Lecture 8: Monte Carlo

All relevant macroscopic properties of a molecular systems can be derived from the partition function:

$$\begin{aligned} Z &= \frac{1}{h^{3N}N!}\int..\int \exp[-\beta\sum_i \frac{p_i^2}{2m}]d\mathbf{p}_1..d\mathbf{p}_N \int..\int \exp[-\beta U(\mathbf{q}_1,..\mathbf{q}_N)]d\mathbf{q}_1..d\mathbf{q}_N \\ &= \frac{V^N}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}N} \times \frac{1}{V^N}\int..\int \exp[-\beta U(\mathbf{q}_1,..\mathbf{q}_N]d\mathbf{q}_1..d\mathbf{q}_N \end{aligned} \tag{1}$$

where we assumed that all particles have the same mass.

However, the partition function itself can only be obtained analytically for the most simple systems, such as harmonic oscillators and ideal gases. If there are interactions between the particles, *i.e.*, $U(\mathbf{q}_1,..\mathbf{q}_N) \neq 0$, the configurational part of the partition function

$$Q = \frac{1}{V^N}\int..\int \exp[-\beta U(\mathbf{q}_1,..\mathbf{q}_N)]d\mathbf{q}_1..d\mathbf{q}_N \tag{2}$$

cannot be evaluated analytically and we need numerical methods instead for calculating expectation values of observables.

One such numerical method is the Metropolis Monte Carlo algorithm. The idea is to only evaluate the integral in equation 2 at points that have a significant Boltzmann factor.

Assume that we have a realistic starting configuration (*i.e.*, precise information about the initial positions of all atoms) of the system we're interested in. This might for instance be an x-ray structure, or a configuration from a previous simulation. This we call the old configuration, o, with energy $U(o)$. We assume furthermore that we can evaluate that potential energy function for any configuration, or at least approximate it (note that evaluating this energy at a given point in configuration space might be difficult, but is far less complicated than evaluating the

multi-dimensional integral over all of configuration space).

The way to proceed is to make some random displacement of (few) atom(s) in the old configuration to generate a new configuration n with potential energy $U(n)$. Imagine that we do a very large number of Monte Carlo simulations in parallel, say M. Then, for the M simulated systems to remain in equilibrium, the number of moves that go from o to n in the M simulations must be identical to the number of moves from n to o, otherwise the condition for equilibrium would be violated. This is called detailed balance and implies:

$$N(o)\pi(o \to n) = N(n)\pi(n \to o) \tag{3}$$

where $\pi(o \to n)$ is the probability for making a move from o to n and $N(o)$ and $N(n)$ are the number of the M simulations, which are in configuration o and n. Because at equilibrium, $N(o) = M \exp[-\beta U(o)]/Z$, and likewise for n, we have that

$$\frac{M}{Z} \exp[-\beta U(o)]\pi(o \to n) = \frac{M}{Z} \exp[-\beta U(n)]\pi(n \to o) \tag{4}$$

A trial move is a two step procedure: First, we select a move (*e.g.*, displacing a randomly chosen atom, or group of atoms): $\alpha(o \to n)$. Second, we accept or reject that move: $\text{acc}(o \to n)$. Thus, the total probability of the move is:

$$\pi(o \to n) = \alpha(o \to n) \times \text{acc}(o \to n) \tag{5}$$

If we further enforce that $\alpha(o \to n)$ is symmetric, *i.e.*, $\alpha(o \to n) = \alpha(n \to o)$, which is the case if we randomly select atoms for displacement, the condition for detailed balance is

$$\exp[-\beta U(o)] \times \text{acc}(o \to n) = \exp[-\beta U(n)] \times \text{acc}(n \to o) \tag{6}$$

For the acceptance probabilities we thus get

$$\frac{\text{acc}(o \to n)}{\text{acc}(n \to o)} = \exp[-\beta[(U(n) - U(o))] \tag{7}$$

In the first computer simulation, Metropolis, Rosenbluth, Rosenbluth, Teller and Teller used the following criteria for accepting or rejecting trial moves:

$$\begin{aligned} \text{acc}(o \to n) &= \exp[-\beta[(U(n) - U(o))] \quad \text{if} \quad U(n) > U(o) \\ &= 1 \qquad\qquad\qquad\qquad\qquad\quad \text{if} \quad U(n) \leq U(o) \end{aligned} \tag{8}$$

If we use a random number generator to get a random number R on the interval $[0, 1]$, we accept a move to a configuration with a higher energy if

$$\exp[-\beta(U(n) - U(o))] > R \tag{9}$$

while a move to a configuration of lower enegy than o is always accepted.