Simulation of Polymers

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

Lesar, Chapter 8. Frenkel and Smit Chapter 11.

“Computer simulation methods for polymer physics”

Kurt Kramer *in MC and MD in Condensed Matter Systems*

“MC and MD simulations in polymer science”

K. Binder editor, Oxford, 1995.

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 1step/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 visits each site once.
- **Bead spring model**
  - Bonding interaction holds the chain together. This is a key feature of polymer. *A bead does not represent an atom, but a blob--a section of the chain.*
  - Non-bonded excluded volume interaction (e.g. LJ)

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

$$\textit{Modified harmonic potential } (\textit{with } k = 20, \sigma = 1.95\sigma_{HS})$$

$$\gamma_h = \tfrac{1}{2}\kappa(r - r_0)^2 \qquad \gamma_{hl} = -\tfrac{1}{2}k\sigma \ln[1 - (r/\sigma)^2]$$

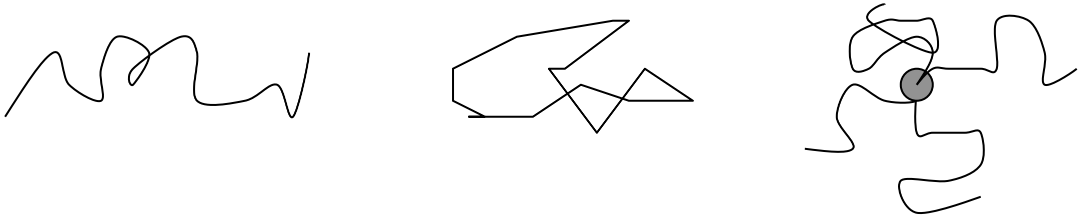
Polymer Phases

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

$$\langle (r_n - r_0)^2 \rangle \rightarrow N^{2\nu}$$

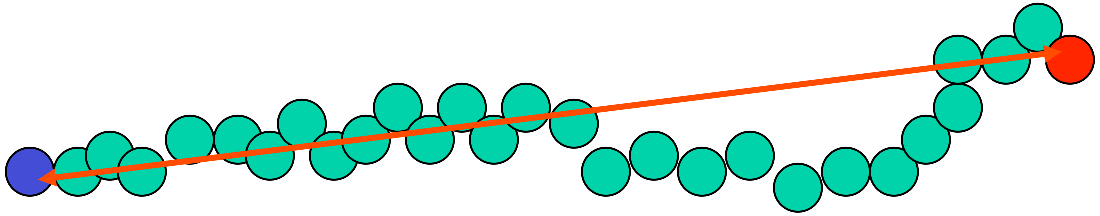
$\nu \sim 0.588$ SAW or 0.5 RW.

- 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)

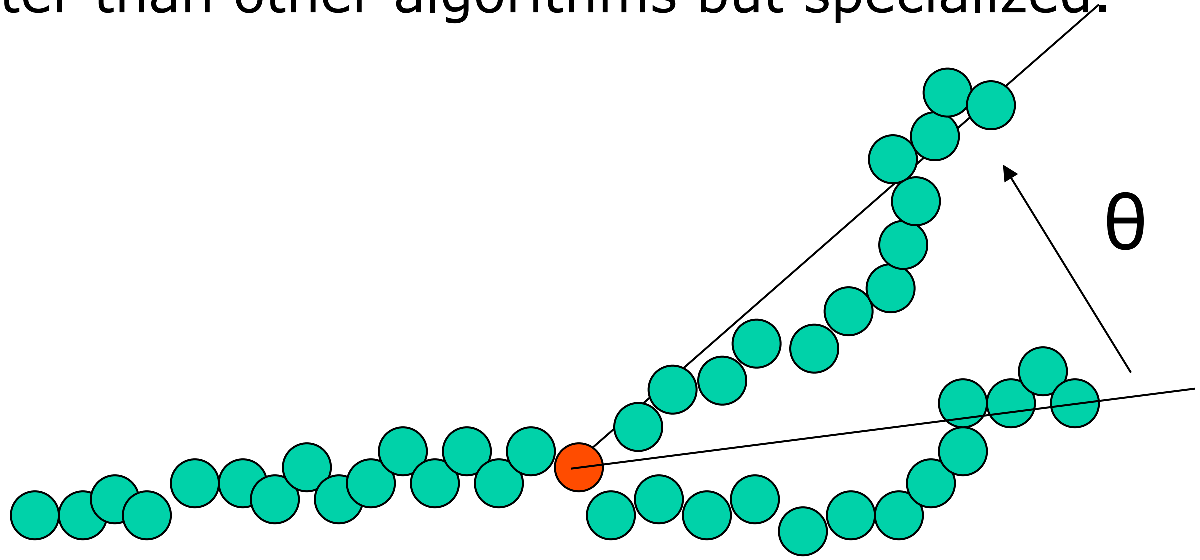
- Polymers move very slowly because of entanglement.
- Local MC just as slow as MD.
- A good algorithm is "reptation."
  - *Cut off one end and stick onto the other end.*
  - *Choose end at random or "bounce" with rejection.*



- Sample directly the bonding interaction
- Acceptance probability will be the 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. (This is the theory of Degennes)

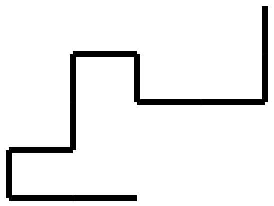
Pivot algorithm

- Take a polymer. Pick an atom at random.
- Rotate one segment with respect to the pivot point a random angle θ.
- Accept or reject.
- Most efficient method for a single chain. Exponent of relaxation of end-end distance is $N^{0.2}$.
- Better than other algorithms but specialized.



Lattice models for polymers

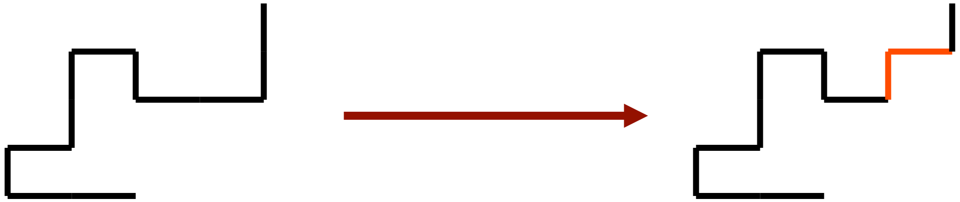
- Maybe we can speed up the algorithm by forcing the polymer to lie on a lattice.
- SAW = “self-avoiding random walk”: a walk on a lattice with N steps which cannot visit a site more than once.



- 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

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.

$$W_n = W_{n-1}\left[\frac{q_i}{q}\right] \qquad < R^2 >= \frac{\sum W_j R_j^2}{W_i}$$

$$q_i = \#\, of\;\; open\;\; moves$$

- 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

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