2)} \quad (3.76)$$

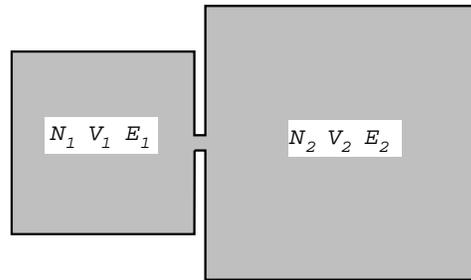
Taking into account that  $Q_1$  depends also upon  $N_1$  and  $V_1$  and that  $Q_2$  depends on  $N_2$  and  $V_2$ , Eq. (3.76) can be written as

$$\frac{\partial \log Q_1(N_1, V_1, E_1)}{\partial E_1} = \frac{\partial \log Q_2(N_2, V_2, E_2)}{\partial E_2} \quad (3.77)$$

This equilibrium condition will agree with Eq. (3.70), the thermodynamic condition for equilibrium, if we identify  $S(N, E, V)$  for any system as

$$S(N, E, V) = k \log Q(N, E, V) + K \quad (3.78)$$

where  $k$  and  $K$  are two constants that may, however, depend on  $N$  and  $V$ .



**Fig. 3.10** The two systems can transfer both energy and particles. The final distribution of both quantities will be such as to maximize the entropy of the combined system.

In order to obtain information about the  $N$  dependence of  $S$ , it is necessary to consider the equilibrium of two subsystems that can exchange particles as well as energy. Such a situation is depicted in Fig. 3.10. The system contains a total of  $N_T$  particles and has an energy  $E_T$ . The problem is now to determine the values of  $E_1$  and  $N_1$  at equilibrium. Let the left domain be called  $\mathbf{V}_L$ . The characteristic function of  $\mathbf{V}_L$  is defined as

$$C_L(\mathbf{r}) = \begin{cases} 1, & \mathbf{r} \in \mathbf{V}_L \\ 0, & \text{otherwise} \end{cases} \quad (3.79)$$

As is shown in Exercise 3.4, the observable described by the phrase “the number of particles on the left” is

$$N_L(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{i=1}^{N_T} C_L(\mathbf{r}_i) \quad (3.80)$$

For any particular configuration of the system, we can write  $H_T = H_L + H_R$ , where  $H_L$  is the energy of all the particles on the left and  $H_R$  is the energy of those on the right. The probability of finding exactly  $N_1$  particles on the left with an energy  $E_1$  is given by

$$P_L(N_1, E_1) = \frac{\int \delta(N_1 - N_L) \delta(E_1 - H_L) \delta(E_T - H_L - H_R) d^K x d^K p}{Q_T(N_T, V_T, E_T)} \quad (3.81)$$

The discrete Kronecker delta function,  $\delta(N_1 - N_L(x))$ , is zero except for configurations in which exactly  $N_1$  particles are on the left. There are  $\binom{N_T}{N_1}$  ways of choosing those particles. When that is taken into account, one finds that

$$P_L(N_1, E_1) = \frac{N_T!}{N_1! N_2!} \frac{Q_L(N_1, V_1, E_1) Q_R(N_2, V_2, E_2)}{Q_T(N_T, V_T, E_T)} \quad (3.82)$$

The most probable state is determined by setting  $\partial P_L / \partial E_1 = 0$  and  $\partial P_L / \partial N_1 = 0$ . The first equation gives the same result obtained in Eq. (3.77). The second condition will give

$$\frac{\partial \log(Q_L / N_1!)}{\partial N_1} = \frac{\partial \log(Q_R / N_2!)}{\partial N_2} \quad (3.83)$$

which shows that  $\log Q$  should be replaced by  $\log(Q/N!)$  in Eq. (3.78). This change will have no effect on the solution of the energy equilibrium equation. There is one further modification that must be made. In Chapter 4, which treats quantum-mechanical systems, we will define the entropy as the logarithm of the number of discrete quantum states that have energy less than  $E$ . In order to prevent having the classical and quantum-mechanical definitions of the entropy differ by a constant (which would not have any effect on the equilibrium states that the entropy functions would predict), we must divide the phase-space integral that defines  $Q$  by the factor  $h^K$ , where  $h = 2\pi\hbar$  is Planck's constant and  $2K$  is the dimensionality of the phase-space. The appearance of Planck's constant clearly reveals the quantum-mechanical origin of this term. One might say that Planck's constant supplies a natural or fundamental unit of phase-space volume, namely  $h^K$ , just as the velocity of light supplies a fundamental unit of velocity. The net result is that, for any system that can be described by classical mechanics, the thermodynamic entropy is given by the formula

$$\begin{aligned} S &= k \log \left[ \frac{1}{h^K N!} \int \delta(E - H(x, p)) d^K x d^K p \right] \\ &= k \log [Q / h^K N!] \end{aligned} \quad (3.84)$$

The absolute temperature is defined in terms of the entropy by

$$\frac{1}{T} = \frac{\partial S}{\partial E} \quad (3.85)$$

Thus, the choice of a temperature unit fixes the arbitrary constant  $k$ . For the Kelvin temperature scale,  $k$  must be chosen to be Boltzmann's constant.

Because of the geometrical properties of high-dimensional spaces that were discussed in Section 3.7, it would make no difference if the microcanonical normalization integral  $Q$  were replaced in Eq. (3.84) by the normalization integral for the uniform ensemble  $C$  defined in Eq. (3.16).

### 3.21 THERMODYNAMIC CALCULATIONS

This formula, giving the entropy as a phase-space integral, is the basis for another method of computing many important macroscopic observables that is much more efficient than the standard calculational procedure. In Chapter 5 it will be shown that, once the entropy function is known, the equilibrium values of most macroscopic observables may be computed using thermodynamic identities, directly from that function. As

an example, we will derive the equations of state of an ideal gas from Eq. (3.20), which gives the value of  $C(N, E, V)$ . From that equation, we get that

$$\begin{aligned} S &= k \log[C/h^K N!] \\ &= Nk(\log V + \frac{3}{2} \log E + \phi(N)) \end{aligned} \quad (3.86)$$

where  $\phi$  is a function of  $N$  that could easily be calculated but will not be needed here. Using the thermodynamic formulas\*  $1/T = \partial S/\partial E$  and  $p/T = \partial S/\partial V$ , we immediately obtain the desired relations.

$$\frac{1}{T} = \frac{3kN}{2E} \quad (3.87)$$

and

$$\frac{p}{T} = \frac{kN}{V} \quad (3.88)$$

### 3.22 THE PRESSURE FORMULA\*

The temperature is fundamentally a statistical variable. From the equation  $1/T = \partial S/\partial E$ , it is clear that it conveys information on how fast the number of microstates available to the system increases with energy. But the pressure, being a force over an area, is a mechanical variable. For a system of  $N$  particles in a cylinder closed by a piston, the force on the piston is a well-defined function of the positions and momenta of the particles. That is exactly what defines a mechanical variable. Therefore, the formula  $p = T \partial S/\partial V$ , which equates a mechanical variable to a statistical variable, is particularly remarkable. In Chapter 5, it will be derived by a thermodynamic argument. However, the thermodynamic argument, because it makes no reference to microscopic dynamics, somewhat hides the detailed mechanical origin of the relation. Therefore, in this section, we will give an alternative derivation of the formula, using a microcanonical ensemble.

We consider a system of  $N$  particles in a cylinder whose left wall is a moveable but fixed piston (Fig. 3.11). In other words, the piston could be located at any point, but while the particles of the system move, it remains fixed and is not a dynamical variable in the system. We model the interaction between the  $i$ th particle and the piston by a "wall potential"  $U(x_i - X)$ , which smoothly becomes infinite as  $x_i - X \rightarrow 0$  but is equal to zero for  $x_i - X$  larger than some fixed microscopic distance  $a$ . Thus the Hamiltonian of the system, when the piston is at position  $X$ , is

$$H = H_o(\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{p}_1, \dots, \mathbf{p}_N) + \sum_1^N U(x_i - X) \quad (3.89)$$

where  $H_o$  contains the kinetic energy and interaction potentials for the  $N$  particles. For any finite energy, the wall potential guarantees that no particle's  $x$  coordinate becomes less than  $X$ . For any state of the system, the instantaneous force that the piston is exerting on the particles is

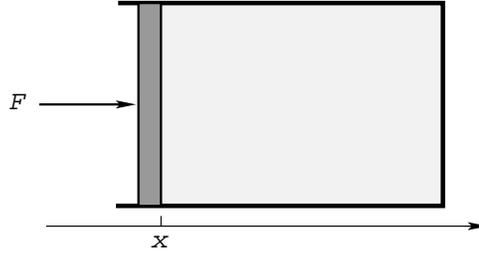
$$F = - \sum_1^N \frac{\partial U(x_i - X)}{\partial x_i} \quad (3.90)$$

The pressure on the wall is defined as  $F/A$ , where  $A$  is the area of the piston.

$$p = -A^{-1} \sum_1^N \frac{\partial U(x_i - X)}{\partial x_i} \quad (3.91)$$

The pressure resembles a one-body macroscopic observable, in that it is a one-body function, summed over all the particles in the system. But, in the thermodynamic limit, it would not be appropriate to scale the wall potential  $U(x_i - X)$ . Even for a macroscopic system, a particle only interacts with the wall when it is microscopically close to it. Therefore, it is really necessary to repeat the thermodynamic limit analysis

\*The second relation is derived in the next section and also in Chapter 5.



**Fig. 3.11** The piston is fixed at position  $X$ . The particles within the cylinder exert an average force  $F = pA$  on the piston.

separately for this case. The details have been left as an exercise (see Problem 3.25). One must assume that, for  $x$  and  $x'$  in the range  $X < x, x' < X + a$ ,

$$F_2(x, sy, sz, \mathbf{p}, x', sy', sz', \mathbf{p}') \rightarrow F_1(x, sy, sz, \mathbf{p}) F_1(x', sy', sz', \mathbf{p}') \quad (3.92)$$

as  $s \rightarrow \infty$ . That is, particles at large distances from one another on the surface of the piston are assumed not to be statistically correlated. With that assumption, the observed pressure is almost certain to be the average pressure for a microcanonical ensemble at the system energy. Thus, we can assume that

$$p = -A^{-1} \int \sum \frac{\partial U}{\partial x_i} \delta(E - H) d^{3N} r d^{3N} p / \int \delta(E - H) d^{3N} r d^{3N} p \quad (3.93)$$

But, by the definition of  $H$ , it is easy to see that

$$-\sum \frac{\partial U}{\partial x_i} \delta(E - H) = -\frac{\partial}{\partial X} \theta(E - H) \quad (3.94)$$

which implies that

$$\begin{aligned} p &= -A^{-1} \frac{\partial}{\partial X} \int \theta(E - H) d^{3N} r d^{3N} p / \int \delta(E - H) d^{3N} r d^{3N} p \\ &= -A^{-1} \frac{\partial C(E, X)}{\partial X} / Q(E, X) \end{aligned} \quad (3.95)$$

Using the facts that  $Q(E, X) = \partial C(E, X) / \partial E$  and that  $dV = -A dX$ , where  $V$  is the container volume, the pressure can be written as

$$\begin{aligned} p &= \frac{\partial C / \partial V}{\partial C / \partial E} \\ &= \frac{\partial \log C / \partial V}{\partial \log C / \partial E} \\ &= \frac{\partial S / \partial V}{\partial S / \partial E} \\ &= T \frac{\partial S}{\partial V} \end{aligned} \quad (3.96)$$

## PROBLEMS

3.1 For a system with a Hamiltonian function of the form of Eq. (3.4), verify that Hamilton's equations (Eqs. 3.5 and 3.6) are equivalent to Newton's equation  $\mathbf{F}_i = m d^2\mathbf{r}_i/dt^2$ .

3.2 For a particle, constrained to the  $z$  axis, in a uniform gravitational field, draw a few energy surfaces in the two-dimensional phase-space and indicate the trajectory of a system point in the phase-space.

3.3 Choose a potential function  $U(x)$  so that the energy surfaces in the two-dimensional phase-space of the Hamiltonian,  $H(x, p) = p^2/2m + U(x)$ , are each composed of two disconnected parts.

3.4 (a) If a point is chosen at random in an  $N$ -dimensional unit sphere, what is the probability of falling inside the sphere of radius 0.99999999? (b) Evaluate your answer for  $N = 3$  and  $N = N_A$ .

3.5 The unit cube in  $N$  dimensions is the set of points defined by the inequalities  $0 \leq x_i \leq 1$  for  $i = 1, \dots, N$ . The *inscribed sphere* is the largest  $N$ -dimensional sphere that can fit within the unit cube. It has a unit diameter. (a) If a point is chosen at random within the unit cube, what is the probability that it will fall within the inscribed sphere? (b) The *circumscribed sphere* is the smallest sphere that contains the unit cube. If a point is chosen at random in the circumscribed sphere, what is the probability that it will fall within the unit cube? (c) For very large  $N$ , give simplified, approximate forms for your answers to (a) and (b). (Hint: Simplify the logarithm of the answer and then exponentiate it.)

3.6 The transformation from four-dimensional Cartesian coordinates  $(x, y, z, w)$  to spherical coordinates  $(r, \psi, \theta, \phi)$  is  $x = r \sin \psi \sin \theta \cos \phi$ ,  $y = r \sin \psi \sin \theta \sin \phi$ ,  $z = r \sin \psi \cos \theta$ , and  $w = r \cos \psi$ . The ranges of the angles are  $0 \leq \psi \leq \pi$ ,  $0 \leq \theta \leq \pi$ , and  $0 \leq \phi \leq 2\pi$ . Determine the volume element in spherical coordinates and, by direct integration, the volume of a four-dimensional sphere of radius  $R$ . Check your result with the general formula given in the Mathematical Appendix.

3.7 Consider a system composed of two weakly interacting subsystems, so that the Hamiltonian function of the system can be approximated by  $H(x, p) = H_1(x_1, p_1) + H_2(x_2, p_2)$ . Show that

$$Q(E) = \int Q_1(E_1)Q_2(E - E_1) dE_1 \quad (3.97)$$

where  $Q_1$  and  $Q_2$  are the microcanonical normalization constants (defined in Eq. (3.27) for the subsystems separately.  $(x_1, p_1) = (x_1, \dots, x_K, p_1, \dots, p_K)$  are the coordinates and momenta of subsystem 1 and  $(x_2, p_2) = (x'_1, \dots, x'_L, p'_1, \dots, p'_L)$  are those of subsystem 2.

3.8 A system of  $N$  noninteracting one-dimensional particles are constrained to an interval of length  $L$  and have a total energy  $E = N\varepsilon$ . (a) Write an explicit formula for the uniform ensemble probability density  $P(x_1, \dots, x_N, p_1, \dots, p_N)$ . (b) By integrating over all coordinates and momenta except  $p_N$ , determine the probability distribution for the momentum of the  $N$ th particle. (c) Take the logarithm of the result obtained in (b), assuming that  $N \gg 1$ , use Stirling's approximation to rewrite it, and then exponentiate the result to show that the momentum distribution associated with the uniform ensemble is just the Maxwell distribution.

3.9 (a) For  $N$  one-dimensional particles in a harmonic oscillator potential, using the uniform ensemble, write an expression for the probability density  $P(x_1, \dots, x_N, p_1, \dots, p_N)$  and, by integrating over all coordinates and moments except  $x_N$ , calculate the probability density for the position of the  $N$ th particle. (b) Assume that  $N \gg 1$  and write a simpler, approximate, expression for your answer. (Hint: Take the logarithm of your answer, simplify it, and then exponentiate it.)

3.10 For a system of identical particles,  $H = \sum p_i^2/2m + V(x)$ . Verify the identity,  $\langle \sum p_i^2/2m \rangle = m(\partial C/\partial m)/(\partial C/\partial E)$ , where  $C$  is the normalization constant for the uniform ensemble. Check the identity for an ideal gas, using Eq. (3.20) for  $C$ .

3.11 For an ideal gas, calculate  $Q(E)$  as an explicit function of  $E$ ,  $m$ ,  $N$ , and  $V$ .

3.12 Define the function  $a(\mathbf{r}, \mathbf{p})$  for the one-body observable described by the phrase “the fraction of particles with kinetic energy greater than  $K$ ”.

3.13 Write a two-body observable whose average value is equal to the average number of pairs of particles with relative separation less than  $d$ . (Hint: Do not count  $(1, 2)$  and  $(2, 1)$  as *two* pairs.)

3.14 Define the function  $a(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}')$  for the two-body observable described by the phrase “the number of pairs of particles that are separated by a distance less than  $d$  and are approaching one another”. (Hint: “approaching one another” means that the distance between them is getting smaller.)

3.15 Prove that the normalization integrals of  $F_1$  and  $F_2$ , given in Eqs. (3.38) and (3.39), are correct.

3.16 Consider a system of  $N$  noninteracting particles, confined to move within a smooth circular cylinder of radius  $R$  and length  $\ell$ . The axis of the cylinder is the  $z$  axis. Suppose that, besides fixing the number of particles in the system, we fix the total energy to be  $E$  and the  $z$  component of angular momentum to be  $L_z$ . (a) By the method used to derive the Maxwell-Boltzmann distribution in the previous chapter, show that the equilibrium distribution function is of the form,  $f(\mathbf{r}, \mathbf{v}) = C \exp[-\beta(mv^2/2 - m\Omega(xv_y - yv_x))]$ . (b) Calculate the average velocity of particles at position  $(x, y, z)$  and show that it is identical to what would be obtained for rigid body rotation about the  $z$  axis with angular velocity  $\Omega$ . (c) Show that the particle density  $n(\mathbf{r})$  has the form  $C \exp[-\phi(\mathbf{r})/kT]$ , where  $\phi = -\frac{1}{2}m\Omega^2(x^2 + y^2)$  is the centrifugal potential.

3.17 (a) Show that the minimum value of the energy per particle for a three-dimensional Ising lattice is  $-3V$ . (b) At very high temperatures, the spins in an Ising lattice become statistically independent random variables. Show that, in that case,  $\langle E \rangle/N = 0$  and that  $\Delta E/N \approx 0$ .

3.18 William Cleghorn, one of the early proponents of the caloric theory of heat, according to which heat is a fundamental conserved substance, called caloric, whose density in a body determines the body’s temperature, gave the following objection to the competing theory that temperature was a measure of the vibrational or translational motion of the minute particles that comprised the body. If heat and temperature were measures of the vibrational motions of the particles of solid bodies, then they would propagate through solid bodies at very high speeds, as vibrations are known to do. The temperature differences in an ordinary sized object would be expected to vanish in a time so small as to be difficult to measure. This is clearly contradicted by the observed slow diffusion of heat through objects. With your much more detailed knowledge of the internal structure of bodies, and the motions of the particles comprising them, can you give a clear refutation of Cleghorn’s objection to the kinetic theory of heat?

3.19\* [Starred problems are those that are associated with optional sections.] Consider a system of  $N$  noninteracting particles in a box of volume  $V = L^3$  subject to a uniform gravitational field  $g$ . According to Eq. (2.20), the density at height  $z$  is given by  $n(z) = n_o \exp(-z/h)$ , where  $h = kT/mg$  and  $n_o$  is determined by the normalization condition  $\int_0^L dx dy dz n(z) = N$ . (a) Take  $g$  as fixed and consider a thermodynamic sequence  $N = s^3 N_o$  and  $L = s L_o$ . Show that, as  $s \rightarrow \infty$ , for any fixed  $z$ ,  $n(z) \rightarrow \infty$ , but  $n(sz) \rightarrow 0$ . Thus the density in fixed or scaled units behaves badly in the thermodynamic limit. (b) Take  $g = g_o/s$  [this is the prescription of Eq. (3.63)] and show that  $n(z) = n_o$  and  $n(sz) = n_o e^{-z/h_o}$ , where  $h_o$  and  $n_o$  are independent of  $s$ . Thus, with this prescription, the density in scaled units gives the expected exponential distribution.

3.20\* Show that any intensive one-body observable [an observable defined by Eq. (3.65)] satisfies the zero-fluctuation theorem.

3.21\* Show that, if  $A$  is an extensive observable, as defined in Eq. (3.64), and  $\langle A \rangle \neq 0$ , then, in the thermodynamic limit,  $\langle A \rangle$  is proportional to  $N$  but  $\Delta A/\langle A \rangle \rightarrow 0$ .

3.22\* For a system of particles in a box described by the inequalities  $0 < x, y, z < L$ , the particle density

$n(x, y, z)$  can be written in terms of its Fourier coefficients  $n_{klm}$  as

$$n(x, y, z) = \sum_{k,l,m} n_{klm} \sin\left(\frac{k\pi x}{L}\right) \sin\left(\frac{l\pi y}{L}\right) \sin\left(\frac{m\pi z}{L}\right)$$

Show that  $n_{klm} = \langle A_{klm} \rangle$ , where  $A_{klm}$  is an intensive one-body observable as defined by Eq. (3.65).

3.23\* Consider a starting system composed of  $N_o$  particles with a total energy of  $E_o$ , within a symmetric three-dimensional harmonic oscillator potential  $U_o = \frac{1}{2}k_o(x^2 + y^2 + z^2)$ . Calculate the parameters  $C$  and  $\beta$  in a Maxwell–Boltzmann distribution [Eq. (2.16)] in terms of  $N_o$ ,  $E_o$ , and  $k_o$ . Let  $N = s^3 N_o$  and  $E = s^3 E_o$  and determine how the force constant  $k_o$  must be scaled in order for  $C$  and  $\beta$  to be independent of  $s$ . Show that the required scaling satisfies Eq. (3.63).

3.24 Calculate the function  $\phi(N)$  defined in Eq. (3.86).

3.25 Using the uniform ensemble, evaluate the entropy  $S(N, E)$  for a system of  $N$  distinguishable one-dimensional harmonic oscillators. When the particles are distinguishable, the factor of  $1/N!$  is left out of the definition of  $S$  given in Eq. (3.84).

3.26\* Using the formula for the pressure given in Eq. (3.91), the assumption about  $F_2$  given in Eq. (3.92), and the fact that the area of the piston goes as  $s^2 A_o$  in the thermodynamic limit, show that the pressure satisfies the no-fluctuation theorem.