Quiz 13 Polymer Properties November 22, 2013

1. Flory proposed the following equation for the osmotic pressure:

$$\Pi = \frac{kT}{V_c}\left(\frac{\phi}{N} + \left(\frac{1}{2} - \chi\right)\phi^2 + \ldots\right)$$

   a) The first term is an energy balance assuming each polymer molecule has translational energy of kT. Derive the first term of this equation.
   b) The second term is a value for the second virial coefficient. Give a definition of the interaction parameter in this term explaining how chi is based on a different structural unit compared to the first term.
   c) Do you think it is appropriate to use these two different structural units for the basis of the two terms in the same equation? Explain why or why not.
   d) For colloidal suspension of nano size spheres, such as polystyrene latex particles or colloidal silica, could you use the first term to obtain the number average mass of the spheres? Why or why not?
   e) What kind of expression would you use for the second virial coefficient for a colloidal suspension of nano-size spheres?

2. des Cloizeaux proposed use of the concentration blob model to account for deviations of the osmotic pressure from Flory's expression at high concentrations above Φ*. des Cloizeaux proposed an expression dependent on the first term in Flory's expression times $(\Phi/\Phi^*)^P$, where P can be determined under the condition that the osmotic pressure does not depend on the molecular weight of the chain, N, above the overlap concentration.

   a) Find the power "P" in terms of the fractal dimension of the chain above the blob size.
   b) What is the concentration scaling of osomtic pressure for $d_f = 5/3$? How does this compare with experimental observations?
   c) What is the concentration scaling of osmotic pressure for $d_f = 2$? How does it compare with the Flory expression?
   d) Does the des Cloizeaux approach really depend on the existance of a concentration blob? Explain your answer.
   e) Vapor pressure osmometry can be used to measure molecular weight from changes in the vapor pressure of a solvent in a polymer solution. Do you think that this method would measure number average molecular weight? Why or why not?

ANSWERS: **Quiz 13 Polymer Properties November 22, 2013**

1) a) PV is a measure of energy. nkT is a measure of the kinetic energy of diffusing molecules, where n is the number of molecules. n/V is the number concentration. The mass concentration for a polymer is $nN/V = \Phi$. So we have $\pi V = kT\,\Phi/N$.

b) The first term of part "a" considers the translational motion of the whole polymer molecule. The second term considers Kuhn units and their kinetic energy, kT. The interaction parameter is the average energy of mixing per Kuhn unit per kT so the second term is based on a different structural unit than the first term, which considers kinetic motion of translation of the chain as a whole.

c) This is a somewhat open-ended question. Either answer is correct. It would seem that there is a problem with using a different structural basis for two terms in the same equation. On the other hand this is a well excepted method to determine the interaction parameter. The values from this method typically differ from those obtained using light scattering or neutron scattering.

d) The first term can be used for colloidal particles.

e) The second term could be replaced by the excluded volume for a sphere, $4\,V_0$. The chi term would not be appropriate for spheres since they are not made up of Kuhn units.

2) a) $\pi/(kT\,\Phi) = (1/N)\,(\Phi/\Phi^*)^P$ We have from earlier that $\Phi^* \sim N^{1-3/df}$, so if $\pi \sim N^0$, then $P(3/d_f-1) -1 = 0$, so $P = 1/(3/d_f-1)$.

b) $P = 5/4$ and $\pi \sim \Phi^{9/4}$. This matches experimental observations.

c) $P = 2$ and $\pi \sim \Phi^3$. This doesn't match the Flory prediction.

d) The des Cloizeaux approach relies on Φ/Φ^* being the basis of the concentration dependence. This is a kind of renormalization of the concentration that is common to the blob model. The assumption that the dimension is 5/3 above the overlap concentration is inherent to the concentration blob model.

e) Vapor pressure osmometry relies on Raoult's law which is a colligative law, depending on counting of molecular species. So it measures the number average molecular weight.