Simulation of Polymers

- Physics of polymers
- MD of polymers?
- MC methods
- Lattice models
- Reptation Monte Carlo
- Rosenbluth growth methods
- Pivot method

“Computer simulation methods for polymer physics”
Kurt Kramer in MC and MD in Condensed Matter Systems

“MC and MD simulations in polymer science”
Time estimate for MD

- **Time scales**
  - Local oscillations are $10^{-13}$ s so time step is $10^{-14}$ s
  - Important motions in polymers take seconds or hours (real time) requiring $10^{14}$ to $10^{18}$ steps!
  - A system of 100 chains of 50 monomers (20,000 particles) takes about 1 step/sec for $10^{-4}$ s (real time) would take about $10^{10}$ secs or 300 years!

- **Distance scales**
  - Local effects are order 1Å.
  - Volume of cell is $(100\text{Å})^3$.

- **Solvent** is important. Hydrodynamic effects dominate.

- **Conclusion:** You need to make a simplified model of the polymer to do research in this area unless you have a much faster computer.
Polymer Hamiltonian

- **Self-avoiding random walk. (SAW)**
  Consider a simple lattice and take a random walk on the lattice--one which only visit each site once.

- **Bead spring model**
  - Bonding interaction holds the chain together. Key feature of polymer. *A bead does not represent an atom, but a blob--a section of the chain.*
  - Non-bonded excluded volume interaction (LJ)

\[
V = \sum_{i<j} \phi(r_{ij}) + \sum_i \gamma(|r_i - r_{i+1}|)
\]

Modified harmonic potential (with \( k=20, \sigma=1.94\sigma_{HS} \))

\[
\gamma = \frac{1}{2} \kappa (r - r_0)^2 \quad \phi = -\frac{1}{2} k \sigma \ln \left[ 1 - \left( \frac{r}{\sigma} \right)^2 \right]
\]
Polymer Phases

• For a repulsive interaction--the chains stretch out, swell.
• Characterize size by mean square end-end distance.

\[ \langle (r_n - r_0)^2 \rangle \propto N^{2\nu} \]
\[ \nu \sim 0.588 \text{ SAW} \quad \text{or} \quad 0.5 \text{ RW.} \]

• This means MD will be very slow. Relaxation time $= N^{2.2}$.  
• As attractive interaction are added in  
  - at some point the polymers collapse. (Theta point collapse.)  
  - Right at collapse point--walks are uncorrelated random walks.  
  - This is a type of phase transition ($R_{\text{gyr}} \sim N^{3/5} \rightarrow N^{1/2} \rightarrow N^{1/3}$).
• Big question: how does the dynamics scale with the length of the chain-entanglement?
• Other topologies for polymers: linear, rings, stars,
Polymer Reptation (slithering snake)

- Polymers move very slowly because of entanglement.
- Local MC just as slow as MD.
- A good algorithm is “reptation.”
  - Cut off one end and stick onto the other end.
  - Choose end at random or “bounce” with rejection.
- Sample directly the bonding interaction
- Acceptance probability is change in non-bonding potential.
- Simple moves go quickly through polymer space.
  - But Ergodic? Not always (what if both ends get trapped?)
- Decorrelation time is $O(N^2)$. Works for many chains.
- Completely unphysical dynamics or is it?
  - This may be how entangled polymers actually move. (theory of Degennes)
Pivot algorithm

- Take a polymer. Pick an atom at random.
- Rotate one segment with respect to the pivot point a random angle $\theta$.
- Accept or reject.
- Most efficient method for a single chain. Exponent of relaxation of end-end distance is $N^{0.2}$
• Maybe we can speed up the algorithm by forcing the polymer to lie on a lattice.
• SAW = “self-avoiding random walk”: a walk on a lattice with N steps which cannot visit a site more than once.

Lattice model for polymers

* Partition function=sum over all such possible walks.
* Monte Carlo=sample the distribution of the walks and take averages such as end-end distribution.
* You can also put a “non-bonded” interaction to make polymer collapse.
How to move polymers

- Growth
- Reptation
- Crankshaft moves

- If move is allowed, accept it.
- Pivot moves
- ....

Ergodic questions arise:

Can you go everywhere in chain space?
Make a mixture of moves.
Growth algorithms

\textbf{CBMC} = Configurational Bias MC/Rosenbluth

** Chapters 11,13  FS**

- Simply grow polymer, stopping when you get any overlap.
- Use importance sampling to direct the walk in favorable directions.

\[ W_n = W_{n-1} \left[ \frac{q_i}{q} \right] \]

\[ \langle R^2 \rangle = \frac{\sum W_j R_j^2}{W_i} \]

\( q_i = \# \text{ of open moves} \)

- Problem: \textcolor{orange}{can you get really long polymers?}
- Use branching when weights fluctuate too much.
- Easily generalized to continuum models.
- In CBMC we grow a new section and accept or reject it

\[ \text{acc. prob} = \min \left[ 1, \frac{W_{\text{new}}}{W_{\text{old}}} \right] \]