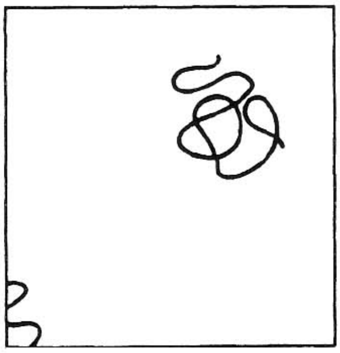
4. Polymer solutions and blends

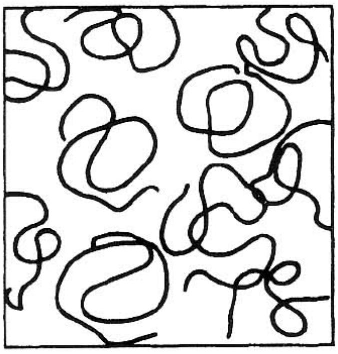
4.1 Introduction

Polymer solutions at different concentrations c



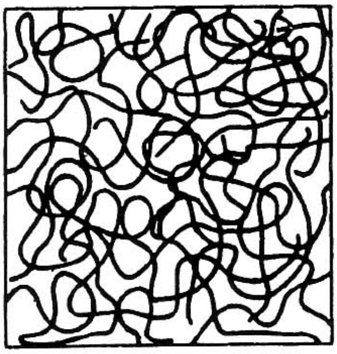
$c < c^*$

dilute solution



$c \cong c^*$

semi-dilute solution



$c > c^*$

concentrated solution

with overlap concentration $c^* \approx \frac{M}{N_A}\frac{3}{4\pi\left\langle r^2\right\rangle^{3/2}}$ and molar mass M

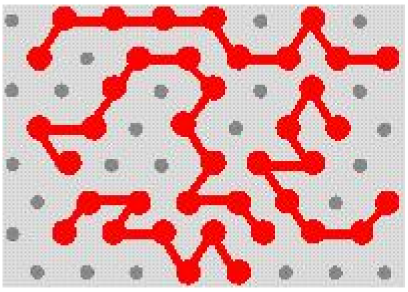
$c < c^*$: polymer chain described by radius of gyration = characteristic length
$c \cong c^*$: the polymer chains start to touch
$c > c^*$: characteristic length scale is mesh size

goal: solve the interaction of a many-body system
→ idea: replace n-body system by a 1-body problem with external field

at and above c^* the solution is reasonably uniform in composition
→ mean field situation, no large regions of pure solvent

Mean field: the interactions between molecules are assumed to be due to the interaction of a given molecule and an *average field,* caused by 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).



→ Mean field Flory Huggins lattice theory

(P. J. Flory, J. ChemPhys. 10, 51 (1942), M. L. Huggins, J. Phys. Chem. 46, 151 (1942).)

4.2 Thermodynamic Potentials

A **thermodynamic potential** is a scalar function used to represent the thermodynamic state of a system.

Five common thermodynamic potentials are: internal energy U, Helmholtz free energy F, enthalpy H, Gibbs free energy G and grand potential J

A *state function* describes the equilibrium state of a system using *natural variables* such as volume V, number of particles N, entropy S, temperature T, pressure p and chemical potential μ.

a) **internal energy U with the natural variables S,V,N**

U(S,V,N) : $dU=TdS-pdV+\mu dN$

from partial derivatives $T=\left.\frac{\partial U}{\partial S}\right|_{V,N}$ $\quad -p=\left.\frac{\partial U}{\partial V}\right|_{S,N}$ $\quad \mu=\left.\frac{\partial U}{\partial N}\right|_{V,S}$

b) **Helmholtz free energy F with the natural variables T,V,N**

F(T,V,N) : $dF=dU-SdT = -SdT-pdV+\mu dN$

Of interest in technical applications because many processes operate at constant temperature.

c) **Enthalpy H with the natural variables S,p,N**

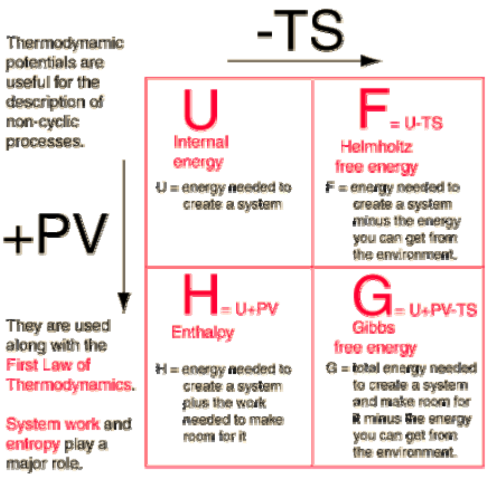
H(S,p,N) : $dH=dU+pdV+Vdp = TdS+Vdp+\mu dN$

Of interest in chemistry because chemical reactions frequently happen in open containers and thus at atmospheric pressure.

d) **Gibbs free energy G with the natural variables T,p,N**

G(T,p,N) : $dG=-SdT+Vdp+\mu dN$

In physical experiments it is easier to keep the pressure instead of the volume constant.



Thermodynamic potentials are useful for the description of non-cyclic processes.

They are used along with the First Law of Thermodynamics.

System work and entropy play a major role.

U = energy needed to create a system

F = energy needed to create a system minus the energy you can get from the environment.

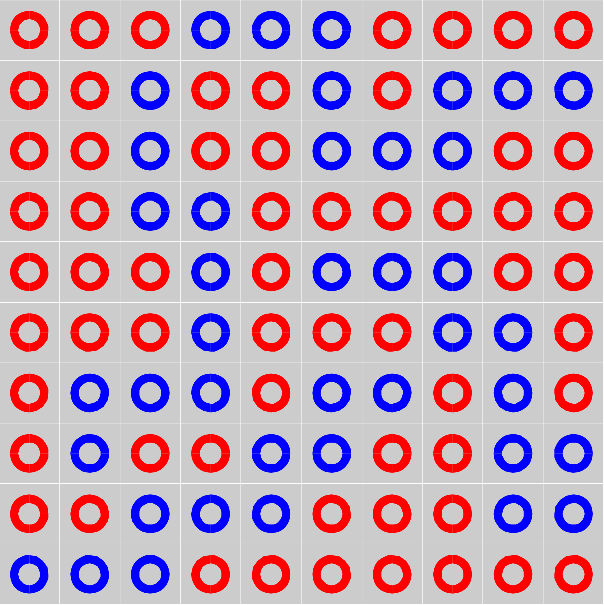
H = energy needed to create a system plus the work needed to make room for it

G = total energy needed to create a system and make room for it minus the energy you can get from the environment.

Legendre-Transformations, to transform one set of variables into the next one.

4.3 Entropy of mixing of monomers

Calculating the entropy of mixing of an athermal mixture with the aid of a lattice model:



Assumptions:

- No interaction between the particles
- Not two particles on one lattice position (one particle per lattice position) ⇒ take excluded volume into account
- All lattice positions are occupied ($n = n_1 + n_2$)

The **entropy** ***S*** is given by **the number of possible configurations Ω** of the particles on the lattice:

$$S = k_B \ln \Omega$$

$$\Omega = \frac{n!}{n_1! \cdot n_2!}$$

$$S = k_B (\ln n! - \ln n_1! - \ln n_2!)$$

Stirling equation: $\ln(n!) = n \ln n - n$

$$S = k_B (n \ln n - n - n_1 \ln n_1 + n_1 - n_2 \ln n_2 + n_2)$$
$$S = k_B (n \ln n - n_1 \ln n_1 - n_2 \ln n_2)$$
$$S = k_B (n_1 \ln n + n_2 \ln n - n_1 \ln n_1 - n_2 \ln n_2)$$

Volume fraction: $\phi_1 = \frac{n_1}{n_1 + n_2}$; $\phi_2 = \frac{n_2}{n_1 + n_2}$

$$S = -n k_B \left(\phi_1 \ln \phi_1 + \phi_2 \ln \phi_2 \right)$$

n:	*total number of lattice positions = total number of particles $n = n_1 + n_2$*
n_1:	*number of particles type 1*
n_2:	*number of particles type 2*
$\phi_{1,2}$:	*volume fraction $\phi_{1,2} = n_{1,2}/n$ of particle 1 and 2*
S:	*entropy*
k_B:	*Boltzmann constant*
Ω:	*number of possible configurations of the particles on the lattice.*
$R = N_A k_B$:	*gas constant*

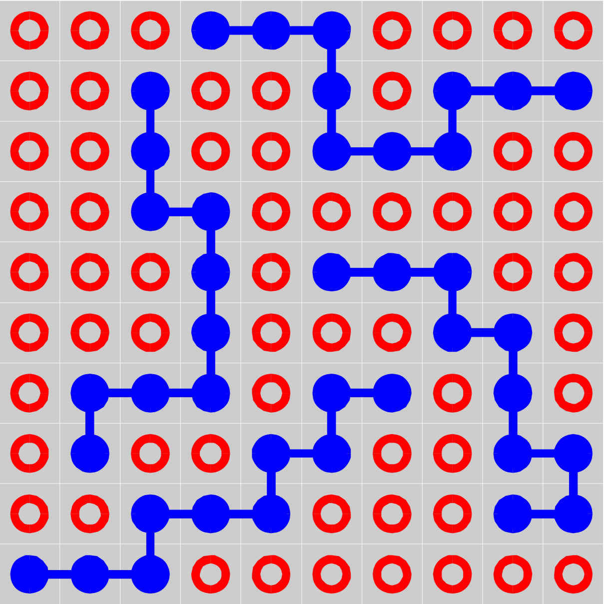
Ideal mixture of monomers related to one mole:

$$S = -R(\phi_1 \ln \phi_1 + \phi_2 \ln \phi_2)$$

The entropic contribution to ΔG is thus seen to always favor mixing if the random mixing approximation is used.

4.4 Entropy of mixing of polymer in solvent

Polymerize the particles of type 2 ⇒ number of possible configurations is drastically reduced (calculate with lattice model):



Assumptions:

- No interaction between the particles
- Not two particles on one lattice position (one particle per lattice position) ⇒ take excluded volume into account
- All lattice positions are occupied ($n = n_1 + Nn_2$)

The **entropy** ***S*** is given by **the number of possible configurations Ω** of the particles on the lattice:

$$S = k_B \ln \Omega$$

with Ansatz of the possible configurations of the polymer (by Flory):

$$\Omega = \frac{1}{n_2!} \prod_{i=1}^{n_2} \nu_i$$

Lattice occupied with *i* polymer chain segments, place segment number *i+1*:

$$\nu_{i+1} = \prod_{k=1}^{N} n_k^{i+1}$$

n:	*total number of lattice positions*
n_1:	*number of solvent molecules*
n_2:	*number of polymer chains*
N:	*degree of polymerization (number of monomers/chain)*
$\phi_{1,2}$:	*volume fraction of particle 1 and 2*
fi:	*available empty lattice positions*
z:	*coordination number*
S:	*entropy*
k_B:	*Boltzmann constant*
Ω:	*number of possible configurations of the particles on the lattice.*
ν_{i+1}:	*number of possible configurations of the of i+1 polymer chain*

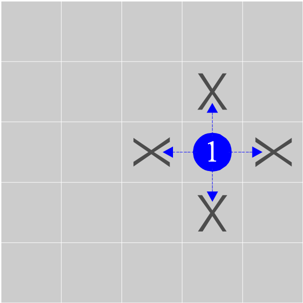
Descriptive:

segment 1:

$$n_1^{(i+1)} = n - iN$$

segment 2:

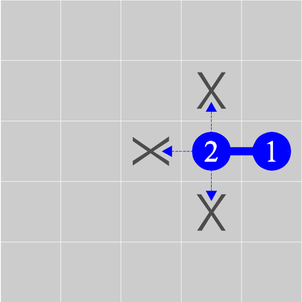
$$n_2^{(i+1)} \approx z(1 - f_i) = z\left(1 - \frac{iN}{n}\right)$$



segment 3 and 4:

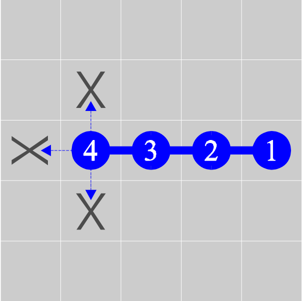
$$n_3^{(i+1)} \approx (z-1)\cdot\left(1-\frac{iN}{n}\right)$$

$$n_4^{(i+1)} \approx (z-1)\cdot\left(1-\frac{iN}{n}\right)$$

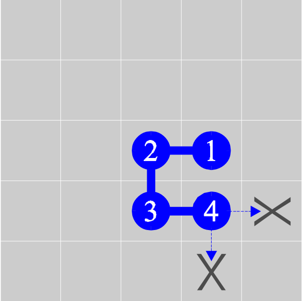


segment 5:

$$n_5^{(i+1)} \approx (z-1)\cdot\left(1-\frac{iN}{n}\right)$$



Situation which contradicts to the excluded volume of the polymer is not possible!



Summarized:

$$v_{i+1} = [n-iN]\cdot\left[z\left(1-\frac{iN}{n}\right)\right]\cdot\left[(z-1)\left(1-\frac{iN}{n}\right)\right]^{N-2}$$

$$v_{i+1} = \boxed{z(z-1)^{N-2}}\cdot\boxed{(n-iN)}\cdot\boxed{(1-\frac{iN}{n})^{N-1}}$$

Coordination number

Still available lattice positions

availability of empty lattice positions

$$v_{i+1} = (n-iN)\left(1-\frac{iN}{n}\right)^{N-1} z(z-1)^{N-2} \qquad \Big|\ (n-iN) = n\frac{n-iN}{n}$$

With the approximation *(z-1)≈z* we obtain

$$v_{i+1} \approx n\left(\frac{n-iN}{n}\right)^{N}(z-1)^{N-1} = n\left(\frac{N}{n}\right)^{N}\left(\frac{n}{N}-i\right)^{N}(z-1)^{N-1}$$

and

$$S = k_B \ln\left[\frac{1}{n_2!}\prod_{i=1}^{n2} n\left(\frac{N}{n}\right)^{N}\left(\frac{n}{N}-i\right)^{N}\frac{(z-1)^{N-1}}{1}\right]$$

Longer calculation (see textbook) gives entropy:

$$S = -k_B\left[n_1 \ln\frac{n_1}{n_1 + Nn_2} + n_2 \ln\frac{n_2}{n_1 + Nn_2} - n_2(N-1)\ln\frac{z-1}{e}\right]$$

Entropy consists of two parts, one part from conformation S_{dis} (disordering entropy) cause by the differences between the polymers and one part due to the mixing S_m:

$$S = S_m + S_{dis}$$

Of interest is only the part related with the mixing between polymer and solvent S_m. The other part S_{dis} is calculated with $n_1 = 0$ yielding:

$$S_{dis} = S(n_1 = 0) = n_2 k_B\left[\ln N + (N-1)\ln\left(\frac{z-1}{e}\right)\right]$$

$$S_m = S - S_{dis} = -k_B\left[n_1 \ln\frac{n_1}{n_1 + Nn_2} + n_2 \ln\frac{Nn_2}{n_1 + Nn_2}\right]$$

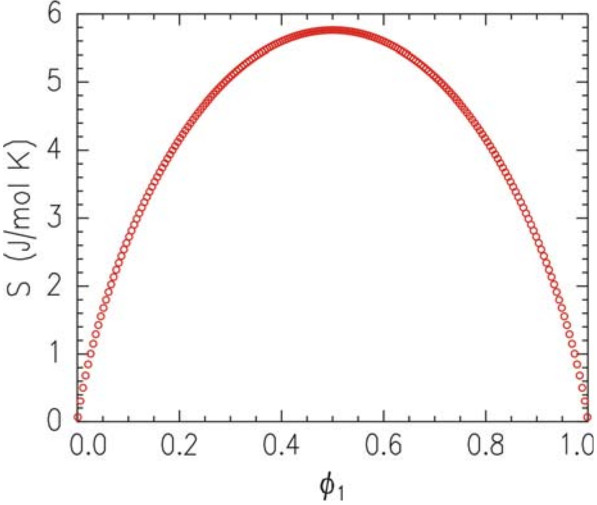
and with volume fractions $\phi_1 = \frac{n_1}{n_1 + n_2}$; $\phi_2 = \frac{n_2}{n_1 + n_2}$:

Ideal solution of polymer related to one mole:

$$S_m = -R\left[\phi_1 \ln\phi_1 + \frac{\phi_2}{N}\ln\phi_2\right]$$

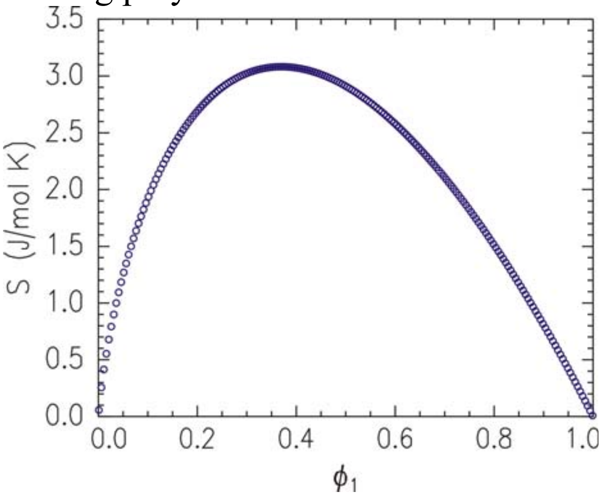
Entropy is reduced, because polymer chain has less degree of freedom due to covalent bonds along backbone of chain

Mixing monomers



symmetric

Mixing polymer and solvent



asymmetric

ϕ_2 is polymer component (N=100)

4.5 Entropy of mixing of polymer in polymer

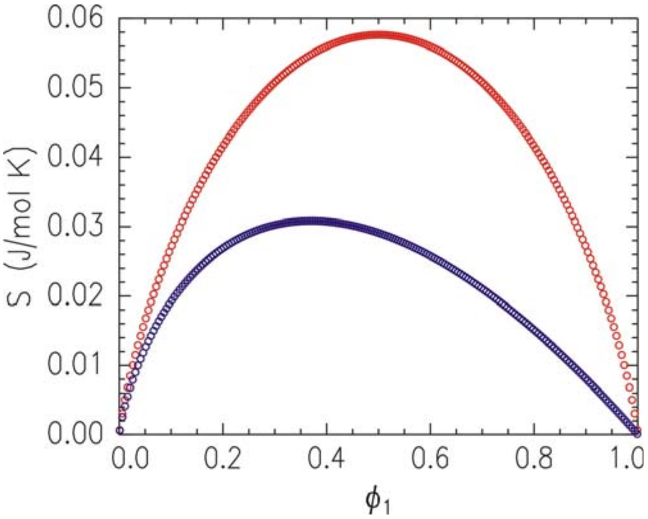
In analogy to the calculation for polymer solution, but now $N_{1,2}$ *degree of polymerization of polymer 1 and 2*

Ideal mixture of two polymers related to one mole:

$$S_m = -R\left[\frac{\phi_1}{N_1}\ln\phi_1 + \frac{\phi_2}{N_2}\ln\phi_2\right]$$

Entropy is further reduced – mixing less favored in polymer blends!

$N_{1,2}=100$
$N_1=100$
$N_2=10000$



4.6 Free energy of polymer blend

Attention: So far only positioning of 2 particles or 2 parts of polymer chains on one lattice position was not allowed, but the interaction between polymers was not considered!

To calculate the **enthalpy of mixing** the interaction between neighboring monomers of type 1 and 2 is taken into account – change in enthalpy due to mixing of polymers

$$\Delta w = w_{12} - \frac{1}{2}(w_{11} + w_{22})$$

and thus for the complete mixture

$$\Delta E = (z-2)\Delta w N_2 n_2 \phi_1$$

with $N_2 n_2 \phi_1 = \frac{N_2 n_2 N_1 n_1}{N_1 n_1 + N_2 n_2} = n\phi_1\phi_2$

$$\Delta E = nk_B T\chi\phi_1\phi_2$$

The polymer-polymer interaction parameter χ is:

$$\chi = \frac{(z-2)\Delta w}{k_B T}$$

n:	*total number of polymer chains*
$n_{1,2}$:	*number of polymer chains of polymer 1 or 2*
$N_{1,2}$:	*degree of polymerization of Polymer chain 1 or 2*
$\phi_{1,2}$:	*volume fraction of polymer 1 or 2*
z: *$(z-2)$:*	*coordination number* *available positions*
k_B: *w:*	*Boltzmann constant* *interaction between the monomers*
χ:	*interaction parameter*

The value of the interaction parameter can be estimated from the **Hildebrand solubility parameters** δ_a and δ_b

$$\chi = \frac{V_{seg}\left(\delta_a - \delta_b\right)^2}{RT}$$

where V_{seg} is the actual volume of a polymer segment.

Change in free energy due to mixing:

$$\Delta F_m = \Delta E_m + T\Delta S_m$$

Assumption: Interaction has no influence on the entropy of mixing

$$\Delta F_m = nk_B T\left[\frac{\phi_1}{N_1}\ln\phi_1 + \frac{\phi_2}{N_2}\ln\phi_2 + \chi\phi_1\phi_2\right]$$

E:	*energy*
H:	*enthalpy*
F:	*Helmholz free energy*
G:	*Gibbs free Enthalpy*

Because the pressure *p* and temperature *T* are the typical laboratory parameters the Gibbs free enthalpy needs to be taken instead of the free energy.

Gibbs free enthalpy of mixing two polymers related to one mole:

$$\Delta G_m = RT\left[\frac{\phi_1}{N_1}\ln\phi_1 + \frac{\phi_2}{N_2}\ln\phi_2 + \chi\phi_1\phi_2\right]$$

In case of $N_1 = 1$ this equation transforms into the equation for **polymer solutions** and for $N_1 = N_2 = 1$ into a **solvent mixture**:

$$\Delta G_m = RT\left[\phi_1\ln\phi_1 + \frac{\phi_2}{N_2}\ln\phi_2 + \chi\phi_1\phi_2\right] \text{ and } \Delta G_m = RT\left[\phi_1\ln\phi_1 + \phi_2\ln\phi_2 + \chi\phi_1\phi_2\right]$$

Corrections to polymer-polymer interaction parameter:

a) Modification by Tanaka

If the polymer-polymer interaction parameter χ would be only of enthalpic origin, the approach $\chi \propto 1/T$ would be sufficient. However, the entry of a polymer mixture is different as compared with the simple Flory-Huggins approach. Although these deviations are of entropic origin, the empiric corrections is put to the enthalpic term χ:

Flory-Huggins Parameter χ of polymer blend:

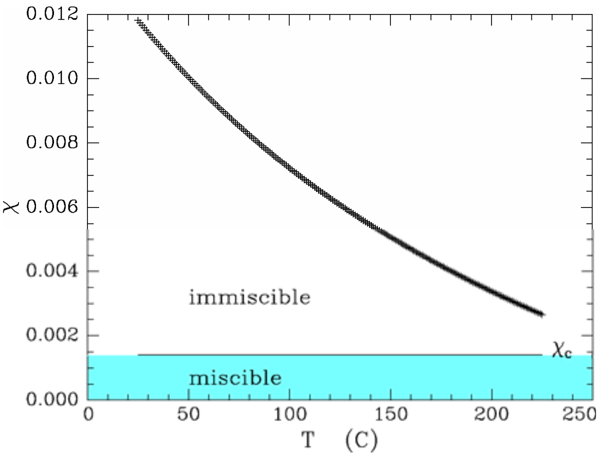
$$\chi = \frac{a}{k_B T} + b$$

with two constants *a* and *b*.

Widely discussed entropic contributions are from the presence of excess free volume, monomer structure, chain flexibility, and chain-end effects.

Example: deuterated polystyrene (dPS) and polyparamethylstyrene (PpMS)

$\chi = b + a/T$
with $b = -0.011 \pm 0.002$ and $a = 6.8 \pm 1$ K



b) Model of Bawendi and Freed (1988)

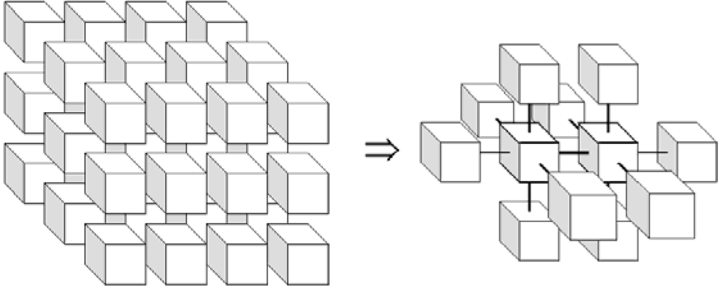
Based on lattice model and lattice cluster theory a field-theoretical description, which involves generalized interaction parameters g_{ij} between the different components results in a Flory-Huggins Parameter χ of polymer blend, which confirms the empiric approach by Tanaka:

$$\chi = \frac{\Gamma_H}{T} + \Gamma_\sigma$$

entropic portion of the Flory–Huggins parameter depends on components

$$\Gamma_\sigma = -\frac{2}{V_{cell} z^2}\left(\frac{1}{N_1} - \frac{1}{N_2}\right)^2 \left(10 + z + \left(-18 + \frac{22}{N_1}\right)\phi_1 + \left(-18 + \frac{22}{N_1}\right)\phi_2 + 12\left(\left(1 - \frac{1}{N_1}\right)\phi_1 + \left(1 + \frac{1}{N_2}\right)\phi_2\right)\right)$$

Calculated from 3d lattice approach



http://www.dp-e.de/web/dawt/dawt.htm#kap3.1.htm

c) Model of Mumby und Sher (1994)

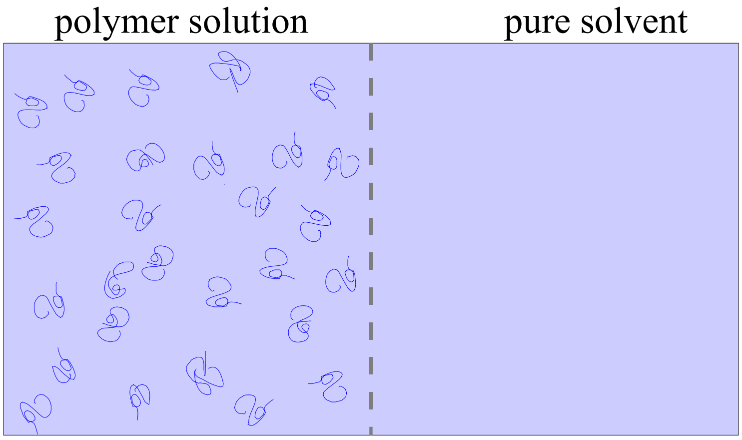
Empiric model which modifies the interaction parameter to be not only dependent on temperature T but also on the volume fractions $\phi_{1,2}$. Such model is successful for more complex phase diagrams which exhibit LCST and UCST behavior at the same time.

$$\chi = \left(1 + b_1\phi_1 + b_2\phi_2^2\right)\left(d_0 + \frac{d_1}{T} + d_2 \ln(T)\right)$$

with b_i and d_i are adjustable constants

4.7 Example: Osmotic pressure

n: total number of polymer chains; $n_{1,2}$*: number of polymer chains type 1 and type 2;* $N_{1,2}$*: degree of polymerization of polymer 1 and 2;* $\phi_{1,2}$*: volume fraction of polymer 1 and 2;* μ_1*:chemical potential of polymer solution,* μ_1^0*: chemical potential of solvent; P: pressure; T: temperature;* ΔG *Gibbs free energy;* Π*: osmotic pressure*



$$\mu_1(P,T) = \mu_1^0(P',T)$$

Chemical potential calculated from Flory-Huggins approach:

$$\mu_1(P,T) - \mu_1^0(P,T) = \frac{\partial \Delta G_m}{\partial n_1}$$

$$= RT[\ln\phi_1 + (1-\frac{1}{N})\phi_2 + \chi\phi_2^2]$$

Pressure difference between pure solvent P' and solution P:

$$\mu_1^0(P',T) - \mu_1^0(P,T) = -\Pi\frac{\partial \mu_1^0}{\partial P}$$

$$\left.\frac{\partial \mu_1^0}{\partial P}\right|_{T,n_1} = V_1$$

$$RT[\ln\phi_1 + (1+\frac{1}{N})\phi_2 + \chi\phi_2^2] = -\Pi V_1$$

In case of a dilute solution ($\phi_1 << 1$) the logarithm can be expanded in Taylor-series: $\ln\phi_1 = \ln(1-\phi_2) = -\phi_2 - \frac{1}{2}\phi_2^2 + \ldots$

Virial expansion of osmotic pressure:

$$\Pi V_1 = RT\left(\frac{\phi_2}{N} + \left(\frac{1}{2} - \chi\right)\phi_2^2 + \ldots\right)$$

Cut-off Taylor-series after second term:

$$\boxed{\Pi V_1 = RT\left[\frac{\phi_2}{N} + (\frac{1}{2} - \chi)\cdot\phi_2^2\right]}$$

with

$$\chi \propto \frac{1}{T}$$

R: gas constant
k_B*: Bolzmann constant*
T: temperature
V_1*: mol volume solvent*
Π*: osmotic pressure*
ϕ_2*: volume fraction polymer*
χ*: interaction parameter*
a: Enthalpy coefficient
b: Entropy coefficient

Discussion of 3 possible cases, because the term 1/2-χ can change the sign as function of temperature T:

1) high temperature ⇨ χ is small ⇨ quadratic term is positive:

$$\Pi V_1 = RT\left[\frac{\phi_2}{N} + \frac{1}{2}\phi_2^2 + \dots\right]$$

- Osmotic pressure is increased as compared with ideal interaction-free scenario
- With increasing concentration the polymers act with increased osmotic pressure
- Polymers are in a good solvent ⇨ polymers have tendency to expand and repel each other

2) low temperature ⇨ χ is large ⇨ quadratic term is negative:

$$\Pi V_1 = RT\left[\frac{\phi_2}{N} - \dots\right]$$

- Osmotic pressure is decreased as compared with ideal interaction-free scenario
- Polymers are in a bad solvent ⇨ polymers have tendency to collapse and cluster together ⇨ phase separation can occur

3) θ-temperature ⇨ $\chi = ½$ ⇨ quadratic term is zero:

$$\Pi V_1 = RT\frac{\phi_2}{N}$$

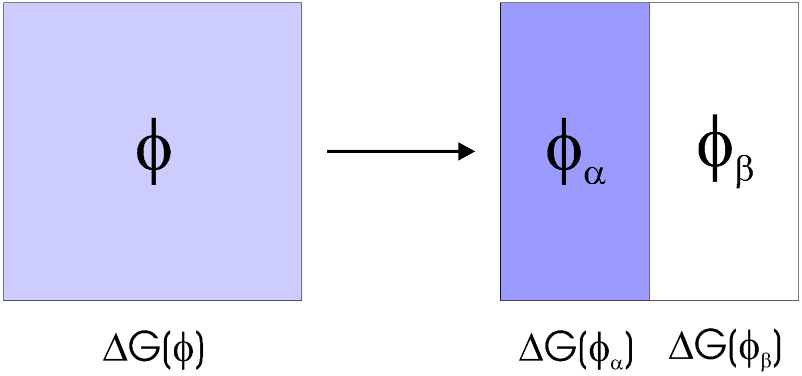
- Osmotic pressure is equal to ideal gas ⇨ repulsive and attractive contributions compensate each other
- the ideal chain conformation is reached

4.8 Limits of the Flory-Huggins-Theory

- Ansatz is a mean-field theory, which means that the averaged surrounding of all atoms acts on each monomer
- Fluctuation are completely neglected
- Theory will work well for medium and high concentrations which not exhibit strong density fluctuations
- At low concentration, which have dominating fluctuations, the theory is only appropriate very close to the θ–point

4.9 Phase-separation based on Flory-Huggins-Theory

a) Polymer solution: with concentration ϕ



divide ϕ in $\phi \Rightarrow \phi_\alpha + \phi_\beta$ with $\phi_{\alpha,\beta}$: *volume fraction of phase α and β*

$$\phi = \alpha\phi_\alpha + \beta\phi_\beta \quad \text{with} \quad \alpha + \beta = 1$$

For an adiabatic system in equilibrium, the Gibbs free energy ***ΔG is minimal***. As a consequence, no phase separation can occur if:

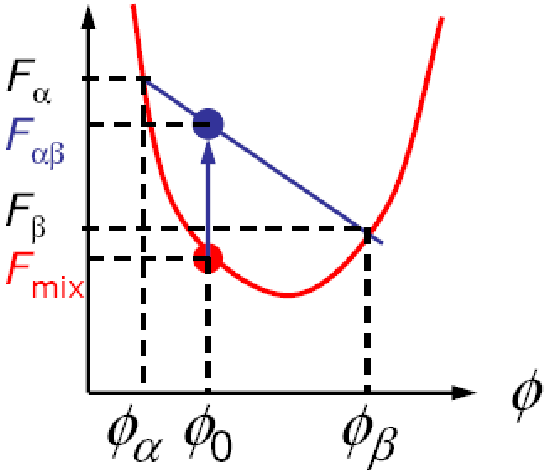
Gibbs's stability criteria

$$\Delta G(\phi) < \alpha\Delta G(\phi_\alpha) + \beta\Delta G(\phi_\beta)$$

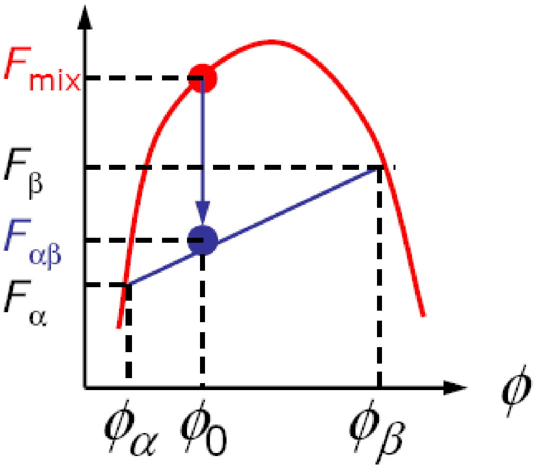
Analog inequation in case of Helmholz free energy *dF= dG-Vdp-pdV*

The stability of a mixture is depending on the Gibbs/Helmholz free energies: local stability of homogeneous mixture of composition ϕ_0

energy of two phases α and β: weighted average of F_α and F_β = straight line



curve *ΔG(ϕ)* is convex
Solution is stable: phase separation would increase the Gibbs free energy

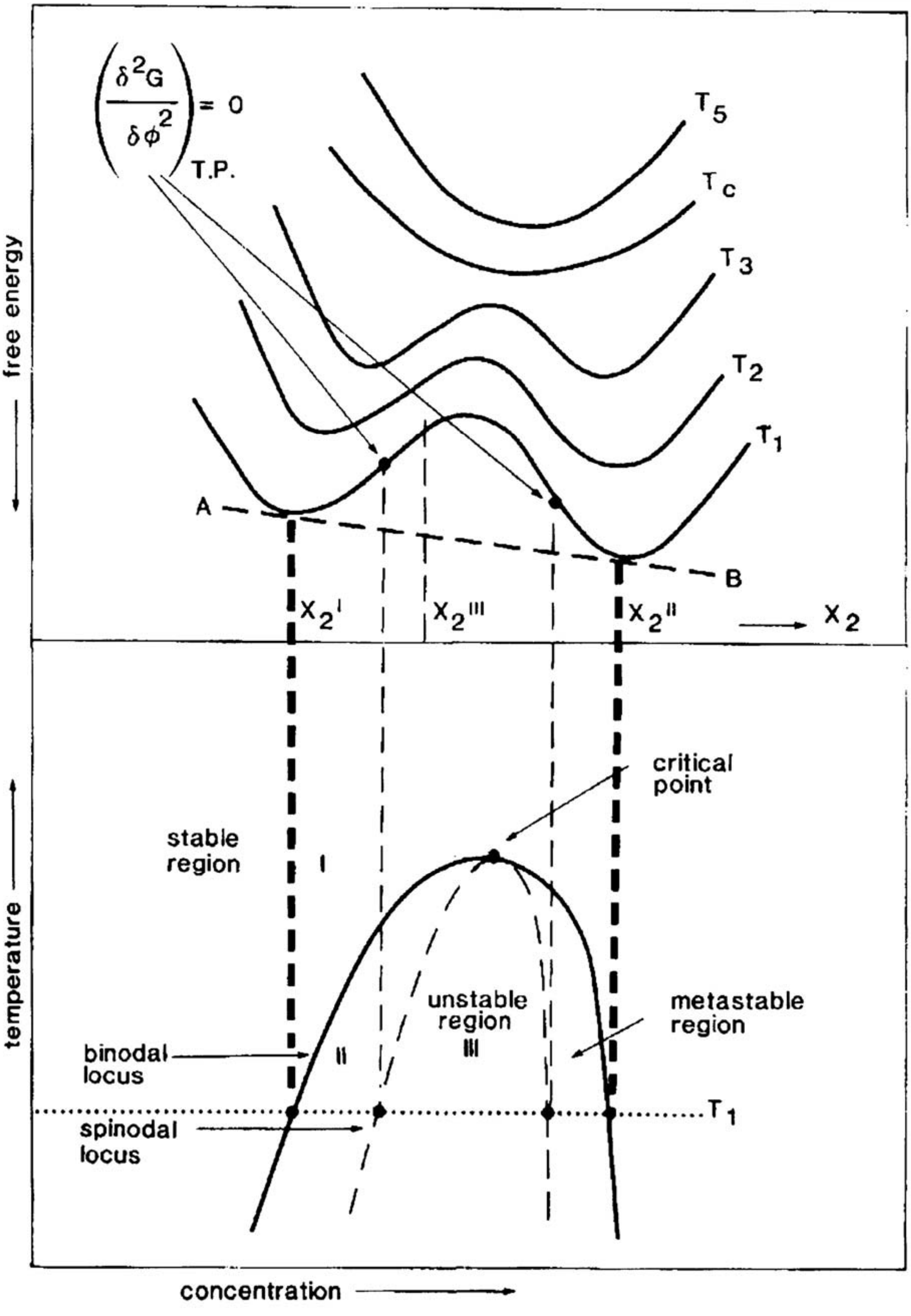


curve *ΔG(ϕ)* concave
Solution is unstable: phase separation would decrease Gibbs free energy

⇒ calculation of α and β

Construction of phase diagrams:

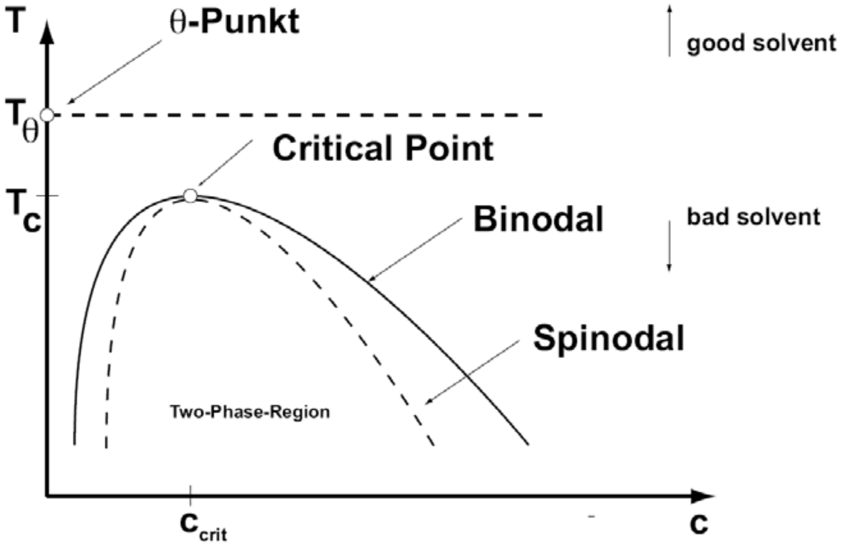
1) Determination of the Gibbs free energy as function of the volume fraction ϕ for different temperature T_1, T_2, T_3, ….
2) Determination of stable and instable regions from a projection to the Tϕ-plot



Where to find in the Gibbs free energy (for a fixed temperature) the stable, meta- and instable regions:

- The ***binodal line*** (separation between the single- and two-phase region) is resulting from the tangent-construction
- The ***spinodal line*** (separation between meta-stable and stable demixed / phase separated region) is resulting from the inflection points

Resulting phase diagram has a lower miscibility gap and has a upper critical solution temperature (LCST):



Exact location of binodal and spinodal line from curve sketching:

Gibbs free energy of polymer solution with $\phi_2 = \phi$ and $\phi_1 = 1 - \phi$

$$\frac{\Delta G}{RT} = (1-\phi)\ln(1-\phi) + \frac{\phi}{N}\ln\phi + \chi\phi(1-\phi)$$

Zeros of the first derivative with respect to ϕ yield positions of the extremes and the minima are the positions of the binodal line:

$$\frac{\partial}{\partial\phi}\frac{\Delta G}{RT} = -\ln(1-\phi) + \frac{1}{N}\ln\phi - 1 + \frac{1}{N} + (1-2\phi)\chi = 0$$

Zeros of the second derivative with respect to ϕ yield the positions of the inflection points and give the limit of local stability (<0: unstable with spontaneous demixing and >0: stable):

$$\frac{\partial^2}{\partial\phi^2}\frac{\Delta G}{RT} = \frac{1}{N\phi} + \frac{1}{1-\phi} - 2\chi = 0$$

Inside the spinodal a spontaneous demixing occurs. In the metastable area demixing needs grains (impurities).

Zeros of the third derivative with respect to ϕ yield the extremes of the second derivative:

$$\frac{\partial^3}{\partial\phi^3}\frac{\Delta G}{RT} = \frac{1}{N\phi^2} + \frac{1}{(1-\phi)^2} = 0$$

Define the point where spinodal and binodal meet at the critical volume fraction ϕ_c:

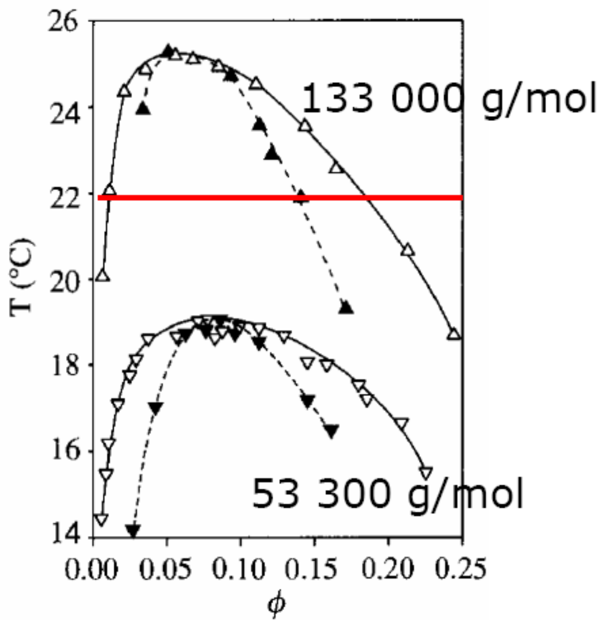
$$\phi_c = \frac{1}{1+\sqrt{N}} \approx \frac{1}{\sqrt{N}} \qquad \text{for } N >> 1$$

knowing ϕ_c the critical polymer-polymer interaction parameter χ_c can be determined:

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

The values (T_c,ϕ_c) give the critical point in the phase diagram.

Example: polyisoprene solutions in dioxane



→ strongly asymmetric phase diagrams

for 133 000 g/mol at 22°C:
miscibility only for
$\phi < \sim 0.02$ and $\phi > 0.20$

for 53 300 g/mol at 22°C:
miscibility for all ϕ

Takano at al., *Polym. J.*, **17**, 1123 (1985)

b) Polymer blends

Gibbs free energy in the framework of Flory-Huggins theory:

$$\Delta G_m = RT\left[\frac{\phi_1}{N_1}\ln\phi_1 + \frac{\phi_2}{N_2}\ln\phi_2 + \chi\phi_1\phi_2\right]$$

Determine critical point:

$$\frac{\partial^3}{\partial\phi^3}\frac{\Delta G}{RT} = \frac{1}{N_1(1-\phi)^2} - \frac{1}{N_2\phi^2} = 0 \quad \text{yields: } \phi_c = \frac{1}{\sqrt{N_2/N_1}+1}$$

with ϕ_c and the second derivative, the critical polymer-polymer interaction parameter is determined χ_c:

$$\frac{\partial^2}{\partial\phi^2}\frac{\Delta G}{RT} = \frac{1}{N_1(1-\phi)} + \frac{1}{N_2\phi} - 2\chi = 0 \qquad \text{and thus: } \chi_c = \frac{1}{2N_2}\left(1+\sqrt{N_2/N_1}\right)^2$$

Special case:

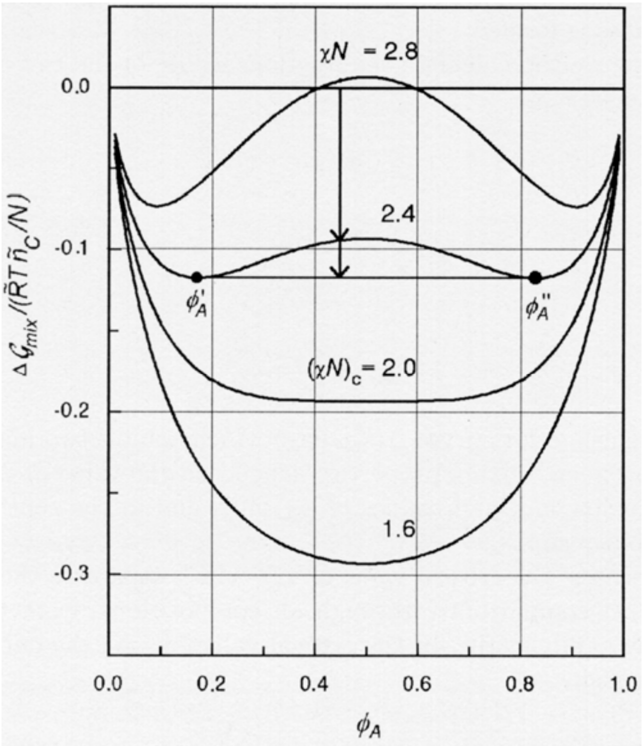
Equal degree of polymerization $N_1 = N_2 := N$:

Critical volume fraction:

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

Critical polymer-polymer interaction parameter:

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



$(\chi N_c)<2$ curve convex = blend stable = miscible

$(\chi N_c)=2$ curve linear = critical point = phase boundary

$(\chi N_c)>2$ curve concave = blend instable = non miscible

- In case of equal degree of polymerization N the phase diagram is symmetric with respect to ϕ_c
- Monomers are covalently connected ⇨ reduced disorder ⇨ entropic part in mixing is small ⇨ Monomer interaction determines the miscibility
- χ_c is reduced with a factor 1/N ⇨ thus it is small value ⇨ a weak repulsion of the monomers results already in a demixing

⇩

Miscibility of polymers is reduced as compared with low molecular weight systems.

Miscibility is only possible in case of special monomer interaction as for example: dipole-dipole interaction, hydrogen bonds, donor-acceptor interaction

→ phase diagram is well described but how to explain the resulting structures?

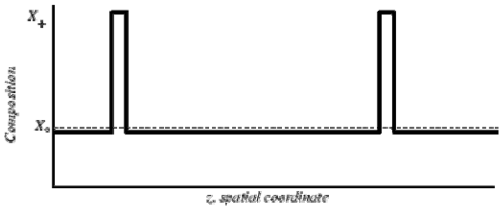
4.10 Phase separation kinetics

Polymers phase separate by the same mechanisms as small molecule mixtures, that is by *nucleation and growth* or by *spinodal decomposition,* according to what part of the phase diagram one quenches them into.

a) nucleation and growth

Between binodal and spinodal line the system is metastable, meaning that the system is stable with respect to small fluctuations but unstable with respect to infinitesimal composition fluctuations.

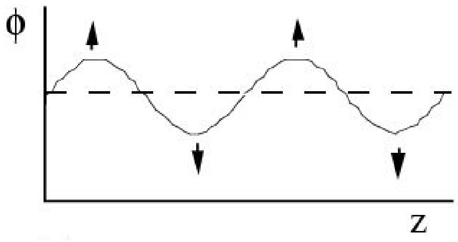
A process requiring a large composition fluctuation is called ``nucleation." After the nucleus forms, the new phase grows. Together, the process is called *nucleation and growth.*



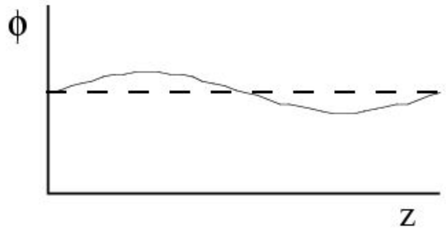
The new phase must initiate with a composition that is *not* near that of the parent phase.

b) spinodal decomposition

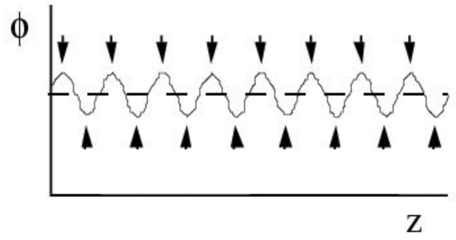
Within the spinodal line, any small local change in composition lowers the free energy. The system is unstable, and any small fluctuation in composition is amplified.



In the unstable part of the phase diagram, random concentration fluctuations are unstable and grow in amplitude.



Long wavelength fluctuations grow slowly because of the large distances through which material needs to be transported.



Short fluctuations are suppressed, because of the high free energy penalty associated with sharp concentration gradients.

→ Fluctuations on an intermediate length scale grow the fastest and dominate the resulting morphology free energy leads to a modified diffusion equation; this has a solution

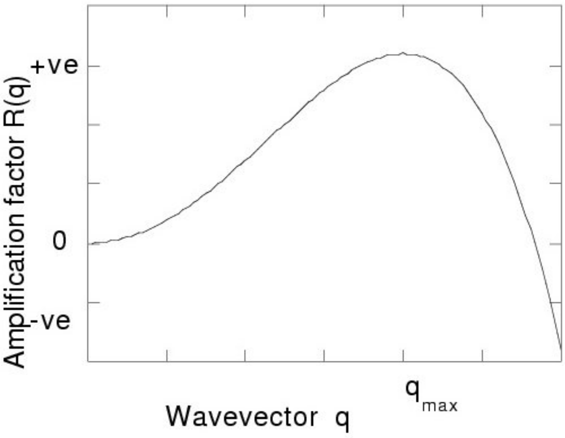
$$\phi(x,t) = A\cos(qx)\exp\left(-D_{eff}q^2\left(1+\frac{2kq^2}{f_0''}\right)t\right) \quad \text{with} \quad f_0'' = \frac{d^2 f_0}{d\phi^2}$$

Thus a composition fluctuation with wavevector q grows exponentially (as D_{eff} is negative) with an amplification factor

$$R(q) = -D_{eff}\left(1+\frac{2kq^2}{f_0''}\right)q^2$$

Inside the spinodal region f_0'' is negative, so $R(q)$ has a maximum value.

This defines a fastest growing wavevector q_{max}, which sets the length scale on which spinodal decomposition occurs.

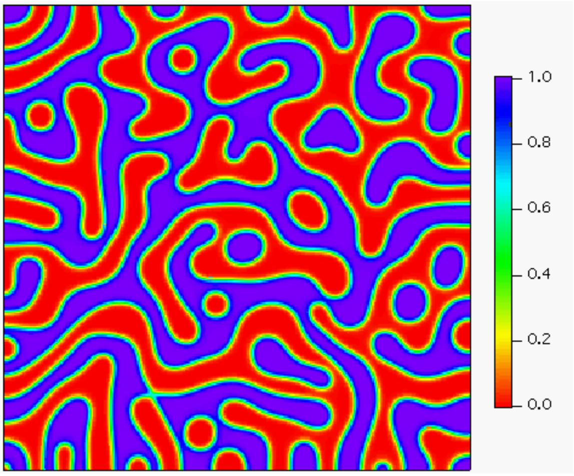


Simulation of pattern formed by spinodal decomposition in real space.

Characteristic pattern with dominant length scale

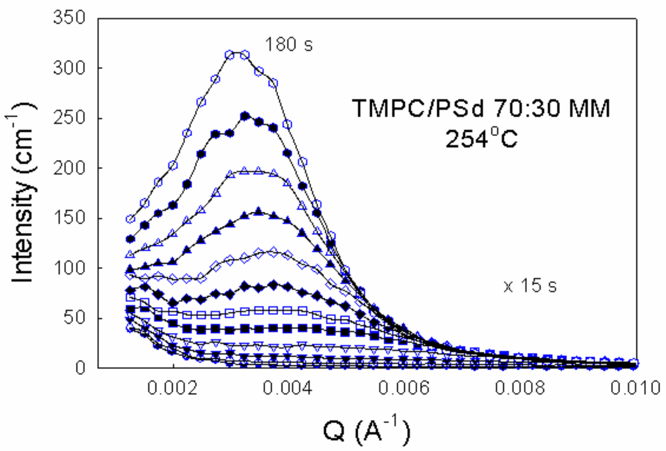
$$\Lambda = \frac{2\pi}{q_{\max}}$$

ctcms.nist.gov

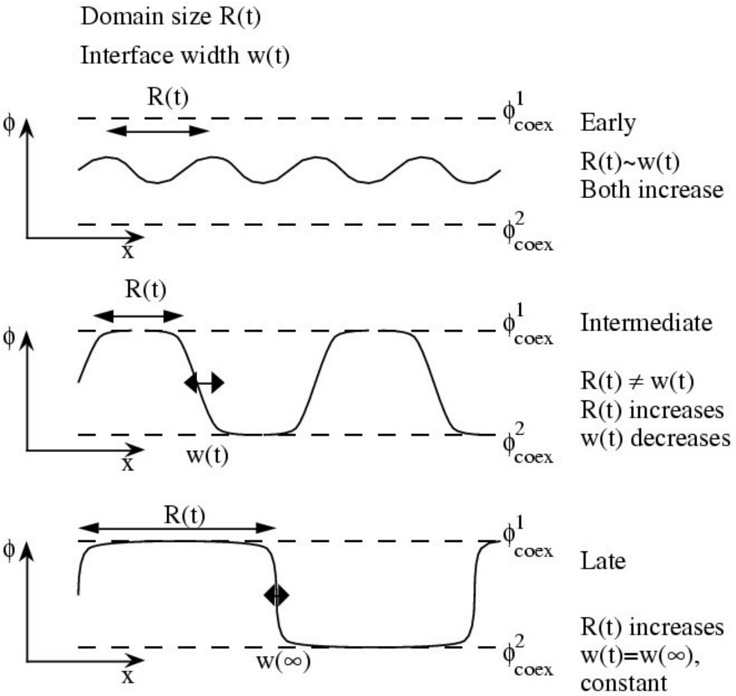


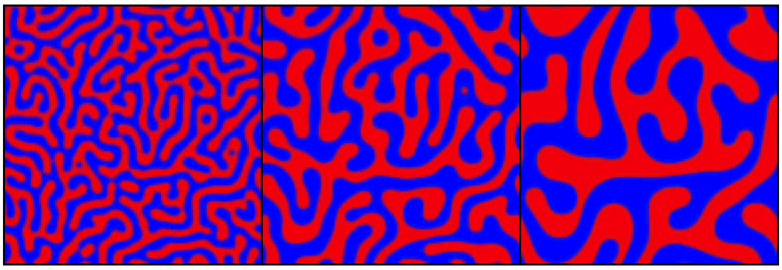
X-ray or neutron scattering is well suited to probe the characteristic wavelength Λ and one sees a maximum in the scattering pattern at a wavevector corresponding to the fastest growing wavevector of the spinodal pattern.

Cabral et al. *Physica B* 276-278, 408 (2000)



So far only the early stages of spinodal decomposition are described. At later stages the morphology transforms further.

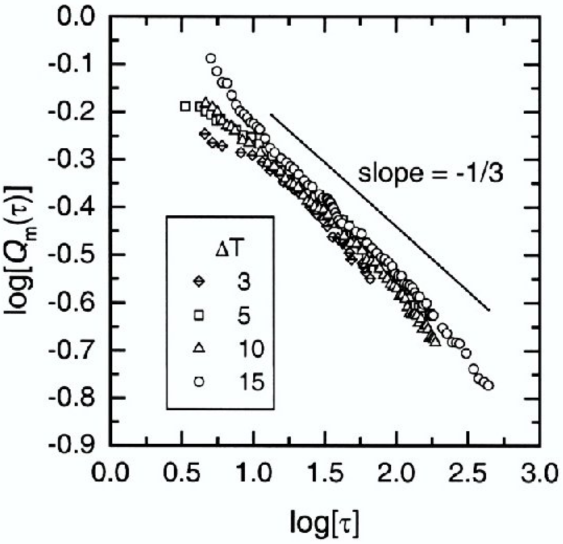




In the late stage of phase separation, there is only one important length scale, the characteristic size of the domains L(t). This leads to the idea of dynamical scaling.

The growth of the domains is driven by the reduction of interfacial energy, with the transport of material being controlled by diffusion.

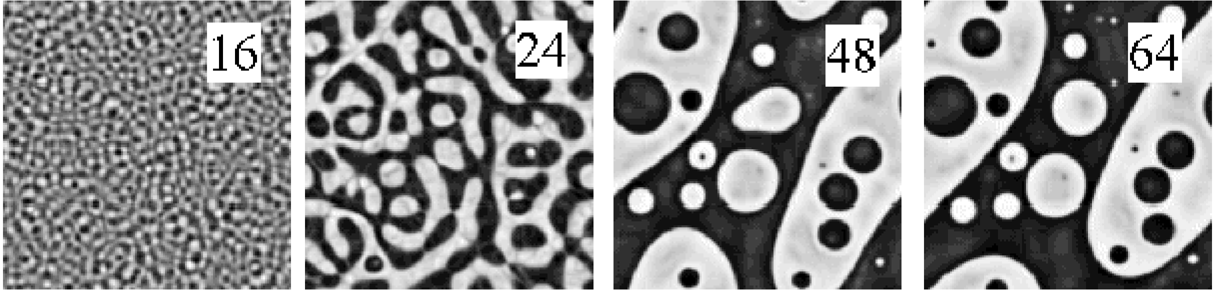
Lifshitz-Slyozov law: $L(t) \sim (D\,\gamma\,t)^{1/3}$



Boom Jung’s PhD thesis (University of Cambridge 1999)

Effects of hydrodymic flow on phase separation dynamics of fluid mixtures: Numerical simulations show that the spinodal decomposition of fluid mixtures is strongly dependent upon their fluidity.

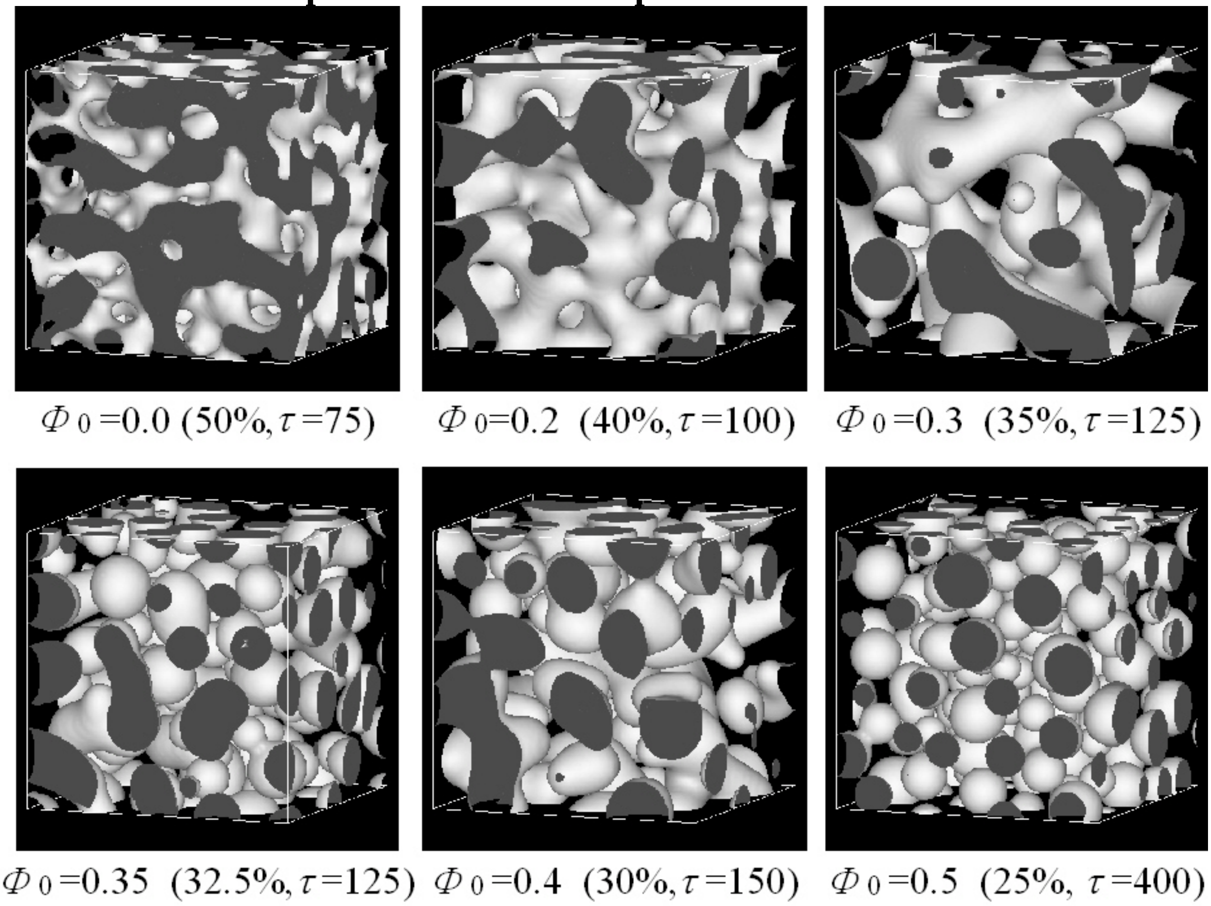
Example in 2D:



Tanaka et al; Phys. Rev. Lett. **81**, 389 (1998)

Two relevant transport mechanisms are acting: hydrodynamic flow and diffusion. In case of a high fluidity a *spontaneous double phase separation* can occur, because high fluidity causes rapid geometrical coarsening of domains due to a hydrodynamic process, which is too fast for diffusion to follow. This brings the system out of equilibrium and induces secondary phase separation.

Volume fraction dependence of domain pattern of fluid mixtures



$\Phi_0=0.0$ (50%, $\tau=75$) $\Phi_0=0.2$ (40%, $\tau=100$) $\Phi_0=0.3$ (35%, $\tau=125$)

$\Phi_0=0.35$ (32.5%, $\tau=125$) $\Phi_0=0.4$ (30%, $\tau=150$) $\Phi_0=0.5$ (25%, $\tau=400$)

Araki, Kyoto University

4.11 Phase diagrams: UCST / LCST behavior

In a ϕ/T-phase diagram the shape of binodal and spinodal is determined by $\chi(T)$ and different temperature dependence will result in UCST and LCST behavior.

a) Low temperature decomposition

(UCST = Upper Critical Solution Temperature)

Example: PS/PB, PS/PαMS, PS/PMMA

Results from a polymer blend with a polymer-polymer interaction parameter which has a general shape

$$\chi \propto \frac{1}{T}$$

In case of ***symmetric polymer blend*** with $N_1 = N_2 := N$ is:

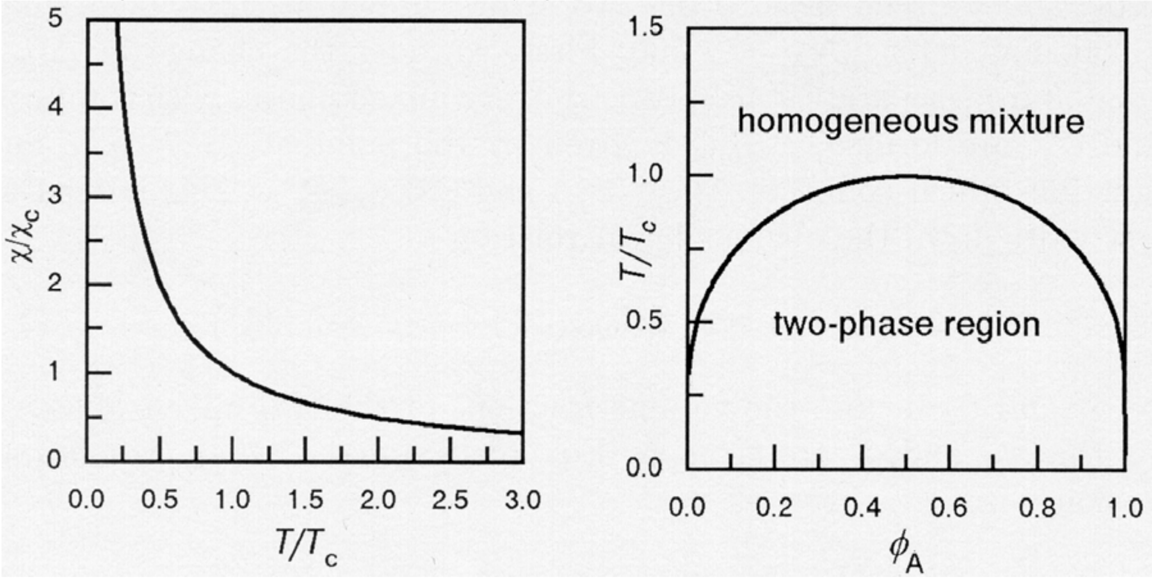
$$\chi_c = \frac{2}{N} \text{ for } \chi(T) \Rightarrow \chi = \frac{2}{N}\frac{T_c}{T}$$

with $\frac{\partial}{\partial\phi}\frac{\Delta G}{RT} = 0$ results: $\chi \cdot N = \frac{1}{1-2\phi}\ln\left(\frac{1-\phi}{\phi}\right)$

The boundary between homogeneous mixture at high temperatures and the two-phase region at low temperatures is given by:

$$\frac{T}{T_c} = \frac{2(1-2\phi)}{\ln\left(\frac{1-\phi}{\phi}\right)}$$

Phase diagram with lower miscibility gap:

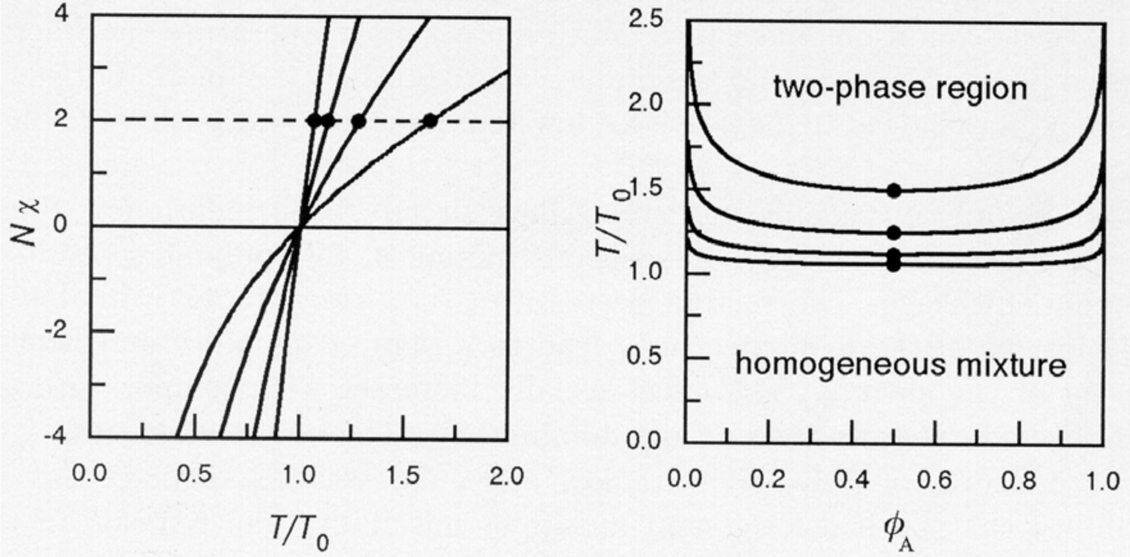


b) High temperature decomposition

(LCST= Lower Critical Solution Temperature)

Example: PS/PVME

In case of exothermic polymer blends upper miscibility gaps are known as well.



Demixing occurs independent of the volume fraction ϕ, for $\chi \geq 0$.

The prerequisite for an upper miscibility gap is a polymer-polymer interaction parameter χ.which increases with temperature T.

Possible mechanisms:

Mechanism 1:

Competition between

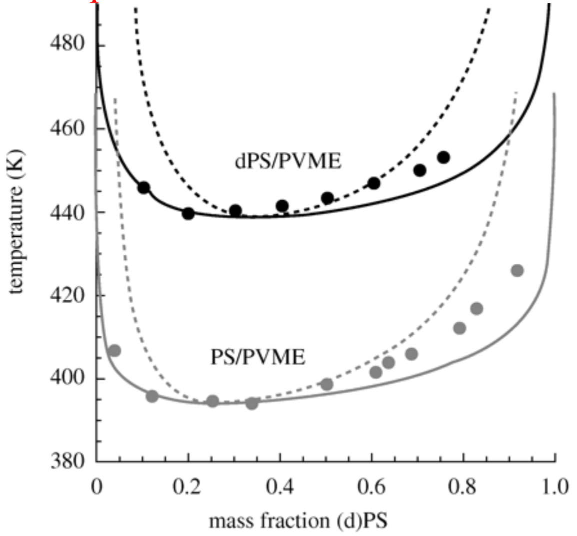
- Attractive interaction of special groups in both polymers (hydrogen-bonds)
- Repulsive interaction of the remaining monomers without these special groups (e.g. in case of copolymers)

Mechanism 2:

Mixing reduces the volume as compared with the demixed system. Therefore the volume is reduced for the local movement of the polymer chains. This reduced mobility of the monomers decreases the entropy.

This effect is increasing with temperature and overcompensates the initially dominating attractive interaction.

Example: hPS/PVME and dPS/PVME phase diagrams



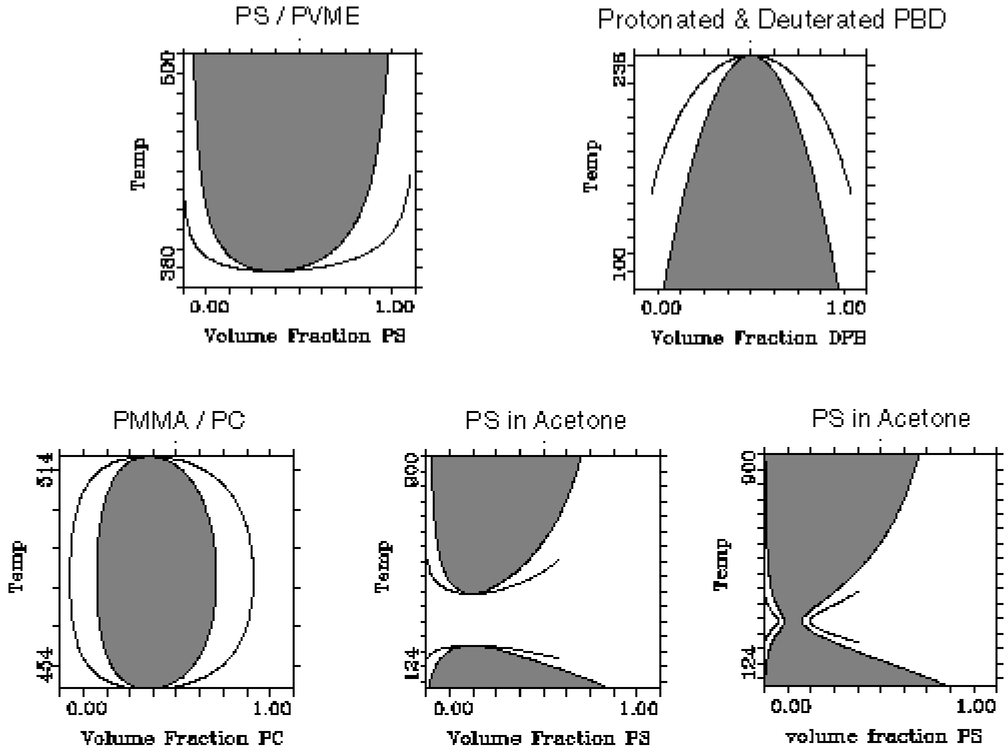
theoretical binodal (solid) and spinodal (dashed) curves

hPS/PVME blend: molecular weights of 120000/99000 g/mol; experimental data from Beaucage *et al.* (1991)

dPS/PVME blend: molecular weights of 119000/99000 g/mol; experimental data from Yang *et al.* (1986)

Higgins et al.; *Phil. Trans. R. Soc. A 368, 1009 (2010)*

c) more complex phase diagrams



Adapted from a Review published in *Trends in Polymer Science*, **2**, 1994 by F.H. Case and J.D. Honeycutt