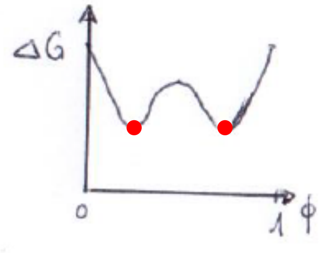
Solutions to Soft Matter exercise 6: Phase separations in polymer solutions

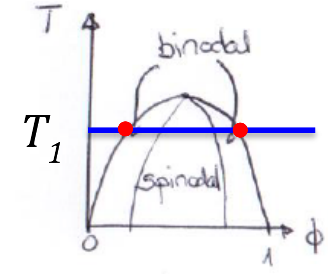
1. Spinodal decomposition

For a binodal mixture, we assume $N_1 = N_2 = 1$ and thus obtain

a. $\frac{\Delta G}{k_B T} = \phi ln\phi + (1-\phi)\ln(1-\phi) + \chi\phi(1-\phi)$



b. The phase diagram is constructed from graphs of $\Delta G(\phi)$ measured for different temperatures. The spinodal curve connects the points from the graphs of $\Delta G(\phi)$ measured for different temperatures where $\frac{\partial^2 G(\phi)}{\partial\phi^2} = 0$, the binodal curve the minima in the graphs of $\Delta G(\phi)$ measured for different temperatures where $\frac{\partial G(\phi)}{\partial\phi} = 0$.



c. The compositions are indicated in (a) and (b) and indicated with red circles.

d. The spinodal decomposition is a spontaneous phase separation that occurs because of small fluctuations in temperature or concentrations. It can occur if $\frac{\partial^2 G}{\partial\phi^2} < 0$ and results in two interconnected phases.

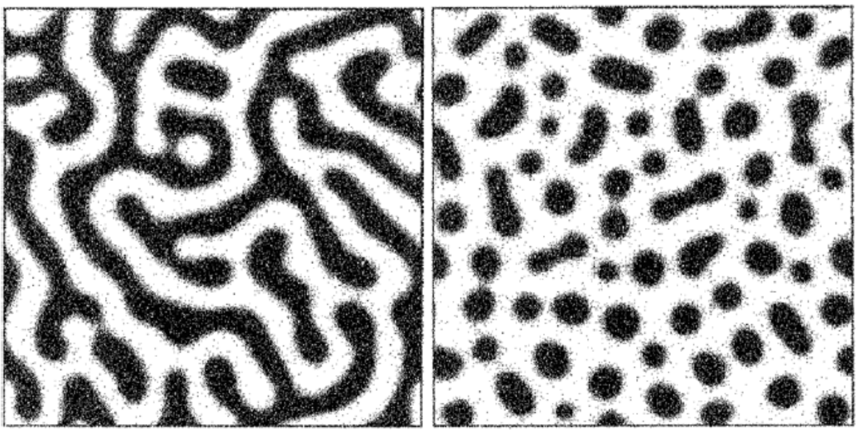
e. The flux can be described using Fick's law: $J = -\left(D_x \frac{\partial c_x}{\partial x} + D_y \frac{\partial c_y}{\partial y} + D_z \frac{\partial c_z}{\partial z}\right)$

In the case of phase separation, diffusion is caused by the gradient in the chemical potential and not the gradient in the concentration. Hence, one can re-write Fick's equation as

$$J = -\left(D_x \frac{c_x}{RT}\frac{\partial \mu_x}{\partial x} + D_y \frac{c_y}{RT}\frac{\partial \mu_y}{\partial y} + D_z \frac{c_z}{RT}\frac{\partial \mu_z}{\partial z}\right)$$

Using $\mu_i = \left(\frac{\partial G}{\partial N}\right)_{T,p,N_{i\neq j}}$ one finds $J = -\left(M_x \frac{\partial^2 G}{\partial \phi^2}\frac{\partial c}{\partial x} + M_y \frac{\partial^2 G}{\partial \phi^2}\frac{\partial c}{\partial y} + M_z \frac{\partial^2 G}{\partial \phi^2}\frac{\partial c}{\partial z}\right)$ such that the diffusion coefficient can be described as $D_{eff} = M\frac{\partial^2 G}{\partial \phi^2}$, here M is the positive diffusion coefficient. Within the spinodal line, $\frac{\partial^2 G}{\partial \phi^2} < 0$. Hence, D_{eff} is negative such that mass is transported in the direction of the concentration gradients (from locations with low concentrations of solutes to locations with high concentrations of solutes).

f.



Spinodal Binodal

Gebauer, D.; Kellermeier, M.; Gale, J. D.; Bergstrom, L.; Coelfen, H. *Chemical Society Reviews* **2014**, *43*, 2348

The microstructure is different. A spinodal decomposition results in interconnected phases, a binodal decomposition into islands that are surrounded by a continuous matrix. However, the composition of the two phases is the same for binodally and spinodally decomposed systems. If any of these decompositions occurs in polymer solutions used to produce e.g. coatings, the resulting coatings are rough.

2. Solubility

a. hexane and water are two solvents such that N_1 = N_2 = 1. Hence we can write the equation for the changes in the Gibbs free energy as

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

.

To calculate the solubility, we must determine the binodal line where

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

For hexane we have

$n_C = 6$

such that $\chi = 3.04 + 1.37 n_C = 11.26$

And we find

$$\phi_{H2O} = 0.999987$$

$$\phi_{nC} = 1 - \phi_{H2O} = 0.000013$$

b. For octane we have $n_C = 8$

such that

$$\chi = 3.04 + 1.37 n_C = 14$$

$$\phi_{nC} = 1 - \phi_{H2O} = 8.35 \times 10^{-7}$$

c. for dodecane we have $n_C = 12$

such that

$$\chi = 3.04 + 1.37 n_C = 19.48$$

$$\phi_{nC} = 1 - \phi_{H2O} = 3.47 \times 10^{-9}$$

3. Phase diagram of a liquid mixture

a. If we have two solvents, we have $N_1 = N_2 = 1$. Hence, we can describe the change in the Gibbs free energy as

$$\Delta G = \phi ln\phi + (1-\phi)\ln(1-\phi) + \chi\phi(1-\phi)$$

At the critical point ϕ_c, we have

$$\frac{\partial}{\partial\phi}\frac{\Delta G}{k_B T} = \frac{\partial^2}{\partial\phi^2}\frac{\Delta G}{k_B T} = \frac{\partial^3}{\partial\phi^3}\frac{\Delta G}{k_B T} = 0$$

Hence, we obtain

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

$$\frac{\partial^2 G(\phi)}{\partial\phi^2} = 0 = \frac{1}{\phi} + \frac{1}{1-\phi} - 2\chi$$

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

such that

$$\phi_c^2 = 1 - 2\phi_c + \phi_c^2$$

and

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

hence

$$\chi_c = \frac{1}{2}\left(\frac{1}{\phi_c} + \frac{1}{1-\phi_c}\right) = \frac{1}{2}(2+2) = 2 = \frac{600K}{T_c}$$

such that

$T_c = 300$ K

b. This is a lower critical solution temperature where phase separation occurs if the temperature is below the critical temperature T_c. 273 K < 300 K ➔ Hence, yes, phase separation occurs at 273 K.

c. The volume fractions correspond to the fractions at the binodal line where $\frac{\partial G}{\partial \phi} = 0$.

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

at 5°C = 278 K

$$\chi = \frac{600K}{278K} = 2.16$$

Hence, we find

$$\phi_1 = 0.27$$

$$\phi_2 = 1 - \phi_1 = 0.73$$

d. If we have two a polymer solution, we have N_1 =1000>> N_2 = 1. Hence, we can describe the change in the Gibbs free energy as

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

At the critical point ϕ_c, we have

$$\frac{\partial}{\partial\phi}\frac{\Delta G}{k_B T} = \frac{\partial^2}{\partial\phi^2}\frac{\Delta G}{k_B T} = \frac{\partial^3}{\partial\phi^3}\frac{\Delta G}{k_B T} = 0$$

Hence, we obtain

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

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

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

such that

$$\Phi_c^2(1-N) - 2\Phi + 1 = 0$$

and

$$\Phi_c = \frac{1}{1+\sqrt{N}}$$

$$\chi_c = \frac{1}{2}\left(\frac{1}{1-\Phi_c} + \frac{1}{N\Phi_c}\right)$$

For N = 1000 we can approximate

$$\Phi_c \approx \frac{1}{\sqrt{N}}$$

and hence

$$\chi_c = \frac{1}{2}\left(\frac{1}{1-\frac{1}{\sqrt{N}}} + \frac{1}{\sqrt{N}}\right) = \frac{1}{2}\left(\frac{1}{1-\frac{1}{\sqrt{1000}}} + \frac{1}{\sqrt{1000}}\right) = 0.532$$

Because this system is not an ideal solution any more, the formula to calculate T_c from the critical interaction parameter does not apply any more. Instead, it has the form $\chi_c = A + \frac{B}{T_c}$.

In this, case we can estimate the interaction parameter using $\chi = \frac{z}{2k_B T}\left(2E_{AB} - E_{AA} - E_{BB}\right)$

4. Phase diagram of a polymer mixture

a. The composition of the solution is different to the critical composition where the system transitions from the liquid phase directly into the spinodally decomposed region. Hence, upon cooling, the system first reaches the region where it undergoes binodal decomposition such that it contains individual, isolated nuclei that are contained in a continuous matrix.

b. In this case, the composition of the liquid is equal to the critical composition such that the system transitions from the liquid directly into the spinodal region upon cooling. Hence, the microstructure is composed of two percolating, interconnected networks.

c. In an ideal solution one has two solvents such that $N_1 = N_2 = 1$. Hence the Gibbs free energy plotted as a function if the composition is symmetric and $\Phi_c = 0.5$. This is also the case if the degree of polymerization for two polymers is the same such that $N_1 = N_2 > 1$. However, if the degree of polymerization of the two polymers that are mixed is not the same N_1 is different from N_2, such that $\Delta G(\Phi)$ is not symmetric and $\Phi_c \neq 0.5$.