

# Mean Field Flory Huggins Lattice Theory

- Mean field: the interactions between molecules are assumed to be due to the interaction of a given molecule and an *average field* due to all the other molecules in the system. To aid in modeling, the solution is imagined to be divided into a set of cells within which molecules or parts of molecules can be placed (lattice theory).
- The total volume,  $V$ , is divided into a lattice of  $N_o$  cells, each cell of volume  $v$ . The molecules occupy the sites randomly according to a probability based on their respective volume fractions. To model a polymer chain, one occupies  $x_i$  adjacent cells.

$$N_o = N_1 + N_2 = n_1 x_1 + n_2 x_2$$

$$V = N_o v$$

- Following the standard treatment for small molecules ( $x_1 = x_2 = 1$ )

$$\Omega_{1,2} = \frac{N_o!}{N_1! N_2!}$$

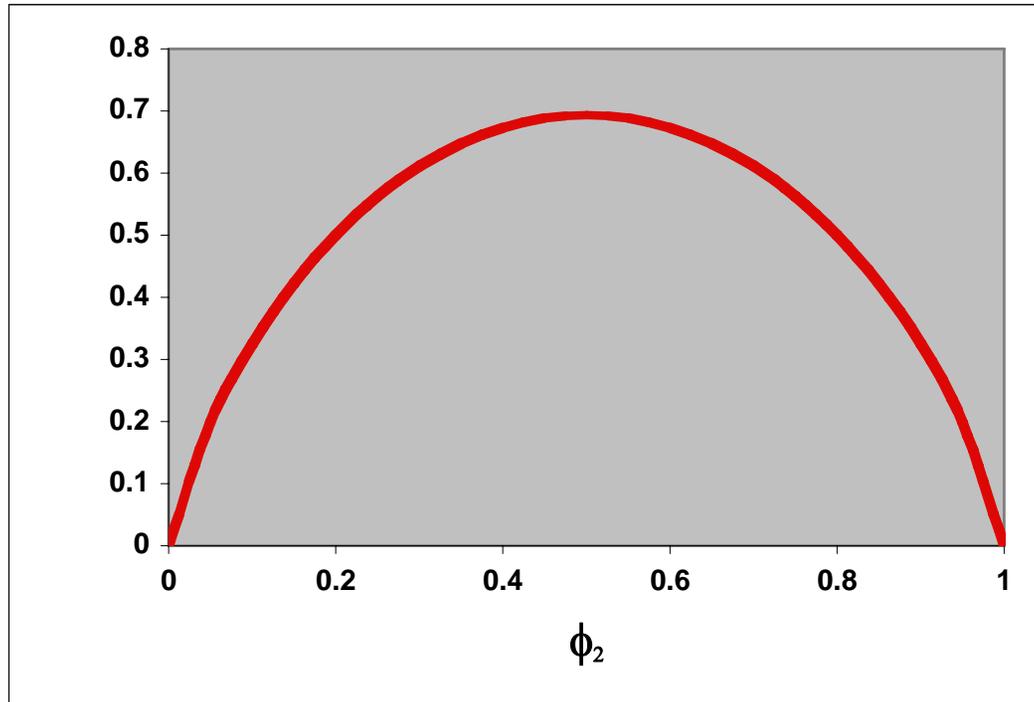
using Stirling's approximation:  $\ln M! = M \ln M - M$  for  $M \gg 1$

$$\Delta S_m = k(-N_1 \ln \phi_1 - N_2 \ln \phi_2) \quad \phi_1 = ?$$

# Entropy Change on Mixing $\Delta S_m$

$$\frac{\Delta S_m}{N_o} = +k(-\phi_1 \ln \phi_1 - \phi_2 \ln \phi_2)$$

Remember this is  
for small molecules  
 $x_1 = x_2 = 1$



Note the symmetry

The entropic contribution to  $\Delta G_m$  is thus seen to always favor mixing if the random mixing approximation is used.

# Enthalpy of Mixing $\Delta H_m$

- Assume lattice has  $z$  nearest-neighbor cells.
- To calculate the enthalpic interactions we consider the number of *pairwise* interactions. The probability of finding adjacent cells filled by component  $i$ , and  $j$  is given by assuming the probability that a given cell is occupied by species  $i$  is equal to the volume fraction of that species:  $\phi_i$ .

# $\Delta H_m$ cont'd

$$v_{ij} = \# \text{ of } i,j \text{ interactions}$$

$$v_{12} = N_1 z \phi_2$$

$$v_{11} = N_1 z \phi_1 / 2$$

$$v_{22} = N_2 z \phi_2 / 2$$

Mixed state enthalpic interactions

$$H_{1,2} = v_{12} \epsilon_{12} + v_{11} \epsilon_{11} + v_{22} \epsilon_{22}$$

$$H_{1,2} = z N_1 \phi_2 \epsilon_{12} + \frac{z}{2} N_1 \phi_1 \epsilon_{11} + \frac{z}{2} N_2 \phi_2 \epsilon_{22}$$

Pure state enthalpic interactions

$$H_1 = \frac{z N_1}{2} \epsilon_{11} \qquad H_2 = \frac{z N_2}{2} \epsilon_{22}$$

$$\Delta H_M = z \left[ N_1 \phi_2 \epsilon_{12} + \frac{N_1 \epsilon_{11}}{2} (\phi_1 - 1) + \frac{N_2 \epsilon_{22}}{2} (\phi_2 - 1) \right]$$

recall

$$N_1 + N_2 = N_0$$

Some math

$$\Delta H_M = z N_0 \left[ \epsilon_{12} - \frac{1}{2} (\epsilon_{11} + \epsilon_{22}) \right] \phi_1 \phi_2 \qquad \text{Note the symmetry}$$

# $\chi$ Parameter

- Define  $\chi$ : 
$$\chi = \frac{z}{kT} \left[ \varepsilon_{12} - \frac{1}{2} (\varepsilon_{11} + \varepsilon_{22}) \right]$$

$\chi$  represents the chemical interaction between the components

$$\frac{\Delta H_M}{N_0} = k T \chi \phi_1 \phi_2$$

*Ned: add eqn for  
Computing Chi from  
 $V_{seg} (\Delta\Delta)^2/RT$*

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- $\Delta G_M$ : 
$$\Delta G_M = \Delta H_M - T \Delta S_M$$

$$\frac{\Delta G_M}{N_0} = kT \chi \phi_1 \phi_2 - kT \left[ -\phi_1 \ln \phi_1 - \phi_2 \ln \phi_2 \right]$$

$$\frac{\Delta G_M}{N_0} = kT \left[ \chi \phi_1 \phi_2 + \phi_1 \ln \phi_1 + \phi_2 \ln \phi_2 \right]$$

Note:  $\Delta G_M$  is symmetric in  $\phi_1$  and  $\phi_2$ .

**This is the Bragg-Williams result for the change in free energy for the mixing of binary metal alloys.**

# $\Delta G_M(T, \phi, \chi)$

- Flory showed how to pack chains onto a lattice and correctly evaluate  $\Omega_{1,2}$  for polymer-solvent and polymer-polymer systems. Flory made a complex derivation but got a very simple and intuitive result, namely that  $\Delta S_M$  is decreased by factor  $(1/x)$  due to connectivity of  $x$  segments into a single molecule:

$$\frac{\Delta S_M}{N_0} = -k \left[ \frac{\phi_1}{x_1} \ln \phi_1 + \frac{\phi_2}{x_2} \ln \phi_2 \right] \quad \text{For polymers}$$

- Systems of Interest**

- |                     |                      |                      |
|---------------------|----------------------|----------------------|
| - solvent – solvent | $x_1 = 1$            | $x_2 = 1$            |
| - solvent – polymer | $x_1 = 1$            | $x_2 = \text{large}$ |
| - polymer – polymer | $x_1 = \text{large}$ | $x_2 = \text{large}$ |

$$\frac{\Delta G_M}{N_0} = kT \left[ \chi \phi_1 \phi_2 + \frac{\phi_1}{x_1} \ln \phi_1 + \frac{\phi_2}{x_2} \ln \phi_2 \right]$$

Note possible huge asymmetry in  $x_1, x_2$

$$\chi = \frac{z}{kT} \left[ \epsilon_{12} - \frac{1}{2} (\epsilon_{11} + \epsilon_{22}) \right]$$

Need to examine variation of  $\Delta G_M$  with  $T, \chi, \phi_i,$  and  $x_i$  to determine phase behavior.

# Flory Huggins Theory

- **Many Important Applications**

1. Phase diagrams
2. Fractionation by molecular weight, fractionation by composition
3.  $T_m$  depression in a semicrystalline polymer by 2<sup>nd</sup> component
4. Swelling behavior of networks (when combined with the theory of rubber elasticity)

The two parts of free energy per site  $\frac{\Delta G_M}{N_0 k T}$

$$\text{S} \quad \Delta S_M = -\frac{\phi_1}{x_1} \ln(\phi_1) - \frac{\phi_2}{x_2} \ln(\phi_2)$$

$$\text{H} \quad \Delta H_M = \chi \phi_1 \phi_2$$

- $\Delta H_M$  can be measured for low molar mass liquids and estimated for nonpolar, noncrystalline polymers by the Hildebrand solubility approach.

# Solubility Parameter

- Liquids 
$$\delta = \left( \frac{\Delta E}{V} \right)^{1/2} = \sqrt{\frac{\text{cohesive energy}}{\text{density}}} = \left[ \frac{\Delta H_v - RT}{V_m} \right]^{1/2}$$

$\Delta H_v$  = molar enthalpy of vaporization

Hildebrand proposed that compatibility between components 1 and 2 arises as their solubility parameters approach one another  $\delta_1 \rightarrow \delta_2$ .

- $\delta_p$  for polymers

Take  $\delta_p$  as equal to  $\delta$  solvent for which there is:

- (1) maximum in intrinsic viscosity for soluble polymers
- (2) maximum in swelling of the polymer network

or (3) calculate an approximate value of  $\delta_p$  by chemical group contributions for a particular monomeric repeat unit.

# Estimating the Heat of Mixing

Hildebrand equation:

$$\Delta H_M = V_m \phi_1 \phi_2 (\delta_1 - \delta_2)^2 \geq 0$$

$V_m$  = average molar volume of solvent/monomers

$\delta_1, \delta_2$  = solubility parameters of components

Inspection of solubility parameters can be used to estimate possible compatibility (miscibility) of solvent-polymer or polymer-polymer pairs. This approach works well for non-polar solvents with non-polar amorphous polymers.

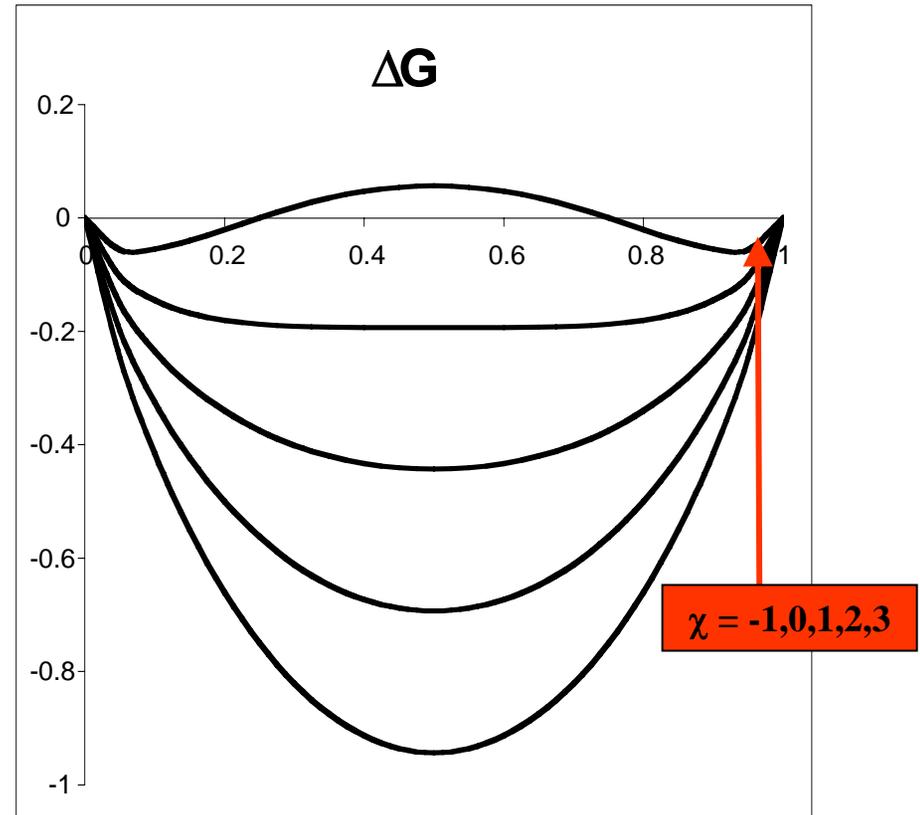
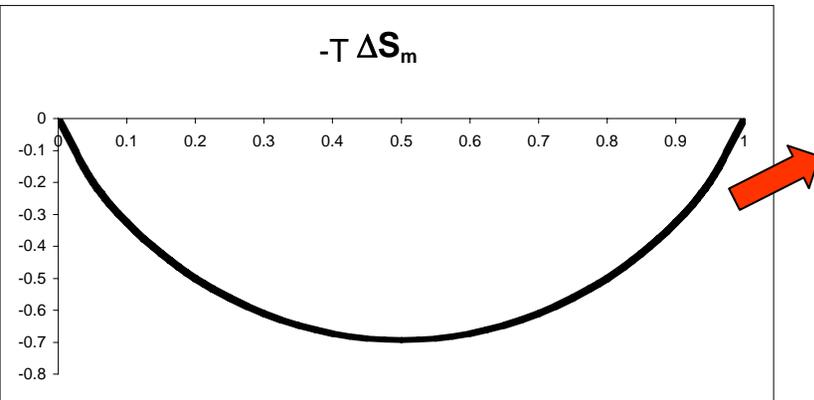
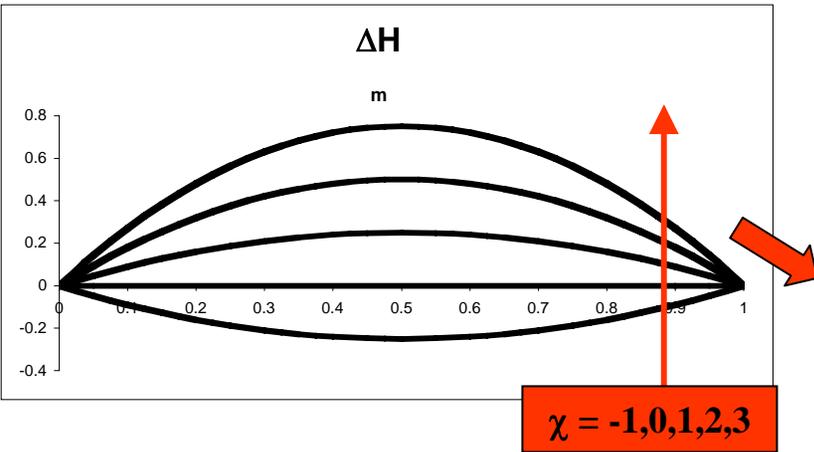
Think: usual phase behavior for a pair of polymers?

Note: this approach is not appropriate for systems with specific interactions, for which  $\Delta H_M$  can be *negative*.

# Influence of $\chi$ on Phase Behavior

Assume  $kT = 1$  and  $x_1 = x_2$

Expect symmetry



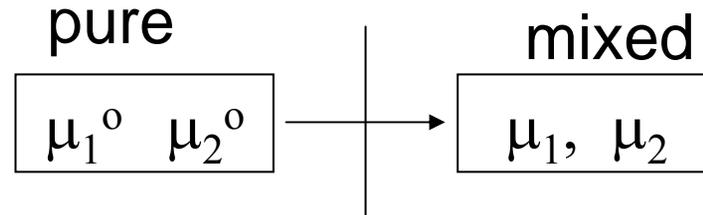
At what value of  $\chi$  does the system go biphasic?

What happens to entropy for a pair of polymers?

# Polymer-Solvent Solutions

- Equilibrium: Equal Chemical potentials: so need partial molar quantities

$$\mu_i = \left[ \frac{\partial G}{\partial n_i} \right]_{T,P,n,j}$$



$$\mu_i - \mu_i^0 \equiv RT \ln a_i \quad \text{where } a \text{ is the activity} \equiv \left[ \frac{\partial \Delta G_m}{\partial n_i} \right]_{T,P,n,j} = \frac{\partial \Delta G_m}{\partial \phi_i} \frac{\partial \phi_i}{\partial n_i}$$

and  $\mu_i^0$  is the chemical potential in the standard state

$$\mu_1 - \mu_1^0 = RT \left[ \ln \phi_1 + \left( 1 - \frac{1}{x_2} \right) \phi_2 + \chi \phi_2^2 \right] \quad \text{solvent}$$

P.S. #1

$$\mu_2 - \mu_2^0 = RT \left[ \ln \phi_2 - (x_2 - 1) \phi_1 + x_2 \chi \phi_1^2 \right] \quad \text{polymer}$$

Note: For a polydisperse system of chains, use  $x_2 = \langle x_2 \rangle$  the number average

$$\text{Recall at equilibrium} \quad \mu_i^\alpha = \mu_i^\beta \quad \text{etc}$$

# Construction of Phase Diagrams

$$\frac{\Delta G_m}{N_0} = kT \left[ \chi \phi_1 \phi_2 + \frac{\phi_1}{x_1} \ln \phi_1 + \frac{\phi_2}{x_2} \ln \phi_2 \right]$$

- Chemical Potential  $\mu_i = \left[ \frac{\partial G}{\partial n_i} \right]_{T,P,n,j}$
- Binodal - curve denoting the region of 2 distinct coexisting phases or equivalently

$$\mu_1' = \mu_1'' \quad \mu_2' = \mu_2''$$

$$\mu_1' - \mu_1^0 = \mu_1'' - \mu_1^0 \quad \text{Phases called prime and double prime}$$

$$\mu_2' - \mu_2^0 = \mu_2'' - \mu_2^0$$

$$\left[ \frac{\partial \Delta G_m}{\partial n_2} \right]_{T,P} = \Delta \mu_2 \quad \text{and since} \quad \left[ \frac{\partial \Delta G_m}{\partial n_2} \right] = \left[ \frac{\partial \Delta G_m}{\partial \phi_2} \right] \left[ \frac{\partial \phi_2}{\partial n_2} \right]$$

Binodal curve is given by finding common tangent to  $\Delta G_m(\phi)$  curve for each  $\phi$ , T combination. Note with lattice model ( $\mathbf{x}_1 = \mathbf{x}_2$ ) (can use volume fraction of component in place of moles of component)

# Construction of Phase Diagrams

## cont'd

- Spinodal (Inflection Points)

$$\left[ \frac{\partial^2 \Delta G_m}{\partial \phi_2^2} \right]^\alpha = 0 \quad \left[ \frac{\partial^2 \Delta G_m}{\partial \phi_2^2} \right]^\beta = 0$$

- Critical Point

$$\chi_c \left[ \frac{\partial^2 \Delta G_m}{\partial \phi_2^2} \right] = 0 \quad \text{and} \quad \left[ \frac{\partial^3 \Delta G_m}{\partial \phi_2^3} \right] = 0$$

$\phi_{1,c}$

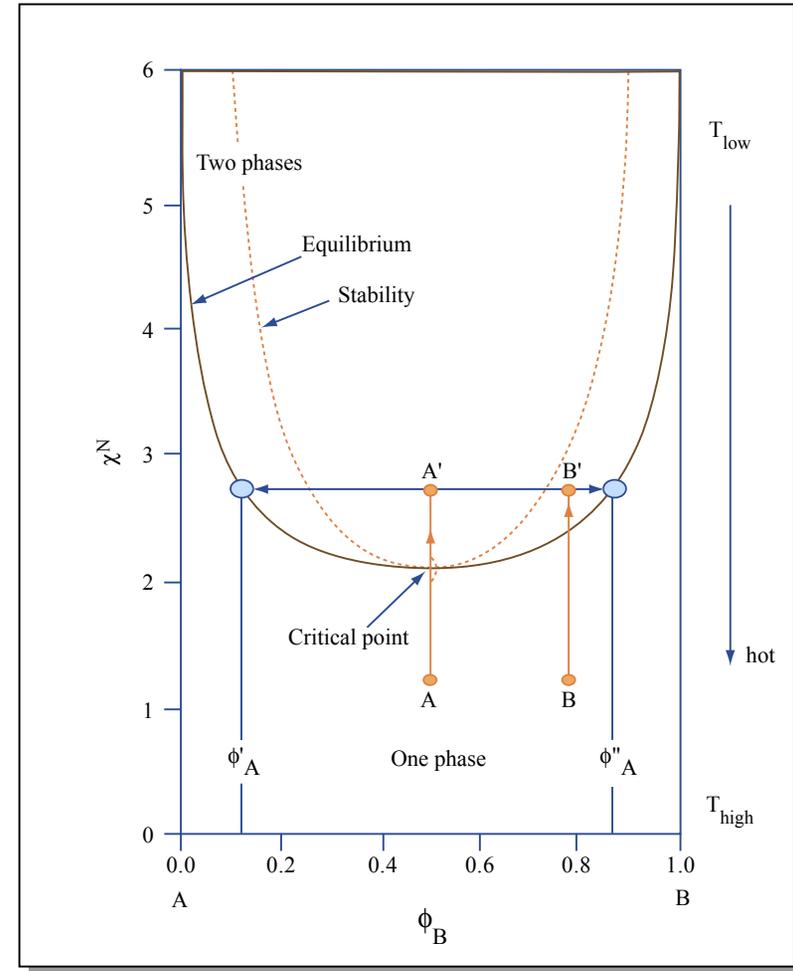


Figure by MIT OCW.

# Dilute Polymer Solution

- # moles of solvent ( $n_1$ )  $\gg$  polymer ( $n_2$ ) and  $n_1 \gg n_2 x_2$

$$\phi_1 = \frac{n_1 v_1}{n_1 v_1 + n_2 x_2 v_2} \qquad \phi_2 = \frac{n_2 x_2 v_2}{n_1 v_1 + n_2 x_2 v_2} \sim \frac{n_2 x_2}{n_1}$$

Useful Approximations

$$\phi_2 \equiv \frac{n_2 x_2}{n_1} \sim X_2 x_2 \qquad \text{Careful...}$$

$$\ln(1+x) \cong x - \frac{x^2}{2} + \frac{x^3}{3} - \dots$$

$$\ln(1-x) \cong -x - \frac{x^2}{2} - \frac{x^3}{3} - \dots$$

- For a dilute solution:

Let's do the math:

$$\mu_1 - \mu_1^0 = RT \left[ -\frac{\phi_2}{x_2} + \left( \chi - \frac{1}{2} \right) \phi_2^2 \right]$$

# Dilute Polymer Solution cont'd

- Recall for an **Ideal Solution** the chemical potential is proportional to the activity which is equal to the mole fraction of the species,  $X_i$

$$\mu_1 - \mu_1^0 = RT \ln X_1 = RT \ln(1 - X_2) \cong -RTX_2 = -RT \frac{\phi_2}{x_2}$$

- Comparing to the  $\mu_1 - \mu_1^0$  expression we have for the dilute solution, we see the first term corresponds to that of an ideal solution. The 2<sup>nd</sup> term is called the excess chemical potential

$$\mu_1 - \mu_1^0 = RT \left[ -\frac{\phi_2}{x_2} + \left( \chi - \frac{1}{2} \right) \phi_2^2 \right]$$

– This term has 2 parts due to

- Contact interactions (solvent quality)  $\chi \phi_2^2 RT$
- Chain connectivity (excluded volume)  $-(1/2) \phi_2^2 RT$

- Notice that for the special case of  $\chi = 1/2$ , the entire 2<sup>nd</sup> term disappears!**

This implies that in this special situation, the dilute solution acts as an **Ideal solution**.

*The excluded volume effect is precisely compensated by the solvent quality effect.*

Previously we called this the  **$\theta$  condition**, so  $\chi = 1/2$  is also the theta point

# F-H Phase Diagram at/near $\theta$ condition

- $x_1 = 1, x_2 \gg 1$  and  $n_1 \gg n_2 x_2$

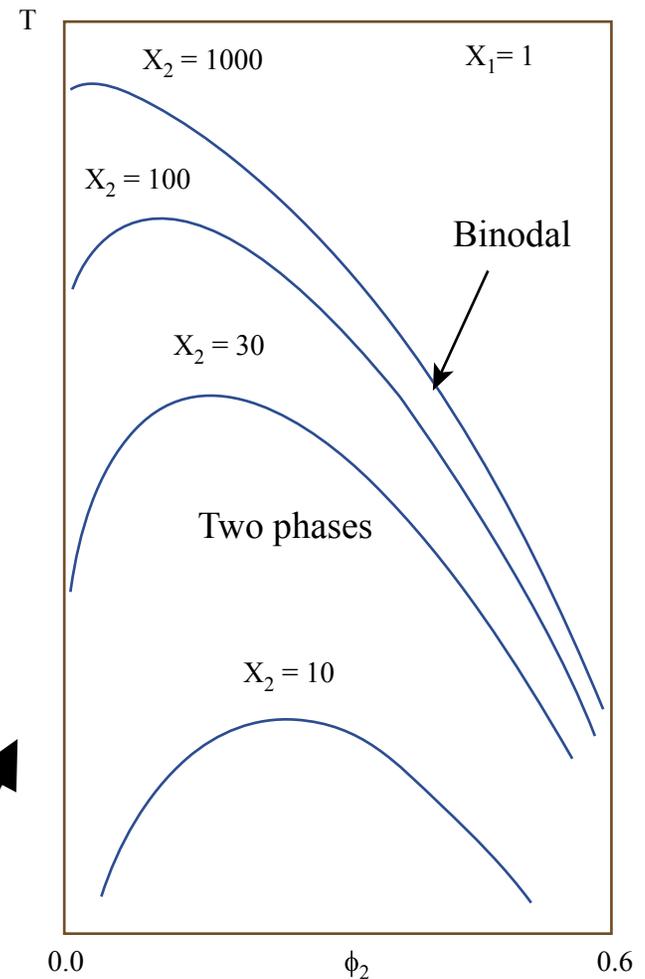
Find:

$$\chi_c = \frac{1}{2} \left( \frac{1}{\sqrt{x_1}} + \frac{1}{\sqrt{x_2}} \right)^2$$

$$\phi_{1,c} = \frac{\sqrt{x_2}}{\sqrt{x_1} + \sqrt{x_2}}$$

Note strong asymmetry!

Symmetric when  $x_1 = 1 = x_2$



# Critical Composition & Critical Interaction Parameter

Binary System		$\phi_{1,c}$	$\chi_c$
2 low molar mass liquids	$x_1 = x_2 = 1$	0.5	2
Solvent-polymer	$x_1 = 1;$ $x_2 = N$	$\frac{\sqrt{x_2}}{1 + \sqrt{x_2}}$	$\frac{1}{2} \left( 1 + \frac{1}{\sqrt{x_2}} \right)^2$
Symmetric Polymer-Polymer	$x_1 = x_2 = N$	0.5	$\frac{2}{N}$
General	$x_1, x_2$	$\frac{\sqrt{x_2}}{\sqrt{x_1} + \sqrt{x_2}}$	$\frac{1}{2} \left( \frac{1}{\sqrt{x_1}} + \frac{1}{\sqrt{x_2}} \right)^2$

# Polymer Blends

Good References on Polymer Blends:

- O. Olasbisi, L.M. Robeson and M. Shaw, *Polymer-Polymer Miscibility*, Academic Press (1979).
- D.R. Paul, S. Newman, *Polymer Blends*, Vol I, II, Academic Press (1978).
- Upper Critical Solution Temperature (UCST) Behavior  
Well accounted for by F-H theory with  $\chi = a/T + b$
- Lower Critical Solution Temperature (LCST) Behavior  
FH theory cannot predict LCST behavior. Experimentally find that blend systems displaying hydrogen bonding and/or large thermal expansion factor difference between the respective homopolymers often results in LCST formation.

# Phase Diagram for UCST Polymer Blend

Predicted from FH Theory

$$\chi = \frac{A}{T} + B$$

$$x_1 = x_2 = N$$

$$\frac{\partial \Delta G_m}{\partial \phi} = 0 \quad \text{binodal}$$

$$\frac{\partial^2 \Delta G_m}{\partial \phi^2} = 0 \quad \text{spinodal}$$

$$\frac{\partial^3 \Delta G_m}{\partial \phi^3} = 0 \quad \text{critical point}$$

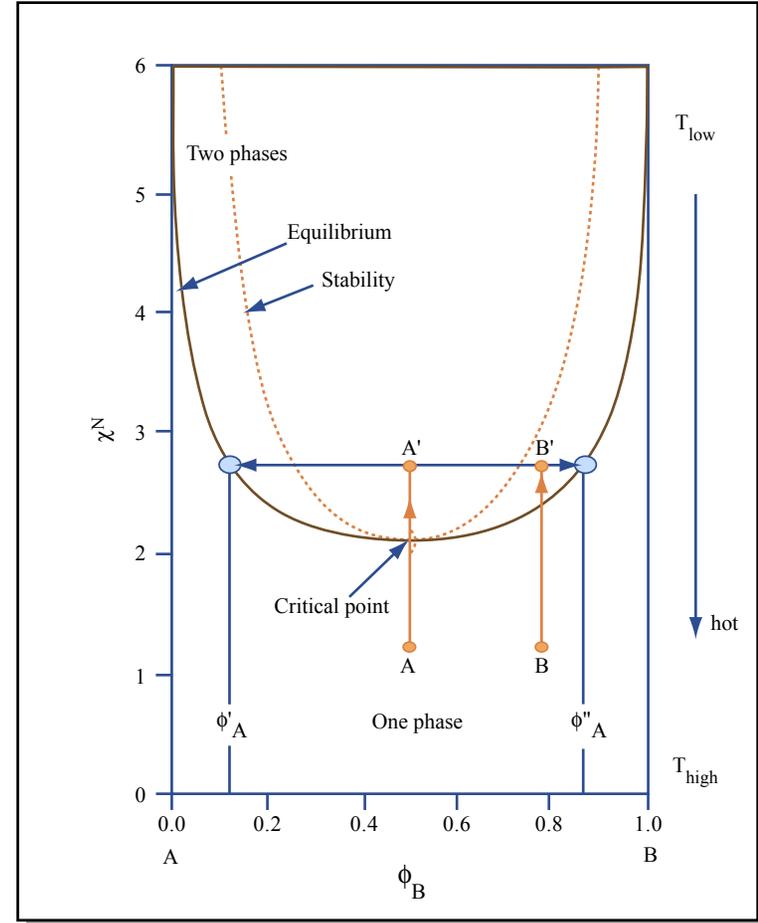


Figure by MIT OCW.

A polymer  
B polymer

$x_1$  segments  
 $x_2$  segments

$$v_1 \approx v_2 \ \& \ x_1 \approx x_2$$

# 2 Principal Types of Phase Diagrams

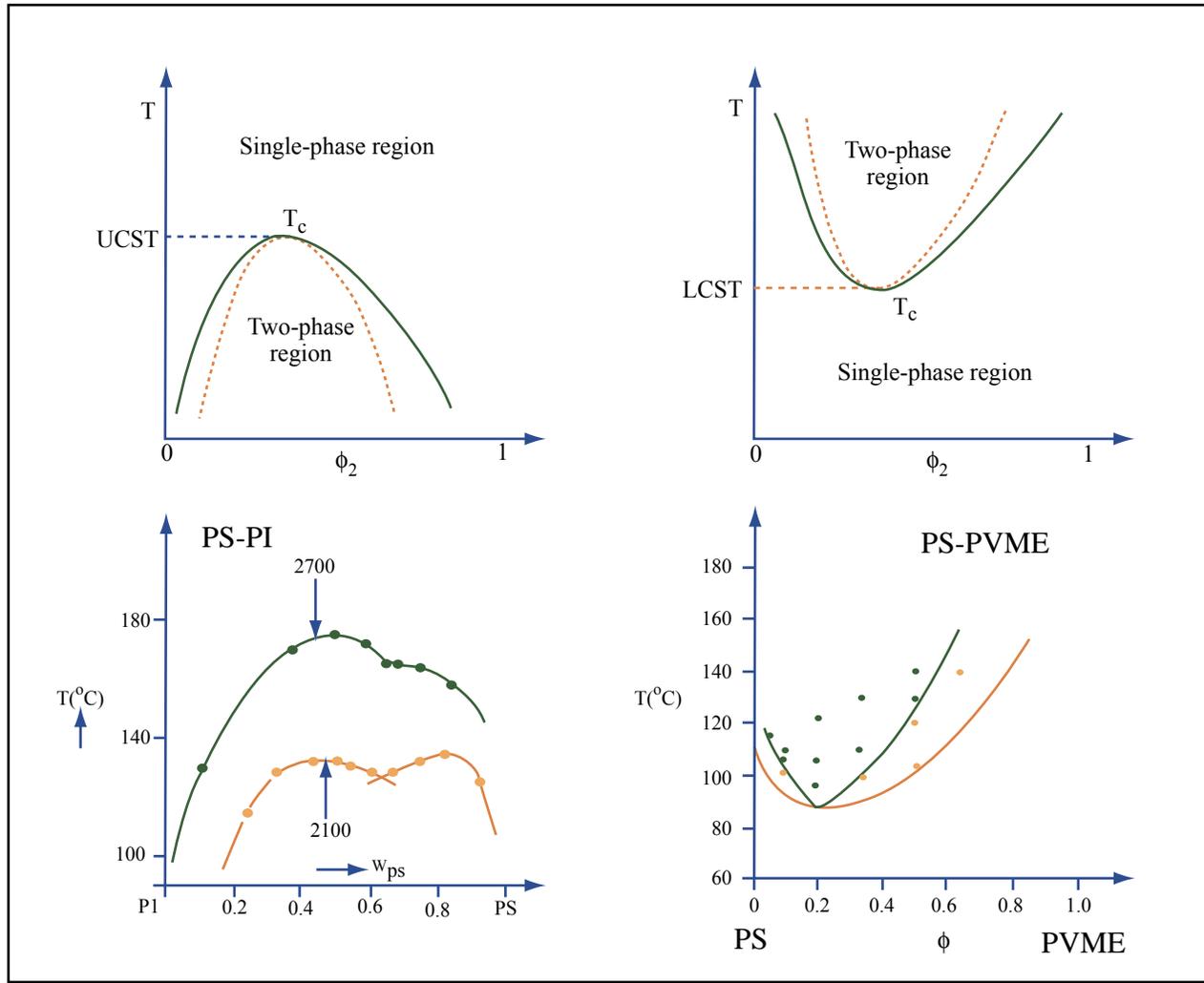


Figure by MIT OCW.

Konigsveld, Klentjens, Schoffeleers  
Pure Appl. Chem. 39, 1 (1974)

Nishi, Wang, Kwei  
Macromolecules, 8, 227 (1995)

# Assignment - Reminder

- Problem set #1 is due in class on February 15th.