## 060331 Quiz 1 Polymer Properties

This week we discussed the difference between the view of a polymer chain by a chemist, physicist and engineer (rheologist). We also discussed differences between *models*, *simulations* and *experiments*. An example of the *assumptions* made in the development of a *simulation* for a simple polymer chain were given, which were framed on the concepts of *short* and *long range interactions*. The results for two *models* for long range interactions (Brownian and self-avoidance) were described. An outline for a simulation of a random walk including the assumptions involved was given.

1) A chemist views the polymer chain as composed of chemical units called mers. Flory followed this approach when he developed the *rotational isomeric state model (RISM)* which is based on calculations of chain energy for various bond rotations. Consider the difference between Flory's *model* to calculate chain energy based on bond rotations and a *simulation* of a polymer chain conformation.

a) Make a Neumann projection of 4 carbons showing how the bond rotation angle  $\psi$  might affect the chain segment energy. (Plot energy versus  $\psi$  and show the projection to explain the plot).

b) List the assumptions given in class for a simulation of a *random walk*.

c) Discuss the application of a model (*RISM*) and the use of a simulation to determine the melting point of a polymer (as best you can, i.e. guess if you need to).

d) Discuss the application of a model (*Random Walk*) or the use of a simulation to determine the total size of a polymer chain (you shouldn't have to guess much here).

e) Explain why a *simulation* that included *long-range interactions* would take longer to run than a *simulation* that ignored *long-range interactions*.



**Left:** End to end distance versus chain index for Gaussian Chain shown to the right. **Right:** Position for spherical units on a Cartesian coordinate system following Brownian chain scaling. (Simulation by Beaucage using Igor by Wavemetrics.)

 We discussed two *models* for long range interactions (Gaussian and Excluded Volume) that yield two functions for mean chain size, R, in terms of the number of persistence steps, N and the persistence length 1

N, and the persistence length, l<sub>p</sub>.

- a) What are the assumptions for these two models?
- b) Give these two functions.

c) For a chain of 10,000 persistence units what difference in chain size is expected between the two models?

d) For a single *simulation* of a polymer chain following a Gaussian assumption (figure above) the chain size (end to end distance) fell between the expected result from the two models (Left above). Explain this result. Which line is predicted to be correct?

e) A 3d plot for this *simulation* (Right above) seems to show non-random behavior with clustering of the chain path into nodules. Explain this observation. Is this truly a random path?

 In class you saw a simulation of a Brownian walk (below) where a large bead was driven in 2d space by collisions from a large number of smaller beads (this should mimic pollen grains and gas atoms).

a) Describe in words the persistence length for this simulation.

b) What is the effect of changing the mass ratio (m2/m1) between the two types of beads on persistence length? Explain.

c) In a polymer chain simulation what assumptions (initial values) play the role of the mass ratio in this simulation? Explain.

d) How would long-range exclusion (if the path of the large particle avoided itself on long distances) affect persistence?

e) If the left image below were scaled smaller (shrunken) it might look identical to a small part of the right image. Guess at why this might be important.



http://www.phy.ntnu.edu.tw/ntnujava/viewtopic.php?t=41

Simulation results where large (red) (M2) is a heavy particle and small (grey) (M1) are light gas atoms for instance, **Left:** Large (Red) is of comparable mass to small (grey) (M2/M1 = 5), **Right:** Large (Red) is much heavier than Small (grey) (M2/M1 = 50).





- b) i) assume a lattice (x,y,z)
- ii) assume a starting point (0,0,0)
- iii) assume a step size l
- iv) assume restrictions on direction (along x-y-z only)

iii) and iv) lead to  $l_p$  the persistence length

v) assume the nature of long range interactions (excluded volume or a phantom chain that can be passed through freely) Assume a chain that has no LRI for Gaussian.

vi) you might want to list assumptions concerning branching and other things. (none for Gaussian)

c) The calculation of a melting point requires a detailed knowledge of the energetics of various rotational isomeric states for the chain. These can be compared with the available thermal energy (kT) to see if the chain favors certain helical conformations associated with crystallization (planar zig-zag for polyethylene). A discrete transition can be determined in this way where planar zig-zag becomes favored over a more random conformation at a certain temperature,  $kT_m$ . At the melting point a crystal has a the same free energy as a molten chain.

For a simulation similar energetic information might be used to choose bond rotations but the chain would be allowed to randomly probe free energy space by trial and error using the total chain conformational energy as a basis for skewing a random distribution such as would be used in a Monte-Carlo method (see web notes). At the melting point the average equilibrated volume of a chain shows a discrete transition from a low density to a higher density. Also, the simulation result should display long-range order associated with the crystalline lattice.

d) For a simulation the chain size is determined by application of a set of assumptions such as those listed in b) above repetitively. The chain size is the result of the repetitive calculation. A number of these calculations need to be averaged to obtain a reasonable answer.

For a model such as the random walk model an analytic function to predict average chain size is determined based on some assumptions and physics. The analytic function,  $R \sim N^{1/2} l_p$ , results in a direct value for the chain size.

e) The LRI simulation takes more time since it must check if the next step is exclude by the existing chain.

2) a) The Gaussian model assumes no long range interactions so the chain can pass directly through itself at long distances. The SAW model assumes total exclusion of the chain at long distances. This is the equivalent of a *hard core potential* in simulation literature.

b)  $R \sim N^{1/2} l_p$  Gaussian, Browian, Random Walk  $R \sim N^{3/5} l_p$  SAW, Excluded volume, Good Solvent Scaling

c)  $R_{SAW}/R_{Gaussian} \sim N^{1/10} = (1e4)^{1/10} = 2.51$ 

d) A single simulation for a single chain is not sufficient since the results are a random sample of a wide variety of possible results. Any end-to-end distance from 0 to Nl is possible from a random simulation. On average the Gaussian simulation should follow Gaussian statistics except at very short lengths (N < 10) where chain persistence comes into play.

e) As noted in class the nature of "random" differs from the perception of "random". An interesting example of this is in the random i-pod player. A number of purchasers have returned the random players for not being "random" because they sometimes play the same song twice. We expect clustering in a random process. Another analogy is to throw darts with a blind fold on. You would expect some to hit the bulls eye if you throw a sufficient number of darts.

3) a) There are many ways to describe persistence length. One way (the wikipedia way) is to consider the probability that a particle will continue traveling in a given direction. For the simulation on the left this probability is rather high. It is much lower for the simulation on the right. We can consider a correlation function as the dot product of two vectors for chain steps separated by n steps. The average of this dot product should be 0 for a random path. The average of the square of this dot product is a measure of path persistence.

 $\langle \mathbf{r}(i)\mathbf{\dot{r}}(j) \rangle = 0$  and  $\langle (\mathbf{r}(i)\mathbf{\dot{r}}(j))^2 \rangle \sim l_p$ . There are many other ways to measure persistence.

b) Larger mass ratio results in a smaller persistence since the energy transferred in an elastic collision between a grey dot and the red is small and the motion of the large dot requires many collisions so shorter persistence results from a more jagged path.

c) The initial step length or lattice size and the probabilities for different directional motion as well as the lattice shape determine the persistence length.

d) No effect.

e) This is called self-similarity if it is true within a single object (fractal). Here it means that the solution for one random walk is the same except for scale as the solution for any other random walk. The value of M2/M1 has no relevance except that it defines the scale of the walk, i.e. the persistence length.