

Chapter 4. Thermodynamics of Mixing



- 4.1. Entropy of binary mixing
- 4.2 Energy of binary mixing
- 4.3 Equilibrium and stability
- 4.4 Phase diagram
- 4.5 Experimental investigation



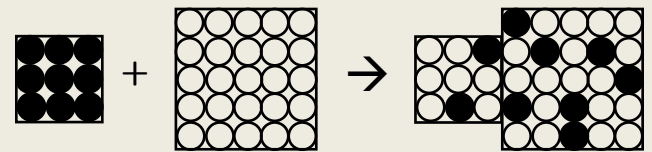
4.1. Entropy of binary mixing

- ❑ **Mixtures** are systems consisting of two or more different chemical species.
- ❑ Whether an equilibrium state of a given mixture is homogeneous heterogeneous is determined by the dependence of the entropy and energy changes on mixing.
 - ❑ Entropy always favors mixing, but energetic interaction between species can either promote or inhibit mixing.
- ❑ Assumption
 - ① Two species A and B mix together to form a single-phase homogeneous liquid.
 - ② There is no volume change on mixing.

❖ The volume fraction of the two components

$$\phi_A = \frac{V_A}{V_A + V_B} \quad \phi_B = \frac{V_B}{V_A + V_B} = 1 - \phi_A$$

→ the mixing of two small molecules of equal molecular volumes



4.1. Entropy of binary mixing

□ In the more general case, *the lattice volume v_0* is defined by the smallest units (solvent molecules or monomers), and larger molecules occupy multiple connected lattice sites.

❖ Molar volume of species A and B

$$v_A = N_A v_0$$

$$v_B = N_B v_0$$

where N_A, N_B : the numbers of lattice sites occupied by each respective molecule

□ Three cases of interest : regular solution / polymer solution / polymer blend

- ❖ Regular solutions : mixtures of low molar mass species with $N_A=N_B=1$
- ❖ Polymer solutions : mixtures of macromolecules ($N_A=N \gg 1$) with the low molar mass solvent defining the lattice ($N_B=1$)
- ❖ Polymer blends : mixtures of macromolecules of different chemical species ($N_A \gg 1$ and $N_B \gg 1$)

The lattice sites occupied by the combined system of volume V_A+V_B

$$: n = \frac{V_A + V_B}{v_0}$$

All molecules of species A occupy $V_A/v_0 = n\Phi_A$ sites

	N_A	N_B
Regular solutions	1	1
Polymer solutions	N	1
Polymer blends	N_A	N_B

4.1. Entropy of binary mixing

□ The entropy

$$S = k \ln \Omega$$

where k : Boltzmann constant

Ω : the number of state (to arrange molecules on the lattice)

❖ In a homogeneous mixture of A and B,

$$\Omega_{AB} = n$$

❖ Before mixing, the number of state of each molecule of A is

$$\Omega_A = n\phi_A$$

❖ For a single molecule of A, the entropy change on mixing is

$$\begin{aligned} \Delta S_A &= k \ln \Omega_{AB} - k \ln \Omega_A = k \ln \left(\frac{\Omega_{AB}}{\Omega_A} \right) \\ &= k \ln \left(\frac{1}{\phi_A} \right) = -k \ln \phi_A > 0 \quad (\text{since } \phi_A < 1) \end{aligned}$$



4.1. Entropy of binary mixing

- The total entropy of mixing
: summation of the entropy contribution from each molecule

$$\Delta S_{mix} = n_A \Delta S_A + n_B \Delta S_B = -k(n_A \ln \phi_A + n_B \ln \phi_B)$$

where no. of molecules $n_A = n\phi_A / N_A$, $n_B = n\phi_B / N_B$

- The entropy of mixing per lattice site (n)

$$\Delta \bar{S}_{mix} = \Delta S_{mix} / n = -k \left[\frac{\phi_A}{N_A} \ln \phi_A + \frac{\phi_B}{N_B} \ln \phi_B \right] \quad \text{For polymer blends}$$

- ❖ For a regular solution ; $N_A = N_B = 1$

$$\Delta \bar{S}_{mix} = -k [\phi_A \ln \phi_A + \phi_B \ln \phi_B]$$

- ❖ For a polymer solution ; $N_A = N$ and $N_B = 1$

$$\Delta \bar{S}_{mix} = -k \left[\frac{\phi_A}{N} \ln \phi_A + \phi_B \ln \phi_B \right]$$

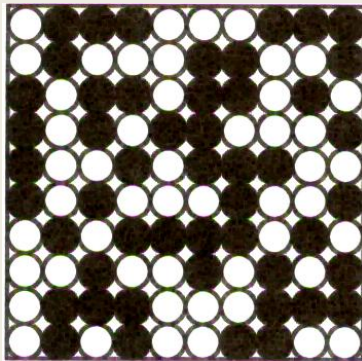


4.1. Entropy of binary mixing

□ Schematic example for the binary mixture

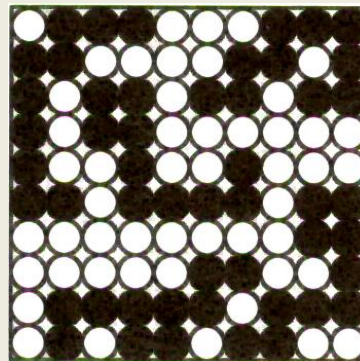
❖ Consider the 10 x 10 square lattice with different mixtures ($\Phi_A = \Phi_B = 0.5$)

Regular solution



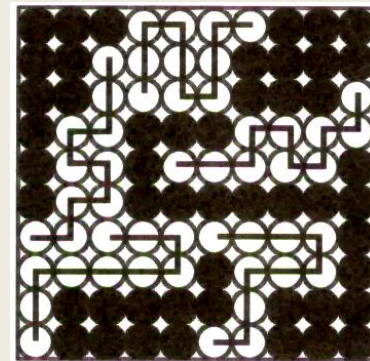
50 white balls and
50 black balls

Polymer solution



five black 10-ball chains

Polymer blend



five white 10-ball chains and
five black 10-ball chains.

The mixing entropy per site for the three situations

Mixture	$\Delta \bar{S}_{mix} / k$
50 black balls and 50 white balls	0.69
Five 10-ball black chains and 50 white balls	0.38
Five 10-ball black chains and five 10-ball white chains	0.069

Calculate
yourself !!!

4.1.

Entropy of binary mixing

- ❖ For polymer solutions,
N is large, the first term \rightarrow negligible
 \rightarrow entropy is roughly half of that for the regular solution

$$\Delta \bar{S}_{mix} = -k \left[\frac{\phi_A}{N} \ln \phi_A + \phi_B \ln \phi_B \right]$$

- ❖ For polymer blends,
 N_A and N_B are large, \rightarrow entropy is very small
 \rightarrow polymer have stymied entropy.
 - Connecting monomers into chains drastically reduces the no. of possible states.
 - Simply try to recreate the illustrations of polymer blends with a different state in the previous page!

\rightarrow Despite the entropy is small for polymer blends, it is always positive and hence promotes mixing.

- ❖ Mixtures with no difference in interaction energy between components
 \rightarrow *Ideal mixture*



4.1. Entropy of binary mixing

- ❖ The free energy of mixing per site for ideal mixtures is purely entropic,

$$\Delta\bar{F}_{mix} = -T\Delta\bar{S}_{mix} = kT \left[\frac{\phi}{N_A} \ln \phi + \frac{1-\phi}{N_B} \ln(1-\phi) \right] \quad \text{where } \Phi_A = \phi, \Phi_B = 1-\phi$$

: Ideal mixtures are always homogeneous as a result of the entropy always being positive

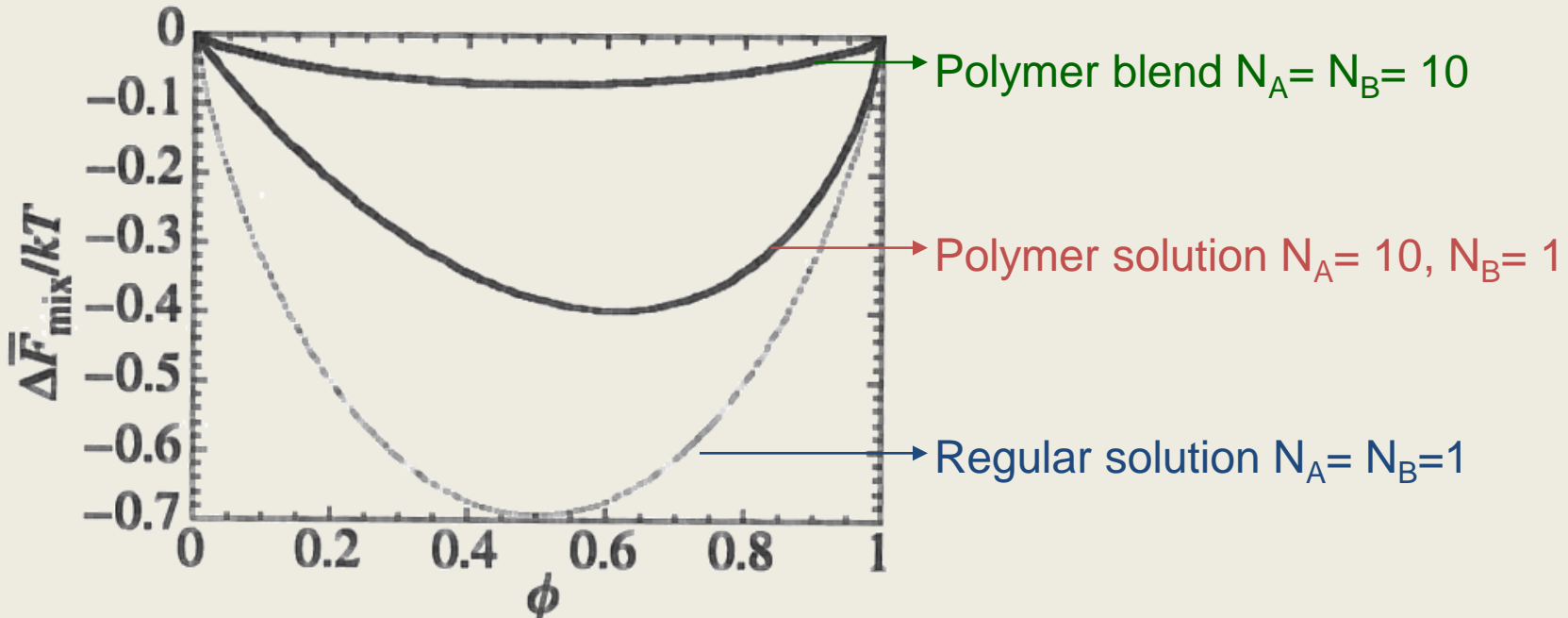


Fig. 4.1 The mixing free energy of an ideal mixture is always favorable and all compositions are stable.

4.2. Energy of binary mixing

❖ In most experimental situations, mixing occurs at constant pressure and the **enthalpic interactions** between species must be analyzed to find a minimum of the **Gibbs free energy of mixing**. $G(T, P) = H - TS$

❖ In the simplified lattice model, components are mixed at constant volume and therefore we will be studying the **energy of interaction** between components and the change in the **Helmholtz free energy of mixing**. $A(T, V) = U - TS$

❖ The energy of mixing → negative : promotes mixing
→ positive : opposes mixing

□ Regular solution theory

❖ Assumption

: For all mixtures, favorable or unfavorable interaction between monomers are assumed to be small enough that they do not affect the random placement.

: For simplicity, it is assumed that in polymer blends the monomer volumes of species A and B are identical



4.2. Energy of binary mixing

□ Regular solution theory

: The energy in terms of three pairwise interaction energies (u_{AA} , u_{AB} , and u_{BB}) between adjacent lattice sites occupied by the two species

❖ The interaction energy of an A- or B-monomer with one of its neighboring

$$U_A = u_{AA}\phi_A + u_{AB}\phi_B \quad U_B = u_{AB}\phi_A + u_{BB}\phi_B$$

❖ Each lattice site has z nearest neighbors (z : the coordination number)

: for example, $z=4$ for a square lattice, and $z=6$ for a cubic lattice

: The interaction energy of an A monomer with all of its z neighbors : zU_A

: The energy per monomer : $zU_A/2$ (pairwise interaction is counted twice)

: The number of sites occupied by species A : $n\phi_A$

❖ The total interaction energy of mixture :

$$U = \frac{zn}{2} [U_A\phi_A + U_B\phi_B]$$

$$U = \frac{zn}{2} \{ [u_{AA}\phi + u_{AB}(1-\phi)]\phi + [u_{AB}\phi + u_{BB}(1-\phi)](1-\phi) \}$$

$$= \frac{zn}{2} [u_{AA}\phi^2 + 2u_{AB}\phi(1-\phi) + u_{BB}(1-\phi)^2]$$

where $\phi = \phi_A = 1 - \phi_B$

4.2. Energy of binary mixing

- ❖ The total energy of species A and B before mixing

$$\frac{zn}{2} u_{AA} \phi \quad \frac{zn}{2} u_{BB} (1 - \phi)$$

- ❖ The total energy of both species before mixing

$$U_0 = \frac{zn}{2} [u_{AA} \phi + u_{BB} (1 - \phi)]$$

- ❖ The energy change on mixing

$$\begin{aligned} U - U_0 &= \frac{zn}{2} [u_{AA} \phi^2 + 2u_{AB} \phi(1 - \phi) + u_{BB} (1 - \phi)^2 - u_{AA} \phi - u_{BB} (1 - \phi)] \\ &= \frac{zn}{2} [u_{AA} (\phi^2 - \phi) + 2u_{AB} \phi(1 - \phi) + u_{BB} (1 - 2\phi + \phi^2 - 1 + \phi)] \\ &= \frac{zn}{2} [u_{AA} \phi(\phi - 1) + 2u_{AB} \phi(1 - \phi) + u_{BB} \phi(\phi - 1)] \\ &= \frac{zn}{2} \phi(1 - \phi)(2u_{AB} - u_{AA} - u_{BB}) \end{aligned}$$

- ❖ The energy change on mixing per site

$$\Delta \bar{U}_{mix} = \frac{U - U_0}{n} = \frac{z}{2} \phi(1 - \phi)(2u_{AB} - u_{AA} - u_{BB})$$

4.2. Energy of binary mixing



- ❖ The Flory interaction parameter

$$\chi \equiv \frac{z}{2} \frac{(2u_{AB} - u_{AA} - u_{BB})}{kT}$$

: a dimensionless measure of the difference in the strength of pairwise interaction energies between species in a mixture (compared with the same species in their pure components state)

- ❖ The energy of mixing per lattice site

$$\Delta \bar{U}_{mix} = \chi \phi (1 - \phi) kT$$

- ❖ The Helmholtz free energy of mixing per lattice site

$$\begin{aligned} \Delta \bar{F}_{mix} &= \Delta \bar{U}_{mix} - T \Delta \bar{S}_{mix} \\ &= kT \left[\frac{\phi}{N_A} \ln \phi + \frac{1 - \phi}{N_B} \ln (1 - \phi) + \chi \phi (1 - \phi) \right] \end{aligned}$$

- First calculated by Huggins and latter independently derived by Flory,
- Commonly referred to as the *Flory-Huggins equation*



4.2. Energy of binary mixing

- ❖ For non-polymeric mixtures with $N_A=N_B=1$, *regular solution theory* by Hildebrand

$$\Delta\bar{F}_{mix} = kT[\phi \ln \phi + (1-\phi) \ln(1-\phi) + \chi\phi(1-\phi)]$$

- ❖ For polymeric solutions, $N_A=N$ and $N_B=1$, *Flory-Huggins eqn.* for polymer solution

$$\Delta\bar{F}_{mix} = kT\left[\frac{\phi}{N} \ln \phi + (1-\phi) \ln(1-\phi) + \chi\phi(1-\phi)\right]$$

Entropic origin

Energetic origin

↓
Promote mixing

↓
Depending on χ

- positive : opposing mixing
- zero : ideal mixture (Fig.4.1)
- negative : promoting mixing

- ❖ If there is a **net attraction** between species (like each other better than themselves)
; $\chi < 0 \rightarrow$ single phase mixture favorable
- ❖ If there is a **net repulsion** between species (like themselves more than each other)
; $\chi > 0$



It is very important to know the value of the Flory interaction parameter χ .

4.2. Energy of binary mixing

❖ For non-polymeric mixtures with interacting mainly by dispersion forces,

→ **solubility parameter** $\delta_A \equiv \sqrt{\frac{\Delta E_A}{v_A}}$

minus value due to $u_{AA} < 0$
 v_0 : volume per site

❖ The interaction energy per site in the pure A : $-\frac{zu_{AA}}{2} = v_0 \frac{\Delta E_A}{v_A} = v_0 \delta_A^2$

❖ The interaction energy per site in the pure B : $-\frac{zu_{BB}}{2} = v_0 \frac{\Delta E_B}{v_B} = v_0 \delta_B^2$

❖ The cohesive energy density of interaction between A and B : $-\frac{zu_{AB}}{2} = v_0 \delta_A \delta_B$

❖ Flory-Huggins interaction parameter in terms of solubility parameter difference

$$\chi \equiv \frac{z}{2} \frac{(2u_{AB} - u_{AA} - u_{BB})}{kT} = v_0 \frac{[\delta_A^2 + \delta_B^2 - 2\delta_A \delta_B]}{kT}$$

$$\chi = \frac{v_0}{kT} (\delta_A - \delta_B)^2$$

Temp. dependence

$$\chi(T) \cong A + \frac{B}{T}$$

Entropic part

Enthalpic part

4.2. Energy of binary mixing

$$\chi(T) \cong A + \frac{B}{T}$$

Temperature dependence of the Flory interaction parameters of polymer blends with $v_0=100 \text{ \AA}^3$

Polymer blend	A	B (K)	T range (°C)
dPS/PS	-0.00017	0.117	150-220
dPS/PMMA	0.0174	2.39	120-180
PS/dPMMA	0.0180	1.96	170-210
PS/PMMA	0.0129	1.96	100-200
dPS/dPMMA	0.0154	1.96	130-210
PVME/PS	0.103	-43.0	60-150
dPS/PPO	0.059	-32.5	180-330
dPS/TMPC	0.157	-81.3	190-250
PEO/dPMMA	-0.0021	-	80-160
PP/hhPP	-0.00364	1.84	30-130
PIB/dhhPP	0.0180	-7.74	30-170

Let's think about the miscibility at each case

dPS-deuterated polystyrene; PVME-poly(vinyl methyl ether); PPO-poly(2,6-dimethyl 1,4-phenylene oxide); TMPC-tetramethylpolycarbonate; PEO-poly(ethylene oxide); hhPP-head-to-head polypropylene; PIB-polyisobutylene; dhhPP-deuterium-labelled head-to-head polypropylene

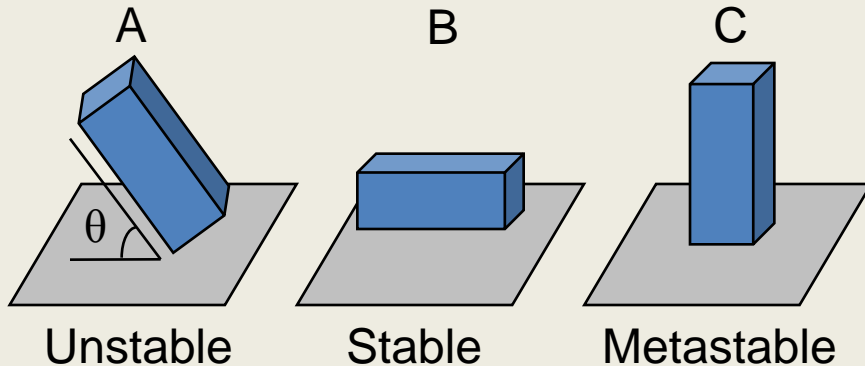
(Ref. N. P. Balsara, "Physical Properties of Polymers Handbook", AIP Press, 1996, Chapter 19)



4.3. Equilibrium and Stability

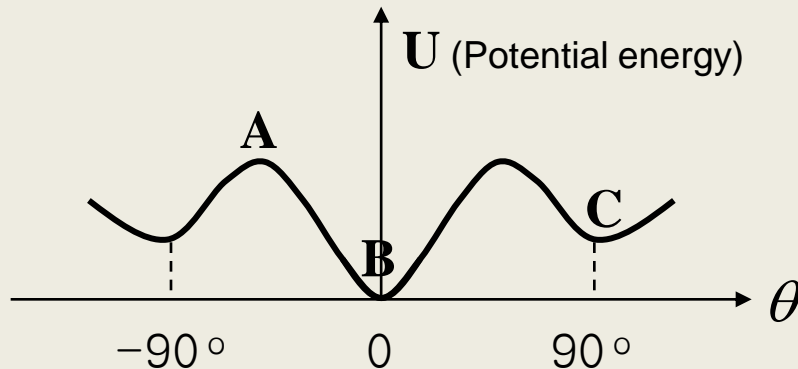
□ The definition of thermodynamic equilibrium

: the state of the system with minimum free energy



B : stable or ground state

∵ any perturbations in the angle
→ higher center-of-mass → increase U

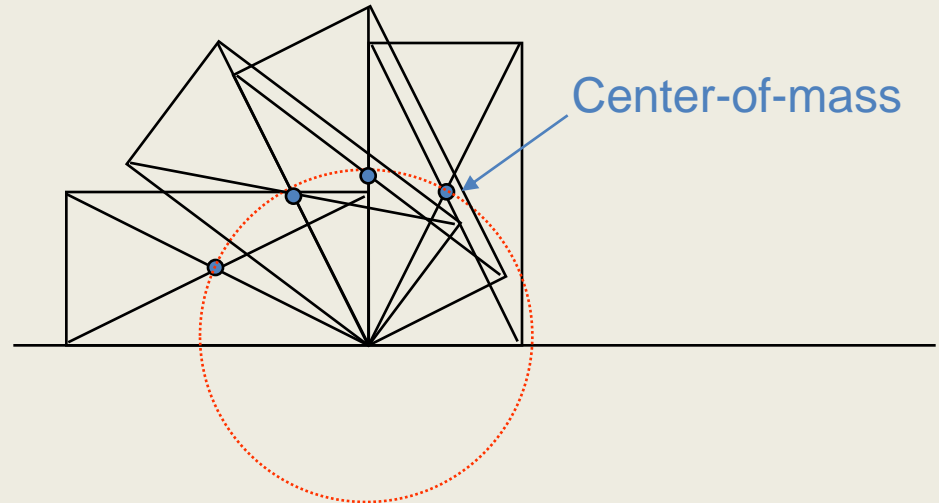
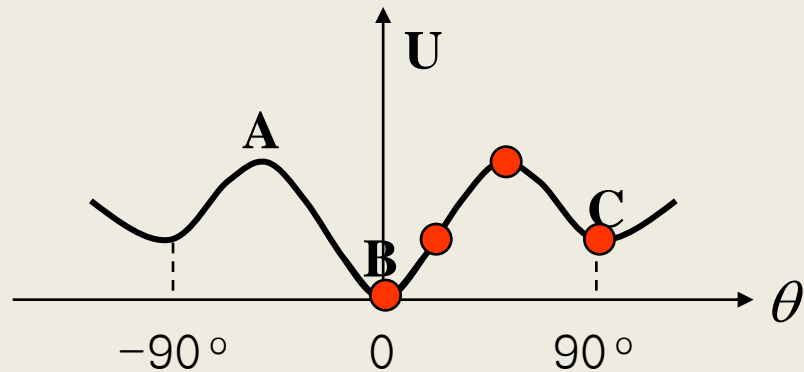
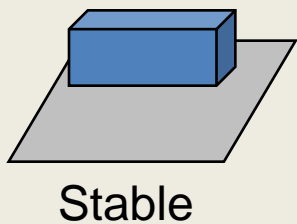
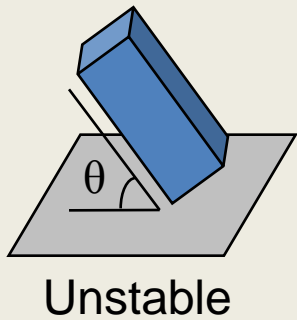
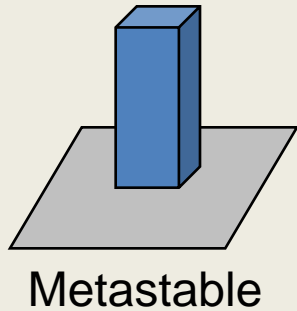


→ The potential energy of the brick
as a function of angle Θ



4.3. Equilibrium and Stability

✧ Potential energy and center-of-mass



4.3. Equilibrium and Stability

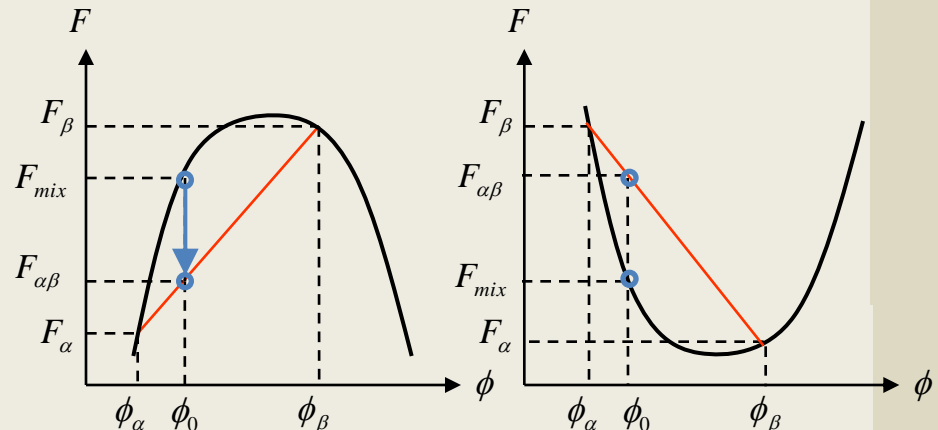
- ❖ The local stability of a homogeneous mixture of composition Φ_0 with free energy $F_{\text{mix}}(\Phi_0) \rightarrow$ shown by concave or convex
- ❖ The relative amounts of each phase (α , β) are determined from the **lever rule**.
 - the system in a state with two phases, the vol. fraction of A in the α phase : Φ_α
the vol. fraction of A in the β phase : Φ_β
 - the fraction of the material having composition Φ_α : f_α ($f_\beta = 1 - f_\alpha$)
 - the total vol. fraction of A component in the system

$$\phi_0 = f_\alpha \phi_\alpha + f_\beta \phi_\beta \qquad f_\alpha = \frac{\phi_\beta - \phi_0}{\phi_\beta - \phi_\alpha} \qquad f_\beta = 1 - f_\alpha = \frac{\phi_0 - \phi_\alpha}{\phi_\beta - \phi_\alpha}$$

- The free energy of the demixed state is the weighted average of the free energy of the material in each of the two states (F_α and F_β)

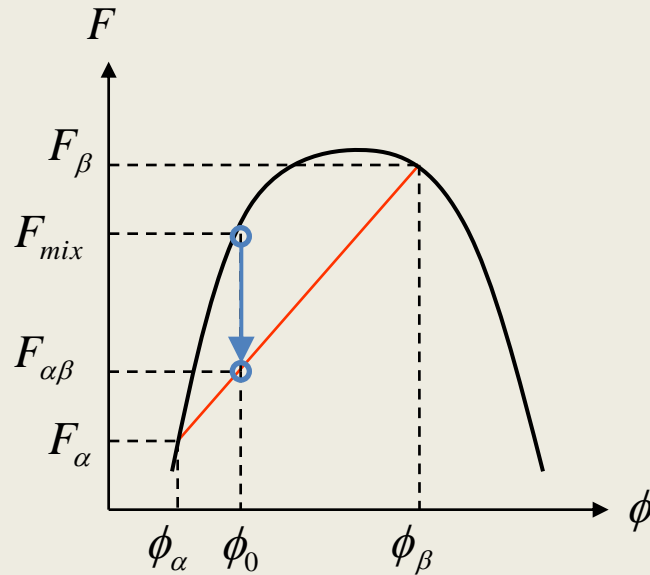
$$\begin{aligned} F_{\alpha\beta}(\phi_0) &= f_\alpha F_\alpha + f_\beta F_\beta \\ &= \frac{(\phi_\beta - \phi_0)F_\alpha + (\phi_0 - \phi_\alpha)F_\beta}{\phi_\beta - \phi_\alpha} \end{aligned}$$

Straight line ; linear dependence of $F_{\alpha\beta}$



4.3. Equilibrium and Stability

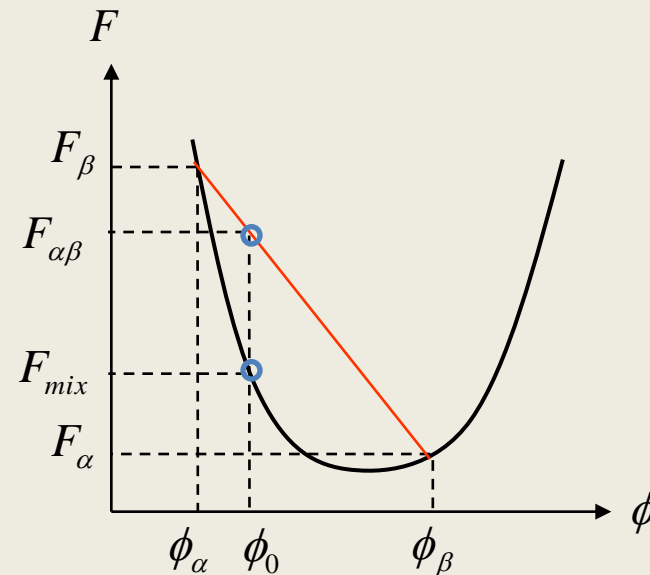
- Stability is determined by whether $F_{mix}(\Phi_0)$ is higher or lower than $F_{\alpha\beta}(\Phi_0)$ ($F_{\alpha\beta}(\Phi_0)$: the free energy of a phase separated state)



concave

$$F_{\alpha\beta}(\Phi_0) < F_{mix}(\Phi_0)$$

The system can spontaneously lower its free energy by phase separating in two phases



convex

$$F_{\alpha\beta}(\Phi_0) > F_{mix}(\Phi_0)$$

The mixed state has lower free energy than any state : stable

$$\frac{\partial^2 F_{mix}}{\partial \phi^2} < 0$$

unstable

$$\frac{\partial^2 F_{mix}}{\partial \phi^2} > 0$$

locally stable

4.3. Equilibrium and Stability

❖ **Ideal mixtures** with $\Delta\bar{U}_{mix} = 0$ have their free energy of mixing convex (Fig.4.1)

❖ Why it is convex?

Free energy of ideal mixture

$$\Delta\bar{F}_{mix} = -T\Delta\bar{S}_{mix} = kT \left[\frac{\phi}{N_A} \ln \phi + \frac{1-\phi}{N_B} \ln(1-\phi) \right]$$

Differentiate with respect to composition

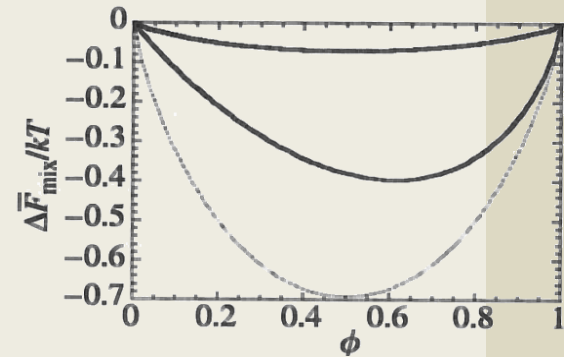
$$\frac{\partial\Delta\bar{F}_{mix}}{\partial\phi} = -T \frac{\partial\Delta\bar{S}_{mix}}{\partial\phi} = kT \left[\frac{\ln \phi}{N_A} + \frac{1}{N_A} - \frac{\ln(1-\phi)}{N_B} - \frac{1}{N_B} \right]$$

Differentiating

$$\frac{\partial^2\Delta\bar{F}_{mix}}{\partial\phi^2} = -T \frac{\partial^2\Delta\bar{S}_{mix}}{\partial\phi^2} = kT \left[\frac{1}{N_A\phi} + \frac{1}{N_B(1-\phi)} \right] > 0$$

Homogeneous ideal mixtures are stable for all compositions because entropy always acts to promote mixing and does not have any energetic contribution.

→ opposite case in next page



4.3. Equilibrium and Stability

- ❖ The opposite case where the **energy dominates** is found at $T = 0$ K, because the entropic contribution banishes.

$$\Delta \bar{F}_{mix} = \Delta \bar{U}_{mix} = \chi \phi(1-\phi)kT$$

$$\frac{\partial^2 \Delta \bar{F}_{mix}}{\partial \phi^2} = \frac{\partial^2 \Delta \bar{U}_{mix}}{\partial \phi^2} = -2\chi kT$$

$$\frac{\partial^2 \Delta \bar{F}_{mix}}{\partial \phi^2} = -z(2u_{AB} - u_{AA} - u_{BB}) = -2kB$$

$$\chi \equiv \frac{z(2u_{AB} - u_{AA} - u_{BB})}{kT}$$

$$\chi(T) \cong A + \frac{B}{T}$$

- If like themselves more than each other

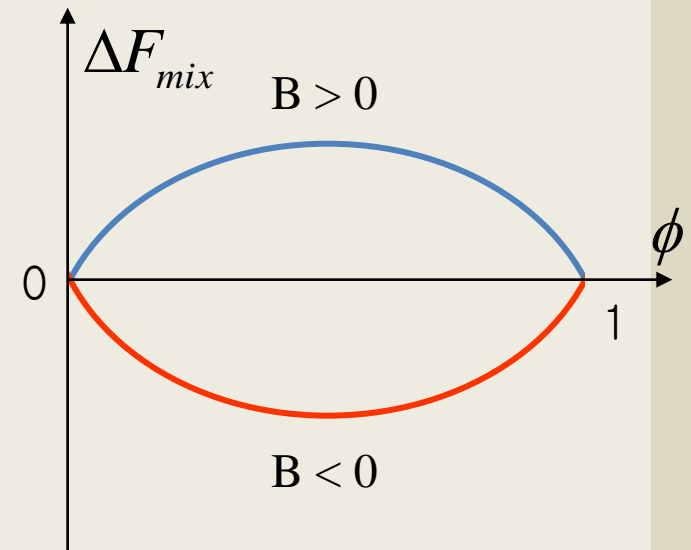
$$u_{AB} > \frac{u_{AA} + u_{BB}}{2} \quad \text{or} \quad B > 0$$

$$\frac{\partial^2 F_{mix}}{\partial \phi^2} < 0, \text{ concave, } \chi > 0 \quad \text{unstable and phase separate}$$

- If like each other more than themselves

$$u_{AB} < \frac{u_{AA} + u_{BB}}{2} \quad \text{or} \quad B < 0$$

$$\frac{\partial^2 F_{mix}}{\partial \phi^2} > 0, \text{ convex, } \chi < 0 \quad \text{stable}$$



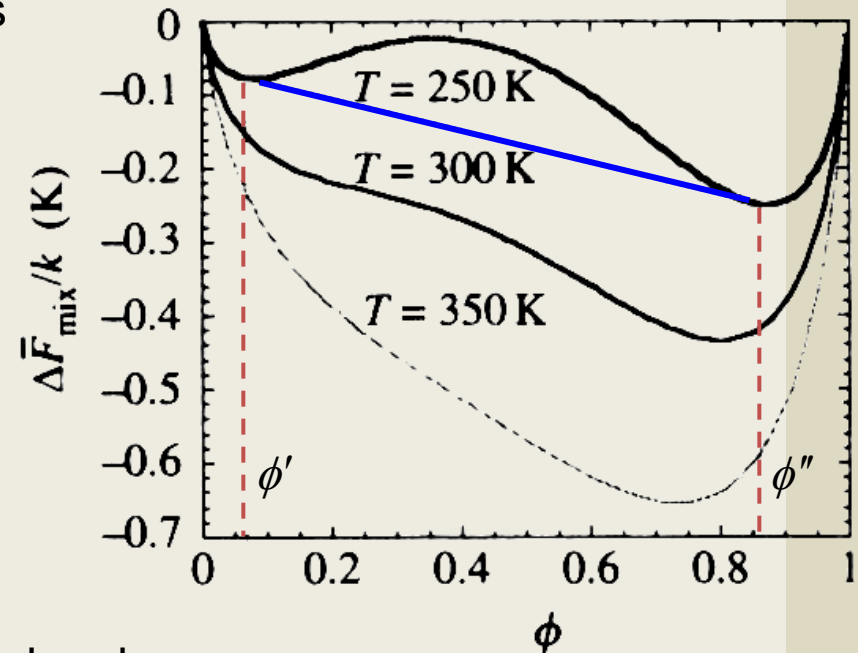
4.3. Equilibrium and Stability

- ❖ Real mixture have both energetic and entropic contributions.

$$\frac{\partial^2 \Delta \bar{F}_{mix}}{\partial \phi^2} = \frac{\partial^2 \Delta \bar{U}_{mix}}{\partial \phi^2} - T \frac{\partial^2 \Delta \bar{S}_{mix}}{\partial \phi^2} = kT \left[\frac{1}{N_A \phi} + \frac{1}{N_B (1-\phi)} \right] - 2\chi kT$$

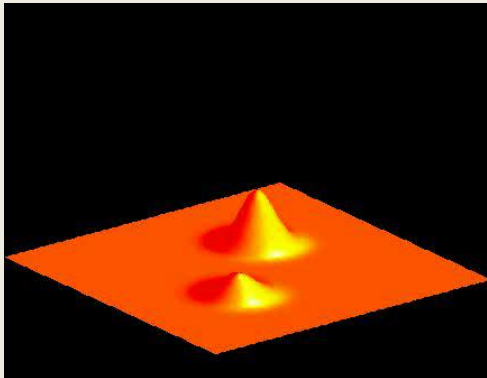
- ❖ Consider a polymer blend with $N_A=200$ and $N_B=100$, for which $\chi = (5K)/T$

- At high temp. the entropic term dominates
→ stable ($T=350$ K)
- Below critical temp. T_c (detail in Ch.4.4)
→ concave range appears ($T=300$ K)
→ a range of phase separated state
- **Straight line** connecting the two phase compositions (ϕ' and ϕ'') determines the free energy of the phase separated state
→ **common tangent rule**
- For any overall compositions in the **miscibility gap** (between ϕ' and ϕ'')
→ the system can minimize its free energy by phase separating into two phases of composition ϕ' and ϕ'' .



4.3. Equilibrium and Stability

- Within the **miscibility gap**, there are unstable and metastable regions, separated by inflection points ($\partial^2 \Delta \bar{F}_{mix} / \partial \phi^2 = 0$)
- ① Between the inflection points, $\partial^2 \Delta \bar{F}_{mix} / \partial \phi^2 < 0$, mixed state is unstable
→ **Spinodal decomposition** ; Even the smallest fluctuation in composition lowers the free energy, leading to spontaneous phase separation
- ② Between the inflection points and phase separated composition (Φ' or Φ'')
→ **Binodal decomposition** ; The mixed state is locally stable to small composition fluctuations (metastable)
→ phase separation occurs by **nucleation and growth**



4.4. Phase diagram

❖ **Phase diagram** can be constructed to summarize the phase behavior of the mixture, showing the regions of stability, instability, and metastability.

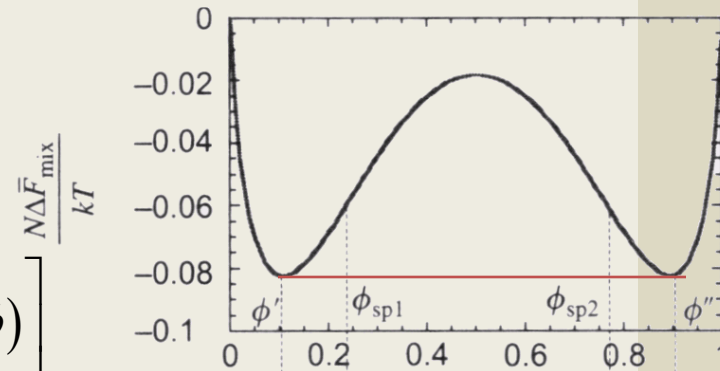
❖ The free energy of mixing for a polymer blend

$$\Delta\bar{F}_{mix} = kT \left[\frac{\phi}{N_A} \ln \phi + \frac{1-\phi}{N_B} \ln(1-\phi) + \chi\phi(1-\phi) \right]$$

▪ The phase boundary is determined by the common tangent of the free energy at the compositions ϕ' and ϕ''

$$\left(\frac{\partial \Delta\bar{F}_{mix}}{\partial \phi} \right)_{\phi=\phi'} = \left(\frac{\partial \Delta\bar{F}_{mix}}{\partial \phi} \right)_{\phi=\phi''}$$

$$\frac{\partial \Delta\bar{F}_{mix}}{\partial \phi} = kT \left[\frac{\ln \phi}{N_A} + \frac{1}{N_A} - \frac{\ln(1-\phi)}{N_B} - \frac{1}{N_B} + \chi(1-2\phi) \right]$$



For a simple example of a symmetric polymer blend with $N_A=N_B=N$

$$\left(\frac{\partial \Delta\bar{F}_{mix}}{\partial \phi} \right)_{\phi=\phi'} = \left(\frac{\partial \Delta\bar{F}_{mix}}{\partial \phi} \right)_{\phi=\phi''} = kT \left[\frac{\ln \phi}{N} - \frac{\ln(1-\phi)}{N} + \chi(1-2\phi) \right] = 0$$

Common tangent line is horizontal

4.4. Phase diagram

- The above eqn. can be solved for the interaction parameter corresponding to the phase boundary - **binodal** (solid line)

$$\chi_b = \frac{1}{2\phi - 1} \left[\frac{\ln \phi}{N} - \frac{\ln(1-\phi)}{N} \right] = \frac{\ln(\phi/(1-\phi))}{(2\phi - 1)N}$$

- temperature-composition dependence

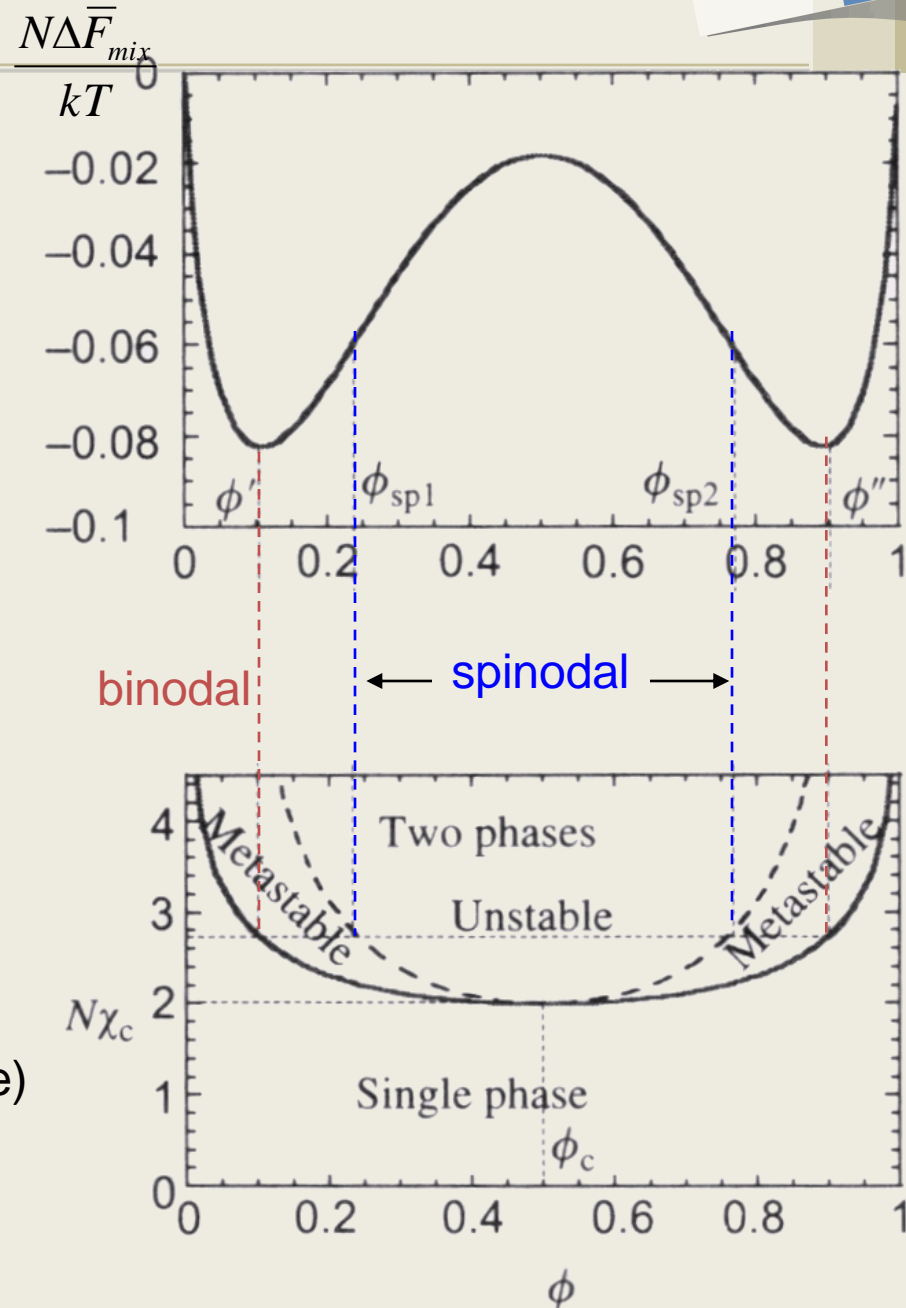
$$T_b = \frac{B}{\ln[\phi/(1-\phi)] / [(2\phi - 1)N] - A}$$

- Inflection point for an asymmetric blend,

$$\frac{\partial^2 \Delta \bar{F}_{mix}}{\partial \phi^2} = kT \left[\frac{1}{N_A \phi} + \frac{1}{N_B (1-\phi)} - 2\chi \right] = 0$$

- the boundary between unstable and metastable regions - **spinodal** (dashed line)

$$\chi_s = \frac{1}{2} \left[\frac{1}{N_A \phi} + \frac{1}{N_B (1-\phi)} \right]$$



4.4. Phase diagram

- In binary blend the lowest point on the spinodal curve corresponds to the critical point.

$$\frac{\partial \chi_s}{\partial \phi} = \frac{1}{2} \left[-\frac{1}{N_A \phi^2} + \frac{1}{N_B (1-\phi)^2} \right] = 0$$

→ the solution of above eqn. : the **critical composition**

$$\phi_c = \frac{\sqrt{N_B}}{\sqrt{N_A} + \sqrt{N_B}}$$

→ Substitution the critical composition into eqn. of the spinodal,
critical interaction parameter

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

critical temperature

$$T_c = \frac{B}{\chi_c - A} = \frac{B}{\frac{1}{2} \left(1/\sqrt{N_A} + 1/\sqrt{N_B} \right)^2 - A}$$



4.4. Phase diagram

- ❖ For a symmetric polymer blend ($N_A=N_B=N$),
: the whole phase diagram is symmetric with the critical composition

$$\phi_c = \frac{1}{2}$$

and very small critical interaction parameter

$$\chi_c = \frac{2}{N}$$

- For long chains polymer blends (N : large) \rightarrow most polymer blends $\chi > \chi_c$
 \rightarrow phase separated over some composition range (within the miscibility gap)
- Only blends with very weak repulsion ($0 < \chi < \chi_c$), or a net attraction ($\chi < 0$)
 \rightarrow form homogeneous (single phase) blends over the whole composition range
- ❖ In polymer solutions ($N_A=N$ and $N_B=1$), the phase diagram is strongly asymmetric with low critical composition

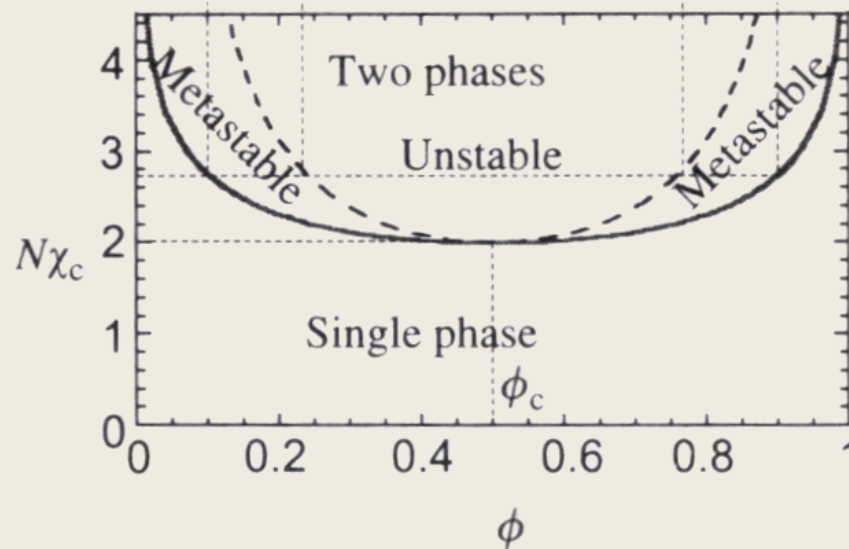
$$\phi_c = \frac{1}{\sqrt{N} + 1} \cong \frac{1}{\sqrt{N}}$$

and critical interaction parameter close to 1/2

$$\chi_c = \frac{1}{2} + \frac{1}{\sqrt{N}} + \frac{1}{2N} \cong \frac{1}{2} + \frac{1}{\sqrt{N}}$$

4.4. Phase diagram

- ❖ Note that the spinodal and binodal for any binary mixture meet at the critical point



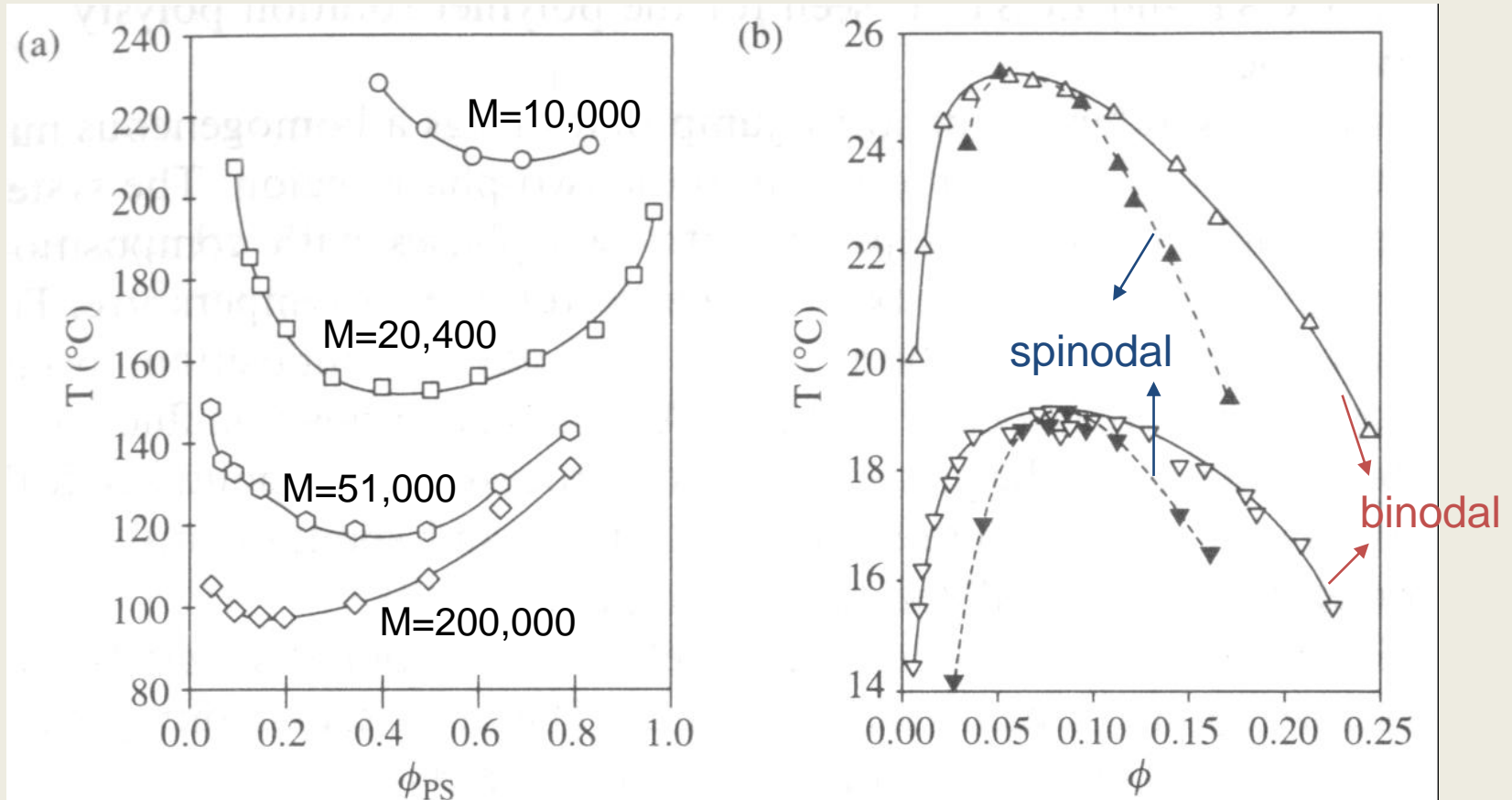
- For $\chi < \chi_c$, the homogeneous mixture is stable at any composition $0 \leq \Phi \leq 1$
- For $\chi > \chi_c$, there is a miscibility gap \rightarrow for any composition in a miscibility gap, the equilibrium state correspond to two phases



4.4. Phase diagram

$$\chi(T) \cong A + \frac{B}{T}$$

- ❖ Experimentally, the interaction parameter is changed by varying temperature T
- ❖ Phase diagrams are typically plotted in the temperature-composition plane.

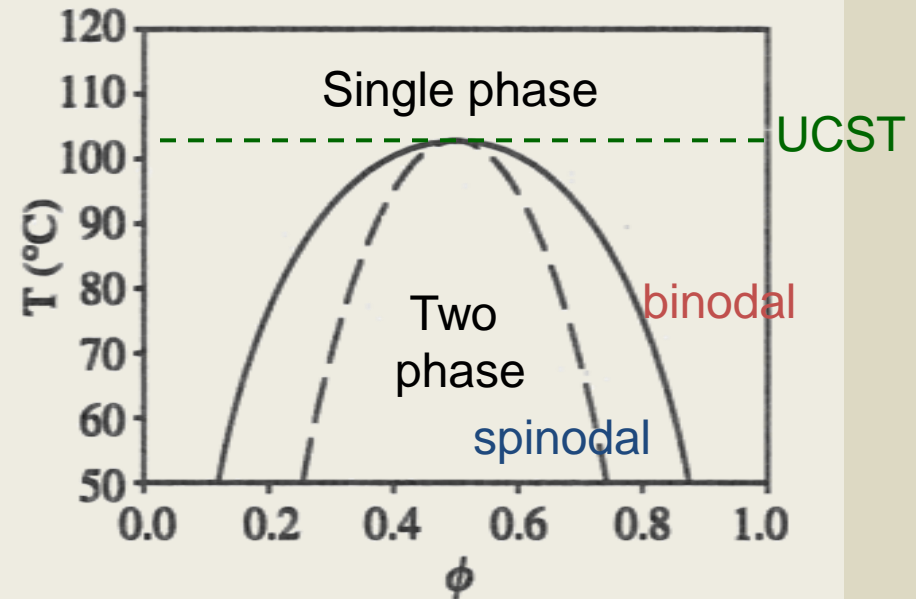
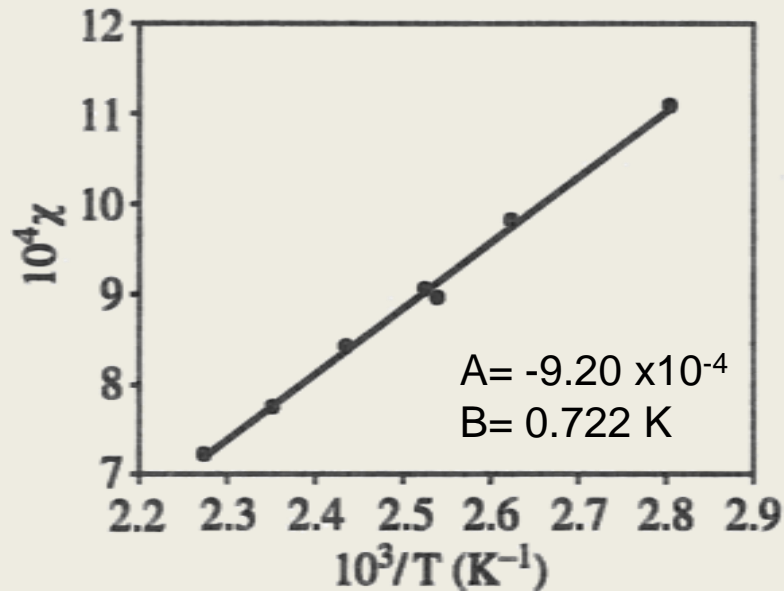


- Phase diagram of polymer blends and solutions. (a) Polymer blends of poly(vinyl methyl ether) (M=51,500 g mol⁻¹) and various molar masses of polystyrene. (b) polyisoprene solution in dioxane ($\triangle \blacktriangle$: 1,330,000 g mol⁻¹, $\nabla \blacktriangledown$: 53,300 g mol⁻¹)

4.4. Phase diagram

$\chi(T) \cong A + \frac{B}{T}$; In $B > 0$, then χ decreases as temperature is raised.

- ❖ The *upper critical solution temperature (UCST)* T_c
 - : The highest temperature of the two-phase region
 - : For all $T > T_c$, the homogeneous mixtures are stable.



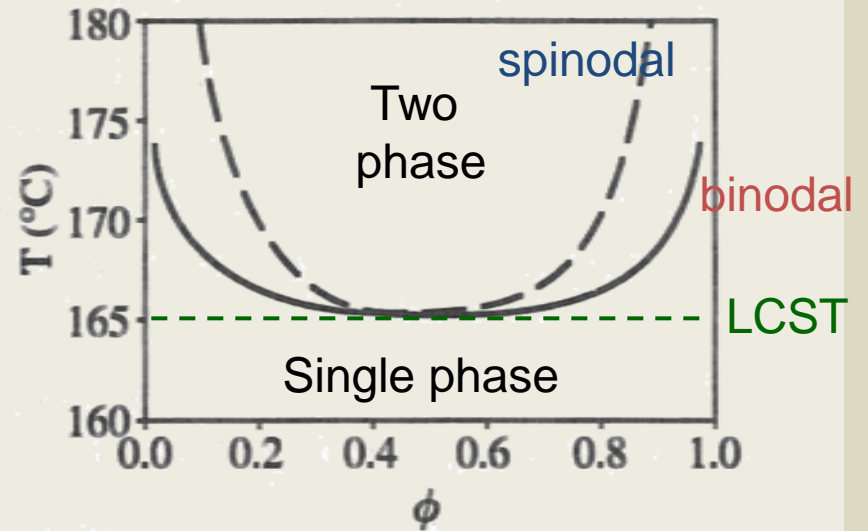
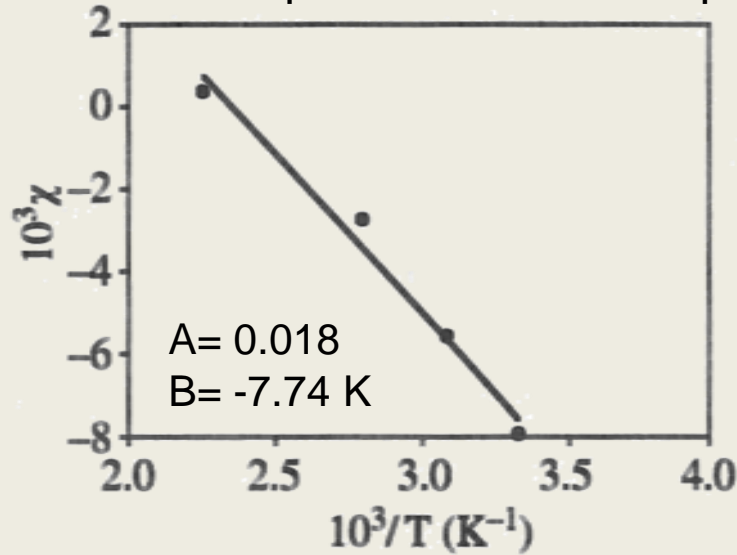
Temperature dependence of χ for mixtures of hydrogenated polybutadiene and deuterated polybutadiene with $N_A = N_B = 2000$ and $v_0 = 100 \text{ \AA}^3$.



4.4. Phase diagram

$\chi(T) \cong A + \frac{B}{T}$; In $B < 0$, then χ decreases as temperature is lowered.

- ❖ The *lower critical solution temperature (LCST)* T_c
: The lowest temperature of the two-phase region



Temperature dependence of χ for mixtures of polyisobutadiene and deuterated head-to-head polypropylene with $N_A = N_B = 6000$ and $v_0 = 100 \text{ \AA}^3$.



4.4. Phase diagram

□ Summary of phase separation and phase diagram

- ❖ Consider a sudden temperature jump that brings a homogeneous mixture at Φ_c into the two-phase region.
 - The system will spontaneously phase separate into two phase with compositions given by the values on the coexistence curve at new temperature
 - This spontaneous phase separation, called **spinodal decomposition**, occurs because the mixtures is locally unstable.
 - Any small composition fluctuation is sufficient to initiate the phase separation.
- ❖ The points of the phase diagram between the spinodal and binodal curves correspond to metastable mixtures.
 - The metastable homogeneous state is stable against small composition fluctuations and requires a larger nucleation event to initiate phase separation
 - This phase separation process is called **nucleation and growth** (binodal decomposition)



4.5. Experimental investigation

- ❖ Determination of Flory interaction parameter χ : by **measuring composition fluctuations using scattering**.
- ❖ Consider a homogeneous blend at equilibrium with composition of A monomers $\bar{\phi}$
 - In a small volume containing n monomers with $n_A = \Phi n$ A monomers, a small fluctuation in composition $\delta\phi$ can occur spontaneously at equilibrium.

$$\delta\phi \equiv \phi - \bar{\phi}$$

- fluctuation \rightarrow transfer of δn_A A monomers from the rest of blend \rightarrow transfer of the same number of B monomer out of small volume (effective exchange of A and B)

$$\delta n_A = n\delta\phi$$

$$\Delta F_{mix}(\phi) = \Delta F_{mix}(\bar{\phi}) + \frac{\partial \Delta F_{mix}}{\partial \phi} \delta\phi + \frac{1}{2} \frac{\partial^2 \Delta F_{mix}}{\partial \phi^2} (\delta\phi)^2 + \dots$$

- rewritten in terms of the number of monomers exchanged

$$\frac{\partial \Delta F_{mix}}{\partial \phi} \delta\phi = \frac{\partial \Delta F_{mix}}{\partial (n\phi)} n\delta\phi = \frac{\partial \Delta F_{mix}}{\partial n_A} \delta n_A$$

Exchange chemical potential

: change in free energy of mixing arising from the exchange of one A monomer for one B monomer



4.5. Experimental investigation

- exchange \rightarrow changes the free energy in the rest of the blend : $\frac{\partial \Delta F_{mix}}{\partial n_A} (-\delta n_A)$
- The free energy change in the system (δF) arising from this fluctuation

$$\delta F = \Delta F_{mix}(\phi) - \Delta F_{mix}(\bar{\phi}) - \frac{\partial \Delta F_{mix}}{\partial n_A} \delta n_A = \frac{1}{2} \frac{\partial^2 \Delta F_{mix}}{\partial \phi^2} (\delta \phi)^2$$

- ※ Note that the rest of the blend is considered very large
exchange of δn_A A monomers does not change its composition
- The typical free energy change is of order of the thermal energy, $\delta F \approx kT$

$$\langle (\delta \phi)^2 \rangle \approx kT \left(\frac{\partial^2 \Delta F_{mix}}{\partial \phi^2} \right)^{-1} = \frac{kT}{n} \left(\frac{\partial^2 \Delta \bar{F}_{mix}}{\partial \phi^2} \right)^{-1} \rightarrow \text{Appendix 4.1}$$

- : composition fluctuation $\propto 1/(\text{volume}) \approx n$ (number of site)
- : Small volumes with a few monomers (small n) \rightarrow large fluctuations



4.5. Experimental investigation

- ❖ *The mean-square fluctuation* is related to the low wavevector limit of the scattering function

$$S(q) = \frac{\langle (\delta n_A)^2 \rangle}{n} = n \langle (\delta \phi)^2 \rangle \quad \text{where no. of monomers in the small volume : } n = (qb)^{-3}$$

→ Appendix 4.2

- Since $\langle (\delta \phi)^2 \rangle \sim 1/n$, $S(q)$ saturates at small values of the wavevector
- The scattering function at zero wavevector $S(0) \sim$ second derivative of $\Delta \bar{F}_{mix}$

$$S(0) = n \langle (\delta \phi)^2 \rangle = kT \left(\frac{\partial^2 \Delta \bar{F}_{mix}}{\partial \phi^2} \right)^{-1}$$

- The Flory-Huggins theory predicts

$$\frac{1}{S(0)} = \frac{1}{kT} \frac{\partial^2 \Delta \bar{F}_{mix}}{\partial \phi^2} = \frac{1}{N_A \phi} + \frac{1}{N_B (1-\phi)} - 2\chi$$

where N_A : no. of A monomer
 Φ : volume fraction of A chains
→ Appendix 4.3

: Flory interaction parameter χ can be determined from the low wavevector limit of the scattering function



4.5. Experimental investigation

- ❖ The standard assumption, called the random-phase approximation, extends to non-zero wavevectors q using the form factor of ideal chain $P(q, N)$

$$\frac{1}{S(q)} = \frac{1}{N_A \phi P(q, N_A)} + \frac{1}{N_B \phi P(q, N_B)} - 2\chi$$

- The form factor for an ideal chain is the Debye function.
- The high q limit of the Debye function is

$$P(q, N) \cong \frac{2}{q^2 \langle R_g^2 \rangle} = \frac{12}{q^2 N b^2} \quad \text{for } q \gg 1/R_g \quad \text{where } \langle R_g^2 \rangle = N b^2 / 6$$

- The low q limit of any form factor is $P(q, N) = 1$, and a simple crossover expression emerges for the reciprocal of the Debye function.

$$\frac{1}{P(q, N)} = 1 + \frac{q^2 N b^2}{12}$$

- A simple result for the reciprocal scattering function by combining above eqns.

$$\begin{aligned} \frac{1}{S(q)} &= \frac{1}{N_A \phi} + \frac{q^2 b^2}{12 \phi} + \frac{1}{N_B (1-\phi)} + \frac{q^2 b^2}{12(1-\phi)} - 2\chi = \frac{1}{N_A \phi} + \frac{1}{N_B (1-\phi)} - 2\chi + \frac{q^2 b^2}{12} \left(\frac{1}{\phi} + \frac{1}{1-\phi} \right) \\ &= \frac{1}{S(0)} + \frac{q^2 b^2}{12 \phi (1-\phi)} \end{aligned}$$

4.5. Experimental investigation

$$\frac{1}{S(q)} = \frac{1}{S(0)} + \frac{q^2 b^2}{12\phi(1-\phi)}$$

- This form for scattering is actually far more general, valid for random fluctuation
- ❖ Small angle neutron scattering data on miscible polymer blends are customarily fit to the *Ornstein-Zernike scattering function*

$$S(q) = \frac{S(0)}{1+(q\xi)^2}$$

$\xi = \sqrt{\frac{b^2 S(0)}{12\phi(1-\phi)}}$: *correlation length* for the mean-field theory for binary mixtures

$$\left(\begin{array}{l} \text{For } q \ll 1/\xi, S(q) \rightarrow S(0) \\ \text{For } q \gg 1/\xi, S(q) \sim q^{-2} \end{array} \right)$$



4.5. Experimental investigation

27 °C $I(q)=1180\text{m}^{-1}$, $\xi =3.3\text{nm}$

51 °C $I(q)=2180\text{m}^{-1}$, $\xi =4.5\text{nm}$

83 °C $I(q)=2180\text{m}^{-1}$, $\xi =4.5\text{nm}$

- temperature $\uparrow \rightarrow$ scattering intensity \uparrow
 \rightarrow fluctuation stronger
- at high $q \gg 1/\xi$, the scattering intensity is independent to temperature because

$$S(q) = \frac{S(0)}{(q\xi)^2} = \frac{12\phi(1-\phi)}{(qb)^2} \quad \text{for } q \gg 1/\xi$$

SANS intensity for a $\Phi=0.5$ miscible blend of polyisobutylene and a random copolymer of ethylene and butene at three temperatures

Ref. *Macromolecules*, **28** (1995) 1252



4.5. Experimental investigation

- ❖ The correlation length ξ has important significance and is related to concentration fluctuation.
- On length scales smaller than the correlation length ($q^{-1} < \xi$),
: $S(q) \sim \langle (\delta n_A)^2 \rangle \sim (qb)^{-2} \rightarrow$ independent to ξ or χ
 \rightarrow independent to temperature at high q (above Fig)
- On length scale larger than the correlation length ($q^{-1} > \xi$),
: $S(q) \rightarrow S(0) \sim (\xi/b)^2$
: Both $S(0)$ and ξ^2 contain the same information about Flory interaction parameter χ
: This information is only obtained at low q , by **Ornstein-Zernike scattering function**

$$\chi = \frac{v_0}{2} \left[\frac{1}{v_A \phi} + \frac{1}{v_B (1-\phi)} \right] - \frac{1}{2S(0)}$$

$$S(q) = \frac{S(0)}{1 + (q\xi)^2}$$





Keywords in Chapter 5

- Birefringence
- Small-Angle Neutron Scattering (SANS) & Wide-angle X-ray scattering (WAXS)
 - Freely jointed chain model
 - The Rouse-Bueche Theory

