Computational Nanoscience
NSE C242 & Phys C203
Spring, 2006

Lecture 8:
Monte Carlo Methods - Part II
February 14, 2008

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Review of Metropolis

Our goal is the evaluation of integrals such as:

\[
\langle A \rangle = \frac{\int dR A(R) \exp[-\beta V(R)]}{\int dR \exp[-\beta V(R)]}
\]

As a quick way of thinking of Metropolis:

It is an approach that generates configuration states with a probability of \( \exp[-\beta \Delta \varepsilon] \) and then counts each of them equally when computing the average.

The Metropolis scheme obeys detailed balance - i.e., we are sampling equilibrium as dictated by the canonical distribution (NVT).

Conventional MC samples NVT (whereas conventional MD, as we saw before, samples NVE).
Review - Metropolis Algorithm

1. Assign an initial configuration (non-trivial!!) for your system, record it’s energy.

2. Choose a second configuration for the system (e.g. move an atom by a diffusion step in a random direction, flip a spin, move all of the atoms, etc), and compute the change in energy $\Delta \varepsilon$ associated with the change in configuration.

3. If $\Delta \varepsilon < 0$ : accept the change
   
   If $\Delta \varepsilon > 0$ : accept the change with probability $e^{-\beta(\Delta \varepsilon)}$
   
   - i.e. generate a random number $r$ uniformly distributed between 0 and 1.
   
   - If $r < e^{-\beta(\Delta \varepsilon)}$, accept the change. Otherwise, reject it.

   This accepting and rejecting ensures that we choose our configurations consistently with the Boltzmann population distribution.

4. Repeat steps 2 and 3 as long as reasonable. We can use these successive configurations to obtain an estimate for the desired average.

Basic idea: The Metropolis algorithm obeys detailed balance and exhibits the dynamics of a canonical distribution.
The balance condition states that when you are sampling configuration space consistently with equilibrium distribution, then the relative probability of being in a given state must remain constant.

That is, the total transition rate out of a given state must equal the total transition rate (from all other states) into that state.

In practice, for convenience we use a more stringent condition known as detailed balance. This states that the transition rate from state “c” to state “n” is the same as the transition rate from state “n” to “c”

\[
N(c)\pi(c \to n) = N(n)\pi(n \to c)
\]

\[
N(c)\alpha(c \to n)acc(c \to n) = N(n)\alpha(n \to c)acc(n \to c)
\]

In Metropolis, \(\alpha\) is symmetric. Thus, the relative acceptance rates must satisfy:

\[
\frac{acc(c \to n)}{acc(n \to c)} = \frac{N(n)}{N(c)} = \exp[-\beta \varepsilon_n] = \exp[-\beta (\varepsilon_n - \varepsilon_c)]
\]

Many ways to do this, but Metropolis approach is:

\[
acc(c \to n) = \begin{cases} 
\exp[-\beta (\varepsilon_n - \varepsilon_c)] & \text{if } \varepsilon_n > \varepsilon_c \\
1 & \text{if } \varepsilon_n < \varepsilon_c
\end{cases}
\]
MC vs. MD?

Discussion: Describe some differences between molecular dynamics and Monte Carlo.

MONTE CARLO:
• Ease of programming, no calculation of forces or time step concerns.
• When dealing with systems that have no natural dynamics (discrete degrees of freedom like Ising spins).
• Discrete systems, lattice models in general use Monte Carlo.
• We can perform unphysical trial moves (have no counterpart in MD) but are necessary for equilibration. Sometimes, the natural dynamics of the system are too slow to allow the system to equilibrate on accessible time scales.
• Global moves allow for more independent, uncorrelated measurements of configuration space
• Probabilistic, rather than deterministic approach

MOLECULAR DYNAMICS:
• It’s all in the name -- dynamics, dynamics, dynamics.
• Deterministic approach (albeit, with high sensitivity to initial conditions)
Examples of Metropolis Monte Carlo

Hard-Sphere Monte Carlo Model in 2D

\[ \nu(r) = +c \text{ if } r \leq \sigma \text{ and } 0 \text{ otherwise} \]

36 particles; step-size 0.05 \( \sigma \); kT/c = 0.1; 1000 Metropolis sweeps

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Frames from Simulation:

- sweep 1
- sweep 200
- sweep 400
- sweep 600
- sweep 800
- sweep 1000
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• Look what happens when we change the step-size.

• What else could we change? (Temperature)
Examples of Metropolis Monte Carlo

Hard-Sphere Monte Carlo Model in 2D

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Frames from Simulation

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Say I construct a series of n configurations using Metropolis Monte Carlo. I arrive at an estimate for the average value for the parameter of interest:

\[ \bar{x} = \frac{1}{n} \sum_{i=1}^{n} x_i \]

How “good” is my estimate? What can we say about the certainty of our estimate? What’s the best guess for the peak \( \langle x \rangle \) and the width \( \sigma \) of the distribution?

Thanks to some handy theorems (namely, the Central Limit Theorem and Bayes Theorem), there are ways to estimate the uncertainty.

For a rigorous proof, see, e.g., Reif. We’ll outline the process here….

68% of the values drawn from a normal distribution lie within one \( \sigma \) of the peak, etc. etc.
Error Estimation

Let $X$ = the event that the distribution has true average $<x>$

Let $Y$ = the event that the $n$ configurations selected are $\{x_1, x_2, \ldots, x_n\}$

The question that we want to ask is: “Given that our simulation generated the configurations $\{x_1, x_2, \ldots, x_n\}$, what is the probability that the true average is $<x>$?”

\[
p\left(\langle x \rangle \mid \{x_1, x_2, \ldots, x_n\}\right) = \frac{p\left(\{x_1, x_2, \ldots, x_n\} \mid \langle x \rangle\right)p\left(\langle x \rangle\right)}{p\left(\{x_1, x_2, \ldots, x_n\}\right)} \quad \text{Baye’s Theorem}
\]

\[
= \prod_{i=1}^{n} \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{(x_i - \langle x \rangle)^2}{2\sigma^2}\right) \quad \text{Central Limit Theorem*}
\]

* CLT: Many things in life look like gaussians. (There exist, of course, more rigorous statements of the CLT.)
Error Estimation

We can find the $<x>$ that gives the highest probability by solving

$$\frac{d}{d\langle x \rangle} p\left(\langle x \rangle \mid \{x_1, x_2, \ldots, x_n\}\right) = 0$$

which gives us, not surprisingly, that the peak (that is, our best guess for the value of the mean) occurs at

$$\langle x \rangle = \frac{1}{n} \sum_{i=1}^{n} x_i = \bar{x}$$

The best estimate for the width of the distribution comes also from our data:

$$\sigma = \left\{ \frac{1}{n-1} \sum_{i=1}^{n} (x_i - \bar{x})^2 \right\}^{1/2}$$

Thus, we can guess that the mean has a standard error of

$$\langle x \rangle = \bar{x} \pm \frac{\sigma}{\sqrt{n}}$$

As the sample size grows, we can expect that the calculated average becomes closer to the true average.

The standard error tells us how much, on average, our predicted average varies from the real average, given a distribution of width $\sigma$. 
Beyond NVT to Grand Canonical MC

- It is possible to conduct Monte Carlo simulations in the Grand Canonical Ensemble, where \((\mu, P, T)\) are held fixed.
- Note how the number of particles in the system is now free to vary.
- Why would one want to do this?

Procedure is the same as before:

1. Find the partition function for the system.
   - The “system” is now a coupled system.
2. Determine transition rules are consistent with it - detailed balance.

After M. Dijkstra,

\[
\sum_{N=0}^{M} \frac{V^N}{N! \Lambda^{3N}} \int ds^N \exp[-\beta U(s^N; V)] \times \frac{(V_0 - V)^{M-N}}{(M-N)! \Lambda^{3(M-N)}}
\]

The probability of acceptance of a trial move in which a particle is transferred from the ideal reservoir to our system

\[
\frac{\text{acc}(N \rightarrow N + 1)}{\text{acc}(N + 1 \rightarrow N)} = \frac{V^{N+1}(V_0 - V)^{M-N-1} \exp[-\beta U(s^{N+1})]}{(N+1)!(M-N-1)!} \\
\times \frac{(N)!(M-N)!}{V^N(V_0 - V)^{M-N} \exp[-\beta U(s^N)]}
\]

\[
= \frac{V(M-N)}{(V_0 - V)(N+1)} \exp[-\beta(U(s^{N+1}) - U(s^N))]
\]

\[
= \frac{V}{\Lambda^3(N+1)} \exp[\beta(\mu - U(s^{N+1}) + U(s^N))]
\]

where we considered the limit that the reservoir tends to infinity, i.e. \( V_0 \rightarrow \infty, M \rightarrow \infty \), while \( (M - N)/(V_0 - V) \rightarrow M/V_0 = \rho = \exp[\beta \mu]/\Lambda^3 \).
Grand Canonical MC Example

formation of a graphene cap on a spherical catalyst

- $\mu = -5 \text{ eV}; T = 1000K$
- $\mu = -5 \text{ eV}; T = 2000K$
- $\mu = -5 \text{ eV}; T = 3000K$
Grand Canonical MC Example

First 1/2 million iterations …

Energy (eV)

Monte Carlo Iteration

T = 1000K
T = 2000K
T = 3000K
Grand Canonical MC Example

Last 7 million iterations …

Monte Carlo Iteration

Energy (eV)

-300
-320
-340
-360
-380
-400

0 1x10^6 2x10^6 3x10^6 4x10^6 5x10^6 6x10^6 7x10^6

T = 1000K
T = 2000K
T = 3000K

In-Class Simulation:

Hard-Sphere Monte Carlo

Bring your wireless-enabled laptop.