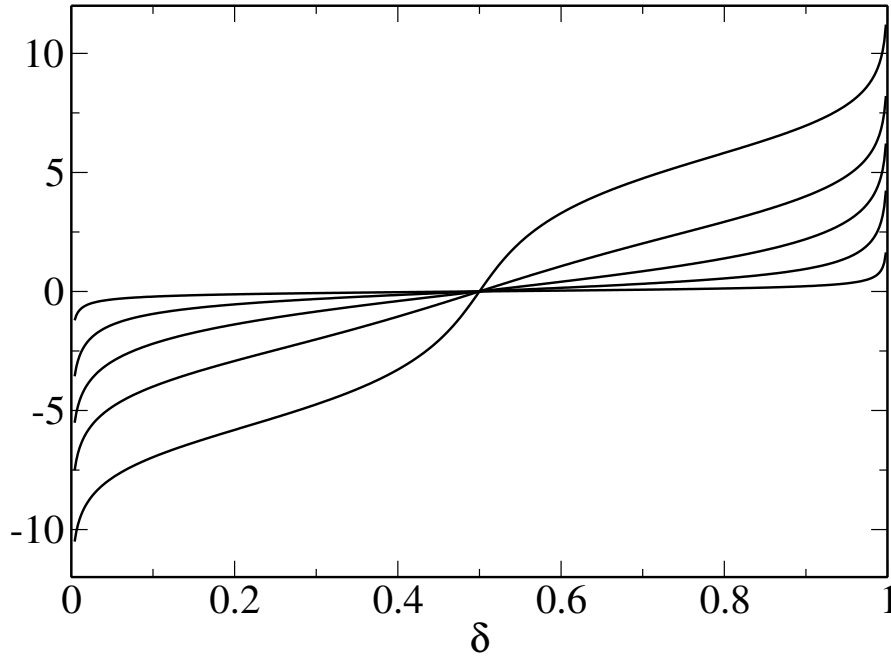


$$+ \frac{1}{l_\alpha - l_\beta} \frac{\partial N_{\alpha\beta}^*}{\partial M_\alpha} \frac{\partial}{\partial N_{\alpha\beta}^*} \left(-kT \ln g - \frac{w N_{\alpha\beta}^*}{2} \right)$$

The last part vanishes due to the definition of $N_{\alpha\beta}^*$. Now using Stirling's formula we find

Figure 15: force-length relation for the interacting 2-component model $-\ln \frac{\xi+1-2\delta}{\xi-1+2\delta}$ is shown as a function of δ for $w/kT = 0, \pm 2, \pm 5$



$$\frac{\partial}{\partial M_\alpha} \ln g = \ln \frac{M_\alpha}{M - M_\alpha} + \ln \frac{M - M_\alpha - \frac{N_{\alpha\beta}^*}{2}}{M_\alpha - \frac{N_{\alpha\beta}^*}{2}} = \ln \frac{\delta}{1 - \delta} + \ln \frac{1 - \delta - \gamma}{\delta - \gamma}$$

and substituting γ we have finally

$$\kappa \frac{(l_\alpha - l_\beta)}{kT} = \ln \frac{z_\beta e^{-w\beta\beta/kT}}{z_\alpha e^{-w\alpha\alpha/kT}} - \ln \frac{\xi(\delta) + 1 - 2\delta}{\xi(\delta) - 1 + 2\delta}$$

For negative w a small force may lead to much larger changes in length than without interaction. This explains, for example, how in proteins huge channels may open although the acting forces are quite small. In the case of Myoglobine, that is how the penetration of oxygen in the protein becomes possible.

2 Flory-Huggins Theory for Biopolymer solutions

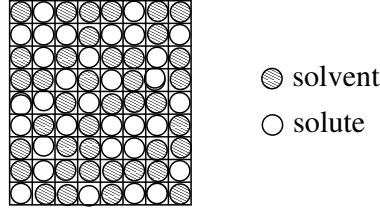
In the early 1940s, Paul Flory and Maurice Huggins, working independently, developed a theory based upon a simple lattice model that could be used to

understand the nonideal nature of polymer solutions. We consider a lattice model where the lattice sites are chosen to be of the size of a solvent molecule and where all lattice sites are occupied by one molecule.

2.1 monomeric solution

As the simplest example, consider the mixing of a low-molecular-weight solvent (component α) with a low-molecular-weight solute (component β). The solute molecule is assumed to have the same size as a solvent molecule and therefore every lattice site is occupied by one solvent molecule or by one solute molecule at a given time.

Figure 16: two-dimensional Flory-Huggins lattice



The increase in entropy ΔS_m due to mixing of solvent and solute is given by

$$\Delta S_m = k \ln \Omega = k \ln \left(\frac{N!}{N_\alpha! N_\beta!} \right)$$

where $N = N_\alpha + N_\beta$ is the total number of lattice sites. Using Stirling's approximation leads to

$$\begin{aligned} \Delta S_m &= k(N \ln N - N - N_\alpha \ln N_\alpha + N_\alpha - N_\beta \ln N_\beta + N_\beta) \\ &= k(N \ln N - N_\alpha \ln N_\alpha - N_\beta \ln N_\beta) \\ &= -kN_\alpha \ln \frac{N_\alpha}{N} - kN_\beta \ln \frac{N_\beta}{N} \end{aligned}$$

Inserting the volume fractions

$$\phi_\alpha = \frac{N_\alpha}{N_\alpha + N_\beta} \quad \phi_\beta = \frac{N_\beta}{N_\alpha + N_\beta}$$

the mixing entropy can be written in the well known form

$$\Delta S_m = -Nk(\phi_\alpha \ln \phi_\alpha + \phi_\beta \ln \phi_\beta)$$

Neglecting boundary effects (or using periodic b.c.) the number of nearest neighbour pairs is (c is the coordination number)

$$N_{nn} = N \frac{c}{2}$$

These are divided into

$$N_{\alpha\alpha} = \frac{N_\alpha c}{2} \phi_\alpha = \frac{N \phi_\alpha^2 c}{2} \quad N_{\beta\beta} = \frac{N_\beta c}{2} \phi_\beta = \frac{N \phi_\beta^2 c}{2} \quad N_{\alpha\beta} = N \phi_\alpha \phi_\beta c$$

The average interaction energy is

$$\bar{w} = \frac{1}{2} N c \phi_\alpha^2 w_{\alpha\alpha} + \frac{1}{2} N c \phi_\beta^2 w_{\beta\beta} + N c \phi_\alpha \phi_\beta w_{\alpha\beta}$$

which after the substitution

$$w_{\alpha\beta} = \frac{1}{2} (w_{\alpha\alpha} + w_{\beta\beta} - w)$$

becomes

$$\bar{w} = -\frac{1}{2} N c \phi_\alpha \phi_\beta w + \frac{1}{2} N c \phi_\alpha (\phi_\alpha w_{\alpha\alpha} + \phi_\beta w_{\alpha\alpha}) + \frac{1}{2} N c \phi_\beta (\phi_\beta w_{\beta\beta} + \phi_\alpha w_{\beta\beta})$$

and since $\phi_\alpha + \phi_\beta = 1$

$$\bar{w} = -\frac{1}{2} N c \phi_\alpha \phi_\beta w + \frac{1}{2} N c (\phi_\alpha w_{\alpha\alpha} + \phi_\beta w_{\beta\beta})$$

Now the partition function is

$$\begin{aligned} Z &= z_\alpha^{N_\alpha} z_\beta^{N_\beta} e^{-N_\alpha c w_{\alpha\alpha} / 2kT} e^{-N_\beta c w_{\beta\beta} / 2kT} e^{N_\alpha N_\beta c w / 2NkT} \frac{N!}{N_\alpha! N_\beta!} \\ &= (z_\alpha e^{-c w_{\alpha\alpha} / 2kT})^{N_\alpha} (z_\beta e^{-c w_{\beta\beta} / 2kT})^{N_\beta} e^{N_\alpha N_\beta c w / 2NkT} \frac{N!}{N_\alpha! N_\beta!} \end{aligned}$$

The free energy is

$$\begin{aligned} F = -kT \ln Z &= -N_\alpha kT \ln z_\alpha - N_\beta kT \ln z_\beta + N_\alpha \frac{c}{2} w_{\alpha\alpha} + N_\beta \frac{c}{2} w_{\beta\beta} - \frac{N_\alpha N_\beta c w}{2N} \\ &\quad + NkT (\phi_\alpha \ln \phi_\alpha + \phi_\beta \ln \phi_\beta) \end{aligned}$$

for the pure solvent the free energy is

$$F(N_\alpha = N, N_\beta = 0) = -N_\alpha kT \ln z_\alpha + N_\alpha \frac{c}{2} w_{\alpha\alpha}$$

and for the pure solute

$$F(N_\alpha = 0, N_\beta = N) = -N_\beta kT \ln z_\beta + N_\beta \frac{c}{2} w_{\beta\beta}$$

hence the change in free energy is

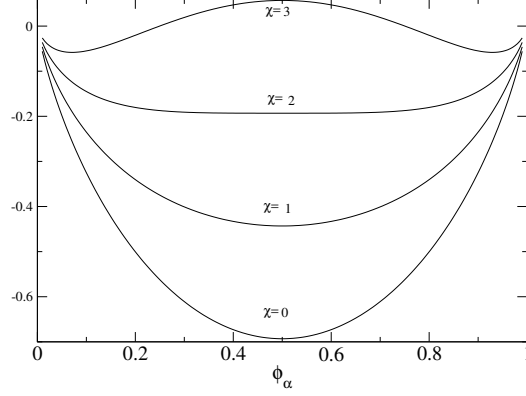
$$\Delta F_m = -\frac{N_\alpha N_\beta c w}{2N} + NkT (\phi_\alpha \ln \phi_\alpha + \phi_\beta \ln \phi_\beta)$$

with the energy change (van Laar heat of mixing)

$$\Delta E_m = -\frac{N_\alpha N_\beta c w}{2N} = -N \frac{c w}{2} \phi_\alpha \phi_\beta = NkT \chi \phi_\alpha \phi_\beta$$

The last equation defines the Flory interaction parameter $\chi = -\frac{cw}{2kT}$.

Figure 17: Free energy change $\Delta F/NkT$ of a binary mixture with interaction



For $\chi > 2$ the free energy has two minima and two stable phases exist. This is seen from solution of

$$\begin{aligned} 0 &= \frac{\partial \Delta F}{\partial \phi_\alpha} = NkT \frac{\partial}{\partial \phi_\alpha} (\chi \phi_\alpha (1 - \phi_\alpha) + \phi_\alpha \ln \phi_\alpha + (1 - \phi_\alpha) \ln (1 - \phi_\alpha)) \\ &= NkT (\chi (1 - 2\phi_\alpha) + \ln \frac{\phi_\alpha}{1 - \phi_\alpha}) \end{aligned}$$

This equation has as one solution $\phi_\alpha = 1/2$. This solution becomes unstable for $\chi > 2$ as can be seen from the sign change of the second derivative

$$\frac{\partial^2 \Delta F}{\partial \phi_\alpha^2} = NkT \left(\frac{1 - 2\chi \phi_\alpha + 2\chi \phi_\alpha^2}{\phi_\alpha^2 - \phi_\alpha} \right) = NkT (4 - 2\chi)$$

2.2 Polymeric solution

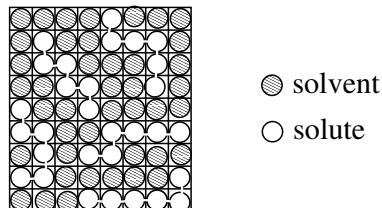
Now consider N_β polymer molecules which consist of M units and hence occupy a total of MN_β lattice sites. The volume fractions are now

$$\phi_\alpha = \frac{N_\alpha}{N_\alpha + MN_\beta} \quad \phi_\beta = \frac{MN_\beta}{N_\alpha + MN_\beta}$$

and the number of lattice sites is

$$N = N_\alpha + MN_\beta$$

Figure 18: lattice model for a polymer



The entropy is given by

$$\Delta S = \Delta S_m + \Delta S_d = k \ln \Omega(N_\alpha, N_\beta)$$

It consists of the mixing entropy and a contribution due to the different conformations of the polymers (disordering entropy). The latter can be eliminated by subtracting the entropy for $N_\alpha = 0$.

$$\Delta S_m = \Delta S - \Delta S_d = k \frac{\ln \Omega(N_\alpha, N_\beta)}{\ln \Omega(0, N_\beta)}$$

In the following we will calculate $\Omega(N_\alpha, N_\beta)$ in an approximate way. We use a mean-field method where one polymer after the other is distributed over the lattice, taking into account only the available volume but not the configuration of all the other polymers. Under that conditions Ω factorizes

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

where ν_i counts the number of possibilities to put the i -th polymer onto the lattice. It will be calculated by adding one segment after the other and counting the number of possible ways.

$$\nu_{i+1} = \prod_{s=1}^M n_s^{i+1}$$

The first segment of the $(i+1)$ -th polymer molecule can be placed onto

$$n_1^{i+1} = N - iM$$

lattice sites.

The second segment has to be placed on a neighbouring position. Depending on the coordination number of the lattice there are c possible neighbouring sites. But only a fraction of

$$f = 1 - \frac{iM}{N}$$

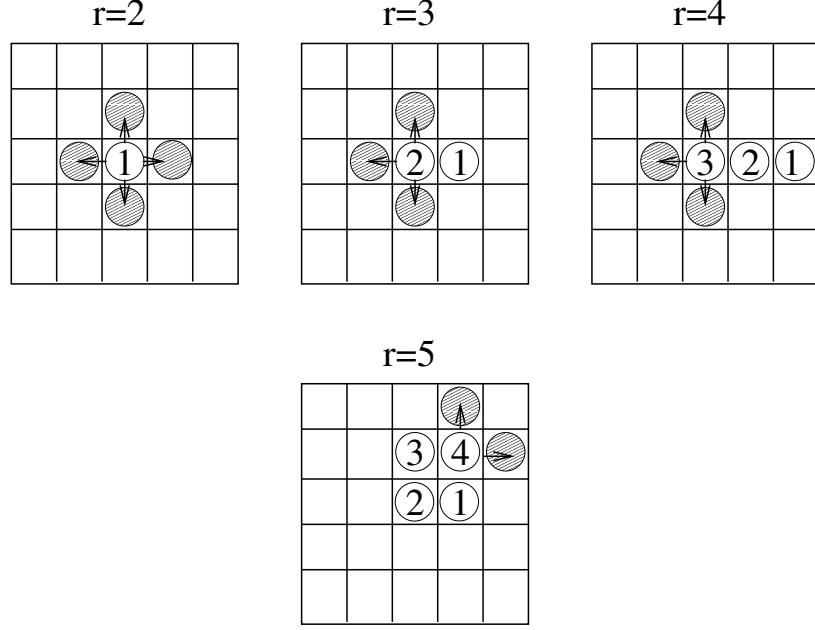
of these is unoccupied. Hence for the second segment we have

$$n_2^{i+1} = c \left(1 - \frac{iM}{N} \right)$$

For the third segment only $c - 1$ neighbouring positions are available

$$n_3^{i+1} = (c - 1) \left(1 - \frac{iM}{N} \right)$$

Figure 19: available positions



For the following segments $r = 4 \dots M$ we assume that the number of possible sites is the same as for the third segment. This introduces some error since for some configurations the number is reduced due to the excluded volume. This error, however is small compared with the crudeness of the whole model. Multiplying all the factors we have

$$\begin{aligned} \nu_{i+1} &= (N - iM)c(c - 1)^{M-2} \left(1 - \frac{iM}{N} \right)^{M-1} \\ &\approx (N - iM)^M \left(\frac{c-1}{N} \right)^{M-1} \end{aligned}$$

and the entropy is

$$\begin{aligned} \Delta S &= k \ln \left[\frac{1}{N_\beta!} \prod_{i=1}^{N_\beta} (N - iM)^M \left(\frac{c-1}{N} \right)^{M-1} \right] \\ &= -kN_\beta \ln N_\beta + kN_\beta + kN_\beta(M - 1) \ln \left(\frac{c-1}{N} \right) + kM \sum_{i=1}^{N_\beta} \ln(N - iM) \end{aligned}$$

The sum will be approximated by an integral

$$\begin{aligned} \sum_{i=1}^{N_\beta} \ln(N - iM) &\approx \int_0^{N_\beta} \ln(N - Mx) dx = \left(x - \frac{N}{M} \right) (\ln(N - Mx) - 1) \Big|_0^{N_\beta} \\ &= -\frac{N_\alpha}{M} (\ln N_\alpha - 1) + \frac{N}{M} (\ln N - 1) \end{aligned}$$

Finally we get

$$\Delta S = -kN_\beta \ln N_\beta + kN_\beta + kN_\beta(M-1) \ln\left(\frac{c-1}{N}\right) + k(N \ln N - N + N_\alpha - N_\alpha \ln N_\alpha)$$

The disorder entropy is obtained by substituting $N_\alpha = 0$ and $N = MN_\beta$

$$\Delta S_d = \Delta S(N_\alpha = 0) = -kN_\beta \ln N_\beta + kN_\beta + kN_\beta(M-1) \ln\left(\frac{c-1}{MN_\beta}\right) + k(MN_\beta \ln MN_\beta - MN_\beta)$$

and the difference gives the mixing entropy

$$\begin{aligned} \Delta S_m = \Delta S - \Delta S_d &= k(N \ln N - N + N_\alpha - N_\alpha \ln N_\alpha - MN_\beta \ln MN_\beta + MN_\beta) \\ &\quad + kN_\beta(M-1)(\ln MN_\beta - \ln N) \end{aligned}$$

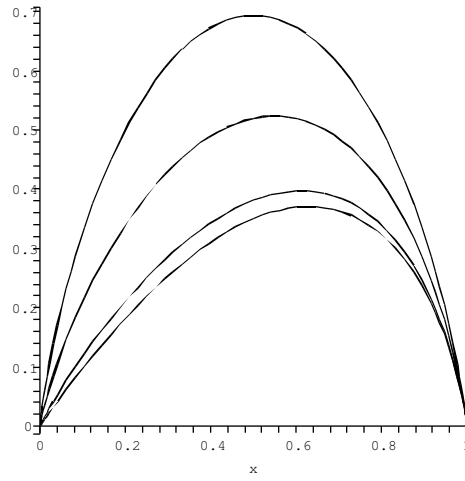
$$= k(N \ln N - N_\alpha \ln N_\alpha - MN_\beta \ln MN_\beta + MN_\beta \ln MN_\beta - MN_\beta \ln N - N_\beta \ln MN_\beta + N_\beta \ln N)$$

$$= -k\left(N_\alpha \ln \frac{N_\alpha}{N} + N_\beta \ln \frac{MN_\beta}{N}\right) = -kN_\alpha \ln \phi_\alpha - kN_\beta \ln \phi_\beta$$

$$= -Nk\left(\phi_\alpha \ln \phi_\alpha + \frac{\phi_\beta}{M} \ln \phi_\beta\right)$$

Figure 20: mixing entropy

$\Delta S_m/Nk$ is shown as a function of ϕ_β for $M=1,2,10,100$



In comparison with the expression for a solution of molecules without internal flexibility we obtain an extra contribution to the entropy of

$$-N_{\beta}k \ln \frac{MN_{\beta}}{N} + N_{\beta}k \ln \frac{N_{\beta}}{N} = -N_{\beta}k \ln M$$

Next we calculate the change of energy due to mixing ΔE_m . $w_{\alpha\alpha}$ is the interaction energy between nearest-neighbour solvent molecules, $w_{\beta\beta}$ between nearest-neighbour polymer units (not chemically bonded) and $w_{\alpha\beta}$ between one solvent molecule and one polymer unit. The probability that any site is occupied by a solvent molecule is ϕ_{α} and by a polymer unit is ϕ_{β} . We introduce an effective coordination number \bar{c} which takes into account that a solvent molecule has c neighbours whereas a polymer segment interacts only with $c-2$ other molecules.

Then

$$N_{\alpha\alpha} = \bar{c}\phi_{\alpha} \frac{N_{\alpha}}{2} \quad N_{\beta\beta} = M\bar{c}\phi_{\beta} \frac{N_{\beta}}{2}$$

$$N_{\alpha\beta} = \bar{c}\phi_{\alpha}N_{\beta}$$

In the pure polymer $\phi_{\beta} = 1$ and $N_{\beta\beta} = M\bar{c}N_{\beta}/2$ whereas in the pure solvent $N_{\alpha\alpha} = \bar{c}N_{\alpha}/2$.

The energy change is

$$\begin{aligned} \Delta E_m &= \bar{c}w_{\alpha\alpha}\phi_{\alpha} \frac{N_{\alpha}}{2} + w_{\beta\beta}M\bar{c}\phi_{\beta} \frac{N_{\beta}}{2} + w_{\alpha\beta}M\bar{c}\phi_{\alpha}N_{\beta} \\ &\quad - w_{\alpha\alpha}\bar{c} \frac{N_{\alpha}}{2} - w_{\beta\beta}M\bar{c} \frac{N_{\beta}}{2} \\ &= -\bar{c}w_{\alpha\alpha} \frac{N_{\alpha}}{2} \phi_{\beta} - \bar{c}Mw_{\beta\beta} \frac{N_{\beta}}{2} \phi_{\alpha} + w_{\alpha\beta}M\bar{c}\phi_{\alpha}N_{\beta} \\ &= (w_{\alpha\beta} - \frac{w_{\alpha\alpha} + w_{\beta\beta}}{2})\bar{c}N\phi_{\alpha}\phi_{\beta} \\ &= -\frac{w}{2}\bar{c}N\phi_{\alpha}\phi_{\beta} \\ &= NkT\chi\phi_{\alpha}\phi_{\beta} \end{aligned}$$

with the Flory interaction parameter

$$\chi = -\frac{w\bar{c}}{2kT}$$

For the change in free energy we find

$$\frac{\Delta F_m}{NkT} = \frac{\Delta E_m}{NkT} - \frac{\Delta S_m}{Nk} = \phi_{\alpha} \ln \phi_{\alpha} + \frac{\phi_{\beta}}{M} \ln \phi_{\beta} + \chi\phi_{\alpha}\phi_{\beta}$$

2.3 phase transitions

In equilibrium the free energy (if volume is constant) has a minimum value. Hence a homogeneous system becomes unstable and separates into two phases if the free energy of the two-phase system is lower, i.e. the following equation can be fulfilled

stability criterion

A phase separation is energetically favourable if

$$\Delta F_m(\phi_\beta, N) > \Delta F_m(\phi'_\beta, N') + \Delta F_m(\phi''_\beta, N - N')$$

But since $\Delta F_m = N\Delta f_m(\phi_\beta)$ is proportional to N , this condition becomes

$$N\Delta f_m(\phi_\beta) > N'\Delta f_m(\phi'_\beta) + (N - N')\Delta f_m(\phi''_\beta)$$

Since the total numbers N_α, N_β are conserved we have

$$N\phi_\beta = N'\phi'_\beta + (N - N')\phi''_\beta$$

or

$$N' = N \frac{\phi_\beta - \phi''_\beta}{\phi'_\beta - \phi''_\beta} \quad (N - N') = N \frac{\phi'_\beta - \phi_\beta}{\phi'_\beta - \phi''_\beta}$$

But since N as well as $(N - N')$ should be positive numbers there are two possible cases:

$$\phi'_\beta - \phi''_\beta > 0 \quad \phi_\beta - \phi''_\beta > 0 \quad \phi'_\beta - \phi_\beta > 0$$

$$\phi'_\beta - \phi''_\beta < 0 \quad \phi_\beta - \phi''_\beta < 0 \quad \phi'_\beta - \phi_\beta < 0$$

which means that one of ϕ'_β and ϕ''_β must be larger than ϕ_β and one smaller. By renaming we always can choose the order

$$\phi'_\beta < \phi_\beta < \phi''_\beta$$

The stability criterion becomes

$$\Delta f_m(\phi_\beta) > \frac{\phi''_\beta - \phi_\beta}{\phi''_\beta - \phi'_\beta} \Delta f_m(\phi'_\beta) + \frac{\phi_\beta - \phi'_\beta}{\phi''_\beta - \phi'_\beta} \Delta f_m(\phi''_\beta)$$

or with the abbreviation

$$h' = \phi_\beta - \phi'_\beta \quad h'' = \phi''_\beta - \phi_\beta$$

as

$$\frac{\Delta f(\phi_\beta - h') - \Delta f(\phi_\beta)}{h'} + \frac{\Delta f(\phi_\beta + h'') - \Delta f(\phi_\beta)}{h''} < 0$$

but that means the curvature has to be negative or locally

$$\frac{\partial^2 \Delta f(\phi_\beta)}{\partial \phi_\beta^2} < 0$$

Figure 21: stability criterion for the free energy

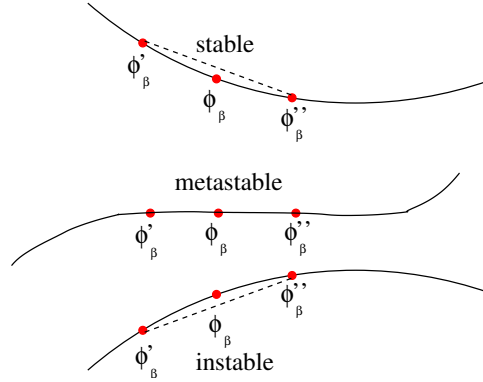
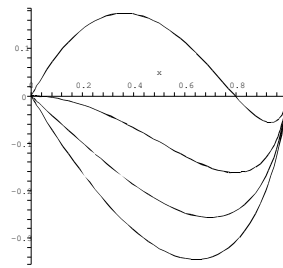
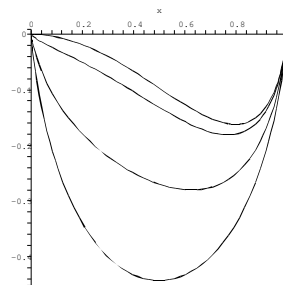


Figure 22: Free energy as a function of solute concentration



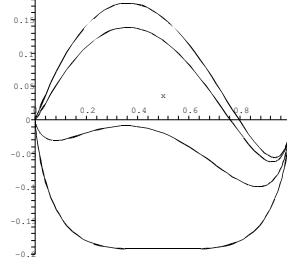
$\Delta F_m/NkT$ is shown for $M=1000$ and $\chi = 0.1, 0.5, 1.0, 2.0$

Figure 23: Free energy as a function of solute concentration



$\Delta F_m/NkT$ is shown for $\chi = 1.0$ and $M=1, 2, 10, 1000$

Figure 24: Free energy as a function of solute concentration



$\Delta F_m/NkT$ is shown for $\chi = 2.0$ and $M=1,2,10,1000$

critical coupling

Above a certain value of $\chi = \chi_c(M)$ instabilities appear. To find this critical value we have to look for the metastable case with

$$0 = \frac{\partial^2}{\partial^2 \phi_b} \Delta f(\phi_b) = \frac{1}{1 - \phi_b} + \frac{1}{M\phi_b} - 2\chi$$

In principle the critical χ value can be found from solving this quadratic equation for ϕ_b and looking for real roots in the range $0 \leq \phi_b \leq 1$. Here, however a simpler strategy can be applied. At the boundaries of the interval $[0, 1]$ of possible ϕ_b -values the second derivative is positive

$$\frac{\partial^2}{\partial^2 \phi_b} \Delta f(\phi_b) \rightarrow \frac{1}{M\phi_b} > 0 \quad \text{for } \phi_b \rightarrow 0$$

$$\frac{\partial^2}{\partial^2 \phi_b} \Delta f(\phi_b) \rightarrow \frac{1}{1 - \phi_b} > 0 \quad \text{for } \phi_b \rightarrow 1$$

Hence we look for a minimum of the second derivative, i.e. we solve

$$0 = \frac{\partial^3}{\partial^3 \phi_b} \Delta f(\phi_b) = \frac{1}{(1 - \phi_b)^2} - \frac{1}{M\phi_b^2}$$

this gives immediately

$$\phi_{bc} = \frac{1}{1 + \sqrt{M}}$$

Above the critical point the minimum of the second derivative is negative. Hence we are looking for a solution of

$$\frac{\partial^2}{\partial^2 \phi_b} \Delta f(\phi_b) = \frac{\partial^3}{\partial^3 \phi_b} \Delta f(\phi_b) = 0$$

Inserting ϕ_{bc} into the second derivative gives

$$0 = 1 + \frac{1}{M} + \frac{2}{\sqrt{M}} - 2\chi$$

which gives the critical value of χ

$$\chi_c = \frac{(1 + \sqrt{M})^2}{2M} = \frac{1}{2} + \frac{1}{\sqrt{M}} + \frac{1}{2M}$$

chemical potential and vapor pressure

From $dF = -SdT + \mu_\alpha dN_\alpha + \mu_\beta dN_\beta$ we obtain the change of the chemical potential as

$$\begin{aligned} \mu_\alpha - \mu_\alpha^0 &= \Delta\mu_\alpha = \left. \frac{\partial \Delta F}{\partial N_\alpha} \right|_{N_\beta, T} = \left(\frac{\partial N}{\partial N_\alpha} \frac{\partial}{\partial N} + \frac{\partial \phi_\beta}{\partial N_\alpha} \frac{\partial}{\partial \phi_\beta} \right) N \Delta f(\phi_\beta) \\ &= \Delta f(\phi_\beta) - \phi_\beta \Delta f'(\phi_\beta) = kT \left(\ln(1 - \phi_\beta) + \left(1 - \frac{1}{M}\right) \phi_\beta + \chi \phi_\beta^2 \right) \end{aligned}$$

Now the derivatives of $\Delta\mu_\alpha$ are

$$\begin{aligned} \frac{\partial}{\partial \phi_\beta} \Delta\mu_\alpha &= -\phi_\beta \Delta f''(\phi_\beta) \\ \frac{\partial^2}{\partial \phi_\beta^2} \Delta\mu_\alpha &= -\Delta f''(\phi_\beta) - \phi_\beta \Delta f'''(\phi_\beta) \end{aligned}$$

Hence the critical point can be also found by solving

$$\frac{\partial^2}{\partial \phi_\beta^2} \Delta\mu_\alpha = \frac{\partial}{\partial \phi_\beta} \Delta\mu_\alpha = 0$$

employing the ideal gas approximation this gives for the vapor pressure

$$\frac{p_\alpha}{p_\alpha^0} = e^{\frac{\mu_\alpha - \mu_\alpha^0}{kT}} = (1 - \phi_\beta) e^{(\chi \phi_\beta^2 + (1 - 1/M) \phi_\beta)}$$

and since the exponential is a monotonous function another condition for the critical point is

$$\frac{\partial}{\partial \phi_\beta} \frac{p_\alpha}{p_\alpha^0} = \frac{\partial^2}{\partial \phi_\beta^2} \frac{p_\alpha}{p_\alpha^0} = 0$$

Figure 25: ideal gas approximation for the vapor pressure

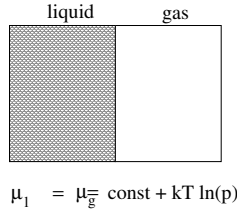


Figure 26: vapor pressure of a binary mixture with interaction (M=1)

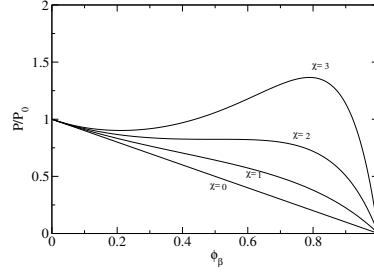
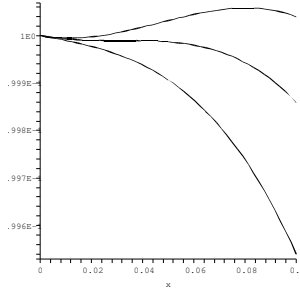


Figure 27: vapor pressure of a polymer solution with interaction (M=1000)



$$\chi = 0.5, 0.532, 0.55$$

phase diagram

In the simple Flory-Huggins theory the interaction parameter is proportional to $\frac{1}{T}$. Hence we can write it as

$$\chi = \frac{T_0 \chi_0}{T}$$

and discuss the free energy change as a function of ϕ_β and T.

$$\Delta F = NkT \left((1 - \phi_\beta) \ln(1 - \phi_\beta) + \frac{\phi_\beta}{M} \ln \phi_\beta \right) + NkT_0 \chi_0 \phi_\beta (1 - \phi_\beta)$$

The turning points follow from

$$0 = \frac{\partial^2}{\partial \phi_\beta^2} \Delta F = Nk \left(\frac{T}{1 - \phi_\beta} + \frac{T}{M \phi_\beta} - 2T_0 \chi_0 \right)$$

as

$$\phi_{\beta,TP} = \frac{1}{2} + \frac{T(1 - M) \pm \sqrt{T^2(M - 1)^2 + 4T_0 \chi_0 M (T_0 \chi_0 M - T - 4MT)}}{4T_0 \chi_0 M}$$

This defines the spinodal curve which separates the instable from the metastable region

Figure 28: Spinodal for M=1

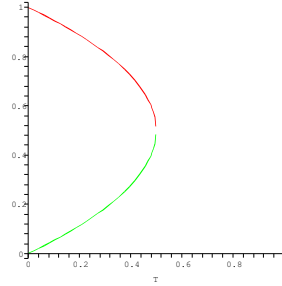
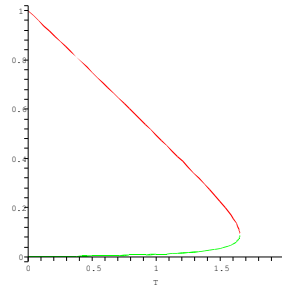


Figure 29: Spinodal for M=100



Which is the minimum free energy of a two-phase system? The free energy has the form

$$\Delta F = \Delta F^1 + \Delta F^2 = N^1 kT \Delta f(\phi_\beta^1) + N^2 kT \Delta f(\phi_\beta^2)$$

with

$$N^j = N_\alpha^j + MN_\beta^j \quad \phi_\beta^j = \frac{MN_\beta^j}{N^j}$$

The minimum free energy can be found from the condition that exchange of solvent or solute molecules between the two phases does not change the free energy, i.e. the chemical potentials in the two phases are the same

$$0 = d\Delta F = \left(\frac{\partial \Delta F^1}{\partial N_\alpha^1} - \frac{\partial \Delta F^2}{\partial N_\alpha^2} \right) dN_\alpha + \left(\frac{\partial \Delta F^1}{\partial N_\beta^1} - \frac{\partial \Delta F^2}{\partial N_\beta^2} \right) dN_\beta$$

$$0 = \mu_\alpha^1 - \mu_\alpha^2 = \mu_\beta^1 - \mu_\beta^2$$

or

$$0 = (\Delta f^1 - \phi_\beta^1 \frac{\partial}{\partial \phi_\beta^1} \Delta f^1) - (\Delta f^2 - \phi_\beta^2 \frac{\partial}{\partial \phi_\beta^2} \Delta f^2)$$

$$0 = (\delta f^1 + (1 - \phi_\beta^1) \frac{\partial}{\partial \phi_\beta^1} \Delta f^1) - (\Delta f^2 + (1 - \phi_\beta^2) \frac{\partial}{\partial \phi_\beta^2} \Delta f^2)$$

From the difference of these two equations we find

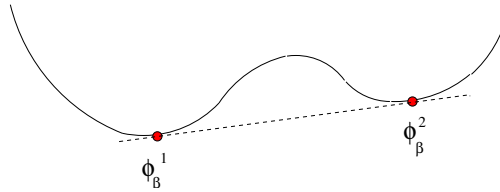
$$\frac{\partial \Delta f^1}{\partial \phi_\beta^1} = \frac{\partial \Delta f^2}{\partial \phi_\beta^2}$$

and hence the slope of the free energy has to be the same for both phases. Inserting into the first equation then gives

$$\Delta f^1 - \Delta f^2 = (\phi_\beta^1 - \phi_\beta^2) \Delta f'$$

which shows that the concentrations of the two phases can be found by the wellknown “common tangent” construction

Figure 30: common tangent construction



These so called binodal points give the border to the stable one-phase region. Between spinodal and binodal the system is metastable. It is stable against small fluctuations since the curvature of the free energy is positive. It is, however unstable against larger scale fluctuations.

Figure 31: phase diagram

