THERMODYNAMICS

1. **Flory-Huggins Theory**. We introduced a simple lattice model for polymer solutions in lectures 24 and 25. The Flory-Huggins model for polymer solutions is a close relative of the regular solution model of small-molecule binary solutions, and the free energy of mixing per lattice site in the Flory-Huggins model looks somewhat like the expression for the regular solution:

$$\frac{\Delta G^{mix}}{M} = \chi kT \phi_P \phi_S + kT\left[\frac{\phi_P}{N}\ln\phi_P + \phi_S \ln\phi_S\right]$$

…where χ is the Flory-Huggins interaction parameter and ϕ_s and ϕ_p are the volume fractions of solvent and polymer, respectively.
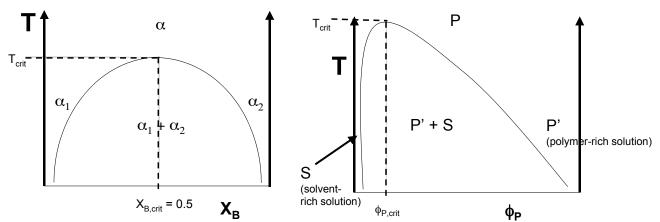
  a. We showed earlier that the critical temperature in the regular solution model is $T_{crit} = \Omega/2R$. We obtained this result by determining the value of T when the second derivative of the free energy of mixing with respect to composition is equal to zero, *at the composition X_B = 0.5* ($\frac{\partial^2 \Delta\overline{G}^{mix}}{\partial X_B^2}\Big|_{X_B=0.5} = 0$). In this case we knew the miscibility gap would first appear at X_B = 0.5 because the enthalpy and entropy of mixing functions in the regular solution are *symmetric* about X_B = 0.5. However, these functions are **not** symmetric about ϕ_p = 0.5 in the Flory-Huggins model. (This is why the miscibility gap on the polymer solution phase diagram is 'canted' strongly toward the ϕ_p = 0 vertical axis for long-chain polymers.) The Flory-Huggins model thus has both a critical temperature and a critical volume fraction (illustrated below).

Regular solution of small molecules:

Solution of polymer in a small molecule solvent:

Typically, instead of calculating a critical temperature for polymer solutions, one instead calculates χ_{crit}, the critical value of the interaction parameter at the onset of the miscibility gap (which, as you can see by looking at the definition of χ, is inversely proportional to the critical temperature). In order to determine the critical volume fraction, we use an additional condition on the free energy: The critical point is located at the temperature and composition where the following two criteria are met:

$$\frac{\partial^2\left(\Delta\overline{G}^{mix}/M\right)}{\partial\phi_P^2} = 0$$

$$\frac{\partial^3\left(\Delta\overline{G}^{mix}/M\right)}{\partial\phi_P^3} = 0$$

(We use here the free energy change on mixing per lattice site). Use these equations to determine the critical volume fraction $\phi_{P,crit}$ and χ_{crit} for the Flory-Huggins model, and show how they depend on N, the number of segments in the polymer chains.

We first put the free energy of mixing expression in terms of ϕ_P alone:

$$\frac{\Delta\overline{G}^{mix}}{M} = \chi kT\phi_P\left(1-\phi_P\right) + kT\left[\frac{\phi_P}{N}\ln\phi_P + \left(1-\phi_P\right)\ln\left(1-\phi_P\right)\right]$$

Next, we simply calculate the derivatives:

$$\frac{\partial\left(\Delta\overline{G}^{mix}/M\right)}{\partial\phi_P} = kT\left[\chi\left(1-2\phi_P\right) + \frac{1}{N}\ln\phi_P - \ln\left(1-\phi_P\right) + \frac{1}{N} - 1\right]$$

$$\frac{\partial^2\left(\Delta\overline{G}^{mix}/M\right)}{\partial\phi_P^2} = -2\chi kT + kT\left[\frac{1}{N\phi_P} + \frac{1}{\left(1-\phi_P\right)}\right] = 0$$

$$\frac{\partial^3\left(\Delta\overline{G}^{mix}/M\right)}{\partial\phi_P^3} = kT\left[-\frac{1}{N\phi_P^2} + \frac{1}{\left(1-\phi_P\right)^2}\right] = 0$$

Solving for ϕ_P in the third derivative expression, we have for the critical volume fraction of polymer:

$$\phi_{P,crit} = \frac{1}{1+\sqrt{N}}$$

Note that if N = 1, the critical volume fraction is 1/2, exactly the result from the regular solution model.

We can plug this critical volume fraction into the second derivative expression to obtain the critical value of the interaction parameter:

$$\chi_{crit} = \frac{\left(1 + \sqrt{N}\right)^2}{2N}$$

For large values of N, the critical interaction parameter will vary only slightly from 1/2:

$$\chi_{crit} \cong \frac{1}{2} + \frac{1}{\sqrt{N}} \approx \frac{1}{2}$$

      b. We showed in class how the entropy change on mixing a polymer with a small-molecule solvent, $\Delta \overline{S}^{mix}$, is obtained. Use this information to derive an expression for the entropy change on mixing a polymer A with chains each comprised of N_A segments with a *second polymer B*, which has chains comprised of N_B segments.

What must change in this scenario? First, the entropy of the unmixed state is changed. A pure lattice of single-segment small molecules has an entropy of zero, but we showed in class that the entropy of a polymer-filled lattice is:

$$W_{\text{pure polymer}} = \left(\frac{z-1}{M}\right)^{n_p(N-1)} \frac{M!}{\left(M - Nn_p\right)! n_p!} = \left(\frac{z-1}{Nn_p}\right)^{n_p(N-1)} \frac{(Nn_p)!}{n_p!}$$

$$S^{\text{pure polymer}} = k_b \ln W_{\text{pure polymer}}$$

We will have an entropy term from both pure polymer A and pure polymer B. In the solution, we now have to place nA A chains and nB B chains on the lattice. We simply extend our calculation from the polymer + small molecule solvent mixing. The number of configurations for the A and B chains on the lattice are obtained as a product of placement terms:

$$W_{solution} = \frac{\nu_{first,A} \nu_{subsequent,A} \nu_{first,B} \nu_{subsequent,B}}{n_{p,A}! n_{p,B}!}$$

The counting for placing the A chains is the same as we did in class; we place the first segment of all of the A chains into the lattice, and then follow with the subsequent segments of each chain:

$$\nu_{first,A} = \frac{M!}{(M - n_A)!}$$

$$\nu_{subsequent,A} = \left(\frac{z-1}{M}\right)^{n_A(N_A - 1)} \frac{(M - n_A)!}{(M - N_A n_A)!}$$

We then use the same counting approach to place the B chains into the lattice which is already filled by the A chains:

$$\nu_{first,B} = \left(M - N_A n_A\right)\left(M - N_A n_A - 1\right)\left(M - N_A n_A - 2\right)\cdots\left(M - N_A n_A - \left(n_B - 1\right)\right) = \frac{\left(M - N_A n_A\right)!}{\left(M - N_A n_A - n_B\right)!}$$

$$\nu_{subsequent} = \left[\left(z-1\right)\left(\frac{M - N_A n_A - n_B}{M}\right)\right]\left[\left(z-1\right)\left(\frac{M - N_A n_A - n_B - 1}{M}\right)\right]\cdots\left[\left(z-1\right)\left(\frac{M - N_A n_A - N_B\left(n_B - 1\right) - \left(N_B - 1\right)}{M}\right)\right]$$

$$\therefore \nu_{subsequent,B} = \left(\frac{z-1}{M}\right)^{n_B\left(N_B - 1\right)}\frac{\left(M - N_A n_A - n_B\right)!}{\left(M - N_A n_A - N_B n_B\right)!}$$

Since the lattice must be completely full, **M = N_A n_A + N_B n_B**, so $\nu_{subsequent,B}$ reduces to:

$$\therefore \nu_{subsequent,B} = \left(\frac{z-1}{M}\right)^{n_B\left(N_B - 1\right)}\frac{\left(M - N_A n_A - n_B\right)!}{\left(0\right)!} = \left(\frac{z-1}{M}\right)^{n_B\left(N_B - 1\right)}\left(M - N_A n_A - n_B\right)!$$

Putting these expressions together, we have for the polymer A + polymer B solution:

$$W_{solution} = \frac{1}{n_A! n_B!}\left(\frac{M!}{\left(M - n_A\right)!}\right)\left(\left(\frac{z-1}{M}\right)^{n_A\left(N_A - 1\right)}\frac{\left(M - n_A\right)!}{\left(M - N_A n_A\right)!}\right)\left(\frac{\left(M - N_A n_A\right)!}{\left(M - N_A n_A - n_B\right)!}\right)\left(\left(\frac{z-1}{M}\right)^{n_B\left(N_B - 1\right)}\left(M - N_A n_A - n_B\right)!\right)$$

We can use these expressions to calculate the entropy of mixing when we have 2 different polymers to mix:

$$\Delta S^{mix} = S^{solution} - S^{unmixed} = S^{solution} - \left(S^{\text{pure polymer A}} + S^{\text{pure polymer B}}\right) = k_b \ln\frac{W_{solution}}{W_{\text{pure polymer A}}W_{\text{pure polymer B}}}$$

$$\therefore \Delta S^{mix} = k_b \ln\frac{\frac{1}{n_A! n_B!}\left(\frac{M!}{\left(M - n_A\right)!}\right)\left(\left(\frac{z-1}{M}\right)^{n_A\left(N_A - 1\right)}\frac{\left(M - n_A\right)!}{\left(M - N_A n_A\right)!}\right)\left(\frac{\left(M - N_A n_A\right)!}{\left(M - N_A n_A - n_B\right)!}\right)\left(\left(\frac{z-1}{M}\right)^{n_B\left(N_B - 1\right)}\left(M - N_A n_A - n_B\right)!\right)}{\left[\left(\frac{z-1}{N_A n_A}\right)^{n_A\left(N_A - 1\right)}\frac{\left(N_A n_A\right)!}{n_A!}\right]\left[\left(\frac{z-1}{N_B n_B}\right)^{n_B\left(N_B - 1\right)}\frac{\left(N_B n_B\right)!}{n_B!}\right]}$$

Many terms cancel out in this expression:

$$\Delta S^{mix} = k_b \ln\phi_A^{n_A\left(N_A - 1\right)}\phi_B^{n_B\left(N_B - 1\right)}\left(\frac{M!}{\left(N_A n_A\right)!\left(N_B n_B\right)!}\right) = -k_b\left[n_A \ln\phi_A + n_B \ln\phi_B\right]$$

or, per lattice site:

$$\frac{\Delta S^{mix}}{M} = -k_b \left[\frac{\phi_A}{N_A} \ln \phi_A + \frac{\phi_B}{N_B} \ln \phi_B \right]$$

As you might expect, this looks like the entroa pair of entropy terms similar to the polymer term from the entropy of mixing in the polymer solution case.

2. **The ideal solution as a lattice model**. We can derive the free energy of mixing for ideal solutions using a lattice model similar to the Flory-Huggins theory- but simpler. Suppose components A and B of the solution both occupy one lattice site each (and are the same size). Following the conceptual procedure we used in class (determining the entropy S from the number of configurations for the system W), answer the following questions:

   a. What is the entropy of the **unmixed** system of pure A molecules + pure B molecules?

   b. What is the entropy of the homogeneously mixed system of A + B?

   c. Using these two results, what is the molar entropy change on mixing for this model system? Compare your answer to the ideal solution entropy of mixing we gave earlier in class.

The entropy of mixing change has two parts:

$$\Delta S^{mix} = S^{solution} - S^{umixed}$$

First, the entropy of the unmixed regular solution: What is the entropy of a lattice of pure A molecules and a lattice of pure B molecules? We count the number of unique configurations for the molecules on the lattice: $W^{unmixed} = 1$ (There is only one way to fill a lattice with one type of molecule). The entropy is thus:

$$S^{umixed} = k_b \ln W^{unmixed} = 0$$

Let us denote the number of A molecules in the solution as n_a and the number B molecules as n_B. For the solution, we now need to determine the number of ways to load these two sets of molecules into the lattice. This is a relatively straightforward extension of counting the configurations for placing the first bead of a polymer chain into a lattice:

$$v = M(M-1)(M-2)\cdots(M-n_A)(M-n_A-1)\cdots(M-n_A-(n_B-1))$$

$$v = \frac{M!}{(M-n_A-n_B)!} = \frac{M!}{(0)!} = M!$$

$$W_{solution} = \frac{v}{n_A! n_B!} = \frac{M!}{n_A! n_B!}$$

$$\therefore \Delta S^{mix} = S^{solution} - S^{unmixed} = k_b \ln W_{solution} - 0 = k_b \ln \frac{M!}{n_A! n_B!}$$

$$\Delta S^{mix} = k_b \left[\ln M! - \ln n_A! - \ln n_B! \right]$$

Applying Stirling's approximation (also used in lecturein our Flory-Huggins derivation):

$$\Delta S^{mix} = k_b \left[M \ln M - M - n_A \ln n_A + n_A - n_B \ln n_B + n_B \right]$$

$$\Delta S^{mix} = k_b \left[n_A \ln M + n_B \ln M - n_A \ln n_A - n_B \ln n_B \right]$$

$$\Delta S^{mix} = -k_b \left[n_A \ln X_A + n_B \ln X_B \right]$$

We have made use of the fact that $n_A/M = X_A$ and $n_B/M = X_B$, the mole fractions of A and B, respectively (note volume fraction and mole fraction are the same here, since the molecules have the same volumes). The entropy per lattice site reduces to a familiar expression:

$$\frac{\Delta S^{mix}}{M} = -k_b \left[X_A \ln X_A + X_B \ln X_B \right]$$

3. **Practice with the partition function.** In class, we gave a number of useful relationships that allow you to directly determine thermodynamic quantities from the partition function. An example is the expression for the internal energy:

$$U = <E> = -\frac{\partial \ln Q}{\partial \beta} = kT^2 \frac{\partial \ln Q}{\partial T}$$

Show that this expression is equivalent to the ensemble average of the internal energy:

$$U = <E> = \sum_{i=1}^{W} E_i p_i$$

$$U = <E> = kT^2 \frac{\partial \ln Q}{\partial T} = kT^2 \left(\frac{\partial \ln Q}{\partial Q} \left(\frac{\partial Q}{\partial T} \right) \right) = kT^2 \left(\frac{1}{Q} \frac{\partial Q}{\partial T} \right) = \frac{kT^2}{Q} \left(\frac{\partial \left(\sum_{i=1}^{W} e^{-\frac{E_i}{kT}} \right)}{\partial T} \right)$$

$$U = <E> = \frac{kT^2}{Q} \sum_{i=1}^{W} \left(\frac{E_i}{kT^2} \right) e^{-\frac{E_i}{kT}} = \sum_{i=1}^{W} (E_i) \left(\frac{e^{-\frac{E_i}{kT}}}{Q} \right) = \sum_{i=1}^{W} (E_i)(p_i)$$

4. **Practice with the Boltzmann distribution**. Consider an imaginary crystal where a collection of 3 atoms vibrate as simple 1D harmonic oscillators, and each atoms has access only to the first 4 energy levels (the ground state and the first 3 excited states). The energies of the 4 states are 75k, 225k, 375k, and 525k from the ground state to the higher energy states (where k is the Boltzmann constant). The atoms are identical and distinguishable.

   a. What is the probability of finding **one atom** of the system in each possible energy level at T = 200K?

We need the partition function of one atom at T = 200 K:

$$q = \sum_{i=1}^{W} e^{-\frac{E_i}{kT}} = e^{-\frac{75k}{kT}} + e^{-\frac{225k}{kT}} + e^{-\frac{375k}{kT}} + e^{-\frac{525k}{kT}} = e^{-\frac{75}{200}} + e^{-\frac{225}{200}} + e^{-\frac{375}{200}} + e^{-\frac{525}{200}} = 1.2378$$

The probability of observing an atom in each of the four energy levels is:

$$p_{75k} = \frac{e^{-\frac{75k}{kT}}}{q} = 0.5553 \qquad\qquad p_{225k} = \frac{e^{-\frac{225k}{kT}}}{q} = 0.2623$$

$$p_{75k} = \frac{e^{-\frac{375k}{kT}}}{q} = 0.1239 \qquad\qquad p_{525k} = \frac{e^{-\frac{525k}{kT}}}{q} = 0.0585$$

…the Boltzmann distribution shows a reduced probability of finding an atom in single states of increasing energy.

   b. Compute the probability of observing the **system** with a total energy of 225k.

To make a calculation for the system, we need the partition function of the collection of atoms:

$$Q = q^N = q^3 = 1.8965$$

How many different unique states can be observed with a total energy of 225k? For the collection of 3 atoms, the only state with this energy is the ground state (all 3 atoms in their lowest energy level). The probability of observing this state is:

$$p_{\text{system 225k}} = \frac{e^{-\frac{225k}{kT}}}{Q} = 0.1712$$

Remember that the energy in the Boltzmann factor here is the total energy of the system (sum of energies of each independent atom).

    c. Compute the probability of observing the **system** with a total energy of 375k.

How many different unique states of the system provide a total energy of 375k? This energy is obtained when one of the atoms is in the first excited state and the other two are in the ground state. Because the atoms are distinguishable, each possible arrangement (first atom excited, 2nd and 3rd in ground state; second atom excited, 1st and 3rd in ground state; third atom excited, 1st and 2nd in ground state) is uniquely identifiable. The probability of any one of these 3 states is:

$$p_{\text{one system state 375k}} = \frac{e^{-\frac{375k}{kT}}}{Q}$$

Because we have 3 of these states, the total probability of observing the system with this energy is:

$$p_{\text{system 375k}} = 3p_{\text{one system state 375k}} = 3\frac{e^{-\frac{375k}{kT}}}{Q} = 0.2425$$

    d. Explain why it is more probable to find the **system** with an energy greater than the ground state energy (all atoms in the ground state energy level), despite the fact that the probabilities of finding **one atom** of the system in an excited state (part a) decrease with increasing energy.

In this problem, we see why excited states become the most likely states at elevated temperatures. Because the number of *possible* states for a system increases as the total energy increases, this **degeneracy** of the available states (number of states that have the same total energy) competes against the dwindling probability of occupation of any **individual** state of increasing energy dictated by the Boltzmann distribution. Even though any **single** state at elevated energy is less likely than any single lower-energy state, there are **many more** unique states at elevated energies relative to lower energy conditions (e.g., the lowest energy of the system is obtained in only one single unique state, the ground state). When we ask the probability of observing the system with a given particular energy, we are asking the likelihood of observing the system in **any** of the degenerate states of that energy. At high temperatures, the many states available at elevated energies make it most probable that we will observe a higher-energy state. This is how the continuously-decreasing probabilities of the Boltzmann distribution can lead to a mean energy which is not always the ground state energy.