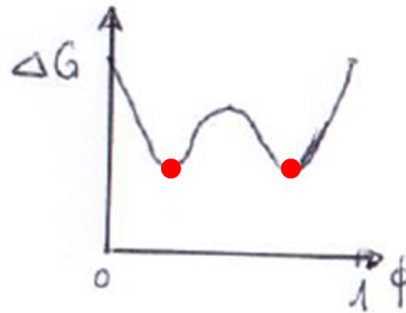


## Solutions to Soft Matter Exercise - Chapter 6: Phase Transitions

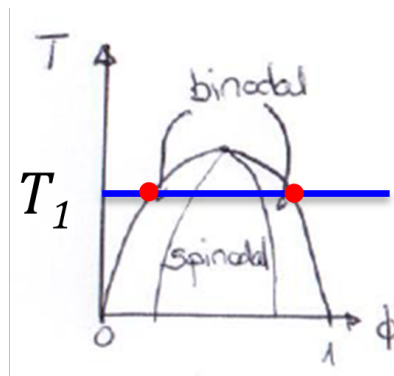
### 1. Spinodal Decomposition

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

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



b. The phase diagram is constructed from graphs of  $\Delta G(\phi)$  at 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  $\frac{\partial G(\phi)}{\partial \phi} = 0$ .



- The compositions are indicated in (a) and (b) and indicated with red circles.
- 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.
- The flux can be determined using Fick's law:

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

$$J = -D \nabla c$$

In the case of phase separation, diffusion is caused by the gradient in the chemical potential and not the gradient in the concentration. Therefore, we can use the relationship between chemical potential and concentration:

$$\nabla c = \frac{c}{RT} \nabla \mu$$

to re-write Fick's law as:

$$J = -\frac{Dc}{RT} \nabla \mu$$

Which expands to:

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

Using  $\mu_i = (\partial G / \partial N)_{T,p,N_{i \neq j}}$ , we find:

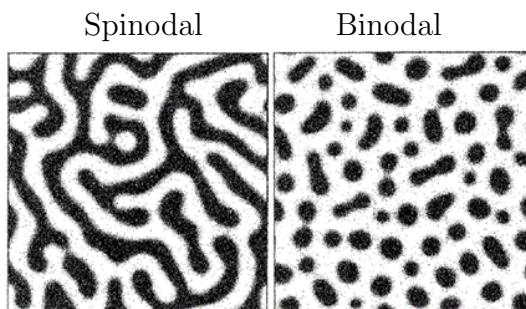
$$J = -\left(M_x \frac{\partial^2 G}{\partial \phi^2} \frac{\partial c}{\partial x} + M_y \frac{\partial^2 G}{\partial \phi^2} \frac{\partial c}{\partial y} + M_z \frac{\partial^2 G}{\partial \phi^2} \frac{\partial c}{\partial z}\right)$$

With this, 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 ( $\frac{\partial^2 G}{\partial \phi^2} < 0$ ), which results in a negative  $D_{eff}$  such that mass is transported in the direction of the concentration gradient (from locations with low concentrations of solute to locations with high concentrations of solute).

- f. Spinodal decomposition results in interconnected phases, while binodal decomposition results in islands that are surrounded by a continuous matrix. If any of these decompositions occur in polymer solutions used to produce coating, the resultant coating is rough.



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## 2. Solubility

- a. Hexane and water are two solvents where  $N_1 = N_2 = 1$ . Therefore, we can write the equation for the changes in 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:

$$\begin{aligned}\chi &= 3.04 + 1.37n_c = 11.26 \\ \phi_{H_2O} &= 0.999987 \\ \phi_{nC} &= 1 - \phi_{H_2O} = 1.3 \times 10^{-5}\end{aligned}$$

b. For octane, we have  $n_C = 8$ , such that:

$$\begin{aligned}\chi &= 3.04 + 1.37n_C = 14 \\ \phi_{nC} &= 1 - \phi_{H_2O} = 8.35 \times 10^{-7}\end{aligned}$$

c. For dodecane, we have  $n_C = 12$ , such that:

$$\begin{aligned}\chi &= 3.04 + 1.37n_C = 19.48 \\ \phi_{nC} &= 1 - \phi_{H_2O} = 3.47 \times 10^{-9}\end{aligned}$$

### 3. Phase Diagram of a Liquid Mixture

a. if we have two solvents, we have  $N_1 = N_2 = 1$ . Therefore, 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  $\phi_c$ , we have:

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

From this, 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:  $\phi_c^2 = 1 - 2\phi_c + \phi_c^2$  where  $\phi_c = 1/2$

Therefore:

$$\chi_c = \frac{1}{2} \left( \frac{1}{\phi_c} + \frac{1}{1-\phi_c} \right) = \frac{1}{2}(2 + 2) = 2 = \frac{600}{T_c} \rightarrow T_c = 300K$$

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  $\rightarrow$  phase separation occurs at 273 K.

c. The volume fractions correspond to the fractions at the binodal line where:

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

At  $5^\circ\text{C}$  (278 K):  $\chi = \frac{600 \text{ K}}{278 \text{ K}} = 2.16$ , therefore we find that  $\phi_1 = 0.27$ ,  $\phi_2 = 1 - \phi_1 = 0.73$ .

- d. If we have a polymer solution wherein  $N_1 = 1000 \gg N_2 = 1$ , 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  $\phi_c$ , we have:

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

From this, 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  $\phi_c^2(1 - N) - 2\phi_c + 1 = 0$  and  $\phi_c = 1/(1 + \sqrt{N})$ ,  $\chi_c = \frac{1}{2}(\frac{1}{1 - \phi_c} + \frac{1}{N\phi_c})$ .

For  $N = 1000$ , we can approximate  $\phi_c \approx 1/\sqrt{N}$ , and therefore:

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

Because this system is not an ideal solution, the formula to calculate  $T_c$  from the critical interaction parameter does not apply. Instead, it has the form  $\chi_c = A + \frac{B}{T_c}$ . In this case, we can estimate the interaction parameter with:

$$\chi = \frac{z}{2k_B T} (2E_{AB} - E_{AA} - E_{BB})$$

#### 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. Upon cooling, the system first reaches the region where it undergoes binodal decomposition wherein individual, isolated nuclei are contained in a continuous matrix.
- b. In this case, the composition of the liquid is equal to the critical composition. The system transitions from the liquid phase directly to the spinodal region upon cooling. The microstructure is composed of two percolating, interconnected networks.
- c. In an ideal solution, two solvents are mixed where  $N_1 = N_2 = 1$ . Thus, the Gibbs free energy plotted as a function of 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 mixed polymers is not the same (i.e.  $N_1 \neq N_2$ ),  $\Delta G(\phi)$  is not symmetric and  $\phi_c \neq 0.5$ .