

# Statistical Mechanics

The greater part of this chapter is devoted to a summary of the principles of classical statistical mechanics, a discussion of the link between statistical mechanics and thermodynamics, and the definition of certain equilibrium and time-dependent distribution functions of fundamental importance in the theory of liquids. It also establishes much of the notation used in later parts of the book. The emphasis is on atomic systems; some of the complications that arise in the study of molecular liquids are discussed in [Chapter 11](#). The last two sections deal with computer simulation, an approach that can be described as “numerical” statistical mechanics and which has played a major role in improving our understanding of the liquid state.

## 2.1 TIME EVOLUTION AND KINETIC EQUATIONS

Consider an isolated, macroscopic system consisting of  $N$  identical, spherical particles of mass  $m$  enclosed in a volume  $V$ . An example would be a one-component, monatomic gas or liquid. In classical mechanics the dynamical state of the system at any instant is completely specified by the  $3N$  coordinates  $\mathbf{r}^N \equiv \mathbf{r}_1, \dots, \mathbf{r}_N$  and  $3N$  momenta  $\mathbf{p}^N \equiv \mathbf{p}_1, \dots, \mathbf{p}_N$  of the particles. The values of these  $6N$  variables define a *phase point* in a  $6N$ -dimensional *phase space*. Let  $\mathcal{H}$  be the hamiltonian of the system, which we write in general form as

$$\mathcal{H}(\mathbf{r}^N, \mathbf{p}^N) = K_N(\mathbf{p}^N) + V_N(\mathbf{r}^N) + \Phi_N(\mathbf{r}^N) \quad (2.1.1)$$

where

$$K_N = \sum_{i=1}^N \frac{|\mathbf{p}_i|^2}{2m} \quad (2.1.2)$$

is the kinetic energy,  $V_N$  is the interatomic potential energy and  $\Phi_N$  is the potential energy arising from the interaction of the particles with some spatially varying, external field. If there is no external field, the system will be both spatially uniform and isotropic. The motion of the phase point along its *phase*

*trajectory* is determined by Hamilton's equations:

$$\dot{\mathbf{r}}_i = \frac{\partial \mathcal{H}}{\partial \mathbf{p}_i}, \quad \dot{\mathbf{p}}_i = -\frac{\partial \mathcal{H}}{\partial \mathbf{r}_i} \quad (2.1.3)$$

These equations are to be solved subject to  $6N$  initial conditions on the coordinates and momenta. Since the trajectory of a phase point is wholly determined by the values of  $\mathbf{r}^N, \mathbf{p}^N$  at any given time, it follows that two different trajectories cannot pass through the same point in phase space.

The aim of equilibrium statistical mechanics is to calculate observable properties of a system of interest either as averages over a phase trajectory (the method of Boltzmann), or as averages over an ensemble of systems, each of which is a replica of the system of interest (the method of Gibbs). The main features of the two methods are reviewed in later sections of this chapter. Here it is sufficient to recall that in Gibbs's formulation of statistical mechanics the distribution of phase points of systems of the ensemble is described by a *phase space probability density*  $f^{[N]}(\mathbf{r}^N, \mathbf{p}^N; t)$ . The quantity  $f^{[N]} d\mathbf{r}^N d\mathbf{p}^N$  is the probability that at time  $t$  the physical system is in a microscopic state represented by a phase point lying in the infinitesimal,  $6N$ -dimensional phase space element  $d\mathbf{r}^N d\mathbf{p}^N$ . This definition implies that the integral of  $f^{[N]}$  over phase space is

$$\iint f^{[N]}(\mathbf{r}^N, \mathbf{p}^N; t) d\mathbf{r}^N d\mathbf{p}^N = 1 \quad (2.1.4)$$

for all  $t$ . Given a complete knowledge of the probability density it would be possible to calculate the average value of any function of the coordinates and momenta.

The time evolution of the probability density at a fixed point in phase space is governed by the Liouville equation, which is a  $6N$ -dimensional analogue of the equation of continuity of an incompressible fluid; it describes the fact that phase points of the ensemble are neither created nor destroyed as time evolves. The Liouville equation may be written either as

$$\frac{\partial f^{[N]}}{\partial t} + \sum_{i=1}^N \left( \frac{\partial f^{[N]}}{\partial \mathbf{r}_i} \cdot \dot{\mathbf{r}}_i + \frac{\partial f^{[N]}}{\partial \mathbf{p}_i} \cdot \dot{\mathbf{p}}_i \right) = 0 \quad (2.1.5)$$

or, more compactly, as

$$\frac{\partial f^{[N]}}{\partial t} = \{\mathcal{H}, f^{[N]}\} \quad (2.1.6)$$

where  $\{A, B\}$  denotes the Poisson bracket:

$$\{A, B\} \equiv \sum_{i=1}^N \left( \frac{\partial A}{\partial \mathbf{r}_i} \cdot \frac{\partial B}{\partial \mathbf{p}_i} - \frac{\partial A}{\partial \mathbf{p}_i} \cdot \frac{\partial B}{\partial \mathbf{r}_i} \right) \quad (2.1.7)$$

Alternatively, by introducing the Liouville operator  $\mathcal{L}$ , defined as

$$\mathcal{L} \equiv i\{\mathcal{H}, \} \quad (2.1.8)$$

the Liouville equation becomes

$$\frac{\partial f^{[N]}}{\partial t} = -i\mathcal{L}f^{[N]} \quad (2.1.9)$$

the formal solution to which is

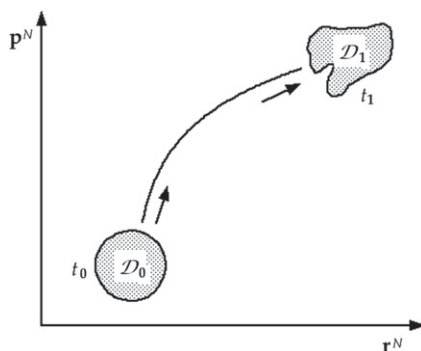
$$f^{[N]}(t) = \exp(-i\mathcal{L}t)f^{[N]}(0) \quad (2.1.10)$$

The Liouville equation can be expressed even more concisely in the form

$$\frac{df^{[N]}}{dt} = 0 \quad (2.1.11)$$

where  $d/dt$  denotes the total derivative with respect to time. This result is called the Liouville theorem; it shows that the probability density, as seen by an observer moving with a phase point along its phase space trajectory, is independent of time. To see its further significance, consider the phase points that at time  $t = t_0$ , say, are contained in the region of phase space labelled  $\mathcal{D}_0$  in Figure 2.1 and which at time  $t_1$  are contained in the region  $\mathcal{D}_1$ . The region will have changed in shape but no phase points will have entered or left, since that would require phase space trajectories to have crossed. The Liouville theorem therefore implies that the volumes (in  $6N$  dimensions) of  $\mathcal{D}_0$  and  $\mathcal{D}_1$  must be the same. Volume in phase space is said to be ‘conserved’, which is equivalent to saying that the jacobian corresponding to the coordinate transformation  $\mathbf{r}^N(t_0)\mathbf{p}^N(t_0) \rightarrow \mathbf{r}^N(t_1)\mathbf{p}^N(t_1)$  is equal to unity; this is a direct consequence of Hamilton’s equations and is easily proved explicitly.<sup>1</sup>

The time dependence of any function of the phase space variables,  $B(\mathbf{r}^N, \mathbf{p}^N)$  say, may be represented in a manner similar to (2.1.10). Although  $B$  is not an explicit function of  $t$ , it will in general change with time as the system



**FIGURE 2.1** Conservation of volume in phase space. The phase points contained in the region  $\mathcal{D}_0$  at a time  $t = t_0$  move along their phase space trajectories in the manner prescribed by Hamilton’s equations to occupy the region  $\mathcal{D}_1$  at  $t = t_1$ . The Liouville theorem shows that the two regions have the same volume.

moves along its phase space trajectory. The time derivative of  $B$  is therefore given by

$$\frac{dB}{dt} = \sum_{i=1}^N \left( \frac{\partial B}{\partial \mathbf{r}_i} \cdot \dot{\mathbf{r}}_i + \frac{\partial B}{\partial \mathbf{p}_i} \cdot \dot{\mathbf{p}}_i \right) \quad (2.1.12)$$

or, from Hamilton's equations:

$$\frac{dB}{dt} = \sum_{i=1}^N \left( \frac{\partial B}{\partial \mathbf{r}_i} \cdot \frac{\partial \mathcal{H}}{\partial \mathbf{p}_i} - \frac{\partial B}{\partial \mathbf{p}_i} \cdot \frac{\partial \mathcal{H}}{\partial \mathbf{r}_i} \right) = i\mathcal{L}B \quad (2.1.13)$$

which has as its solution

$$B(t) = \exp(i\mathcal{L}t)B(0) \quad (2.1.14)$$

Note the change of sign in the propagator compared with (2.1.10).

The description of the system that the full phase space probability density provides is for many purposes unnecessarily detailed. Normally we are interested only in the behaviour of a subset of particles of size  $n$ , say, and the redundant information can be eliminated by integrating  $f^{[N]}$  over the coordinates and momenta of the other  $(N - n)$  particles. We therefore define a *reduced phase space distribution function*  $f^{(n)}(\mathbf{r}^n, \mathbf{p}^n; t)$  by

$$f^{(n)}(\mathbf{r}^n, \mathbf{p}^n; t) = \frac{N!}{(N - n)!} \iint f^{[N]}(\mathbf{r}^N, \mathbf{p}^N; t) d\mathbf{r}^{(N-n)} d\mathbf{p}^{(N-n)} \quad (2.1.15)$$

where  $\mathbf{r}^n \equiv \mathbf{r}_1, \dots, \mathbf{r}_n$  and  $\mathbf{r}^{(N-n)} \equiv \mathbf{r}_{n+1}, \dots, \mathbf{r}_N$ , etc. The quantity  $f^{(n)} d\mathbf{r}^n d\mathbf{p}^n$  determines the probability of finding a subset of  $n$  particles in the reduced phase space element  $d\mathbf{r}^n d\mathbf{p}^n$  at time  $t$  irrespective of the coordinates and momenta of the remaining particles; the combinatorial factor  $N!/(N - n)!$  is the number of ways of choosing a subset of size  $n$ .

To find an equation of motion for  $f^{(n)}$  we consider the special case when the total force acting on particle  $i$  is the sum of an external force  $\mathbf{X}_i$ , arising from an external potential  $\phi(\mathbf{r}_i)$ , and of pair forces  $\mathbf{F}_{ij}$  due to other particles  $j$ , with  $\mathbf{F}_{ii} = 0$ . The second of Hamilton's equations (2.1.3) then takes the form

$$\dot{\mathbf{p}}_i = \mathbf{X}_i + \sum_{j=1}^N \mathbf{F}_{ij} \quad (2.1.16)$$

and the Liouville equation becomes

$$\left( \frac{\partial}{\partial t} + \sum_{i=1}^N \frac{\mathbf{p}_i}{m} \cdot \frac{\partial}{\partial \mathbf{r}_i} + \sum_{i=1}^N \mathbf{X}_i \cdot \frac{\partial}{\partial \mathbf{p}_i} \right) f^{[N]} = - \sum_{i=1}^N \sum_{j=1}^N \mathbf{F}_{ij} \cdot \frac{\partial f^{[N]}}{\partial \mathbf{p}_i} \quad (2.1.17)$$

We now multiply through by  $N!/(N - n)!$  and integrate over the  $3(N - n)$  coordinates  $\mathbf{r}_{n+1}, \dots, \mathbf{r}_N$  and  $3(N - n)$  momenta  $\mathbf{p}_{n+1}, \dots, \mathbf{p}_N$ . The probability

density  $f^{[N]}$  is zero when  $\mathbf{r}_i$  lies outside the volume occupied by the system and must vanish as  $\mathbf{p}_i \rightarrow \infty$  to ensure convergence of the integrals over momenta in (2.1.4). Thus  $f^{[N]}$  vanishes at the limits of integration and the derivative of  $f^{[N]}$  with respect to any component of position or momentum will contribute nothing to the result when integrated with respect to that component. On integration, therefore, all terms disappear for which  $i > n$  in (2.1.17). What remains, given the definition of  $f^{(n)}$  in (2.1.15), is

$$\begin{aligned} & \left( \frac{\partial}{\partial t} + \sum_{i=1}^n \frac{\mathbf{p}_i}{m} \cdot \frac{\partial}{\partial \mathbf{r}_i} + \sum_{i=1}^n \mathbf{X}_i \cdot \frac{\partial}{\partial \mathbf{p}_i} \right) f^{(n)} \\ &= - \sum_{i=1}^n \sum_{j=1}^n \mathbf{F}_{ij} \cdot \frac{\partial f^{(n)}}{\partial \mathbf{p}_i} \\ & \quad - \frac{N!}{(N-n)!} \sum_{i=1}^n \sum_{j=n+1}^N \iint \mathbf{F}_{ij} \cdot \frac{\partial f^{[N]}}{\partial \mathbf{p}_i} d\mathbf{r}^{(N-n)} d\mathbf{p}^{(N-n)} \quad (2.1.18) \end{aligned}$$

Because the particles are identical,  $f^{[N]}$  is symmetric with respect to interchange of particle labels and the sum of terms for  $j = n+1$  to  $N$  on the right-hand side of (2.1.18) may be replaced by  $(N-n)$  times the value of any one term. This simplification makes it possible to rewrite (2.1.18) in a manner which relates the behaviour of  $f^{(n)}$  to that of  $f^{(n+1)}$ :

$$\begin{aligned} & \left( \frac{\partial}{\partial t} + \sum_{i=1}^n \frac{\mathbf{p}_i}{m} \cdot \frac{\partial}{\partial \mathbf{r}_i} + \sum_{i=1}^n \left( \mathbf{X}_i + \sum_{j=1}^n \mathbf{F}_{ij} \right) \cdot \frac{\partial}{\partial \mathbf{p}_i} \right) f^{(n)} \\ &= - \sum_{i=1}^n \iint \mathbf{F}_{i,n+1} \cdot \frac{\partial f^{(n+1)}}{\partial \mathbf{p}_i} d\mathbf{r}_{n+1} d\mathbf{p}_{n+1} \quad (2.1.19) \end{aligned}$$

The system of coupled equations represented by (2.1.19) was first obtained by Yvon and subsequently rederived by others. It is known as the Bogoliubov–Born–Green–Kirkwood–Yvon or BBGKY hierarchy. The equations are exact, though limited in their applicability to systems for which the particle interactions are pairwise additive. They are not immediately useful, however, because they merely express one unknown function,  $f^{(n)}$ , in terms of another,  $f^{(n+1)}$ . Some approximate ‘closure relation’ is therefore needed.

In practice the most important member of the BBGKY hierarchy is that corresponding to  $n = 1$ :

$$\begin{aligned} & \left( \frac{\partial}{\partial t} + \frac{\mathbf{p}_1}{m} \cdot \frac{\partial}{\partial \mathbf{r}_1} + \mathbf{X}_1 \cdot \frac{\partial}{\partial \mathbf{p}_1} \right) f^{(1)}(\mathbf{r}_1, \mathbf{p}_1; t) \\ &= - \iint \mathbf{F}_{12} \cdot \frac{\partial}{\partial \mathbf{p}_1} f^{(2)}(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2; t) d\mathbf{r}_2 d\mathbf{p}_2 \quad (2.1.20) \end{aligned}$$

Much effort has been devoted to finding approximate solutions to (2.1.20) on the basis of expressions that relate the two-particle distribution function  $f^{(2)}$  to the single-particle function  $f^{(1)}$ . From the resulting *kinetic equations* it is possible to calculate the hydrodynamic transport coefficients, but the approximations made are rarely appropriate to liquids because correlations between particles are mostly treated in a very crude way.<sup>2</sup> The simplest possible approximation is to ignore pair correlations altogether by writing

$$f^{(2)}(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}'; t) \approx f^{(1)}(\mathbf{r}, \mathbf{p}; t) f^{(1)}(\mathbf{r}', \mathbf{p}'; t) \quad (2.1.21)$$

This leads to the Vlasov equation:

$$\left( \frac{\partial}{\partial t} + \frac{\mathbf{p}}{m} \cdot \frac{\partial}{\partial \mathbf{r}} + [\mathbf{X}(\mathbf{r}, t) + \bar{\mathbf{F}}(\mathbf{r}, t)] \cdot \frac{\partial}{\partial \mathbf{p}} \right) f^{(1)}(\mathbf{r}, \mathbf{p}; t) = 0 \quad (2.1.22)$$

where the quantity

$$\bar{\mathbf{F}}(\mathbf{r}, t) = \iint \mathbf{F}(\mathbf{r}, \mathbf{r}'; t) f^{(1)}(\mathbf{r}', \mathbf{p}'; t) d\mathbf{r}' d\mathbf{p}' \quad (2.1.23)$$

is the average force exerted by other particles, situated at points  $\mathbf{r}'$ , on a particle that at time  $t$  is at a point  $\mathbf{r}$ ; this is an approximation of classic, mean field type. Though obviously not suitable for liquids, the Vlasov equation is widely used in plasma physics, where the long-range character of the Coulomb potential justifies a mean field treatment of the interactions.

Equation (2.1.20) may be rewritten schematically in the form

$$\left( \frac{\partial}{\partial t} + \frac{\mathbf{p}_1}{m} \cdot \frac{\partial}{\partial \mathbf{r}_1} + \mathbf{X}_1 \cdot \frac{\partial}{\partial \mathbf{p}_1} \right) f^{(1)} = \left( \frac{\partial f^{(1)}}{\partial t} \right)_{\text{coll}} \quad (2.1.24)$$

where the term  $(\partial f^{(1)}/\partial t)_{\text{coll}}$  is the rate of change of  $f^{(1)}$  due to collisions between particles. The collision term is given rigorously by the right-hand side of (2.1.20) but in the Vlasov equation it is eliminated by replacing the true external force  $\mathbf{X}(\mathbf{r}, t)$  by an effective force – the quantity inside square brackets in (2.1.22) – which depends in part on  $f^{(1)}$  itself. For this reason the Vlasov equation is called a ‘collisionless’ approximation.

In the most famous of all kinetic equations, derived by Boltzmann in 1872, the collision term is evaluated with the help of two assumptions, which in general are justified only at low densities: that two-body collisions alone are involved and that successive collisions are uncorrelated.<sup>2</sup> The second of these assumptions, that of ‘molecular chaos’, corresponds formally to supposing that the factorisation represented by (2.1.21) applies prior to any collision, though not subsequently. In simple terms it means that when two particles collide, no memory is retained of any previous encounters between them, an assumption that breaks down when recollisions are frequent events. A binary collision at

a point  $\mathbf{r}$  is characterised by the momenta  $\mathbf{p}_1, \mathbf{p}_2$  of the two particles before collision and their momenta  $\mathbf{p}'_1, \mathbf{p}'_2$  afterwards; the post-collisional momenta are related to their pre-collisional values by the laws of classical mechanics. With Boltzmann's approximations the collision term in (2.1.24) becomes

$$\left(\frac{\partial f^{(1)}}{\partial t}\right)_{\text{coll}} = \frac{1}{m} \iint \sigma(\Omega, \Delta p) [f^{(1)}(\mathbf{r}, \mathbf{p}'_1; t) f^{(1)}(\mathbf{r}, \mathbf{p}'_2; t) - f^{(1)}(\mathbf{r}, \mathbf{p}_1; t) f^{(1)}(\mathbf{r}, \mathbf{p}_2; t)] d\Omega d\mathbf{p}_2 \quad (2.1.25)$$

where  $\Delta p \equiv |\mathbf{p}_2 - \mathbf{p}_1|$  and  $\sigma(\Omega, \Delta p)$  is the differential cross-section for scattering into a solid angle  $d\Omega$ . As Boltzmann showed, this form of the collision term is able to account for the fact that many-particle systems evolve irreversibly towards an equilibrium state. That irreversibility is described by Boltzmann's H-theorem; its source is the assumption of molecular chaos.

Solution of the Boltzmann equation leads to explicit expressions for the hydrodynamic transport coefficients in terms of certain 'collision integrals'.<sup>3</sup> The differential scattering cross-section and hence the collision integrals themselves can be evaluated numerically for a given choice of two-body interaction, though for hard spheres they have a simple, analytical form. The results, however, are applicable only to dilute gases. In the case of hard spheres the Boltzmann equation was later modified semi-empirically by Enskog in a manner that extends its range of applicability to considerably higher densities. Enskog's theory retains the two key assumptions involved in the derivation of the Boltzmann equation, but it also corrects in two ways for the finite size of the colliding particles. First, allowance is made for the modification of the collision rate by the hard-sphere interaction. Because the same interaction is also responsible for the increase in pressure over its ideal gas value, the enhancement of the collision rate relative to its low-density limit can be calculated if the hard-sphere equation of state is known. Secondly, 'collisional transfer' is incorporated into the theory by rewriting (2.1.25) in a form in which the distribution functions for the two colliding particles are evaluated not at the same point,  $\mathbf{r}$ , but at points separated by a distance equal to the hard-sphere diameter. This is an important modification of the theory, since at high densities interactions rather than particle displacements provide the dominant mechanism for the transport of energy and momentum.

The phase space probability density of a system in thermodynamic equilibrium is a function of the time-varying coordinates and momenta, but is independent of  $t$  at each point in phase space. We shall use the symbol  $f_0^{[N]}(\mathbf{r}^N, \mathbf{p}^N)$  to denote the equilibrium probability density; it follows from (2.1.6) that a sufficient condition for a probability density to be descriptive of a system in equilibrium is that it should be some function of the hamiltonian. Integration of  $f_0^{[N]}$  over a subset of coordinates and momenta in the manner of (2.1.15) yields a set of equilibrium phase space distribution functions

$f_0^{(n)}(\mathbf{r}^n, \mathbf{p}^n)$ . The case when  $n = 1$  corresponds to the equilibrium single-particle distribution function; if there is no external field the distribution is independent of  $\mathbf{r}$  and has the familiar maxwellian form, i.e.

$$\begin{aligned} f_0^{(1)}(\mathbf{r}, \mathbf{p}) &= \frac{\rho \exp(-\beta|\mathbf{p}|^2/2m)}{(2\pi mk_B T)^{3/2}} \\ &\equiv \rho f_M(\mathbf{p}) \end{aligned} \quad (2.1.26)$$

where  $f_M(\mathbf{p})$  is the Maxwell distribution of momenta, normalised such that

$$\int f_M(\mathbf{p}) d\mathbf{p} = 1 \quad (2.1.27)$$

The corresponding distribution of particle velocities,  $\mathbf{u}$ , is

$$\phi_M(\mathbf{u}) = \left( \frac{m}{2\pi k_B T} \right)^{3/2} \exp\left(-\frac{1}{2}m\beta|\mathbf{u}|^2\right) \quad (2.1.28)$$

## 2.2 TIME AVERAGES AND ENSEMBLE AVERAGES

Certain thermodynamic properties of a physical system may be written as averages of functions of the coordinates and momenta of the constituent particles. These are the so-called ‘mechanical’ properties, which include internal energy and pressure; ‘thermal’ properties such as entropy are not expressible in this way. In a state of thermal equilibrium such averages must be independent of time. To avoid undue complication we again suppose that the system of interest consists of  $N$  identical, spherical particles. If the system is isolated from its surroundings, its total energy is constant, i.e. the hamiltonian is a constant of the motion.

As before, let  $B(\mathbf{r}^N, \mathbf{p}^N)$  be some function of the  $6N$  phase space variables and let  $\langle B \rangle$  be its average value, where the angular brackets represent an averaging process of a nature as yet unspecified. Given the coordinates and momenta of the particles at some instant, their values at any later (or earlier) time can in principle be obtained as the solution to Newton’s equations of motion, i.e. to a set of  $3N$  coupled, second-order, differential equations that, in the absence of an external field, have the form

$$m\ddot{\mathbf{r}}_i = \mathbf{F}_i = -\nabla_i V_N(\mathbf{r}^N) \quad (2.2.1)$$

where  $\mathbf{F}_i$  is the total force on particle  $i$ . It is therefore natural to view  $\langle B \rangle$  as a time average over the dynamical history of the system, i.e.

$$\langle B \rangle_t = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau B[\mathbf{r}^N(t), \mathbf{p}^N(t)] dt \quad (2.2.2)$$



A simple example of the use of (2.2.2) arises in the calculation of the thermodynamic temperature of the system from the time average of the total kinetic energy. If

$$\mathcal{T}(t) = \frac{2}{3Nk_B} K_N(t) = \frac{1}{3Nk_B m} \sum_{i=1}^N |\mathbf{p}_i(t)|^2 \quad (2.2.3)$$

then

$$T \equiv \langle \mathcal{T} \rangle_t = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau \mathcal{T}(t) dt \quad (2.2.4)$$

As a more interesting example we can use (2.2.2) and (2.2.4) to show that the equation of state is related to the time average of the *virial function* of Clausius. The virial function is defined as

$$\mathcal{V}(\mathbf{r}^N) = \sum_{i=1}^N \mathbf{r}_i \cdot \mathbf{F}_i \quad (2.2.5)$$

From previous formulae, together with an integration by parts, we find that

$$\begin{aligned} \langle \mathcal{V} \rangle_t &= \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau \sum_{i=1}^N \mathbf{r}_i(t) \cdot \mathbf{F}_i(t) dt = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau \sum_{i=1}^N \mathbf{r}_i(t) \cdot m \ddot{\mathbf{r}}_i(t) dt \\ &= - \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau \sum_{i=1}^N m |\dot{\mathbf{r}}_i(t)|^2 dt = -3Nk_B T \end{aligned} \quad (2.2.6)$$

or

$$\langle \mathcal{V} \rangle_t = -2 \langle K_N \rangle_t \quad (2.2.7)$$

which is the virial theorem of classical mechanics. The total virial function may be separated into two parts: one,  $\mathcal{V}_{\text{int}}$ , comes from the forces between particles; the other,  $\mathcal{V}_{\text{ext}}$ , arises from the forces exerted by the walls and is related in a simple way to the pressure,  $P$ . The force exerted by a surface element  $d\mathbf{S}$  located at  $\mathbf{r}$  is  $-P\mathbf{n} d\mathbf{S}$ , where  $\mathbf{n}$  is a unit vector directed outwards, and its contribution to the average virial is  $-P\mathbf{r} \cdot \mathbf{n} d\mathbf{S}$ . On integrating over the surface we find that

$$\langle \mathcal{V}_{\text{ext}} \rangle = -P \int \mathbf{r} \cdot \mathbf{n} d\mathbf{S} = -P \int \nabla \cdot \mathbf{r} dV = -3PV \quad (2.2.8)$$

Equation (2.2.7) may therefore be rearranged to give the *virial equation*:

$$PV = Nk_B T + \frac{1}{3} \langle \mathcal{V}_{\text{int}} \rangle_t = Nk_B T - \frac{1}{3} \left\langle \sum_{i=1}^N \mathbf{r}_i(t) \cdot \nabla_i V_N [\mathbf{r}^N(t)] \right\rangle_t \quad (2.2.9)$$

or

$$\frac{\beta P}{\rho} = 1 - \frac{\beta}{3N} \left\langle \sum_{i=1}^N \mathbf{r}_i(t) \cdot \nabla_i V_N [\mathbf{r}^N(t)] \right\rangle_t \quad (2.2.10)$$

In the absence of interactions between particles, i.e. when  $V_N = 0$ , the virial equation reduces to the equation of state of an ideal gas,  $PV = Nk_B T$ .

The alternative to the time-averaging procedure described by (2.2.2) is to average over a suitably constructed *ensemble*. A statistical mechanical ensemble is an arbitrarily large collection of imaginary systems, each of which is a replica of the physical system of interest and characterised by the same macroscopic parameters. The systems of the ensemble differ from each other in the assignment of coordinates and momenta of the particles and the dynamics of the ensemble as a whole is represented by the motion of a cloud of phase points distributed in phase space according to the probability density  $f^{[N]}(\mathbf{r}^N, \mathbf{p}^N; t)$  introduced in Section 2.1. The equilibrium ensemble average of the function  $B(\mathbf{r}^N, \mathbf{p}^N)$  is therefore given by

$$\langle B \rangle_e = \iint B(\mathbf{r}^N, \mathbf{p}^N) f_0^{[N]}(\mathbf{r}^N, \mathbf{p}^N) d\mathbf{r}^N d\mathbf{p}^N \quad (2.2.11)$$

where  $f_0^{[N]}$  is the equilibrium probability density. For example, the thermodynamic internal energy is the ensemble average of the hamiltonian:

$$U \equiv \langle \mathcal{H} \rangle_e = \iint \mathcal{H} f_0^{[N]} d\mathbf{r}^N d\mathbf{p}^N \quad (2.2.12)$$

The explicit form of the equilibrium probability density depends on the macroscopic parameters that describe the ensemble. The simplest case is when the systems of the ensemble are assumed to have the same number of particles, the same volume and the same total energy,  $E$  say. An ensemble constructed in this way is called a *microcanonical* ensemble and describes a system that exchanges neither heat nor matter with its surroundings. The microcanonical equilibrium probability density is

$$f_0^{[N]}(\mathbf{r}^N, \mathbf{p}^N) = C \delta(\mathcal{H} - E) \quad (2.2.13)$$

where  $\delta(\dots)$  is the Dirac  $\delta$ -function and  $C$  is a normalisation constant. The systems of a microcanonical ensemble are therefore uniformly distributed over the region of phase space corresponding to a total energy  $E$ ; from (2.2.13) we see that the internal energy is equal to the value of the parameter  $E$ . The constraint of constant total energy is reminiscent of the condition of constant total energy under which time averages are taken. Indeed, time averages and ensemble averages are identical if the system is *ergodic*, by which is meant that after a suitable lapse of time the phase trajectory of the system will have passed an equal number of times through every phase space element in the region defined by (2.2.13). In practice, however, it is almost always easier to calculate ensemble averages in one of the ensembles described in the next two sections.

## 2.3 CANONICAL AND ISOTHERMAL–ISOBARIC ENSEMBLES

A *canonical* ensemble is a collection of systems characterised by the same values of  $N$ ,  $V$  and  $T$ . It therefore represents a system immersed in a heat bath of fixed temperature. The equilibrium probability density for a system of identical, spherical particles is now

$$f_0^{[N]}(\mathbf{r}^N, \mathbf{p}^N) = \frac{1}{h^{3N} N!} \frac{\exp(-\beta \mathcal{H})}{Q_N} \quad (2.3.1)$$

where  $h$  is Planck's constant and the normalisation constant  $Q_N$  is the canonical *partition function*, given by

$$Q_N = \frac{1}{h^{3N} N!} \iint \exp(-\beta \mathcal{H}) d\mathbf{r}^N d\mathbf{p}^N \quad (2.3.2)$$

Inclusion of the factor  $1/h^{3N}$  in these definitions ensures that both  $f_0^{[N]} d\mathbf{r}^N d\mathbf{p}^N$  and  $Q_N$  are dimensionless and consistent in form with the corresponding quantities of quantum statistical mechanics, while division by  $N!$  ensures that microscopic states are correctly counted.

The *thermodynamic potential* appropriate to a situation in which  $N$ ,  $V$  and  $T$  are chosen as independent thermodynamic variables is the Helmholtz free energy,  $F$ , defined as

$$F = U - TS \quad (2.3.3)$$

where  $S$  is the entropy. Use of the term 'potential' refers to the fact that equilibrium at constant values of  $N$ ,  $V$  and  $T$  is reached when  $F$  is a minimum with respect to variations in any internal constraint. The link between statistical mechanics and thermodynamics is established via a relation between the thermodynamic potential and the partition function:

$$F = -k_B T \ln Q_N \quad (2.3.4)$$

Let us assume that there is no external field and hence that the system of interest is homogeneous. Then the change in internal energy arising from infinitesimal changes in  $N$ ,  $V$  and  $S$  is

$$dU = T dS - P dV + \mu dN \quad (2.3.5)$$

where  $\mu$  is the chemical potential. Since  $N$ ,  $V$  and  $S$  are all extensive variables it follows that

$$U = TS - PV + \mu N \quad (2.3.6)$$

Combination of (2.3.5) with the differential form of (2.3.3) shows that the change in free energy in an infinitesimal process is

$$dF = -S dT - P dV + \mu dN \quad (2.3.7)$$

Thus  $N$ ,  $V$  and  $T$  are the natural variables of  $F$ ; if  $F$  is a known function of those variables, all other thermodynamic functions can be obtained by differentiation:

$$S = - \left( \frac{\partial F}{\partial T} \right)_{V,N}, \quad P = - \left( \frac{\partial F}{\partial V} \right)_{T,N}, \quad \mu = \left( \frac{\partial F}{\partial N} \right)_{T,V} \quad (2.3.8)$$

and

$$U = F + TS = \left( \frac{\partial(F/T)}{\partial(1/T)} \right)_{V,N} \quad (2.3.9)$$

To each such thermodynamic relation there corresponds an equivalent relation in terms of the partition function. For example, it follows from (2.2.12) and (2.3.1) that

$$U = \frac{1}{h^{3N} N! Q_N} \iint \mathcal{H} \exp(-\beta \mathcal{H}) d\mathbf{r}^N d\mathbf{p}^N = - \left( \frac{\partial \ln Q_N}{\partial \beta} \right)_V \quad (2.3.10)$$

This result, together with the fundamental relation (2.3.4), is equivalent to the thermodynamic formula (2.3.9). Similarly, the expression for the pressure given by (2.3.8) can be rewritten as

$$P = k_B T \left( \frac{\partial \ln Q_N}{\partial V} \right)_{T,N} \quad (2.3.11)$$

and shown to be equivalent to the virial equation (2.2.10).<sup>4</sup>

If the hamiltonian is separated into kinetic and potential energy terms in the manner of (2.1.1), the integrations over momenta in the definition (2.3.2) of  $Q_N$  can be carried out analytically, yielding a factor  $(2\pi m k_B T)^{1/2}$  for each of the  $3N$  degrees of freedom. This allows the partition function to be rewritten as

$$Q_N = \frac{1}{N!} \frac{Z_N}{\Lambda^{3N}} \quad (2.3.12)$$

where  $\Lambda$  is the de Broglie thermal wavelength defined by (1.1.1) and

$$Z_N = \int \exp(-\beta V_N) d\mathbf{r}^N \quad (2.3.13)$$

is the *configuration integral*. If  $V_N = 0$ :

$$Z_N = \int \cdots \int d\mathbf{r}_1 \cdots d\mathbf{r}_N = V^N \quad (2.3.14)$$

Hence the partition function of a uniform, ideal gas is

$$Q_N^{\text{id}} = \frac{1}{N!} \frac{V^N}{\Lambda^{3N}} = \frac{q^N}{N!} \quad (2.3.15)$$

where  $q = V/\Lambda^3$  is the single-particle translational partition function, familiar from elementary statistical mechanics. If Stirling's approximation is used for  $\ln N!$ , the Helmholtz free energy is

$$\frac{F^{\text{id}}}{N} = k_{\text{B}}T (\ln \Lambda^3 \rho - 1) \quad (2.3.16)$$

and the chemical potential is

$$\mu^{\text{id}} = k_{\text{B}}T \ln \Lambda^3 \rho \quad (2.3.17)$$

The partition function of a system of interacting particles is conveniently written in the form

$$Q_N = Q_N^{\text{id}} \frac{Z_N}{V^N} \quad (2.3.18)$$

Then, on taking the logarithm of both sides, the Helmholtz free energy separates naturally into 'ideal' and 'excess' parts:

$$F = F^{\text{id}} + F^{\text{ex}} \quad (2.3.19)$$

where  $F^{\text{id}}$  is given by (2.3.16) and the excess part is

$$F^{\text{ex}} = -k_{\text{B}}T \ln \frac{Z_N}{V^N} \quad (2.3.20)$$

The excess part contains the contributions to the free energy that arise from interactions between particles; in the case of an inhomogeneous fluid there will also be a contribution that depends explicitly on the external potential. A similar division into ideal and excess parts can be made of any thermodynamic function obtained by differentiation of  $F$  with respect to either  $V$  or  $T$ . For example, the internal energy derived from (2.3.10) and (2.3.18) is

$$U = U^{\text{id}} + U^{\text{ex}} \quad (2.3.21)$$

where  $U^{\text{id}} = \frac{3}{2}Nk_{\text{B}}T$  and

$$U^{\text{ex}} = \langle V_N \rangle = \frac{1}{Z_N} \int V_N \exp(-\beta V_N) \mathbf{dr}^N \quad (2.3.22)$$

Note the simplification compared with the expression for  $U$  given by the first equality in (2.3.10); because  $V_N$  is a function only of the particle coordinates, the integrations over momenta cancel between numerator and denominator.

In the *isothermal-isobaric* ensemble pressure rather than volume is a fixed parameter. The thermodynamic potential for a system having specified values of  $N$ ,  $P$  and  $T$  is the Gibbs free energy,  $G$ , defined as

$$G = F + PV \quad (2.3.23)$$

and other state functions are obtained by differentiation of  $G$  with respect to the independent variables. The link with statistical mechanics is now made through the relation

$$G = -k_B T \ln \Delta_N \quad (2.3.24)$$

where the isothermal–isobaric partition function  $\Delta_N$  is generally written<sup>5</sup> as a Laplace transform of the canonical partition function:

$$\begin{aligned} \Delta_N &= \frac{1}{h^{3N} N!} \frac{1}{V_0} \int_0^\infty dV \iint \exp[-\beta(\mathcal{H} + PV)] d\mathbf{r}^N d\mathbf{p}^N \\ &= \frac{1}{V_0} \int_0^\infty \exp(-\beta PV) Q_N dV \end{aligned} \quad (2.3.25)$$

where  $V_0$  is a reference volume, inclusion of which makes  $\Delta_N$  dimensionless. The form of (2.3.25) implies that the process of forming the ensemble average involves first calculating the canonical ensemble average at a volume  $V$  and then averaging over  $V$  with a weight factor  $\exp(-\beta PV)$ .

## 2.4 THE GRAND CANONICAL ENSEMBLE AND CHEMICAL POTENTIAL

The discussion of ensembles has thus far been restricted to uniform systems containing a fixed number of particles (‘closed’ systems). We now extend the argument to situations in which the number of particles may vary by interchange with the surroundings, but retain the assumption that the system is homogeneous. The thermodynamic state of an ‘open’ system is defined by specifying the values of  $\mu$ ,  $V$  and  $T$  and the corresponding thermodynamic potential is the grand potential,  $\Omega$ , defined in terms of the Helmholtz free energy by

$$\Omega = F - N\mu \quad (2.4.1)$$

When the internal energy is given by (2.3.6), the grand potential reduces to

$$\Omega = -PV \quad (2.4.2)$$

and the differential form of (2.4.1) is

$$d\Omega = -S dT - P dV - N d\mu \quad (2.4.3)$$

The thermodynamic functions  $S$ ,  $P$  and  $N$  are therefore given as derivatives of  $\Omega$  by

$$S = -\left(\frac{\partial \Omega}{\partial T}\right)_{V, \mu}, \quad P = -\left(\frac{\partial \Omega}{\partial V}\right)_{T, \mu}, \quad N = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T, V} \quad (2.4.4)$$

An ensemble of systems having the same values of  $\mu$ ,  $V$  and  $T$  is called a *grand canonical ensemble*. The phase space of the grand canonical ensemble is the union of phase spaces corresponding to all values of the variable  $N$  for given values of  $V$  and  $T$ . The ensemble probability density is therefore a function of  $N$  as well as of the phase space variables  $\mathbf{r}^N, \mathbf{p}^N$ ; at equilibrium it takes the form

$$f_0(\mathbf{r}^N, \mathbf{p}^N; N) = \frac{\exp[-\beta(\mathcal{H} - N\mu)]}{\mathcal{E}} \quad (2.4.5)$$

where

$$\mathcal{E} = \sum_{N=0}^{\infty} \frac{\exp(N\beta\mu)}{h^{3N}N!} \iint \exp(-\beta\mathcal{H}) d\mathbf{r}^N d\mathbf{p}^N = \sum_{N=0}^{\infty} \frac{z^N}{N!} Z_N \quad (2.4.6)$$

is the grand partition function and

$$z = \frac{\exp(\beta\mu)}{\Lambda^3} \quad (2.4.7)$$

is the *activity*. The definition (2.4.5) means that  $f_0$  is normalised such that

$$\sum_{N=0}^{\infty} \frac{1}{h^{3N}N!} \iint f_0(\mathbf{r}^N, \mathbf{p}^N; N) d\mathbf{r}^N d\mathbf{p}^N = 1 \quad (2.4.8)$$

and the ensemble average of a microscopic variable  $B(\mathbf{r}^N, \mathbf{p}^N)$  is

$$\langle B \rangle = \sum_{N=0}^{\infty} \frac{1}{h^{3N}N!} \iint B(\mathbf{r}^N, \mathbf{p}^N) f_0(\mathbf{r}^N, \mathbf{p}^N; N) d\mathbf{r}^N d\mathbf{p}^N \quad (2.4.9)$$

The link with thermodynamics is established through the relation

$$\Omega = -k_B T \ln \mathcal{E} \quad (2.4.10)$$

Equation (2.3.17) shows that  $z = \rho$  for a uniform, ideal gas and in that case (2.4.6) reduces to

$$\mathcal{E}^{\text{id}} = \sum_{N=0}^{\infty} \frac{\rho^N V^N}{N!} = \exp(\rho V) \quad (2.4.11)$$

which, together with (2.4.2), yields the equation of state in the form  $\beta P = \rho$ .

The probability  $p(N)$  that at equilibrium a system of the ensemble contains precisely  $N$  particles, irrespective of their coordinates and momenta, is

$$p(N) = \frac{1}{h^{3N}N!} \iint f_0 d\mathbf{r}^N d\mathbf{p}^N = \frac{1}{\mathcal{E}} \frac{z^N}{N!} Z_N \quad (2.4.12)$$

The average number of particles in the system is

$$\langle N \rangle = \sum_{N=0}^{\infty} N p(N) = \frac{1}{\mathcal{E}} \sum_{N=0}^{\infty} N \frac{z^N}{N!} Z_N = \frac{\partial \ln \mathcal{E}}{\partial \ln z} \quad (2.4.13)$$

which is equivalent to the last of the thermodynamic relations (2.4.4). A measure of the fluctuation in particle number about its average value is provided by the mean-square deviation, for which an expression is obtained if (2.4.13) is differentiated with respect to  $\ln z$ :

$$\begin{aligned} \frac{\partial \langle N \rangle}{\partial \ln z} &= z \frac{\partial}{\partial z} \left( \frac{1}{\mathcal{E}} \sum_{N=0}^{\infty} N \frac{z^N}{N!} Z_N \right) \\ &= \frac{1}{\mathcal{E}} \sum_{N=0}^{\infty} N^2 \frac{z^N}{N!} Z_N - \left( \frac{1}{\mathcal{E}} \sum_{N=0}^{\infty} N \frac{z^N}{N!} Z_N \right)^2 \\ &= \langle N^2 \rangle - \langle N \rangle^2 \equiv \langle (\Delta N)^2 \rangle \end{aligned} \quad (2.4.14)$$

or

$$\frac{\langle (\Delta N)^2 \rangle}{\langle N \rangle} = \frac{k_B T}{\langle N \rangle} \frac{\partial \langle N \rangle}{\partial \mu} \quad (2.4.15)$$

The right-hand side of this equation is an intensive quantity and the same must therefore be true of the left-hand side. Hence the relative root-mean-square deviation,  $\langle (\Delta N)^2 \rangle^{1/2} / \langle N \rangle$ , tends to zero as  $\langle N \rangle \rightarrow \infty$ . In the *thermodynamic limit*, i.e. the limit  $\langle N \rangle \rightarrow \infty$ ,  $V \rightarrow \infty$  with  $\rho = \langle N \rangle / V$  held constant, the number of particles in the system of interest (the thermodynamic variable  $N$ ) may be identified with the grand canonical average,  $\langle N \rangle$ . More generally, in the same limit, thermodynamic properties calculated in different ensembles become identical.

The intensive ratio (2.4.15) is related to the isothermal compressibility  $\chi_T$ , defined as

$$\chi_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \quad (2.4.16)$$

To show this we note first that because the Helmholtz free energy is an extensive property it must be expressible in the form

$$F = N\phi(\rho, T) \quad (2.4.17)$$

where  $\phi$ , the free energy per particle, is a function of the intensive variables  $\rho$  and  $T$ . From (2.3.8) we find that

$$\mu = \phi + \rho \left( \frac{\partial \phi}{\partial \rho} \right)_T \quad (2.4.18)$$

$$\left( \frac{\partial \mu}{\partial \rho} \right)_T = 2 \left( \frac{\partial \phi}{\partial \rho} \right)_T + \rho \left( \frac{\partial^2 \phi}{\partial \rho^2} \right)_T \quad (2.4.19)$$



while

$$P = \rho^2 \left( \frac{\partial \phi}{\partial \rho} \right)_T \quad (2.4.20)$$

$$\left( \frac{\partial P}{\partial \rho} \right)_T = 2\rho \left( \frac{\partial \phi}{\partial \rho} \right)_T + \rho^2 \left( \frac{\partial^2 \phi}{\partial \rho^2} \right)_T = \rho \left( \frac{\partial \mu}{\partial \rho} \right)_T \quad (2.4.21)$$

Because  $(\partial P / \partial \rho)_T = -(V^2 / N)(\partial P / \partial V)_{N,T} = 1 / \rho \chi_T$  and  $(\partial \mu / \partial \rho)_T = V(\partial \mu / \partial N)_{V,T}$  it follows that

$$N \left( \frac{\partial \mu}{\partial N} \right)_{V,T} = \frac{1}{\rho \chi_T} \quad (2.4.22)$$

and hence, from (2.4.15), that

$$\frac{\langle (\Delta N)^2 \rangle}{\langle N \rangle} = \rho k_B T \chi_T \quad (2.4.23)$$

Thus the compressibility cannot be negative, since  $\langle N^2 \rangle$  is always greater than or equal to  $\langle N \rangle^2$ .

Equation (2.4.23) and other fluctuation formulae of similar type can also be derived by purely thermodynamic arguments. In the thermodynamic theory of fluctuations described in Appendix A the quantity  $N$  in (2.4.23) is interpreted as the number of particles in a subsystem of macroscopic dimensions that forms part of a much larger thermodynamic system. If the system as a whole is isolated from its surroundings, the probability of a fluctuation within the subsystem is proportional to  $\exp(\Delta S_t / k_B)$ , where  $\Delta S_t$  is the total entropy change resulting from the fluctuation. Since  $\Delta S_t$  can in turn be related to changes in the properties of the subsystem, it becomes possible to calculate the mean-square fluctuations in those properties; the results thereby obtained are identical to their statistical mechanical counterparts. Because the subsystems are of macroscopic size, fluctuations in neighbouring subsystems will in general be uncorrelated. Strong correlations can, however, be expected under certain conditions. In particular, number fluctuations in two infinitesimal volume elements will be highly correlated if the separation of the elements is comparable with the range of the interparticle forces. A quantitative measure of these correlations is provided by the equilibrium distribution functions to be introduced later in Sections 2.5 and 2.6.

The definitions (2.3.1) and (2.4.5), together with (2.4.12), show that the canonical and grand canonical ensemble probability densities are related by

$$\frac{1}{h^{3N} N!} f_0(\mathbf{r}^N, \mathbf{p}^N; N) = p(N) f_0^{[N]}(\mathbf{r}^N, \mathbf{p}^N) \quad (2.4.24)$$

The grand canonical ensemble average of any microscopic variable is therefore given by a weighted sum of averages of the same variable in the canonical

ensemble, the weighting factor being the probability  $p(N)$  that the system contains precisely  $N$  particles.

In addition to its significance as a fixed parameter of the grand canonical ensemble, the chemical potential can also be expressed as a canonical ensemble average. This result, due to Widom,<sup>6</sup> provides some useful insight into the meaning of chemical potential. From (2.3.8) and (2.3.20) we see that

$$\mu^{\text{ex}} = F^{\text{ex}}(N+1, V, T) - F^{\text{ex}}(N, V, T) = k_B T \ln \frac{V Z_N}{Z_{N+1}} \quad (2.4.25)$$

or

$$\frac{V Z_N}{Z_{N+1}} = \exp(\beta \mu^{\text{ex}}) \quad (2.4.26)$$

where  $Z_N, Z_{N+1}$  are the configuration integrals for systems containing  $N$  or  $(N+1)$  particles, respectively. The ratio  $Z_{N+1}/Z_N$  is

$$\frac{Z_{N+1}}{Z_N} = \frac{\int \exp[-\beta V_{N+1}(\mathbf{r}^{N+1})] d\mathbf{r}^{N+1}}{\int \exp[-\beta V_N(\mathbf{r}^N)] d\mathbf{r}^N} \quad (2.4.27)$$

If the total potential energy of the system of  $(N+1)$  particles is written as

$$V_{N+1}(\mathbf{r}^{N+1}) = V_N(\mathbf{r}^N) + \epsilon \quad (2.4.28)$$

where  $\epsilon$  is the energy of interaction of particle  $(N+1)$  with all others, (2.4.27) can be re-expressed as

$$\frac{Z_{N+1}}{Z_N} = \frac{\int \exp(-\beta \epsilon) \exp[-\beta V_N(\mathbf{r}^N)] d\mathbf{r}^{N+1}}{\int \exp[-\beta V_N(\mathbf{r}^N)] d\mathbf{r}^N} \quad (2.4.29)$$

If the system is homogeneous, translational invariance allows us to take  $\mathbf{r}_{N+1}$  as origin for the remaining  $N$  position vectors and integrate over  $\mathbf{r}_{N+1}$ ; this yields a factor  $V$  and (2.4.29) becomes

$$\frac{Z_{N+1}}{Z_N} = \frac{V \int \exp(-\beta \epsilon) \exp(-\beta V_N) d\mathbf{r}^N}{\int \exp(-\beta V_N) d\mathbf{r}^N} = V \langle \exp(-\beta \epsilon) \rangle \quad (2.4.30)$$

where the angular brackets denote a canonical ensemble average for the system of  $N$  particles. Substitution of (2.4.30) in (2.4.25) gives

$$\mu^{\text{ex}} = -k_B T \ln \langle \exp(-\beta \epsilon) \rangle \quad (2.4.31)$$

Hence the excess chemical potential is proportional to the logarithm of the mean Boltzmann factor of a test particle introduced randomly into the system.

Equation (2.4.31) is commonly referred to as the Widom insertion formula, particularly in connection with its use in computer simulations, where it provides a powerful and easily implemented method of determining the chemical

potential of a fluid. It is also called the potential distribution theorem, since it may be written in the form

$$\beta\mu^{\text{ex}} = -\ln \int \exp(-\beta\epsilon) p(\epsilon) d\epsilon \quad (2.4.32)$$

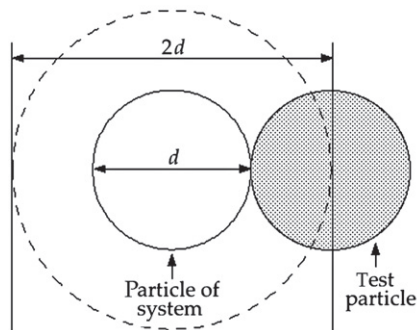
where the quantity  $p(\epsilon) d\epsilon$  is the probability that the potential energy of the test particle lies in the range  $\epsilon \rightarrow \epsilon + d\epsilon$ . Given a microscopic model of the distribution function  $p(\epsilon)$ , use of (2.4.32) provides a possible route to the calculation of the chemical potential of, say, a solute molecule in a liquid solvent. This forms the basis of what is called a ‘quasi-chemical’ theory of solutions.<sup>7</sup>

Equation (2.4.31) has a particularly simple interpretation for a system of hard spheres. Insertion of a test hard sphere can have one of two possible outcomes: either the sphere that is added overlaps with one or more of the spheres already present, in which case  $\epsilon$  is infinite and the Boltzmann factor in (2.4.31) is zero, or there is no overlap, in which case  $\epsilon = 0$  and the Boltzmann factor is unity. The excess chemical potential may therefore be written as

$$\mu^{\text{ex}} = -k_B T \ln p_0 \quad (2.4.33)$$

where  $p_0$  is the probability that a hard sphere can be introduced at a randomly chosen point in the system without creating an overlap. Calculation of  $p_0$  poses a straightforward problem provided the density is low. As Figure 2.2 illustrates, centred on each particle of the system is a sphere of radius  $d$  and volume  $v_x = \frac{4}{3}\pi d^3$ , or eight times the hard-sphere volume, from which the centre of the test particle is excluded if overlap is to be avoided. If the density is sufficiently low, the total excluded volume in a system of  $N$  hard spheres is to a good approximation  $N$  times that of a single sphere. It follows that

$$p_0 \approx \frac{V - Nv_x}{V} = 1 - \frac{4}{3}\pi\rho d^3 \quad (2.4.34)$$



**FIGURE 2.2** Widom's method for determining the excess chemical potential of a hard-sphere fluid. The broken line shows the sphere centred on a particle of the system into which the centre of a test hard sphere cannot penetrate without creating an overlap.

and hence, from (2.4.33), that at low densities:

$$\beta\mu^{\text{ex}} \approx \frac{4}{3}\pi\rho d^3 \quad (2.4.35)$$

As we shall see in Section 3.9, this is the correct result for the leading term in the density expansion of the excess chemical potential of the hard-sphere fluid. However, the argument used here breaks down as the density increases, because overlaps between the exclusion spheres around neighbouring particles can no longer be ignored. Use of the approximation represented by (2.4.34) therefore overestimates the coefficients of all higher-order terms in the expansion.

## 2.5 PARTICLE DENSITIES AND DISTRIBUTION FUNCTIONS

It was shown in Section 2.3 that a factorisation of the equilibrium phase space probability density  $f_0^{[N]}(\mathbf{r}^N, \mathbf{p}^N)$  into kinetic and potential terms leads naturally to a separation of thermodynamic properties into ideal and excess parts. A similar factorisation can be made of the reduced phase space distribution functions  $f_0^{(n)}(\mathbf{r}^n, \mathbf{p}^n)$  defined in Section 2.1. We assume again that there is no external field and hence that the hamiltonian is  $\mathcal{H} = K_N + V_N$ , where  $K_N$  is a sum of independent terms. For a system of fixed  $N$ ,  $V$  and  $T$ ,  $f_0^{[N]}$  is given by the canonical distribution (2.3.1). If we recall from Section 2.3 that integration over each component of momentum yields a factor  $(2\pi mk_B T)^{1/2}$ , we see that  $f_0^{(n)}$  can be written as

$$f_0^{(n)}(\mathbf{r}^n, \mathbf{p}^n) = \rho_N^{(n)}(\mathbf{r}^n) f_M^{(n)}(\mathbf{p}^n) \quad (2.5.1)$$

where

$$f_M^{(n)}(\mathbf{p}^n) = \frac{1}{(2\pi mk_B T)^{3n/2}} \exp\left(-\beta \sum_{i=1}^n \frac{|\mathbf{p}_i|^2}{2m}\right) \quad (2.5.2)$$

is the product of  $n$  independent Maxwell distributions of the form defined by (2.1.26) and  $\rho_N^{(n)}$ , the equilibrium  $n$ -particle density is

$$\begin{aligned} \rho_N^{(n)}(\mathbf{r}^n) &= \frac{N!}{(N-n)!} \frac{1}{Q_N} \iint \exp(-\beta\mathcal{H}) d\mathbf{r}^{(N-n)} d\mathbf{p}^N \\ &= \frac{N!}{(N-n)!} \frac{1}{Z_N} \int \exp(-\beta V_N) d\mathbf{r}^{(N-n)} \end{aligned} \quad (2.5.3)$$

The quantity  $\rho_N^{(n)}(\mathbf{r}^n) d\mathbf{r}^n$  determines the probability of finding  $n$  particles of the system with coordinates in the volume element  $d\mathbf{r}^n$  irrespective of the positions of the remaining particles and irrespective of all momenta. The particle densities and the closely related, equilibrium *particle distribution functions*, defined below, provide a complete description of the structure of a fluid, while

knowledge of the low-order particle distribution functions, in particular of the pair density  $\rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ , is often sufficient to calculate the equation of state and other thermodynamic properties of the system.

The definition of the  $n$ -particle density means that

$$\int \rho_N^{(n)}(\mathbf{r}^n) d\mathbf{r}^n = \frac{N!}{(N-n)!} \quad (2.5.4)$$

and in particular that

$$\int \rho_N^{(1)}(\mathbf{r}) d\mathbf{r} = N \quad (2.5.5)$$

The single-particle density of a uniform fluid is therefore equal to the overall number density:

$$\rho_N^{(1)}(\mathbf{r}) = N/V = \rho \quad (\text{uniform fluid}) \quad (2.5.6)$$

In the special case of a uniform, ideal gas we know from (2.3.14) that  $Z_N = V^N$ . Hence the pair density is

$$\rho_N^{(2)} = \rho^2 \left(1 - \frac{1}{N}\right) \quad (\text{uniform ideal gas}) \quad (2.5.7)$$

The appearance of the term  $1/N$  in (2.5.7) reflects the fact that in a system containing a fixed number of particles the probability of finding a particle in the volume element  $d\mathbf{r}_1$ , given that another particle is in the element  $d\mathbf{r}_2$ , is proportional to  $(N-1)/V$  rather than  $\rho$ .

The  $n$ -particle distribution function  $g_N^{(n)}(\mathbf{r}^n)$  is defined in terms of the corresponding particle densities by

$$g_N^{(n)}(\mathbf{r}^n) = \frac{\rho_N^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n)}{\prod_{i=1}^n \rho_N^{(1)}(\mathbf{r}_i)} \quad (2.5.8)$$

which for a homogeneous system reduces to

$$\rho^n g_N^{(n)}(\mathbf{r}^n) = \rho_N^{(n)}(\mathbf{r}^n) \quad (2.5.9)$$

The particle distribution functions measure the extent to which the structure of a fluid deviates from complete randomness. If the system is also isotropic, the pair distribution function  $g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$  is a function only of the separation  $r_{12} = |\mathbf{r}_2 - \mathbf{r}_1|$ ; it is then usually called the *radial distribution function* and written simply as  $g(r)$ . When  $r$  is much larger than the range of the interparticle potential, the radial distribution function approaches the ideal gas limit; from (2.5.7) this limit can be identified as  $(1 - 1/N) \approx 1$ .

The particle densities defined by (2.5.3) are also expressible in terms of  $\delta$ -functions of position in a form that is very convenient for later purposes. From

the definition of a  $\delta$ -function it follows that

$$\begin{aligned}\langle \delta(\mathbf{r} - \mathbf{r}_1) \rangle &= \frac{1}{Z_N} \int \delta(\mathbf{r} - \mathbf{r}_1) \exp[-\beta V_N(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)] \mathbf{d}\mathbf{r}^N \\ &= \frac{1}{Z_N} \int \dots \int \exp[-\beta V_N(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)] \mathbf{d}\mathbf{r}_2 \dots \mathbf{d}\mathbf{r}_N\end{aligned}\quad (2.5.10)$$

The ensemble average in (2.5.10) is a function of the coordinate  $\mathbf{r}$  but is independent of the particle label (here taken to be 1). A sum over all particle labels is therefore equal to  $N$  times the contribution from any one particle. Comparison with the definition (2.5.3) then shows that

$$\rho_N^{(1)}(\mathbf{r}) = \left\langle \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \right\rangle \quad (2.5.11)$$

which represents the ensemble average of a microscopic particle density  $\rho(\mathbf{r})$ . Similarly, the average of a product of two  $\delta$ -functions is

$$\begin{aligned}\langle \delta(\mathbf{r} - \mathbf{r}_1) \delta(\mathbf{r}' - \mathbf{r}_2) \rangle &= \frac{1}{Z_N} \int \delta(\mathbf{r} - \mathbf{r}_1) \delta(\mathbf{r}' - \mathbf{r}_2) \\ &\quad \exp[-\beta V_N(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)] \mathbf{d}\mathbf{r}^N \\ &= \frac{1}{Z_N} \int \dots \int \exp[-\beta V_N(\mathbf{r}, \mathbf{r}', \mathbf{r}_3, \dots, \mathbf{r}_N)] \\ &\quad \mathbf{d}\mathbf{r}_3 \dots \mathbf{d}\mathbf{r}_N\end{aligned}\quad (2.5.12)$$

which implies that

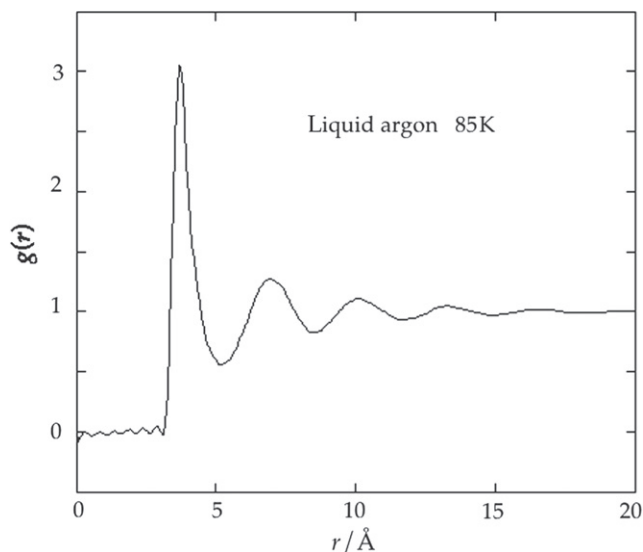
$$\rho_N^{(2)}(\mathbf{r}, \mathbf{r}') = \left\langle \sum_{i=1}^N \sum_{j=1}^{N'} \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j) \right\rangle \quad (2.5.13)$$

where the prime on the summation sign indicates that terms for which  $i = j$  must be omitted. Finally, a useful  $\delta$ -function representation can be obtained for the radial distribution function. It follows straightforwardly that

$$\begin{aligned}\left\langle \frac{1}{N} \sum_{i=1}^N \sum_{j=1}^{N'} \delta(\mathbf{r} - \mathbf{r}_j + \mathbf{r}_i) \right\rangle &= \left\langle \frac{1}{N} \int \sum_{i=1}^N \sum_{j=1}^{N'} \delta(\mathbf{r}' + \mathbf{r} - \mathbf{r}_j) \delta(\mathbf{r}' - \mathbf{r}_i) \mathbf{d}\mathbf{r}' \right\rangle \\ &= \frac{1}{N} \int \rho_N^{(2)}(\mathbf{r}' + \mathbf{r}, \mathbf{r}') \mathbf{d}\mathbf{r}'\end{aligned}\quad (2.5.14)$$

Hence, if the system is both homogeneous and isotropic:

$$\left\langle \frac{1}{N} \sum_{i=1}^N \sum_{j=1}^{N'} \delta(\mathbf{r} - \mathbf{r}_j + \mathbf{r}_i) \right\rangle = \frac{\rho^2}{N} \int g_N^{(2)}(\mathbf{r}, \mathbf{r}') \mathbf{d}\mathbf{r}' = \rho g(r) \quad (2.5.15)$$



**FIGURE 2.3** Results of neutron scattering experiments for the radial distribution function of argon near the triple point. The ripples at small  $r$  are artefacts of the data analysis. After Yarnell et al.<sup>8</sup>

The radial distribution function plays a key role in the physics of monatomic liquids. There are several reasons for this. First,  $g(r)$  is measurable by radiation scattering experiments. The results of such an experiment on liquid argon are pictured in Figure 2.3;  $g(r)$  shows a pattern of peaks and troughs that is typical of all monatomic liquids, tends to unity at large  $r$ , and vanishes as  $r \rightarrow 0$  as a consequence of the strongly repulsive forces that act at small particle separations. Secondly, the form of  $g(r)$  provides considerable insight into what is meant by the structure of a liquid, at least at the level of pair correlations. The definition of  $g(r)$  implies that on average the number of particles lying within the range  $r$  to  $r + dr$  from a reference particle is  $4\pi r^2 \rho g(r) dr$  and the peaks in  $g(r)$  represent ‘shells’ of neighbours around the reference particle. Integration of  $4\pi r^2 \rho g(r)$  up to the position of the first minimum therefore provides an estimate of the nearest-neighbour ‘coordination number’. The concepts of a ‘shell’ of neighbours and a ‘coordination number’ are obviously more appropriate to solids than to liquids, but they provide useful measures of the structure of a liquid provided the analogy with solids is not taken too far. The coordination number ( $\approx 12.2$ ) calculated from the distribution function shown in the figure is in fact very close to the number (12) of nearest neighbours in the face-centred cubic structure into which argon crystallises. Finally, if the atoms interact through pairwise-additive forces, thermodynamic properties can be expressed in terms of integrals over  $g(r)$ , as we shall now show.

Consider a uniform fluid for which the total potential energy is given by a sum of pair terms:

$$V_N(\mathbf{r}^N) = \sum_{i=1}^N \sum_{j>i}^N v(r_{ij}) \quad (2.5.16)$$

According to (2.3.22), the excess internal energy is

$$U^{\text{ex}} = \frac{N(N-1)}{2} \iint v(r_{12}) \left( \frac{1}{Z_N} \int \cdots \int \exp(-\beta V_N) d\mathbf{r}_3 \cdots d\mathbf{r}_N \right) d\mathbf{r}_1 d\mathbf{r}_2 \quad (2.5.17)$$

because the double sum over  $i, j$  in (2.5.16) gives rise to  $\frac{1}{2}N(N-1)$  terms, each of which leads to the same result after integration. Use of (2.5.3) and (2.5.9) allows (2.5.17) to be rewritten as

$$U^{\text{ex}} = \frac{N^2}{2V^2} \iint v(r_{12}) g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (2.5.18)$$

We now take the position of particle 1 as the origin of coordinates, set  $\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1$  and integrate over the coordinate  $\mathbf{r}_1$  (which yields a factor  $V$ ) to give

$$U^{\text{ex}} = \frac{N^2}{2V^2} \iint v(r_{12}) g(r_{21}) d\mathbf{r}_1 d\mathbf{r}_{12} = \frac{N^2}{2V} \int v(r) g(r) dr \quad (2.5.19)$$

or

$$\frac{U^{\text{ex}}}{N} = 2\pi\rho \int_0^\infty v(r) g(r) r^2 dr \quad (2.5.20)$$

This result, usually referred to as the *energy equation*, can also be derived in a more intuitive way. The mean number of particles at a distance between  $r$  and  $r + dr$  from a reference particle is  $n(r) dr = 4\pi r^2 \rho g(r) dr$  and the total energy of interaction with the reference particle is  $v(r)n(r) dr$ . The excess internal energy per particle is then obtained by integrating  $v(r)n(r)$  between  $r = 0$  and  $r = \infty$  and dividing the result by two to avoid counting each interaction twice.

It is also possible to express the equation of state (2.2.10) as an integral over  $g(r)$ . Given the assumption of pairwise additivity of the interparticle forces, the internal contribution to the virial function can be written, with the help of Newton's Third Law, as

$$\mathcal{V}_{\text{int}} = \sum_{i=1}^N \sum_{j>i}^N \mathbf{r}_i \cdot \mathbf{F}_{ij} = - \sum_{i=1}^N \sum_{j>i}^N r_{ij} v'(r_{ij}) \quad (2.5.21)$$

where  $v'(r) \equiv dv(r)/dr$ . Then, starting from (2.2.10) and following the steps involved in the derivation of (2.5.20) but with  $v(r_{ij})$  replaced by  $r_{ij} v'(r_{ij})$ :

$$\frac{\beta P}{\rho} = 1 - \frac{2\pi\beta\rho}{3} \int_0^\infty v'(r) g(r) r^3 dr \quad (2.5.22)$$

Equation (2.5.22) is called either the *pressure equation* or, in common with (2.2.10), the *virial equation*.



Equations (2.5.20) and (2.5.22) are superficially simpler in form than (2.3.22) and (2.2.10), but the difficulty has merely shifted to that of determining the radial distribution function from the pair potential via (2.5.3) and (2.5.8). The problem is yet more complicated if there are many-body forces acting between particles or if the pair potential is not spherically symmetric. The presence of three-body forces, for example, leads to the appearance in expressions for the internal energy and pressure of integrals over the triplet distribution function  $g_N^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ . We shall not pursue this matter further, since no new point of principle is involved, but the generalisation to systems of non-spherical particles is treated in detail in Chapter 11.

Because the pressure equation involves the derivative of the pair potential, it is not directly applicable in the calculation of the equation of state of hard spheres, or of other systems for which the pair potential contains a discontinuity. The problem can be overcome by rewriting (2.5.22) in terms of a function  $y(r)$  defined as

$$y(r) = \exp[\beta v(r)]g(r) \quad (2.5.23)$$

We show in Chapter 4 that  $y(r)$  is a continuous function of  $r$  even when there are discontinuities in  $v(r)$  and hence in  $g(r)$ ;  $y(r)$  is called the *cavity distribution function* for reasons that will become clear in Section 4.6. On introducing the definition of  $y(r)$  into (2.5.22) we find that

$$\begin{aligned} \frac{\beta P}{\rho} &= 1 - \frac{2\pi\beta\rho}{3} \int_0^\infty v'(r)e(r)y(r)r^3 dr \\ &= 1 + \frac{2\pi\rho}{3} \int_0^\infty e'(r)y(r)r^3 dr \end{aligned} \quad (2.5.24)$$

where

$$e(r) = \exp[-\beta v(r)] \quad (2.5.25)$$

is the Boltzmann factor for a pair of particles separated by a distance  $r$  and  $e'(r) \equiv de(r)/dr$ . In the case of hard spheres,  $e(r)$  is a unit step function, the derivative of which is a  $\delta$ -function, i.e.  $e(r) = 0$  for  $r < d$ ,  $e(r) = 1$  for  $r > d$  and  $e'(r) = \delta(r - d)$ , where  $d$  is the hard-sphere diameter. Thus

$$\begin{aligned} \frac{\beta P}{\rho} &= 1 + \frac{2\pi\rho}{3} \int_0^\infty r^3 y(r) \delta(r - d) dr \\ &= 1 + \frac{2\pi\rho}{3} \lim_{r \rightarrow d^+} r^3 y(r) = 1 + \frac{2\pi\rho}{3} d^3 g(d) \end{aligned} \quad (2.5.26)$$

The pressure of the hard-sphere fluid is therefore determined by the value of the radial distribution function at contact of the spheres, where  $g(r)$  goes discontinuously to zero. We show in the next section that  $g(r) \approx e(r)$  and hence that  $g(d) \rightarrow 1$  in the limit  $\rho \rightarrow 0$ . Thus, at low densities:

$$\frac{\beta P}{\rho} \approx 1 + \frac{2}{3}\pi\rho d^3 \quad (2.5.27)$$

This expression represents the first two terms in the *virial expansion* of the equation of state in powers of the density, which we derive in a systematic way in Section 3.9.

The contact value of  $g(r)$  also appears in the theory of transport processes in gases. Elementary kinetic theory<sup>9</sup> shows that at low densities the mean time between collisions suffered by a given particle is  $\lambda/\bar{u}$ , where  $\bar{u} = (8k_B T/\pi m)^{1/2}$  is the mean speed appropriate to a Maxwell distribution of momenta and  $\lambda$  is the mean free path. If the gas particles are treated as hard spheres of diameter  $d$ , the mean free path is  $\lambda = 1/\sqrt{2}\pi\rho d^2$ . Thus the collision rate in the dilute gas is

$$\Gamma_0 = \bar{u}/\lambda = 4\rho d^2(\pi k_B T/m)^{1/2} \quad (2.5.28)$$

At higher densities the collision rate is enhanced by the interactions between particles. Since the ‘forces’ between hard spheres act only at collisions, the collision rate is proportional to the non-ideal contribution to the pressure, as given by the hard-sphere equation of state (2.5.26). It follows that  $\Gamma_E = g(d)\Gamma_0$  where  $\Gamma_E$ , the collision rate in the dense gas, is the quantity that arises in the Enskog theory discussed in Section 2.1. This enhancement of the collision rate leads to a corresponding reduction in the self-diffusion coefficient relative to the value obtained from the Boltzmann equation by a factor  $1/g(d)$ .

## 2.6 PARTICLE DENSITIES IN THE GRAND CANONICAL ENSEMBLE

The fact that in the canonical ensemble the pair distribution function behaves asymptotically as  $(1 - 1/N)$  rather than tending strictly to unity is often irrelevant since the term of order  $N^{-1}$  vanishes in the thermodynamic limit. On the other hand, if a term of that order is integrated over the volume of the system, a result of order  $V/N$  is obtained, which usually cannot be ignored. The difficulties that this situation sometimes creates can be avoided by working in the grand canonical ensemble. As we shall see in later chapters, the grand canonical ensemble also provides a convenient framework for the derivation of density expansions of the particle distribution functions and, more generally, for the development of the theory of inhomogeneous fluids.

In the grand canonical ensemble the  $n$ -particle density is defined in terms of its canonical ensemble counterparts as the sum

$$\begin{aligned} \rho^{(n)}(\mathbf{r}^n) &= \sum_{N \geq n}^{\infty} p(N) \rho_N^{(n)}(\mathbf{r}^n) \\ &= \frac{1}{\Xi} \sum_{N=n}^{\infty} \frac{z^N}{(N-n)!} \int \exp(-\beta V_N) d\mathbf{r}^{(N-n)} \end{aligned} \quad (2.6.1)$$

where  $p(N)$  is the probability (2.4.12). Integration of (2.6.1) over the coordinates  $\mathbf{r}_1, \dots, \mathbf{r}_n$  shows that  $\rho^{(n)}$  is normalised such that

$$\int \rho^{(n)}(\mathbf{r}^n) d\mathbf{r}^n = \left\langle \frac{N!}{(N-n)!} \right\rangle \quad (2.6.2)$$

In particular:

$$\int \rho^{(1)} d\mathbf{r} = \langle N \rangle \quad (2.6.3)$$

and

$$\iint \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 = \langle N^2 \rangle - \langle N \rangle \quad (2.6.4)$$

Equation (2.6.3) confirms that the single-particle density in a homogeneous system is

$$\rho^{(1)} = \langle N \rangle / V \equiv \rho \quad (\text{uniform fluid}) \quad (2.6.5)$$

We know from Section 2.4 that for a homogeneous, ideal gas the activity  $z$  is equal to  $\rho$ , while the integral in (2.6.1) is equal to  $V^{(N-n)}$ . Hence the particle densities of the ideal gas are

$$\rho^{(n)} = \rho^n \quad (\text{uniform ideal gas}) \quad (2.6.6)$$

The relation between the grand canonical  $n$ -particle density and the corresponding distribution function is the same as in the canonical ensemble, i.e.

$$g^{(n)}(\mathbf{r}^n) = \frac{\rho^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n)}{\prod_{i=1}^n \rho^{(1)}(\mathbf{r}_i)} \quad (2.6.7)$$

or  $\rho^{(n)}(\mathbf{r}^n) = \rho^n g^{(n)}(\mathbf{r}^n)$  if the system is homogeneous, but now  $g^{(n)}(\mathbf{r}^n) \rightarrow 1$  for all  $n$  as the mutual separations of all pairs of particles becomes sufficiently large. In particular, the *pair correlation function*, defined as

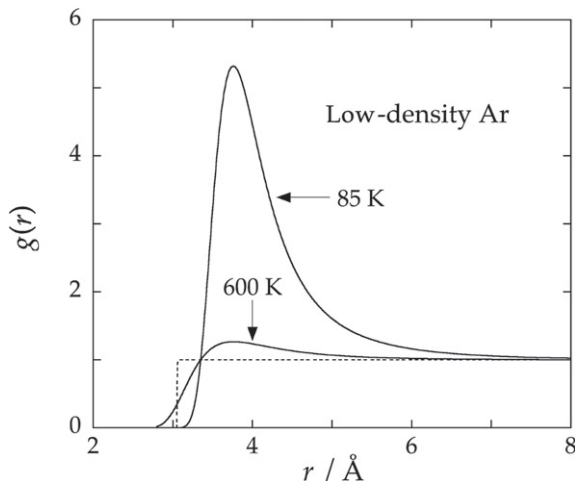
$$h^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - 1 \quad (2.6.8)$$

vanishes in the limit  $|\mathbf{r}_2 - \mathbf{r}_1| \rightarrow \infty$ . If we insert the definition (2.6.1) into (2.6.7) we obtain an expansion of the  $n$ -particle distribution function of a uniform fluid as a power series in  $z$ , which starts as

$$\mathcal{E} \left( \frac{\rho}{z} \right)^n g^{(n)}(\mathbf{r}^n) = \exp[-\beta V_n(\mathbf{r}^n)] + \mathcal{O}(z) \quad (2.6.9)$$

The first term on the right-hand side is the one corresponding to the case  $N = n$  in (2.6.1). As  $\rho \rightarrow 0$ , it follows from earlier definitions that  $z \rightarrow 0$ ,  $\rho/z \rightarrow 1$  and  $\mathcal{E} \rightarrow 1$ . Hence, taking  $n = 2$ , we find that the low-density limit of the radial distribution function is equal to the Boltzmann factor of the pair potential:

$$\lim_{\rho \rightarrow 0} g(r) = \exp[-\beta v(r)] \quad (2.6.10)$$



**FIGURE 2.4** Low-density limit of the radial distribution function for argon at two temperatures, calculated from (2.6.10) for the accurate pair potential pictured in Figure 1.3. The dotted line shows the low-density distribution function for a system of hard spheres of diameter 3.23 Å (see text).

Figure 2.4 shows the low-density limit of the radial distribution function of argon for the accurate, gas phase potential pictured in Figure 1.3. Results are shown for two temperatures, one some four times greater than the experimental critical temperature (150.7 K) and one close to the experimental triple point (83.8 K). The strong peak seen at 85 K in the region of the minimum in the pair potential is indicative of the known tendency for argon to form weakly bound, van der Waals dimers at low temperatures.<sup>10</sup> At 600 K, by contrast, the distribution function closely resembles that of a hard-sphere gas, with the attractive part of the potential playing only a minor role. The hard-sphere results are for hard spheres of diameter equal to 3.23 Å, corresponding to the pair separation at which the gas phase potential is equal to  $k_B T$ ; this is known to provide a realistic estimate of the effective ‘size’ of an atom as a function of temperature.

The  $\delta$ -function representations of  $\rho_N^{(1)}(\mathbf{r})$ ,  $\rho_N^{(2)}(\mathbf{r}, \mathbf{r}')$  and  $g(r)$  provided by (2.5.11), (2.5.13) and (2.5.15), respectively, are also valid (without the subscript  $N$ ) in the grand canonical ensemble, as are the energy and pressure equations, (2.5.20) and (2.5.22). On the other hand, the *compressibility equation*, which expresses  $\chi_T$  as an integral over  $g(r)$ , can be derived only in the grand canonical ensemble because the compressibility is related to fluctuations in an open system via (2.4.23). The normalisations (2.6.3) and (2.6.4) show that

$$\iint \left[ \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - \rho^{(1)}(\mathbf{r}_1)\rho^{(1)}(\mathbf{r}_2) \right] d\mathbf{r}_1 d\mathbf{r}_2 = \langle N^2 \rangle - \langle N \rangle^2 \quad (2.6.11)$$

In the homogeneous case it follows immediately that

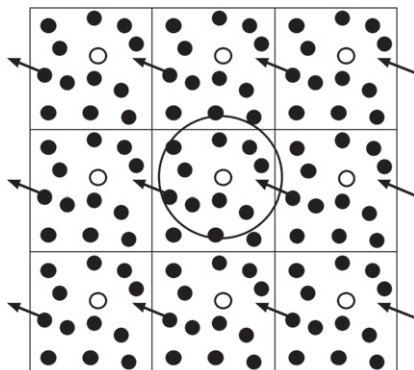
$$1 + \rho \int [g(r) - 1] \mathbf{dr} = \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} = \rho k_B T \chi_T \quad (2.6.12)$$

Unlike the energy and pressure equations, the applicability of this relation does not rely on the assumption of pairwise additivity of the interparticle forces. For an ideal gas in the grand canonical ensemble,  $g(r) = 1$  for all  $r$ ; it follows from (2.6.12) that  $\chi_T^{\text{id}} = \beta/\rho$ , in agreement with the result obtained by differentiation of the ideal gas equation of state.

## 2.7 MOLECULAR DYNAMICS SIMULATION

As we briefly mentioned at the end of [Chapter 1](#), the behaviour of liquids, solids and dense gases at the microscopic level can be simulated in one of two ways: by the method of molecular dynamics or by a Monte Carlo method. The importance of computer simulation from the standpoint of liquid state theory is the fact that it provides essentially exact, quasi-experimental data on well-defined models, particularly on those that are prototypical models of simple liquids. In this section we give a brief account of how classical computer simulations are carried out. Excellent books exist that provide much fuller descriptions of the principles underlying the large variety of techniques that are now available and of the computer codes needed for their implementation.<sup>1,11</sup>

We begin by considering the method of molecular dynamics. In a conventional molecular dynamics simulation of a bulk fluid a system of  $N$  particles is allocated a set of initial coordinates within a cell of fixed volume, most commonly a cube. A set of velocities is also assigned, usually drawn from a Maxwell distribution appropriate to the temperature of interest and selected in such a way that the net linear momentum of the system is zero. The subsequent calculation tracks the motion of the particles through space by integration of the classical equations of motion. Equilibrium properties are obtained as time averages over the dynamical history of the system in the manner outlined in [Section 2.2](#) and correspond to averages over a microcanonical ensemble. In modern work  $N$  is typically of order  $10^3$  or  $10^4$ , though much larger systems have occasionally been studied. To minimise surface effects, and thereby simulate more closely the behaviour expected of a macroscopic system, it is customary to use a periodic boundary condition. The way in which the periodic boundary condition is applied is illustrated for the two-dimensional case in [Figure 2.5](#). The system as a whole is divided into cells. Each cell is surrounded on all sides by periodic images of itself and particles that are images of each other have the same relative positions within their respective cells and the same momenta. When a particle enters or leaves a cell, the move is balanced by an image of that particle leaving or entering through the opposite face.



**FIGURE 2.5** Periodic boundary conditions used in computer simulations. The circle represents the truncation sphere around a white particle in the central cell. When a particle leaves a cell it is replaced by an image of that particle entering through the opposite face.

A key question that arises in both the molecular dynamics and Monte Carlo methods is whether the properties of an infinite, periodic fluid with a unit cell containing, typically, of order  $10^3$  particles are representative of the properties of the macroscopic system that the calculation is designed to simulate. There is no easy or general answer to this,<sup>12</sup> but broadly speaking it appears that bulk properties are only weakly dependent on sample size beyond  $N \approx 500$ , and that the remaining errors, relative to the  $N \rightarrow \infty$  limit, are no larger than the inevitable statistical uncertainties. Nonetheless, the restriction on sample size does have some drawbacks. For example, it is impossible to study collective, spatial fluctuations of wavelength greater than  $L$ , the length of the cell. Use of a periodic boundary condition also has an effect on time correlations. In a molecular dynamics simulation a local disturbance will move through the periodic system and reappear at the same place, albeit in attenuated form, after a recurrence time of order  $L/c$ , where  $c$  is a speed of propagation that can be roughly equated to the speed of sound. The effects of periodicity will manifest themselves in spurious contributions to time correlations calculated over time intervals greater than this. Another difficulty, which is particularly acute for small samples, is the so-called quasi-ergodic problem. In the context of a computer simulation the term refers to the possibility that the system may become trapped in some region of phase space. Near the melting temperature, for example, an initial, lattice-type arrangement of particles may persist for very long times unless the density is appreciably less than the freezing density of the fluid. Whatever the starting conditions, time must be allowed for the system to equilibrate before the ‘production’ stage of the calculation begins, while throughout the simulation it is important to monitor the properties of the system in such a way as to detect any tendency towards a long-time drift. Non-ergodic behaviour is also observed in simulations in which a liquid is quenched

below a ‘glass transition’ temperature into a disordered, glassy state which is metastable with respect to the equilibrium, crystalline phase. Such states are characterised by very slow relaxation processes of the type to be discussed in Section 8.8.

The interactions between particles can be of any form but in the great majority of cases they are assumed to be pairwise additive. For economy in computing time it is customary to truncate the interaction at a separation  $r_c \leq \frac{1}{2}L$ , where the cut-off radius  $r_c$  is typically a few particle diameters. When a truncation sphere is used, the interaction of a particle with its neighbours is calculated with a ‘nearest-neighbour’ convention. The principle of this convention is illustrated in Figure 2.5: a particle  $i$  lying within a given cell is assumed to interact only with the nearest image of any other particle  $j$  (including  $j$  itself), the interaction being set equal to zero if the distance from the nearest image is greater than  $r_c$ . The upper limit imposed on  $r_c$  ensures that interactions with other images of  $j$  are automatically ignored. Use of such a cut-off is inappropriate when the interparticle forces are long ranged, particularly for ionic systems, since there is no guarantee that the truncation sphere would be electrically neutral. One way to overcome this difficulty is to calculate the coulombic interaction of a particle not only with all other particles in the same cell but with all images in other cells. An infinite lattice sum of this type can be evaluated by the method of Ewald, the essence of which is to convert the slowly convergent sum in  $r^{-1}$  into two series that are separately rapidly convergent. One series is a sum in real space of a short-range potential that may safely be truncated, and the other is a sum over reciprocal-lattice vectors of the periodic array of cells. Strongly polar systems also require special treatment.

The earliest applications of the molecular dynamics method were those of Alder and Wainwright<sup>13</sup> to systems of hard spheres and other hard-core particles. A feature of hard-sphere dynamics is that the velocities of the particles change only as the result of collisions; between collisions, the particles move in straight lines at constant speeds. The time evolution of a many particle, hard-sphere system may therefore be treated as a sequence of strictly binary, elastic collisions. Thus the algorithm for calculation of the trajectories consists of first advancing the coordinates of all particles until such a time as a collision occurs somewhere in the system, and then of exploiting the fact that both energy and momentum are conserved to calculate the changes in velocities of the colliding particles. Since that calculation is exact, the trajectories of the particles can be computed with a precision limited only by round-off errors. The instantaneous temperature of the system remains constant because the total kinetic energy is conserved.

When the potentials are continuous, the trajectories of the particles, unlike those of hard spheres, can no longer be calculated exactly. In the case of spherically symmetric potentials the equations of motion are the  $3N$  coupled, second-order differential equations (2.2.1). These equations must be solved numerically by finite difference methods, which leads unavoidably to errors in

the particle trajectories. One of the simplest but also most successful algorithms is that first used by Verlet<sup>14</sup> in studies of the properties of the Lennard-Jones fluid. Let the coordinates of particle  $i$  at time  $t$  be  $\mathbf{r}_i(t)$ . The coordinates at times  $t \pm \Delta t$  are given by Taylor expansions forwards and backwards in time around  $\mathbf{r}_i(t)$ :

$$\mathbf{r}_i(t \pm \Delta t) = \mathbf{r}_i(t) \pm \Delta t \dot{\mathbf{r}}_i(t) + \frac{1}{2} \Delta t^2 \ddot{\mathbf{r}}_i(t) \pm \mathcal{O}(\Delta t^3) \quad (2.7.1)$$

By adding together the two expansions in (2.7.1), we obtain an estimate for the particle coordinates at time  $t + \Delta t$ :

$$\mathbf{r}_i(t + \Delta t) \approx -\mathbf{r}_i(t - \Delta t) + 2\mathbf{r}_i(t) + \frac{\Delta t^2}{m} \mathbf{F}_i(t) \quad (2.7.2)$$

where  $\mathbf{F}_i(t)$  is the total force acting on particle  $i$  at time  $t$ . The error in the predicted coordinates is of order  $\Delta t^4$ . If we subtract the two expansions in (2.7.1), we obtain an estimate of the velocity of particle  $i$  at time  $t$ :

$$\dot{\mathbf{r}}_i(t) \approx \frac{1}{2\Delta t} [\mathbf{r}_i(t + \Delta t) - \mathbf{r}_i(t - \Delta t)] \quad (2.7.3)$$

The error now is of order  $\Delta t^2$ , but velocities play no part in the integration scheme and the particle trajectories are therefore unaffected. In one of a number of variants of the Verlet algorithm, the ‘velocity’ version, the predicted coordinates are obtained solely from the forward expansion in (2.7.1), i.e.

$$\mathbf{r}_i(t + \Delta t) \approx \mathbf{r}_i(t) + \Delta t \dot{\mathbf{r}}_i(t) + \frac{1}{2} \Delta t^2 \ddot{\mathbf{r}}_i(t) \quad (2.7.4)$$

and the velocity is calculated as

$$\dot{\mathbf{r}}_i(t + \Delta t) \approx \dot{\mathbf{r}}_i(t) + \frac{1}{2} \Delta t [\ddot{\mathbf{r}}_i(t + \Delta t) + \ddot{\mathbf{r}}_i(t)] \quad (2.7.5)$$

Taken together, (2.7.4) and (2.7.5) are equivalent to (2.7.2). In other words, the particle trajectories in configuration space are identical in the two versions of the algorithm, but different estimates are obtained for the velocities.

Although simple in form, the original Verlet algorithm and its modifications are at least as satisfactory as higher-order schemes that make use of derivatives of the particle coordinates beyond  $\ddot{\mathbf{r}}_i(t)$ . It may be less accurate than others at short times but, more importantly, it conserves energy well even over very long times; it is also time reversible, as it should be for consistency with the equations of motion. Some understanding of the reasons for the stability of the algorithm may be obtained in the following way.<sup>15</sup>

The true dynamics of a system of particles is described by the action of the operator  $\exp(i\mathcal{L}t)$  on the phase space coordinates  $\mathbf{r}^N, \mathbf{p}^N$  in the manner described by (2.1.14). Let the time interval  $t$  be divided into  $P$  equal intervals of length  $\Delta t$ . Then

$$\exp(i\mathcal{L}t) = [\exp(i\mathcal{L}\Delta t)]^P \quad (2.7.6)$$



If the Liouville operator is divided in the form

$$i\mathcal{L} = i\mathcal{L}_{\mathbf{r}} + i\mathcal{L}_{\mathbf{p}} \quad (2.7.7)$$

where

$$i\mathcal{L}_{\mathbf{r}} \equiv \sum_{i=1}^N \dot{\mathbf{r}}_i \cdot \frac{\partial}{\partial \mathbf{r}_i}, \quad i\mathcal{L}_{\mathbf{p}} = \sum_{i=1}^N \mathbf{F}_i \cdot \frac{\partial}{\partial \mathbf{p}_i} \quad (2.7.8)$$

and if  $\Delta t$  is sufficiently small, the operator  $\exp(i\mathcal{L}\Delta t)$  can be written as<sup>16</sup>

$$\exp(i\mathcal{L}\Delta t) \approx \exp\left(i\frac{1}{2}\mathcal{L}_{\mathbf{p}}\Delta t\right) \exp(i\mathcal{L}_{\mathbf{r}}\Delta t) \exp\left(i\frac{1}{2}\mathcal{L}_{\mathbf{p}}\Delta t\right) \quad (2.7.9)$$

This relationship is only approximate, since the operators  $\mathcal{L}_{\mathbf{r}}$  and  $\mathcal{L}_{\mathbf{p}}$  do not commute; the error involved is of order  $\Delta t^3$ . The action of an exponential operator of the type appearing in (2.7.9) is

$$\exp\left(a\frac{\partial}{\partial x}\right)f(x) \equiv 1 + a\frac{\partial f}{\partial x} + \frac{1}{2}a^2\frac{\partial^2 f}{\partial x^2} + \cdots = f(x+a) \quad (2.7.10)$$

The effect of operating with  $\exp(i\mathcal{L}_{\mathbf{r}}\Delta t)$  or  $\exp(i\mathcal{L}_{\mathbf{p}}\Delta t)$  on  $\mathbf{r}^N, \mathbf{p}^N$  is therefore to displace the position or momentum, respectively, of each particle according to the rules

$$\begin{aligned} \mathbf{r}_i &\rightarrow \mathbf{r}_i + \Delta t \dot{\mathbf{r}}_i = \mathbf{r}_i + (\Delta t/m)\mathbf{p}_i \\ \mathbf{p}_i &\rightarrow \mathbf{p}_i + \Delta t \dot{\mathbf{p}}_i = \mathbf{p}_i + \Delta t \mathbf{F}_i \end{aligned} \quad (2.7.11)$$

The three operations involved in (2.7.9) may be regarded as successive steps in a simple, predictor–corrector scheme. The first step yields an estimate of the momentum of the particle at time  $t + \Delta t/2$ :

$$\mathbf{p}_i(t + \Delta t/2) = \mathbf{p}_i(t) + \frac{1}{2}\Delta t \dot{\mathbf{p}}_i(t) = \mathbf{p}_i(t) + \frac{1}{2}\Delta t \mathbf{F}_i(t) \quad (2.7.12)$$

In the second step this estimate of the momentum is used to predict the coordinates of the particle at time  $t + \Delta t$ :

$$\begin{aligned} \mathbf{r}_i(t + \Delta t) &= \mathbf{r}_i(t) + (\Delta t/m)\mathbf{p}_i(t + \Delta t/2) \\ &= \mathbf{r}_i(t) + \Delta t \dot{\mathbf{r}}_i(t) + (\Delta t^2/2m)\mathbf{F}_i(t) \end{aligned} \quad (2.7.13)$$

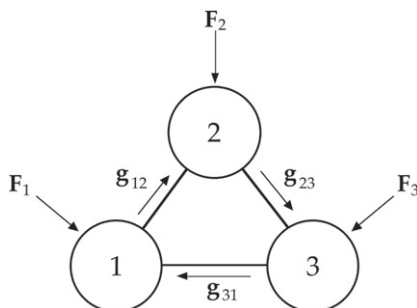
Finally, an improved estimate is obtained for the momentum, based on the value of the force acting on the particle at its predicted position:

$$\begin{aligned} \mathbf{p}_i(t + \Delta t) &= \mathbf{p}_i(t + \Delta t/2) + \frac{1}{2}\Delta t \dot{\mathbf{p}}_i(t + \Delta t) \\ &= \mathbf{p}_i(t) + \frac{1}{2}\Delta t [\mathbf{F}_i(t) + \mathbf{F}_i(t + \Delta t)] \end{aligned} \quad (2.7.14)$$

The results thereby obtained for  $\mathbf{r}_i(t + \Delta t)$ ,  $\mathbf{p}_i(t + \Delta t)$  are precisely those that appear in the velocity version of the Verlet algorithm, (2.7.4) and (2.7.5). It is remarkable that a practical and widely used algorithm can be derived from a well-defined approximation for the propagator  $\exp(i\mathcal{L}t)$ . What is more significant, however, is that each of the three steps implied by use of (2.7.9) is time reversible and conserves volume in phase space in the sense of Section 2.1; the same is therefore true of the algorithm overall. The fact that the Verlet algorithm preserves these key features of hamiltonian dynamics is almost certainly the reason why it is numerically so stable. Other time-reversible algorithms can be derived by dividing the Liouville operator in ways different from that adopted in (2.7.9).

A molecular dynamics calculation is organised as a loop over time. At each step, the time is incremented by  $\Delta t$ , the total force acting on each particle is computed and the particles are advanced to their new positions. In the early stages of the simulation it is normal for the temperature to move away from the value at which it was set and some occasional rescaling of particle velocities is therefore needed. Once equilibrium is reached, the system is allowed to evolve undisturbed, with both potential and kinetic energies fluctuating around steady, mean values; the temperature of the system is calculated from the time-averaged kinetic energy, as in (2.2.4). The choice of the time step  $\Delta t$  is made on the basis of how well total energy is conserved. In the case of a model of liquid argon, for example, an acceptable level of energy conservation is achieved with a time step of  $10^{-14}$  s, and a moderately long run would be one lasting about  $10^5$  time steps, corresponding to a real time span of the order of a nanosecond. By treating argon atoms as hard spheres of diameter  $3.4 \text{ \AA}$ , the mean ‘collision’ time in liquid argon near its triple point can be estimated as roughly  $10^{-13}$  s. Hence the criterion for the choice of time step based on energy conservation leads to the physically reasonable result that  $\Delta t$  should be roughly an order of magnitude smaller than the typical time between ‘collisions’. As the time step is increased, the fluctuations in total energy become larger, until eventually an overall, upward drift in energy develops. Even when a small time step is used, deviations from the true dynamics are inevitable, and the phase space trajectory of the system can be expected to diverge exponentially from that given by the exact solution of the equations of motion. In this respect an error in the algorithm plays a similar role to a small change in initial conditions. Any such change is known to lead to a divergence in phase space that grows with time as  $\exp(\lambda t)$ , where  $\lambda$  is a ‘Lyapunov exponent’; the consequences in terms of loss of correlation between trajectories can be dramatic.<sup>17</sup>

The methods outlined above are easily extended to models of molecular fluids in which the molecules consist of independent atoms bound together by continuous intramolecular forces, but small molecules are in general more efficiently treated as rigid particles. One approach to the solution of the equations of motion of a rigid body involves a separation of internal and centre-of-mass coordinates. Another is based on the method of ‘constraints’, in which



**FIGURE 2.6** The method of constraints applied to a triatomic molecule:  $\mathbf{F}_i$  is the total intermolecular force on atom  $i$  and  $\mathbf{g}_{ij}$  is the force of constraint that maintains the rigidity of the bond between  $i$  and  $j$ .

the equations of motion are solved in Cartesian form.<sup>18</sup> As an illustration of the use of constraint dynamics, consider the example of the triatomic molecule shown in Figure 2.6, in which each internuclear bond is of length  $L$  and each atom (labelled 1–3) is of mass  $m$ . The geometry of the molecule is described by three constraints,  $\sigma_{ij}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ , such that

$$\sigma_{ij} = \frac{1}{2}(\mathbf{r}_{ij} \cdot \mathbf{r}_{ij} - L^2) = 0 \quad (2.7.15)$$

where  $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$ . The total force acting on atom 1, say, at time  $t$  is the sum of three terms:  $\mathbf{F}_1(t)$ , the force due to interactions with other molecules; a force of constraint,  $\mathbf{g}_{12}(t)$ , which ensures that the bond vector  $\mathbf{r}_{12}$  remains of fixed length; and a second force of constraint,  $\mathbf{g}_{13}(t)$ , which preserves the bond length between atoms 1 and 3. Similar considerations apply to the other atoms. The forces of constraint are directed along the corresponding bond vectors and the law of action and reaction requires that  $\mathbf{g}_{ij} = -\mathbf{g}_{ji}$ . Thus  $\mathbf{g}_{ij} = \lambda_{ij}\mathbf{r}_{ij}$ , where  $\lambda_{ij}$  is a time-dependent scalar quantity, with  $\lambda_{ij} = \lambda_{ji}$ . The newtonian equations of motion are therefore of the form

$$\begin{aligned} m\ddot{\mathbf{r}}_1(t) &= \mathbf{F}_1(t) + \lambda_{12}\mathbf{r}_{12}(t) + \lambda_{13}\mathbf{r}_{13}(t) \\ m\ddot{\mathbf{r}}_2(t) &= \mathbf{F}_2(t) - \lambda_{12}\mathbf{r}_{12}(t) + \lambda_{23}\mathbf{r}_{23}(t) \\ m\ddot{\mathbf{r}}_3(t) &= \mathbf{F}_3(t) - \lambda_{13}\mathbf{r}_{13}(t) - \lambda_{23}\mathbf{r}_{23}(t) \end{aligned} \quad (2.7.16)$$

Comparison with (2.7.15) shows that the total force of constraint on atom  $i$ ,  $\mathbf{G}_i$ , can be written as

$$\mathbf{G}_i = - \sum_{j \neq i} \lambda_{ij} \frac{\partial \sigma_{ij}}{\partial \mathbf{r}_i} \quad (2.7.17)$$

As is to be expected, the sum of the forces of constraint is zero:  $\sum_i \mathbf{G}_i = 0$ .

It is possible to eliminate the unknown quantities  $\lambda_{12}$ ,  $\lambda_{13}$  and  $\lambda_{23}$  from (2.7.16) by requiring the second time derivative of the constraint conditions

(2.7.15) to vanish, i.e. by setting  $\ddot{\sigma}_{ij} = \dot{\mathbf{r}}_{ij} \cdot \dot{\mathbf{r}}_{ij} + \mathbf{r}_{ij} \cdot \ddot{\mathbf{r}}_{ij} = 0$  and replacing  $\ddot{\mathbf{r}}_i$  by  $(\mathbf{F}_i + \mathbf{G}_i)/m$ . The resulting system of equations for the constrained coordinates can then be integrated numerically. In practice this procedure does not work; the errors inherent in any approximate algorithm cause the bond lengths to drift away rapidly from their initial values. What is done instead is to require the constraints to be satisfied exactly after each time step in a manner dictated by the chosen integration scheme. If the original Verlet algorithm is used, for example, we find that

$$\begin{aligned}\mathbf{r}_1(t + \Delta t) &= \mathbf{r}'_1(t + \Delta t) + (\Delta t^2/m)[\lambda_{12}\mathbf{r}_{12}(t) + \lambda_{13}\mathbf{r}_{13}(t)] \\ \mathbf{r}_2(t + \Delta t) &= \mathbf{r}'_2(t + \Delta t) + (\Delta t^2/m)[- \lambda_{12}\mathbf{r}_{12}(t) + \lambda_{23}\mathbf{r}_{23}(t)] \\ \mathbf{r}_3(t + \Delta t) &= \mathbf{r}'_3(t + \Delta t) + (\Delta t^2/m)[- \lambda_{13}\mathbf{r}_{13}(t) - \lambda_{23}\mathbf{r}_{23}(t)]\end{aligned}\quad (2.7.18)$$

where  $\mathbf{r}'_i(t + \Delta t)$  are the predicted coordinates of atom  $i$  in the absence of constraints, given by (2.7.4). Equations (2.7.18) must be solved subject to the requirement that  $|\mathbf{r}_{ij}(t + \Delta t)|^2 = L^2$  for all  $i, j$ . This leads to three simultaneous equations for the quantities  $\lambda_{ij}(t)$ , to which a solution can be obtained by an iterative method; three to four iterations per molecule are normally sufficient to maintain the bond lengths constant to within one part in  $10^4$ .

Apart from its simplicity, a particular merit of the method of constraints is the fact that it can be used for both rigid and flexible molecules. A partially flexible chain molecule, for example, can be treated by employing a suitable mixture of constraints on bond angles and bond lengths in a way that allows for torsional motion and bending but freezes the fast vibrations.<sup>19</sup>

The algorithms discussed thus far are limited to the calculation of the trajectories of particles moving solely under the influence of the interparticle forces. However, some of the most interesting applications of the molecular dynamics method have involved the incorporation into the dynamics of one or more additional degrees of freedom that describe, for example, a coupling between the physical system of interest and its surroundings or some fluctuating molecular property such as an induced dipole moment. The equations of motion of the resulting 'extended' system are most easily derived within the framework of Lagrangian mechanics. As an example of this approach we shall briefly describe the scheme, developed in a classic paper by Andersen,<sup>20</sup> which allows a molecular dynamics simulation to be carried out for state conditions corresponding to constant pressure rather than constant volume.

The Lagrangian of a mechanical system is defined as the difference between the kinetic and potential energies taken as functions of a set of generalised coordinates, one for each degree of freedom of the system, and a corresponding set of generalised velocities. In the case of an atomic fluid there are  $3N$  degrees of freedom and the generalised coordinates are simply the Cartesian coordinates, denoted collectively by  $\mathbf{r}^N$ , with generalised velocities similarly denoted by  $\dot{\mathbf{r}}^N$ .

The Lagrangian for a one-component system is therefore

$$L(\mathbf{r}^N, \dot{\mathbf{r}}^N) = \frac{1}{2}m \sum_{i=1}^N |\dot{\mathbf{r}}_i|^2 - V_N(\mathbf{r}^N) \quad (2.7.19)$$

and the equations of motion of the particles are given by

$$\frac{\partial}{\partial t} \left( \frac{\partial L}{\partial \dot{\mathbf{r}}_i} \right) = \frac{\partial L}{\partial \mathbf{r}_i} \quad (2.7.20)$$

The generalised momenta are

$$\mathbf{p}_i = \frac{\partial L}{\partial \dot{\mathbf{r}}_i} \quad (2.7.21)$$

and the link with the hamiltonian description of the system is provided by the relation

$$\mathcal{H}(\mathbf{r}^N, \mathbf{p}^N) = \sum_{i=1}^N \mathbf{p}_i \cdot \dot{\mathbf{r}}_i - L(\mathbf{r}^N, \dot{\mathbf{r}}^N) \quad (2.7.22)$$

In the simple case just described, use of (2.7.20) leads to the Newtonian equations (2.2.1) and the hamiltonian is that given by (2.1.1), with the contribution from the external field omitted.

Consider a system of structureless particles enclosed in a cube of volume  $V$ . The ‘extended Lagrangian’ proposed by Andersen differs from (2.7.19) in two ways. First, the Cartesian coordinates and associated velocities are replaced by the scaled variables  $\boldsymbol{\tau}_i$  and  $\dot{\boldsymbol{\tau}}_i$ , defined as

$$\boldsymbol{\tau}_i = V^{-1/3} \mathbf{r}_i, \quad \dot{\boldsymbol{\tau}}_i = V^{-1/3} \dot{\mathbf{r}}_i \quad (2.7.23)$$

Secondly,  $V$  itself is treated as an additional, generalised coordinate. The extended system may then be visualised as one that fluctuates in volume against a fixed external pressure equal to  $P_{\text{ext}}$ . With that picture in mind the Lagrangian is assumed to have the form

$$L(\boldsymbol{\tau}^N, \dot{\boldsymbol{\tau}}^N, V, \dot{V}) = \frac{1}{2}m \sum_{i=1}^N |\dot{\boldsymbol{\tau}}_i|^2 + \frac{1}{2}W \dot{V}^2 - V_N(V^{1/3} \boldsymbol{\tau}^N) - P_{\text{ext}}V \quad (2.7.24)$$

where the quantities  $\frac{1}{2}W \dot{V}^2$  and  $P_{\text{ext}}V$  are respectively the kinetic and potential energies associated with the coordinate  $V$ ;  $W$  is an inertial factor which plays the role of a ‘mass’ in the kinetic energy term. The equations of motion derived from the analogues of (2.7.20) for the scaled variables are

$$\ddot{\boldsymbol{\tau}}_i = \frac{\mathbf{F}_i}{mV^{1/3}} - \frac{2}{3V} \dot{V} \dot{\boldsymbol{\tau}}_i \quad (2.7.25)$$

where  $\mathbf{F}_i$  is the total force on particle  $i$ , and

$$W \ddot{V} = \frac{m}{3V^{1/3}} \sum_{i=1}^N |\dot{\boldsymbol{\tau}}_i|^2 + \frac{1}{3V^{2/3}} \sum_{i=1}^N \boldsymbol{\tau}_i \cdot \mathbf{F}_i - P_{\text{ext}} \quad (2.7.26)$$

Equation (2.7.25) shows that the motion of the particles is now coupled to the motion of the coordinate  $V$ , while the meaning of (2.7.26) is most easily grasped by rewriting it in terms of the unscaled variables:

$$W \ddot{V} = \frac{m}{3V} \sum_{i=1}^N |\dot{\mathbf{r}}_i|^2 + \frac{1}{3V} \sum_{i=1}^N \mathbf{r}_i \cdot \mathbf{F}_i - P_{\text{ext}} \quad (2.7.27)$$

Comparison with (2.2.9) shows that the sum of the first two terms on the right-hand side is the instantaneous value of the internal pressure  $P$  of the system and hence that

$$\ddot{V} = \frac{1}{W} (P - P_{\text{ext}}) \quad (2.7.28)$$

Thus the difference between internal and external pressures represents the ‘force’ that causes the volume of the system to change. When averaged over a sufficiently long time, the ‘force’ must vanish, and the mean value of the internal pressure will be equal to the pre-set value  $P_{\text{ext}}$ .

The generalised momenta conjugate to the generalised coordinates  $\dot{\mathbf{r}}_i$  and  $V$ , respectively, are

$$\pi_i = \frac{\partial L}{\partial \dot{\mathbf{r}}_i} = m V^{2/3} \dot{\mathbf{r}}_i, \quad \pi_V = \frac{\partial L}{\partial \dot{V}} = W \dot{V} \quad (2.7.29)$$

The hamiltonian of the extended system, which is conserved by the equations of motion, is therefore

$$\begin{aligned} \mathcal{H}(\boldsymbol{\tau}^N, \boldsymbol{\pi}^N; V, \pi_V) &= \sum_{i=1}^N \pi_i \cdot \dot{\mathbf{r}}_i + \pi_V \dot{V} - L(\boldsymbol{\tau}^N, \dot{\mathbf{r}}^N; V, \dot{V}) \\ &= \frac{1}{2m V^{2/3}} \sum_{i=1}^N |\pi_i|^2 + V_N (V^{1/3} \boldsymbol{\tau}^N) \\ &\quad + \frac{\pi_V^2}{2W} + P_{\text{ext}} V \end{aligned} \quad (2.7.30)$$

This is equal to the enthalpy,  $H$ , of the physical system apart from the presence of the fictitious kinetic energy term  $\pi_V^2/2W$ . Since the extra term is a quadratic function of momentum its average value is

$$\left\langle \frac{\pi_V^2}{2W} \right\rangle = \frac{1}{2} k_B T \quad (2.7.31)$$

which, relative to the remaining terms in (2.7.30), becomes negligibly small in the limit  $N \rightarrow \infty$ . Thus, to a good approximation, time averages over the trajectories of the particles correspond to averages in the constant  $N$ ,  $P$  and  $H$  or isobaric–isoenthalpic ensemble. This is true irrespective of the value chosen

for the inertial parameter  $W$ . However, if the value used is too small, the motion of the coordinate  $V$  is effectively decoupled from that of the particles; if it is too large, the phase space of the extended system is inefficiently sampled. In the limit  $W \rightarrow \infty$ , and assuming that  $\dot{V}$  is initially zero, the equations of motion reduce to those of conventional molecular dynamics at constant  $N$ ,  $V$  and  $E$ .

Andersen's paper also describes a method for controlling the temperature of the system by adding a stochastic collision term to the equations of motion. Later work by Nosé<sup>21</sup> showed that the same effect could be achieved by use of the equations of motion derived from an extended Lagrangian in which a variable is introduced that scales the velocities of the particles; this mimics the interaction between the system and a reservoir of fixed temperature. Nosé's method was later reformulated by Hoover<sup>22</sup> in a way that made it easier to implement and the so-called Nosé–Hoover 'thermostat' is now very widely used in molecular dynamics calculations at constant  $N$ ,  $V$  and  $T$  or  $N$ ,  $P$  and  $T$ .

## 2.8 MONTE CARLO METHODS

Given a set of initial conditions, a conventional molecular dynamics simulation is, in principle, entirely deterministic in nature. By contrast, as the name suggests, a stochastic element is an essential part of any Monte Carlo calculation. In a Monte Carlo simulation a system of  $N$  particles, subject to the same boundary condition used in molecular dynamics calculations and interacting through some known potentials, is again assigned a set of arbitrarily chosen, initial coordinates. A sequence of configurations is then generated, which in the simplest case would occur by random displacements of randomly chosen particles, usually of one particle at a time. Not all configurations that are generated are added to the sequence. The decision whether to 'accept' or 'reject' a trial configuration is made in such a way that asymptotically configuration space is sampled according to the probability density corresponding to a particular statistical mechanical ensemble. The ensemble average of any function of the particle coordinates, such as the total potential energy, is then obtained as an unweighted average over the resulting set of configurations. The particle momenta do not enter the calculation, there is no time scale involved, and the order in which the configurations occur has no special significance. The method is therefore limited to the calculation of static properties.

The problem of devising a scheme for sampling configuration space according to a specific probability distribution is most easily formulated in terms of the theory of Markov processes.<sup>23</sup> Suppose we have a sequence of random variables. Here the 'variable' consists of the coordinates of the particles, and possibly also the volume of the system or the number of particles it contains, while its range is the set of all accessible states of the system. Hence, instead of speaking of the 'value' of the variable at a given point in the sequence, it is more natural to say that at that point the system occupies a particular state.

If the probability of finding the system in a state  $n$  at ‘time’  $(t + 1)$  is dependent only on the state it occupied at the previous time,  $t$ , the sequence of states constitutes a Markov chain. Note that the concept of ‘time’ is introduced merely for descriptive purposes; there is no connection with any physical time scale.

Let  $q_n(t)$  be the probability that the system is in a state  $n$  at time  $t$ . A Markov process is one for which

$$q_n(t) = \sum_m p_{n \leftarrow m} q_m(t - 1) \quad (2.8.1)$$

where  $p_{n \leftarrow m}$  is a transition probability, with  $\sum_n p_{n \leftarrow m} = 1$ . If we regard the probabilities  $\{q_n(t)\}$  as the components of a column vector  $\mathbf{q}(t)$  and the quantities  $\{p_{n \leftarrow m}\}$  as the elements of a square *transition matrix*  $\mathbf{p}$ , (2.8.1) may be rewritten in more compact form as

$$\mathbf{q}(t) = \mathbf{p} \cdot \mathbf{q}(t - 1) \quad (2.8.2)$$

Equation (2.8.2) can be immediately generalised to yield the probability distribution at time  $t$  given an initial distribution  $\mathbf{q}(0)$ :

$$\mathbf{q}(t) = \overbrace{\mathbf{p} \cdots \mathbf{p}}^{t \text{ times}} \cdot \mathbf{q}(0) \equiv \mathbf{p}^t \cdot \mathbf{q}(0) \quad (2.8.3)$$

where  $\mathbf{p}^t \equiv \{p_{n \leftarrow m}^{(t)}\}$  is the  $t$ -fold product of  $\mathbf{p}$  with itself. If all elements of the matrix  $\mathbf{p}^t$  are non-zero for some finite  $t$ , each state of the system can be reached from any other state in a finite number of steps (or finite ‘time’), and the Markov chain is said to be *ergodic*; it is clear that this usage of the term ‘ergodic’ is closely related to its meaning in statistical mechanics. When the chain is ergodic, it can be shown that the limits

$$Q_n = \lim_{t \rightarrow \infty} p_{n \leftarrow m}^{(t)} q_m(0) \quad (2.8.4)$$

exist and are the same for all  $m$ . In other words there exists a limiting probability distribution  $\mathbf{Q} \equiv \{Q_n\}$  that is independent of the initial distribution  $\mathbf{q}(0)$ . When the limiting distribution is reached, it persists, because  $\mathbf{p} \cdot \mathbf{Q} = \mathbf{Q}$  or, in component form:

$$Q_n = \sum_m p_{n \leftarrow m} Q_m \quad (2.8.5)$$

This result is called the *steady-state condition*. In the context of statistical mechanics the limiting distribution is determined by the appropriate equilibrium probability density, which in the case of the canonical ensemble, for example, is proportional to the Boltzmann factor, so the desired limits are  $Q_n \propto \exp[-\beta V_N(n)]$ . The task of finding a set of transition probabilities consistent



with the known, limiting distribution is greatly simplified by seeking a transition matrix that satisfies *microscopic reversibility*, i.e. one for which

$$Q_n p_{m \leftarrow n} = Q_m p_{n \leftarrow m} \quad (2.8.6)$$

If this relation holds, the steady-state condition is automatically satisfied.<sup>24</sup>

Let us suppose that the system is in state  $m$  at a given time and that a trial state  $n$  is generated in some way. If the probability of choosing  $n$  as the trial state is the same as that of choosing  $m$  when  $n$  is the current state, a choice of transition probabilities that satisfies (2.8.6) is

$$\begin{aligned} p_{n \leftarrow m} &= 1, \quad \text{if } Q_n \geq Q_m \\ &= \frac{Q_n}{Q_m}, \quad \text{if } Q_n < Q_m \end{aligned} \quad (2.8.7)$$

with  $p_{m \leftarrow m} = 1 - p_{n \leftarrow m}$ . The transition matrix defined by (2.8.7) is the one proposed in the pioneering work of Metropolis et al.<sup>25</sup> and remains much the most commonly used prescription for  $\mathbf{p}$ . In practice, in the case of the canonical ensemble, the trial state is normally generated by selecting a particle  $i$  at random and giving it a small, random displacement,  $\mathbf{r}_i \rightarrow \mathbf{r}_i + \Delta \mathbf{r}$ , where  $\Delta \mathbf{r}$  is chosen uniformly within prescribed limits. If the difference in potential energy of the two states is  $\Delta U = V_N(n) - V_N(m)$ , the trial state is accepted unconditionally when  $\Delta U \leq 0$  and with a probability  $\exp(-\beta \Delta U)$  when  $\Delta U > 0$ , i.e.

$$p_{n \leftarrow m} = \min \{1, \exp(-\beta \Delta U)\} \quad (2.8.8)$$

The procedure takes a particularly simple form for a system of hard spheres: trial configurations in which two or more spheres overlap are rejected, but all others are accepted. One important point to note about the Metropolis scheme is that the system remains in its current state if the trial state  $n$  is rejected. In that case, state  $m$  appears a further time in the Markov chain, and the contribution it makes to any ensemble average must be counted again.

Monte Carlo methods similar to that outlined above are easily devised for use in other ensembles. All that changes are the form of the equilibrium probability density and the way in which trial states are generated. In the case of the isothermal–isobaric ensemble random displacements of the particles must be combined with random changes in volume. The corresponding probability density can be deduced from the form of the partition function (2.3.25), but allowance needs to be made for the fact that a change in volume alters the range of integration over particle coordinates. That can be done, in the case where the periodic cell is cubic, by switching to the scaled coordinates  $\tau_i$  defined by (2.7.23). This has the effect of transforming the integral over the region  $V$  into an integral over the unit cube  $\omega$ :

$$\int_V \dots d\mathbf{r}^N \rightarrow V^N \int_\omega \dots d\boldsymbol{\tau}^N \quad (2.8.9)$$

and the partition function, after integration over momenta, takes the form

$$\Delta_N = \frac{1}{N!} \frac{V_0^{-1}}{\Lambda^{3N}} \int_0^\infty dV V^N \int \exp[-\beta(U_N + PV)] d\tau^N \quad (2.8.10)$$

where, to avoid confusion, we use the symbol  $U_N$  rather than  $V_N$  to denote the total potential energy. The required probability density is therefore proportional to  $V^N \exp[-\beta(U_N + PV)]$ . Thus the selection rule for displacements is the same as in the canonical ensemble while that for a change in volume from  $V$  to  $V + \Delta V$  is

$$p_{n \leftarrow m} = \min \left\{ 1, \exp \left[ -\beta(\Delta U + P \Delta V) + N \ln \left( 1 + \frac{\Delta V}{V} \right) \right] \right\} \quad (2.8.11)$$

where  $\Delta U$  is the change in potential energy brought about by the change in volume. As in the case of particle displacements, the choice of  $\Delta V$  must be made within prescribed limits.

In simulations in the grand canonical ensemble displacements are combined with random attempts to insert or delete particles, a choice that must be made randomly but with equal probabilities. By switching to scaled coordinates and integrating over momenta in the definition of the grand partition function (2.4.6) we find that the equilibrium probability density is

$$\frac{(zV)^N}{N!} \exp(-\beta U_N)$$

The acceptance rule for displacements is again given by (2.8.8) and those for insertion and deletion of particles by

$$p_{n \leftarrow m} = \min \left\{ 1, \frac{zV}{N+1} \exp(-\beta \Delta U) \right\}, \quad \text{insertion, } N \rightarrow N+1 \quad (2.8.12)$$

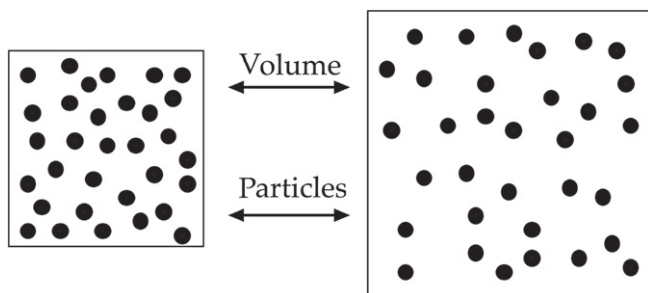
and

$$p_{n \leftarrow m} = \min \left\{ 1, \frac{N}{zV} \exp(-\beta \Delta U) \right\}, \quad \text{deletion, } N \rightarrow N-1 \quad (2.8.13)$$

where  $\Delta U$  is the change in potential energy associated with the gain or loss of a particle.

The extension to molecular systems is straightforward. Interactions between particles are now dependent on their mutual orientation and ‘displacements’ are either random translational moves or random reorientations. The choice of which type of move is to be attempted at any given stage should be made randomly to guarantee that microscopic reversibility is preserved.

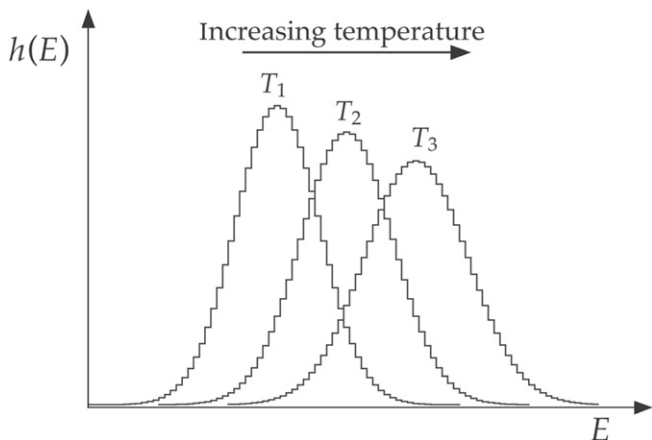
Monte Carlo methods are widely used in the study of phase equilibria for model systems, particularly that of equilibrium between liquid and vapour. The liquid–vapour coexistence curve of a one-component system can be determined



**FIGURE 2.7** The Gibbs ensemble. The system of interest consists of two sub-systems A and B held at a constant temperature and between which volume and particles can be exchanged while keeping the total volume  $V = V_A + V_B$  and total number of particles  $N = N_A + N_B$  constant.

if the chemical potential is known as a function of density and temperature over the relevant region of the phase diagram. The necessary data may be obtained by working either in the grand canonical ensemble, where the chemical potential is an input parameter, or in the isobaric–isothermal ensemble<sup>26</sup> if supplemented by calculation of the chemical potential by the particle insertion method.<sup>27</sup> A more direct approach to the problem of liquid–vapour coexistence is provided by the ‘Gibbs ensemble’ methodology developed by Panagiotopoulos.<sup>28</sup> Consider a system held at a constant temperature  $T$  and divided into two sub-systems, A and B, which represent the two phases, as pictured in Figure 2.7. The equilibrium properties of the composite system can be determined from a Monte Carlo simulation involving particle displacements within each sub-system and exchanges of volume and particles between them, while keeping both the total volume  $V$  and total number of particles  $N$  constant. If the temperature and overall density are well chosen, the ensemble averages will be those corresponding to phase equilibrium in which subsystem A, say, has a density equal to that of the vapour, and B has a density equal to that of the liquid, while the pressure in the two subsystems will be the same and equal to the vapour pressure. The coexistence curve in the density – temperature plane can therefore be determined without measurement of the chemical potential, which should, however, be the same for A and B; this can be checked by use of a test particle method<sup>29</sup> to ensure that a true equilibrium state has been reached.

The Gibbs ensemble approach is straightforward to implement and requires only modest computing resources. If high accuracy is required, however, other methods must be used, of which the most powerful is based on calculations in the grand canonical ensemble combined with a ‘histogram reweighting’ scheme. Such schemes are ones in which data obtained from multiple simulations for the same values of  $\mu$  and  $V$  but different temperatures are pooled in such a way as to minimise the statistical uncertainties in the results of the individual simulations. The principle involved can be readily understood by focusing on the simpler problem of the calculation of the internal energy from data obtained in canonical ensemble simulations.



**FIGURE 2.8** Histograms showing the number of times a system is found to have a total potential energy lying in an interval  $\Delta E$  around a value  $E$  in typical Monte Carlo calculations in the canonical ensemble.

If a Monte Carlo run is carried out at constant  $N$ ,  $V$  and  $T$  it is a trivial matter to construct a histogram,  $h(E)$ , incremented at each step in the calculation, which records the number of times that the potential energy  $V_N(\mathbf{r}^N)$  of the system is found to lie in a narrow interval  $\Delta E$  around a value  $E$ . The histogram typically has the form pictured in Figure 2.8, where results are plotted for three different temperatures; as the temperature increases, the histogram broadens and the peak shifts to higher energies. The excess internal energy is the mean value of  $E$ , given in terms of histogram entries by

$$U^{\text{ex}}(T) = \frac{\sum_E E h(E)}{\sum_E h(E)} \quad (2.8.14)$$

Let  $p(E) dE$  be the probability of finding the system in a state of potential energy in the range  $E$  to  $E + dE$ . An estimate of the probability density  $p(E)$  is provided by the quantity

$$p(E) = \frac{h(E)}{\mathcal{N} \Delta E} \quad (2.8.15)$$

where  $\mathcal{N}$  is the total number of steps in the Monte Carlo run. The probability density is the product of an energy density of states,  $W(N, V, E)$ , and a Boltzmann factor,  $\exp(-\beta E)$ :

$$p(E) = \frac{1}{\mathcal{Z}} W(N, V, E) \exp(-\beta E) \quad (2.8.16)$$

where

$$\mathcal{Z} = \sum_E W(N, V, E) \exp(-\beta E) \quad (2.8.17)$$

is an unknown, run-dependent, normalisation constant.<sup>30</sup> Since the density of states is independent of temperature, an estimate of the excess internal energy at a temperature  $T'$  can be derived from (2.8.14) if  $h(E)$  is replaced by a histogram  $h'(E)$ , reweighted to match the target temperature:

$$h(E) \rightarrow h'(E) = h(E) \exp[(-\beta' + \beta)E] \quad (2.8.18)$$

This makes it possible to determine the excess internal energy over a limited range of temperature from data accumulated in a single simulation, while other physical properties can be determined by extensions of the basic method.<sup>31</sup> As the temperature difference  $|T' - T|$  increases, however, greater weight is placed on the contributions to  $\langle E \rangle$  from the wings of the histogram, which correspond to energies rarely sampled in the simulation. This leads to a rapidly growing loss in accuracy.

A more efficient method is one based on multiple histograms<sup>32</sup> obtained from independent simulations at the same values of  $N$  and  $V$  but different temperatures,  $T_m$  say. The temperatures should be sufficiently closely spaced to ensure a significant degree of overlap between neighbouring histograms, as exemplified in Figure 2.8. Equations (2.8.15) and (2.8.16) together show that each simulation provides an estimate of the density of states in the form

$$W_m(N, V, E) \approx \mathcal{Z}_m \frac{h_m(E)}{\mathcal{N} \Delta E} \exp(\beta_m E) \quad (2.8.19)$$

where  $\mathcal{N}$  and  $\Delta E$  are assumed to be the same in each case. The results for different temperatures can then be combined to provide an estimate of the density of states over the full range of energies sampled by the simulations in the form of a weighted sum:

$$W(N, V, E) \approx \frac{\sum_m c_m W_m(N, V, E)}{\sum_m c_m} \quad (2.8.20)$$

How are the coefficients  $c_m$  to be chosen? Let us imagine that not one but  $n$  simulations are carried out at a temperature  $T_m$ , where  $n$  is a very large number and let  $\langle h_m(E) \rangle$  be the histogram obtained by averaging over the  $n$  sets of results, which in the limit  $n \rightarrow \infty$  is related to the exact density of states by

$$\mathcal{Z}_m \frac{\langle h_m(E) \rangle}{\mathcal{N} \Delta E} \exp(\beta_m E) \rightarrow W(N, V, E), \quad n \rightarrow \infty \quad (2.8.21)$$

The limiting value of the quantity  $\langle h_m(E) \rangle$  provides a natural choice of weight factor in (2.8.20). Though the limiting value cannot be computed, it is sufficient to know that the limit exists; justification<sup>33</sup> for its use as a weight factor rests ultimately on the fact that the error associated with an individual histogram is proportional to  $\langle h_m(E) \rangle^{-1/2}$ . That given, it follows from (2.8.19) and (2.8.21)

that the best estimate of the density of states is

$$\begin{aligned} W(N, V, E) &\approx \frac{\sum_m \langle h_m(E) \rangle W_m(N, V, E)}{\sum_m \langle h_m(E) \rangle} \\ &= \frac{1}{\mathcal{N} \Delta E} \frac{\sum_m h_m(E)}{\sum_m [\mathcal{Z}_m]^{-1} \exp(-\beta_m E)} \end{aligned} \quad (2.8.22)$$

This expression cannot be used as it stands, since the normalisation constants remain unknown, but substitution of (2.8.22) in (2.8.17) shows that  $\mathcal{Z}_{m'}$ , corresponding to a temperature  $T_{m'}$ , is given in closed form by

$$\begin{aligned} \mathcal{Z}_{m'} &= \sum_E W(N, V, E) \exp(-\beta_{m'} E) \\ &= \sum_E \frac{\sum_m h_m(E)}{\mathcal{N} \Delta E \sum_m [\mathcal{Z}_m]^{-1} \exp[(\beta_{m'} - \beta_m) E]} \end{aligned} \quad (2.8.23)$$

The set of equations represented by (2.8.23) can be solved self-consistently to yield values of the normalisation constants relative to that at one, arbitrarily chosen temperature. The density of states given by (2.8.22) can then be constructed, from which the excess internal energy is easily computed at any temperature in the range originally chosen.

Application of histogram reweighting to the grand canonical ensemble involves the accumulation of data on both potential energy and particle number in a two-dimensional histogram.<sup>34</sup> This allows reweighting to be made to other values of chemical potential as well as temperature. The method has proved particularly valuable in studies of the critical region, where high precision in the calculation of physical properties is needed but is also difficult to achieve. In the case of Gibbs ensemble simulations, for example, fluctuations in density in the two subsystems at temperatures close to  $T_c$  become comparable with the difference between the equilibrium densities of liquid and vapour, making accurate measurement of the individual densities impossible.

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