Lecture 9:
Polymer solutions – Phase behavior

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1 Suggested reading

- *Molecular Driving Forces* – Dill and Bromberg: Chapter 32
- *Polymer Physics* – Rubinstein and Colby: Chapters 4,5
- *Soft Condensed Matter* – Jones: Chapters 3,9

2 Flory-Huggins Theory

In the last lecture, we derived the Flory-Huggins Theory for the Free Energy of mixing of polymer solutions. The derivation was general for species 1 and 2 with degree of polymerization x_1 and x_2 and is a more general expression of regular solution theory. In this discussion, we will look at what the Flory-Huggins theory tells us about phase behavior of polymers and how this differs from the behavior of small molecules. As we are no longer considering a lattice with N sites, we will revert back to using the term N as the degree of polymerization of our two species. Again we will consider two generic species A and B with degrees of polymerization N_A and N_B. Recall the form of the Free Energy of mixing per site from Flory-Huggins Theory:

$$\boxed{\frac{\Delta F^M}{N k_B T} = \Delta \bar{F}^M = \frac{\phi_A}{N_A}\ln\phi_A + \frac{\phi_B}{N_B}\ln\phi_B + \chi\phi_A\phi_B}. \tag{1}$$

We will now use the term $\Delta\bar{F}^M$ as the Free Energy of mixing per site.

3 Phase behavior of polymer solutions

In order to work with polymer solutions for industrial and biomedical applications, it is essential to understand the phase behavior of the systems. For example, we need to know under which conditions a polymer will dissolve in a solvent or if two polymers will be miscible. Polymer blends, or mixtures of multiple types of polymers, are commonly used in materials design - as discussed in the slides - and their behavior and properties depend on whether the blend is miscible or phase separates. To calculate the conditions for miscibility or phase separation we can generate model phase diagrams for the system and look at the critical points in terms of volume fraction ϕ_c and interaction parameter χ_c. For this it is convenient to define $\phi_A = \phi$ and $\phi_B = (1-\phi)$. Therefore, we can write the Flory-Huggins Theory as:

$$\Delta\bar{F}^M = \frac{\phi}{N_A}\ln\phi + \frac{1-\phi}{N_B}\ln(1-\phi) + \chi\phi(1-\phi). \tag{2}$$

Recall that a coexistence curve is defined by the common tangent:

$$\left(\frac{\partial\Delta\bar{F}^M}{\partial\phi}\right)^{'} = \left(\frac{\partial\Delta\bar{F}^M}{\partial\phi}\right)^{''} \tag{3}$$

where $'$ and $''$ denote the two phases that are in equilibrium with volume fractions $\phi^{'}$ and $\phi^{''}$, respectively. Further, the spinodal decomposition curve is determined by solving for the values of ϕ that set the second derivative of Eq. 2 = 0:

$$\frac{\partial^2}{\partial\phi^2}\Delta\bar{F}^M = 0. \tag{4}$$

Finally, the critical point is when the spinodal curve (from Eq. 4) and its derivate = 0:

$$\frac{\partial^2}{\partial\phi^2}\Delta\bar{F}^M = \frac{\partial^3}{\partial\phi^3}\Delta\bar{F}^M = 0. \tag{5}$$

In this exercise, we will explore mathematically and conceptually the phase behavior of different polymer solutions.

Solve for the critical point in terms of ϕ_c and χ_c:

4 Polymer solution phase diagrams are asymmetric

Now consider the case where you have a long polymer A and a solvent B. Define $N = N_A \gg 1$ and $N_B = 1$.
Rewrite the critical point ϕ_c and χ_c:

χ can be modeled as:

$$\chi(T) = \alpha + \frac{\beta}{T} \tag{6}$$

where α is referred to as the 'entropic part' and $\frac{\beta}{T}$ is referred to as the 'enthalpic part'. This approach accounts for some of the shortcoming of the Flory-Huggins Theory and implies that $\chi \propto \frac{1}{T}$. Therefore, χ^{-1} can be seen as an analog of T.
Sketch a phase diagram of χ^{-1} as a function of ϕ:

5 Polymer blends are often immiscible

Hydrocarbon based polymers are often immiscible with other hydrocarbon polymers. Why is this the case? If $\chi < 0$ then mixing is favorable, but this will only occur if there is a selective benefit of monomer A associating with monomer B. For most non-polar hydrocarbon chains this is not the case and $\chi \geq 0$. Now consider the mixing of two long polymers of the same length $N = N_A = N_B$.
Rewrite the critical point ϕ_c and χ_c:

Sketch a miscibility phase diagram for this system of χ^{-1} as a function of ϕ for various values of N:

Describe qualitatively why polymer-polymer miscibility is less likely than for small molecule systems: