## 060512 Quiz 7 Polymer Properties

This week we covered the concentration dependencies of the osmotic pressure of a polymer solution using the concentration blob model and the Flory-Huggins (F-H) equation for polymer solutions and blends.

1) Last weeks quiz discussed an analogy between a gas in a container and the Pfeffer cell for measurement of osmotic pressure.

a) Consider a lattice with two types of gas atoms, A and B of identical size that are randomly arranged. Wikipedia describes the entropy of mixing by:

We can use Boltzmann's equation for the entropy change as applied to the mixing process

 $\Delta S_m = k_B ln \Omega$ 

where  $\,k_B$  is Boltzmann's constant. We then calculate the number of ways  $\,\Omega$  of arranging  $\,N_1$  molecules of component 1 and  $\,N_2$  molecules of component 2 on a lattice, where

 $N = N_1 + N_2$ 

is the total number of molecules, and therefore the number of lattice sites. Calculating the number of permutations of N objects, correcting for the fact that  $N_1$  of them are *identical* to one another, and likewise for  $N_2$ ,

 $\Omega = N!/N_1!N_2!$ 

After applying Stirling's approximation, the result is

 $\Delta S_m = -k_B [N_1 ln(N_1/N) + N_2 ln(N_2/N)]$ 

Sterling's Approximation  $\ln n! \cong n \ln n - n$ 

Explain the connection or disagreement with the F-H Equation for an ideal gas (N = 1).

b) How does this expression differ from the expression for a polymer solution. Explain the reasoning for this difference.

c) Add to this expression a term representing the average enthalpic interaction per lattice site per kT.

d) From the discussion of chain overlap we know that there is a finite limit to dilution for a polymer coil. Comment on how this might effect the phase diagram and implementation of the F-H equation.

e) What is the critical value of  $\chi$ ,  $\chi_c$ , for the gas and for the polymer solution? Explain the difference.

2) a) Plot the Flory-Huggins equation for the gas mixture of question "1a" in a plot of free energy per kT per lattice site versus volume fraction of A for  $\chi = 0$ ,  $\chi = 0.5$ ,  $\chi = 1$ ,  $\chi = 2$ ,  $\chi = 2.5$ .

b) Show graphically the location of the critical point, the binodal points and the spinodal points in part "a".

c) The binodal regime is considered a meta-stable region of the phase diagram while the spinodal regime is considered unstable. Explain the difference between stable: meta-stable and unstable in the context of the free energy plot of part "a".

d) Sketch a phase diagram for a gas mixture following the Flory-Huggins-like gas equation.

- e) Explain the connection between the plot in part "a" and the plot in part "d".
- 3) a) In models and simulations of polymer mixing the critical  $\chi$  is calculated from N  $\chi_c = 2$ , show how this can be obtained from the F-H equation.

b) In class we observed the phase separation of PVME (polyvinylmethylether) in water when the solution was heated. If we consider N in the Flory-Huggins equation to be the number of thermal blobs in a chain how would changes in the size of thermal blobs with temperature effect miscibility? Could this explain the observation of an LCST in this system (phase separation on heating)?

c) If we do not invoke the thermal blob, how can the Flory-Huggins equation be modified to allow for the observed LCST behavior?

d) Would it be possible to have both an LSCT and an UCST in the same polymer blend according to your answer to "c"?

e) Explain what happens to thermodynamic fluctuations at the critical point.

## **ANSWERS: 060512 Quiz 7 Polymer Properties**

1a)  $S/(NkT) = \phi_A \ln \phi_A + (1-\phi_A) \ln(1-\phi_A)$ 

The two equations are identical

b) The polymer term is divided by the chain molecular weight z. The number of ways to arrange the units remains random since the chain is Gaussian but the number of molecules is reduced by z.

c)  $S/(NkT) = (\phi_A \ln \phi_A)/z + (1-\phi_A) \ln(1-\phi_A) + \phi_A(1-\phi_A)\chi$ 

d) F-H assumes that infinite dilution is possible. This is not true at very low number fractions. The free energy plot will show a horizontal tail at the polymer end of the curve.

e) For the gas  $\chi_c = 2$  while for the solution  $\chi_c = 1/2$ . This is because the second derivative using the critical volume fraction from the third derivative yields,

 $\chi_c = 1/2 (1/\sqrt{N_A} + 1/\sqrt{N_B})^2 \qquad \text{which when } N_A = N_B = 1 \text{ yields } 2 \text{ and when } N_A >>>1 \text{ yields } 1/2.$ 

2)



c) Stable indicates the one phase region where any fluctuation in composition leads to a net increase in the free energy. Unstable indicates the spinodal region where any fluctuation in

composition lowers the free energy so phase separation is spontaneous. Meta-Stable indicates the binodal region where small fluctations dissipate due to a weak increase in free energy but large fluctuations decay into phase separation with a net lowering of the free energy.

3) a) We consider a symmetric blend of two polymers. Then the F-H free energy of mixing is given by,

$$\begin{aligned} \int_{A^{1}} \frac{d^{2}}{dt} &= \frac{d}{N} \frac{\ln d}{N} + \frac{(1-4)\ln(1-4)}{N} + \frac{d(1-4)\pi}{N} \\ & Nf(4) &= \frac{d}{N} \frac{\ln d}{t} + \frac{(1-4)\ln(1-4)}{N} + \frac{d(1-4)N\pi}{N} \\ & N \frac{d}{dt} \frac{f(4)}{dt} &= \ln t + (1 - \ln(1-4) - 1 + N\pi - 2 \frac{d}{t}N\pi) \\ & N \frac{d^{2}f(4)}{dt^{2}} &= \frac{1}{t} + \frac{1}{(1-t)} - 2N\pi \\ & N \frac{d^{2}f(4)}{dt^{2}} &= \frac{1}{t^{2}} + \frac{2}{(1-t)^{2}} \\ & N \frac{d^{2}f(4)}{dt^{2}} &= \frac{1}{t^{2}} + \frac{2}{(1-t)^{2}} \\ & \int_{Nm} \frac{d^{2}f(4)}{dt^{2}} &= 0 \quad we \text{ field} \quad t_{e} = 0.5 \\ & U(5,n) \frac{d^{2}f(4)}{dt^{2}} &= 0 \quad we \text{ field} \quad t_{e} = 2N\pi_{c} \\ & \frac{d^{2}f(4)}{dt^{2}} &= 0 \quad we \text{ field} \quad t_{e} = 2N\pi_{c} \end{aligned}$$

b)  $N_T = N/n_T = N (1 - 2\chi)^2$  as temperature rises  $N_T$  drops and the entropy for the system drops reducing miscibility.

c) Traditionally, we redefine  $\chi$  as  $\chi = A - B/T$  where A is the noncombinatorial entropy and B is the conventional enthalpic part of  $\chi$ .

d) It would require higher order terms in (1/T) such as  $\chi = A - B/T + C/T^2$ . Such systems have been observed (see book by Olabisi on polymer blends).

e) At the critical point the free energy as a function of composition is essentially flat meaning that there is no penalty to but also no gain from large composition fluctuations on large scales. The fluctuations are random and not really governed by thermodynamics. Since there is no driving force for these fluctuations the kinetics (rate of composition fluctuation) becomes slow (critical slowing down). Basically the system becomes unpredictable near the critical point.