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 1A.
  - Volume of cell is $(100A)^3$.
- 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 \( k = 20, \sigma = 1.95\sigma_{HS} \))

\[ \gamma_h = \frac{1}{2} k (r - r_0)^2 \quad \gamma_{hl} = -\frac{1}{2} k \sigma \ln[1 - \left(\frac{r}{\sigma}\right)^2] \]

Polymer Phases

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

\[ \langle (r_n - r_0)^2 \rangle \propto N^{2\nu} \]

\[ \nu \sim 0.588 \text{ SAW or 0.5 RW.} \]

- 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.
- 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 $N^{0.2}$
Lattice model for polymers

- 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.

\[ \text{\ldots} \]

- 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

\[ \text{\ldots} \]

- 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

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.
  \[ W_n = W_{n-1} \left[ \frac{q_i}{q} \right] \quad < R^2 > = \frac{\sum W_i R_i^2}{W_i} \]
  
  \( q_i \) = # of open moves

- Problem: 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.

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