

Chem 860. Lecture 16

Advanced Monte Carlo: different ensembles

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1 Monte Carlo simulation of various ensembles

It is very straightforward to develop Monte Carlo methods for different ensembles. All we have to do is to include new types of moves that reflect the character of the ensemble (e.g., volume move for isobaric), and develop acceptance rule for the move such that detailed balance is satisfied. In general, if we make the move-generation step symmetric (i.e., $\alpha(o \rightarrow n)$ symmetric), the task of developing acceptance rule is reduced to finding the probability distribution associated with the move variable (e.g., volume); because we can always use the Metropolis scheme:

$$acc(o \rightarrow n) = \min\left\{1, \frac{\mathcal{N}(n)}{\mathcal{N}(o)}\right\}$$

1.1 Isobaric-isothermal ensemble - NPT

Consider that the system of interest (N, V, T) is in contact with a much larger bath system ($M - N, V_0, T$) through a piston; the latter contain ideal gas of fixed pressure P . The volume V can fluctuate such that the pressure of the system of interest is a constant. To develop a Monte Carlo scheme for the NPT ensemble, we simply have to add a move that changes the volume V . For the corresponding acceptance rule, we have find $\mathcal{N}(V)$ or $\mathcal{N}(V, \mathbf{r}^N)$.

The canonical partition function for a NVT system is given as:

$$Q_{NVT} = \frac{1}{\Lambda^{3N} N!} \int d\mathbf{r}^N e^{-\beta U(\mathbf{r}^N)}$$

where Λ is the thermal wavelength ($h/\sqrt{2\pi m k_B T}$).

Assuming that we deal with a cube of box length L , we can define a set of scaled coordinates:

$$\mathbf{s}^N = L^{-3} \mathbf{r}^N$$

and the partition function has explicit V -dependence

$$Q_{NVT} = \frac{V^N}{\Lambda^{3N} N!} \int d\mathbf{s}^N e^{-\beta U(\mathbf{s}^N; L)}$$

Taking the ideal gas in the bath-system into account, the total partition function is

$$Q_{NVT; M, V_0} = \frac{V^N (V_0 - V)^{M-N}}{\Lambda^{3M} N! (M - N)!} \int d\mathbf{s}^N e^{-\beta U(\mathbf{s}^N; L)}$$

Note that there is no configuration integral contribution from the bath because it contains ideal gas.

Using this expression, we can write the distribution of volume,

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

We note that if we take the bath to be extremely large, i.e., $M \rightarrow \infty$, $V_0 \rightarrow \infty$, we have the approximation,

$$(V_0 - V)^{M-N} = V_0^{M-N} \left\{1 - \frac{V}{V_0}\right\}^{M-N} = V_0^{M-N} e^{-(M-N)V/V_0} = V_0^{M-N} e^{-\beta PV}$$

where we used the fact that the bath contains ideal gas of well defined volume, pressure and temperature. Substituting this result into the expression of $\mathcal{N}(V)$, it is easy to see that

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

which means that the acceptance rule for the volume move is

$$acc(V_{old} \rightarrow V_{new}) = \min\{1, \exp\{-\beta[\Delta U(\mathbf{s}^N; L) + P\Delta V - N\beta^{-1} \ln(V_{new}/V_{old})]\}\}$$

Note that the potential energy contributes because the inter-particle distances change once the volume of the system changes (i.e., it is \mathbf{s}^N held fixed during the volume move). As a result, the volume move is expensive because the total potential energy has to be calculated. In realistic simulations, one should invoke the volume move with the probability of $1/N$, N being the number of particles in the system.

1.2 Grand Canonical ensemble - GCMC

Grand canonical ensemble is very powerful when studying absorption or water distribution in the interior of biomolecules, for example. We use the same bath-system “trick” to think about GCMC, except that now the system and bath can exchange particles as well. For simplicity, we consider the μVT ensemble in which the volume of the system is constant.

The canonical partition function of the entire system-bath is given as

$$Q_{M,V,V_0,T} = \sum_{N=0}^M \frac{V^N (V_0 - V)^{M-N}}{\Lambda^{3M} N! (M-N)!} \int d\mathbf{s}^N e^{-\beta U(\mathbf{s}^N; L)}$$

The probability distribution for N is then given as

$$\mathcal{N}(N, \mathbf{s}^N) = \frac{V^N (V_0 - V)^{M-N} e^{-\beta U(\mathbf{s}^N; L)}}{Q_{M,V,V_0,T} \Lambda^{3M} N! (M-N)!}$$

Using the same large-bath limit, one can show that the probability distribution is simplified to be

$$\mathcal{N}(N, \mathbf{s}^N) \sim \frac{e^{\beta \mu N} V^N e^{-\beta U(\mathbf{s}^N; L)}}{\Lambda^{3N} N!}$$

where μ is the chemical potential imposed by the bath.

This immediately suggests the following acceptance rules:

$$acc(N \rightarrow N+1) = \min\left\{1, \frac{V}{\Lambda^3(N+1)} \exp[\beta(\mu - U(N+1) + U(N))]\right\}$$

$$acc(N \rightarrow N-1) = \min\left\{1, \frac{\Lambda^3 N}{V} \exp[-\beta(\mu + U(N-1) - U(N))]\right\}$$

where notations such as $U(N+1)$ indicate the potential energy of the system containing a specific number of particles. One can show that this set of acceptance rule satisfy the detailed balance.

In practical simulations, the difficulty is associated with the insertion move because one has to be careful about where to insert the new particle; otherwise, the acceptance probability is very small. For a recent example of implementation for studying water/ion distribution in biomolecules, see *J. Chem. Phys.*, **121**, 6392.