Lecture 8:
Polymer solutions – Flory-Huggins Theory

Prof. Mark W. Tibbitt – ETH Zürich – 19 März 2019

1 Suggested reading

- *Molecular Driving Forces* – Dill and Bromberg: Chapter 32
- *Polymer Physics* – Rubinstein and Colby: Chapters 4,5

2 Flory-Huggins Theory

In the last lecture, we developed the regular solution theory from a lattice model combining the entropy and energy of mixing to calculate the free energy of mixing for regular solutions of two species with equal molecular volume. We now want to develop a theory that can account for the fact that we do not always consider only molecules that are of equivalent volume and equal volume to the lattice site. The includes the mixing of polymer chains and here we want to consider how our previous calculations change when we consider the free energy of mixing for polymers. Ideally, we would like a general approach that can handle binary polymer-polymer solutions as well as polymer-solvent solutions. To do this we will follow the method developed by Flory and Huggins known as the **Flory-Huggins Theory** and follow a lattice approach with a mean-field estimate as we did for the regular solution theory. We will calculate the entropy of mixing and the energy of mixing and combine these terms to develop a formulation for the free energy of mixing.

Here we define the system similarly as a lattice consisting of N sites of equal volume v_0. We take n_1 and n_2 as the number of molecules of species 1 and 2, respectively, with degree of polymerizations x_1 and x_2, monomer volumes v_1 and v_2 and total volumes V_1 and V_2. For the sake of simplifying the lattice model, we assume that the monomer volume is equal to the volume of a lattice site $v_1 = v_2 = v_0$. Therefore, each molecule occupies x_i lattice sites and there are n_i molecules so the total volume for species i is given as:

$$V_i = n_i x_i v_0. \tag{1}$$

From this we can see that the volume fractions ϕ_1 and ϕ_2 are given as:

$$\phi_i = \frac{n_i x_i}{n_1 x_1 + n_2 x_2} = \frac{n_i x_i}{N}. \tag{2}$$

3 Entropy of mixing for polymers

We first consider conceptually how the entropy of mixing changes as we move from regular solutions to polymer solutions. We have already explored how entropy of polymer chains is heavily dominated by the number of conformations available to the chain, which dictactes the size of a polymer and imparts entropic elasticity when a polymer chain is stretched or compressed. However, we do not predict that the conformational entropy of the polymer chains will change significantly when transitioning from free polymers in space to polymers in solution, **if we assume the chains are ideal**. That is, we ignore the excluded volume from other chains. This is to say that we expect that the number of conformations available to a polymer is approximately the same in free space and in solution. Thus, the major source of entropy associated with mixing polymers should be translational – or the fact that the whole polymer chain can access more configurations by being moved from a sample of pure polymer into a polymer blend or a solvent. In this light, we can view the whole chain as a large molecule gains translational entropy by having more locations to place its center of mass as we had in the regular solutions theory. Note: this is equivalent to the entropy of an ideal gas. Thus, the entropy per molecule can be written as:

$$S_i = k_B \ln V_i \tag{3}$$

Therefore, we can write down the entropy per molecule for the following conditions where P denotes pure and M denotes mixed:

$$\begin{aligned}
S_1^P &= k_B \ln V_1 = k_B \ln(n_1 x_1 v_0) && (4)\\
S_2^P &= k_B \ln V_2 = k_B \ln(n_2 x_2 v_0) && (5)\\
S_1^M &= k_B \ln N = k_B \ln[(n_1 x_1 + n_2 x_2) v_0] && (6)\\
S_2^M &= k_B \ln N = k_B \ln[(n_1 x_1 + n_2 x_2) v_0] && (7)
\end{aligned}$$

Therefore, we can calculate the total change in entropy on mixing:

$$\begin{aligned}
\Delta S^M &= n_1 S_1^M + n_2 S_2^M - n_1 S_1^P - n_2 S_2^P && (8)\\
&= -k_B \left[n_1 \ln\left(\frac{n_1 x_1}{n_1 x_1 + n_2 x_2}\right) + n_2 \ln\left(\frac{n_2 x_2}{n_1 x_1 + n_2 x_2}\right)\right] && (9)\\
&= -k_B \left[n_1 \ln \phi_1 + n_2 \ln \phi_2 \right] && (10)\\
\frac{\Delta S^M}{N} &= -k_B \left[\frac{n_1}{N} \ln \phi_1 + \frac{n_2}{N} \ln \phi_2 \right] && (11)\\
\frac{\Delta S^M}{N} &= -k_B \left[\frac{\phi_1}{x_1} \ln \phi_1 + \frac{\phi_2}{x_2} \ln \phi_2 \right] && (12)
\end{aligned}$$

Note that in Eq. 12, we have an analogous form of what we found for regular solution theory. Mole fraction is replaced by volume fraction and we have scaled the pre-factors by the degree of polymerization. Note that in the case where the degree of polymerization goes to 1 (solvents; $x_1 = x_2 = 1$) the equations become equivalent.

4 Energy of mixing for polymers

Last time we derived the interaction parameter χ for regular solution theory using a mean-field approximation. As above, we assume ideal chain behavior and re-derive this for the case where we have polymers with degrees of polymerization x_1 and x_2. We can expect that the energy of mixing for polymers can either be negative (promotes mixing) or positive (opposes mixing). Again, we use a lattice model with a mean-field approximation that posits that the local variations in concentration are not significantly different that the overall concentration. That is, the favorable or unfavorable interactions between monomers are small enough that they do not significantly affect random placement on the lattice. Further, in the regular solution theory all species are freely able to move and there is no local 'connection' to other species of the same type. Clearly, this is not the case for polymer chains as each monomer has to be associated to two neighbors of the same type (only one at the chain ends). However, in the Flory-Huggins approach we ignore this fact and account for the energy of mixing as if it is a mixture of ideal gases as before. This is analogous to the assumption of the dilute gas of monomers used in the Flory theory of real polymer chains. Essentially, this will lead to the same derivation as we did in the note from Lecture 7 for the energy of mixing per lattice site where we substitute the mole fractions with volume fractions ϕ_1 and ϕ_2:

$$\frac{\Delta U^M}{N k_B T} = \chi \phi_1 \phi_2. \tag{13}$$

Where as before, we have:

$$\chi = \frac{z}{k_B T}\left(w_{12} - \frac{w_{11} + w_{22}}{2}\right). \tag{14}$$

5 Flory-Huggins free energy of mixing for polymers

As before we can combine Eqs. 12 and 13 to calculate the full free energy of mixing in this system.

$$\Delta F^M = \Delta U^M - T \Delta S^M. \tag{15}$$

Writing the free energy normalized per lattice site we find that:

$$\boxed{\frac{\Delta F^M}{N k_B T} = \chi \phi_1 \phi_2 + \frac{\phi_1}{x_1} \ln \phi_1 + \frac{\phi_2}{x_2} \ln \phi_2}. \tag{16}$$

We can have a few cases of mixtures:

- solvent–solvent: $x_1 = x_2 = 1$
- solvent–polymer: $x_1 = 1$, $x_2 =$ large
- polymer–polymer: $x_1 =$ large, $x_2 =$ large

By inspection, we see that the solvent–solvent case reduces to the regular solution theory and, thus, the Flory-Huggins theory is a more general result. In the solvent–polymer and polymer–polymer cases we have asymmetric free energies dictated by the degrees of polymerization.

Furthermore, we can see that the favorable entropy of mixing decreases as the degree of polymerization of either or both species increases; that is polymers are less likely to mix if either species is very large. In addition, we can see that $\chi \propto \frac{1}{T}$ and thus the energy of mixing will vary with temperature. This leads to interesting behavior where polymer solutions can change solubility dramatically over small ranges of temperatures. We will explore this in more detail in future lectures.