

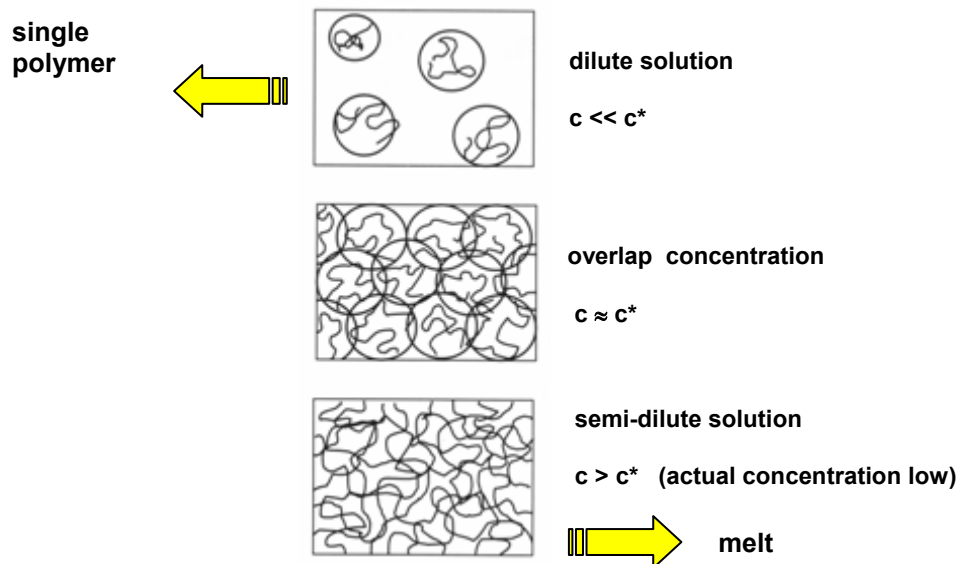
Chapter 4: POLYMER SOLUTIONS AND MIXTURES

4.1 Excluded volume interaction & Flory theory

- idea of excluded volume interactions
- θ -temperature
- Flory approach for the free energy and scaling behavior of R_E with excluded volume interactions

Up to here (see script Chap. 3) we looked at the properties of a single chain with increasing concentration polymer will interpenetrate each other. We can distinguish the following concentration regions:

Range of concentrations



Overlap concentration c^*

pervaded volume $V \sim R^3$

overlap of single polymer if $c^* = \frac{Nv_{mon}}{V} \approx \frac{Nv_{mon}}{R^3} = \frac{Nv_{mon}}{(N^{\nu}l)^3}$ (with ν = Flory exponent)

$\Rightarrow c^* \sim N^{1-3\nu} \sim N^{-0.8}$ if $\nu = \frac{3}{5}$ for good solvent conditions.

For high degrees of polymerization, the overlap concentration can be rather low!

Now we look at the thermodynamic properties of polymers in solutions at $c \geq c^*$ and in polymer mixtures (dense systems).

i.e. phase separations & osmotic pressure

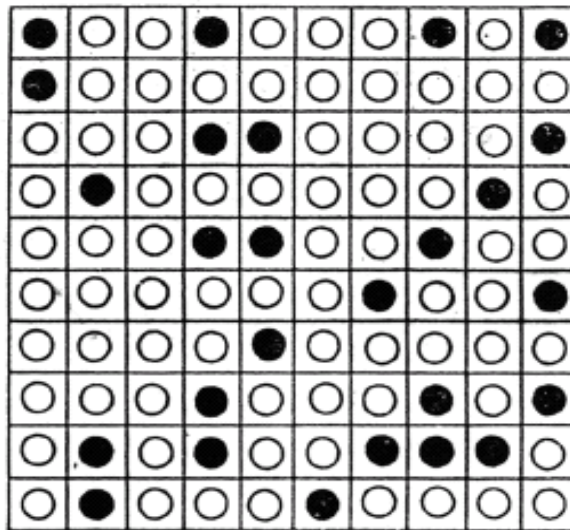
Flory-Huggins theory

A mixture is miscible if the free enthalpy of mixing $\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} < 0$ where ΔH_{mix} and ΔS_{mix} are the enthalpy and entropy of mixing, respectively.

First we look at a mixture of **low molecular weight substances**

- distribution on lattice without change in volume
- both components have lattice volume so in this theory; number fraction=volume fraction

Entropy of mixing



n_1 = number of lattice sites for component 1
 n_2 = number of lattice sites for component 2
 $n = n_1 + n_2$ = total number of lattice sites

Calculation of entropy change

$\Delta S_{mix} = k_B \ln \Omega$ where $\Omega =$ number of possible distributions of component 1 & 2 on lattice sites

$\Omega = \frac{n!}{n_1! n_2!}$ the denominator takes permutations of component 1&2 among each other into account

with $\ln x! \approx x \ln x - x$

$$\Rightarrow \Delta S_{mix} = -k_B \left[n_1 \ln \left(\frac{n_1}{n} \right) + n_2 \ln \left(\frac{n_2}{n} \right) \right] \text{ with number fractions } c_1 = \frac{n_1}{n} \text{ and } c_2 = \frac{n_2}{n}$$

since component 1&2 have same lattice volume: number fraction=volume fraction

$$\Rightarrow \Delta S_{mix} = -nk_B [c_1 \ln(c_1) + c_2 \ln(c_2)]$$

$$\Rightarrow \text{if } n=N_A \quad \Delta S_{mix}^n = -R [c_1 \ln(c_1) + c_2 \ln(c_2)] \quad \text{per mole!}$$

with gas-constant $R=k_B N_A$

Calculation of enthalpy change

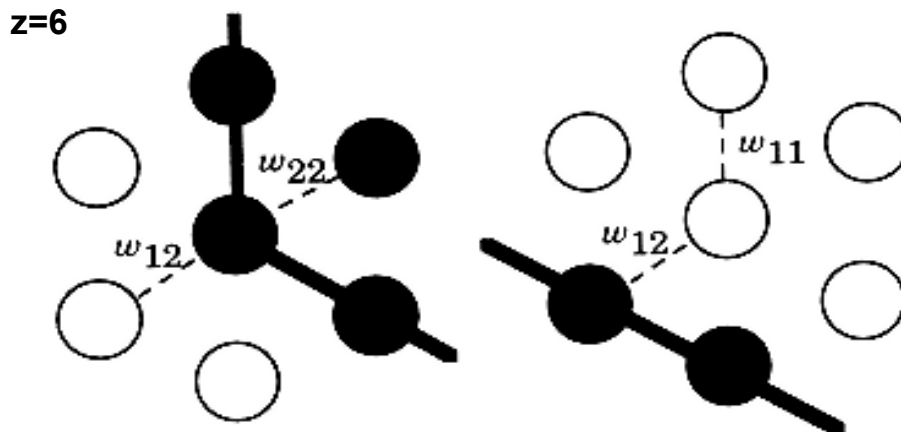
Every lattice site is in the average surrounded

by $c_1 z$ neighbors of component 1

by $c_2 z$ neighbors of component 2 (z = coordination number)

Looking at averages implies that concentration fluctuations are small. The Flory-Huggins theory is a mean-field theory.

Enthalpy of mixing



$$\Rightarrow \text{interaction enthalpy of component 1: } H_1 = \frac{1}{2} n c_1 (c_1 z w_{11} + c_2 z w_{12})$$

$$\text{component 2: } H_2 = \frac{1}{2} n c_2 (c_1 z w_{12} + c_2 z w_{22})$$

with w_{ij} =pair-wise interaction energies

The factor 0.5 arises from the fact, that all pairs are counted twice.

$$\text{The expressions for the pure components are: } H_i^0 = \frac{1}{2} n c_i z w_{ii}, \quad i=1,2$$

$$\Delta H_{mix} = (H_1 + H_2) - (H_1^0 + H_2^0) = \frac{1}{2} n z c_1 c_2 (2w_{12} - w_{11} - w_{22}) \quad \text{with } c_1 + c_2 = 1$$

$$= n z c_1 c_2 \Delta w_{12} \quad \text{with } \Delta w_{12} = w_{12} - \frac{1}{2}(w_{11} + w_{22})$$

$$\Rightarrow \quad \Delta H_{mix}^M = n z c_1 c_2 \Delta w_{12} \quad \text{per mole!}$$

$\Delta w_{12} < 0$ exothermal mixing process
 $\Delta w_{12} > 0$ endothermal mixing process
 $\Delta w_{12} = 0$ athermal mixing process

introduction of the interaction parameter: $\chi_{12} = \Delta w_{12} \frac{1}{RT} \propto \frac{1}{T}$

$$\Rightarrow \quad \Delta H_{mix}^M = RT \chi_{12} c_1 c_2$$

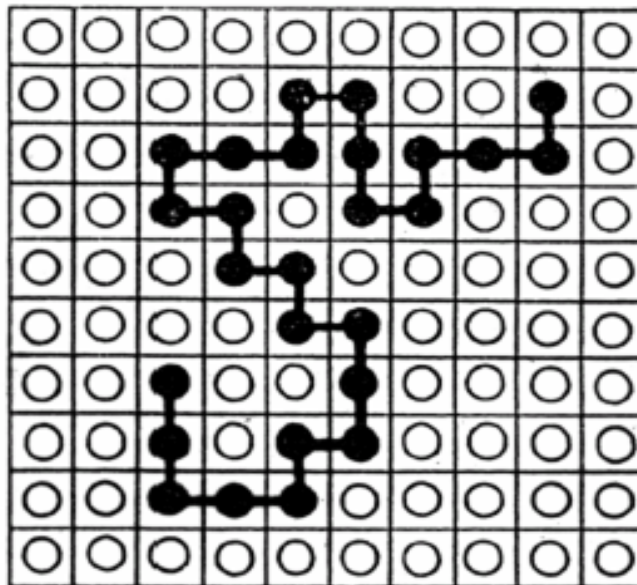
$$\Rightarrow \quad \text{free enthalpy of mixing:} \quad \Delta G_{mix}^M = RT [c_1 \ln c_1 + c_2 \ln c_2 + \chi_{12} c_1 c_2] \quad \text{per mole}$$

Polymer solutions

The calculation of the enthalpy of mixing is the same for mixtures of low molecular weight and polymeric substances. It was based on pairwise interaction of segments/molecules. Connectivity of the segment plays no role!

Calculation of entropy change

Entropy of mixing



- $n_1 =$ number of solvent molecules
- $n_2 =$ number of polymers
- $N =$ lattice sites per polymer = degree of polymerization
- $n = n_1 + n_2 N =$ total number of lattice sites

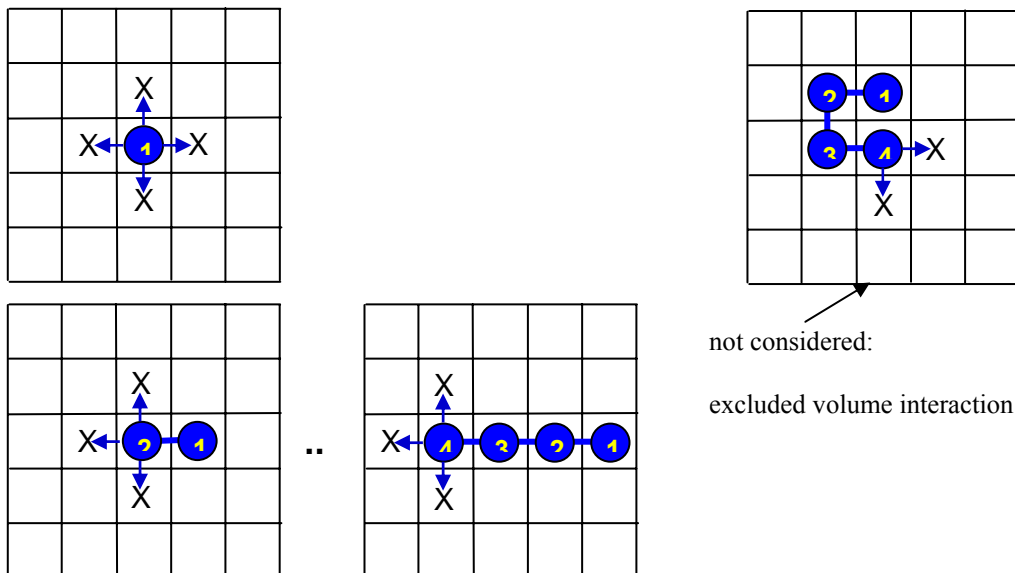
Assume that i polymers are already distributed on the lattice

- \Rightarrow number of free sites is: $n - N \times i$
- \Rightarrow for the first segment of the $(i+1)$ polymer there are $(n - N \times i)$ possibilities to find a site
- \Rightarrow for the second segment there are $z \times$ (number of free sites)
- \Rightarrow for the third to x th segment there are $(z-1) \times$ (number of free sites)

number of free sites is replaced by the average number: $\frac{n - N \times i}{n}$

- $n \gg N$ otherwise there would be a significant reduction with each segment added

Entropy of mixing



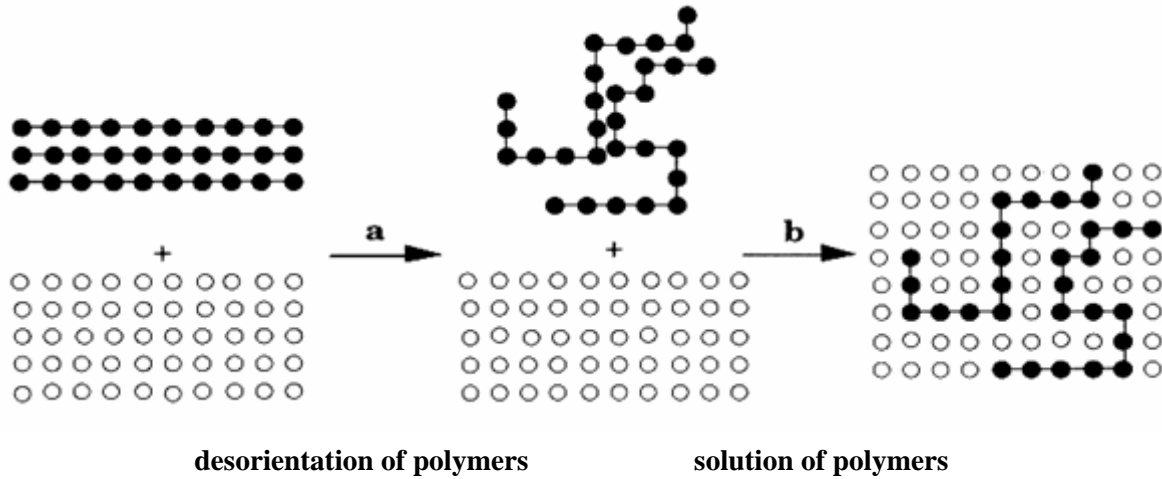
\Rightarrow number of possibilities to distribute the $(i+1)$ th polymer on the lattice:

$$V_{i+1} = \underbrace{(n - Ni)}_{1st} \cdot z \cdot \underbrace{\frac{(n - Ni)}{n}}_{2nd} \cdot \underbrace{(z-1)^{N-2} \left[\frac{(n - Ni)}{n} \right]^{N-2}}_{\text{all other (N-2) segments}} \stackrel{\text{if } z \gg 1}{\approx} (n - Ni)^N \left(\frac{z-1}{n} \right)^{N-1}$$

\Rightarrow number of possibilities to distribute all polymers on n_2 lattice sites:

$$P_2 = \frac{V_1 \cdot V_2 \cdot \dots \cdot V_{n_2}}{n_2!} \quad \text{denominator takes into account indistinguishability of polymers!}$$

for $n \gg N \Rightarrow P_2 \approx \left(\frac{z-1}{n} \right)^{n_2(n-1)} \frac{n!}{(n - n_2 N)! n_2!}$



entropy of the solution: $S = k_B \ln P_2$ with $n = n_1 + n_2 N$ and $c_i = \frac{n_i}{n_1 + n_2 N}$

$$\Rightarrow S = k_B \left\{ -n_1 \ln c_1 - n_2 \ln c_2 + n_2 (N-1) \ln \left(\frac{z-1}{e} \right) \right\}$$

The final stage has been reached by

- (1) disorientation of the polymer (creation of an amorphous state)
- (2) dissolution of the disoriented polymer

substraction of the entropy change due to step (1)

entropy of a polymer melt $s(n_1 = 0) = k_B n_2 \ln N + k_B n_2 (z-1) \ln \left(\frac{z-1}{e} \right)$

$$\Rightarrow \text{change solely due to step (2): } \Delta S_{mix} = S - S(n_1 = 0) = -k_B [c_1 \ln c_1 + c_2 \ln c_2]$$

$$\Rightarrow \Delta S_{mix}^M = -R \left[c_1 \ln c_1 + \frac{c_2}{N} \ln c_2 \right] \quad \text{polymer in solution}$$

$$\Delta S_{mix}^M = -R \left[\frac{c_1}{N_1} \ln c_1 + \frac{c_2}{N_2} \ln c_2 \right] \quad \text{polymer mixture}$$

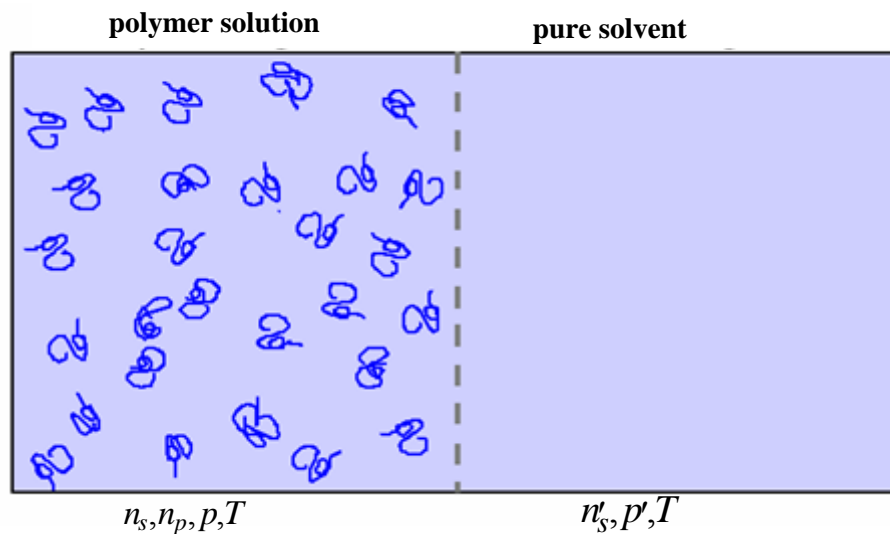
$$\Rightarrow \Delta G_{mix}^M = RT \left\{ \frac{c_1}{N_1} \ln c_1 + \frac{c_2}{N_2} \ln c_2 + \chi_{12} c_1 c_2 \right\}$$

in general $\Delta w_{12} \propto \chi_{12} > 0$ (endothermal mixing)

The entropy of mixing is for high molecular weights small.

\Rightarrow Polymers are poorly miscible!

Osmotic pressure & membrane osmometry



semipermeable membrane: exchange of solvent until the chemical potential of the solvent is equal on both sides`.

chem. potential pure solvent = $\mu_s^0(p', T) = \mu_s(p, T)$ = chem. potential solvent in polymer solution

$$\Delta\mu_s = \mu_s(p, T) - \mu_s^0(p, T) = \left. \frac{\partial \Delta G_{mix}}{\partial n_s} \right|_{p, T, n_p} \quad \text{enthalpy for dilution(*)}$$

remember: $\Delta G_{mix} = nk_B T \left\{ c_s \ln c_s + \frac{c_p}{N} \ln c_p + \chi c_s c_p \right\}$ with $c_s = \frac{n_s}{n}$; $c_p = \frac{n_p}{n}$; $n = n_s + n_p N$

$$\Rightarrow \Delta\mu_s = \frac{\partial \Delta G_{mix}}{\partial n_s} = nk_B T \left\{ \ln c_s + \left(1 - \frac{1}{N}\right) c_p + \chi c_p^2 \right\} = \mu_s(p, T) - \mu_s^0(p, T)$$

$$\Rightarrow \Delta\mu_s^M = RT \left\{ \ln c_s + \left(1 - \frac{1}{N}\right) c_p + \chi c_p^2 \right\} \text{ per mole} \quad (**)$$

The osmotic pressure is the pressure difference $p - p' = \Pi$

In a linear approximation (in equilibrium):

$$\mu_s(p, T) = \mu_s^0(p', T) = \mu_s^0(p, T) - (p - p') \underbrace{\left. \frac{\partial \mu_s^0}{\partial p} \right|_{T, n_s}}_{= v_s} = \mu_s^0(p, T) - \Pi v_s$$

= molar volume

with (*) $\Rightarrow \Delta\mu_s = -\Pi v_s$

with (**) $\Rightarrow -\Pi v_s = RT \left\{ \ln c_s + \left(1 - \frac{1}{N}\right) c_p + \chi c_p^2 \right\}$

for low polymer concentrations $c_p \ll 1$: $\ln c_s = \ln(1 - c_p) \approx -c_p - \frac{1}{2}c_p^2 + \dots$

$$\Rightarrow -\Pi v_s = RT \left\{ \frac{c_p}{N} + \left(\frac{1}{2} - \chi \right) c_p^2 + \dots \right\}$$

with $\Pi v_s = RT \frac{c_p}{N}$ **van't Hoff Law**

and the other terms are derivations from ideal behavior, they disappear for $\chi = \frac{1}{2}$

remember: (1) $\chi \propto T^{-1}$
 (2) osmotic pressure is the pressure difference between polymer solution and pure solution

\Rightarrow

1. for $\chi < \frac{1}{2}$ (high temperatures):

osmotic pressure is higher compared to ideal gas condition; solvent is incorporated into the polymer and results in extension of the polymers; polymers repel each other.

good solvent conditions

2. for $\chi > \frac{1}{2}$ (low temperatures):

osmotic pressure is reduced compared to ideal gas condition; solvent is suppressed from polymer and results in shrinkage of the polymers; polymers attract each other.

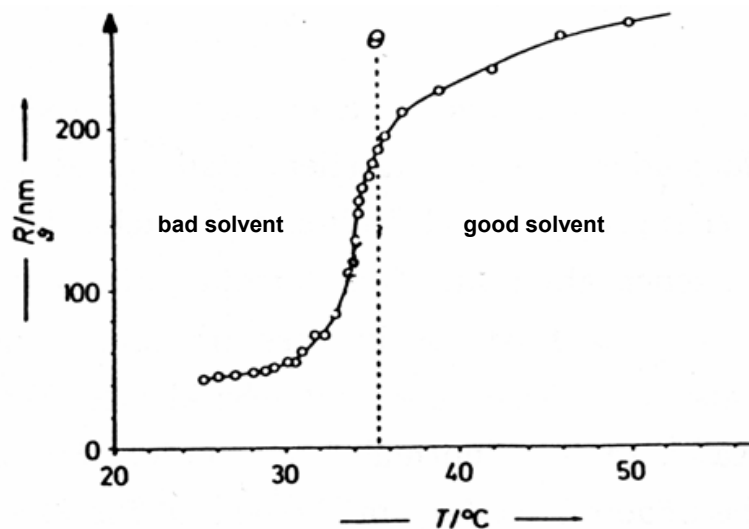
bad solvent conditions

3. for $\chi = \frac{1}{2}$:

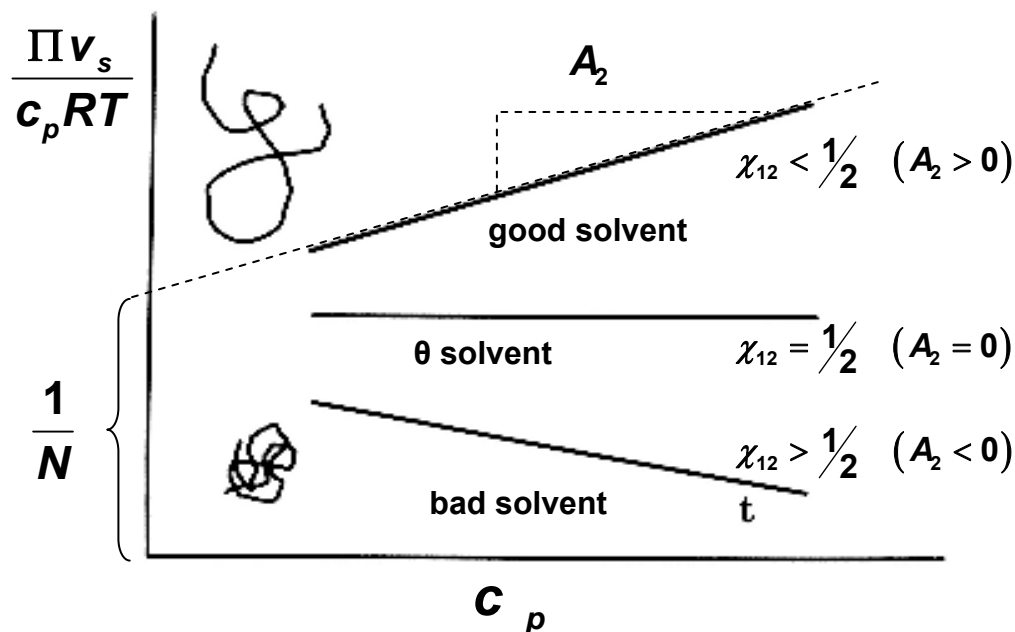
osmotic pressure corresponds to ideal gas condition.

θ -conditions

Radius of PS in cyclohexane as a function of the solvent quality



Dependance of osmotic pressure on polymer concentration and solvent quality



Question: How can we determine N and χ ?

Answer: plot $\frac{\Pi v_s}{c_p RT}$ versus c_p !

$$\frac{\Pi v_s}{c_p RT} = \left[\frac{1}{N} + \left(\frac{1}{2} - \chi \right) c_p + \dots \right]$$

\Rightarrow axis intercept $= \frac{1}{N}$

\Rightarrow slope $= \frac{1}{2} - \chi = 2\text{nd virial coefficient } A_2$

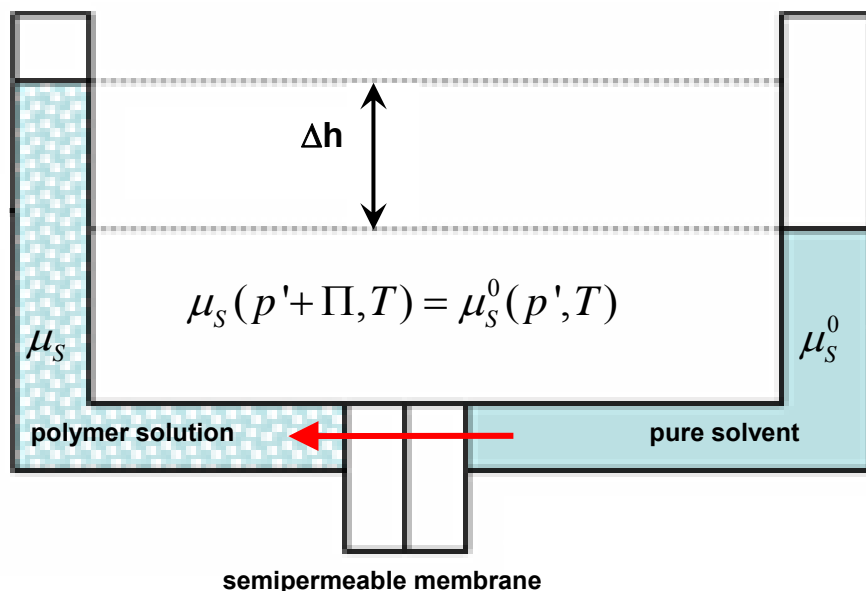
Question: How can we measure Π ?

Answer: Membrane osmometry

The membrane is impermeable for the polymer. Solvent permeates through the membrane until the chemical potential of the solvent is the same in both chambers. The excess column is a measure of the hydrostatic pressure which is in equilibrium equal to the osmotic pressure.

$$\rho_s g \Delta h = \Pi = RT \left[\frac{1}{N} \frac{1}{v_s} c_p + \left(\frac{1}{2} - \chi \right) c_p^2 + \dots \right]$$

with ρ_s = solvent density; g = acceleration of gravity; Δh = excess column height;
 v_s = molar volume solvent



Question: What kind of molecular weight average is measured by membrane osmometry?
 [see “Physical chemistry of polymer solutions”, Kamide & Dobast]

$$-\Pi v_s = RT \left\{ \ln c_s + \left(1 - \frac{1}{N}\right) c_p + \chi c_p^2 \right\}$$

for very (!) dilute solutions: $\Pi v_s = -RT \ln c_s = -RT \ln(1 - \sum_i c_{p,i})$

$$\text{with } \sum_i c_{p,i} = \frac{\sum_i n_{p,i}}{n_s + \sum_i n_{p,i}} \approx \frac{\sum_i n_{p,i}}{n_s}$$

$$\text{with (*)} \Rightarrow \Pi = -\frac{RT}{v_s} \ln \left(1 - \frac{\sum_i n_{p,i}}{n_s} \right) \stackrel{(\times)}{\approx} RT \frac{\sum_i n_{p,i}}{v_s n_s}$$

$$\text{total concentration of solute } v = v_s n_s + \sum_i n_{p,i} \stackrel{(\times)}{\approx} v_s n_s$$

$$c = \frac{\sum_i n_{p,i} M_i}{v} = \underbrace{\left(\frac{\sum_i n_{p,i} M_i}{\sum_i n_{p,i}} \right)}_{=\bar{M}_n} \left(\frac{\sum_i n_{p,i}}{v} \right) = \bar{M}_n \frac{\sum_i n_{p,i}}{v_s n_s} \quad \text{notice: concentration in } \frac{\text{weight}}{\text{volume}}$$

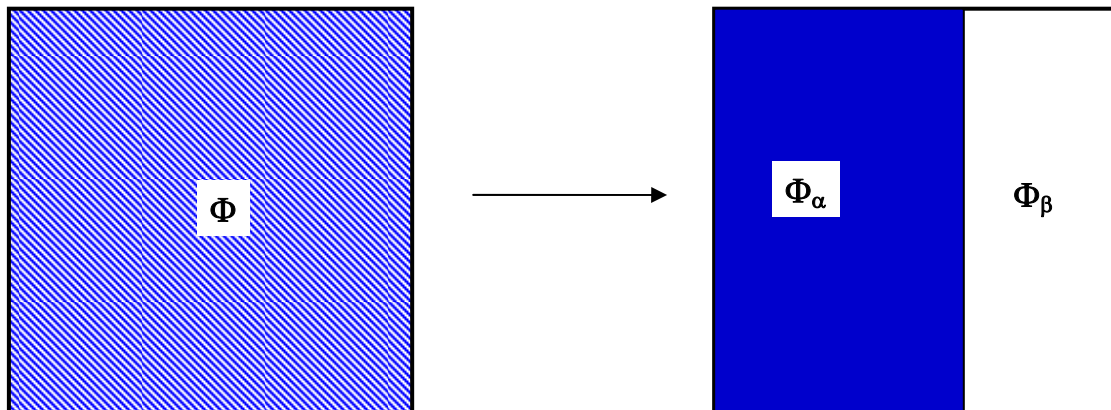
$$\text{with } (\times) \Rightarrow \sum_i n_{p,i} \ll n_s : \ln \left(1 - \frac{\sum_i n_{p,i}}{n_s} \right) \approx -\frac{\sum_i n_{p,i}}{n_s}$$

$$\Rightarrow \Pi = RT \frac{c}{\bar{M}_n}$$

\Rightarrow **Answer:** Membrane osmometry determines the number averaged molecular weight! (in very dilute solutions)

Phase diagrams for polymer solutions and –mixtures

Phase diagrams (the basics)

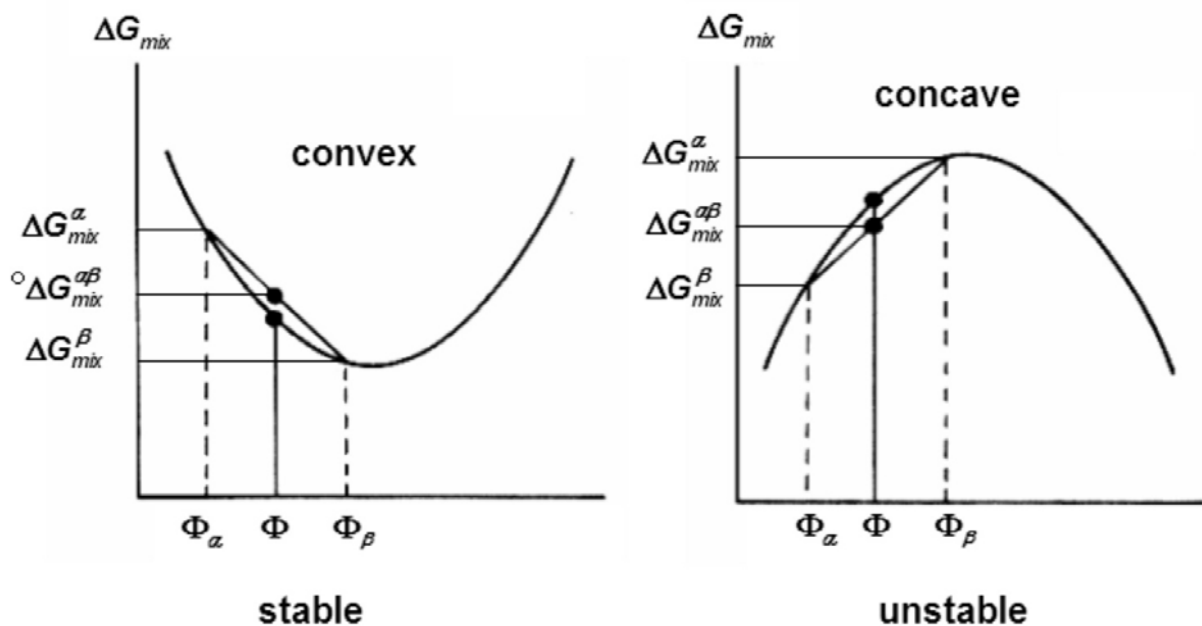


Assume a mixture with composition Φ separates into two phases with composition Φ_α and Φ_β with volume fractions α and β , respectively. $\Phi = \alpha \Phi_\alpha + \beta \Phi_\beta$ with $\alpha + \beta = 1$

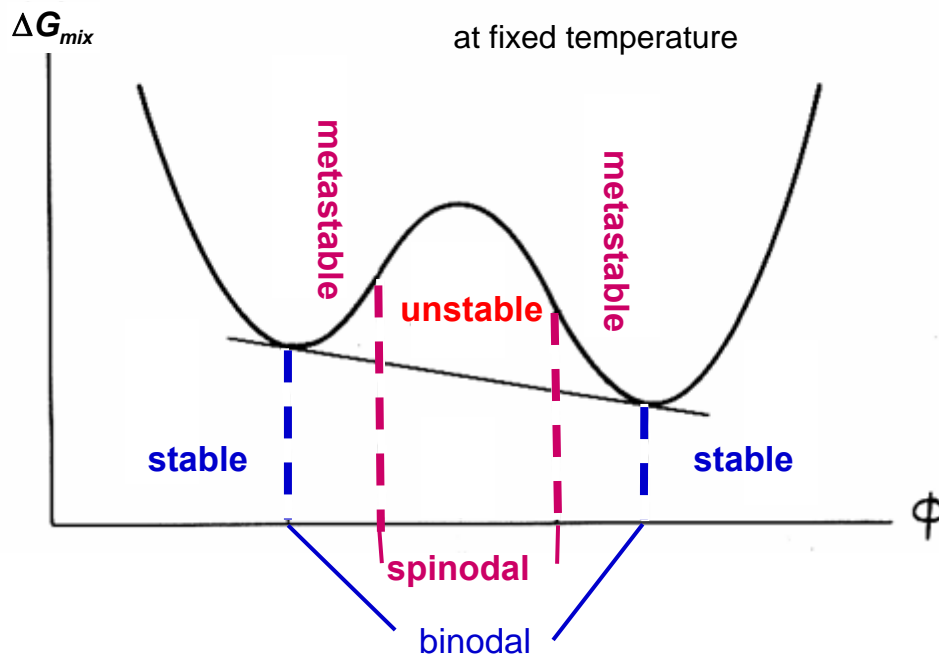
The original phase is stable, if

$$\Delta G_{mix} \leq \alpha \Delta G_{mix}(\Phi_\alpha) + (1 - \alpha) \Delta G_{mix}(\Phi_\beta) = \Delta G_{mix}^{\alpha\beta} \quad \text{Gibbs stability criterion}$$

free enthalpy of mixing as a function of volume fraction of one component



more complex situation: convex and concave curve regions
stable, metastable and unstable regions



- (1) The binodal defines the boundary between the one-and two-phase region and can be determined by tangent construction

$$\left(\frac{\partial \Delta G_{mix}}{\partial \Phi} \right)_{T,p} = 0 \quad (\text{minima})$$

- (2) The spinodal defines the boundary between the metastable and unstable region and can be determined from the points of inflection

$$\left(\frac{\partial^2 \Delta G_{mix}}{\partial \Phi^2} \right)_{T,p} = 0$$

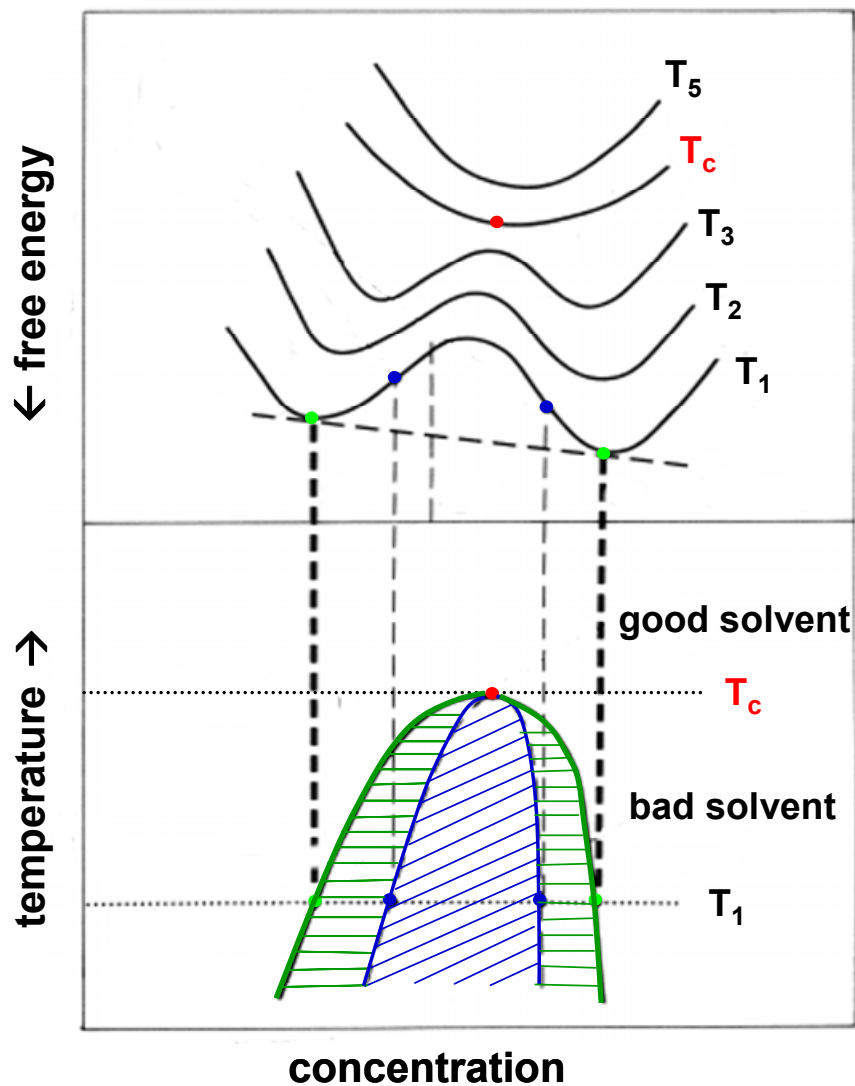
unstable: small fluctuations in concentration lead to spontaneous demixing

metastable: system is stable in respect to small fluctuations; only if a sufficient large nucleus with equilibrium composition is formed it growth in size. The nucleus has to be large enough because of the surface tension between the two phases.
keyword: separation by nucleation

- (3) There is a temperature T_c and a composition Φ_c where spinodal and binodal merge called critical point

$$\left(\frac{\partial^3 \Delta G_{mix}}{\partial \Phi^3} \right)_{T,p} = 0 \quad (\text{extremum of the spinodal curve})$$

Construction of a phase diagram



- (1) Determination of the free enthalpy as a function of Φ at various temperatures
- (2) Determination of stable and unstable regions and projection into the (T, Φ) space

Flory $\Delta G_{mix}^M = RT \left\{ \frac{\Phi_1}{N_1} \ln \Phi_1 + \frac{\Phi_2}{N_2} \ln \Phi_2 + \chi_{12} \Phi_1 \Phi_2 \right\} < 0$ as condition for miscibility

$$\chi_{12} \propto \frac{1}{T}$$

\Rightarrow In Flory-theory always lower miscibility gap and upper critical point (miscibility at high temperatures)

Polymer solution

$$N_1=N; N_2=1; \Phi_1 = \Phi; \Phi_2 = (1-\Phi)$$

$$(1) \text{ binodal: } \frac{\partial}{\partial \Phi} \frac{\Delta G_{mix}^M}{RT} = \frac{1}{N} \ln \Phi + \frac{1}{N} - \ln(1-\Phi) - 1 + (1-2\Phi)\chi = 0$$

$$(2) \text{ spinodal: } \frac{\partial^2}{\partial \Phi^2} \frac{\Delta G_{mix}^M}{RT} = \frac{1}{N\Phi} + \frac{1}{(1-\Phi)} - 2\chi = 0$$

$$(3) \text{ critical point: } \frac{\partial^3}{\partial \Phi^3} \frac{\Delta G_{mix}^M}{RT} = -\frac{1}{N\Phi_c^2} + \frac{1}{(1-\Phi_c)^2} = 0$$

$$\Rightarrow \Phi_c = \frac{1}{\sqrt{N+1}} \approx N^{-\frac{1}{2}} \quad \text{for large } N \gg 1$$

insertion of Φ_c into (2):

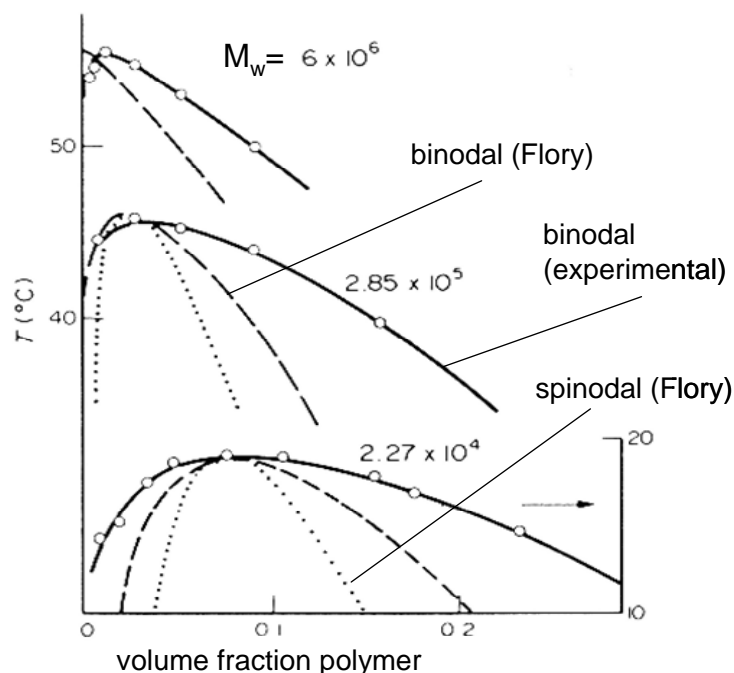
$$\frac{\partial^2}{\partial \Phi^2} \frac{\Delta G_{mix}^M}{RT}(\Phi_c) = 0 \Rightarrow \frac{1}{N\Phi_c} + \frac{1}{(1-\Phi_c)} - 2\chi_c = 0$$

$$\Rightarrow \chi_c = \frac{1}{2} \left(\frac{1}{\sqrt{N}} + 1 \right)^2 = \frac{1}{2} \left(\frac{1}{N} + 2 \frac{1}{\sqrt{N}} + 1 \right) = \frac{1}{2} + N^{-\frac{1}{2}} + \frac{1}{2} N^{-1} \propto T_c^{-1}$$

\Rightarrow Asymmetric miscibility gap which shifts to very small polymer contents for high molecular weight polymers.

$\Rightarrow T_c$ increases with molecular weight of polymer

Binodal experimentally determined from precipitation temperature



- No good description of experimental data!
- The dependence of χ on Φ has to be taken into account; also bad description of T dependence!

Polymer mixtures

$$\Phi_1 = \Phi ; \Phi_2 = (1 - \Phi)$$

$$\Delta G_{mix}^M = RT \left\{ \frac{\Phi_1}{N_1} \ln \Phi_1 + \frac{\Phi_2}{N_2} \ln \Phi_2 + \chi_{12} \Phi_1 \Phi_2 \right\} < 0 \quad \text{as condition for miscibility}$$

$$(1) \quad \text{binodal: } \frac{\partial}{\partial \Phi} \frac{\Delta G_{mix}^M}{RT} = \frac{1}{N_1} \ln \Phi + \frac{1}{N_1} - \frac{\ln(1-\Phi)-1}{N_2} + (1-2\Phi)\chi = 0$$

$$(2) \quad \text{spinodal: } \frac{\partial^2}{\partial \Phi^2} \frac{\Delta G_{mix}^M}{RT} = \frac{1}{N_1 \Phi} + \frac{1}{N_2(1-\Phi)} - 2\chi = 0$$

$$(3) \quad \text{critical point: } \frac{\partial^3}{\partial \Phi^3} \frac{\Delta G_{mix}^M}{RT} = -\frac{1}{N_1 \Phi_c^2} + \frac{1}{N_2(1-\Phi_c)^2} = 0 \Rightarrow \Phi_c = \frac{1}{\sqrt{N_1/N_2} + 1}$$

$$\text{with (2)} \Rightarrow \chi_c = \frac{1}{2} \left(\frac{1}{\sqrt{N_1}} + \frac{1}{\sqrt{N_2}} \right)^2 \propto T_c^{-1}$$

$\Rightarrow T_c$ increases with increasing N_1 or N_2

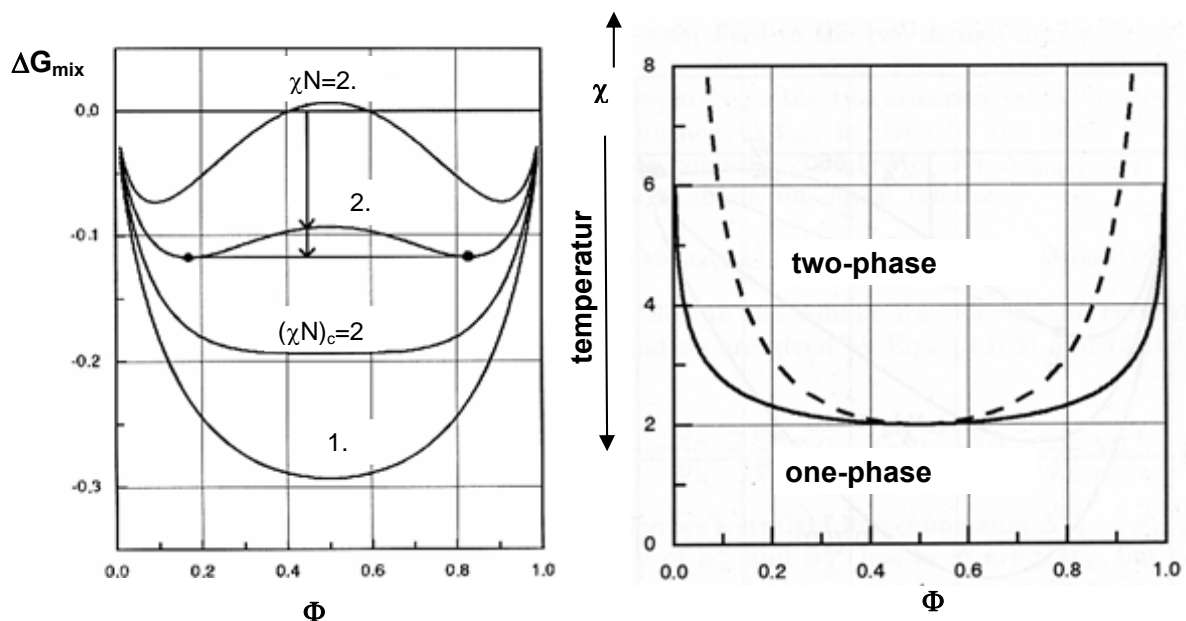
$\Rightarrow N_1 \ll N_2$ or $N_2 \ll N_1 \Rightarrow \Phi_c$ shifts towards very low concentrations of the longer component.

Special case: Polymer with the same degree of polymerization: $N_1 = N_2 = N$

$$\Rightarrow \Phi_c = 1/2 \quad \text{and} \quad \chi_c = 2/N \propto T_c^{-1} \quad \Rightarrow \quad \begin{array}{ll} (\chi_c N) = 2 & \text{critical point} \\ (\chi_c N) < 2 & \text{one-phase region} \\ (\chi_c N) > 2 & \text{two-phase region} \end{array}$$

\Rightarrow Phase diagram is symmetrical at Φ_c for polymer mixtures with identical degree of Polymerization

Mixture of symmetric polymers



In summary

- Connectivity of polymers \Rightarrow degree of possible disorder is limited \Rightarrow entropy of mixing is reduced by prefactor $1/N$ \Rightarrow monomer-monomer interaction determines mixing behavior.
- As higher the molecular weight as higher the critical temperature; weak repulsive interaction between the monomers leads to demixing.
- Miscibility of polymers as significantly reduced compared to low molecular weight substances.
- Attractive interaction, such as dipole-dipole interaction / hydrogen bonds / donor acceptor interaction, is necessary.

Flory-Huggins theory yields bad description of experimental data

The simple lattice model does not describe the behavior of dilute polymer solutions very well

- (1) Approach is based on mean-field-theory, i.e. lattice site occupation is uniform and every molecule/ monomer sees the same averaged surrounding. It was assumed that the monomer/ molecule distribution on the lattice is purely statistically.
 \Rightarrow only true if $\Delta w_{12} = 0$
 \Rightarrow fluctuations in particular relevant in dilute solutions are neglected
- (2) Volume changes due to mixing having an impact on the mobility/ flexibility (\Rightarrow entropy) are neglected.
 $\Rightarrow \chi$ is concentration dependent!
- (3) Interaction is assumed to be between nearest neighbors only. Any specific interaction (longer ranged, inducing order or specific interaction involving only some specific groups) between component A and B like: dipole-dipole interaction, hydrogen bonding, donor-acceptor interaction, solvent orientation in polar solvent close to the chain.

Ansatz: χ parameter comprises on enthalpic χ_H and entropic χ_S contribution

$$\chi = \chi_S + \chi_H = A + \frac{B}{k_B T}$$

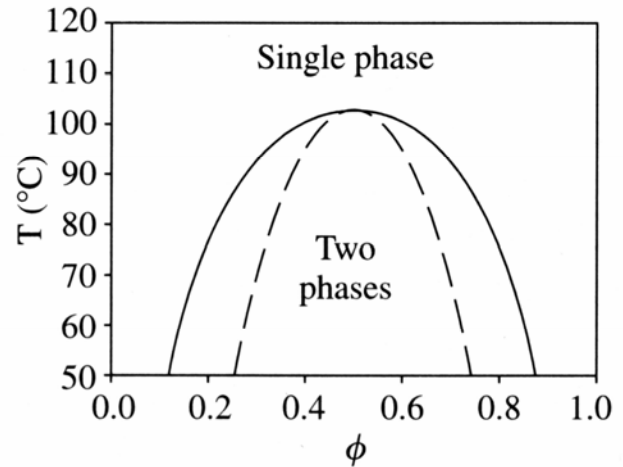
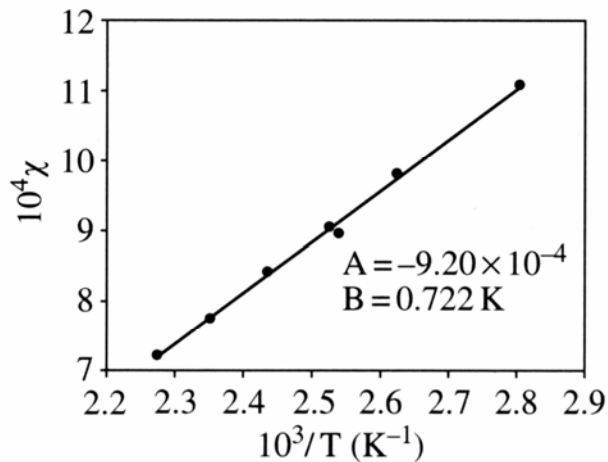
$$\text{with } \chi_H = -T \left(\frac{d\chi}{dT} \right) = \frac{B}{k_B T} \quad \text{and} \quad \chi_S = \frac{d(\chi T)}{dT} = A = -\frac{\Delta S}{k_B}$$

from experiments \Rightarrow major contribution from non-combinatorial change in entropy: χ_S

UCST = upper critical solution temperature

χ decreases with increasing temperature

e.g. polybutadiene (88% vinyl, protonated; 78% vinyl, deuterated)



mixing leads to increase in volume;

volume for local movements of the chains is larger \Rightarrow increase in mobility/flexibility

\Rightarrow increase in entropy.

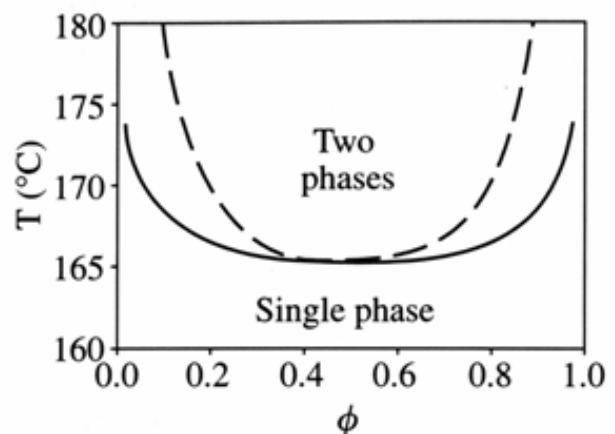
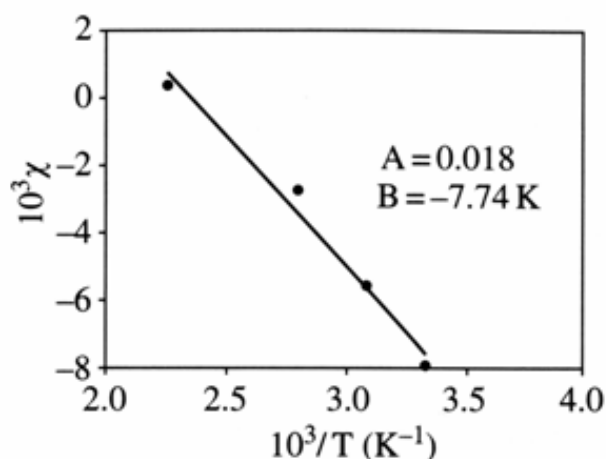
\Rightarrow effect more dominant with increasing temperature

$\Rightarrow \chi_s$ is negative and decreases with T , i.e. increases with $1/T$

LCST = lower critical solution temperature

χ increases with increasing temperature

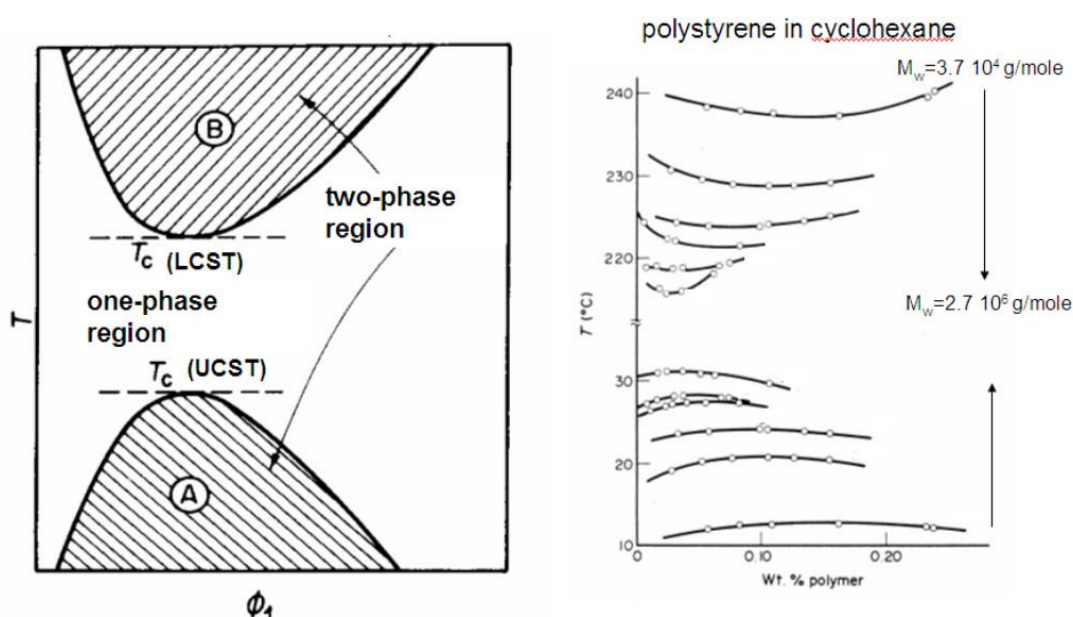
e.g. polyisobutylene (protonated); head-to-head polypropylene (deuterated)



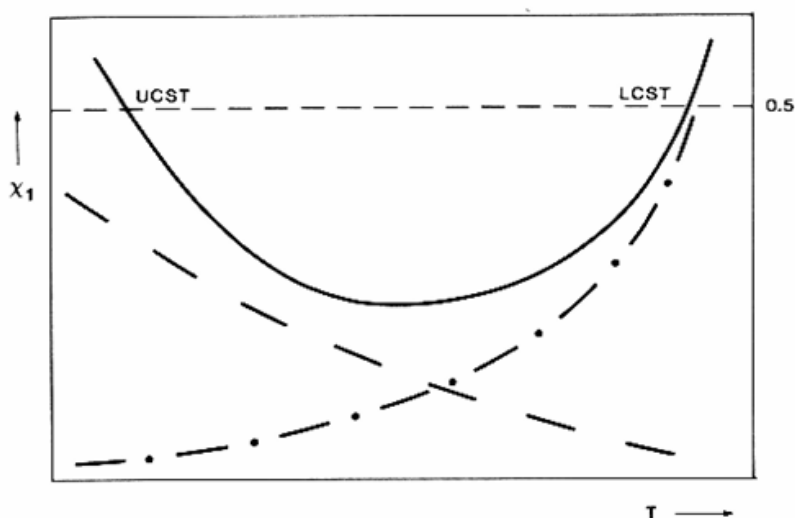
Mechanism:

- (1) Mixing leads to reduction in volume; volume for local movements of the chains is reduced
 \Rightarrow reduction in mobility/ flexibility \Rightarrow reduction in entropy.
 Effect becomes more dominant with increasing temperature \Rightarrow
 χ_s is positive and increases with temperature/ decreases with $1/T$
- (2) Competition between attractive interaction of “special” groups of both components and repulsive interaction between remaining groups (e.g. copolymers). Attractive interaction: dipole-dipole interaction; hydrogen bonds; donor acceptor interaction
 Increasing temperature weakens bonds and repulsive interaction dominates
 \Rightarrow both LCST and UCST

Phase diagram with lower and upper miscibility gap



Flory-Huggins parameter as a function of temperature



4.4 Flory-Krigbaum Theory

On the foundation of the excluded volume interactions an enthalpy parameter H and an entropy parameter Ψ for dilution are defined describing deviations from ideal behaviour.

Flory-Huggins:
$$\Delta G^d = \frac{\partial \Delta G_{mix}^M}{\partial n_s} = \Delta \mu_s^M = RT \left[\ln c_s + \left(1 - \frac{1}{N}\right) c_p + \chi c_p^2 \right]$$

with $c_p \ll 1 \Rightarrow \ln c_s = \ln(1 - c_p) \approx -c_p - \frac{1}{2} c_p^2 + \dots$ as for osmotic pressure

$$\Rightarrow \Delta G^d = \Delta \mu_s^M = -RT \left[\frac{c_p}{N} + \underbrace{\left(\frac{1}{2} - \chi \right) c_p^2}_{\text{deviations from ideal behavior}} + \dots \right]$$

Flory-Krigbaum: dilution enthalpy: $\Delta H_{ni}^d = RTHc_p^2$
 dilution entropy: $\Delta S_{ni}^d = R\Psi c_p^2$ (c_p^2 due to pair contacts)

\Rightarrow free enthalpy of dilution: $\Delta G_{ni}^d = RT(H - \Psi)c_p^2$

\Rightarrow comparison Flory-Huggins and Flory-Krigbaum theory: $-(H - \Psi) = \left(\frac{1}{2} - \chi \right)$

θ conditions: $\chi = \frac{1}{2} \Leftrightarrow H = \Psi$; i.e. $\Delta H_{ni}^d = T\Delta S_{ni}^d$

define: $\theta = T \frac{H}{\Psi}$ (only defined if H and Ψ have equal sign)

non-ideal behavior disappears for $T = \theta$!

replace $\frac{1}{2} - \chi = \Psi \left(1 - \frac{\theta}{T}\right) = 2^{\text{nd}}$ virial coefficient A_2 !

$$\Rightarrow \Delta G^d = \Delta \mu_s^M = -RT \left[\frac{c_p}{N} + \Psi \left(1 - \frac{\theta}{T}\right) c_p^2 + \dots \right]$$

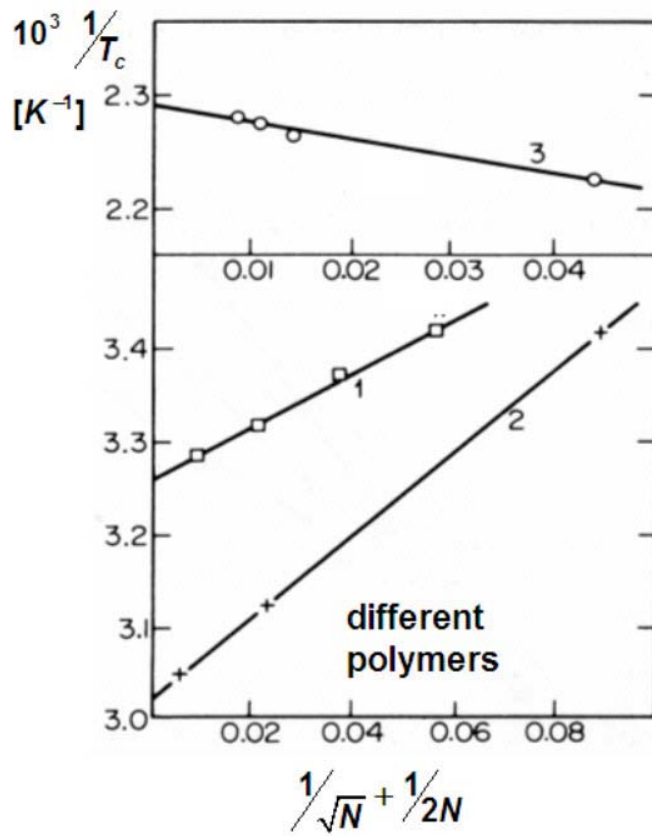
Determination of the θ temperature in polymer solutions

(A) From the determination of the critical phase separation temperature T_c as a function of the degree of polymerization

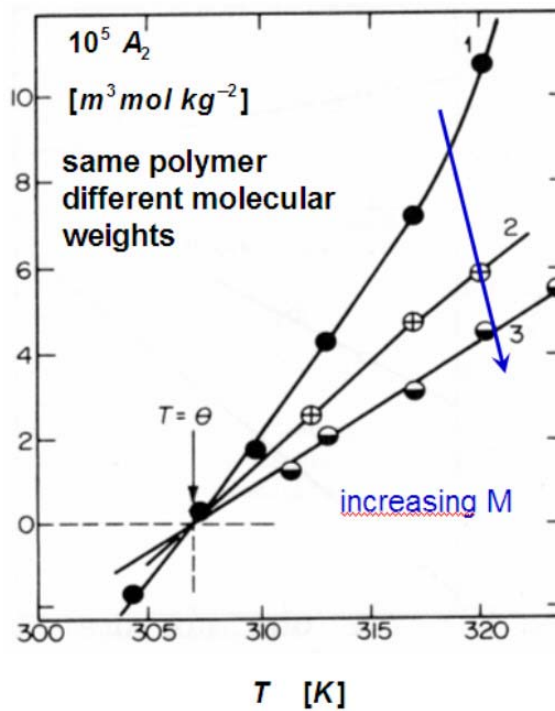
$$\frac{1}{2} - \chi_c = \Psi \left(1 - \frac{\theta}{T_c}\right) = N^{-1/2} - \frac{1}{2} N^{-1} \Rightarrow \frac{1}{T_c} = \frac{1}{\Psi \theta} \left(N^{-1/2} + \frac{1}{2} N^{-1} \right) + \frac{1}{\theta}$$

$\Rightarrow \theta$ can be determined from axis intersection $N \rightarrow \infty$ and $N^{-1/2} + \frac{1}{2} N^{-1} \rightarrow 0$

$\Rightarrow \Psi$ from slope



(B) From A_2 measurement (osmotic pressure) as a function of the temperature $A_2 = \Psi \left(1 - \frac{\theta}{T} \right)$
 intersection with T axis ($A_2=0$) $\Rightarrow T = \theta$

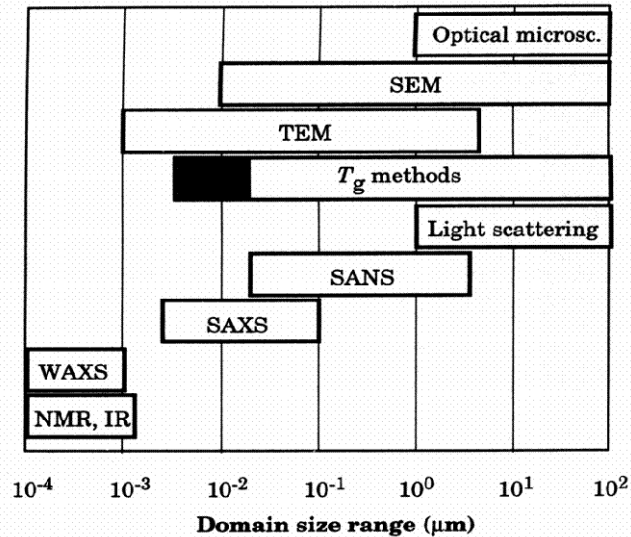


4.5 Phase separation mechanisms

Separation process

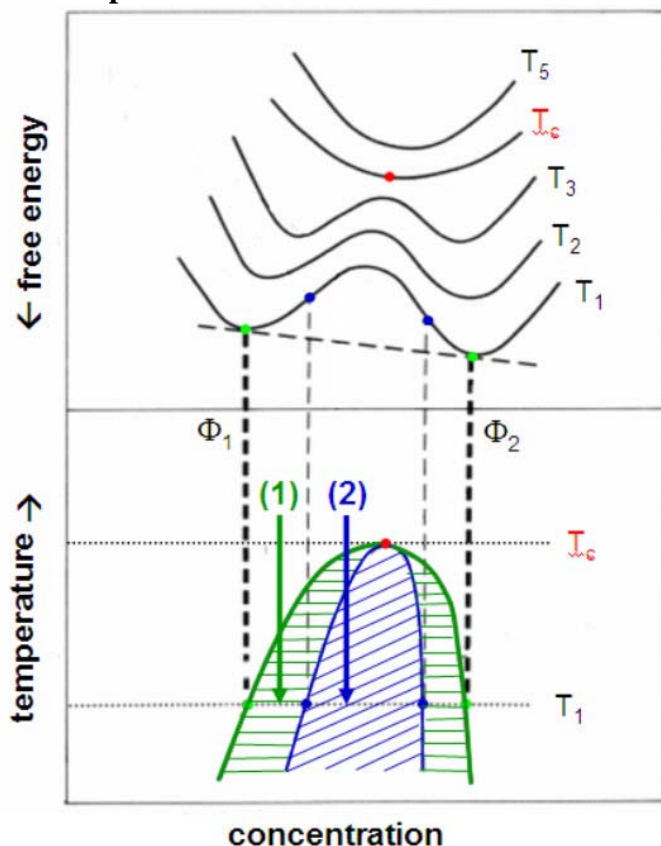
time resolution possible due to high viscosity of polymer or by quenching to temperatures below glass transition temperature

Methods for the determination of the cloud point



Depending on method of investigation different length scales can be resolved.

Phase separation mechanisms



cooling from one-phase region into:

(1) binodal (metastable region)

segregation by nucleation

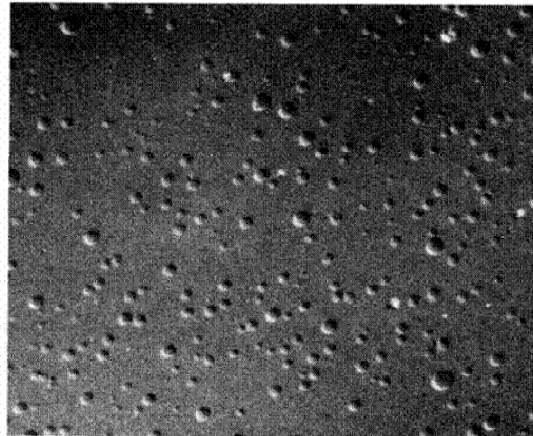
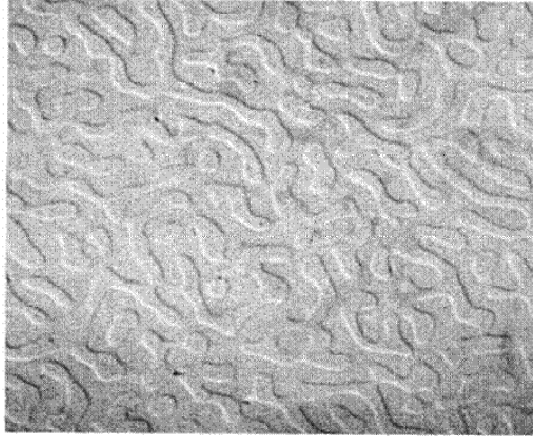
(2) spinodal (unstable region)

spinodal segregation



Cooling from one-phase region into two-phase region

Resulting structure depends strongly whether cooling down ends in metastable or unstable region. In unstable region any small concentration fluctuation can grow. In metastable region the concentration fluctuation has to be large enough in respect to concentration difference $\Delta\Phi$ and size R



spinodal segregation

segregation by nucleation

PS/PBr₂S

$\Phi(\text{PS})=0.8$

$\Phi(\text{PS})=0.5$

- (1) spinodal decomposition results in interpenetrating, continuous structure with specific length scale.
- (2) binodal decomposition by nucleation, spherical precipitates growing in time.

Spontaneous local concentration fluctuation

$\delta\Phi$ in volume d^3r and $-\delta\Phi$ in adjacent volume d^3r

\Rightarrow change of free enthalpy in terms of free enthalpy g per unit volume

$$\delta G = \frac{1}{2} [g(\Phi_0 + \delta\Phi) + g(\Phi_0 - \delta\Phi)] d^3r - g(\Phi_0) d^3r$$

series expansion of g up to second order in Φ yields

$$\delta G = \frac{1}{2} \frac{\partial^2 g}{\partial \Phi^2}(\Phi_0) \delta\Phi^2 d^3r = \frac{1}{2} \frac{1}{v} \frac{\partial^2 \Delta G_{mix}}{\partial \Phi^2}(\Phi_0) \delta\Phi^2 d^3r$$

\Rightarrow depending on the sign of the curvature $\frac{\partial^2 \Delta G_{mix}}{\partial \Phi^2}$ a small fluctuation in concentration leads to an increase or decrease of the free enthalpy (Gibbs stability criterion)

- (1) $\left(\frac{\partial^2 \Delta G_{mix}}{\partial \Phi^2}\right) > 0$ (convex) $\delta G > 0$ phase is stable against small perturbation;
amplitude of small perturbation decays
- (2) $\left(\frac{\partial^2 \Delta G_{mix}}{\partial \Phi^2}\right) < 0$ (concave) $\delta G < 0$ phase is unstable against small perturbation;
amplitude of small perturbation growth

Separation by nucleation

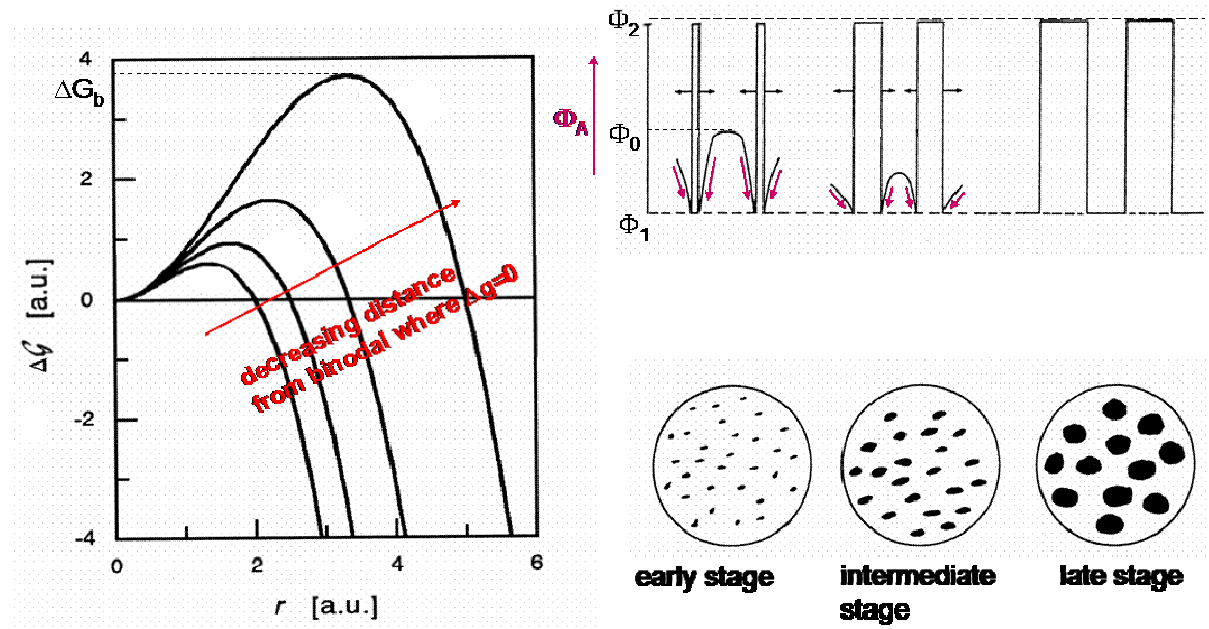
- a small concentration fluctuation decays.
- concentration difference of the nucleus must correspond to that of the equilibrium phases.
- nucleus must have critical size.

free enthalpy for nucleation: $\Delta G(r) = \underbrace{-\frac{4\pi}{3} r^3 \Delta g}_{\text{Term I}} + \underbrace{4\pi r^2 \sigma}_{\text{Term II}}$ with $\Delta g = g(\Phi_0) - g(\Phi_2)$ (*)

Term I: volume term corresponds to reduction in enthalpy by generation of the new phases.

Term II: surface term corresponds to increase in enthalpy due to surface generation with σ being the free enthalpy per unit surface.

segregation by nucleation



⇒ overcome energy barrier before nucleus can growth

⇒ nucleation rate increases with Arrhenius law: $\nu_{nucleus} \propto \exp\left(-\frac{\Delta G_b}{k_B T}\right)$

with the barrier height $\Delta G_b = \frac{16\pi}{3} \frac{\sigma^3}{(\Delta g)^2}$ which is the maximum of (*) $\Delta G(r)$

⇒ energy barrier ΔG_b increases with decreasing distance from the binodal (approaching from spinodal); at the binodal $\Delta g = 0 \Rightarrow \Delta G_b \rightarrow \infty$

⇒ mixture needs to be supercooled (or overheated) to achieve relevant nucleation rates.

In summary

- nucleus growth diffusion controlled; downhill-diffusion towards decreasing concentrations (chemical potential gradient supports feeding nucleus).
- decreasing temperature \Rightarrow diffusion slower (nucleus growth slower); nucleation rate increases (for lower miscibility gap) \Rightarrow number of nuclei increases
- droplet size, number and distance depend on time and temperature
- at later stages coalescence, coarsening and ripening until there are two large phases with composition Φ_1 and Φ_2

Spinodal Decomposition

- at spinodal $\frac{\partial^2 \Delta G_{mix}}{\partial \Phi^2} \rightarrow 0 \Rightarrow$ spontaneous demixing; no activation energy
- no sharp transition from phase separation by nucleation to spontaneous demixing since $\frac{\partial^2 \Delta G_{mix}}{\partial \Phi^2}$ vanishes continuously

Kinetics of spinodal decomposition in polymer mixtures

- local chemical potential difference caused by concentration fluctuations

$$\Delta\mu = \mu_s - \mu_s^0 = \underbrace{\frac{\partial \Delta G_{mix}}{\partial \Phi}}_{\text{Term I}} - \underbrace{2\kappa \nabla^2 \Phi}_{\text{Term II}}$$

Term I: homogenous system

Term II: gradient energy term associated with departure from uniformity

κ = gradient energy coefficient (empirical constant)

- difference in the chemical potentials causes interdiffusion flux. Linear response between flux and gradient in chemical potential:

$$-j = \Omega \nabla(\Delta\mu) = \Omega \left[\frac{\partial^2 \Delta G_{mix}}{\partial \Phi^2} \nabla \Phi - 2\kappa \nabla^3 \Phi \right]$$

with Ω = Onsager-type phenomenological coefficient

- substitution into equation of continuity which equates the net flux over a surface with the loss

or gain of material within the surface

$$\frac{\partial \Phi}{\partial t} = -\nabla \cdot j = \Omega \left[\frac{\partial^2 \Delta G_{mix}}{\partial \Phi^2} \nabla^2 \Phi - 2\kappa \nabla^4 \Phi \right]$$

Cahn-Hilliard relation

- comparison to conventional diffusion equation

$$\frac{\partial \Phi}{\partial t} = D \nabla^2 \Phi \quad (D = \text{diffusion coefficient})$$

$$\Rightarrow D \approx \Omega \frac{\partial^2 \Delta G_{mix}}{\partial \Phi^2} < 0 \quad \text{in unstable region}$$

diffusion against concentration gradient at spinodal ($T \rightarrow T_{sp}$) $D \rightarrow 0$ “critical slowing down”

general solution for Cahn-Hilliard relation:

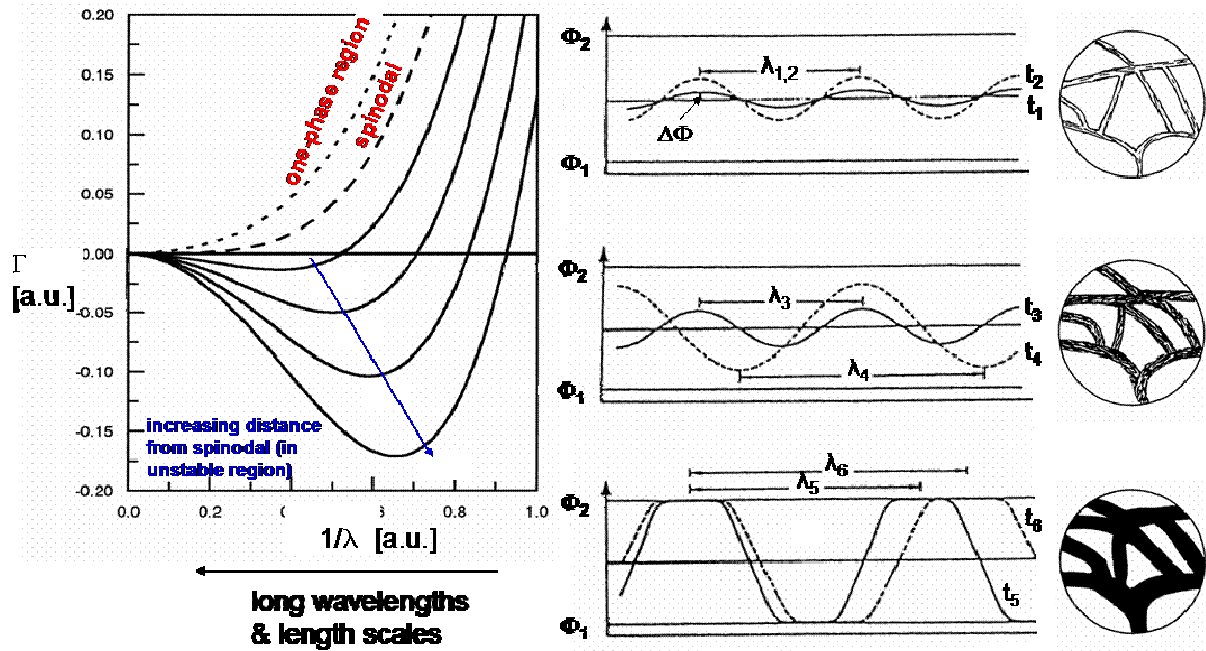
$$\Phi - \Phi_0 = \sum_{\beta} \exp(\Gamma(\beta) \cdot t) \cdot [A(\beta) \cos(\beta x) + B(\beta) \sin(\beta x)]$$

$$\text{with } \lambda = \frac{2\pi}{\beta} \quad \text{and} \quad \Gamma(\beta) = -\Omega \beta^2 \left[\frac{\partial^2 \Delta G_{mix}}{\partial \Phi^2} - \underbrace{2\kappa \beta^2}_{>0} \right]$$

stable region: $\frac{\partial^2 \Delta G_{mix}}{\partial \Phi^2} > 0 \Rightarrow \Gamma(\beta) < 0 \Rightarrow$ instabilities rapidly decay

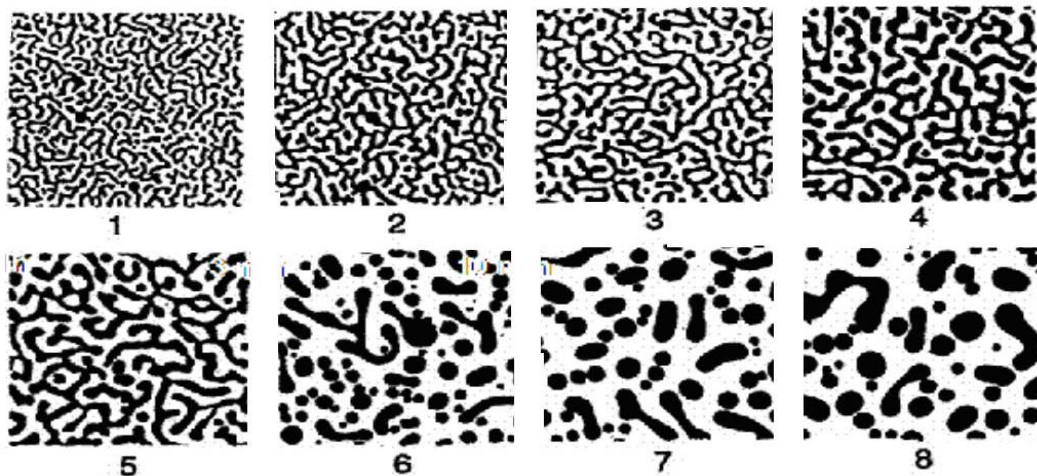
unstable region: $\frac{\partial^2 \Delta G_{mix}}{\partial \Phi^2} < 0 \Rightarrow \Gamma(\beta) > 0 \Rightarrow$ some wavelengths notably the long wavelengths (small β) will grow

Spinodal segregation



- (1) **early stages:** amplitudes of fluctuations growth for preferred wavelength $\lambda = (\text{length scale})^{-1}$; modes are independent.
- (2) **intermediate stages:** amplitudes growth, modes interact with each other; wavelength growth and structure coarsens; deviations from cosine wave form.
- (3) **late stages:** fluctuation reaches the upper and lower limit Φ_1 and Φ_2 of equilibrium coexistence curve; wave form becomes rectangular and domain structure appears. Domain boundaries have finite thickness but extension is small compared to domain size.

Late stages of spinodal segregation

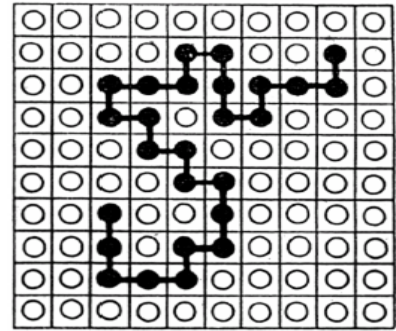


Finally: system tends to minimize its interfacial free energy by minimizing the amount of interface area. Sphere contains the most volume and the least surface area. \Rightarrow

- (1) interwoven structure coarsens by an interfacial-energy driven viscous flow mechanism
- (2) tendency to spherical precipitates

4.6 Summary

Miscibility of mixtures if $\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} < 0$



Flory-Huggins Theory (mean field theory)

considers a random distribution of polymer monomers & solvent molecules on a lattice

calculation of ΔH_{mix} in terms of pair interaction energies; every molecule or monomer sees the same average surrounding.

calculation of ΔS_{mix} number possible distributions of both component on the lattice under preservations of the connectivity of the polymer(s).

further assumptions:

- distribution on lattice without volume change; both components have same lattice volume: volume fractions = number fractions.
- number of lattice sites much larger than the degree of polymerization.
- large coordination number (nearest neighbors on lattice).

Flory-Huggins Theory

$$\Delta G_{mix}^M = RT \left[\frac{c_1}{N_1} \ln c_1 + \frac{c_2}{N_2} \ln c_2 + \chi_{12} c_1 c_2 \right]$$

$$\chi_{12} = \frac{z\Delta w_{12}}{RT} \propto T^{-1} \quad \text{with} \quad \Delta w_{12} = w_{12} - \frac{1}{2}(w_{11} + w_{22})$$

for polymers with high degree of polymerization the entropy gain due to mixing very is small (reduced by factor $1/N$)

for most substances endothermal mixing $\chi_{12} > 0$

⇒ small enthalpic contribution leads to demixing!

in Flory-Huggins theory $\chi_{12} \propto T^{-1}$

⇒ mixing at high temperatures & demixing at low temperatures

Osmotic pressure

is the pressure produced by a solution in a space that is enclosed by a semi-permeable membrane. $\Pi =$ pressure polymer solution – pressure pure solvent

$$\Pi V_s = RT \left[\frac{c_p}{N} + \left(\frac{1}{2} - \chi \right) c_p^2 + \dots \right]$$

$\chi < \frac{1}{2}$ good solvent - high temperatures - polymer swells

$\chi > \frac{1}{2}$ bad solvent - low temperatures - polymer shrinks

$\chi = \frac{1}{2}$ θ solvent

Membrane osmometry (measures excess column height)

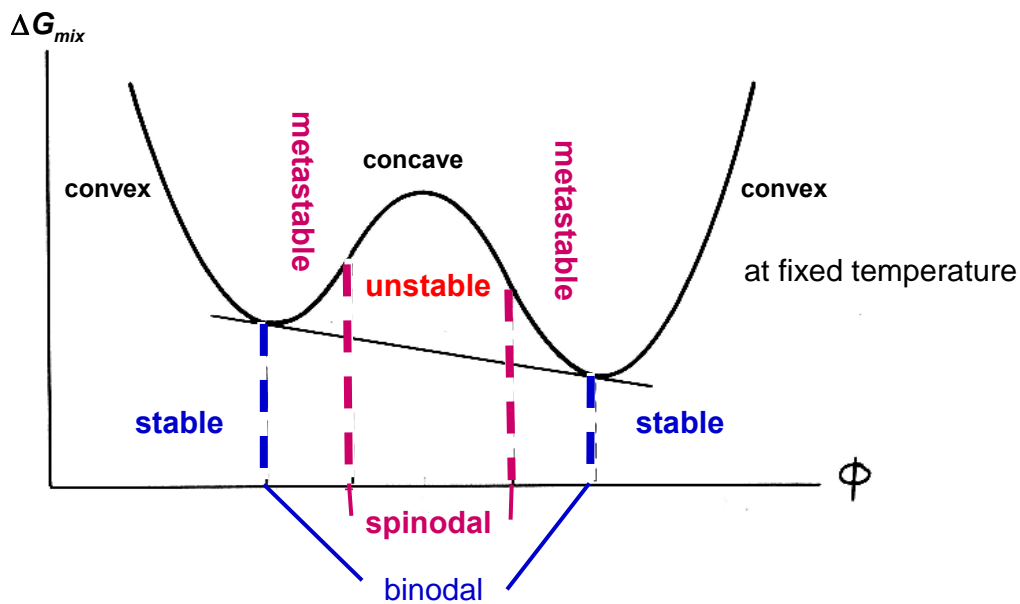
hydrostatic pressure = osmotic pressure
dilute solutions:

$$\frac{\Pi V_s}{RT c_p} = \left[\frac{1}{N} + \left(\frac{1}{2} - \chi \right) c_p + \dots \right]$$

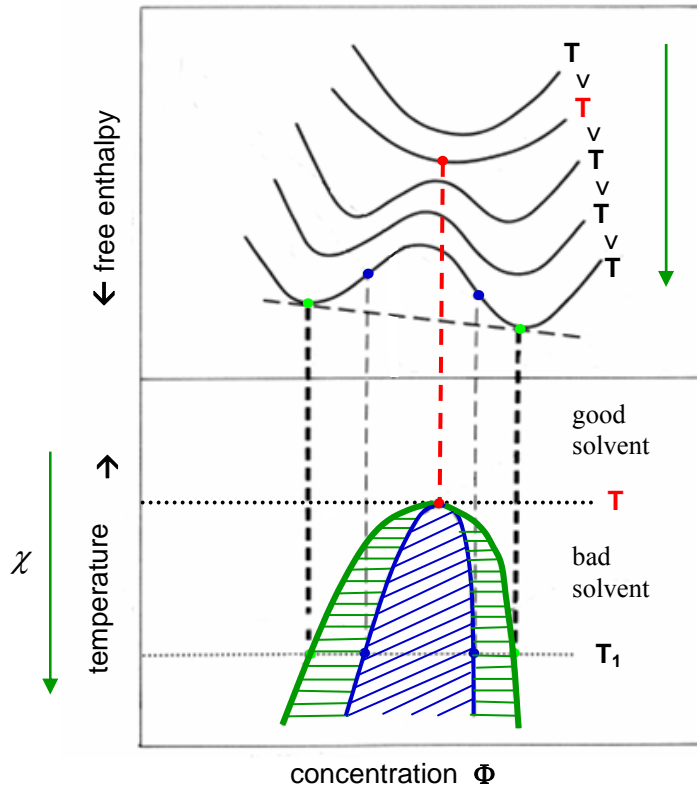
in very dilute solution: the number averaged molecular weight is measured

Phase diagrams

Gibbs stability criterion: $\Delta G_{\text{mix}} \leq \alpha \Delta G_{\text{mix}}(\Phi_\alpha) + (1 - \alpha) \Delta G_{\text{mix}}(\Phi_\beta) = \Delta G_{\text{mix}}^{\alpha\beta}$



Construction of phase diagrams



binodal (metastable region)

$$\left(\frac{\partial \Delta G_{mix}}{\partial \Phi} \right)_{T,p} = 0$$

spinodal (unstable region)

$$\left(\frac{\partial^2 \Delta G_{mix}}{\partial \Phi^2} \right)_{T,p} = 0$$

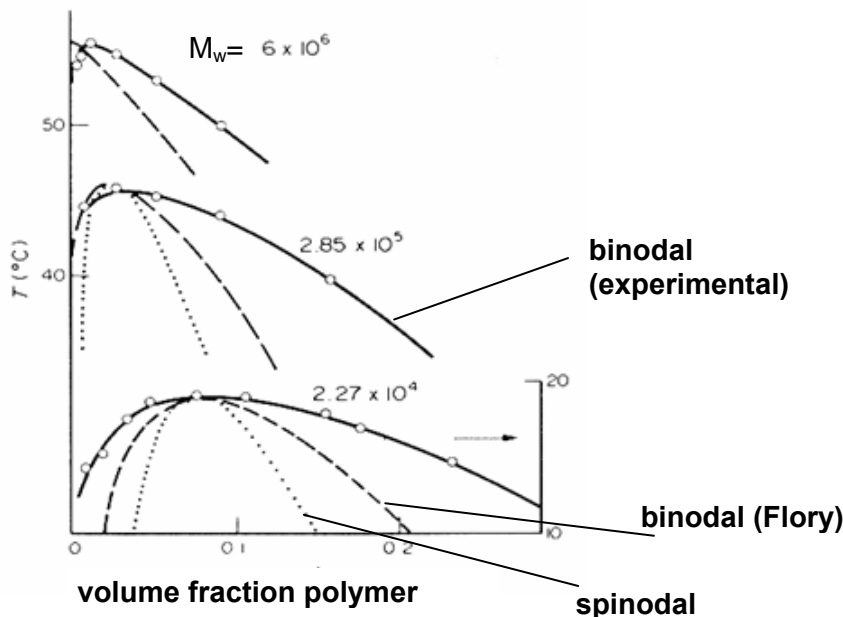
critical point

$$\left(\frac{\partial^3 \Delta G_{mix}}{\partial \Phi^3} \right)_{T,p} = 0$$

binodal and spinodal merge; determined by (T_c, Φ_c)

Flory-Huggins Theory : $\chi \propto \frac{1}{T}$ always lower miscibility gap & upper critical point

Polymer solution



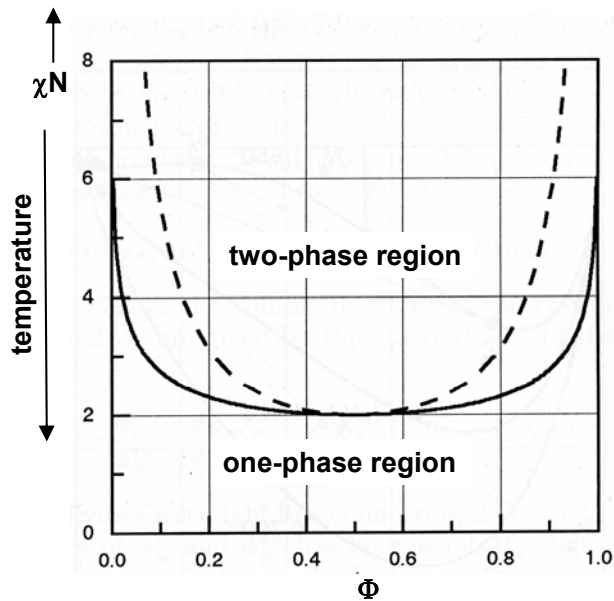
$$\Phi_c = \frac{1}{\sqrt{N+1}} \approx N^{-1/2}$$

$$\chi_c = \frac{1}{2} + N^{-1/2} + \frac{1}{2} N^{-1} \propto T_c^{-1}$$

miscibility gap is highly asymmetric, shifts to very small polymer concentrations for high N

T_c increases with N

Polymer mixtures



$$\Phi_c = \frac{1}{\sqrt{N_1/N_2 + 1}}$$

$$\chi_c = \frac{1}{2} (N_1^{-1/2} + N_2^{-1/2})^2 \propto T_c^{-1}$$

- for $N_1 \ll N_2$ or $N_2 \ll N_1$: Φ_c shifts towards very concentrations of the shorter component.
- T_c increases with N_1 or N_2
- miscibility gap is symmetric at critical point for $N_1 = N_2$

$$\Phi_c = 1/2$$

$$\chi_c = 2/N \propto T_c^{-1}$$

Limitation of the Flory theory

Mean field approach but distribution of the monomers + molecules on the lattice is not purely statistically due to non-equal interaction between identical and non-identical components: χ becomes concentration dependent. Concentration fluctuations are also neglected.

Main lack of the Flory Huggins theory originates from an additional non-combinatorial entropical contribution to the enthalpy of mixing resulting from volume changes due to mixing.

Ansatz: $\chi = \chi_S + \chi_H = A(T) + B/(k_B T)$

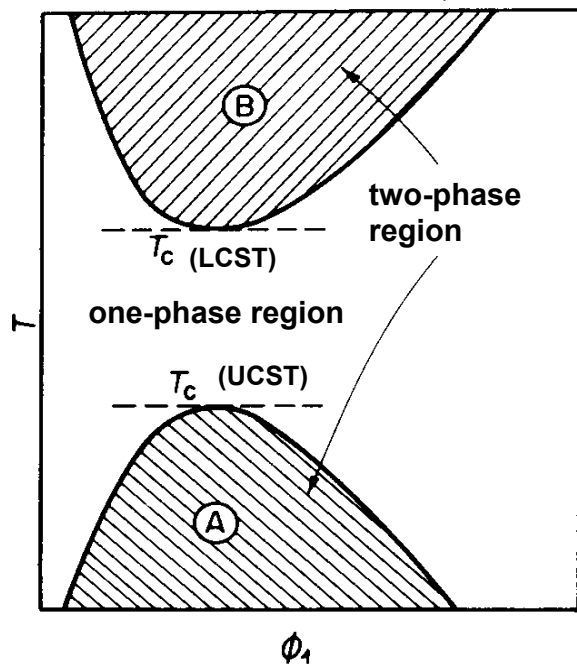
- (1) mixing leads to increase in volume - gain of entropy due to higher chain mobility - χ_S is negative and decreases with temperature \Rightarrow UCST- Lower miscibility gap
- (2) mixing leads to decrease in volume - loss of entropy due to higher chain mobility - χ_S is positive and increases with temperature \Rightarrow LCST- Upper miscibility gap

Combinations of enthalpic contribution and (2) to χ can lead to both UCST + LCST

also in combination with:

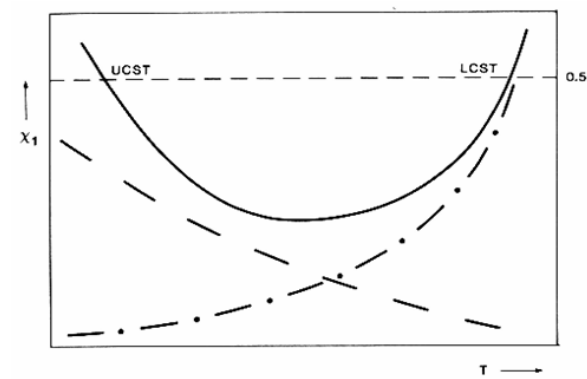
- (3) competition of attractive bonds of certain groups on the polymer and repulsive interaction between remaining groups. Weakening of the attractive bonds with increasing temperature \Rightarrow repulsive interaction dominates.

Phase diagram with lower and upper miscibility gap



Flory-Huggins enthalpy of mixing:

$$\Delta G_{mix}^M = RT \left[\frac{c_1}{N_1} \ln c_1 + \frac{c_2}{N_2} \ln c_2 + \chi_{12} c_1 c_2 \right] < 0$$



Flory Krigbaum theory

introduces an enthalpy κ and an entropy ψ parameter for dilution describing deviations from ideal behavior due to excluded volume interaction,

introduction of the **θ temperature**: $\theta = T \kappa / \psi$

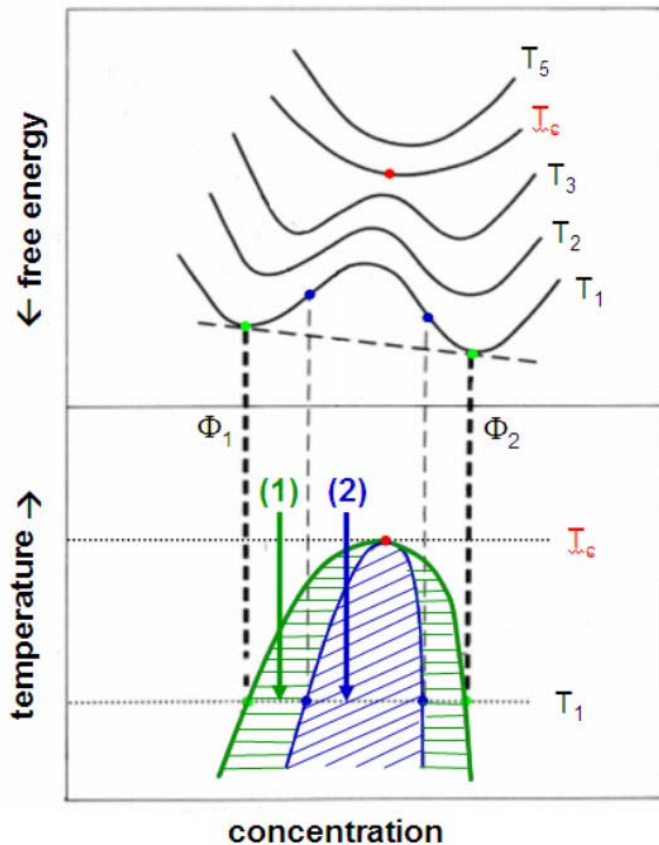
$$\frac{\partial \Delta G_{mix}^M}{\partial n_s} = \Delta \mu_s^M = -RT (\Psi - \kappa) c_p^2 = -\Psi \left(1 - \frac{\theta}{T} \right) c_p^2$$

2nd virial coefficient $A_2 \sim (1/2 - \chi) = \psi(1 - \theta/T)$

- θ temperature can be determined from A_2 measurements
- θ temperature and entropy parameter ψ can be determined from molecular weight

dependency on T_c

Phase separation mechanisms



cooling from one-phase region into:

(1) binodal (metastable region)

segregation by nucleation

results in spherical precipitates growing with time.

(2) spinodal (unstable region)

spinodal segregation

results in interpenetrating, continuous structure with specific length scale.

Separation by nucleation

- a small concentration fluctuation decays.
- concentration difference of the nucleus must correspond to that of the equilibrium phases. and nucleus must have critical size.
- nucleus growth diffusion controlled; downhill-diffusion towards decreasing concentrations (chemical potential gradient supports feeding nucleus).
- decreasing temperature \Rightarrow diffusion slower (nucleus growth slower); nucleation rate increases (for lower miscibility gap) \Rightarrow number of nuclei increases
- droplet size, number and distance depend on time and temperature
- at later stages coalescence, coarsening and ripening until there are two large phases with composition Φ_1 and Φ_2

Spinodal segregation

- a small concentration fluctuation growth.
- diffusion against concentration gradient at spinodal ($T \rightarrow T_{sp}$) $D \rightarrow 0$ "critical slowing down"

Stages

- (1) **early stages:** amplitudes of fluctuations growth for preferred wavelength $\lambda = (\text{length scale})^{-1}$; modes are independent.
- (2) **intermediate stages:** amplitudes growth, modes interact with each other; wavelength growth and structure coarsens; deviations from cosine wave form.
- (3) **late stages:** fluctuation reaches the upper and lower limit Φ_1 and Φ_2 of equilibrium coexistence curve; wave form becomes rectangular and domain structure appears. Domain boundaries have finite thickness but extension is small compared to domain size.
- (4) **Finally:** system tends to minimize its interfacial free energy by minimizing the amount of interface area. Sphere contains the most volume and the least surface area. \Rightarrow
 - interwoven structure coarsens by an interfacial-energy driven viscous flow mechanism
 - tendency to spherical precipitates

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