

1 Other ensembles in MC

In a conventional Molecular Dynamics simulation, the total energy E and the total linear momentum \mathbf{P} are constants of motion. Hence, Molecular Dynamics simulations measure (time) averages in an ensemble that is very similar to the microcanonical); namely, the constant-NVE ensemble. In contrast, a conventional Monte Carlo simulation probes the canonical (i.e., constant-NVT) ensemble. The fact that these ensembles are different leads to observable differences in the statistical averages computed in Molecular Dynamics and Monte Carlo simulations. Most of these differences disappear in the thermodynamic limit and are already relatively small for systems of a few hundred particles. However, the choice of ensemble does make a difference when computing the mean-squared value of fluctuations in thermodynamic quantities. Fortunately, techniques exist to relate fluctuations in different ensembles [80]. Moreover, nowadays it is common practice to carry out Molecular Dynamics simulations in ensembles other than the microcanonical. In particular, it is possible to do Molecular Dynamics at constant pressure, at constant stress, and at constant temperature. The choice of ensembles for Monte Carlo simulations is even wider: isobaric-isothermal, constant-stress-isothermal, grand canonical (i.e., constant μVT), and even microcanonical [88-93]. A more recent addition to this list is a Monte Carlo method that employs the Gibbs ensemble technique [94], which was developed to study phase coexistence in moderately dense (multicomponent) fluids. The Gibbs ensemble method is discussed in detail in Chapter 8.

As explained in section 3.1 the principal idea of importance sampling is to use a Monte Carlo procedure to generate a random walk in those regions of phase space that have an important contribution to the ensemble averages. The acceptance rules are chosen such that these configurations occur with a frequency prescribed by the desired

probability distribution. In section 3.1 it is shown that such a procedure indeed yields the correct distribution of configurations. Essential in the demonstration that our Monte Carlo scheme samples the desired distribution is the condition of detailed balance. To be more precise, detailed balance, in fact, is too strong a condition, but if detailed balance is obeyed we are guaranteed to have a correct sampling scheme. It may very well be possible that a scheme that does not obey detailed balance still samples the correct distribution. In a Monte Carlo scheme errors are easily introduced, so one should be extremely careful. We will give some examples where we can show that detailed balance is not obeyed and the results show systematic errors. We have found that we could demonstrate that detailed balance was not obeyed in all cases where we observed strange results.

1.1 General Approach

In the following sections, we will use the following procedure to demonstrate the validity of our Monte Carlo algorithms:

- 1. Decide which distribution we want to sample. This distribution, denoted \mathcal{N} will depend on the details of the ensemble.
- 2. Impose the condition of detailed balance,

$$\mathcal{K}(o \rightarrow n) = \mathcal{K}(n \rightarrow o)$$

where $\mathcal{K}(o \rightarrow n)$ is the flow of configuration o to n . This flow is given by the product of the probability of being in configuration o , the probability of generating configuration n , and the probability of accepting this move,

$$\mathcal{K}(o \rightarrow n) = \mathcal{N}(o) \times \alpha(o \rightarrow n) \times acc(o \rightarrow n)$$

- 3. Determine the probabilities of generating a particular configuration.

- 4. Derive the condition that needs to be fulfilled by the acceptance rules.

2 Isobaric-Isothermal – Frenkel Smith

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.

2.1 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-N V-I- 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

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

It is convenient to rewrite this equation 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

$$\mathbf{r}_i = L\mathbf{s}_i$$

If we now insert these scaled coordinates in the expression for the partition function, we obtain

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

In this equation 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

$$F(N, V, T) = -k_B T \ln Q(N, V, T) = -k_B T \ln \frac{V^N}{\Lambda^{3N} N!} - k_B T \ln \int_0^1 \dots \int_0^1 \exp[-\beta \mathcal{U}(\mathbf{s}^N, L)] d\mathbf{s}^N$$

$$F^{idealgas}(N, V, T) + F^{excess}(N, V, T)$$

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 from an ideal gas reservoir (see Figure 5.2).

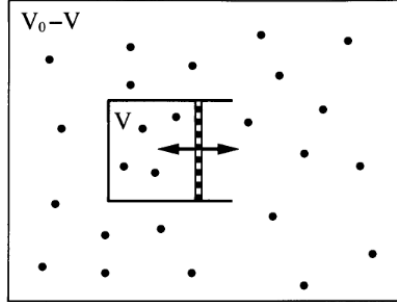


Figure 5.2: Ideal gas (m particles, volume $V_0 - V$) can exchange volume with an N -particle system (volume V).

The total volume of this 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: The system S subsystem is defined by the N particle in the volume V , with

$$Q_S(N, V, T) = \frac{V^N}{\lambda^{3N} N!} \int d\mathbf{s}^N \exp[-\beta \mathcal{U}(\mathbf{s}^N, L)] \quad (1)$$

while the reservoir R subsystem, composed by ideal gas particles, has

$$Q_R(M - N, V_0 - V, T) = \frac{(V_0 - V)^{M-N}}{\lambda^{3(M-N)} (M - N)!} \int d\mathbf{s}^{M-N}$$

The final partition function $Q(N, MV, V_0, T)$ is the product

$$Q(N, MV, V_0, T) = Q_S(N, V, T) Q_R(M - 1, V_0 - V, T)$$

For the sake of compactness, we have assumed that the thermal wavelength of the ideal gas molecules is also equal to λ . The total free energy of this combined system is $F^{tot} = -k_B T \ln Q(N, MV, V_0, T)$.

We now consider the limit that the size of the reservoir tends to infinity, ($V_0 \rightarrow \infty$, $M \rightarrow \infty$, $(M - V)/V_0 \rightarrow \rho$). 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 Eq. 2.1.

Remembering the thermodynamic relations

$$F = U - TS, \quad G = N\mu = F + PV, \quad \beta F = N\beta\mu - \beta PV$$

and the relation

$$\beta F_R = -\ln[Q_R(M - N, V_0 - V, T)]$$

then

$$Q_R(M - N, V_0 - V, T) = \exp[-\beta F_R(M - N, V_0 - V, T)] = \exp[-(M - N)\beta\mu + \beta P(V_0 - V)]$$

where the only dependence on the small system volume is in the $\exp[-\beta PV]$ contribution.

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. If we now allow the composed system to change the volume, then we need to sum over all possible V values. Then Eq. 2.1, integrated over all possible volumes can be written as

$$\begin{aligned} Q(N, P, T) &\equiv \beta P \int_0^\infty dV \exp[-(M - N)\beta\mu] \exp[+\beta P(V_0 - V)] Q_S(N, V, T) = \\ &= \beta P \exp[-(M - N)\beta\mu] \exp[+\beta P V_0] \int_0^\infty dV \exp[-\beta PV] Q_S(N, V, T) \end{aligned}$$

Focusing only on the V -dependent part

$$\beta P \int dV V^N \exp[-\beta PV] \int ds^N \exp[-\beta \mathcal{U}(\mathbf{s}^N, L)],$$

Since N , P , T and M are fixed quantities, they can all be reassorbed in the normalization, leaving

$$Q(N, P, T) \equiv \beta P \int dV V^N \exp[-\beta PV] \int ds^N \exp[-\beta \mathcal{U}(\mathbf{s}^N, L)]$$

where we have included a factor βP to make $Q(N, P, T)$ dimensionless (this choice is not obvious). Note that the corresponding generalized thermodynamic potential is the Gibbs free energy

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

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

$$\mathcal{N}_{N,P,T}(V) = \frac{V^N \exp[-\beta PV] \int ds^N \exp[-\beta \mathcal{U}(\mathbf{s}^N, L)]}{\int dV' V'^N \exp[-\beta PV'] \int ds^N \exp[-\beta \mathcal{U}(\mathbf{s}^N, L)]}, \quad (2)$$

Equation Eq 2 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 \mathbf{s}^N) at a given volume V is given by

$$\mathcal{N}(V, \mathbf{s}^N) \sim V^N \exp[-\beta PV] \int ds^N \exp[-\beta \mathcal{U}(\mathbf{s}^N, L)] \quad (3)$$

$$= \exp[-\beta \mathcal{U}(\mathbf{s}^N, L) + PV - N\beta^{-1} \ln V] \quad (4)$$

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 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 ΔV 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

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

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 for the acceptance rule. The partition function $Q(N, P, T)$ can be rewritten as

$$Q(N, P, T) = \frac{\beta P}{\lambda^{3N} N!} \int d \ln V V^{N+1} \exp[-\beta P V] \int d\mathbf{s}^N \exp[-\beta \mathcal{U}(\mathbf{s}^N, V)]$$

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

$$\mathcal{N}(V, \mathbf{s}^N) \sim V^{N+1} \exp[-\beta P V] \exp[-\beta \mathcal{U}(\mathbf{s}^N, V)]$$

This distribution can be sampled with the following acceptance rule:

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

2.2 Implementation

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

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

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,

$$\mathcal{U}_n = \sum_{i < j} \epsilon \left(\frac{\sigma}{r_{ij}} \right)^n = \sum_{i < j} \epsilon \left(\frac{\sigma}{L s_{ij}} \right)^n$$

or, possibly, a linear combination of such sums (the famous Lennard-Jones potential is an example of the latter category). Note that \mathcal{U}_n in the previous equation changes in a trivial way if the volume is modified such that the linear dimensions of the system change for L to L'

$$\mathcal{U}_n(L') = \left(\frac{L}{L'} \right)^n \mathcal{U}_n$$

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 if at the same time one uses a cutoff (say r_c) on the range of the potential. Use of the previous equation implicitly assumes that the cutoff radius r_c scales with L . e.g. $r'_c = (L'/L)r_c$. The corre-

sponding 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.

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

$$P_v(V) = - \left(\frac{\partial F}{\partial V} \right)_{N,T}$$

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

$$Q(N, P, T) = \beta P \int dV \exp[-\beta(F(V) + PV)]$$

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

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

Integrating by parts

$$\begin{aligned} &\int dV \frac{\partial \exp[-\beta(F(V))]}{\partial V} \exp[-\beta PV] = \\ &\exp[-\beta(F(V)) \exp[-\beta PV]]_0^\infty - \int \exp[-\beta(F(V))] d \exp[-\beta PV] \end{aligned}$$

and assuming that $F(0) = \infty$ (infinite high density, since N is fixed)

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

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 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 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.

2.3 Equation of state

2.4 $\mathcal{P}(V)$

$\mathcal{P}(V)$, 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. 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 unless special sampling techniques are used.

3 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).

In this case, one defines the box coordinates by three vectors \mathbf{a} , \mathbf{b} , \mathbf{c} such that the volume is $\det|\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}|$. A change in these three vectors generates a volume change and, at the same time, a change in the box geometry. Particles are located by the scaled vectors \mathbf{s}_i , related to the real coordinates by the transform

$$\begin{bmatrix} x_i \\ y_i \\ z_i \end{bmatrix} = \begin{bmatrix} a_x & b_x & c_x \\ a_y & b_y & c_y \\ a_z & b_z & c_z \end{bmatrix} \begin{bmatrix} s_{xi} \\ s_{yi} \\ s_{zi} \end{bmatrix} \quad (5)$$

or defining the matrix \mathbf{h}

$$\mathbf{h} = \begin{bmatrix} a_x & b_x & c_x \\ a_y & b_y & c_y \\ a_z & b_z & c_z \end{bmatrix} \quad (6)$$

$$\mathbf{r}_i = \mathbf{h}\mathbf{s}_i$$

Of the nine elements of \mathbf{h} only six are independent, since a rotation of the box does not change the system. Hence, one can fix \mathbf{a} along \hat{x} and \mathbf{b} in the xy plane.

$$\mathbf{h} = \begin{bmatrix} a_x & b_x & c_x \\ 0 & b_y & c_y \\ 0 & 0 & c_z \end{bmatrix} \quad (7)$$

or without loss of generality we can choose \mathbf{h} to be a symmetric matrix.

A MC step in any of the six non-vanishing element of h can be performed and the move can be accepted or rejected with the previously derived probability for volume changes.

4 Grand Canonical Simulations (Frenkel)

The original Metropolis scheme could not be used to determine those thermodynamic properties of a system that depend explicitly on the configurational integral. Examples of such thermal properties are the Helmholtz free energy F , the entropy S , and the Gibbs free energy G . However, although the Metropolis method cannot be used to measure, for instance, free energies directly, it can be used to measure the difference in free energy between two possible states of an N -body system. This fact is exploited in the grand-canonical Monte Carlo method first implemented for classical fluids by Norman and Filinov [91], and later extended and improved by a number of other groups [92, 106-113]. The basic idea of the grand-canonical Monte Carlo method is explained next. To understand the statistical mechanical basis for the grand-canonical Monte Carlo technique, let us recall the equation that gives the partition function of a combined system of N interacting particles in volume V and $M - N$ ideal gas molecules in volume $V - V_0$

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

Now, instead of allowing the two systems to exchange volume, let us see what happens if the systems can exchange particles. To be more

precise, we assume that the molecules in the two sub-volumes are actually identical particles. The only difference is that when they find themselves in volume V , they interact and, when they are in volume $V_0 - V$, they do not. If we transfer a molecule i from a reduced coordinate \mathbf{s}_i in the volume $V_0 - V$ to the same reduced coordinate in volume V , then the potential energy function \mathcal{U} changes from $\mathcal{U}(\mathbf{s}^N)$ to $\mathcal{U}(\mathbf{s}^{N+1})$. The expression for the total partition function of the system, including all possible distributions of the M particles over the two sub-volumes (that creates the $\sum_{N=0}^M$) is

$$Q(N, M, V, V_0, T) = \sum_{N=0}^M \frac{V^N (V_0 - V)^{M-N}}{\Lambda^{3M} N! (M - N)!} \int d\mathbf{s}^{M-N} \int d\mathbf{s}^N \exp[-\beta \mathcal{U}(\mathbf{s}^N)]$$

The probability density $\mathcal{N}(\mathbf{s}^N, V, \mathbf{s}^{M-N}, V_0 - V)$ to find a system with $M - N$ particles at reduced coordinates \mathbf{s}^{M-N} in volume $V' = V_0 - V$ and N particles at reduced coordinates \mathbf{s}^N in volume V is

$$\mathcal{N}(\mathbf{s}^N, V, \mathbf{s}^{M-N}, V_0 - V) = \frac{V^N V'^{M-N}}{Q(N, M, V, V_0, T) \Lambda^{3M} N! (M - N)!} \exp[-\beta \mathcal{U}(\mathbf{s}^N)]$$

such that

$$\sum_{N=0}^M \int d\mathbf{s}^{M-N} \int d\mathbf{s}^N \mathcal{N}(\mathbf{s}^N, V, \mathbf{s}^{M-N}, V_0 - V) = 1$$

Now let us consider the limit that the ideal gas system is very much larger than the interacting system: $M \rightarrow \infty$, $V' \rightarrow \infty$, $(M/V') \rightarrow \rho$. As we did before, we can write in the thermodynamic limit

$$\begin{aligned} Q_R(N, V, T) &= \exp[-\beta F_R] = \exp[-(M - N)\beta\mu + \beta P(V - V_0)] \\ &= \exp[N\beta\mu] \exp[-M\beta\mu + \beta P(V - V_0)] \end{aligned}$$

where the only part depending on N is $\exp[N\beta\mu]$.

Therefore, in the limit $M/N \rightarrow \infty$, reabsorbing in the normalization all quantities which do not depend on N (being V , T , μ fixed) the partition function becomes

$$Q(\mu, V, T) = \sum_{N=0}^{\infty} \frac{V^N}{\lambda^{3N} N!} \exp[N\beta\mu] \int d\mathbf{s}^N \exp[-\beta\mathcal{U}(\mathbf{s}^N)]$$

and the corresponding probability density

$$\mathcal{N}_{\mu, V, T}(N, \mathbf{s}^N) \sim \frac{V^N}{\lambda^{3N} N!} \exp[N\beta\mu] \exp[-\beta\mathcal{U}(\mathbf{s}^N)]$$

The last two equations are the basic equations for Monte Carlo simulations in the grand-canonical ensemble. Note that, in these equations, all explicit reference to the ideal gas system has disappeared.

5 Grand Canonical Simulation

We have seen that any acceptance rule that allows for detailed balance with the proper probability distribution is a proper rule for sampling the desired ensemble. We recall that detailed balance requires (if the probability to select the move $o \rightarrow n$ and $n \rightarrow o$ have the same probability by construction (e.g. same amounts of attempt to insert or delete a particle))

$$P(o)acc(o \rightarrow n) = \mathcal{N}(N)acc(n \rightarrow o)$$

In the case of the grand canonical ensemble, at fixed V and T

$$\mathcal{Z}(V, T, z) = \sum_{N=0}^{\infty} \frac{z^N V^N}{\Lambda^{3N} N!} \int d\mathbf{r}^N \exp[-\beta\mathcal{U}(\mathbf{s}^N, V)]$$

and the probability to find a system with N particles in \mathbf{s}^N is

$$\mathcal{N}(N, \mathbf{s}^N, z, V) = \frac{1}{\mathcal{Z}(V, T, z)} \frac{z^N V^N}{\Lambda^{3N} N!} \exp[-\beta \mathcal{U}(\mathbf{s}^N, V)]$$

If in the MC code the probability that an attempt is made to remove a particle is equal to the probability of attempting to add one (e.g. $\alpha(N \rightarrow N+1) = \alpha(N+1 \rightarrow N)$) then the probability distribution $\mathcal{N}(N, \mathbf{s}^N, z, V)$ suggests a Metropolis rule of the type

$$\begin{aligned} & \text{acc}(N_{\text{initial}} \rightarrow N_{\text{final}}) = \\ & \text{Min} \left(1, \frac{z^{N_{\text{final}} - N_{\text{initial}}} V^{N_{\text{final}} - N_{\text{initial}}} N_{\text{initial}}!}{\Lambda^{3(N_{\text{final}} - N_{\text{initial}})} N_{\text{final}}!} \exp[-\beta \mathcal{U}(\mathbf{s}^{N_{\text{final}}}, V) + \beta \mathcal{U}(\mathbf{s}^{N_{\text{initial}}}, V)] \right) \end{aligned}$$

that gives for the addition of a particle

$$\text{acc}(N \rightarrow N+1) = \text{Min} \left(1, \frac{zV}{\Lambda^3(N+1)} \exp[-\beta \mathcal{U}(\mathbf{s}^{N+1}, V) + \beta \mathcal{U}(\mathbf{s}^N, V)] \right)$$

and, for the delation of a particle,

$$\text{acc}(N \rightarrow N-1) = \text{Min} \left(1, \frac{\Lambda^3 N}{zV} \exp[-\beta \mathcal{U}(\mathbf{s}^{N-1}, V) + \beta \mathcal{U}(\mathbf{s}^N, V)] \right)$$

5.1 What do we learn from a GC simulation

In principle, a well converged GC simulation provides an accurate estimate of $\mathcal{N}(N, z)$. If the histogram of the potential energy for each N has also been saved, then one has the reacher $\mathcal{N}(N, E, z)$ distribution.

From $\mathcal{N}(N, z)$, several interesting quantities can be calculated. The simplest is the density, $\rho = \frac{\sum_N N \mathcal{N}(N)}{V}$.

It is also possible to evaluate the pressure. Since the grand potential is $\exp(\beta PV)$, then

$$\sum_N z^N Z_N = \exp(\beta PV)$$

Hence

$$\mathcal{N}(N) = \frac{1}{\exp(\beta PV)} z^N Z_N$$

But since $Z_0 = 1$,

$$\mathcal{N}(0) = \frac{1}{\exp(\beta PV)}$$

or

$$\beta PV = -\ln(\mathcal{N}(0))$$

Thus, if the simulation is able to sample all densities down to $N = 0$, then it is possible to evaluate P without calculating any virial. This is convenient for example for hard-bodies, when impulsive forces are present.

A GC simulation is surely rather expensive, since to be well converged, it has to sample all different N and all different configuration at fixed N . Assuming this is the case, then one can recover canonical quantities from the grand canonical data. Remembering that $Z(0) = 1$,

$$\frac{\mathcal{N}(N)}{\mathcal{N}(0)} = \frac{z^N}{\lambda^{3N} N!} Z_N$$

and that $\exp[-\beta F_N] = \frac{Z_N}{\lambda^{3N} N!}$

$$\frac{\mathcal{N}(N)}{\mathcal{N}(0)} = z^N \exp[-\beta F_N]$$

Then it is possible to evaluate the free energy

$$-\beta F_N = \ln \left[\frac{\mathcal{N}(N)}{\mathcal{N}(0)} \right] - N \ln z$$

(where z is the activity of the GC run).

Let's now consider the ratio

$$\frac{\mathcal{N}(N)}{\mathcal{N}(N+1)} = \frac{1}{z} \exp[\beta F_{N+1} - \beta F_N]$$

If N is rather large, then one make use of the thermodynamic relation

$$\frac{\partial F}{\partial N} = \mu \approx \frac{F_{N+1} - F_N}{1}$$

so that

$$z \frac{\mathcal{N}(N)}{\mathcal{N}(N+1)} = \exp[\beta \mu_N]$$

Exploiting the thermodynamic definitions

$$N\beta\mu_N = \beta A_N + \beta P_N V$$

one can find the entire equation of states

$$\begin{aligned} \beta P_N V &= N \ln \left[z \frac{\mathcal{N}(N)}{\mathcal{N}(N+1)} \right] + \ln \left[\frac{\mathcal{N}(N)}{\mathcal{N}(0)} \right] - N \ln z = N \ln \left[\frac{\mathcal{N}(N)}{\mathcal{N}(N+1)} \right] + \ln \left[\frac{\mathcal{N}(N)}{\mathcal{N}(0)} \right] = \\ &= (N+1) \ln \mathcal{N}(N) - N \ln \mathcal{N}(N+1) - \ln \mathcal{N}(0) \end{aligned}$$

Hence, $\mathcal{N}(0)$ acts as a constant, but the entire N (or ρ) dependence is encoded in $\mathcal{N}(N)$ and $\mathcal{N}(N+1)$. Interestingly, this expression is independent on z (we will understand this better later on, when discussing histogram reweigh).

5.2 Histogram Reweigh

5.2.1 In z

Consider we have performed a GCMC simulation at one selected value of the activity z_1 and we are interested in predicting $\mathcal{N}(N)$ at a different z_2 value. The ratio between $\mathcal{N}(N, z_1)$ and $\mathcal{N}(N, z_2)$ is

$$\frac{\mathcal{N}(N, z_1)}{\mathcal{N}(N, z_2)} = \frac{\frac{1}{\mathcal{Z}(V, T, z_1)} \frac{z_1^N}{\Lambda^{3N} N!} Z_N}{\frac{1}{\mathcal{Z}(V, T, z_2)} \frac{z_2^N}{\Lambda^{3N} N!} Z_N} = \frac{\mathcal{Z}(V, T, z_2)}{\mathcal{Z}(V, T, z_1)} \left(\frac{z_1}{z_2} \right)^N$$

Since the only N dependence is in the exponent, we obtain (calling $\mathcal{K} = \frac{\mathcal{Z}(V, T, z_1)}{\mathcal{Z}(V, T, z_2)}$)

$$\mathcal{N}(N, z_2) = \mathcal{K} \mathcal{N}(N, z_1) \left(\frac{z_2}{z_1} \right)^N$$

where the constant \mathcal{K} can be determined by imposing $\sum_N \mathcal{N}(N, z_2) = 1$.

If we go back to the previous expression for the equation of state,

$$\begin{aligned} & (N + 1) \ln \mathcal{N}(N, z_2) - N \ln \mathcal{N}(N + 1, z_2) - \ln \mathcal{N}(0, z_2) = \\ & (N + 1) \ln \mathcal{N}(N, z_1) - N \ln \mathcal{N}(N + 1, z_1) - \ln \mathcal{N}(0, z_1) + (N + 1) \ln \mathcal{K} - N \ln \mathcal{K} - \ln \mathcal{K} + \\ & (N + 1) \ln \left(\frac{z_2}{z_1} \right)^N - N \ln \left(\frac{z_2}{z_1} \right)^N - \ln \left(\frac{z_2}{z_1} \right)^N \end{aligned}$$

e.g.

$$\begin{aligned} & (N + 1) \ln \mathcal{N}(N, z_2) - N \ln \mathcal{N}(N + 1, z_2) - \ln \mathcal{N}(0, z_2) \\ & = (N + 1) \ln \mathcal{N}(N, z_1) - N \ln \mathcal{N}(N + 1, z_1) - \ln \mathcal{N}(0, z_1) \end{aligned}$$

that proves that the equation of state does not depend on the value of z selected in the GCMC simulation

5.2.2 In T

If the entire histogram of potential energy values E has been recorded during the simulation, it is also possible to calculate $\mathcal{N}(N, E)$ at a T different from the one used in the simulation. Indeed

$$\mathcal{N}(N, E, z, \beta) = \frac{1}{\mathcal{Z}(V, T, z)} \frac{z^N}{\Lambda^{3N} N!} \Omega(E) \exp[-\beta E]$$

where we have written

$$Z_N = \sum_E \Omega(E) \exp[-\beta E]$$

Assuming we are interested into a different β_2 . Then

$$\frac{\mathcal{N}(N, E, z, \beta_1)}{\mathcal{N}(N, E, z, \beta_2)} = \frac{\mathcal{Z}(V, T_2, z) \exp[-\beta_1 E]}{\mathcal{Z}(V, T_1, z) \exp[-\beta_2 E]} = \mathcal{K} \exp[-(\beta_1 - \beta_2)E]$$

so that

$$\mathcal{N}(N, E, z, \beta_2) = \mathcal{N}(N, E, z, \beta_1) \mathcal{K} \exp[-(\beta_2 - \beta_1)E]$$

and

$$\mathcal{N}(N, z, \beta_2) = \mathcal{K} \sum_E \mathcal{N}(N, E, z, \beta_1) \exp[-(\beta_2 - \beta_1)E]$$

Once again, \mathcal{K} can be determined by the normalization of the distribution.

6 Successive Umbrella Sampling

We have seen how convenient GCMC is for providing thermodynamic information on the system. We will later on see how useful GCMC informations are for estimating phase coexistence and surface tension. It is thus of paramount important to be able to generate well converged histograms, both in N and in E . One particularly convenient way has been proposed by Virnau and M. Müller, J. Chem. Phys. 120, 10925 (2004) to exploit the computer power made available by massive clusters, effectively parallellizing the evaluation of $\mathcal{N}(N)$. The trick is based on the distribution of different N intervals over different processors, asking each processor only to evaluate $\mathcal{N}(N+1)/\mathcal{N}(N)$ for a fixed N values. The code thus reject all moves for which the number of particles leave the selected interval $[N, N+1]$.

Note that if the number of particles in the system is already $N+1$, the insertion move is reject, but the histogram is incremented. Similarly, if the number of particles in the system is already N , the deletion move is rejected but the histogram is incremented. Indeed, the rejection due to boundary crossing is equivalent to a unconstrained trajectory that leave the boundary and comes back.

When all products $\mathcal{N}(N+1)/\mathcal{N}(N)$ have been calculated, they can be combined

$$\frac{\mathcal{N}(N)}{\mathcal{N}(N-1)} \frac{\mathcal{N}(N-1)}{\mathcal{N}(N-2)} \cdots \frac{\mathcal{N}(3)}{\mathcal{N}(2)} \frac{\mathcal{N}(2)}{\mathcal{N}(1)} \frac{\mathcal{N}(1)}{\mathcal{N}(0)} = \frac{\mathcal{N}(N)}{\mathcal{N}(0)}$$

and again the unknown $\mathcal{N}(0)$ can be fixed by normalization. We note on passing that in some cases (e.g. in phase separation) can be convenient to sum the log of the ratios to avoid numerical divergences.

$$\ln \mathcal{N}(N) - \ln \mathcal{N}(0) = \sum_{i=1}^N \ln \frac{\mathcal{N}(i)}{\mathcal{N}(i-1)}$$