Quiz 6 Polymer Properties October 2, 2013

1) In class the function $<R^2> = nl^2$ was obtained by integration of the Gaussian probability to obtain the second moment. Flory and Krigbaum modified the Gaussian probability by considering the probability of self-avoidance using the excluded volume of a Kuhn unit.

   a) Write a modified Gaussian probability using this probability of self-avoidance.

   b) This function cannot be integrated. How did Flory and Krigbaum find the end-to-end distance as a function of molecular weight from this probability?

   c) What are the two assumptions involved in this calculation? Discuss the appropriateness of these two assumptions.

   d) Flory and Krigbaum considered the temperature dependence of the excluded volume by calculating the Boltzmann probability for enthalpic interaction. Write and expression for the Boltzmann probability of enthalpic interaction on mixing a polymer chain in a solvent and explain the origin of the terms.

   e) The expression for temperature dependence of excluded volume shows that excluded volume increases with increasing temperature and this is the source of coil expansion. Why might you expect excluded volume to increase with temperature?

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1) a)

$$\exp\left(-\frac{3R^2}{2Nb^2}-\frac{N^2V_c}{2R^3}\right)$$

b) By setting the derivative of $R^2P(R)$ to zero they found the most probable end to end distance, R^*.

c) First it is a perturbation theory so it is assumed that they can use the Gaussian function as a base point then add a small perturbation associated with excluded volume.

Secondly, they obtain

$$\left(\frac{R^*}{R^*_0}\right)^5-\left(\frac{R^*}{R^*_0}\right)^3=\frac{9\sqrt{6}}{16}\frac{V_c}{b^3}\sqrt{N}$$

by minimization of $R^2P(R)$. They assume R^*/R^*_0 is very large so that they can ignore the power 3 term.

The two assumptions are at odds. The ratio cannot be large if it is a small perturbation. The scaling change that is found from their approach is not a small perturbation. Nonetheless, their approach seems to work and has been repeatedly verified by experiment in a wide range of systems from computer simulations of bead models to worm-like micelles and many synthetic polymers.

d)

$$\frac{\langle E(R)\rangle}{kT}=\frac{n^2V_c\chi}{R^3} \qquad P_{Boltzman}(R)=\exp\left(\frac{-\langle E(R)\rangle}{kT}\right)$$

χ is the average change in enthalpic interaction on mixing of the polymer in the solvent, $z\Delta\varepsilon$, per Kuhn site per kT, $\chi = z\Delta\varepsilon/kT$, z is the number of coordination sites per Kuhn site and $\Delta\varepsilon = (\varepsilon_{pp}+\varepsilon_{ss}-2\varepsilon_{ps})/2$. Vc is the volume per Kuhn site, n is the number of Kuhn segments in the chain, R is the chain end to end distance. nV_c/R_3 is the volume fraction of polymer and $n\chi$ is the enthalpic interaction per chain per kT.

e) At the theta temperature excluded volume vanishes just before the coil collapses. At high temperature we expect a large excluded volume near the hard-core value, $V_c/2$. The excluded volume increases from the theta temperature because the entropic contribution to free energy becomes higher at higher temperature, $kT\Delta S$. So the balance between entropy and enthalpy favors entropic expansion at high temperature. This is reflected in chi being proportional to inverse temperature. In the end, coil expansion is enhanced by thermal motion of the chain Kuhn units which overcome enthalpic attraction.