Substitution of this equation in the condition of detailed balance (6.1.1), with Eq. (6.1.2) and substitution of the desired distribution (6.2.1) gives as condition for the acceptance rules

$$\frac{\mathrm{acc}(o \to n)}{\mathrm{acc}(n \to o)} = \exp\{-\beta[\mathcal{U}(n) - \mathcal{U}(o)]\}. \tag{6.2.5}$$

It is easy to verify that the acceptance rule (6.2.3) obeys this condition.

## 6.3 Isobaric-isothermal ensemble

The isobaric-isothermal (constant-$NPT$) ensemble is widely used in Monte Carlo simulations. This is not surprising because most real experiments are carried at constant pressure and temperature. An advantage of constant-$NPT$ simulations is that they can be used to measure the equation of state of a model system for which the evaluation of the virial expression for the pressure is cumbersome. This is the case, for instance, for systems with non-pairwise additive interactions, but also for certain models of non-spherical hard-core molecules.

Finally, it is often convenient to use constant-$NPT$ Monte Carlo to simulate systems in the vicinity of a first-order phase transition, because, given enough time, a system at constant pressure is free to transform completely into the state of lowest (Gibbs) free energy, whereas in a constant-$NVT$ simulation the system may be kept at a density where, in a macroscopic system, it would separate into two bulk phases of different density, but is prevented from doing so due to finite-size effects.

Monte Carlo simulations at constant pressure were first described by Wood [167] in the context of a simulation study of two-dimensional hard disks. Although the method introduced by Wood is elegant, it is not readily applicable to systems with arbitrary continuous potentials. McDonald [168] was the first to apply constant-$NPT$ simulations to a system with continuous intermolecular forces (a Lennard-Jones mixture), and the constant-pressure method of McDonald is now widely used. It is McDonald's method that we discuss next.

### 6.3.1 Statistical mechanical basis

We will derive the basic equations of constant-pressure Monte Carlo in a way that may appear unnecessarily complicated. However, this derivation has the advantage that the same framework can be used to introduce some of the other non-$NVT$ Monte Carlo methods to be discussed later. For the sake of convenience we shall initially assume that we are dealing with a system of $N$ identical atoms. The partition function for this system is given by

$$Q(N, V, T) = \frac{1}{\Lambda^{3N} N!} \int_0^L \cdots \int_0^L d\mathbf{r}^N \exp[-\beta \mathcal{U}(\mathbf{r}^N)]. \tag{6.3.1}$$

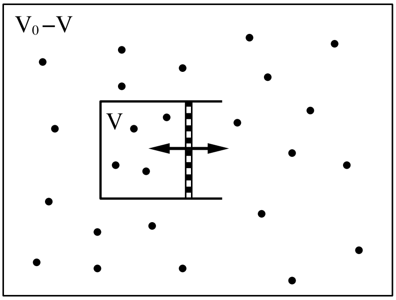

**FIGURE 6.2** Ideal gas ($m$ particles, volume $V_0 - V$) can exchange volume with an $N$-particle system (volume $V$).

It is convenient to rewrite Eq. (6.3.1) in a slightly different way. For convenience, we assume that the system is contained in a cubic box with diameter $L = V^{1/3}$. We now define scaled coordinates $\mathbf{s}^N$ by

$$\mathbf{s}_i \equiv \frac{\mathbf{r}_i}{L} \qquad \text{for} \quad i = 1, 2, \cdots, N. \tag{6.3.2}$$

If we now insert these scaled coordinates in Eq. (6.3.1), we obtain

$$Q(N, V, T) = \frac{V^N}{\Lambda^{3N} N!} \int_0^1 \cdots \int_0^1 d\mathbf{s}^N \exp[-\beta \mathcal{U}(\mathbf{s}^N; L)]. \tag{6.3.3}$$

In Eq. (6.3.3), we have written $\mathcal{U}(\mathbf{s}^N; L)$ to indicate that $\mathcal{U}$ depends on the real rather than the scaled distances between the particles. The expression for the Helmholtz free energy of the system is

$$\begin{aligned} F(N, V, T) &= -k_B T \ln Q \\ &= -k_B T \ln\left(\frac{V^N}{\Lambda^{3N} N!}\right) - k_B T \ln \int d\mathbf{s}^N \exp[-\beta \mathcal{U}(\mathbf{s}^N; L)] \\ &= F^{\mathrm{id}}(N, V, T) + F^{\mathrm{ex}}(N, V, T). \end{aligned} \tag{6.3.4}$$

In the last line of this equation, we have identified the two contributions to the Helmholtz free energy as the ideal gas expression plus an excess part. We now consider the case that the system consists of two non-interacting subsystems with volume $V$ and $V_0 - V$, with $V_0 \gg V$, and $V_0$ fixed. For the sake of visualization, we show the two systems in Fig. 6.2 as two bounded systems separated by a piston, although in reality the subsystems should be considered as completely separate and subject to periodic boundary conditions. We will refer to the system in volume $V_0 - V$ as the *reservoir*. We denote the total number of particles in the combined system by $M$. Of these, $M - N$ are in volume $V_0 - V$, and $N$ are in volume $V$. The partition function of the combined system is simply the product of the partition functions of the two (non-interacting) subsystems:

$$\begin{aligned} Q(N,M,V,V_0,T) &= Q(M,V_0-V,T)\frac{V^N}{\Lambda^{3M}N!}\int \mathrm{d}\mathbf{s}^N \mathrm{e}^{-\beta\mathcal{U}(\mathbf{s}^N;L)} \\ &= \mathrm{e}^{-\beta F_R(M,V_0-V,T)}\frac{V^N}{\Lambda^{3M}N!}\int \mathrm{d}\mathbf{s}^N \mathrm{e}^{-\beta\mathcal{U}(\mathbf{s}^N;L)}\,, \end{aligned} \tag{6.3.5}$$

where $F_R$ denotes the Helmholtz free energy of the reservoir. The total free energy of this combined system is $F^{\mathrm{tot}} = -k_BT\ln Q(N,M,V,V_0,T)$. Now let us assume that the two subsystems can exchange volume. In that case, the volume $V$ of the $N$-particle subsystem can fluctuate. The most probable value of $V$ will be the one that minimizes the free energy of the combined system. The probability density $\mathcal{N}(V)$ that the $N$-particle subsystem has a volume $V$ is given by[1]

$$\mathcal{N}(V) = \frac{\exp[-\beta F_R(M,V_0-V,T)]V^N\int \mathrm{d}\mathbf{s}^N\exp[-\beta\mathcal{U}(\mathbf{s}^N;L)]}{\int_0^{V_0}\mathrm{d}V'\exp[-\beta F_R(M,V_0-V',T)]V'^N\int \mathrm{d}\mathbf{s}^N\exp[-\beta\mathcal{U}(\mathbf{s}^N;L')]}. \tag{6.3.6}$$

We now consider the limit that the size of the reservoir tends to infinity ($V_0 \to \infty$, $M \to \infty$, $(M-N)/V_0 \to \rho$). In that limit, a volume change of the small system does not change the pressure $P_R$ of the reservoir. In other words, the large system works as a barostat for the small system. In that case, we can simplify Eqs. (6.3.5) and (6.3.6). Note that in the limit $V/V_0 \to 0$, we can write

$$\begin{aligned} F_R(M,V_0-V,T) &= F_R(M,V_0,T) + V\left(\frac{\partial F_R(M,V_0-V,T}{\partial V}\right)_{V=0} \\ &= F_R(M,V_0,T) + P_RV\,. \end{aligned} \tag{6.3.7}$$

The combined partition function (6.3.5) can then be written as

$$Q(N,P,T) \equiv \frac{\beta P}{\Lambda^{3N}N!}\int \mathrm{d}V\, V^N\exp(-\beta PV)\int \mathrm{d}\mathbf{s}^N\exp[-\beta\mathcal{U}(\mathbf{s}^N;L)], \tag{6.3.8}$$

where we have included a factor $\beta P$ to make $Q(N,P,T)$ dimensionless (this choice is not obvious —see footnote 1). This gives, for Eq. (6.3.6),

$$\mathcal{N}_{N,P,T}(V) = \frac{V^N\exp(-\beta PV)\int \mathrm{d}\mathbf{s}^N\exp[-\beta\mathcal{U}(\mathbf{s}^N;L)]}{\int_0^{V_0}\mathrm{d}V'\,V'^N\exp(-\beta PV')\int \mathrm{d}\mathbf{s}^N\exp[-\beta\mathcal{U}(\mathbf{s}^N;L')]}. \tag{6.3.9}$$

---

[1] Actually, this step is hard to justify. The reason is that there is no natural “metric” for the volume integration. Unlike the degeneracy of energy levels or the number of particles in a system, we cannot *count* volume. This problem has been addressed by several authors[173,174]. Attard [173] approaches the problem from an information-theory point of view and concludes that the integration variable should be $\ln V$, rather than $V$. In contrast, Koper and Reiss [174] aim to reduce the problem to one of counting the number of quantum states compatible with a given volume. They end up with an expression that is almost identical to the one discussed here.

In the same limit, the difference in free energy of the combined system and that of the reservoir in the absence of the $N$-particle subsystem is the well-known Gibbs free energy $G$:

$$G(N,P,T) = -k_B T \ln Q(N,P,T). \tag{6.3.10}$$

Eq. (6.3.9) is the starting point for constant-$NPT$ Monte Carlo simulations. The idea is that the probability density to find the small system with volume $V$ in a particular configuration of the $N$ atoms, as specified by $\mathbf{s}^N$, is given by

$$\begin{aligned}\mathcal{N}(V;\mathbf{s}^N) &\propto V^N \exp(-\beta PV)\exp[-\beta\mathcal{U}(\mathbf{s}^N;L)]\\ &= \exp\{-\beta[\mathcal{U}(\mathbf{s}^N,V)+PV-N\beta^{-1}\ln V]\}.\end{aligned} \tag{6.3.11}$$

We can now carry out Metropolis sampling on the reduced coordinates $\mathbf{s}^N$ *and* the volume $V$.

In the constant-$NPT$ Monte Carlo method, $V$ is simply treated as an additional coordinate, and trial moves in $V$ must satisfy the same rules as trial moves in $\mathbf{s}$; in particular, we should maintain the microscopic reversibility of the underlying Markov chain. Let us assume that our trial moves consist of an attempted change of the volume from $V$ to $V' = V + \Delta V$, where $\Delta V$ is a random number uniformly distributed over the interval $[-\Delta V_{\max}, +\Delta V_{\max}]$. In the Metropolis scheme such a random, volume-changing move will be accepted with the probability

$$\begin{aligned}\text{acc}(o\to n) = \min\Big(1, \exp\{-\beta[\mathcal{U}(\mathbf{s}^N,V')-\mathcal{U}(\mathbf{s}^N,V)\\ + P(V'-V) - N\beta^{-1}\ln(V'/V)]\}\Big).\end{aligned} \tag{6.3.12}$$

Instead of attempting random changes in the volume itself, one might construct trial moves in the box length $L$ [168] or in the logarithm of the volume [133]. Such trial moves are equally legitimate, as long as the microscopic reversibility of the underlying Markov chain is maintained. However, such alternative schemes result in a slightly different form for Eq. (6.3.12). The partition function (6.3.8) can be rewritten as

$$Q(N,P,T) = \frac{\beta P}{\Lambda^{3N} N!}\int \mathrm{d}(\ln V)\, V^{N+1}\exp(-\beta PV)\int \mathrm{d}\mathbf{s}^N \exp[-\beta\mathcal{U}(\mathbf{s}^N;L)]. \tag{6.3.13}$$

This equation shows that, if we perform a random walk in $\ln V$, the probability of finding volume $V$ is given by

$$\mathcal{N}(V;\mathbf{s}^N) \propto V^{N+1}\exp(-\beta PV)\exp[-\beta\mathcal{U}(\mathbf{s}^N;L)]. \tag{6.3.14}$$

This distribution can be sampled with the following acceptance rule:

$$\mathrm{acc}(o \to n) = \min\Big(1, \exp\{-\beta[\mathcal{U}(\mathbf{s}^N, V') - \mathcal{U}(\mathbf{s}^N, V) + P(V' - V) - (N+1)\beta^{-1}\ln(V'/V)]\}\Big). \tag{6.3.15}$$

### 6.3.2 Monte Carlo simulations

The frequency with which trial moves in the volume should be attempted depends on the efficiency with which volume space is sampled. If, as before, we use as our criterion of efficiency

$$\frac{\text{sum of squares of accepted volume changes}}{t_{\mathrm{CPU}}}, \tag{6.3.16}$$

then it is obvious that the frequency with which we attempt moves depends on their cost. In general, a volume trial move will require that we recompute all intermolecular interactions. It, therefore, is comparable in cost to carrying out $N$ trial moves on the molecular positions. In such cases, it is common practice to perform one volume trial move for every cycle of positional trial moves. Note that to guarantee detailed balance, rather than just balance, volume moves should be attempted with a probability $1/N$. However, attempting volume moves every $N$ steps should satisfy balance, and that should also be OK.

The criteria determining the optimal acceptance of volume moves are no different from those for particle moves.

For one class of potential energy functions, volume trial moves are very cheap, namely those for which the total interaction energy can be written as a sum of powers of the interatomic distances,

$$\begin{aligned} U_n &= \sum_{i<j} \epsilon(\sigma/r_{ij})^n \\ &= \sum_{i<j} \epsilon[\sigma/(L s_{ij})]^n, \end{aligned} \tag{6.3.17}$$

or, possibly, a linear combination of such sums (the well-known Lennard-Jones potential belongs to the latter category). Note that $U_n$ in Eq. (6.3.17) changes in a trivial way if the volume is modified such that the linear dimensions of the system change for $L$ to $L'$:

$$U_n(L') = \left(\frac{L}{L'}\right)^n U_n(L). \tag{6.3.18}$$

Clearly, in this case, computing the probability of acceptance of a volume-changing trial move is extremely cheap. Hence such trial moves may be attempted with high frequency, for example, as frequently as particle moves. One should be careful when using the scaling property (6.3.18) if, at the same time,