121008 Quiz 5 Polymer Properties

1) Polymer coils display two types of entropy, one associated with the number of chain conformations (conformational entropy) and one associated with the arrangement of whole polymer coils relative to solvent molecules (mixing entropy). The first entropy leads to a function for the average change in energy with end-to-end distance R and the Flory-Krigbaum theory; while the second leads to the Flory-Huggins Equation. Both the Flory-Krigbaum Equation and the Flory-Huggins Equation rely on the interaction parameter to describe enthalpic interactions. That is, the same parameter, χ, is used to describe coil collapse and phase separation.
   a) Why would the same enthalpic parameter be used for both the conformational states of a single chain and the mixing of whole chains with solvent?
   b) The basis of the Flory-Krigbaum approach is excluded volume. Consider two spheres. What is the volume excluded to one sphere by another sphere? (Take the center of mass of each sphere at closest approach and calculate the volume denied to the center of mass due to the presence of the second sphere.)
   c) How would this excluded volume change for an asymmetric objects like randomly oriented rods?
   d) In the Flory-Krigbaum theory the exact shape of the chain unit is not known so we define the volume excluded by a chain unit as V_0. This is often replaced by b^3 where b is the length of a chain unit in the chain direction. Do you think that this is a good assumption?
   e) Show how the exponential expansion, $e(-x) = 1-x+x^2-\ldots$ can be used to obtain an exponential expression for the probability of excluded volume in a polymer chain.

2) The following plot shows the behavior of R_g (and R_h) as a function of temperature.

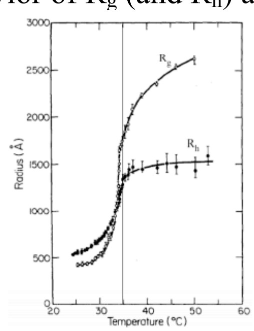

Figure 3. *Radius of gyration, R_g, and hydrodyamic radius R_h versus temperature for polystyrene in cyclohexane. Vertical line indicates the phase separation temperature. From Reference [21].*

   a) What is R_g?
   b) At what temperature is the chain Gaussian? (What is the name of this temperature and what is the value in the plot.)
   c) How can an exponential probability be written to explain a thermal activation energy associated with excluded volume?
   d) Write an expression for this energy and explain its origin.
   e) Give a function for the coil size based on this approach that describes the behavior shown in the plot.

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1) a) This is because enthalpy just adds up linearly, while entropy has to do with the nuances of organization. Enthalpy is a much simpler subject. The total enthalpy of interaction is based on a linear sum of the component interactions. For Flory's theories we base this on simple binary interactions, monomer-monomer, solvent-solvent or monomer-solvent. These are summed over a single chain for Flory-Krigbaum theory and over the entire system for Flory-Huggins equation.

b) The volume excluded by spheres is 8 times the volume of a sphere since the center of mass for the two spheres is separated by 2R and the excluded volume is a sphere of radius 2R.

c) The excluded volume for randomly arranged rods is larger compared to an equivalent (same volume) sphere since the rods would be excluded in a sphere of radius L where L is the length of the rod.

d) It is probably not a great assumption but there is no other option. The chain units are not free to rotate in all directions as rods might be.

e) The probability of avoiding exclusion of a single chain unit is $(1-V_0/R^3)$. There are n-1 other units and this must be considered for n chain units (probabilities multiply). This over counts by 2! The total probability of avoiding exlcluded volume is $(1-V_0/R^3)^{n(n-1)/2!} \sim (1-V_0/R^3)^{n\wedge 2/2}$. To get this probability into an exponential form we take a log of this probability and simplify using the expression given in the problem, $\ln((1-V_0/R^3)^{n\wedge 2/2}) = (n^2/2)\ln(1-V_0/R^3)$, $1- V_0/R^3 \sim \exp(-V_0/R^3)$ so $(n^2/2)\ln(1-V_0/R^3) \sim n^2 V_0/(2 R^3)$ and the probability is $\exp(n^2 V_0/(2 R^3))$.

2) a) R_g is the radius of gyration. It scales with the end-to-end distance.

b) The chain becomes Gaussian at the θ-temperature. For this case θ = 34.5°C.

c) $P_{exclusion} = \exp(\Delta E/kT)$

d) $\Delta E = \chi n^2 V_0/(R^3)$ For a monomer with z sites of interaction we can define a unitless energy parameter $\chi = z\Delta\varepsilon/kT$ that reflects the average enthalpy of interaction per kT for a monomer
The volume fraction of monomers in the polymer coil is nV_c/R^3 And there are n monomers in the chain with a conformational state of end-to-end distance R.

e) $R^* = R_0^* \left(\dfrac{n^{1/2} V_0 (1/2 - \chi)}{b^3} \right)$ where $\chi = \dfrac{z\Delta\varepsilon}{kT}$