Quiz 6 Polymer Properties October 4, 2013

1) In class the function $\langle R^2 \rangle = nl^2$ was obtained by integration of the Gaussian probability to obtain the second moment.
   a) Show how $\langle R^2 \rangle = nl^2$ was obtained by writing out this integration.
   b) Flory and Krigbaum modified the Gaussian probability by considering the probability of self-avoidance using the excluded volume of a Kuhn unit. Give an expression for the probability of excluded volume.
   c) Write a modified Gaussian probability using this probability of self-avoidance.
   d) 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?
   e) What are the two assumptions involved in this calculation? Discuss the appropriateness of these two assumptions.

2) Flory and Krigbaum considered the temperature dependence of the excluded volume by calculating the Boltzmann probability for enthalpic interaction.
   a) 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.
   b) How can this probability be used obtain an expression for the temperature dependence of excluded volume?
   c) Does this expression for temperature dependence modify the chain scaling?
   d) 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?
   e) The expression for temperature dependence of excluded volume has two terms, one associated with the hard-core excluded volume and one with the enthalpic interaction. The interaction parameter can have a negative value if there is a specific enthalpic attraction between the polymer and the solvent. How does the coil expansion behavior for the polymer differ if chi is negative versus if chi is positive?

ANSWERS: **Quiz 6 Polymer Properties October 4, 2013**

1) a)

$$\left\langle R^2 \right\rangle = \int_{-\infty}^{\infty} R^2 P(R)\, dR \qquad P(R) = \left(\frac{3}{2\pi\sigma^2}\right)^{3/2} \exp\left(-\frac{3(R)^2}{2(\sigma)^2}\right)$$

b)

$$P_{Ex}(R) = \left(1 - V_c/R^3\right)^{n^2/2} = \exp\left(\frac{n^2 \ln\left(1 - V_c/R^3\right)}{2}\right) \sim \exp\left(-\frac{n^2 V_c}{2R^3}\right)$$

c)

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

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

e) 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.

2) a)

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

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.

b) This probability multiplies the non-temperature dependent Flory Krigbaum expression,

$\exp\left(-\frac{3R^2}{2Nb^2}-\frac{N^2V_c}{2R^3}\right)$ to yield, $E(R)=kT\left(\frac{3R^2}{2nl^2}+\frac{n^2V_c\left(\frac{1}{2}-\chi\right)}{R^3}\right)$. The excluded volume becomes $V_c(1/2 - \chi)$ and $\chi = z\Delta\varepsilon/kT$.

c) The chain scaling remains the same since the excluded volume does not involve a molecular weight or an end to end distance term.

d) 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.

e) If there is a specific attractive interaction between polymer and solvent and chi is negative then there is no theta temperature since the lowest excluded volume occurs at the highest temperature and is equal to $V_c/2$. At lower temperatures the excluded volume becomes larger not smaller for negative interaction parameters.