School of Engineering
Institute of Materials
Laboratory of Macromolecular
and Organic Materials

Polymer Science 2024/25

Exercise 11 – Solution

1. Use Origin or Excel for this question. The Flory-Huggins equation for a polymer-solvent system is

$$\Delta G_m = RT\left(\frac{\phi_1}{n_1}\ln(\phi_1) + \phi_2\ln(\phi_2) + \chi\phi_1\phi_2\right)$$

where the effective degree of polymerization n_1= 20 and the Flory-Huggins coefficient χ = $270/T$. T is the temperature in K and ϕ_i is the volume fraction of component *i*.

(i) Show that:

$$\frac{d^2\Delta G_m}{d\phi_1^2} = RT\left(\frac{1}{1-\phi_1} + \frac{1}{n_1\phi_1} - 2\chi\right)$$

$$\Delta G_m = RT\left(\frac{\phi_1}{n_1}\ln(\phi_1) + (1-\phi_1)\ln(1-\phi_1) + \chi\phi_1(1-\phi_1)\right)$$

$$\frac{d\Delta G_m}{d\phi_1} = RT\left(\frac{1}{n_1}\ln(\phi_1) + \frac{1}{n_1} - \ln(1-\phi_1) - 1 + \chi(1-\phi_1) - \chi\phi_1\right)$$

$$\frac{d^2\Delta G_m}{d\phi_1^2} = RT\left(\frac{1}{n_1\phi_1} + \frac{1}{1-\phi_1} - 2\chi\right)$$

(ii) The spinodal curve is defined as the condition where the second derivative of the Gibbs free energy of mixing, ΔG_m'', equals zero. Plot the spinodal curve of this system in the (T, ϕ_1)-space for the temperature range −100 ≤ T ≤ 100 °C.

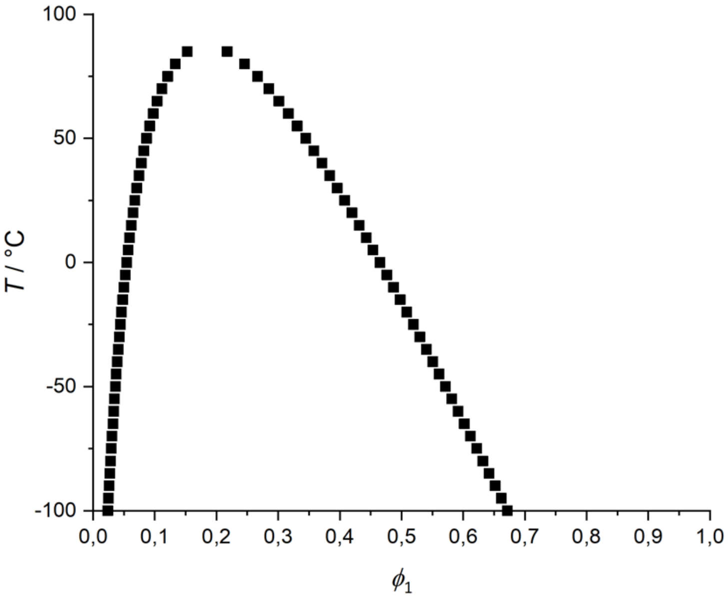
It follows Ffrom the upper expression

$$0 = \frac{1}{n_1\phi_1} + \frac{1}{1-\phi_1} - 2\chi$$

Upon rearrangement, we get the quadratic equation for ϕ_1 :

$$\mathbf{0 = 1 + (n_1 - 1 - 2n_1\chi)\phi_1 + 2n_1\chi\phi_1{}^2}$$

For both roots of the solution, we plot the temperature T against ϕ_1, whereby T is hidden in the interaction parameter.



(iii) Plot ΔG_{m} as a function of ϕ_1 for several values of T between -100 and 100 °C. Using your plots, determine the binodal curve by identifying the points of common tangent.

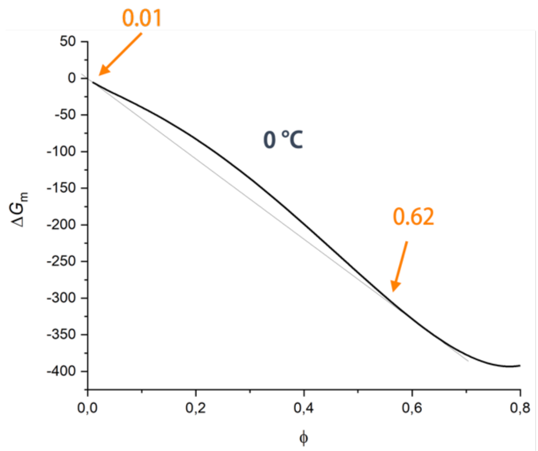
Tip: the binodal represents the boundary of phase coexistence and is defined by the points of ϕ_1 at which the Gibbs free energy curve has a common tangent at a given temperature. These points correspond to the compositions of the two coexisting phases.

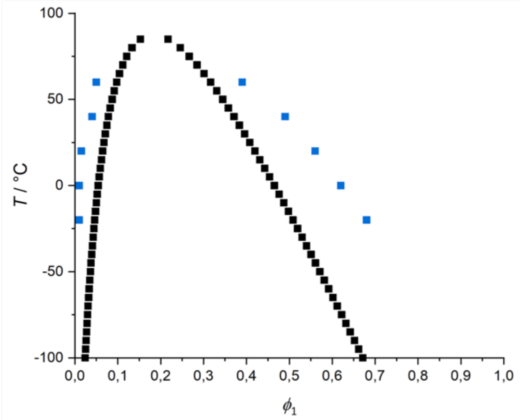
The binodal curve represents equilibrium between two coexisting phases. At each temperature, the two compositions (polymer-poor phase and the polymer-rich phase) are determined by the common tangent constructions, which satisfies the conditions of phase equilibrium:

1. **Equal chemical potential, which is reflected by equal slopes of ΔG_{m} at the two compositions.**
2. **The free energy per unit volume is the same for both phases, which ensures thermodynamic equilibrium between the two phases.**

Note that these coexisting compositions do not correspond to the minima of ΔG_{m} (which represent stable single-phase states). Instead, they are the points where the system minimizes its total free energy by splitting into two phases.

It is perhaps most straightforward to solve this question graphically by plotting ΔG_m as a function of ϕ_1 for a few selected temperatures. Below this is shown for T = 0. It is then necessary to find the points which have a common tangent (if it exists), highlighted by the orange arrows. These values are displayed in the phase diagram shown on the right side, where this procedure was repeated for a few other temperatures between -20 and 60 °C to indicate the binodal (blue).

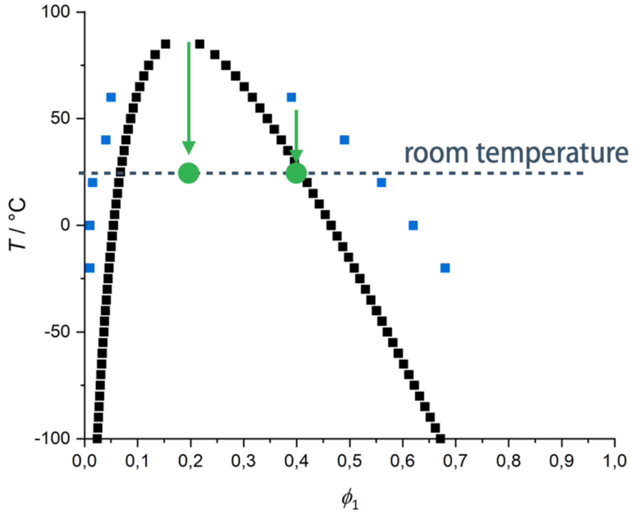




(iv) You mix the polymer and the solvent at 150 °C and cool your mixture slowly. What phase separation mechanisms do you expect for ϕ_1 = 0.18 and for ϕ_1 = 0.4?

For ϕ_1 = 0.18, this composition corresponds roughly to the critical point, where the binodal and the spinodal curves meet (you can confirm this by determining them for a few temperatures just above 80 °C). When cooling a mixture with this composition, the system crosses the binodal and the spinodal at the same time. Therefore, the phase separation mechanism will be spinodal decomposition, characterized by a gradual, continuous formation of composition fluctuations throughout the mixture.

For ϕ_1 = 0.4, the system crosses the binodal curve well before the spinodal curve as the temperature decreases. Phase separation will occur initially via a nucleation and growth mechanism, where the droplets of the new phase nucleate and grow within the existing phase. However, if the cooling is rapid, or if the mobility of the mixture is low, the system may not have sufficient time for nucleation and growth to proceed before reaching the spinodal region. In this case, phase separation may transition to spinodal decomposition, especially at lower temperatures.



(v) Phase separation will result in a polymer-rich phase and a solvent-rich phase. For ϕ_1 = 0.18, estimate the compositions and volume fractions of these two phases at T = 0 °C.

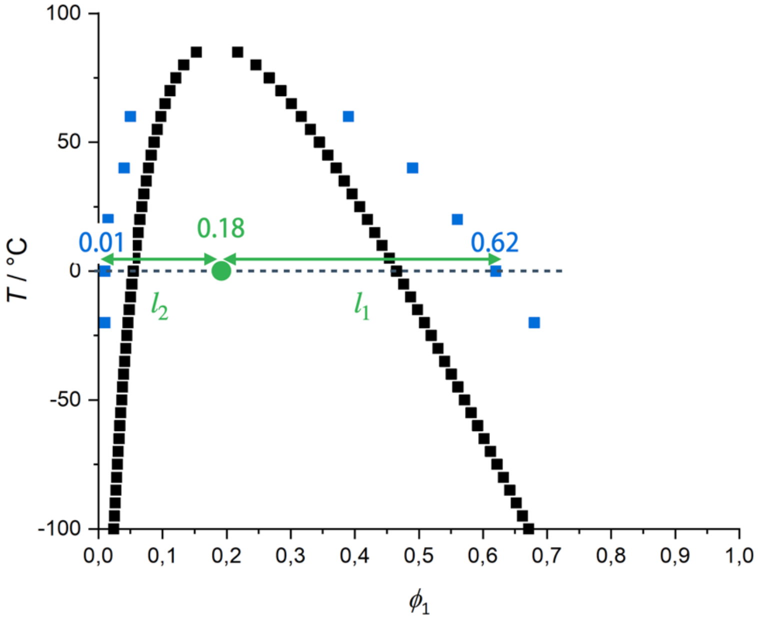
For an overall content of component 1, ϕ_1 = 0.18 and T = 0 (green point), two phases with ϕ_1 = 0.01 and 0.62 respectively will form at equilibrium. Let us call these compositions ϕ_- and ϕ_+. If the volume fraction of the first phase is *f*, the total composition is given by the mass balance:

$$f\phi_- + (1 - f)\phi_+ = \phi_1$$

Rearranging for f:

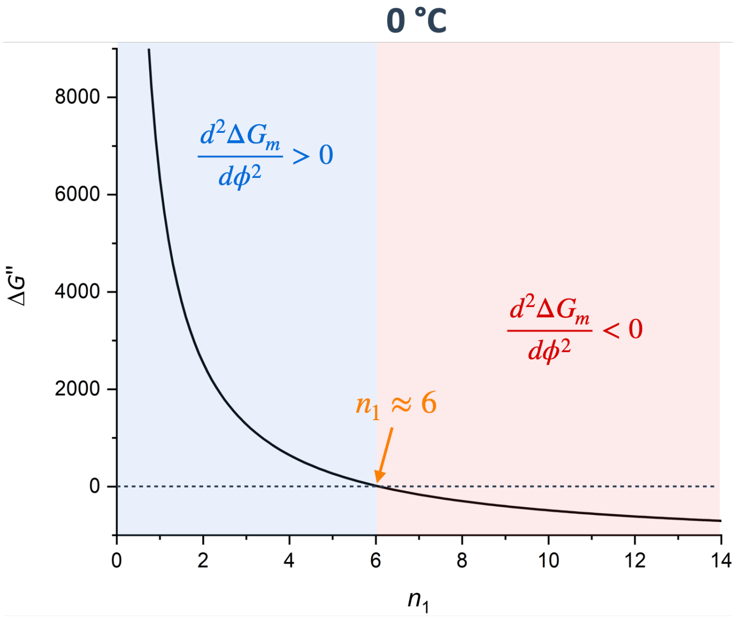
$$f = \frac{\phi_1 - \phi_+}{\phi_- - \phi_+} = \frac{l_1}{l_1 + l_2} = \frac{0.44}{0.62} = 0.72$$

where the l_1 and l_2 are the distances shown in the figure below. This is the Lever rule, which you may have encountered in a similar context elsewhere. The volume fraction of the second phase will accordingly be given by 1 – *f* = 0.28.



(vi) Suppose now that you start with a mixture of the solvent and a volume fraction $\phi_1 = 0.3$ of monomers of the polymer that you let react afterwards. At which value of n_1 (the degree of polymerization) will phase separation occur if the temperature is kept constant at 0 °C?

We must find the value of n_1, where the ΔG_m curve changes its curvature from convex ($\Delta G_m'' > 0$) to concave ($\Delta G_m'' < 0$). I did it again graphically and found n_1 to be about 6.



(vii) Explain qualitatively why high molecular weight polymer blends are most often immiscible over wide ranges of composition below their degradation temperatures.

Simply because n_1 and n_2 are high and the first two terms of the Flory-Huggins equation are close to 0 on a wide range of compositions. ΔG_m is therefore dominated by $\chi\phi_1\phi_2$, which will always be positive if χ is positive. This implies that the mixture is immiscible. χ can be negative if, for example, the specific interactions between the two components are stronger than in the pure components, which is rather exceptional (see the slides/notes for examples).

(viii) How is it possible to improve the dispersion of an immiscible binary mixture of two polymers?

See slides/notes: strong deformation of the domains of the minority phase. Careful adjustment of conditions (viscosity, interfacial tension, etc) is required.