051407 Quiz 6 Polymer Properties

1) In class we discussed the similarity between an ideal gas and a polymer solution using the ideal gas law, $P = \rho kT$, where $\rho = n/V$ and n is the number of gas atoms in the system.

   a) Does the ideal gas law apply to an incompressible or to a compressible system?

   b) The Flory-Huggins equation involves the log of the volume fraction. Show that the thermodynamic expression, $dG_{mixing} = V_{mixing}\ dP$ can be used to obtain an expression similar to the Flory-Huggins entropy of mixing term, $\Delta G_{mixing} = kT\ \ln(P_{mixture}/P_{pure})$.

   c) For an ideal gas the partial pressure is equal to the molar volume. Is this identity appropriate for an incompressible system or for a compressible system?

   d) Explain why equations for gasses (compressible systems) could be appropriate for highly incompressible systems (polymers).

   e). Engraved on Boltzman's tomb in Vienna is $S = k\ \ln\Omega$, where Ω is the number of states that a system can achieve. If $\Omega = n!/(n_1!\ n_2!)$ and using Sterling's approximation, $\ln y! = y\ \ln y - y$ for large y, show that you can obtain an expression similar to the Flory-Huggins Entropy of mixing and to the ideal gas mixing law.

2) Explain how a polymer in an osmometer is similar to an ideal gas by:

   a) Sketch an osmometer and describe the source of the excess pressure on the polymer side.

   b) Write a virial expansion (Taylor Power Series expansion) in concentration from the ideal gas law.

   c) Compare this expression with the expression obtained from the Flory-Huggins Equation,
   $\pi = kT\ c\ [1/N + (1/2 - \chi)\ c]$. Be sure to explain the term 1/N.

   d) Previously we obtained $(1 - 2\chi)$ as an expression for the excluded volume. Why does the virial expansion contain 1/2 of this term?

3) At high concentration the osmotic pressure follows $c^{9/4}$.

   a) Is this consistent with the Flory-Huggins expression of question 2?

   b) What is the overlap concentration? Why is this important to semi-dilute solutions?

   c) Above the overlap concentration can the osmotic pressure depend on molecular weight?

   d) Obtain the $c^{9/4}$ dependence of osmotic pressure on concentration above the overlap concentration by considering the concentration blob and it's scaling dependencies.

4) a) For a mixture of two macromolecular components of molecular weight n_A and n_B give expressions for the critical volume fraction and the critical interaction parameter.

   b) Show that the critical interaction parameter for a polymer solution of extremely high molecular weight is ½.

   c) Show that the critical interaction parameter for a symmetric polymer blend is 2/n.

   d) Temperature can be converted to χ directly making a χ versus composition phase diagram possible. Why would one plot χn versus composition rather than temperature or χ versus composition for a phase diagram?

5) a) Sketch the Gibbs Free energy obtained using the Flory Huggins equation below the critical temperature, at the critical temperature and above the critical temperature.

b) Show from the plot where the critical point, binodal and spinodal curves arise.

c) Sketch the phase diagram (χn versus composition or temperature versus composition) indicating how it was obtained from the free energy curves and show the regions where spinodal decomposition and nucleation and growth would be observed.

d) Why is it rare to observe spinodal decomposition despite the wide area it occupies in the phase diagram?

e) What is special about the critical temperature? Explain the behavior of a system near a critical point.

1) a) The ideal gas law applies to a compressible systems.
b) Substitute the ideal gas law for V and we have:

$$dG = nkT\frac{dP}{P}$$

integration yields $\Delta G_{mixing} = kT \ln(P_{mixture}/P_{pure})$

c) The partial pressure is equal to the molar volume for a compressible system.
d) The Flory-Huggins equation considers the polymer units and solvent molecules as gas molecules and considers the statistical thermodynamics of mixing. The pressure given above is converted to mole fraction and the system is not allowed to display compressibility.
e)
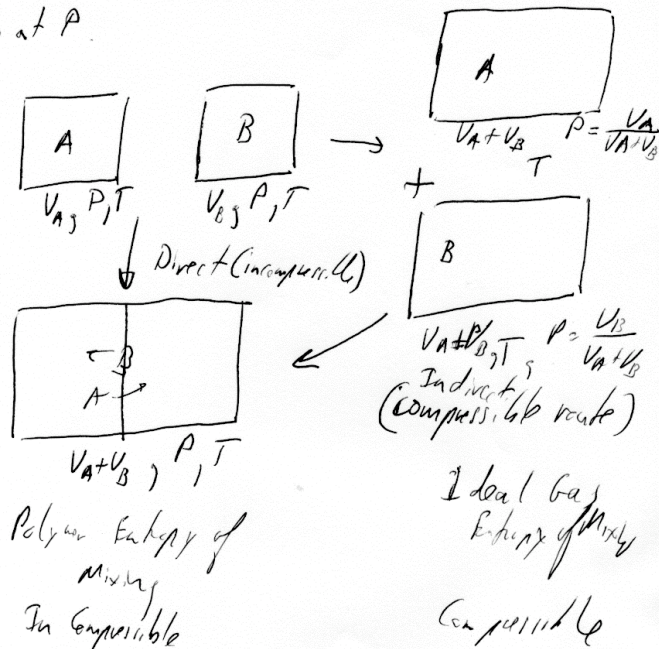
1)e) at
2) a)

$$G = -TS = nKT(x_1 \ln x_1 + x_2 \ln x_2)$$

Solution   Solvent

Polymer Molecules act as if they were ideal gas molecules

leading to a pressure $\Pi \sim \left(\frac{n}{V}\right) KT$

b)

$$\Pi = KT\left(c A_1 + \frac{c^2}{2!} A_2 + \frac{c^3}{3!} A_3 + ...\right)$$

$$c = \frac{n}{V}$$

c)

$A_1 = \frac{1}{N}$ since we count # of Polymer Molecules not

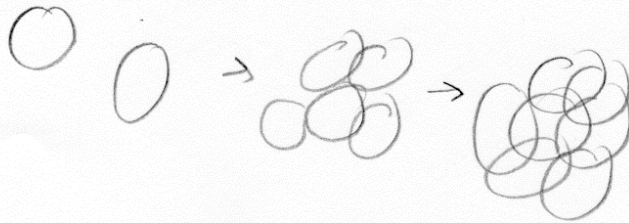mass concentration $\frac{mass}{N}$ = # polymer chains in the solution

$A_2 = B(1 - 2x)$

d) we divide A_2 by $2!$ in the virial expansion.

3a) No $\quad \Pi \sim c^2$ for R-W

b)
$$\phi^* = \frac{N}{R_F^3} \qquad \text{Concentration when coils touch}$$

c) No since you don't see individual coils above ϕ^*

3) (d)
$$R_r = r_c N_c^{1/2}$$
$$r_c = n_c^{3/5} l_k$$
$$\Pi = \frac{kT c}{N}\left(\frac{c}{c^*}\right)^m = \frac{kT c}{N}\left(\frac{c}{c^*}\right)^{5/4} \sim \left(\frac{c}{c^*}\right)^{9/4}$$

$$\left(\frac{c}{c^*}\right) = c\, l_k^3\, N^{4/5}$$

above c^* $\quad \Pi = N^0$

$$\frac{4m}{5} = 0 \qquad m = 5/4$$

4) (a) $\phi_{A_c} = \dfrac{\sqrt{n_a}}{\sqrt{n_a} + \sqrt{n_b}}$

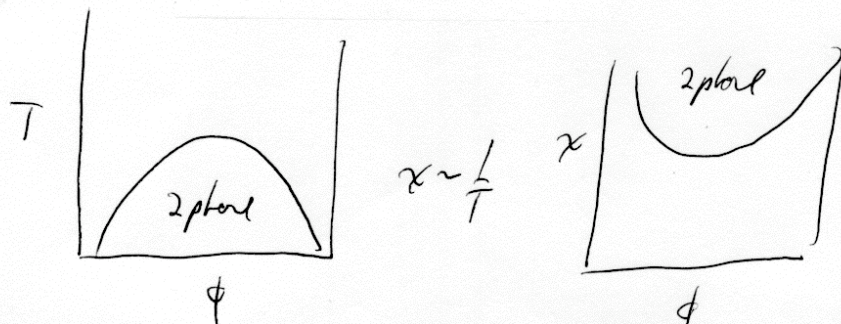$$\chi_c = \frac{1}{2}\left(\frac{1}{\sqrt{n_a}} + \frac{1}{\sqrt{n_b}}\right)^2$$

(b) For solution $n_a = 1$ $n_b \Rightarrow \infty$

$$so \quad \chi_c = \frac{1}{2}\left(1 + \frac{1}{n_b}\right)^2 \Rightarrow \frac{1}{2}$$
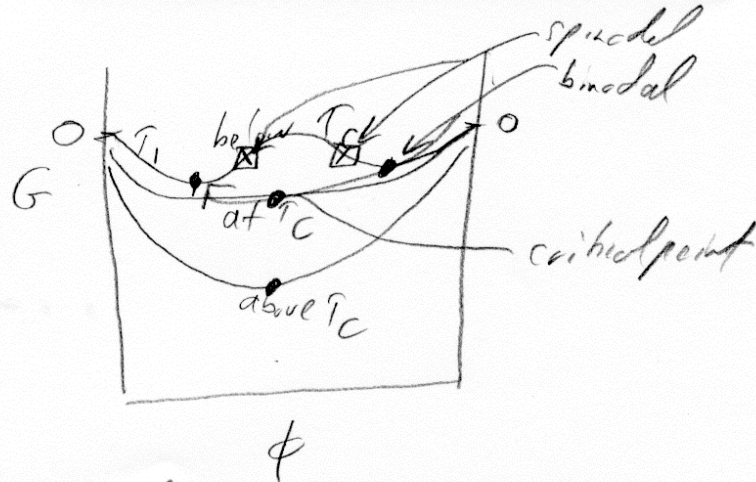
(c) Symmetric $n_a = n_b = n$

$$\chi_c = \frac{1}{2}\left(\frac{2}{\sqrt{n}}\right)^2 = \frac{2}{n}$$

(d)

for symmetric blend $\chi_c n = 2 \equiv$ critical point
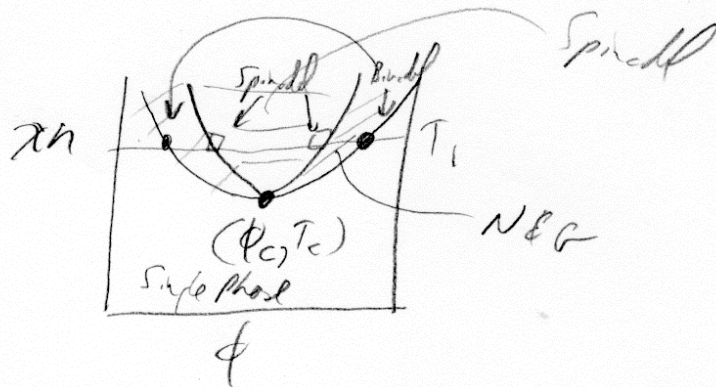
interactions can be changed by χ or by n

χn

5a)

below T_c

spinodal
binodal

O ← T_1

G

at T_c

critical point

above T_c

ϕ

b) for Spinodal Blend

c)

x_n

Spinodal

Binodal

T_1

(ϕ_c, T_c)

N&G

Single Phase

ϕ

d) You Must Travel through N&G regime to
   reach spinodal region

e) No Driving Force for phase separation
   All possible conditions have similar free energy.
   System can't decide what to do at critical point.