ENAS 606: Polymer Physics, Problem Set 1

February 4th, 2013

Solutions are due on Thur 2/14

1. **[15 pts]** *This question involves use of MATLAB to generate trajectories for random walks in three-dimensions.*

Generate ensembles of at least 1000 trajectories for an ideal random walk and a self-avoiding random walk (monomers cannot revisit an occupied point in space) on a cubic lattice. Make calculations for N=100, 500, 1000, 5000 and 10000 monomers or steps. The chain is allowed to take steps of unit length in any of the x, y or z directions.

(a) Provide a plot and show how $\langle R^2 \rangle$ scales with N in each case. Recall that

$$\langle R^2 \rangle = \sum_{i=1}^{N} \sum_{j=1}^{N} \langle (\overrightarrow{R_i}.\overrightarrow{R_j}) \rangle$$

(b) What is the probability distribution function $P(R)$ for N=10000?

(c) Calculate the radius of gyration, $\langle R_g^2 \rangle$ and show how it varies with N. How does $\langle R^2 \rangle / \langle R_g^2 \rangle$ vary with N? Recall that

$$\langle R_g^2 \rangle = 1/N^2 \sum_{i=1}^{N} \langle (\overrightarrow{R_i} - \overrightarrow{R_j})^2 \rangle$$

(d) Subdivide your ideal random walk $N = 10000$ chain by considering only every n$^{\text{th}}$ monomer where $n = 2, 4, 8, 32$ and 128. Are the reduced trajectories still Gaussian in their statistics? At what n do they deviate?

2. **[20 pts]**

Consider the pairwise interaction between uncharged colloidal particles, mediated by a polymer chain attached at their surfaces along a line joining their centers. We examine a linear arrangement of three such particles, as shown in Figure 1.

The attractive interaction between spherical particles due to Van der Waals forces is written as

$$\Phi(s) = -A/6 \left[\frac{2R^2}{s^2 + 4Rs} + \frac{2R^2}{s^2 + 4Rs + 4R^2} + \ln\left(\frac{s^2 + 4Rs}{s^2 + 4Rs + 4R^2} \right) \right]$$

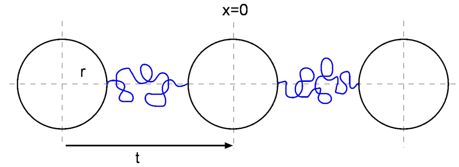

Figure 1: Colloidal particles joined by polymer chains

where s is the separation between the surfaces of the spheres ($t-2r$ in Figure 1), R is the radius of the spheres and A is the Hamaker constant. A good value for the Hamaker constant is $5E-20$ J or about 10 kT at room temperature. For $R \gg s$, this expression reduces to

$$\Phi(s) \approx -\frac{AR}{12s}$$

(a) Make a plot of the inter-particle potential (in units of kT) between the middle and either end particle due solely to the Van der Waals interaction, out to a center-center distance of $10r$.

(b) Consider the displacement of the center particle away from equilibrium ($x = 0$). The free energy change associated with the change in the end-end dimensions of the left and right polymers modifies the interaction potential between the particles. Let's examine polymers with $R_g = r, r/2$ and $r/100$, separated by $t = 4r, 8r$ and $16r$ (9 cases).

i. Construct and plot the modified potentials (i.e. add the contribution from the polymer chains to the potential from part I above) under the assumption that the chains are Gaussian. That is, they follow force-displacement relationships of the form

$$f = 3kT\frac{R}{\langle R_0^2\rangle}$$

where $\langle R_0\rangle$ is the unperturbed end-end distance of the chain.

ii. Construct and plot the modified potentials under the assumption that the chains are worm-like. That is, they follow force-displacement relationships of the form

$$\frac{fb}{kT} \cong \frac{2R}{R_{max}} + \frac{1}{2}\left(\frac{R_{max}}{R_{max}-R}\right)^2 - \frac{1}{2}$$

given $R_{max} = 50b$. In the WLC model, $b = 2l_p$ and the radius of gyration is given by

$$\langle R_g^2\rangle = \frac{1}{3}R_{max}l_p - l_p^2 + \frac{2l_p^3}{R_{max}} - \frac{2l_p^4}{R_{max}^2}\left(1 - \exp\left(-\frac{R_{max}}{l_p}\right)\right)$$

(c) What other factors could be considered in this picture to make it more realistic?

3. **[10 pts]** *Problem 2.12 from the text*

Consider a polymer containing N Kuhn monomers (of length b) in a dilute solution where ideal chain statistics apply. The molar mass of the polymer is M.

(a) What is the mean-square end-to-end distance R_0^2 of the polymer?

(b) What is the fully extended length R_{max}?

(c) What is the mean-square radius of gyration R_g^2 of this polymer?

(d) Estimate the overlap concentration c^* for this polymer, assuming that the pervaded volume of the chain is a sphere of radius R_g

(e) How does this overlap concentration depend on the degree of polymerization

(f) What is the ratio of its fully extended length to the average root mean square end-to-end distance R_{max}/R_0?

(g) Consider an example of a polymer with molar mass $M = 10^4$ g/mol. consisting of $N = 100$ Kuhn monomers (of length $b = 10\mathring{A}$ and determine R_0, R_g, R_{max}, c^* and R_{max}/R_0.

4. **[5 pts]**

The concept of the tension *blob* was introduced to make a simple scaling argument for the force-extension response of a Gaussian chain. Describe the concept and its utility in your own words.