

interaction with the (nearest image) of all the particles in the simulation box is calculated. As a consequence, the potential is not a constant on the surface of a cube around a given particle. Hence, for the same reasons as mentioned in the previous paragraph, the simple minimum image convention should never be used in Molecular Dynamics simulations.

In the preceding, we described some details on how the energy should be calculated. The implementation of a simple, order- $N^2$ , algorithm to compute the energy will be discussed in section 4.2.2 in the context of a Molecular Dynamics simulation (see Algorithm 5). More advanced schemes to simulate large systems efficiently are described in Appendix F.

### Initialization

To start the simulation, we should assign initial positions to all particles in the system. As the equilibrium properties of the system do not (or, at least, should not) depend on the choice of initial conditions, all reasonable initial conditions are in principle acceptable. If we wish to simulate the solid state of a particular model system, it is logical to prepare the system in the crystal structure of interest. In contrast, if we are interested in the fluid phase, we simply prepare the system in any convenient crystal structure. This crystal subsequently melts, because at the temperature and density of a typical liquid-state point, the solid state is not thermodynamically stable. Actually, one should be careful here, because the crystal structure may be metastable, even if it is not absolutely stable. For this reason, it is unwise to use a crystal structure as the starting configuration of a liquid close to the freezing curve. In such cases, it is better to use the final (liquid) configuration of a system at a higher temperature or lower density, where the solid is unstable and has melted spontaneously. In any event, it is usually preferable to use the final (well-equilibrated) configuration of an earlier simulation at a nearby state point as the starting configuration for a new run and adjust the temperature and density to the desired values.

The equilibrium properties of a system should not depend on the initial conditions. If such a dependence nevertheless is observed in a simulation, there are two possibilities. The first is that our results reflect the fact that the system that we simulate really behaves nonergodically. This is the case, for instance, in glassy materials or low-temperature, substitutionally disordered alloys. The second (and much more likely) explanation is the system we simulate is ergodic but our sampling of configuration space is inadequate; in other words, we have not yet reached equilibrium.

### Reduced Units

In simulations it is often convenient to express quantities such as temperature, density, pressure, and the like in reduced units. This means that we choose a convenient unit of energy, length and mass and then express all

other quantities in terms of these basic units. In the example of a Lennard-Jones system, we use a pair potential that is of the form  $u(r) = \epsilon f(r/\sigma)$  (see equation (3.2.3)). A natural (though not unique) choice for our basic units is the following:

- Unit of length,  $\sigma$
- Unit of energy,  $\epsilon$
- Unit of mass,  $m$  (the mass of the atoms in the system)

and from these basic units, all other units follow. For instance, our unit of time is

$$\sigma \sqrt{m/\epsilon}$$

and the unit of temperature is

$$\epsilon/k_B.$$

In terms of these reduced units, denoted with superscript  $*$ , the reduced pair potential  $u^* \equiv u/\epsilon$  is a dimensionless function of the reduced distance  $r^* \equiv r/\sigma$ . For instance, the reduced form for the Lennard-Jones potential is

$$u^{*lj}(r^*) = 4 \left[ \left( \frac{1}{r^*} \right)^{12} - \left( \frac{1}{r^*} \right)^6 \right]. \quad (3.2.10)$$

With these conventions we can define the following reduced units: the potential energy  $U^* = U\epsilon^{-1}$ , the pressure  $P^* = P\sigma^3\epsilon^{-1}$ , the density  $\rho^* = \rho\sigma^3$ , and the temperature  $T^* = k_B T\epsilon^{-1}$ .

One may wonder why it is convenient to introduce reduced units. The most important reason is that (infinitely) many combinations of  $\rho$ ,  $T$ ,  $\epsilon$ , and  $\sigma$  all correspond to the same state in reduced units. This is the law of corresponding states: the same simulation of a Lennard-Jones model can be used to study Ar at 60 K and a density of 840 kg/m<sup>3</sup> and Xe at 112 K and a density of 1617 kg/m<sup>3</sup>. In reduced units, both simulations correspond to the state point  $\rho^* = 0.5$ ,  $T^* = 0.5$ . If we had not used reduced units, we might have easily missed the equivalence of these two simulations. Another, practical, reason for using reduced units is the following: when we work with real (SI) units, we find that the absolute numerical values of the quantities that we are computing (e.g., the average energy of a particle or its acceleration) are either much less or much larger than 1. If we multiply several such quantities using standard floating-point multiplication, we face a distinct risk that, at some stage, we will obtain a result that creates an overflow or underflow. Conversely, in reduced units, almost all quantities of interest are of order 1 (say, between  $10^{-3}$  and  $10^3$ ). Hence, if we suddenly find a very large (or very small) number in our simulations (say,  $10^{42}$ ), then there is a good chance that we have made an error somewhere. In other words, reduced

Quantity	Reduced units		Real units
temperature	$T^* = 1$	$\leftrightarrow$	$T = 119.8 \text{ K}$
density	$\rho^* = 1.0$	$\leftrightarrow$	$\rho = 1680 \text{ kg/m}^3$
time	$\Delta t^* = 0.005$	$\leftrightarrow$	$\Delta t = 1.09 \times 10^{-14} \text{ s}$
pressure	$P^* = 1$	$\leftrightarrow$	$P = 41.9 \text{ MPa}$

**Table 3.1:** Translation of reduced units to real units for Lennard-Jones argon ( $\epsilon/k_B = 119.8 \text{ K}$ ,  $\sigma = 3.405 \times 10^{-10} \text{ m}$ ,  $M = 0.03994 \text{ kg/mol}$ )

units make it easier to spot errors. Simulation results that are obtained in reduced units can always be translated back into real units. For instance, if we wish to compare the results of a simulation on a Lennard-Jones model at  $T^* = 1$  and  $P^* = 1$  with experimental data for argon ( $\epsilon/k_B = 119.8 \text{ K}$ ,  $\sigma = 3.405 \times 10^{-10} \text{ m}$ ,  $M = 0.03994 \text{ kg/mol}$ ), then we can use the translation given in Table 3.1 to convert our simulation parameters to real SI units.<sup>5</sup>

### 3.2.3 Detailed Balance versus Balance

Throughout this book we use the condition of detailed balance as a test of the validity of a Monte Carlo scheme. However, as stated before, the detailed-balance condition is sufficient, but not necessary. Manousiouthakis and Deem [54] have shown that the weaker “balance condition” is a necessary and sufficient requirement. A consequence of this proof is that one has more freedom in developing Monte Carlo moves. For example, in the simple Monte Carlo scheme shown in Algorithm 2 we select a particle at random and give it a random displacement. During the next trial move, the *a priori* probability to select the *same* particle is the same. Thus the reverse trial move has the same *a priori* probability and detailed balance is satisfied. An alternative scheme is to attempt moving all particles sequentially, i.e., first an attempt to move particle one, followed by an attempt to move particle two, etc. In this sequential scheme, the probability that a single-particle move is followed by its reverse is zero. Hence, this scheme clearly violates detailed balance. However, Manousiouthakis and Deem have shown that such a sequential updating scheme does obey balance and does therefore (usually — see Ref. [54]) result in correct MC sampling.

We stress that the detailed-balance condition remains an important guiding principle in developing novel Monte Carlo schemes. Moreover, most algorithms that do not satisfy detailed balance are simply wrong. This is true in particular for “composite” algorithms that combine different trial moves. Therefore, we suggest that it is good practice to impose detailed balance

<sup>5</sup>In what follows we will always use reduced units, unless explicitly indicated otherwise. We, therefore, omit the superscript  $*$  to denote reduced units.

1. After each trial move we compute the change in potential energy of the system,

$$\Delta U = U(\mathbf{q}'^N) - U(\mathbf{q}^N).$$

2. If  $\Delta U < 0$ , we accept the move and increase the energy carried by the demon by  $|\Delta U|$ . If  $\Delta U > 0$ , we test if the demon carries enough energy to make up the difference. Otherwise, we reject the trial move.

Note that no random numbers were used in this decision. Using elementary statistical mechanics it is easy to see that, after equilibration, the probability density to find the demon with an energy  $E_D$  is given by the Boltzmann distribution:

$$\mathcal{N}(E_D) = (k_B T)^{-1} \exp(-E_D/k_B T).$$

Hence, the demon acts as a thermometer. Note that this method does not really simulate the microcanonical ensemble. What is kept (almost) constant is the total potential energy. We can, however, mimic the real  $N, V, E$  ensemble by introducing a demon for every quadratic term in the kinetic energy. We then apply the same rules as before, randomly selecting a demon to pay or accept the potential energy change for every trial move.

Microcanonical Monte Carlo is rarely, if ever, used to simulate molecular systems.

## 5.4 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 also carried out under conditions of controlled pressure and temperature. Moreover, constant-NPT simulations can be used to measure the equation of state of a model system even if the virial expression for the pressure cannot be readily evaluated. This may be the case, for instance, for certain models of nonspherical hard-core molecules, but also for the increasingly important class of models where the (nonpairwise additive) potential energy function is computed numerically for each new configuration. Finally, it is often convenient to use constant-NPT Monte Carlo to simulate systems in the vicinity of a first-order phase transition, because at constant pressure the system is free (given enough time, of course) 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 it would like to phase separate into two bulk phases of different density but is prevented from doing so by finite-size effects.

Monte Carlo simulations at constant pressure were first described by Wood [88] in the context of a simulation study of two-dimensional hard

disks. Although the method introduced by Wood is very elegant, it is not readily applicable to systems with arbitrary continuous potentials. McDonald [89] 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 being used almost universally and that is discussed next.

### 5.4.1 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

$$Q(N, V, T) = \frac{1}{\Lambda^{3N} N!} \int_0^L \cdots \int_0^L d\mathbf{r}^N \exp[-\beta \mathcal{U}(\mathbf{r}^N)]. \quad (5.4.1)$$

It is convenient to rewrite equation (5.4.1) in a slightly different way. We have assumed that the system is contained in a cubic box with diameter  $L = V^{1/3}$ . We now define scaled coordinates  $\mathbf{s}^N$  by

$$\mathbf{r}_i = L\mathbf{s}_i \quad \text{for } i = 1, 2, \dots, N. \quad (5.4.2)$$

If we now insert these scaled coordinates in equation (5.4.1), we obtain

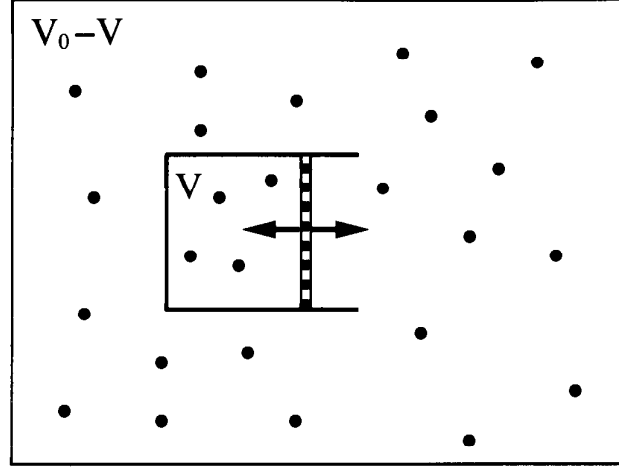
$$Q(N, V, T) = \frac{V^N}{\Lambda^{3N} N!} \int_0^1 \cdots \int_0^1 d\mathbf{s}^N \exp[-\beta \mathcal{U}(\mathbf{s}^N; L)]. \quad (5.4.3)$$

In equation (5.4.3), 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

$$\begin{aligned} F(N, V, T) &= -k_B T \ln Q \\ &= -k_B T \ln \left( \frac{V^N}{\Lambda^{3N} N!} \right) - k_B T \ln \int d\mathbf{s}^N \exp[-\beta \mathcal{U}(\mathbf{s}^N; L)] \\ &= F^{\text{id}}(N, V, T) + F^{\text{ex}}(N, V, T). \end{aligned} \quad (5.4.4)$$

In the last line of this equation we have identified the two contributions to the Helmholtz free energy on the previous line as the ideal gas expression plus an excess part. Let us now assume that the system is separated by a piston<sup>1</sup> from an ideal gas reservoir (see Figure 5.2). The total volume of the

<sup>1</sup>Actually, there is no need to assume a real piston. The systems with volume  $V$  and  $V_0 - V$  may both be isolated systems subject to their individual (periodic) boundary conditions. The only constraint that we impose is that the sum of the volumes of the two systems equals  $V_0$ .



**Figure 5.2:** Ideal gas ( $m$  particles, volume  $V_0 - V$ ) can exchange volume with an  $N$ -particle system (volume  $V$ ).

system plus reservoir is fixed at a value  $V_0$ . The total number of particles is  $M$ . Hence, the volume accessible to the  $M - N$  ideal gas molecules is  $V_0 - V$ . The partition function of the total system is simply the product of the partition functions of the constituent subsystems:

$$Q(N, M, V, V_0, T) = \frac{V^N (V_0 - V)^{M-N}}{\Lambda^{3M} N! (M-N)!} \int d\mathbf{s}^{M-N} \int d\mathbf{s}^N \exp[-\beta \mathcal{U}(\mathbf{s}^N; L)]. \quad (5.4.5)$$

Note that the integral over the  $\mathbf{s}^{M-N}$  scaled coordinates of the ideal gas yields simply 1. For the sake of compactness, we have assumed that the thermal wavelength of the ideal gas molecules is also equal to  $\Lambda$ . The total free energy of this combined system is  $F^{\text{tot}} = -k_B T \ln Q(N, M, V, V_0, T)$ . Now let us assume that the piston between the two subsystems is free to move, so that the volume  $V$  of the  $N$ -particle subsystem can fluctuate. Of course, 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 <sup>2</sup>

$$\mathcal{N}(V) = \frac{V^N (V_0 - V)^{M-N} \int d\mathbf{s}^N \exp[-\beta \mathcal{U}(\mathbf{s}^N; L)]}{\int_0^{V_0} dV' V'^N (V_0 - V')^{M-N} \int d\mathbf{s}^N \exp[-\beta \mathcal{U}(\mathbf{s}^N; L')]} \quad (5.4.6)$$

We now consider the limit that the size of the reservoir tends to infinity

<sup>2</sup>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 [95, 96]. Attard [95] 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 [96] 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.

( $V_0 \rightarrow \infty$ ,  $M \rightarrow \infty$ ,  $(M - N)/V_0 \rightarrow \rho$ ). In that limit, a small volume change of the small system does not change the pressure  $P$  of the large system. In other words, the large system works as a manostat for the small system. In that case, we can simplify equations (5.4.5) and (5.4.6). Note that in the limit  $V/V_0 \rightarrow 0$ , we can write

$$(V_0 - V)^{M-N} = V_0^{M-N} [1 - (V/V_0)]^{M-N} \rightarrow V_0^{M-N} \exp(-(M - N)V/V_0).$$

Note that for  $M - N \rightarrow \infty$ ,  $\exp(-(M - N)V/V_0) \rightarrow \exp(-\rho V)$ . But, as the reservoir contains an ideal gas,  $\rho$  can be written as  $\beta P$ . With these substitutions, the combined partition function (5.4.5) can be written as

$$Q(N, P, T) \equiv \frac{\beta P}{\Lambda^{3N} N!} \int dV V^N \exp(-\beta P V) \int ds^N \exp[-\beta \mathcal{U}(s^N; L)], \quad (5.4.7)$$

where we have included a factor  $\beta P$  to make  $Q(N, P, T)$  dimensionless (this choice is not obvious—see footnote 2). This gives, for equation (5.4.6),

$$\mathcal{N}_{N,P,T}(V) = \frac{V^N \exp(-\beta P V) \int ds^N \exp[-\beta \mathcal{U}(s^N; L)]}{\int_0^{V_0} dV' V'^N \exp(-\beta P V') \int ds^N \exp[-\beta \mathcal{U}(s^N; L)]}. \quad (5.4.8)$$

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

$$G(N, P, T) = -k_B T \ln Q(N, P, T). \quad (5.4.9)$$

Equation (5.4.8) is the starting point for constant-NPT Monte Carlo simulations. The idea is that the probability density to find the small system in a particular configuration of the  $N$  atoms (as specified by  $s^N$ ) at a given volume  $V$  is given by

$$\begin{aligned} \mathcal{N}(V; s^N) &\propto V^N \exp(-\beta P V) \exp[-\beta \mathcal{U}(s^N; L)] \\ &= \exp\{-\beta [\mathcal{U}(s^N, V) + P V - N \beta^{-1} \ln V]\}. \end{aligned} \quad (5.4.10)$$

We can now carry out Metropolis sampling on the reduced coordinates  $s^N$  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  $s$  (in particular, we should maintain the symmetry 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

$$\begin{aligned} \text{acc}(o \rightarrow n) &= \min(1, \exp\{-\beta [\mathcal{U}(s^N, V') - \mathcal{U}(s^N, V) \\ &\quad + P(V' - V) - N \beta^{-1} \ln(V'/V)]\}). \end{aligned} \quad (5.4.11)$$

Instead of attempting random changes in the volume itself, one might construct trial moves in the box length  $L$  [89] or in the logarithm of the volume [97]. Such trial moves are equally legitimate, as long as the symmetry of the underlying Markov chain is maintained. However, such alternative schemes result in a slightly different form for equation (5.4.11). The partition function (5.4.7) can be rewritten as

$$Q(N, P, T) = \frac{\beta P}{\Lambda^{3N} N!} \int d(\ln V) V^{N+1} \exp(-\beta P V) \int ds^N \exp[-\beta \mathcal{U}(s^N; L)]. \quad (5.4.12)$$

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

$$\mathcal{N}(V; s^N) \propto V^{N+1} \exp(-\beta P V) \exp[-\beta \mathcal{U}(s^N; L)]. \quad (5.4.13)$$

This distribution can be sampled with the following acceptance rule:

$$\text{acc}(o \rightarrow n) = \min \left( 1, \exp \{ -\beta [\mathcal{U}(s^N, V') - \mathcal{U}(s^N, V) + P(V' - V) - (N+1)\beta^{-1} \ln(V'/V)] \} \right). \quad (5.4.14)$$

## 5.4.2 Monte Carlo Simulations

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

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

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 the symmetry of the underlying Markov chain, volume moves should not be attempted periodically after a fixed number (say  $N$ ) positional trial moves. Rather, at every step there should be a probability  $1/N$  to attempt a volume move instead of a particle move. The criteria determining the optimal acceptance of volume moves are no different than those for particle moves.

In 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,

$$\begin{aligned} U_n &= \sum_{i<j} \epsilon(\sigma/r_{ij})^n \\ &= \sum_{i<j} \epsilon[\sigma/(Ls_{ij})]^n, \end{aligned} \quad (5.4.15)$$

or, possibly, a linear combination of such sums (the famous Lennard-Jones potential is an example of the latter category). Note that  $U_n$  in equation (5.4.15) changes in a trivial way if the volume is modified such that the linear dimensions of the system change for  $L$  to  $L'$ :

$$U_n(L') = \left(\frac{L}{L'}\right)^n U_n(L). \quad (5.4.16)$$

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 frequent as particle moves. One should be very careful when using the scaling property (5.4.16) if at the same time one uses a cutoff (say  $r_c$ ) on the range of the potential. Use of equation (5.4.16) implicitly assumes that the cutoff radius  $r_c$  scales with  $L$ , such that  $r'_c = r_c(L'/L)$ . The corresponding tail correction to the potential (and the virial) should also be recomputed to take into account both the different cutoff radius and the different density of the system.

Algorithms 2, 10, and 11 show the basic structure of a simulation in the NPT ensemble.

Finally, it is always useful to compute the virial pressure during a constant pressure simulation. On average, the virial pressure should always be equal to the applied pressure. This is easy to prove as follows. First of all, note that the virial pressure  $P_v(V)$  of an  $N$ -particle system at volume  $V$  is equal to

$$P_v(V) = - \left( \frac{\partial F}{\partial V} \right)_{NT}. \quad (5.4.17)$$

In an isothermal-isobaric ensemble, the probability-density  $\mathcal{P}(V)$  of finding the system with volume  $V$  is equal to  $\exp[-\beta(F(V) + PV)]/Q(\text{NPT})$ , where

$$Q(\text{NPT}) \equiv \beta P \int dV \exp[-\beta(F(V) + PV)].$$

**Algorithm 10 (Basic NPT-Ensemble Simulation)**

PROGRAM mc_npt	basic NPT ensemble simulation
do icycle=1,ncycl	perform ncycl MC cycles
ran=ranf()*(npart+1)+1	
if (ran.le.npart) then	
call mcmove	perform particle displacement
else	
call mcvol	perform volume change
endif	
if (mod(icycle,nsamp).eq.0)	
+ call sample	sample averages
enddo	
end	

*Comments to this algorithm:*

1. This algorithm ensures that, after each MC step, detailed balance is obeyed and that per cycle we perform (on average) `npart` attempts to displace particles and one attempt to change the volume.
2. Subroutine `mcmove` attempts to displace a randomly selected particle (Algorithm 2), and subroutine `mcvol` attempts to change the volume (Algorithm 11), and subroutine `sample` updates ensemble averages every `nsamp` cycle.

Let us now compute the average value of the virial pressure:

$$\begin{aligned}
 \langle P_v \rangle &= -\frac{\beta P}{Q(\text{NPT})} \int dV (\partial F(V)/\partial V) \exp[-\beta(F(V) + PV)] \\
 &= \frac{\beta P}{Q(\text{NPT})} \int dV \beta^{-1} (\partial \exp[-\beta F(V)]/\partial V) \exp(-\beta PV) \\
 &= \frac{\beta P}{Q(\text{NPT})} \int dV P \exp[-\beta(F(V) + PV)] \\
 &= P.
 \end{aligned} \tag{5.4.18}$$

The third line in this equation follows from partial integration.

Thus far we have limited our discussion of Monte Carlo at constant pressure to pure, atomic systems. Extension of the technique to mixtures is straightforward. The method is also easily applicable to molecular systems. However, in the latter case, it is crucial to note that only the center-of-mass

**Algorithm 11 (Attempt to Change the Volume)**

SUBROUTINE mcvol	attempts to change the volume
call toterg(box, eno)	total energy old conf.
vo=box**3	determine old volume
lnvn=log(vo) + (ranf() - 0.5) * vmax	perform random walk in $\ln V$
vn=exp(lnvn)	
boxn=vn**(1/3)	new box length
do i=1, npart	
x(i)=x(i)*boxn/box	rescale center of mass
enddo	
call toterg(boxn, enn)	total energy new conf.
arg=-beta*((enn-eno)+p*(vn-vo)	
+ - (npart+1)*log(vn/vo)/beta)	appropriate weight function!
if (ranf().gt.exp(arg)) then	acceptance rule (5.2.3)
do i=1, npart	REJECTED
x(i)=x(i)*box/boxn	restore the old positions
enddo	
endif	
return	
end	

*Comments to this algorithm:*

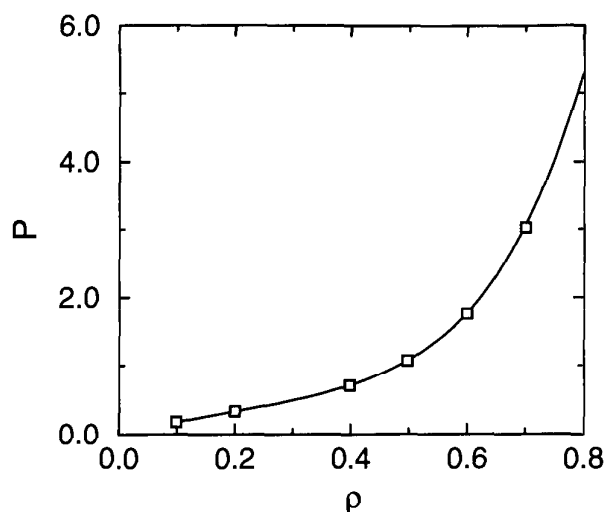
1. A random walk in  $\ln V$  is performed using acceptance rule (5.4.14).
2. The subroutine toterg calculates the total energy. Usually the energy of the old configuration is known; therefore this subroutine is called only once.

positions of the molecules should be scaled in a volume move, never the relative positions of the constituent atoms in the molecule. This has one practical consequence, namely, that the simple scaling relation (5.4.16) can never be used in molecular systems with site-site interactions. The reason is that, even if the center-of-mass separations between molecules scale as a simple power of the system size, the site-site separations do not.

### 5.4.3 Applications

#### Case Study 7 (Equation of State of the Lennard-Jones Fluid)

Simulations at constant pressure can be used also to determine the equation of state of a pure component. In such a simulation the density is determined



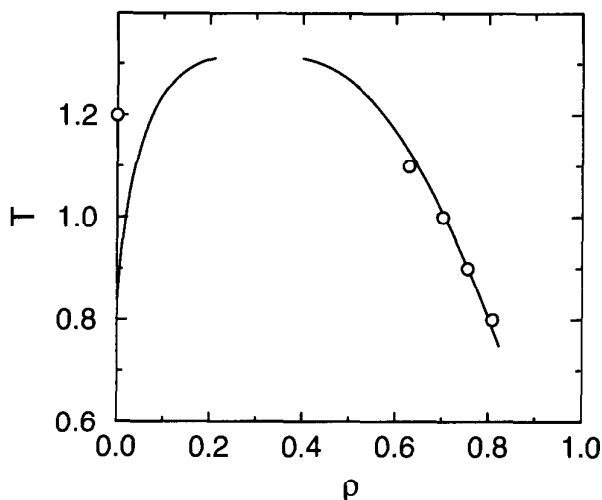
**Figure 5.3:** Equation of state of the Lennard-Jones fluid as obtained from N,P,T simulations; isotherms at  $T = 2.0$ . The solid line is the equation of state of Johnson *et al.* [62] and the squares are the results from the simulations ( $N = 108$ ).

as a function of the applied pressure and temperature. Figure 5.3 shows that, for the Lennard-Jones fluid, the results of an N,P,T simulation compare very well with those obtained in Case Study 1. In simulations of models of real molecules one would like to know whether under atmospheric conditions the model fluid has the same density as the real fluid. One would need to perform several N,V,T simulations to determine the density at which the pressure is approximately 1 atm. In an N,P,T simulation one would obtain this result in a single simulation. Furthermore, 1 atm is a relatively low pressure, and one would need long simulations to determine the pressure from an N,V,T simulation, whereas the density in general is determined accurately from an N,P,T simulation.

#### Case Study 8 (Phase Equilibria from Constant-Pressure Simulations)

In Case Studies 1 and 7 N,V,T or N,P,T simulations are used to determine the equation of state of a pure component. If these equation-of-state data are fitted to an analytical equation of state (for example, the van der Waals equation of state or more sophisticated forms of this equation), the vapor-liquid coexistence curve can be determined from Maxwell's equal area construction. Although this way of determining a coexistence curve is guaranteed to work for all systems, it requires many simulations and, therefore, is a rather cumbersome route. Alternative routes have been developed to determine vapor-liquid coexistence from a single simulation. In this case study we investigate one of them: zero pressure simulation.

A zero pressure simulation provides a quick (and dirty) way to obtain an



**Figure 5.4:** Vapor-liquid coexistence of the Lennard-Jones fluid; for each temperature the solid lines give at a given temperature the coexisting gas density (left curve) and the coexisting liquid density (right curve). The circles are the average densities obtained from N,P,T simulations at zero pressure. Important to note is that for  $T = 1.2$  the zero pressure method fails to predict coexistence.

estimate of the liquid coexistence density. If we perform a simulation at zero pressure and start with a density greater than the liquid density, the average density obtained from a simulation that is not too long will be close to the coexistence density. Such a simulation should not be too long because the probability exists that the system will undergo a large fluctuation in density. If this fluctuation is towards a lower density the system size can become infinitely large, since the equilibrium density that corresponds to zero pressure is exactly zero. Figure 5.4 shows the results for the Lennard-Jones fluid. Not too close to the critical temperature, a reasonable estimate of the liquid density can be obtained via a single simulation. Important to note is that this estimate deviates systematically from the true coexistence densities and this technique should not be used to determine the coexistence curve. This technique is very useful for obtaining a first estimate of the coexistence curve.

As explained below equation (5.4.17),  $\mathcal{P}(V)$ , the probability density of finding a system with volume  $V$  is proportional to  $\exp[-\beta(F(V) + PV)]$ . This probability density can be obtained from a constant-pressure simulation by constructing a histogram of the number of times a certain volume  $V$  is observed during the simulation. Once we know  $F(V)$  as a function of  $V$ , we can locate the coexistence points. In contrast to the zero pressure simula-

tions used in Case Study 8, this histogram technique does lead to a correct estimate of the coexistence density. One of the important applications of this technique is the investigation of finite-size effects. In practice this scheme for deriving  $F(V)$  from  $\mathcal{P}(V)$  only works near the critical point [98–101] unless special sampling techniques are used (see section 7.4).

## 5.5 Isotension-Isothermal Ensemble

The NPT-MC method is perfectly adequate for homogeneous fluids. However, for inhomogeneous systems, in particular crystalline solids, it may not be sufficient that the simulation box can change size. Often we are interested in the transformation of a crystal from one structure to another or even in the change of the shape of the crystalline unit cell with temperature or with applied stress. In such cases it is essential that the shape of the simulation box has enough freedom to allow for such changes in crystal structure without creating grain boundaries or other highly stressed configurations. This problem was first tackled by Parrinello and Rahman [102, 103], who developed an extension of the constant-pressure Molecular Dynamics technique introduced by Andersen [104]. The extension of the Parrinello-Rahman method to Monte Carlo simulations is straightforward (actually, the method is quite a bit simpler in Monte Carlo than in Molecular Dynamics).

To our knowledge, the first published account of constant-stress Monte Carlo is a paper by Najafabadi and Yip [90]. At the core of the constant-stress Monte Carlo method lies the transformation from the scaled coordinates  $\mathbf{s}$  to the real coordinates  $\mathbf{q}$ . If the simulation box is not cubic and not orthorhombic, the transformation between  $\mathbf{s}$  and  $\mathbf{r}$  is given by a matrix  $\mathbf{h}$ :  $r_\alpha = h_{\alpha\beta} s_\beta$ . The volume of the simulation box  $V$  is equal to  $|\det \mathbf{h}|$ . Without loss of generality we can choose  $\mathbf{h}$  to be a symmetric matrix. In the constant-stress Monte Carlo procedure certain moves consist of an attempted change of one or more of the elements of  $\mathbf{h}$ . Actually, it would be equally realistic (but not completely equivalent) to sample the elements of the metric tensor  $\mathbf{G} = \mathbf{h}^T \mathbf{h}$ , where  $\mathbf{h}^T$  is the transpose of  $\mathbf{h}$ . If only hydrostatic external pressure is applied, the constant-stress Monte Carlo method is almost equivalent to constant-pressure Monte Carlo.<sup>3</sup> Under nonhydrostatic pressure (e.g., uniaxial stress), there is again some freedom of choice in deciding how to apply such deforming stresses. Probably the most elegant method (and the method that reflects most closely the statistical thermodynamics of deformed solids)

<sup>3</sup>Except that one should never use the constant-stress method for uniform fluids, because the latter offer no resistance to the deformation of the unit box and very strange (flat, elongated, etc.) box shapes may result. This may have serious consequences because simulations on systems that have shrunk considerably in any one dimension tend to exhibit appreciable finite-size effects.