Chemical Engineering 160/260
Polymer Science and Engineering

Lecture 10 - Phase Equilibria and Polymer Blends

February 7, 2001

Thermodynamics of Polymer Blends: Part 2

Objectives

- To develop the classical **Flory-Huggins** theory for the free energy of mixing of polymer solutions based on a statistical approach on a regular lattice.
- To describe the criteria for **phase stability** and illustrate typical phase diagrams for polymer blends and solutions.

Outline

- **Phase Equilibria**
  - Free energy of mixing for a phase-separated system
  - Spinodal and binodal curves in the Flory-Huggins model
  - Qualitative results from equation-of-state theory

Geometric Mean Mixing Rule

For the systems in which **$\Delta H_m > 0$**, it is common to express ΔH_m in terms of the cohesive energy density, or solubility parameter. Analyze by first considering the (1,1) and (2,2) interactions.

Change in internal energy of vaporization of one mole of (i)

$$\Delta U_{v,i} = \frac{1}{2} Z N_A w_{ii}$$

To evaluate the (1,2) cross interactions, invoke the **geometric mean mixing rule**:

$$w_{12} \cong \sqrt{w_{11} w_{22}}$$

This approximation will be most accurate when both the (1,1) and (2,2) forces are either London dispersion or dipole-dipole. It breaks down for hydrogen bonding or strong specific interactions.

$$-\Delta w = w_{11} + w_{22} - 2\sqrt{w_{11} w_{22}}$$

$$-\Delta w = \left(\sqrt{w_{11}} - \sqrt{w_{22}}\right)^2$$

Cohesive Energy Density

Recall that

$$\Delta H_m = \left(\frac{1}{2}\right) ZN\varphi_1\varphi_2\Delta w$$

$$\Delta U_v = \Delta H_v - P\Delta V$$

$$\Delta U_v = \Delta H_v - P\left(V_g - V_l\right)$$

$$\Delta U_v \cong \Delta H_v - PV_g$$

$$\Delta U_v \cong \Delta H_v - RT$$

$$-\Delta w = \left[\left(\frac{\Delta U_{v,1}}{\frac{1}{2}ZN}\right)^{\frac{1}{2}} - \left(\frac{\Delta U_{v,2}}{\frac{1}{2}ZN}\right)^{\frac{1}{2}}\right]^2$$

Rewrite on a “per unit volume” basis

$$\Delta H_m = V\varphi_1\varphi_2\left[\left(\frac{\Delta U_{v,1}}{V_1^o}\right)^{\frac{1}{2}} - \left(\frac{\Delta U_{v,2}}{V_2^o}\right)^{\frac{1}{2}}\right]^2$$

$$\frac{\Delta U_{v,i}}{V_i^o}$$

Cohesive energy density (CED)

Solubility Parameter

$$\left(\frac{\Delta U_{v,i}}{V_i^o}\right)^{\frac{1}{2}} \equiv (CED)^{1/2} \equiv \delta_i$$

Solvent	CED (cal cm^{-3})	δ (cal cm^{-3})$^{1/2}$
Cyclohexane	67.2	8.2
Carbon tetrachloride	74.0	8.6
Toluene	79.2	8.9
Benzene	84.6	9.2
Methyl acetate	92.2	9.6
Acetone	98.0	9.9
Cyclohexanone	98.0	9.9
Acetic acid	102.0	10.1
Cyclohexanol	130.0	11.4
Methanol	210.3	14.5
Water	547.6	23.4

Polymer Solubility Parameters

Solubility parameters for polymers must be determined **indirectly,** typically by intrinsic viscosity measurements of solutions or by swelling of a crosslinked polymer.

Polymer	δ (cal cm^{-3})$^{1/2}$
Polyisobutylene	7.5-8.0
Polyethylene	7.7-8.2
Natural rubber	8.1-8.5
Polystyrene	9.1-9.4
Poly(ethylene terephthalate)	9.3-9.9
Polyacrylonitrile	12.0-14.0
Nylon-6,6	13.5-15.0

Criterion for Phase Equilibrium

Consider the increment in Gibbs free energy G associated with transfer of dn_i moles of (i) from phase α to phase β at constant temperature T and pressure P.

$$dG = VdP - SdT + \sum_i \mu_i dn_i$$

At equilibrium

$$dG = 0 = dG^\alpha + dG^\beta$$

$$0 = \sum_i \mu_i^\alpha dn_i^\alpha + \sum_i \mu_i^\beta dn_i^\beta$$

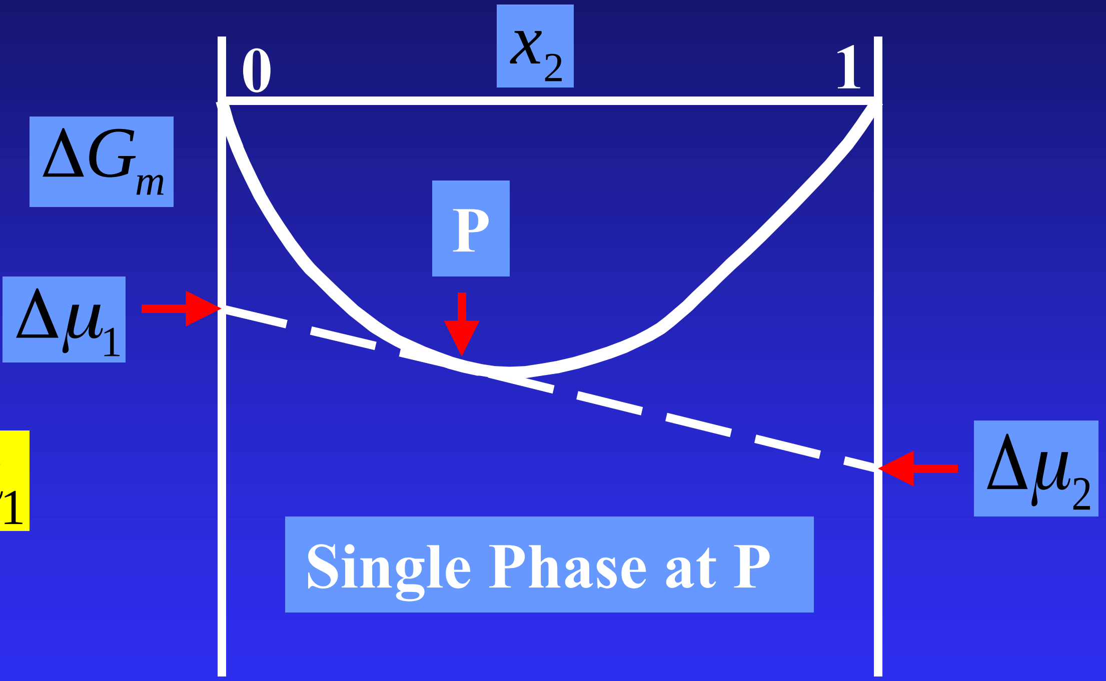
$$0 = \sum_i \left(\mu_i^\alpha - \mu_i^\beta\right) dn_i^\alpha$$

$$\mu_i^\alpha = \mu_i^\beta$$

Free Energy of Mixing for a Single Phase

Recall $\Delta G_m = x_1\Delta\mu_1 + x_2\Delta\mu_2$ where $\Delta\mu_i = \mu_i - \mu_i^o$

$$\Delta G_m = (1 - x_2)\Delta\mu_1 + x_2\Delta\mu_2 = \Delta\mu_1 + x_2(\Delta\mu_2 - \Delta\mu_1)$$



Plot ΔG_m vs x_2:

Slope = $(\Delta\mu_2 - \Delta\mu_1)$

Intercept at $x_2 = 0$ is $\Delta\mu_1$

Plot ΔG_m vs x_1:

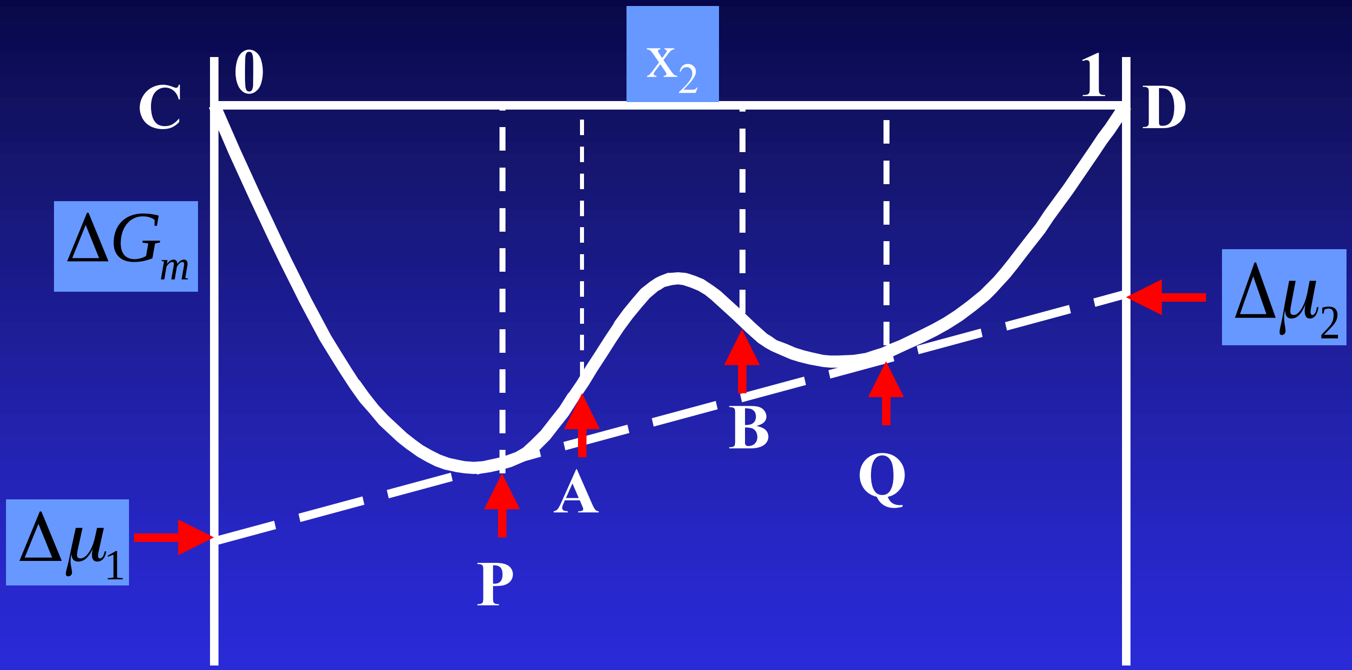
Slope = $-(\Delta\mu_2 - \Delta\mu_1)$

Intercept at $x_1 = 0$ is $\Delta\mu_2$

$$\Delta G_m = \underset{<0}{\Delta H_m} - \underset{>0}{T\Delta S_m} \Rightarrow \Delta G_m < 0$$

ΔG_m for a Phase-Separated System

Suppose that $\Delta H_m > 0$ and $\Delta S_m > 0$. This may lead to the following:



The common tangent to the ΔG_m curve at P and Q implies that phases of compositions (x_2^P, x_1^P) and (x_2^Q, x_1^Q) have the same values of $\Delta\mu_1$ and $\Delta\mu_2$, i.e. $\mu_1^P = \mu_1^Q$ and $\mu_2^P = \mu_2^Q$. Thus, P and Q are in equilibrium, and any mixture having composition between P and Q will phase separate into phases with compositions x_2^P and x_2^Q .

Regions of Phase Stability

Stable Mixtures

For C-P and Q-D regions, all mixtures are stable against separation into different phases.

Metastable Mixtures

For P-A and B-Q regions, where A and B denote inflection points,

$$\frac{\partial^2 \Delta G_m}{\partial x_2^2} > 0$$

and the mixture will be stable against separation into neighboring phases differing only slightly in composition but not against separation into phases of composition P and Q.

Unstable Mixtures

For the A-B region,

$$\frac{\partial^2 \Delta G_m}{\partial x_2^2} < 0$$

and all mixtures are unstable to infinitesimal perturbations.

Spinodal and Binodal Curves

Spinodal Curve

The boundary between the absolutely unstable and the metastable regions is defined by

$$\boxed{\frac{\partial^2 \Delta G_m}{\partial x_2^2} = 0}$$

The locus of all such A, B inflection points as a function of temperature generates the **spinodal curve**.

Binodal Curve

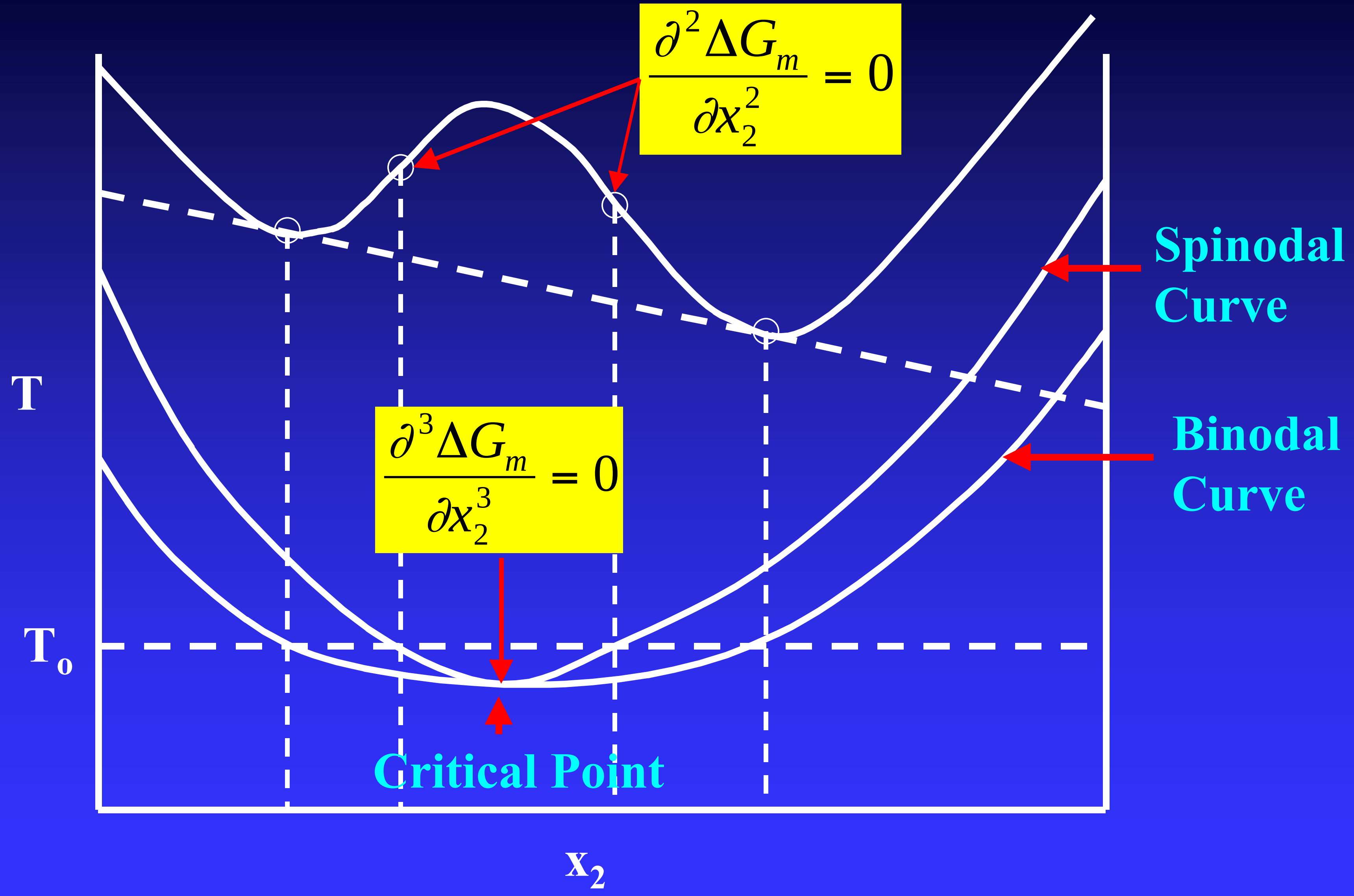
The locus of all points of common tangency P and Q as a function of temperature generates the **binodal curve**.

Critical Point

The critical point is characterized by convergence of the points of common tangency and the inflection points such that

$$\boxed{\frac{\partial^3 \Delta G_m}{\partial x_2^3} = 0}$$

Phase Equilibria in Polymer Solutions



$$\frac{\partial^2 \Delta G_m}{\partial x_2^2} = 0$$

$$\frac{\partial^3 \Delta G_m}{\partial x_2^3} = 0$$

Spinodal Curve

Binodal Curve

Critical Point

Phase Behavior for the Flory-Huggins Model

$$\Delta G_m = RT\left[N\varphi_1\varphi_2\chi + \left(x_1 \ln\varphi_1 + x_2 \ln\varphi_2\right)\right]$$

$$\frac{\partial \Delta G_m}{\partial N_1} = \mu_1 \qquad \frac{\partial \Delta G_m}{\partial N_2} = \mu_2$$

Note that $N_1 = V\varphi_1$ and $\varphi_2 = \frac{nN_2}{N_1 + nN_2}$

Binodal Curves

$$\mu_1 - \mu_1^o = RT\left[\ln(1-\varphi_2) + \varphi_2\left(1-\frac{1}{n}\right) + \chi\varphi_2^2\right]$$

$$\mu_2 - \mu_2^o = RT\left[\ln\varphi_2 + (1-\varphi_2)(1-n) + \chi n(1-\varphi_2)^2\right]$$

Note that differentiation with respect to x_2 is equivalent to φ_2.

Also $\frac{\partial}{\partial x} = \frac{\partial\varphi}{\partial x}\frac{\partial}{\partial\varphi}$

Phase Behavior for the Flory-Huggins Model

Spinodal Curve

$$\frac{\partial^2 \Delta G_m}{\partial x_2^2} = 0 = \frac{\partial \Delta \mu_1}{\partial \varphi_2} = \frac{-1}{1-\varphi_2} + 1 - \frac{1}{n} + 2\chi\varphi_2$$

Critical Point

$$\frac{\partial^3 \Delta G_m}{\partial x_2^3} = 0 = \frac{\partial^2 \Delta \mu_1}{\partial \varphi_2^2} = \frac{-1}{\left(1-\varphi_{2,c}\right)^2} + 2\chi_c$$

$$\chi_c = \frac{1}{2\varphi_{1,c}^2}$$

$$-\frac{1}{\varphi_{1,c}} + 1 - \frac{1}{n} + \frac{1-\varphi_{1,c}}{\varphi_{1,c}^2} = 0$$

$$\chi_c = \frac{1}{2}\left(1 + n^{-1/2}\right)^2$$

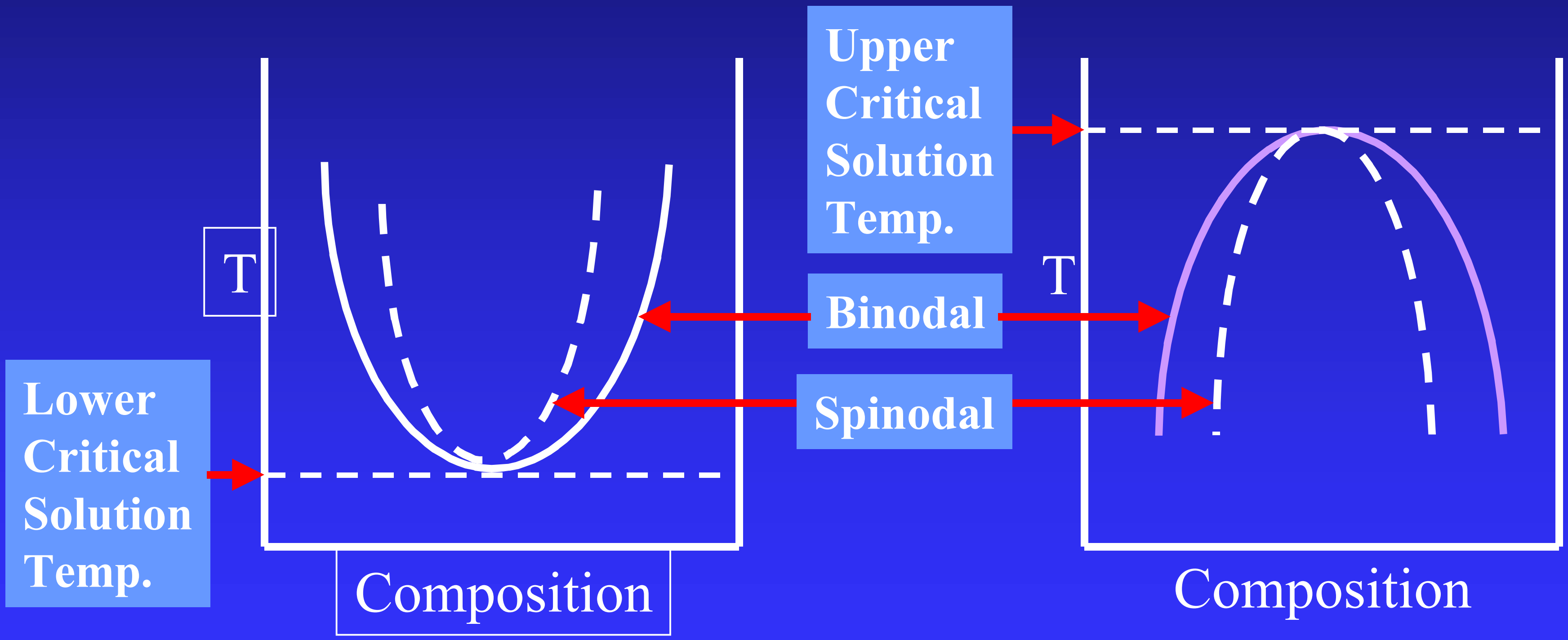
Post Flory-Huggins Thermodynamics

- Flory equation-of-state and Sanchez lattice fluid theories
- LCST behavior is characteristic of exothermic mixing (which could arise from specific chemical interactions) and negative excess entropy (which arises due to densification of the polymers on mixing). Neither one of these phenomena is included in the Flory-Huggins theory.

Typical Phase Diagrams

Typical for Polymer Blend

Typical for Polymer Solution



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Composition

Lower Critical Solution Temp.

Upper Critical Solution Temp.

Binodal

Spinodal

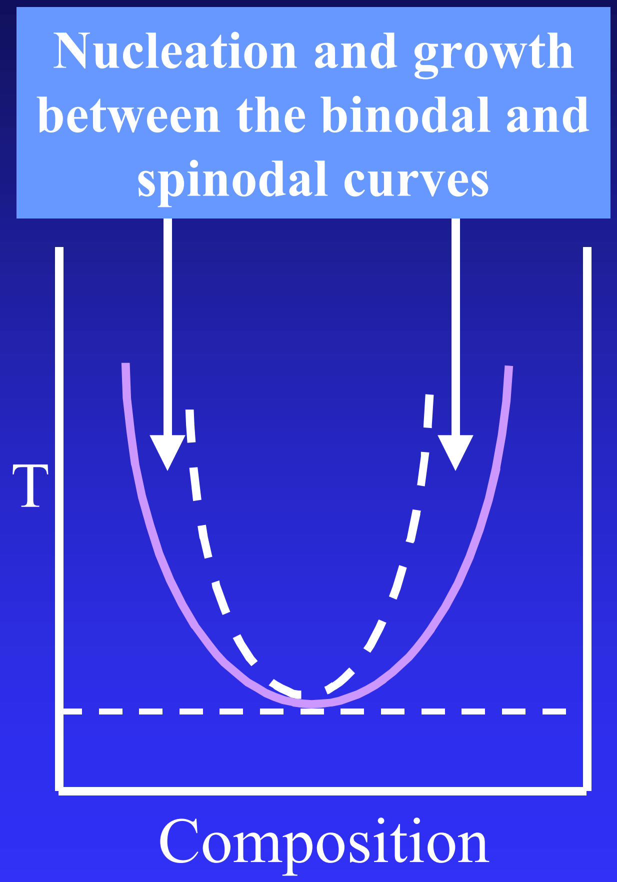
T

Composition

Mechanisms of Phase Separation

Nucleation and Growth

- Initial fragment of more stable phase forms
- Free energy determined by work required to form the surface and the work gained in forming the interior
- Concentration in the immediate vicinity of the nucleus is reduced and diffusion is downhill (diffusion coefficient is positive)
- Droplet size increases by growth initially
- Requires activation energy

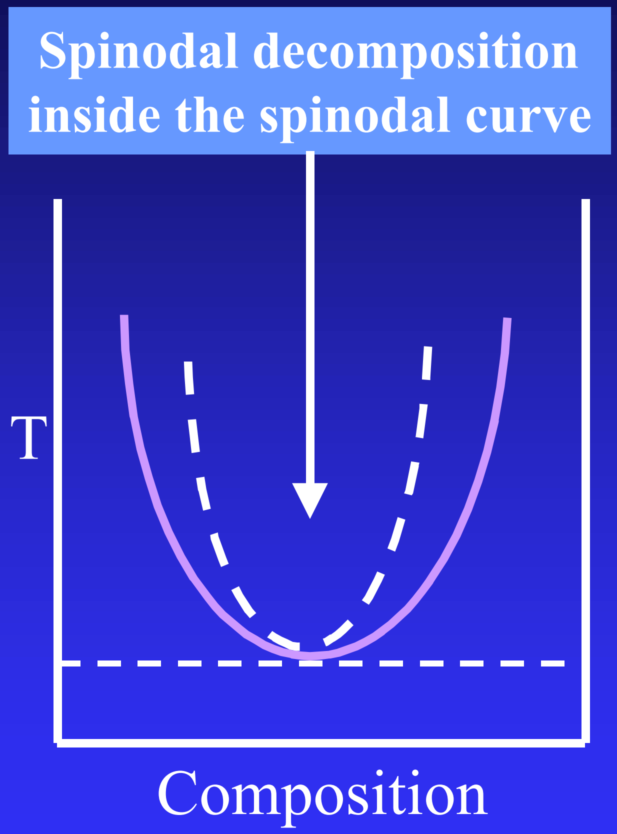


Nucleation and growth between the binodal and spinodal curves

Mechanisms of Phase Separation

Spinodal Decomposition

- Initial small-amplitude composition fluctuations
- Amplitude of wavelike composition fluctuations increases with time
- Diffusion is uphill from the low concentration region into the domain (negative diffusion coefficient)
- Unstable process; no activation energy required
- Phases are interconnected at early time



Spinodal decomposition inside the spinodal curve