9.1 Advanced Topics in Monte Carlo Simulations

One of the advanced topics that we will discuss is Monte Carlo (and molecular
dynamics) simulations of polymers. Another highly relevant topic is the
simulation of systems at negative temperatures. Yet another possible topic is
simulated annealing and applications of MC to operations research problems.
These topics will be discussed in brief.

However, the question of good MC/MD techniques for problems with
long range interactions, such as the two-dimensional Coulomb gas, is a very
important one. We will spend some time in lecture on the methods of Ewald
summation and multipole expansions.

9.2 Simple Models of Polymers (Biomolecules)

One of the simplest models is the freely joined chain. This is a system of
$N$ particles linked by bonds of fixed length $d$. Let the location of particles
be $\vec{x}_1, \vec{x}_2, ..., \vec{x}_N$ where $|\vec{x}_{i+1} - \vec{x}_i| = d$. The assumption of free-jointedness is
equivalent to the independence of the bonds, given by

$$< \vec{d}_i \cdot \vec{d}_j > = d^2 \delta_{ij}$$

||where $\vec{d}_i \equiv \vec{x}_i - \vec{x}_{i-1}$.

Two important quantities are used to characterize a given micro-state or
configuration of the chain $\vec{x} \equiv (\vec{x}_1, \vec{x}_2, ..., \vec{x}_N)$:

(a) $D^2 (N) = < (\vec{x}_N - \vec{x}_1)^2 >$

(a) $R_g^2 = \frac{1}{N-1} \sum_{i=1}^{N} < (\vec{x}_i - \bar{x})^2 >$ where $\bar{x} = \frac{1}{N} \sum_{i=1}^{N} \vec{x}_i$.

The first is the end-to-end separation $D$, and the second is the radius of
gyration $R_g$.

Let us calculate $D^2$ and $R_g^2$, for the freely jointed chain:
\[
D^2(N) = <(\bar{x}_N - \bar{x}_1)^2>
= <(\bar{x}_N - \bar{x}_{N-1} + \bar{x}_{N-1} - \bar{x}_{N-2} + \ldots + \bar{x}_2 - \bar{x}_1)^2>
= <[(\bar{x}_N - \bar{x}_{N-1}) + (\bar{x}_{N-1} - \bar{x}_{N-2}) + \ldots + (\bar{x}_2 - \bar{x}_1)]^2>
= \sum_{i=2}^{N} <(\bar{x}_i - \bar{x}_{i-1})^2> + \sum_{i \neq j} <(\bar{x}_i - \bar{x}_{i-1})(\bar{x}_j - \bar{x}_{j-1})>
= (N - 1) d^2
\]

In the case of \( R^2_y(N) \) we have
\[
R^2_y(N + 1) = \frac{1}{N+1} \sum_{i=1}^{N+1} <(\bar{x}_i - \bar{x})^2>
= \frac{1}{N+1} \sum_{i=1}^{N+1} <\bar{s}_i^2>
(9.1)
\]

where \( \bar{s}_i \equiv \bar{x}_i - \bar{x} \). By a theorem of Lagrange (to be established next) we have
\[
R^2_y(N + 1) = \frac{1}{(N + 1)^2} \sum_{i<j}^{N+1} <r_{ij}^2>
\]

where \( r_{ij} \equiv |\bar{x}_i - \bar{x}_j| \).

9.3 Lagrange’s Theorem

\[
\frac{1}{N+1} \sum_{i=1}^{N+1} (\bar{x}_i - \bar{x})^2 = \frac{1}{(N + 1)^2} \sum_{i<j}^{N+1} |\bar{x}_i - \bar{x}_j|^2
(9.2)
\]

Proof. Let \( \bar{s}_i = \bar{s}_1 + \bar{r}_{1i} \). Substitution into 9.2 gives
\[
\frac{1}{N+1} \sum_{i=1}^{N+1} (\bar{s}_1 + \bar{r}_{1i}) \cdot (\bar{s}_1 + \bar{r}_{1i}) = s_1^2 + \frac{2}{N+1} \bar{s}_1 \cdot (\sum_{i=2}^{N+1} \bar{r}_{1i}) + \frac{1}{N+1} \sum_{i=2}^{N+1} r_{1i}^2
(9.3)
\]
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Since \( \bar{x} \equiv \frac{1}{N+1} \sum_{i=1}^{N+1} x_i \) we have \( \sum_{i=1}^{N+1} \bar{s}_i = 0 \) and therefore,

\[
\bar{s}_i = -\frac{1}{N+1} \sum_{i=2}^{N+1} \bar{r}_{1i}
\]  

(9.4)

follows by summing both sides of \( \bar{s}_i = \bar{s}_i + \bar{r}_{1i} \). Also we have

\[
\bar{s}_1^2 = \frac{1}{(N+1)^2} \sum_{i=2}^{N+1} \sum_{j=2}^{N+1} \bar{r}_{1i} \cdot \bar{r}_{1j}
\]  

(9.5)

Substituting 9.4 and 9.5 into 9.3 we get

\[
\frac{1}{N+1} \sum_{i=1}^{N+1} (\bar{s}_1 + \bar{r}_{1i}) \cdot (\bar{s}_1 + \bar{r}_{1i})
\]

\[
= - \frac{2}{(N+1)^2} \sum_{i=2}^{N+1} \sum_{j=2}^{N+1} \bar{r}_{1i} \cdot \bar{r}_{1j} + \frac{1}{N+1} \sum_{i=1}^{N+1} r_{1i}^2 + \frac{1}{(N+1)^2} \sum_{i=2}^{N+1} \sum_{j=2}^{N+1} \bar{r}_{1i} \cdot \bar{r}_{1j}
\]

\[
= - \frac{1}{(N+1)^2} \sum_{i=2}^{N+1} \sum_{j=2}^{N+1} \bar{r}_{1i} \cdot \bar{r}_{1j} + \frac{1}{N+1} \sum_{i=2}^{N+1} r_{1i}^2
\]

Since \( 2\bar{r}_{1i} \cdot \bar{r}_{1j} = r_{1i}^2 + r_{1j}^2 - r_{ij}^2 \) by the law of cosines, we get:

\[
LHS (9.2) = - \frac{1}{(N+1)^2} \left( \frac{1}{2} \right) \sum_{i=2}^{N+1} \sum_{j=2}^{N+1} \left[ r_{1i}^2 + r_{1j}^2 - r_{ij}^2 \right] + \frac{1}{N+1} \sum_{i=2}^{N+1} r_{1i}^2
\]

\[
= \frac{1}{(N+1)^2} \sum_{i=2}^{N+1} r_{1i}^2 + \frac{1}{(N+1)^2} \left( \frac{1}{2} \right) \sum_{i=2}^{N+1} \sum_{j=2}^{N+1} r_{ij}^2
\]

\[
= \left( \frac{1}{2} \right) \frac{1}{(N+1)^2} \sum_{i=1}^{N+1} \sum_{j=1}^{N+1} r_{ij}^2
\]

Taking expectation values of both sides of Lagrange’s result, we obtain

\[
R_g^2 (N + 1) = \frac{1}{(N+1)^2} \sum_{i<j}^{N+1} < r_{ij}^2 >
\]  

(9.6)

An important conclusion concerning both \( D^2 \) and \( R_g^2 \) is the fact that they are both \( O(N) \), for in the case of the \( R_g^2 \) for the freely-jointed chain,
9.6 becomes
\[
R_g^2 = \frac{1}{(N+1)^2} \sum_{i<j}^{N+1} \left( \sum_{j=i+1}^{N+1} d_k^2 + 2 \sum_{k<i} d_k \cdot d_i \right)
\]
\[
= \frac{1}{(N+1)^2} \sum_{i<j}^{N+1} \left( \sum_{k=i+1}^{j} d_k^2 \right) + 2 \sum_{k<i}^{j} d_k \cdot d_i
\]
\[
= \frac{1}{(N+1)^2} \sum_{i<j}^{N+1} (j-i-1) d_i^2 \sim O( N d^2 )
\]
(9.7)

The probability distribution for a bond-configuration of the freely-jointed model is given by
\[
P \left( \vec{d}_1, \vec{d}_2, ..., \vec{d}_N \right) = \prod_{i=2}^{N+1} \frac{\delta}{4 \pi d^2} \left( |\vec{d}_i| - d \right)
\]
(9.8)

This means that the probability distribution for the end-to-end vector $\vec{x}_{N+1} - \vec{x}_1$ is
\[
P_N \left( \vec{R} \right) = \prod_{i=1}^{N} \int d^3 \vec{r}_i \frac{1}{4 \pi d^2} \delta \left( |\vec{r}_i| - d \right) \delta \left( \vec{R} - \vec{x}_{N+1} + \vec{x}_1 \right)
\]
\[
= \frac{1}{(4 \pi d^2)^N} \prod_{i=1}^{N} \int d^3 \vec{r}_i \delta \left( |\vec{r}_i| - d \right) \delta \left( \vec{R} - \vec{r}_2 - \vec{r}_3 - ... - \vec{r}_{N+1} \right)
\]
(9.9)

One convenient way to look at these probabilities is to consider a bond-configuration $\vec{d} \equiv (\vec{d}_2, \vec{d}_3, ..., \vec{d}_{N+1})$ to be a micro-state in a phase-space $\Omega \subset R^{3N}$ with the constraints that each $\vec{d}_i$ has length $d$. In this picture, the macro-state is given by a collection of bond-configurations $\vec{d}$ with the global (macro) property that $(\vec{x}_{N+1} - \vec{x}_1) = \vec{R}$.

The solution of 9.9 is a nice exercise in Fourier transforms:
\[
\hat{p} \left( \vec{k} \right) = \int d^3 \vec{R} P_N \left( \vec{R} \right) e^{i\vec{k} \cdot \vec{R}}
\]
\[
= \frac{1}{(4 \pi d^2)^{3N}} \prod_{i=2}^{N+1} \left[ d^3 \vec{r}_i e^{i\vec{k} \cdot \vec{r}_i} \delta \left( |\vec{r}_i| - d \right) \right]
\]
(9.10)

Integrating, we obtain that
\[
\hat{p} \left( \vec{k} \right) = \left[ \frac{\sin \left( kd \right)}{kd} \right]^N
\]
where $k = |\vec{k}|$. In the limit of $N \to \infty$, $\left[ \frac{\sin(kd)}{kd} \right]^N$ is sharply localized at $k = 0$ and approximating

$$\ln(\hat{p}) \approx N \ln \left( 1 - \frac{k^2d^2}{6} \right) \approx -\frac{Nk^2d^2}{6}$$

we get that

$$P_N(\vec{R}) \approx \int \frac{d^3k}{(2\pi)^3} \exp \left[ -\frac{Nk^2d^2}{6} - i\vec{k} \cdot \vec{R} \right] \sim \left( \frac{3}{2\pi N d^2} \right)^{\frac{3}{2}} e^{-\frac{3\pi^2}{2Nd^2}} \quad (9.11)$$

to $O\left( \frac{1}{N} \right)$. This is the typical Gaussian distribution for a three-dimensional random walk.

### 9.4 Monte Carlo Simulations of Bio-Macromolecules

We will discuss a simple application of Monte Carlo (MC) methods to polymers. Since the freely-jointed chain is essentially a Gaussian model, and thus exactly solvable, as shown above, we will discuss a Monte Carlo algorithm for simulating this model. For the sake of simplicity, we will simulate a lattice-restricted version of the freely-jointed chain, that is, each bond is not only of fixed length $d$, but can only assume one of 5 directions at a given cubic lattice site. For the purposes of comparison, we recall that for a freely-jointed chain,

$$D^2 = N d^2 \quad (9.12)$$
$$\bar{R}_g^2 = \frac{1}{6} N d^2 \quad (9.13)$$

in the limit as $N \to \infty$.

We will simulate a Gibbs canonical ensemble where

$$\langle Q \rangle = \frac{1}{Z} \int Q(\vec{d}) \exp \left\{ -\beta U(\vec{d}) \right\} D\vec{d} \quad (9.14)$$
where
\[ U(\vec{x}) = \sum_{i<j} \omega(r_{ij}) \]  
(9.15)

and \( \omega(r_{ij}) = 0 \) is the case of the freely-jointed chain (ideal chain) and
\[ \omega_s(r) = \begin{cases} \infty, & r < 0 \\ 0, & r \geq r_0 \end{cases} \]

for a hard-sphere potential of radius \( r_0 \). In other words, the potential \( \omega(r) = 0 \) corresponds to a random lattice walk, while the hard-sphere potential \( \omega_s(r) \) corresponds to a self-avoiding random lattice walk.

### 9.5 The Algorithm

#### 9.5.1 Chain Generation

This is an essential step in MC simulation of polymers, that is, at least one lattice chain configuration \( \vec{d} \) has to be produced.

#### 9.5.2 Normalization

We will normalize things by choosing the origin of the coordinate system to coincide with the starting point of the lattice chain. We will also fix the first step (bond) to be the direction \((0, 0, 1)\) in a cubic lattice.

#### 9.5.3 Bond Selection

The second bond onwards is chosen at random and can take on one of 5 possible directions in a cubic lattice.

#### 9.5.4 Markov Chain Generation

After the initial chain generation part, a Markov chain of polymer configurations are then generated, using the importance sampling (Metropolis) algorithm, discussed in lectures 7 and 8 starting from an arbitrary configuration:
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Change

Select a chain site at random and if it is not an end-site, move to new position

\[ \bar{x}_j = \bar{x}_j + \bar{x}_{j+1} - \bar{x}_j \]  \hspace{1cm} (9.16)

If it is an end-site then pick its new position \( \bar{x}_{\text{end}} \) to be one of the four possibilities given by

\[ (\bar{x}_{\text{end}} - \bar{x}_{\text{next}}) \cdot (\bar{x}_{\text{end}} - \bar{x}_{\text{next}}) = 0 \]  \hspace{1cm} (9.17)

Pictorially, we crank a non end-site along the diagonal, and we make an elbow (or knee) at an end-site.

Decision

A move is accepted or rejected on the basis of the Metropolis rule for the Gibbs Canonical Ensemble 9.14.