3.063
Polymer Physics   Spring 2007

Problem Set 1
Due 2/15/07

1.1
The ideal random walk model for polymer coils has a probability distribution for finding the two ends of the polymer chain comprised of n links of length l a distance r apart:

$$P(r,n) = \left(\frac{2\pi n l^2}{3} \right)^{-3/2} \exp\left(-\frac{3r^2}{2nl^2} \right)$$

(a). Explicitly show that this probability distribution is normalized:
$$\int_0^\infty P(r,n)\, 4\pi r^2\, dr = 1$$

(b). Explicitly show that the mean square end to end distance of the chain is:

$$\langle r^2 \rangle = \int r^2\, P(r,n)\, 4\pi r^2\, dr = nl^2$$

(note: useful integrals are shown on page 238 of Young and Lovell)

(c). When the chain is in a solvent the solvent quality factor changes the characteristic dimensions of the coil and the new probability distribution function is given by:

$$P(r,n,\alpha) = \left(\frac{2\pi \alpha^2 n l^2}{3} \right)^{-3/2} \exp\left(-\frac{3r^2}{2\alpha^2 n l^2} \right)$$

Make a plot (numerical values please, not a sketch) of the segment density distribution for a chain in a good solvent with $\alpha = 1.5$ and compare to the chain in a theta solvent.

(d). Advanced theory shows that the value of solvent quality factor for a good solvent depends on molecular weight to $1/10^{th}$ power. Show that this is consistent with the scaling law for chains in good solvents where
$$\langle r^2 \rangle = n^{\frac{6}{5}} l^2$$

1.2
(a). Write down the scalling law for a random walk and describe the two distinct situations in polymer physics in which the actual chain end to end distance scales as in an ideal random walk.

(b). Random walks are a type of *fractal object*. Fractals are self-similar objects, that is, objects that appear the same when viewed at different magnifications. Fractals are discussed in The Structure of Materials by Allen and Thomas on pages 74-80. Self similar objects can be characterized by their fractal dimension, defined as the scaling exponent D between the mass of the object M and the characteristic size of the object R.

$$M \approx R^D$$

Show by simply relating the mass of the polymer to its characteristic size (i.e. its rms end to end distance) that a polymer chain that has the shape of an ideal random walk (RW) has a fractal dimension of 2.0.

(c). Show that if the polymer is placed in a *good* solvent, the fractal dimension decreases to a value of 1.66. Recall that in a good solvent the chain adopts the shape of a self-avoiding random walk (SARW).

(d). Show that a chain that has collapsed into a compact globule has a fractal dimension of 3.

1.3 (a). Using scaling laws for polymer chains in various environments, estimate the size of a polystyrene chain with 208,000 g/mol molecular weight. Take the length of a C-C single bond as 0.154nm. The characteristic ratio of PS is 10.4 and the density of bulk PS near room temperature is 1.05 g/cm^3
(i). precipitated from a nonsolvent
(ii). in cyclohexane at 36 C
(iii). in THF at 25 C

(b). Compute the percent of the pervaded volume that the chain occupies in each case. The pervaded volume is the volume of the sphere that surrounds the overall chain.

(c). Compute the contour length of the PS molecule in part (a) and calculate the ration of the size of the contour length to the RW size.

1.4
Starting from the Flory Huggins expression for the free energy of mixing of a solvent ($x_1 = 1$) and a polymer having x_2 segments, explicitly derive the following chemical potentials for the solvent and for the polymer:

$$\mu_1 - \mu_1^{0} = RT\left[\ln \phi_1 + \left(1 - \frac{1}{x_2}\right)\phi_2 + \chi \phi_2^{2}\right] \qquad \text{solvent}$$

$$\mu_2 - \mu_2^{0} = RT\left[\ln \phi_2 - \left(x_2 - 1\right)\phi_1 + x_2 \chi \phi_1^{2}\right] \qquad \text{polymer}$$