1 Biased Moves: Beyond Metropolis

The general idea of biased sampling is best explained by considering a simple example. Let us assume that we have developed a Monte Carlo scheme that allows us to generate trial configurations with a probability that depends on the potential energy of that configuration:

$$\alpha(o \to n) = f[\mathcal{U}(n)]$$

For the reverse move, we have

$$\alpha(n \to o) = f[\mathcal{U}(o)]$$

Suppose we want to sample the N,V,T ensemble, which implies that we have to generate configurations with a Boltzmann distribution. Imposing detailed balance yields, as a condition for the acceptance rule,

$$\frac{acc(o \to n)}{acc(n \to o)} = \frac{f[\mathcal{U}(n)]}{f[\mathcal{U}(o)]} \exp[-\beta[\mathcal{U}(n) - \mathcal{U}(o)]$$

A possible acceptance rule that obeys this condition is

$$acc(o \to n) = min\left(1, \frac{f[\mathcal{U}(n)]}{f[\mathcal{U}(o)]} \exp[-\beta[\mathcal{U}(n) - \mathcal{U}(o)]\right)$$

This derivation shows that we can introduce an arbitrary biasing function $f[\mathcal{U}]$ in the sampling scheme and generate a Boltzmann distribution of configurations, provided that the acceptance rule is modified in such a way that the bias is removed from the sampling scheme. Ideally, by biasing the probability to generate a trial conformation in the right way, we could make the term on the right-hand side of equation (13.1.1) always equal to unity. In that case, every trial move will be accepted. However, in general, biased generation of trial moves is simply a technique for enhancing the acceptance of such moves without violating detailed balance. We now give some examples of the use of non-Metropolis sampling techniques to demonstrate how they can be used to enhance the efficiency of a simulation.

1.1 Orientational Bias

To perform a Monte Carlo simulation of molecules with an intermolecular potential that depends strongly on the relative molecular orientation (e.g., polar molecules, hydrogen-bond formers, liquid-crystal forming molecules), it is important to find a position that not only does not overlap with the other molecule but also has an acceptable orientation. If the probability of finding a suitable orientation by chance is very low, we can use biased trial moves to enhance the acceptance.

1.1.1 Algorithm

Let us consider a Monte Carlo trial move in which a randomly selected particle has to be moved and reoriented. We denote the old configuration by o and the trial configuration by n. We use standard random displacement for the translational parts of the move, but we bias the generation of trial orientations, as follows:

- 1. Move the center of mass of the molecule over a (small) random distance and determine all those interactions that do not depend on the orientations. These interactions are denoted by $\mathcal{U}_{pos}(n)$. In practice, there may be several ways to separate the potential into orientation-dependent and orientation-independent parts.
- 2. Generate k trial orientations $\{b_1....b_k\}$ and for each of these trial orientations, calculate the energy $\mathcal{U}_{rot}(b_k)$
- 3. Define the Rosenbluth factor

$$\mathcal{W}(n) = \sum_{i=1}^{k} \exp[-\beta \mathcal{U}_{rot}(b_k)]$$

  Out of these k orientations, we select one, say, n, with a probability

$$p(b_n) = \frac{\exp[-\beta \mathcal{U}_{rot}(b_n)]}{\mathcal{W}(n)}$$

- 4. For the old configuration, o, the part of the energy that does not depend on the orientation of the molecules is denoted by $\mathcal{U}_{pos}$. The orientation of the molecule in the old position is denoted by b_o, and we generate $k-1$ trial orientations denoted by $b_2...b_k$. Using these k orientations, we determine

$$\mathcal{W}(o) = \exp[-\beta \mathcal{U}_{rot}(b_o)] + \sum_{i=2}^{k} \exp[-\beta \mathcal{U}_{rot}(b_k)]$$

- 5. The move is accepted with a probability

$$acc(o \to n) = min\left(1, \frac{\mathcal{W}(n)}{\mathcal{W}(o)} \exp[-\beta[\mathcal{U}_{pos}(n) - \mathcal{U}_{pos}(o)]\right)$$

It is clear that equation ensures that energetically favorable configurations are more likely to be generated. Next, we should demonstrate that the sampling scheme is correct.

1.2 Demonstration for Lattice Models

We assume that the molecules in our lattice model can have k discrete orientations (see Figure 13.1).

We impose the condition of detailed balance:

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

The flow of configurations o to n is

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

In the orientational-bias scheme, the probability of selecting conformation n is

$$\alpha(o \to n) = \frac{\exp[-\beta \mathcal{U}_{or}(n)}{\mathcal{W}(n)}$$

Imposing detailed balance and substitution of the desired distribution for $\mathcal{N}(n)$ and $\mathcal{N}(o)$ imposes the following condition on the acceptance rules:

$$\frac{acc(o \to n)}{acc(n \to o)} = \frac{\exp[-\beta \mathcal{U}(n)]}{\exp[-\beta \mathcal{U}(o)]} \times \frac{\exp[-\beta \mathcal{U}_{or}(n)}{\mathcal{W}(n)} \times \frac{\mathcal{W}(o)}{\exp[-\beta \mathcal{U}_{or}(o)} =$$

$$= \frac{\mathcal{W}(n)}{\mathcal{W}(p)} \exp[-\beta(\mathcal{U}_{pos}(n) - \mathcal{U}_{pos}(o))]$$

Acceptance rule (13.1.5) satisfies this condition. This demonstrates that for a lattice model detailed balance is fulfilled.

1.3 Demonstration for Continuum Model

If the orientation of a molecule is described by a continuous variable, then there is an essential difference with the previous case. In the lattice model all the possible orientations can be considered explicitly, and the corresponding Rosenbluth factor can be calculated exactly. For the continuum case, we can never hope to sample all possible orientations. It is impossible to de- termine the exact Rosenbluth factor since an infinite number of orientations are possible. Hence, the scheme for lattice models, in which the Rosenbluth factor for all orientations is calculated, cannot be used for a continuum model. A possible solution would be to use a large but finite number of trial directions. Surprisingly, this is not necessary. It is possible to devise a rigorous algorithm using an arbitrary subset of all possible trial directions. The answer we get does not depend on the number of trial directions we choose but the statistical accuracy does. Let us consider the case in which we use a set of k trial orientations; this set is denoted by

$$\mathbf{b}_k = \{b_1 .... b_k\}$$

Conformation b_n can be selected only if it belongs to the set $\mathbf{b}_k$. The set of all sets $\mathbf{b}_k$ that includes conformation n is denoted by

$$\mathcal{B}_n = \{\{\mathbf{b}_k\} | b_n \in \{\mathbf{b}\}_k\}$$

Every element of $\mathcal{B}$ can be written as b, b^*, where b^* is the set of $k-1$ additional trial orientations. In the flow of configuration o to n we have to consider the sum over all sets in $\mathcal{B}_n$

$$\mathcal{K}(o \to n) = \mathcal{N}(o) \sum_{i \in \mathcal{B}_n} \alpha((o \to n, i) \times acc((o \to n, i)$$

in which the probability of generating configuration n and the acceptance depend on the particular set of trial orientations i.

Similarly, for the reverse move, we define the set $\mathcal{B}_o$

$$\mathcal{B}_o = \{\{\mathbf{b}_k\} | b_o \in \{\mathbf{b}\}_k$$

for which each element can be written as $(b_o, b^{'*})$. The expression for the reverse flow then becomes

$$\mathcal{K}(n \to o) = \mathcal{N}(n) \sum_{j \in \mathcal{B}_o} \alpha((n \to o, j) \times acc((n \to o, j)$$

It should be stressed that infinitely many different sets of orientations include b, and the same holds for sets that include b_o. Moreover, the probability of selecting b from such a set depends on the remainder of the set b^*. Hence, the acceptance probability must also depend on the sets b^* and $b^{'*}$. Detailed balance is certainly obeyed if we impose a much stronger condition, "super-detailed balance," which states that for every particular choice of the sets b^* and $b^{'*}$, detailed balance should be obeyed,

$$\mathcal{K}(o \to n, b^*, b^{'*}) = \mathcal{K}(n \to o, b^{'*}, b^*)$$
$$\mathcal{N}(o)\alpha(o \to n, b^*, b^{'*})acc(o \to n, b^*, b^{'*}) = \mathcal{N}(n)\alpha(n \to o, b^{'*}, b^*)acc(n \to o, b^{'*}, b^*)$$

in which b^* and $b^{'*}$ are two sets of $k-1$ arbitrary additional trial orientations. It may seem strange that the sets b^* and $b^{'*}$ show up on both sides of the equations. However, bear in mind that, to decide on the acceptance of the forward move, one should generate both the set b^* that includes the new orientation and the set $b^{'*}$ around the old orientation. Hence, the construction of a trial move includes both sets of trial orientations. As the probabilities of generating b^* and $b^{'*}$ appear on both sides of the equations, they cancel each other. Moreover, the a priori probability of generating a random orientation b in the forward move is equal to the a priori probability of generating b_o in the reverse move. So these generation probabilities also cancel each other. This leads to a great simplification of the acceptance criterion. For the canonical ensemble, substitution it yields

$$\frac{acc(o \to n, b^*, b^{'*})}{acc(n \to o, b^{'*}, b^*)} = \frac{\exp[-\beta \mathcal{U}(n)]}{\exp[-\beta \mathcal{U}(o)]} \frac{\exp[-\beta \mathcal{U}^{or}(o)]}{\mathcal{W}(\mathbf{b}_n, b^{'*})} \frac{\mathcal{W}(\mathbf{b}_o, b^*)}{\exp[-\beta \mathcal{U}^{or}(n)]} \exp[-\beta(\mathcal{U}^{pos}(n) - \mathcal{U}^{pos}(o))] =$$
$$\frac{\mathcal{W}(\mathbf{b}_n, b^{'*})}{\mathcal{W}(\mathbf{b}_o, b^*)} \exp[-\beta(\mathcal{U}^{pos}(n) - \mathcal{U}^{pos}(o))]$$

As the previously proposed acceptance rule satisfies this condition, detailed balance is indeed obeyed. Note that, in this demonstration, we did not have to assume that the number of trial orientations k had to be large. In fact, the result is independent of the number of trial orientations.

1.3.1 Application to dipolar spheres

In systems with dipoles, the energy depends on the mutual orientation of the molecules and a bias in the sampling of the orientation can be useful. For models of dipoles embedded in an otherwise spherical particle (e.g., the dipolar hard-sphere fluid) the scheme of section 13.1.2 can be implemented elegantly as pointed out by Caillol [225]. For a dipolar hard sphere (or any point dipole), we can calculate the Rosenbluth factors exactly once the electric field (E) at the position of the inserted particle and that at the position of the old configuration are known:

$$\mathcal{W}(\mathbf{r}) = \int d\mathbf{b} \exp[-\beta\mu \cdot \mathbf{E}(\mathbf{r})] = \frac{sinh[\beta|\mu||\mathbf{E}(\mathbf{r})|}{\beta|\mu||\mathbf{E}(\mathbf{r})|}$$

where μ is the dipole moment of the molecule.

A trial orientation can now be drawn directly from the distribution

$$p(\mathbf{r}, \omega) = \frac{\exp[-\beta\mu \cdot \mathbf{E}(\mathbf{r})]}{\mathcal{W}(r)}$$

2 An example of a biased MC (AVB, Advanced Volume Biasing)

Very often it is necessary to go beyond the simple MC scheme and devise moves that allow for a significantly faster equilibration of a system. The choice of the moves (which must always satisfy the detailed balance condition) is very general and very often need to be optimized for the problem at hand.

One typical example is provided by associating liquids and in all other particle systems in which a small bonding volume is associated to a very strong interaction energy (for example the lock and key interactions in proteins) where bonding can take place only at very high ratios between bonding energy and thermal energy, such that the Boltzmann factor is extremely small.

As a prototipe, we can condider the adhesive sphere model (Baxter model), e.g. the generalization of a square-well potential in the limit of vanishing well width. For this model (and for ranges δ smaller than few per cent of the particle diameterσ the critical temperature is to good approximation given by

$$\beta_c\epsilon = \ln\left[1 + \frac{2.174\sigma^3}{((\sigma+\delta)^3 - \sigma^3}\right] \approx \ln\left[1 + \frac{0.7\sigma}{\delta}\right] \approx \ln 0.7 - \ln\frac{\delta}{\sigma}$$

Since typically when $\beta\epsilon \approx 20$ (e.g. $kT/\epsilon \approx 0.05$) one need $e^{20} \approx 5\ 10^8$ attemps to break a bond, it becomes almost impossible to equilibrate.

One possibility is to devise MC moves that exploit the large entropic component involved in the breaking-forming of the bond to bring back the acceptance probability at reasonable values.

One of this more elaboated MC scheme, developed by XXXX starts by defining a bonding volume for each particle (or site) (the square well width in the AHS case) named V_{in}. Then, with probability p_{bias} and $1 - p_{bias}$ a move that try to break a bond (in $\rightarrow$ out) or to form a bond (out $\rightarrow$ in) is attempted.

In the (out $\rightarrow$ in) move, first a generic particle i is selected among the N particles in the system and the number of particles in the bonding volume N_{in} is calculated. Then a j particle is selected, among the $N_{out} = N - N_{in} - 1$ ones that are NOT in the bonding volume of i (e.g. j is not bonded with i for the ASW model). Then, j is located inside the bonding volume of i and the new energy E_{final} is evaluated. The move is accepted according to the probability

$$\alpha_{(out \rightarrow in)} = min\left(1, \frac{1 - p_{bias}}{p_{bias}} \frac{V_{in}}{V_{out}} \frac{N_{out}}{N_{in} + 1} \exp(-\beta[E_{final} - E_{initial}])\right)$$

In the (in $\rightarrow$ out) move, first a generic particle i is selected among the N particles in the system and the number of particles in the bonding volume N_{in} is calculated. If $N_{in} = 0$ the move is rejected. Else, one particle among N_{in} is selected randomly and located in a random position outside V_{in}. and the new energy E_{final} is evaluated. The move is accepted according to the probability

$$\alpha_{(in \rightarrow out)} = min\left(1, \frac{p_{bias}}{1 - p_{bias}} \frac{V_{out}}{V_{in}} \frac{N_{in}}{N_{out} + 1} \exp(-\beta[E_{final} - E_{initial}])\right)$$

To see how these acceptance probability arises we remember that detailed balance requires, calling *initial* the state in which i has one more neighbour than what i has in the $final$ state (e.g. we always focus on the state of i).

$$P_{initial}\alpha_{(in \rightarrow out)} selection_{(in \rightarrow out)} = P_{final}\alpha_{(out \rightarrow in)} selection_{(out \rightarrow in)}$$

The probability $selection_{(in \rightarrow out)}$ is composed by a factor p_{bias} to select the $(in \rightarrow out)$ move, a factor $\frac{1}{N}$ associated to the choice of i, a factor $\frac{1}{N_{in}}$ associated to the choice of j and $\frac{1}{V_{out}}$ associated to the choice of the position in which the j particle is transfered, e.g.

$$selection_{(in \rightarrow out)} \sim p_{bias} \frac{1}{N} \frac{1}{N_{in}} \frac{1}{V_{out}}$$

The reverse probability $selection_{(out \rightarrow in)}$ is proportional to a factor $1 - p_{bias}$ to select the $(out \rightarrow in)$ move, a factor $\frac{1}{N}$ associated to the choice of i, a factor $\frac{1}{N'_{out}}$ to select one of the outside particles and $\frac{1}{V_{in}}$ to select a point inside the in volume, resulting in

$$selection_{(out \rightarrow in)} \sim (1 - p_{bias}) \frac{1}{N} \frac{1}{N'_{out}} \frac{1}{V_{in}}$$

Note that if we call N_{in} and N_{out} the number of particles in the $selection_{(in\to out)}$ move, then $N'_{out} = N_{out} + 1$, since in the reverse move one particle has gone from the in volume of i to the out volume of i.

It is important to note that the ratio V_{in}/V_{out} now enters in the acceptance probability, compensating the very small Boltzmann factor.

The AVB method is very useful also simulating systems at very low densities and low temperatures. It is also useful in equilibrating limited valence particles, e.g. living polymers.

In the case of living polymers, another possibility is offered by the design of MC moves that perform end-to-end moves, e.g. in which one of the two final particles of the chain is transfered to increase by one the lenght of a randomly selected polymer. In this case the moves can be performed with this acceptance probability

At very low temperatures the Boltzmann factor associated with the energy penalty of breaking a bond completely suppresses the acceptance probability of the unbonding move. To solve this sampling problem, we introduce here the end hopping move, which generates trial moves that leave the en- ergy unchanged. The move proceeds by selecting randomly a chain end, i.e., a particle which is engaged in only one bond, and moving it into the bonding volume of another chain end or of a monomer. Because the move leaves the number of bonds unchanged, its energy cost is null, and, therefore, it is cost-effective at any temperature (provided that chain ends exist in the simulation box). This move allows different chains to exchange particles, and allows efficient exploration of configurations with equal energy. We provide here the details of the algorithm with the trial probabilities in parentheses after each step. The number of chain ends is N_{end} (an end particle has one bond and each polymer contributes with two ends) and the number of monomers is N_{mon} (a monomer particle has no bonds).

- Select a particle i which is also a chain end ($\frac{1}{N_{ends}}$);
- select a target particle j which is either a chain end different from i, or a monomer ($\frac{1}{N_{ends}+N_{mon}-1}$
- place particle i in the in volume of particle j ($1/V_{in}$ if j is a chain end; $2/V_{in}$, if j is a monomer (which has two bonding sites available));
- if after the move particle i is not a chain end, reject the move;
- accept the move with probability

$$acc = \frac{N_{end}(N_{end} + N_{monomers} - 1)}{(N^*_{end} + N^*_{monomers} - 1)N^*_{end}} \times \frac{1 + \delta_{mon}}{1 + \delta^*_{mon}} \exp(-\beta \Delta E)$$

where N^*_{end} and $N^*_{monomers}$ are, respectively, the number ends and the number of monomers in the reverse move, and $\delta_{mon} = 1(0)$, if the target particle in the direct move is a monomer (end) (δ^*_{mon} is the same quantity for the reverse move).