

## Topic 2

# Solution Thermodynamics

### 2.1 Flory-Huggins Theory

9/18: • Outline of the next three lectures.

- Thermodynamics of polymer solutions and blends.
  - Entropy of mixing.
  - Enthalpy of mixing.
  - Flory interaction parameter (definition and measurements).
  - Solutions and melts (the theta temperature).
  - LCST vs. UCST.
- Copolymers.
  - Microparticle separation.
  - Interfacial free energy.
  - Chain stretching and configurational free energy.
- Huggins<sup>[1]</sup>.
- We're going to start by approximating polymers as straight chains on a lattice.

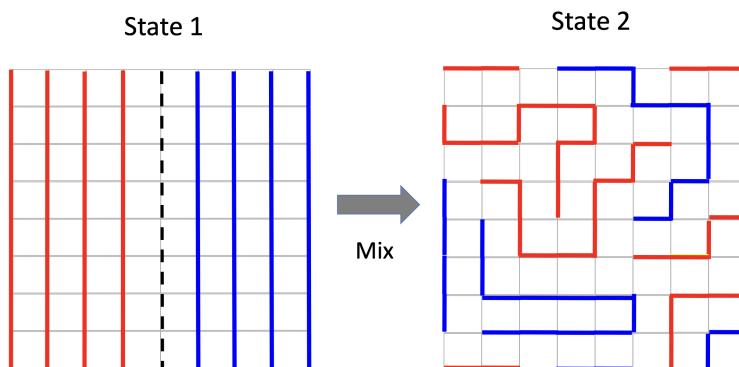


Figure 2.1: Lattice theory for polymer phase behavior.

- When we heat them up, will they stay phase separated or mix (go into State 2)?
- This will depend on how **compatible** they are.

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<sup>1</sup>"HOY-gins"

- **Compatible** (polymers): Two different types of polymers that like to mix with each other to form a single phase.
- The original model for phase behavior was postulated by Bragg and Williams (1934) for small molecules and alloys.
  - Flory (1942) and Huggins (1942) generalized this model to longer things (polymers).
  - Flory was a Stanford prof., but started in the petroleum business (needed to separate chains and understand how they behave).
- The thermodynamics of polymer solutions and blends are important for many applications, such as...
  - Phase diagrams;
  - Fractionation by molecular weight and/or by composition;
  - $T_m$  depression in a semicrystalline polymer by a 2nd component;
  - Swelling behavior of networks/gels;
    - Covered much later in the course.
- High-impact polystyrene (HIPS).

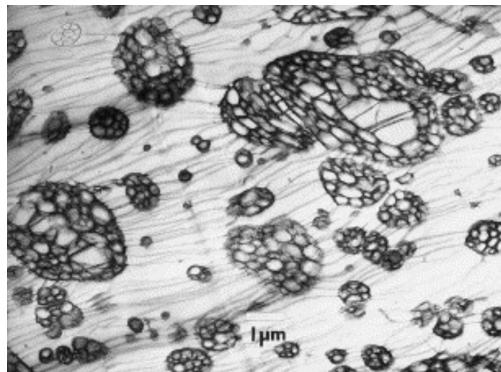


Figure 2.2: Salami phase micrograph in styrene-butadiene mixtures.

- Example: circular plastic dishes in lab. Hard, but very brittle.
- Idea to make better: Mix a stiff but brittle polymer (PS) with a soft elastic polymer (polybutadiene, PB) to get better mechanical properties.
- Cracks cannot propagate because they will hit rubbery phases of PB that have phase separated on the nanoscale, and be absorbed.
  - This is called the **salami phase** because of how micrographs look.
  - Effect: Stress-strain curve elongates significantly (**toughness** increases because that is the area under the curve).
- Aside: Making things look clear requires a lot of polymer engineering, because you have to make things very amorphous and not have nanoscale crystals.
- Thermodynamics of polymer blends.
  - Legos are made of statistical copolymers of acrylonitrile-butadiene-styrene (ABS).
  - Acrylonitrile gives resistance to repeated clicking and unclicking, butadiene makes it rubbery, styrene makes it shiny.
- Today: Derive a free energy functional.

- Last lecture, we derived a free energy functional for single chains.
- Today, we're looking at  $G = H - TS$ .
- What we're really interested in is the free energy of mixing,

$$\Delta G_M = G_{1,2} - (G_1 + G_2)$$

- In multicomponent systems — besides the typical parameters of excluded volume, etc. — we need to know...
  - How many chains we have of each type;
  - What their degree of polymerization is;
  - What total volume do they occupy.
- Thus, in State 1, we have

$$V_1 = n_1 N_1 v_1 \quad V_2 = n_2 N_2 v_2$$

which describes two separate phases...

- Containing  $n_i$  moles of species  $i$ ;
- With degree of polymerization  $N_i$ ;
- Each occupying a total volume  $V_i$ ;
- Where the volume of each monomer/solvent molecule is given by  $v_i$ .
- In State 2, we have a mixed phase with total volume

$$V = \underbrace{n_1 N_1 v_1}_{V_1} + \underbrace{n_2 N_2 v_2}_{V_2}$$

- Note that we're assuming that there is no change in volume  $\Delta V$  during mixing.
- Nomenclature: If a system is comprised of a solvent and polymer, name the solvent “1” and the polymer “2”.

- To understand the thermodynamics of mixing, we'll start with the *entropy* of mixing.
- Comments.
  - In a melt, most chains do not feel themselves because other chains screen the interaction of the original chain with itself.
  - This is great for us, because everything behaves like a truly random walk with scaling relation  $N^{1/2}$ .
    - This realization is what won Flory his Nobel Prize!
- There is only 1 possible way to arrange a pure component in its volume.
  - This follows from the binomial expression  $\binom{n_i N_i}{n_i N_i}$ .
  - Thus, when phases are separated, each phase has entropy  $S = k_B \ln(1) = 0$ .
- Mean field lattice theory.
  - We get another binomial because we're adjacent to a random walk where we have 1 or 2 in each adjacent cell as we go along.
  - As we fill up the grid, we first have access to all  $X_0$  of the objects. Then we have 1 less, then we have 2 less, etc.
    - But since all the objects in group 1 or group 2 are the same, we need to divide out by the number of objects  $X_1$  in category 1. We need to do the same because all objects in  $X_2$  are the same.

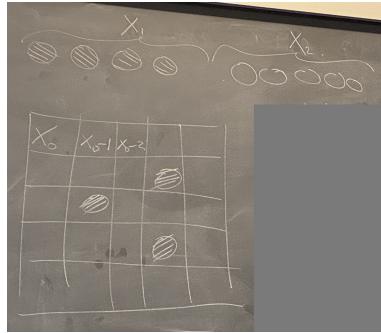


Figure 2.3: Configurations in mean field lattice theory.

■ Thus,

$$\Omega_{1,2} = \frac{X_0!}{X_1!X_2!}$$

– It follows that the change entropy  $\Delta S$  upon mixing is

$$\Delta S_M = k_B \ln \Omega_{1,2} - 0$$

■ Remember that the initial entropy is zero!

– Invoking Stirling's approximation and remembering that  $X_1 + X_2 = X_0$ , we can then get

$$\begin{aligned} \frac{\Delta S_M}{k_B} &= X_0 \ln X_0 - X_0 - [X_1 \ln X_1 - X_1 + X_2 \ln X_2 - X_2] \\ &= X_0 \ln X_0 - X_1 \ln X_1 - X_2 \ln X_2 \end{aligned}$$

– It follows that the entropy of mixing per site  $\Delta S_M/k_B X_0$  is

$$\begin{aligned} \frac{\Delta S_M}{k_B X_0} &= \frac{1}{X_0} [(X_1 + X_2) \ln X_0 - X_1 \ln X_1 - X_2 \ln X_2] \\ &= -\frac{X_1}{X_0} (\ln X_1 - \ln X_0) - \frac{X_2}{X_0} (\ln X_2 - \ln X_0) \\ &= -\frac{X_1}{X_0} \ln \frac{X_1}{X_0} - \frac{X_2}{X_0} \ln \frac{X_2}{X_0} \\ &= -\phi_1 \ln \phi_1 - \phi_2 \ln \phi_2 \end{aligned}$$

where  $\phi_i$  denotes the **volume fraction** of spaces occupied by species  $i$ .

- **Volume fraction** (of  $i$ ): The fraction of lattice sites occupied by species  $i$ . Denoted by  $\phi_i$ . Given by

$$\phi_i := \frac{X_i}{X_0}$$

– It follows from this definition that  $\phi_1 + \phi_2 = 1$ .

- Note: An assumption underlying the use of the Boltzmann equation is that all microstates have equal energy. This isn't strictly true, but it's a good enough approximation.
  - Example: Assume nearest neighbor interactions matter.
  - Let opposing objects in neighboring cells contribute energy  $\varepsilon_1$  to the total energy of the system. This means that in Figure 2.4,  $E_1 = 4\varepsilon_1$  and  $E_2 = 2\varepsilon_2$ .
  - In big systems, the energy won't fluctuate much, though, so Boltzmann equation is more of an approximation, but it's *good enough*.

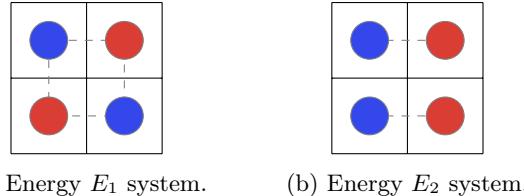


Figure 2.4: Nearest neighbor interactions.

- Mean field mixing enthalpy.
  - Assume the lattice is such that each point has  $z$  nearest neighbor cells.
    - For example, each cell in a square lattice (Figure 2.3) has 4 nearest neighbors: One above, below, right, and left.
  - To calculate enthalpic interactions, we consider the number of pairwise interactions.
  - But in a mean field approximation, we wash out some detail by mixing red and blue to make purple. We say that *on average*, your neighbor one away from you is proportional to the composition (because it might be red, then blue, then red again). Quick exchange of neighbors.
    - You can build on this with weights, but this is the purest sense of a mean field approximation.
  - The mean field approximation breaks down when mixing breaks down, i.e., when you start to get some clusters of pure one thing and pure another thing.
- Enthalpy of mixing.

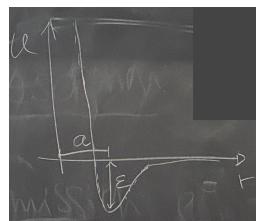


Figure 2.5: Potential well.

- We need to count each interaction. It follows from the above that the number of  $ij$  interactions is

$$\xi_{11} = \frac{X_1 z \phi_1}{2} \quad \xi_{22} = \frac{X_2 z \phi_2}{2} \quad \xi_{12} = X_1 z \phi_2$$

- Let's rationalize the formula for  $\xi_{11}$ .  $X_1$  sites each have  $z$  nearest neighbors, so there are  $X_1 z$  nearest neighbor interactions where one of the species involved is species 1. The probability that a nearest neighbor is also species 1 is  $\phi_1$ . Thus, there are  $X_1 z \phi_1$  interactions where the other partner is also species 1. However, since there are two neighbors involved, we have currently accounted for each interaction twice: Once from the perspective of each neighbor. Thus, we need to divide by 2.
- Same rationalization for  $\xi_{22}$ .
- For  $\xi_{12}$ , a similar rationalization applies but we are not overcounting because we only have the perspective of one of the two interaction partners taken into account, so no dividing by 2 is necessary. Alternatively, from the perspective of both species, we have

$$\xi_{12} = \frac{X_1 z \phi_2}{2} + \frac{X_2 z \phi_1}{2} = X_1 z \phi_2$$

- In a typical attraction well, we have a most probable distance  $a$ , at which the energy depth is  $\epsilon$  (see Figure 2.5).

- Let  $\varepsilon_{ij}$  refer to how deep the well is between species  $i$  and  $j$ , where  $i, j \in \{1, 2\}$ .
- It follows that in a mixed enthalpic state, the interaction energy is the following.

$$\begin{aligned} H_{1,2} &= \xi_{12}\varepsilon_{12} + \xi_{11}\varepsilon_{11} + \xi_{22}\varepsilon_{22} \\ &= zX_1\phi_2\varepsilon_{12} + \frac{zX_1\phi_1\varepsilon_{11}}{2} + \frac{zX_2\phi_2\varepsilon_{22}}{2} \end{aligned}$$

- In pure enthalpic states, the interaction energies are the following.

$$H_1 = \frac{zX_1\varepsilon_{11}}{2} \quad H_2 = \frac{zX_2\varepsilon_{22}}{2}$$

- Note that we are actually computing the energy  $U$  above, not the enthalpy  $H = U + PV$ . However, we equate  $H = U$  by assuming that there is no volume change upon mixing.
- Such an assumption is consistent with the lattice approach (i.e., the assumption that all species fit into a lattice site of equal volume both before and after mixing).
- It follows that

$$\begin{aligned} \Delta H_M &= H_{1,2} - (H_1 + H_2) \\ &= z \left[ X_1\phi_2\varepsilon_{12} + \frac{X_1\varepsilon_{11}}{2}(\phi_1 - 1) + \frac{X_2\varepsilon_{22}}{2}(\phi_2 - 1) \right] \end{aligned}$$

and hence

$$\begin{aligned} \frac{\Delta H_M}{X_0} &= z \left[ \phi_1\phi_2\varepsilon_{12} + \frac{\phi_1\varepsilon_{11}}{2}(-\phi_2) + \frac{\phi_2\varepsilon_{22}}{2}(-\phi_1) \right] \\ \frac{\Delta H_M}{X_0 k_B T} &= \frac{z}{k_B T} \left\{ \phi_1\phi_2 \left[ \varepsilon_{12} - \frac{1}{2}(\varepsilon_{11} + \varepsilon_{22}) \right] \right\} \\ &= \chi\phi_1\phi_2 \end{aligned}$$

where  $\chi$  denotes the **Flory  $\chi$  parameter**.

- **Flory  $\chi$  parameter:** A measure of the degree to which the two species like each other vs. themselves. *Also known as interaction parameter. Denoted by  $\chi$ . Given by*

$$\chi := \frac{z}{k_B T} \left[ \varepsilon_{12} - \frac{1}{2}(\varepsilon_{11} + \varepsilon_{22}) \right]$$

- From its definition, we can see that the sign of  $\chi$  determines whether mixing will be enthalpically favorable or not. Moreover, the sign of  $\chi$  is determined by the interplay between how much the components like each other, and how much they like themselves on average.
- Implication: If the two components like themselves more than they like each other (right diagram at bottom of slide 14),  $\chi$  will be positive and will be between the middle two lines (we don't know here if it will mix or demix)??
- The  $\chi$  parameter is still being debated today; Alfredo is writing a paper on it!
  - The parameter as written is linear, but that's based on a mean field assumption. Should it have a quadratic term? Maybe it does at a (more accurate) higher level of theory.
- At this point, we can assemble everything into the free energy of mixing for monomers.

$$\begin{aligned} \frac{\Delta G_M}{X_0} &= \frac{\Delta H_M}{X_0} - T \frac{\Delta S_M}{X_0} \\ &= k_B T \chi \phi_1 \phi_2 - T \cdot k_B (-\phi_1 \ln \phi_1 - \phi_2 \ln \phi_2) \\ &= k_B T (\chi \phi_1 \phi_2 + \phi_1 \ln \phi_1 + \phi_2 \ln \phi_2) \end{aligned}$$

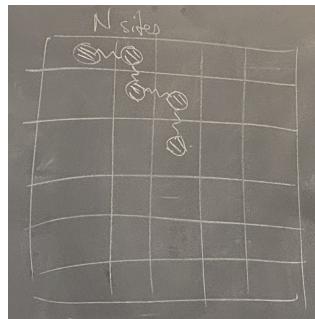
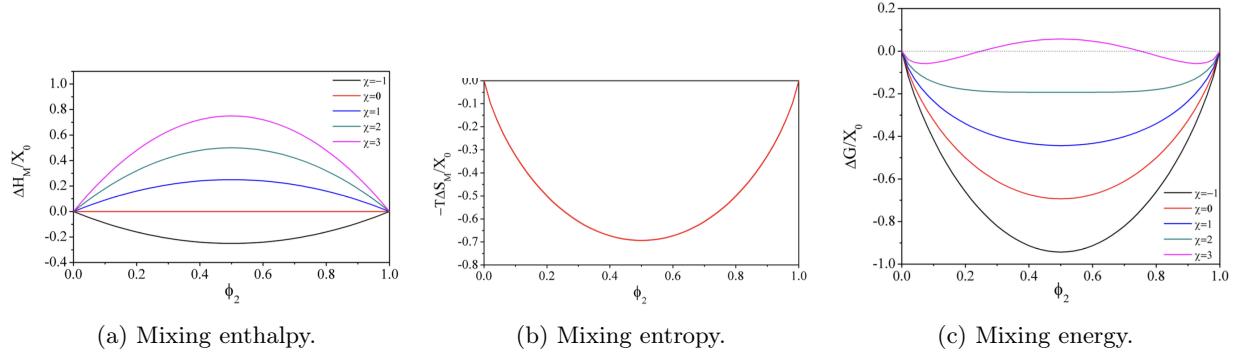


Figure 2.6: Fitting polymers into a square lattice.

- How about for polymers?
    - For enthalpy of mixing, we still use a mean field approximation, so nothing changes. We justify this by noting, as earlier, that in a melt, most chains do not feel themselves because other chains screen the interaction of the original chain with itself.
    - For entropy of mixing, things do change a bit.
      - As in Figure 2.3, we have to pick  $N$  adjacent sites.
      - Then the next time we pick, what's left is the number of sites minus  $N$ . And on and on.
      - This essentially reduces the number of sites by  $N_1$  and  $N_2$ .
      - All of this is part of a complex derivation done by Flory, but the simple and intuitive result is that the entropy of mixing decreases by approximately  $1/N$  due to the connectivity of the  $N$  segments we cannot arrange any further apart. Mathematically, we obtain
- $$\frac{\Delta S_M}{k_B X_0} = -\frac{\phi_1}{N_1} \ln \phi_1 - \frac{\phi_2}{N_2} \ln \phi_2$$
- This equation tells us that when  $N$  is big, entropy doesn't play a huge role in driving mixing (because  $N_1, N_2$  are in the denominator). Thus, enthalpy matters more for the mixing of polymers.
  - Using the modified mixing entropy, we can now finally state the “famous Flory-Huggins theory for the free energy of mixing.”
- $$\frac{\Delta G_M}{X_0} = k_B T \left( \chi \phi_1 \phi_2 + \frac{\phi_1}{N_1} \ln \phi_1 + \frac{\phi_2}{N_2} \ln \phi_2 \right)$$
- This equation is applicable to solvent-solvent ( $1 = N_1 = N_2$ ), polymer-solvent ( $1 = N_1 \neq N_2$ ), and polymer-polymer ( $1 \neq N_1, N_2$ ) mixing.
  - This equation also gives us a tool to investigate phase behavior and how it varies with  $T, \chi, \phi_i, N_i$ . Namely, values of these variables that lead to a negative  $\Delta G_M$  will correspond to mixing, and values of these variables that lead to a positive  $\Delta G_M$  will correspond to demixing.
  - How do we measure  $\chi$  experimentally?
    - We will explore this soon.
  - Influence of  $\chi$  on phase behavior.
    - Notice how adding the curves in Figures 2.7a-2.7b gives the curves in Figure 2.7c.
    - From Figure 2.7c, we can see that when  $\chi$  reaches the range of 2-3, we get demixing.
      - This is because (at  $\chi = 3$  and initially equal volumes of both components, for example) it will be more energetically favorable to form (i) a phase that is approximately 90% component 1 and 10% component 2 and (ii) a phase that is approximately 10% component 1 and 90% component 2 than it will be to completely mix.

Figure 2.7: Mixing or demixing based on the Flory  $\chi$  parameter.

- When  $\chi = 2$ , free energy is largely flat. Thus, very different compositions have similar free energy, which means that the system will “undergo a 2nd order transition where all length scales are viable??”
- A parameter that has gained more importance in recent years: The coordination number  $z$ .
  - It turns out that the more neighbors you have, the better mean-field behavior you get.
  - This is essentially because you’re averaging over more values.
  - Recent finding:  $\chi$  is pretty good if  $z$  is big; if  $z$  is small, quadratic and other higher order corrections may be necessary for  $\chi$ .
- Phase behavior of blends.
  - The critical value  $\chi_c$  of the Flory  $\chi$  parameter is the value of  $\chi$  at which you see phase separation.
  - $\chi_c$  decreases exponentially with increasing chain length  $N_1 = N_2 = N$ .
    - This relates to the phenomenon discussed earlier in which the mixing entropy shrinks as chain length grows. If mixing entropy is shrinking, the system can tolerate less enthalpic repulsion before demixing.
- Preliminaries to next class.

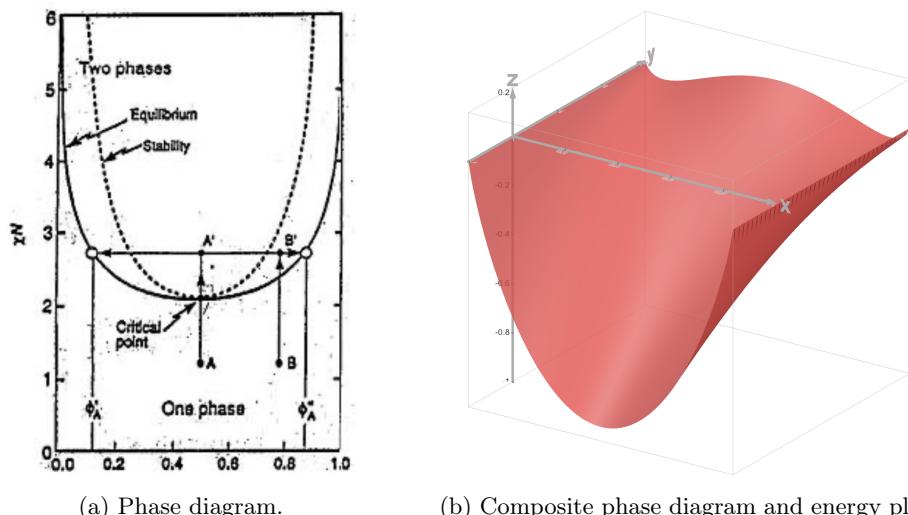


Figure 2.8: Example phase diagram and explanation.

- Construction of phase diagrams.
  - You have a critical point graph that gets flipped??
  - The inside, dashed line is the **spinodal curve**.
  - The outside, solid line is the **binodal curve**.
  - We are essentially thinking of  $\phi_2$  and  $\chi N$  as two independent variables that together define a system. A dependent variable of interest in this system is the mixing energy  $\Delta G_M$ . Therefore, a representation of the set of systems as a 2D graph in 3D space is warranted. Figure 2.7c plots one set of 2D cross sections of this surface (with color as a pseudo-third dimension), and Figure 2.8 plots other important contours of this surface.
- The spinodal curve plots the inflection points in Figure 2.7c.
  - For example, the pink curve has two inflection points around 0.2 and 0.8, and the green curve has one (special) inflection point around 0.5.
  - Between the two inflection points, the system is unstable.
  - Concave curvature puts the sum of two free energies below the points.
  - You will evolve toward the two lowest energy points, phase separating as needed.
- Once we have reached a **metastable** state at the spinodal, demixing to the binodal occurs by nucleation and growth.

## 2.2 The Theta State

9/23:

- Announcements.
  - PSet 2 posted; due midnight next Tuesday.
- Last time: Flory-Huggins polymers.
- Today, let's begin by thinking about the equilibrium between the two different phases of a system.
  - We will quantify this with binodal and spinodal stuff.
- **Chemical potential:** The Gibbs free energy of a substance at a given concentration. *Denoted by  $\mu_i$ . Given by*

$$\mu_i := \left( \frac{\partial G}{\partial n_i} \right)_{T, P, N, n_j} \quad (j \neq i)$$

- **Coexistence curve:** The set of points where the chemical potentials of each component in each phase are equal. *Also known as binodal curve. Constraints*

$$\begin{aligned} \mu'_1 &= \mu''_1 & \mu'_2 &= \mu''_2 \\ \mu'_1 - \mu_1^\circ &= \mu''_1 - \mu_1^\circ & \mu'_2 - \mu_2^\circ &= \mu''_2 - \mu_2^\circ \end{aligned}$$

- Note that one of the phases (e.g., the clumped phase in Figure 2.9) is denoted by a single prime, and the other phase (e.g., the mostly solvent/unclumped phase in Figure 2.9) is denoted by a double prime.
- The lower line of constraints indicates that equal chemical potentials are also equal with respect to the reference chemical potential.
- We include it because  $\mu_i - \mu_i^\circ$  is easier to calculate than just  $\mu_i$ . This is because we have expressions for  $\Delta G_M$ , not  $G_M$ , so we would prefer to use the left derivative below than the right.

$$\mu_i - \mu_i^\circ = \frac{\partial \Delta G}{\partial n_i} \quad \mu_i = \frac{\partial G}{\partial n_i}$$

- The coexistence curve encloses all compositions wherein the mixture demixes into two distinct, coexisting phases.
- Alternatively, the coexistence curve is given by finding, for each  $\Delta G_M(\phi)$  curve, the intersections of said curve with a line tangent to the two wells.<sup>[2]</sup>
- **Spinodal curve:** The set of inflection points along the  $\Delta G_M(\phi)$  curves, generated as  $\chi$  is varied. *Also known as stability limit. Constraint*

$$\frac{\partial^2 \Delta G_M}{\partial \phi_1^2} = 0$$
- Recall that at each inflection point, the 2nd derivative is zero. This is why we use the criterion above.
- **Critical point:** The point on a phase diagram where a solution first begins to demix, or first begins to mix. *Denoted by  $(\phi_{1,c}, \chi_c)$ . Constraints*

$$\left. \frac{\partial^2 \Delta G_M}{\partial \phi_1^2} \right|_{(\phi_{1,c}, \chi_c)} = 0 \quad \left. \frac{\partial^3 \Delta G_M}{\partial \phi_1^3} \right|_{\phi_{1,c}} = 0$$
- The spinodal and coexistence curves intersect at this point.
- Because the critical point lies on the spinodal curve, it will satisfy the left constraint above (i.e., 2nd derivative is zero).
- To explain the right constraint, we need to think a bit more. Usually, an inflection point identifies where the concavity of a curve changes from up to down, or vice versa. At such a point, the concavity is zero. However, on the  $\Delta G_M(\phi)$  curve at the *boundary* between mixing and demixing (e.g., the green line in Figure 2.7c), there is an inflection point where the concavity goes from up, to zero, to up again. At such an inflection point, the second derivative is still equal to zero *but the third derivative is, too*.
- Thus, altogether, the right constraint pinpoints the concentration  $\phi_{1,c}$  at which demixing first occurs as we raise  $\chi$ , and the left constraint relates this concentration to the interaction parameter  $\chi_c$  necessary to produce a mixing curve with an inflection point at  $\phi_{1,c}$ .
- Per the above, a few derivatives suffice to compute the spinodal curve. But if we want to understand the binodal curve, we should find a way to compute the chemical potentials of our solutions.
- The chemical potential of a polymer-solvent solution.

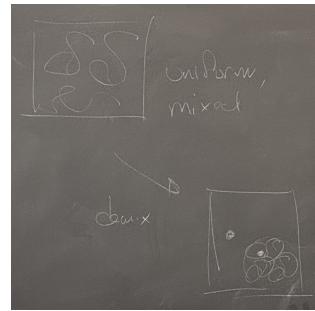


Figure 2.9: Demixing of a polymer-solvent solution.

- An interesting way of thinking about this: Osmometry.
- Imagine a uniform, mixed polymer solution.

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<sup>2</sup>See Office Hours for more on this tangent line.

- We can demix to a state where the polymer is all clumped together, but the clumps still have some solvent in them though.
- The phase separation stops when a solvent molecule *inside* and *outside* the polymer clump has the same chemical potential.
- We now state — without proof — that the change in chemical potentials upon mixing are as follows.

$$\mu_1 - \mu_1^\circ = RT \left[ \ln(1 - \phi_2) + \left(1 - \frac{1}{N_2}\right) \phi_2 + \chi \phi_2^2 \right]$$

$$\mu_2 - \mu_2^\circ = RT \left[ \ln \phi_2 + (N_2 - 1)\phi_2 + N_2 \chi \phi_1^2 \right]$$

- Remember that by convention, phase 1 is the solvent and phase 2 is the polymer.
- Notice the multiplying vs. dividing of  $N_2$ .
- For a polydisperse system of polymer chains, let  $N_2 = \langle N_2 \rangle = M_n$ .
- In PSet 2, Q1a, we'll derive the top one of these expressions.
- We'll now massage the above expressions to get some more mechanistic understanding out of them, specifically for dilute solutions.
  - Since we are postulating a dilute solution, we may use the approximation that the volume fraction of component 2 is small. This will allow us to expand the logarithms.
  - Recall from math class that for small, positive  $x$ , we have the following Taylor series expansion.

$$\ln(1 - x) = -x - \frac{x^2}{2} - \dots - \frac{x^n}{n} - \dots$$

- Additionally, we can approximate  $\ln(1 - x)$  for sufficiently small  $x$  by choosing only the first couple of terms in the expansion.
- It also follows from the assumptions that (1) the solution is dilute (i.e.,  $n_1 \gg n_2 N_2$ ) and (2) that the volume of the monomers is approximately equal (i.e.,  $v_1 \approx v_2$ ) that

$$\phi_1 = \frac{n_1 v_1}{n_1 v_1 + n_2 N_2 v_2} \quad \phi_2 = \frac{n_2 N_2 v_2}{n_1 v_1 + n_2 N_2 v_2} \approx \frac{n_2 N_2}{n_1}$$

- We thus expand

$$\ln(1 - \phi_2) \approx -\phi_2 - \frac{1}{2} \phi_2^2$$

- It follows that

$$\begin{aligned} \frac{\mu_1 - \mu_1^\circ}{RT} &= \ln(1 - \phi_2) + 1 \cdot \phi_2 - \frac{1}{N_2} \cdot \phi_2 + \chi \phi_2^2 \\ &\approx -\phi_2 - \frac{1}{2} \phi_2^2 + \phi_2 - \frac{\phi_2}{N_2} + \chi \phi_2^2 \\ &= -\frac{\phi_2}{N_2} + \left( \chi - \frac{1}{2} \right) \phi_2^2 \end{aligned}$$

- This expression implies that when  $\chi < 1/2$ , the whole thing will be negative.
  - It follows that if  $\chi < 1/2$ , the chemical potential  $\mu_1$  will be less than that of the standard, unmixed state  $\mu_1^\circ$ . Therefore, to lower the energy of the system, everything will want to mix.
  - In a subsequent course, we describe more results based off of the above equation!
- This chemical potential expression allows us to get a more precise definition of the  $\theta$  condition.

- First, recall from thermodynamics that for an **ideal solution**, the chemical potential of the solvent is related to its mole fraction  $x_1$  via

$$\mu_1 = \mu_1^\circ + RT \ln x_1$$

- Substituting  $x_1 = 1 - x_2$  and using the same small logarithm approximation as above, we can learn that for an ideal solution,

$$\frac{\mu_1 - \mu_1^\circ}{RT} = \ln(1 - x_2) \approx -x_2 = -\frac{\phi_2}{N_2}$$

- Let's now compare this expression to the one we just derived for the chemical potential of a polymer-solvent solution.

- Doing so, we'll see that they both have a  $-\phi_2/N_2$  term, but the polymer-solvent solution *also* has the following term.

$$RT \left( \chi - \frac{1}{2} \right) \phi_2^2$$

- This term is called the **excess chemical potential**.

- The excess chemical potential describes...

- Contact interactions, which relate to solvent quality as follows;

$$\chi \phi_2^2 RT$$

- Excluded volume as follows.

$$-\frac{1}{2} \phi_2^2 RT$$

- When contact interactions and excluded volume balance, this is the  $\theta$  condition. It follows that the  $\theta$  condition occurs when the excess chemical potential equals zero. But mathematically, this happens when  $\chi = 1/2$ !

- It also follows (as might be intuitive) that when we are in the  $\theta$  condition, the solution behaves as an ideal solution (i.e., with its chemical potential expression equal to that of an ideal solution).

- This is our definition of the  $\theta$  condition.

- Moreover,  $\chi > 1/2$  implies an elevated chemical potential for the solvent. The solvent would thus rather be closer to its pure state, and demixing will ensue. In other words,  $\chi > 1/2$  is indicative of a “bad solvent,” one that polymers don't like as much as they like themselves.

- On the other hand,  $\chi < 1/2$  implies a decreased chemical potential for the solvent, one that will be augmented by further mixing. Therefore,  $\chi < 1/2$  is indicative of a “good solvent.”

- Lastly, there is the matter of  $N_2$ . As  $N_2$  increases, the chemical potential of the solvent also increases. This means that as chains get longer, solvents tend to get “worse.”

- Implications of Flory-Huggins theory for the behavior polymer-solvent solutions, as seen on their phase diagrams.

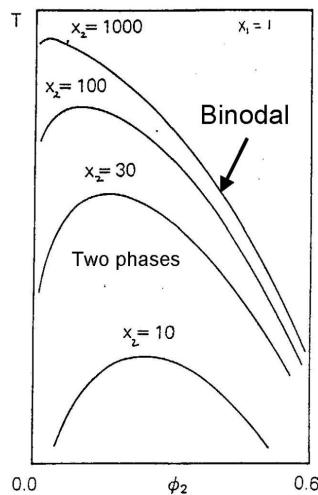
- Recall that a polymer-solvent solution occurs when component 1 is a solvent ( $N_1 = 1$ ), component 2 is a polymer ( $N_2 \gg 1$ ), and the solution is dilute ( $n_1 \gg n_2 N_2$ ).

- It is harder to mix small amounts of high molecular weight polymer into a solvent than it is to mix large amounts of said polymer into a solvent.

- This makes sense because beneath the critical concentration  $c^*$ , polymers will want to coil up into small localized pockets that essentially function as a second phase!

- The temperature required to ensure “even mixing” is the temperature needed to stretch the coils out more.

- Additionally,  $T_c$  increases as  $N$  increases.

Figure 2.10: Binodal curves for polymer-solvent solutions as  $N$  increases.

Binary System	$\phi_{1,c}$	$\chi_c$
Low molar mass liquids	$N_1 = N_2 = 1$	0.5
Polymer-solvent blend	$N_1 = 1, N_2$	$\frac{\sqrt{N_2}}{1 + \sqrt{N_2}}$
Symmetric polymer blend	$N_1 = N = N_2$	0.5
General	$N_1, N_2$	$\frac{\sqrt{N_2}}{\sqrt{N_1} + \sqrt{N_2}}$

Table 2.1: Critical composition and interaction parameters for binary blends.

- This illustrates the point that higher MW polymers require more thermal energy to mix well.
- General expressions for the critical composition and critical interaction parameters.
  - There are four regimes for which it is important to know these parameters: A regular solution of two liquids, a polymer-solvent blend, a **symmetric** polymer-polymer blend, and a general polymer-polymer blend.
  - You will derive these expressions in PSet 2, Q1e.
- **Symmetric** (polymer-polymer blend): A polymer-polymer blend for which the degrees of polymerization for each component are equal. *Constraint*

$$N_1 = N = N_2$$

- The limit of solvents getting “worse” occurs when you mix high molecular weight polymers.
  - Here, you don’t just need  $\chi < 1/2$  for a good solvent, but it turns out you will need  $\chi < 2/N$ .
    - You will prove the  $\chi < 2/N$  rule in PSet 2, Q1e.
    - This is why it is very difficult to mix high MW polymers.
- Let’s now discuss how we can estimate  $\chi$  experimentally using **solubility parameters**.
  - How do you determine  $\chi$  for a mixture? Hildebrand’s interesting idea was to use the molar enthalpy of vaporization  $\Delta\hat{H}_{v,i}$  of each component  $i$  in the mixture.

- Disclaimer: This derivation works better for nonpolar substances than polar substances; you will see why shortly.
- Aside (review): Some thermodynamics where the difference between enthalpy  $H$  and energy  $U$  actually does matter.
  - So far in this class, we have largely ignored the difference between enthalpy and energy, using the two terms interchangeably.
  - However, in Hildebrand's setup, we will experimentally measure the molar enthalpy of vaporization  $\Delta\hat{H}_{v,i}$  while theoretically calculating the molar energy of vaporization  $\Delta\hat{U}_{v,i}$ . Thus, we need to relate these two quantities.
  - Recall from thermodynamics that enthalpy  $H = U + PV$  is defined as the state function describing heat put into a system at constant pressure. It follows (since pressure is constant) that

$$\Delta H = \Delta(U + PV) = \Delta U + \Delta(PV) = \Delta U + P\Delta V$$

- In the specific case of vaporization,

$$\Delta H_v = \Delta U_v + [(PV)_{(g)} - (PV)_{(l)}]$$

- From the ideal gas law,  $PV = nRT$ . Moreover, since gases occupy far more volume than liquids, we may neglect  $(PV)_{(l)}$  and assume that  $P\Delta V \approx (PV)_{(g)}$ . Thus,

$$\Delta H_v = \Delta U_v + nRT$$

- Finally, in the specific case where we are considering only 1 mole of a substance,

$$\begin{aligned}\Delta\hat{H}_v &= \Delta\hat{U}_v + (1)RT \\ \Delta\hat{H}_v &= \Delta\hat{U}_v + RT\end{aligned}$$

- Hildebrand's experimental setup and derivation.

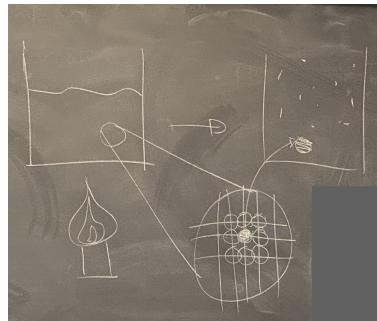


Figure 2.11: Hildebrand's experiment.

- Take a pure liquid, heat it up, and measure how much heat goes into the system before it turns into a gas.
- Consider this experiment from the perspective of lattice theory.
  - In lattice theory, every particle in a liquid corresponds to a point in the lattice. These lattice points interact with each other via enthalpic nearest neighbor interactions, as discussed above extensively (see, for example, Figures 2.4-2.5).
  - But when you transition to the gas phase, every particle is now neighborless. Thus, in terms of lattice theory, nearest neighbor interactions are gone and no particle has any potential energy.

- Essentially, in terms of lattice theory, the process of *vaporization* is equivalent to overcoming each nearest neighbor interaction!
- Let's now investigate these nearest neighbor interactions a bit more.

- Last lecture, we counted each nearest neighbor interaction in a pure substance, and denoted the total by

$$\xi_{ii} = \frac{X_i z \phi_i}{2}$$

- In this scenario (i.e., a pure component), the volume fraction  $\phi_i = 1$ .
- Additionally, since it will be easiest to measure the vaporization of a *molar* quantity, we will be interested in finding the number of nearest neighbor interactions in *one mole* of a pure substance. Thus, we set the number of particles  $X_i$  equal to the number of particles in a mole, which is just Avogadro's number  $N_A$ .
- Therefore, the total number of nearest neighbor interactions broken during the vaporization of one mole of a pure substance is

$$\frac{N_A z}{2}$$

- Continuing to let each nearest neighbor energetic interaction have magnitude  $\varepsilon_{ii}$ , we learn that the molar energy of vaporization  $\Delta\hat{U}_{v,i}$  of component  $i$  is equal to the number of interactions broken times the magnitude of each interaction, or

$$\Delta\hat{U}_{v,i} = \hat{U}_{(g),i} - \hat{U}_{(l),i} = 0 - \frac{N_A z \varepsilon_{ii}}{2} = -\frac{N_A z \varepsilon_{ii}}{2}$$

- Note that since  $\varepsilon_{ii} < 0$ , we have that  $\Delta\hat{U}_{v,i} > 0$ .

- From this equation, we may define the **cohesive energy density** and **solubility parameter**.

- **Cohesive energy density:** The energy needed to make a pure substance  $i$  cohere, or stick together, per unit volume. Denoted by **CED**. Given by

$$\text{CED} := \frac{\Delta\hat{U}_{v,i}}{\hat{V}_i} = \frac{\Delta\hat{H}_{v,i} - RT}{\hat{V}_i}$$

- $\hat{V}_i$  denotes the molar volume of substance  $i$  (i.e., the volume occupied by one mole of substance  $i$ ).
- Note that in this case, the slides use  $E$  instead of  $U$  to denote energy.

- **Solubility parameter:** A numerical estimate of the degree of interaction between materials. Units MPa<sup>1/2</sup>. Denoted by  $\delta$ . Given by

$$\delta := \sqrt{\text{CED}}$$

- Materials with similar solubility parameters are likely to be miscible.

- Let's now continue the derivation of the **Hildebrand equation**.

- We'll focus on a binary mixture of two components, named 1 and 2.
- Let  $v$  denote the volume of a single lattice site. Then from the above definitions, the solubility parameter  $\delta_i$  of each component in a binary mixture is

$$\delta_i = \sqrt{-\frac{N_A z \varepsilon_{ii}}{2\hat{V}_i}} = \sqrt{-\frac{N_A z \varepsilon_{ii}}{2(N_A v)}} = \sqrt{-\frac{z \varepsilon_{ii}}{2v}}$$

- Since 1 and 2 are assumed to be nonpolar, they attract (to themselves and to each other) only through London dispersion forces. In this case, the relevant attraction equation is

$$\varepsilon_{ij} = -\frac{\alpha_1 \alpha_2}{r^6}$$

- We assume that the elements of component  $i$  and component  $j$  are separated by a distance  $r$ , as in Figure 1.13c. Specifically,  $r$  will be equal to the distance between two cells in the lattice.
  - Notice that the attraction energy scales as  $1/r^6$ , and is also dependent on the **polarizability / polarizability volumes**.
  - Origin of the above relation: Related to dipole-induced dipole attractions; when you average over all possible combinations, this relation falls out. And that's what Lennard and Jones based their use of  $1/r^6$  as the attractive term on!
  - In PSet 2, we will prove that this attraction rule is “like likes like.”
- It follows from the above that

$$\varepsilon_{12} = -\sqrt{\varepsilon_{12}^2} = -\sqrt{\frac{\alpha_1^2 \alpha_2^2}{r^{12}}} = -\sqrt{\left(-\frac{\alpha_1 \alpha_1}{r^6}\right) \left(-\frac{\alpha_2 \alpha_2}{r^6}\right)} = -\sqrt{\varepsilon_{11} \varepsilon_{22}}$$

- The above equation is known as **Berthelot’s mixing rule**.
  - It expresses  $\varepsilon_{12}$  as the **geometric mean** of  $\varepsilon_{11}, \varepsilon_{22}$ .
- In light of the above definitions and equations, we may write

$$\begin{aligned} (\delta_1 - \delta_2)^2 &= \delta_1^2 - 2\delta_1\delta_2 + \delta_2^2 \\ &= -\frac{z\varepsilon_{11}}{2v} - 2\sqrt{\frac{z\varepsilon_{11}}{2v} \cdot \frac{z\varepsilon_{22}}{2v}} - \frac{z\varepsilon_{22}}{2v} \\ &= \frac{z}{v} \left[ -\sqrt{\varepsilon_{11}\varepsilon_{22}} - \frac{1}{2}(\varepsilon_{11} + \varepsilon_{22}) \right] \\ &= \frac{z}{v} \left[ \varepsilon_{12} - \frac{1}{2}(\varepsilon_{11} + \varepsilon_{22}) \right] \end{aligned}$$

- Now just multiply by  $v/k_B T$  to get the  $\chi$  parameter:

$$\frac{v}{k_B T} (\delta_1 - \delta_2)^2 = \frac{v}{k_B T} \cdot \frac{z}{v} \left[ \varepsilon_{12} - \frac{1}{2}(\varepsilon_{11} + \varepsilon_{22}) \right] = \underbrace{\frac{z}{k_B T} \left[ \varepsilon_{12} - \frac{1}{2}(\varepsilon_{11} + \varepsilon_{22}) \right]}_{\chi}$$

- Since  $\chi$  is equal to the product of positive quantities (including a perfect square), this equation shows that  $\chi \geq 0$  for a mixture of nonpolar substances!
- From here, we may finally get to the **Hildebrand equation**, which is the last line below.

$$\begin{aligned} \frac{\Delta H_M}{X_0 k_B T} &= \chi \phi_1 \phi_2 \\ \frac{\Delta H_M}{X_0 k_B T} &= \phi_1 \phi_2 \cdot \frac{v}{k_B T} (\delta_1 - \delta_2)^2 \\ \Delta \hat{H}_M &= \hat{V} \phi_1 \phi_2 (\delta_1 - \delta_2)^2 \geq 0 \end{aligned} \quad (\text{Hildebrand equation})$$

- $\Delta \hat{H}_M$  is the molar enthalpy of mixing. We get from the 2nd to the third line by multiplying through by  $N_A k_B T$ .
- $\hat{V}$  is the average molar volume of solvent / monomers.
  - Note that one of the assumptions of lattice theory is that  $\hat{V} = \hat{V}_1 = \hat{V}_2$ .
- This equation justifies why substances with similar solubility parameters are more likely to mix well, as stated in the definition of the solubility parameter.
  - Since  $\chi \geq 0$ , the enthalpy of mixing (for two nonpolar substances) will always be nonnegative. Thus, enthalpy can only cause substances to demix, not to mix better.
  - However, by the form of the Hildebrand equation, we see that as  $\delta_1 \rightarrow \delta_2$  (i.e., as  $|\delta_1 - \delta_2| \rightarrow 0$ ), the enthalpy of mixing will shrink. This makes entropy-driven mixing much more likely.

- Therefore, similar solubility parameters decrease the enthalpic barrier to mixing!
- See Rubinstein and Colby (2003) for an in-depth discussion of this setup.
- At this point, we've written a lot of theoretical equations. Now let's see how Flory-Huggins theory compares with experimental measurements of polymer-solvent blends.

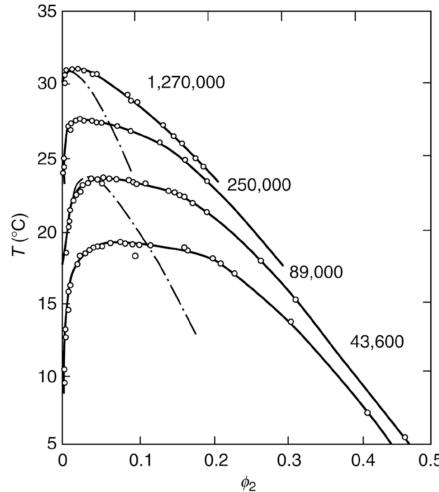


Figure 2.12: Flory-Huggins theory vs. experiment.

- To do so, we'll look at the classic data of Shultz and Flory (1952) on the binodal curves of PS in cyclohexane.
  - Note that Figure 2.12 is lifted from Lodge and Hiemenz (2020, p. 300) rather than the original paper as in the slides, since the textbook's figure is more consistent with the notation used thus far.
  - The dashed lines are the Flory-Huggins theory, which clearly differ significantly from the experimental results.
    - This difference is because of Flory's mean field assumption, which doesn't hold here. Indeed, as you heat up, you will be more likely to have the same neighbor.
    - However, while the predicted curve is wrong, the vertical scaling is correct! This phenomenon happens in several of Flory's theories.
- Phase diagrams of polymer-polymer blends.
  - Recall that the volume fraction that a chain occupies is
 
$$\phi = \frac{Nv}{(N^{1/2}\ell)^3} \propto N^{-1/2}$$
  - Specifically, this is the ratio of a polymer's hard volume to its pervaded volume.
  - The scaling in this equation implies that a polymer with 100 repeat units occupies about 10% of its pervaded volume, a polymer with  $10^4$  repeat units occupies about 1% of its pervaded volume, etc.
  - Therefore, molecules in a polymer chain are far more likely to interact with neighbors on a different polymer chain than they are to interact with themselves.
  - This leads to the melt condition in which excluded volume effects are largely washed out, and hence phase diagrams (as in Figure 2.13) look quite similar to those for a solvent-solvent mixture.
    - This average of the interactions of one polymer with many other chains also justifies the mean field assumption in this case.

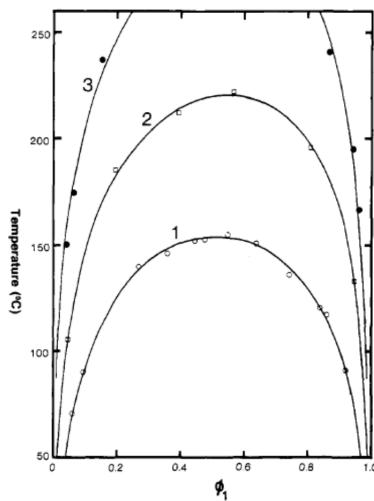


Figure 2.13: Binodal curves for PS-PB blends at almost symmetric compositions.

- At this point, we know what phase diagrams look like and what kinds of curves Flory-Huggins theory predicts they should have.
- However, real systems can exhibit additional phenomena beyond the capacity of Flory-Huggins theory to describe. As such, let's now look at the two principal types of real phase diagrams.

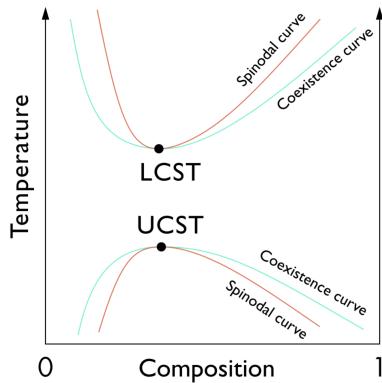


Figure 2.14: The upper and lower critical solution temperatures.

- Up until now, we have only considered solutions that undergo mixing at higher temperatures. Systems like this have a **UCST**.
- However, there also exist systems that *demix* at higher temperatures! Such systems have a **LCST**.
- Some systems, such as the idealized one sketched in Figure 2.14, exhibit both (or more/other!) types of behavior.
- **Upper critical solution temperature:** The critical point on a phase boundary that separates a two-phase region at low temperature from a one-phase region at high temperature. *Also known as UCST.*
- **Lower critical solution temperature:** The critical point on a phase boundary that separates a two-phase region at high temperature from a one-phase region at low temperature. *Also known as LCST.*

- Having covered the fundamentals of real phase diagrams, let's now look at some examples of real systems.
  - Poly(methyl methacrylate) / styrene-*co*-acrylonitrile demixes at increased temperature.
    - This particular system exhibits such behavior because the molecules involved are polar, and thus they preferentially bond to each other provided an excess of thermal energy.
  - Polystyrene / polyisoprene mixes at higher temperatures.
    - This mimicks the systems described by Flory-Huggins theory.
  - PEG and PMMA have a negative  $\chi$  at room temperature. PEG and H<sub>2</sub>O is similar (you heat it up, and the polymer comes out of solution).
  - A polymer-solvent solution of pNIPAM in H<sub>2</sub>O undergoes a transition around 32-34 °C.
    - Specifically, this is the temperature at which water molecules solubilizing pNIPAM will cease their enthalpically stable hydrogen bonding to the C=O and N–H moieties on the polymer.
    - Once the water molecules begin moving around more randomly, they interact more with the hydrophobic C–C backbone, which is not enthalpically favorable. In fact, this new interaction is so unfavorable that phase separation occurs!
- Key takeaway: Strong attraction gives rise to a low or negative  $\chi$ , and this commonly leads to deviations from Flory-Huggins theory.

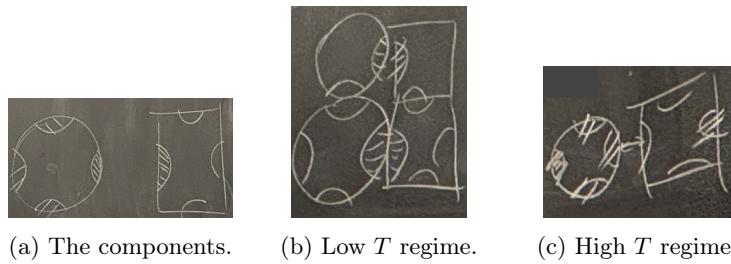


Figure 2.15: Systems with negative Flory  $\chi$  parameters.

- Example system (Figure 2.15a).
  - Consider a model two-component system, where one component is circular and the other component is rectangular. We may consider the components to be either free (like small molecules) or covalently bound together (like polymers); this distinction will not affect the following argument.
  - Suppose these two components have the ability to form productive interactions (e.g., a hydrogen bond) at the shaded regions.
  - At low temperatures (Figure 2.15b), these productive interactions will take hold and drive mixing.
    - Productive enthalpic interactions corresponds to a negative  $\chi$ !
  - At high temperatures (Figure 2.15c), however, we will rupture these attractive interactions and “like dissolves like” will take hold.
    - Notice how the “molecules” are pulling apart.
- Let's now discuss the LCST a bit more, especially as it pertains to polymer blends.
  - You can arrest a spinodal decomposition by **up-quenching** (heating the system into the unstable regime) and then — after a short hold, the time of which you vary on successive experiments — cooling the system very quickly.
    - This process allows you to “trap” the structure of the polymer blend partway through its spinodal decomposition, at a timepoint into the decomposition determined by the length of the hold!

- You can then observe the structure of the material using microscopy (e.g., TEM).
- Results from one such study.
  - McMaster (1975) found that the spinodal decomposition of a SAN/PMMA blend leads to **bicontinuous** structures. We will discuss bicontinuous phases more next class!
  - Allowing the spinodal decomposition to proceed too far will result in coarsening and droplet formation.
  - Note that this behavior mimicks how metal alloys behave under such temperature changes.
- A number of references on polymer blends are included in the slides!
- Applications of FH theory.
  - A Nature paper published just a few days ago used Flory-Huggins theory to explain how free amino acids (solvent) stabilize proteins (polymers) within cells.
  - Biocondensates.
    - These are also known as membrane-free organelles; many of these have been discovered since scientists expanded their definition of “organelle” beyond the requirement of a region cordoned off by a plasma membrane.
    - Examples: The nucleolus and centrioles.
    - These things come together because of FH theory!
- Next time.
  - Self-assembly.
  - The PSet 2 might be a bit long, so start early! We should currently be able to do every problem up to 3, and after Thursday, we should be able to do every problem.

## 2.3 Phase Behavior, Melting Point Depression, Osmometry, and Microphase Separation

9/25:

- Last time.
  - Entities that are not covalently bonded.
- Today.
  - Entities that *are* connected together.
    - You cannot get rigid phase separation here.
    - Self-assembly is a thing.
- Lecture outline.
  - Copolymers.
    - Microphase separation.
    - Interfacial free energy.
    - Chain stretching and configurational free energy.
      - This will bring back concepts from Professor Doyle's class.
- A bit more on biocondensates (not testable material).
  - Correction: The protein discussed last time goes into solution if you *add* salt.
  - Principle in biology: At some point, it gets better to have things that do multiple tasks poorly than one task really well.

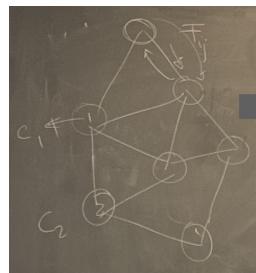


Figure 2.16: Simplified graph of a biochemical network.

- This is because it takes energy to produce proteins.
- Example: In computer science, engineers used to spend a lot of time to make 1 really nice transistor. But now, they go for a lot of transistors that are almost all the same and you connect them in different ways. Now you can do basically any task, but not all of them are great. In D. E. Shaw, they have a computer that *only* runs molecular dynamics (1000 times faster than Nvidia GPUs), but that's the only thing it does.
- So since we need a lot of functions in a cell and we don't want to produce a lot of very specialized proteins, it's better to be a bit more general.
- Suppose you have a (biochemical) network, and we control each transition between nodes locally (Figure 2.16).
  - If we want to actually do complex computation with the system, having junctions that act on a number of different nodes is helpful.
- Takeaway: Random things and disorder in a cell gives you capabilities beyond perfectly folded structures, like proteins and enzymes.
- This concludes content from last time; we now move onto today's content.
- Self-assembly of simplified systems (relative to cells).

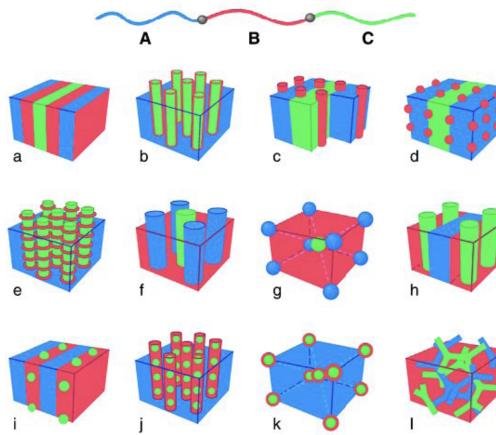


Figure 2.17: Self-assembly of an ABC triblock copolymer.

- What aspects of an ABC triblock copolymer affect its organization?
- There will be **intra interactions**  $\chi_{AB}$ ,  $\chi_{AC}$ , and  $\chi_{BC}$  between the various components of the chain.
- Let the chain have total length  $N$ , and let each of the three segments have length  $N_i$ .
  - Then we have  $N_A$ ,  $N_B$ , and  $N_C = N - N_A - N_B$ .

- If we have something like (a) of Figure 2.17, then we probably have  $N_A = N_B = N_C$  (because everything is nice and equally ordered) and  $\chi_{AC} < \chi_{AB} \approx \chi_{BC}$  (because we have AB and BC interfaces, but not AC interfaces).
- Note: These images are not made up; all of them have been seen.
- If we can do everything in Figure 2.17 with 3 things, imagine how much we can do with the 20 amino acids!
  - Note on the “hydrophobic” amino acids: They have branching (see valine, leucine, isoleucine)! Nature doesn’t just use  $n$ -alkyl chains of different length because the methyl groups sticking off have partial charges of 0.4 (40% the charge of an electron), which makes them still pretty polar.
  - Tyrosine can use its phenolic substituent to *enhance* its  $\pi$ -cation non-covalent interactions relative to phenylalanine.
- Key question: How can a homogeneous state go to a semiordered state, to an even more ordered state?
  - Example: Unfolded protein, to good prions, to rogue prions.
  - Aside: In rogue prions, there is an exposed  $\beta$ -pleated sheet, which will stack vertically with the  $\beta$ -pleated sheets of other prions. This stacking is what causes the brain to shut down in Mad Cow Disease.
- Goals for self-assembly.
  - Understand the key concepts behind the process of self-assembly, in particular for the case of block copolymers.
  - Construct a simple formalism to determine which variables contribute more relative to other ones.
  - Recent stuff on how to control self-assembly using external methods.
- **Min-max principle:** Phases are most stable when we (1) minimize interfacial energy and (2) maximize the conformational entropy of the chains.
- The min-max principle governs self-assembly.

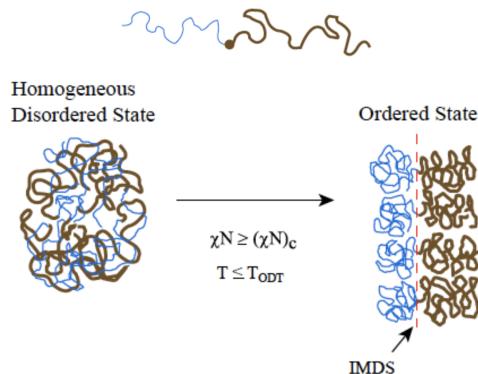


Figure 2.18: Ordering of a diblock copolymer.

- As we transition from a homogeneous, disordered state to an ordered state, we develop an interface.
  - This interface is technically termed the **IMDS**, or inter-material dividing surface.
- In the disordered phase, entropy is maximized... but we’re paying an enthalpic price because of the contact between groups that don’t like each other.
- The subscript  $c$  in Figure 2.18 means “critical.”

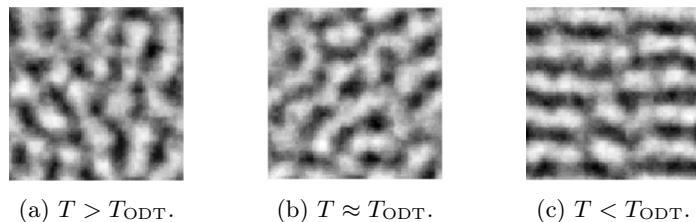


Figure 2.19: Microphase separation in diblock copolymers.

- Remember that  $\chi N$  controls whether or not we develop microdomains (more on this below). We will investigate this in PSet 2, too.
- Principles of self-assembly: Microphase separation in diblock copolymers.
  - $T_{ODT}$  denotes the order-disorder transition temperature.
  - Some domains start to form and you get lamellae in time.
  - Misconception: Things are not perfectly mixed at one extreme; you start seeing domains earlier. As you go from Figure 2.19a-2.19c, you get into a lamellar state.
- Microdomain morphologies: Diblock copolymers.

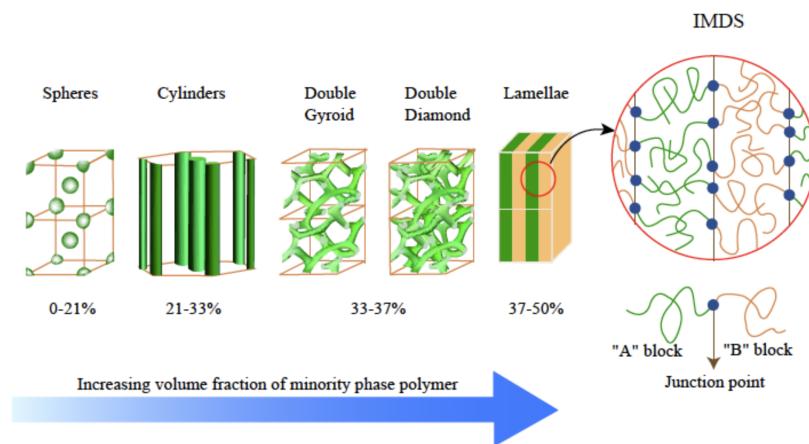


Figure 2.20: Microphase morphologies in diblock copolymers.

- In contrast to Figure 2.20, 40-60% gets you a lamellar state. This accounts for the fact that going on either side of 50% is equivalent.
- On the outskirts of this, you get **bicontinuous phases**.
  - The Double Diamond is heavily sought after in optics.
  - Double Gyroid is more common.
  - Difference is tri- vs. tetracoordination at the nodes.
- Then cylinders.
- And an even smaller amount of green gets you spheres.
- **Bicontinuous** (phases): Two demixed phases such that for any two points in a single phase, there exists a path between them that never crosses a phase boundary.
- Where are the above morphologies used?
  - Example: Krayton's / green rubbers.

- This is a PS-*block*-PB-*block*-PS polymer, with a big PB domain.
- The PS ends either land in another domain, or come back to the same domain.
- Good for high-performance applications, like the rubber in an F1 track.
- We now investigate microdomain spacing for diblock copolymers.
- Variables to be aware of.

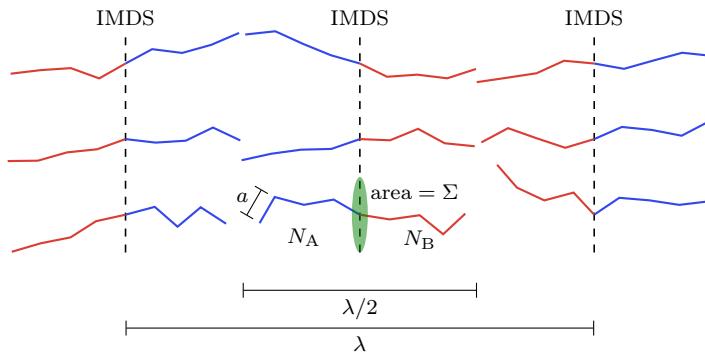


Figure 2.21: Variables describing microdomain spacing.

- $G$  is the free energy *per chain*.
  - $N = N_A + N_B$  is the number of segments per chain.
    - In Figure 2.21 as drawn,  $N_A = N_B = 4$ .
  - $a$  is the step size.
    - This can mean the Kuhn length or bond length, varying depending on the context.
    - For the purposes of this derivation, we assume that the step size for block A is equal to the step size for block B.
  - $\lambda$  is the domain periodicity.
    - This is the length of one of the repeating periods in a lamellar structure.
    - In the context of Figure 2.20's green-yellow-green-yellow lamellae,  $\lambda$  is the width of one pair of green-yellow lamellae back to back. You can think of this as a kind of “repeat unit,” the smallest structure length necessary such that upon repetition of that structure, the full lamellar mesophase is formed.
    - This also means that the left sketch in Figure 2.23 is mislabeled: It should be  $\lambda/2$ , which is also the expected length of a single chain in the microphase separated state.
  - $\Sigma$  is the interfacial area where a single chain's A block interacts with its B block.
  - $\gamma_{AB}$  is the interfacial energy on the IMDS per unit area.
    - We compute this using **Helfand's equation**.
  - $\chi_{AB}$  is the same Flory-Huggins interaction parameter we've been looking at in previous lectures, i.e., between homopolymers of A and B.
- **Helfand's equation:** The following expression of the interfacial energy in terms of other variables. Given by

$$\gamma_{AB} = \frac{k_B T}{a^2} \sqrt{\frac{\chi_{AB}}{6}}$$

- To get a little more comfortable working with these variables, let's discuss the following useful mathematical relation between them.

$$N a^3 = \Sigma \cdot \frac{\lambda}{2}$$

- This essentially equates (1) the total volume occupied by  $N$  monomers, each of volume  $a^3$  and (2) the volume of the cylinder bounding said monomers, a cylinder having height  $\lambda/2$  and base area  $\Sigma$ .
  - We now calculate the change in free energy of a diblock copolymer chain as it phase separates from a melt state and into microdomains.

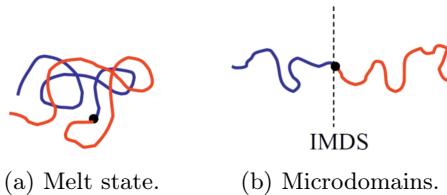


Figure 2.22: Diblock copolymer states.

- Let State 0 denote pure component A or B, State 1 denote a homogeneous melt of AB diblock copolymers (Figure 2.22a), and State 2 denote a phase separation of AB diblock copolymers into microdomains (Figures 2.22b and 2.21).
    - In a homogeneous melt, excluded volume effects are not present. Thus, in State 1, a single polymer chain's end-to-end distance  $R = N^{1/2}a$ .
    - By the definition of  $\lambda$ , a single polymer in State 2 has on average an end-to-end distance of  $R = \lambda/2$ .
  - We want to calculate the change  $\Delta G$  in Gibbs free energy *per polymer chain* upon transitioning from State 1 to State 2. In terms of enthalpy and entropy,  $\Delta G$  is thus given by

$$\Delta G = \underbrace{(H_2 - H_1)}_{\Delta H} - T \underbrace{(S_2 - S_1)}_{\Delta S}$$

- We have already developed extensive theory for polymers in the melt state. Let's use some of it to calculate each  $H_i$  or  $S_i$  in the above equation.
    - Recall from Lecture 1.3 that the entropy  $S$  of a polymer chain without excluded volume effects (as in the melt state) is given by
$$S = -\frac{3k_B R^2}{2Na^2}$$
  - Recall from Lecture 2.1 that the mixing energy per site  $\Delta H_M/X_0$  of components A and B may be related to other parameters by

$$\frac{\Delta H_M}{X_0 k_B T} = \chi_{AB} \phi_A \phi_B$$

- Since there are  $N$  sites in a polymer chain, the mixing energy *per chain* of components A and B is

$$\Delta H_M = Nk_B T \chi_{AB} \phi_A \phi_B$$

- Lastly, by our definitions of States 0-2, the mixing energy is equal to the difference in energy between a chain in State 1 and a chain in State 0. Note that this assumes that State 1 is basically the same as a melt of homopolymers of component A and component B. In this case, we have

$$H_1 - H_0 = Nk_B T \chi_{AB} \phi_A \phi_B$$

- Lastly, let's use some of our new variables.
    - In both State 0 and State 2, like chains will interact with each other enthalpically via at least London dispersion forces. Recall that this is how we got the equations  $H_i = zX_i\varepsilon_{ii}/2$  in Lecture 2.1.

- However, in State 2, there is an additional enthalpic interaction: The interfacial energy on the IMDS. Since we have this energy per unit area on the IMDS ( $\gamma_{AB}$ ) and the interfacial area of a single chain ( $\Sigma$ ), we can obtain the interfacial energy on the IMDS *per chain* by taking the product  $\gamma_{AB}\Sigma$ .
- Thus, the difference in energies between states 0 and 2 is purely equal to this additional enthalpic interaction. Symbolically,

$$H_2 - H_0 = \gamma_{AB}\Sigma$$

- Thus, putting everything together, we obtain

$$\begin{aligned} \Delta G &= [(H_2 - H_0) - (H_1 - H_0)] - T[S_2 - S_1] \\ &= [\underbrace{\gamma_{AB}\Sigma - Nk_B T \chi_{AB} \phi_A \phi_B}_{\text{Enthalpic Term}}] - T \left[ -\frac{3k_B(\lambda/2)^2}{2Na^2} + \frac{3k_B(N^{1/2}a)^2}{2Na^2} \right] \\ &= \underbrace{\gamma_{AB}\Sigma - N\chi_{AB}\phi_A\phi_B k_B T}_{\text{Enthalpic Term}} + \underbrace{\frac{3}{2}k_B T \left[ \frac{(\lambda/2)^2}{Na^2} - 1 \right]}_{\text{Entropic Term}} \end{aligned}$$

- The entropic term quantifies the springiness of the polymer. It is an important observation that  $\Delta S \propto \lambda^2/Na^2$ .
- Now that we have an equation for the change in energy upon microdomain formation, what can we do with it? One useful thing would be to calculate the optimal domain periodicity  $\lambda_{opt}$ .

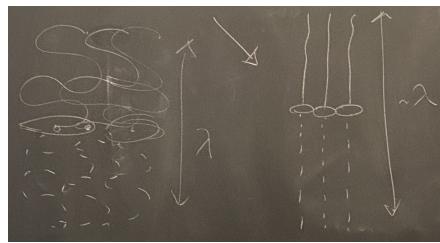


Figure 2.23: Structural changes as diblock copolymers are stretched.

- The idea that such a  $\lambda_{opt}$  exists is based in an important assumption: that polymer chains will want to stretch away from the IMDS.
- Enthalpy goes way down when you have linear strands (as on the right side of Figure 2.23), since this puts most monomers closer to each other on average than they are to monomers of the opposite component.
  - Similarly, enthalpy goes way up when everything squishes near the IMDS (as on the left side of Figure 2.23). This is because in this case, the interfacial area per chain  $\Sigma$  gets way bigger.
- In contrast, entropy goes way up when you have linear strands because we're stretching.
- Thus, the system will try to find the optimal balance between the enthalpic and entropic forces, by which we mean that we want to optimize the length  $\lambda$ .
- Let's now begin calculating  $\lambda_{opt}$ .

- To find the optimal  $\lambda$ , we'll want to find the minimum change in Gibbs free energy upon microphase separation as a function of  $\lambda$ . Symbolically, we want to minimize the following equation.

$$\Delta G(\lambda) = \underbrace{\frac{k_B T}{a^2} \sqrt{\frac{\chi_{AB}}{6}} \frac{Na^3}{\lambda/2}}_{\gamma_{AB}} - N\chi_{AB}\phi_A\phi_B k_B T + \frac{3}{2}k_B T \left[ \frac{(\lambda/2)^2}{Na^2} - 1 \right]$$

- Compressing every non- $\lambda$  variable in the above expression into constants (termed  $\alpha$ ,  $\beta$ ,  $\text{const}_1$ , or  $\text{const}_2$ ) reveals that the above equation is of the following general form.

$$\Delta G(\lambda) = \frac{\alpha}{\lambda} - \text{const}_1 + \beta\lambda^2 - \text{const}_2$$

- Thus, the optimal period of the lamellae repeat unit is

$$\begin{aligned} 0 &= \left. \frac{\partial \Delta G}{\partial \lambda} \right|_{\lambda_{\text{opt}}} \\ &= -\frac{\alpha}{\lambda_{\text{opt}}^2} + 2\beta\lambda_{\text{opt}} \\ \lambda_{\text{opt}} &= \sqrt[3]{\frac{\alpha}{2\beta}} \\ &= \left[ \frac{1}{2} \left( \underbrace{\frac{2k_B T \sqrt{\chi_{AB}} N a}{\sqrt{6}}}_{\alpha} \right) \left( \underbrace{\frac{3k_B T}{8N a^2}}_{\beta} \right)^{-1} \right]^{1/3} \\ &= \left[ \left( \frac{32}{27} \right)^{1/2} a^3 N^2 \chi_{AB}^{1/2} \right]^{1/3} \\ &\approx 1.03 a N^{2/3} \chi_{AB}^{1/6} \\ \lambda_{\text{opt}} &\approx a N^{2/3} \chi_{AB}^{1/6} \end{aligned}$$

- The result that  $\lambda_{\text{opt}}$  scales as  $N^{2/3}$  is important! It implies that chains in microdomains are stretched compared to the homogeneous melt state (in which scaling is the smaller  $N^{1/2}$ ).
- Let's now investigate the order-disorder transition temperature.

- By substituting  $\lambda_{\text{opt}}$  into our expression for  $\Delta G(\lambda)$ , we obtain the estimate that

$$\begin{aligned} \Delta G(\lambda_{\text{opt}}) &= \frac{2}{\sqrt{6}} k_B T N \chi_{AB}^{1/2} a \lambda_{\text{opt}}^{-1} - N \chi_{AB} \phi_A \phi_B k_B T + \frac{3}{8} k_B T \frac{\lambda_{\text{opt}}^2}{N a^2} - \frac{3}{2} k_B T \\ &= \left( \frac{2}{\sqrt{6}} + \frac{3}{8} \right) k_B T N^{1/3} \chi_{AB}^{1/3} - N \chi_{AB} \phi_A \phi_B k_B T - \frac{3}{2} k_B T \\ &\approx 1.2 k_B T N^{1/3} \chi_{AB}^{1/3} - N \chi_{AB} \phi_A \phi_B k_B T - \frac{3}{2} k_B T \\ &\approx 1.2 k_B T N^{1/3} \chi_{AB}^{1/3} - N \chi_{AB} \phi_A \phi_B k_B T \end{aligned}$$

- Since the first two terms in line 3 are both much greater than the third term, we neglect it.
- Thus, the sign of  $\Delta G$  will depend on which of the two terms remaining in line 4 is bigger.
- Let's analyze the case of a 50/50 volume fraction of components A and B. Specifically, we want to know what the critical  $N\chi$  value is above which  $\Delta G = -$  and we form lamellar microdomains, and below which  $\Delta G = +$  and we stay in a homogenous melt.

- In a 50/50 split,  $\phi_A = \phi_B = 1/2$ . Thus,

$$\phi_A \phi_B = \frac{1}{4}$$

- It follows that the critical  $N\chi$  value ( $(N\chi)_c$ ) — at which  $\Delta G(\lambda_{\text{opt}}) = 0$  — is

$$\begin{aligned} \frac{(N\chi)_c}{4} &= 1.2(N\chi)_c^{1/3} \\ (N\chi)_c^{2/3} &= 4.8 \\ (N\chi)_c &\approx 10.5 \end{aligned}$$

- Therefore, if  $N\chi < 10.5$ , we'll get a homogeneous, mixed melt; and if  $N\chi > 10.5$ , we'll get demixing into lamellar microdomains.
- Phase transitions between different microstructures can also be represented on a  $\chi N$  vs. composition phase diagram.

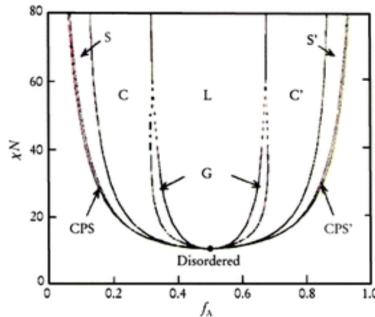


Figure 2.24: Microphase transition diagram.

- As expected,  $(\chi N)_c \approx 10.5$ .
- Moreover, as we go in from the outside (homogeneous, disordered mixed melt), we progressively go through spheres (S), cylinders (C), gyroids (G), and lamellae (L).
- Block copolymer microphases locally look like a series of homopolymers bound to the planar IMDS. This construction is actually very much related to another scenario known as a **polymer brush**.
- **Polymer brush:** A series of homopolymers which have been attached by one end to a hard, planar surface.
  - See Figure 2.25 for a visualization.
  - Variables relevant to polymer brushes.
    - $D$  is the average distance between each grafting site.
    - $H$  is the average height away from the surface to which the polymers stretch.
      - It follows from the definitions of  $D$  and  $H$  that the volume occupied by a single polymer chain is  $HD^2$ .
    - As before,  $N$  and  $a$  are Kuhn parameters.
      - Thus, analogously to before,  $HD^2 = Na^3$ .
    - $c = N/HD^2$  is the (assumed uniform) number density of monomers throughout the brush's volume.
    - $n$  is the total number of chains on the surface.
    - $A$  is the total area of the surface.
    - $\sigma = \rho = n/A = 1/D^2 = H/Na^3$  is the grafting density.
  - The polymer strands stretch out more ( $H$  increases) in two main cases.
    - When they don't want to interact with the 2D interface.
    - When they are so close together that they are crowded away from the surface.
  - Now that we have a language through which to discuss brushes, let's analyze the system as before.
    - What is the energy or enthalpy? If we need to take excluded volume into account, then

$$\Delta H \propto vc^2 \cdot HD^2 = \frac{vN^2}{HD^2}$$

- $v$  is the excluded volume.
  - $c^2$  describes how dense the system is.
    - Explicitly, it is the probability of two segments coming into contact.
  - Together,  $vc^2$  describes how many two body interactions there are (counted by mole).
  - Note the similarity between this term and the Virial expansion's binary term from Lecture 1.3.
- What is the entropy?

$$\Delta S \propto \frac{H^2}{Na^2}$$

- This is analogous to the  $\lambda^2/Na^2$  proportionality from the diblock copolymer case, except with variables changed.
- For the full expression for  $\Delta S$ , the entropy derivation from above is exactly analogous, affording

$$\Delta S = -\frac{3}{2}k_B \left( \frac{H^2}{Na^2} - 1 \right)$$

- Now we may consider how to find the optimal stretching distance  $H$ .
- The enthalpic term goes as  $1/H$  and the entropic term goes as  $H^2$ . Thus, the enthalpic term increases at small  $H$  and the entropic term increases at large  $H$ .
  - Therefore, the Gibbs free energy goes as  $H^2 + 1/H$  and has a proper energy valley. It is the minimum point on this valley that we seek.
  - We will explore this problem more in PSet 2, Q5.

## 2.4 Office Hours (Alexander-Katz)

9/30:

- PSet 2, Q5.

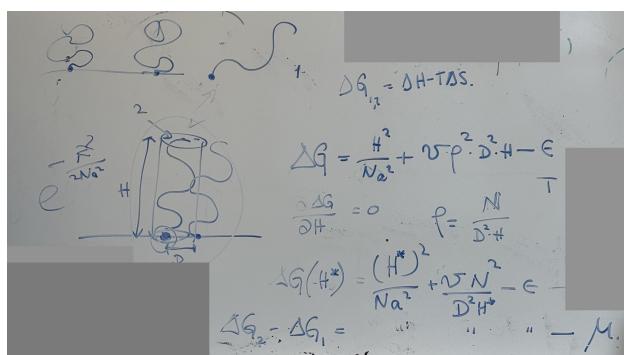


Figure 2.25: PSet 2, Q5 setup.

- Let state 1 be the free chain floating in solution. State 2 is then the brushes stuck/adsorbed to the surface.
- If they're stuck at a particular grafting density  $D$ , you first have to calculate the free energy of a chain being that close to another.
- Bringing in Prof. Doyle's lectures,

$$\Delta G = \frac{H^2}{Na^2} + V_{ex} \rho^2 \cdot HD^2 - \varepsilon$$

- $HD^2$  is a volume.
- $\rho = N/HD^2$  is the number density of monomers.

- So then we need the optimal  $H$ , which we will term  $H^*$ .  $H^*$  minimizes  $\Delta G(H^*)$ , i.e.,  $\langle \partial \Delta G / \partial H \rangle_{H=H^*} = 0$ .
- Then we back feed  $H^*$  into the  $\Delta G$  equation above.
- To find  $D$ , we have to evaluate the stability relative to state 1.
  - $\mu_{\text{bulk}}$  or  $\mu_1$  ( $\mu_1$  seems to be the notation Alexander-Katz used most consistently) can be the chemical potential / energy of state 1. We will have to define this variable.
  - We consider this because we need the energy to take a chain out of state 1 (and into state 2), but changes in state relative to concentration is chemical potential.
- Then the last thing is
 
$$\Delta G_2 - \Delta G_1 = \frac{(H^*)^2}{Na^2} + \frac{vN^2}{H^*D^2} - \varepsilon - \mu_{\text{bulk}}$$
  - And this  $\Delta\Delta G$  must be negative if grafting is going to happen.
- $a$  can be a Kuhn length or segment length or whatever; we're forgetting about all of the chemistry once we get into thermodynamic models.
- We need to figure out the per strand energy, hence why we're concerned with  $\varepsilon$  and not  $N\varepsilon$  (which would be for the whole system).
- You need to account for the entropy of stretching, the enthalpy of sticking, and excluded volume.
  - $vN^2/HD^2$ .
  - Stretching term is  $H^2/Na^2$ . Excluded volume is  $v\rho^2 \cdot HD^2$ .
  - Balance the two terms  $H^2/Na^2$  and  $vN^2/HD^2$  to find  $H^*$ .
  - Then factor in  $\varepsilon$ .
- Phase diagrams.
  - $\chi N$  or  $\chi$  on the  $y$ -axis.
    - This is approximately  $1/T$ , so going up is low  $T$ .
  - Inner dashed line is **spinodal** or **stability** curve.
    - The inflection points on the pink curve in Figure 2.7c defines the spinodal curve.
    - Flat bottomed curve defines critical point!
  - Outer solid line is **binodal** or **equilibrium** or **coexistence** curve.
  - Lowest point where the two curves touch is the **critical** point.
  - Real phase separation is at the binodal line.
    - If we wait a long time.
  - For a symmetric system, we get flat bottomed tangents.
  - Why does the spinodal matter? Won't we just get to the lowest energies?
    - Free energy is the sum of the two states. Downhill from the middle to the spinodal points.
    - Splitting our system in two past the spinodal is not downhill. The way we go beyond this is **nucleation**. You will end up at a higher energy until the nucleating thing is big enough.
  - Nucleation between the curves, spinodal decomposition (to the spinodals) in the middle.
  - Example of utility: QDot synthesis.
    - They first jump into the spinodal zone that will phase separate, creating a bunch of little dots.
    - Then we quickly move the solution (once we have similarly sized nuclei) into the intercurve region. Here we no longer have spontaneous nucleation, but we have growth. And everything will grow at the same rate.
    - People who do nanoparticles play this game all the time. Heterogeneous nucleation: Dumping some trash in to nucleate other stuff, e.g., gold nanoparticles to nucleate silicon-oil phase separation.

- PSet 2, Q3b: When we need to determine  $A$ ? Finding  $\chi_c$  based on other problems, but then how do we get  $A$ ?
  - Critical temperature in the thousands of kelvins? Should be  $A = 45$  and  $\chi_c \approx 8000$  K.
  - We're not accounting for the entropic term in  $\chi$ , so we get an unreasonable value.
- $\Sigma\gamma_{AB}$  is the interfacial energy, which is kind of like the surface tension.
- Helfand parameter.
  - For a particular  $\chi$ , what will be the expected loop crossing the interface into the region of the other polymer.
- PSet 2, Q4 for the star polymer. Is the setup a B cylinder surrounded by AC mixed region?
  - Yes, something like that.
- Aside: It is really hard to get away from the phases in Figure 2.17 and get into new ones.
  - Stadler's goldmine.
- nVT vs. nPT constant regimes.
  - Lowest common energy is the *tangent* line, not the line connecting the two minima.
  - For the calculation for a real phase diagram, the math gets dicey because we have to deal with tangent lines.
  - Implication: The combination of the two unequal wells will give you the total lowest energy, rather than the lowest and the lowest. Moreover, we need to not be at the bottom of the wells, but slightly to the side so we get the tangent line rather than the line connecting the minima.

## 2.5 Review for Quiz 1

- Quiz 1 details.
  - Starts at 3:05 PM sharp.
  - 80 minutes to take it.
    - They're not here to fail us; they will put things appropriate for us to do in 80 minutes.
  - Open book (bring Kwangwook's textbook), notes (print out notes!!), cheat sheets (“you'll probably want one of these”), but no electronic except for the occasional use of a calculator (check TI-84 batteries!! Phone calculator allowed, though).
  - Undergrads need to answer 3/4 questions; grad students must answer all of them.
  - Quiz is based on the HW, so make sure you know how to do it!
- Announcements.
  - 2nd HW solutions will be posted tomorrow.
  - A pre-test has been posted.
- Review starts now.
- Topic 1 (ideal chains) topics to know.
  - General characteristics of polymers: Degree of polymerization  $N$ , tacticity, bond length, etc.
  - Properties of polymer systems:  $M_w$ ,  $M_n$ , architecture.
  - Different models for polymers: Freely jointed chain (FJC), freely rotating chain (FRC), symmetric hindered rotations (and rotational isomeric states).

- Things that come out of these models: End-to-end distances  $\mathbf{R}$  (with  $\langle R^2 \rangle = C_\infty Nl^2$ ), characteristic ratio  $C_\infty$ .
- An important model for polymers: Kuhn's equivalent chain (with its effective bond length  $l_k$  and degree of polymerization  $N_k$ ).
  - This is the only model we've used since we introduced it, as we've increasingly neglected the *chemistry* involved to focus on the thermodynamics.
- The end-to-end distribution is a Gaussian.
  - Since the probability  $p \propto e^{-\Delta G/k_B T}$  and  $\Delta G = F = 3k_B T R^2 / 2Nb^2$ , we get  $\Delta S/k_B T \propto R^2/Nb^2$ .
  - Spring constant in our Hookean spring is  $3k_B T/Nb^2$ .
- Crossover concentrations (Figure 1.10).
  - The chain inhabits a sphere of volume  $R_e^3$ , and the volume per chain is  $V_c \propto R_e^3$ .
  - The number density in the bead is  $c = N/R_e^3$ . When  $c$  is greater than the critical concentration  $N/R_e^3$ , we start to get overlap.
- Topic 2 (real chains) things to know.
  - Excluded volume  $v$  comes from a hard core and the attractive part of the potential.
  - The Mayer- $f$  function is
 
$$f = e^{-U/k_B T} - 1$$
    - The excluded volume is the integral of  $f$  over all space.
    - Intuition for why the integral is excluded volume?
      - The Mayer- $f$  function gives the probability of finding two things close to each other.
      - It essentially tells us how this probability relates to that of an ideal gas where there is no interaction.
      - The attractive component raises the probability that things are close together.
      - The entropic component compensates for this, and doing the integral takes both into account. It measures the effective volume a particle feels like it has when in a sea of other particles.
      - If the interaction is only repulsive, a given particle will feel the volume of the box minus the volume of other monomers.
      - If an attractive component exists, you can eventually balance out repulsion. It's not that the volume has been reduced; it's just that negative excluded volumes mean you don't care about repulsion, you just want to be closer together. So negative excluded volumes effectively reduce the volume the polymer wants to occupy.
    - The  $\theta$  condition for a chain is where excluded volume is zero.
    - Solvent quality.
      - A polymer in a vacuum attracts to itself because of van der Waals forces; it doesn't just float around.
    - Interaction energies.

$$\frac{F_{\text{int}}}{V k_B T} = \frac{1}{2} v c^2 + \frac{1}{3!} \omega c^3$$

- We often call these enthalpic energies.
- $F_{\text{int}}/V$  is an energy density, and dividing by  $k_B T$  takes away the units from the righthand side.
- When  $v < 0$ , we need the next term to the right.
- Volume of the chain, Flory's free energy for a single chain:

$$F = \underbrace{\frac{R^2}{Nb^2}}_{\text{expansion term}} + \underbrace{\frac{Nb^2}{R^2}}_{\text{compression term}} + \frac{1}{2} v \frac{N^2}{R^3} + \frac{1}{3!} \omega \frac{N^3}{R^6}$$

- There is a handwavey and a formal way to come up with the compression term.
- First two terms are the “entropic terms,” in contrast to the latter two “enthalpic terms.”
- Scaling of polymer chains.
  - The size  $R$  will be proportional to  $b$  (the segment length, commonly Kuhn length) times  $N^\nu$ .
  - In a  $\theta$  solvent,  $\nu = 1/2$ . For a good solvent,  $\nu = 3/5$ . For a bad solvent,  $\nu = 1/3$ .
  - We don’t use all terms when we’re minimizing things; we use the ones that matter. If the chain is going to expand, we get rid of the compression term. If one of them is negative, we use the last term. Know when to use which terms!!
- Dimensionality matters.
  - $\nu_{\text{good}} = 1, 2, 3, 4$  for  $\nu = 1, 3/4, 3/5, 1/2$ .
- Topic 3 (Flory-Huggins) things to know.
  - Blends and solutions of polymers and (sometimes) solvents.
  - We’re interested in the free energy of mixing  $\Delta G_M = \Delta H_M - T\Delta S_M$ .
    - An entropic term and enthalpic term come together to make
$$\frac{\Delta G_M}{k_B T X_0} = \frac{\phi_1}{N_1} \ln \phi_1 + \frac{\phi_2}{N_2} \ln \phi_2 + \chi \phi_1 \phi_2$$
    - The Flory  $\chi$  parameter quantifies interactions.
$$\chi = \frac{z}{k_B T} \left[ \varepsilon_{12} - \frac{1}{2}(\varepsilon_{11} + \varepsilon_{22}) \right]$$
    - Take the coordination number, divide by your units of energy, and then compare the interphase attractive energy to the average of the two intraphase attraction energies.
    - $\chi$  scales as  $A/T$ , for some number  $A$ . To make the real world fit the system, we often add another term  $B$  as the “entropic contribution.” Symbolically,
$$\chi = \frac{A}{T} + B$$
    - The above equation allows us to interconvert between  $\chi$  and  $T$ , which we often do in phase diagrams, etc.
  - Phase diagrams.
    - 3 systems of interest.
      - Polymer-polymer systems.
      - Monomer-monomer systems.
      - Polymer-monomer systems.
    - For polymer-polymer and polymer-monomer systems,  $\chi N$  really controls things.
    - Outside the coexistence / equilibrium / binodal curve, you mix into 1 phase.
      - Inside both, you demix to the spinodal. Then with nucleation over a long period of time, you demix to the binodal.
    - Solubility parameters: Interconverting from  $\chi$  to  $\delta$ , as in PSet 2.
    - UCST and LCST transitions. Heating it up goes into an LCST regime, and cooling it down goes into a UCST regime.
  - Topic 4 (self-assembly).
    - Be familiar with the min-max principle of (1) minimizing energy and (2) maximizing entropy.
    - Phases of diblock copolymers.

- Spheres (BCC), cylinders (hexagonal; 20% – 35%), bicontinuous ( $35\% \pm 2\%$ ; gyroid, double diamond, and perforated lamellae), lamellae (40-60%).
- Aside: There is no excluded volume in self-assembly.
- Be familiar with diagrams like the binodal/spinodal one but with many nested curves, each one for a different phase transition (Figure 2.24).
  - Not binodal and spinodal but actual different phases where you have spheres, cylinders, gyroids, lamellae. Happens theoretically around  $(\chi N)_c = 10.5$ ; experimentally around 20.
  - $f$  on the  $x$ -axis; the fraction of one thing relative to the other, which accounts for polymer structure instead of just  $\phi$  for monomers.
- Should we know the polymer names and monomer repeat units?
  - Print this!!
- For the scaling of polymer chains, is this the same as the radius of gyration?
  - Slight difference in prefactor, but for linear chains, it's very close.
  - There's a  $\sqrt{6}$  term in the radius of gyration.

## 2.6 Office Hours (Alexander-Katz)

10/7:

- With the pNIPAM example, wouldn't increasing entropy of mixing at higher temperatures cause everything to mix?
  - Phase separation will occur in systems with negative  $\chi$  as temperature increases *regardless* of the fact that the entropic mixing energy becomes more extreme.
  - That being said, at sufficiently high temperatures, any system will remix due to entropic considerations (but the system may decompose before we are able to reach such a high temperature).
  - This remixing means that binodal lines are *always* “eye-shaped” if we extend the vertical axis to high enough temperatures.
- What are some good resources to read about phase behavior in block copolymers, attachment to surfaces, interfacial energy, and the other topics from Lecture 2.3 that are not covered in Lodge and Hiemenz (2020)?
  - Rubinstein and Colby (2003) has some good information on brushes.
  - Strobl (1997) has some good information on block copolymers.
  - Bates and Fredrickson (1999) — which was also referenced in the slides, though not cited in full — has some good overview of the concepts as well.

## 2.7 Chapter 7: Thermodynamics of Polymer Mixtures

*From Lodge and Hiemenz (2020).*

9/30:

- Goals for this chapter.
  - Thermodynamically analyze a solution of a polymer in a low molecular weight solvent.
  - Determine the phase equilibria relevant to this situation.
- **Polymer blend:** A mixture of two polymers.
- **Pure** (thermodynamics): The purely phenomenological study of observable thermodynamic quantities and the relationships among them.

- **Statistical** (thermodynamics): The atomistic model justifying purely thermodynamic observations.
  - “*Doing* thermodynamics does not even require knowledge that molecules exist... whereas *understanding* thermodynamics benefits considerably from the molecular point of view” (Lodge & Hiemenz, 2020, p. 271).
- In this chapter, we are concerned with the state of a two-component system at equilibrium. The Gibbs free energy relates to this equilibrium, and in this case, it is given by

$$\begin{aligned} dG &= \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2} dP + \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2} dT + \left(\frac{\partial G}{\partial n_1}\right)_{P,T,n_2} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{P,T,n_1} dn_2 \\ &= V dP - S dT + \sum_{i=1}^2 \mu_i dn_i \end{aligned}$$

- **Partial molar** (quantity  $Y$  of component  $i$ ): The amount of  $Y$  contributed to the whole by each mole of component  $i$  in a mixture. *Denoted by  $\bar{Y}_i$ . Units mol<sup>-1</sup>. Given by*

$$\bar{Y}_i := \left(\frac{\partial Y}{\partial n_i}\right)_{P,T,n_j \neq i}$$

- Example: The chemical potential of component  $i$  is the amount of Gibbs free energy contributed to the total Gibbs free energy  $G$  by each mole of  $i$ .
- There exist a partial molar volume, enthalpy, and entropy.
- The value of partial molar quantities depends on the overall composition of the mixture.
  - Example:  $\bar{V}_{H_2O}$  is not the same for a water-alcohol mixture that is 10% water as for one that is 90% water.
  - For a pure substance, partial molar quantities are equal to **molar values**.
    - Example:  $\mu_i = \hat{G}_i$ .
  - Properties of a mixture are linear combinations of mole-weighted contributions of the partial molar properties of the components.

$$Y_m = \sum_i n_i \bar{Y}_i$$

- The value of  $Y_m$  on a per mole basis is given by **mole fractions** as follows.

$$\frac{Y_m}{\sum_i n_i} = \sum_i x_i \bar{Y}_i$$

- Partial molar quantities exhibit the same relations as ordinary thermodynamic variables.
  - Examples:

$$\mu_i = \bar{H}_i - T \bar{S}_i \quad \bar{V}_i = \left(\frac{\partial \mu_i}{\partial P}\right)_{T,n_j \neq i}$$

- **Molar** (quantity  $Y$  of substance  $i$ ): The amount of  $Y$  contributed by each mole of a substance  $i$  when pure. *Denoted by  $\hat{Y}_i$ . Units mol<sup>-1</sup>.*
- **Mole fraction** (of component  $i$ ): The fraction of moles of component  $i$  relative to the total number of moles in the mixture. *Denoted by  $x_i$ . Given by*

$$x_i := \frac{n_i}{\sum_i n_i}$$

- **Standard state** (value of  $Y_i$ ): The value of  $Y_i$  when the substance  $i$  is pure. *Denoted by  $\mathbf{Y}_i^o$ .*

- **Activity:** A thermodynamic concentration and measure of the nonideality of solutions. *Denoted by  $a_i$ . Given by*

$$\mu_i = \mu_i^\circ + RT \ln a_i$$

- Notation.

- We've established  $n_i$  as the number of *moles* of component  $i$ .
- Let  $m_i$  denote the number of *molecules* of component  $i$ . Thus,

$$m_i = N_A n_i$$

where  $N_A = 6.022 \times 10^{23}$  is **Avogadro's number**.

■ This is also equal to  $X_i$  from class!

- **Coordination number:** The number of nearest neighbors that surround a central lattice point. *Denoted by  $z$ .*

- Example: A cell in a 2D square lattice has  $z = 4$ .

- Regular solution theory: A simple statistical model that provides a useful expression for the free energy of mixing for a binary solution of two components.

- Assume that the two molecules in the mixture have equal volumes.
- Assume that the two components have equal (and concentration-independent) partial molar volumes, i.e.,  $\bar{V}_1 = \bar{V}_2$ .
- Imagine each molecule occupying a cell in a lattice with volume equal to the molecular volume.
- Let the lattice have coordination number  $z$ .

10/2:

- Lodge and Hiemenz (2020, p. 275) presents the entropy of mixing in the four useful forms: Original, with  $R$  and number of moles, per site, and per mole of sites.

- This really helps clarify some of the rearrangements in PSet 2, Q1a.

- Comments on the entropy of mixing.

- $\phi_i < 1$  always, so  $\ln \phi_i < 0$  always. This implies that  $\Delta S_M$  is always positive, so configurational entropy always favors spontaneous mixing!
- The expression derived is symmetric with respect to exchange of 1 and 2. Such symmetry comes from the assumption that both mixing molecules are the same size, and is difficult to satisfy in real situations.
- We are assuming that all configurations are equally probable (i.e., that 1 is equally likely to be next to 1 as it is to 2 and vice versa). But if there was an energetic preference, each configuration would need to be weighted by the appropriate Boltzmann factor.

- Lodge and Hiemenz (2020, p. 276) take the perspective that each  $\varepsilon_{ij}$  is negative, rather than being the absolute value of the depth of the well in Figure 2.5.

- It is unclear which perspective we take in class. However, it does make sense for these terms to be negative, as every type of molecule attracts at least a bit to every other type due to London dispersion forces at minimum.

- **Exchange energy:** The difference between the attractive cross-interaction of 1 and 2 and the average self-interaction of 1 with 1 and 2 with 2. *Denoted by  $\Delta\varepsilon$ . Given by*

$$\Delta\varepsilon := \varepsilon_{12} - \frac{1}{2}(\varepsilon_{11} + \varepsilon_{22})$$

- When only London dispersion forces are present, we preferentially have  $\Delta\varepsilon \geq 0$  because “like dissolves like.”
- On the Flory  $\chi$  parameter.
  - This parameter is equal to the exchange energy per molecule, normalized by the thermal energy  $k_B T$ .
  - The Flory  $\chi$  parameter is the energy penalty you must pay (as a fraction of  $k_B T$ ) in order to lift one molecule of type 1 out of a beaker of pure 1, one molecule of type 2 out of a beaker of pure 2, and exchange them. See Lodge and Hiemenz (2020, p. 277). This is because when we do this in a typical square lattice, four things happen.
    1. First, removing a molecule of 1 from a lattice of pure 1 disrupts its interaction with each of its  $z = 4$  nearest neighbors. But as established earlier, each nearest neighbor interaction only contributes  $\varepsilon_{11}/2$  to the total energy/enthalpy of the pure state because we ‘see’ the interaction from the perspective of each molecule involved. Thus, the energy penalty of this removal is  $4 \cdot \varepsilon_{11}/2 = 2\varepsilon_{11}$ .
    2. Removing a molecule of 2 is analogous, and costs  $2\varepsilon_{22}$ .
    3. Adding a molecule of 2 to the now-empty space in a beaker of pure 1 *rewards* you  $2\varepsilon_{12}$ .
    4. Analogously, adding a molecule of 1 to the now-empty space in a beaker of pure 2 rewards you  $2\varepsilon_{12}$ .
  - Adding up all of these contributions gives  $\chi k_B T$ .
  - Then finally dividing by  $k_B T$  makes  $\chi$  unitless, by expressing the energy summed above as a numerical fraction of a known reference energy (namely,  $k_B T$ ).
- **Mean field** (theory): A theory that assumes that the local interactions are determined solely by the bulk average composition.
- On volume fractions.
  - For solvent-solvent systems, volume fractions are equal to mole fractions.
  - For polymer-solvent and polymer-polymer systems, volume fractions are easier to use because calculating them only requires measuring the mass of each component and comparing it against known densities. Measuring mole fractions, on the other hand, requires precise knowledge of the full molecular weight distribution. Therefore, although mole fractions and volume fractions are mathematically equivalent, expressing our results in terms of volume fractions provides an empirically easier to use equation.
- Lodge and Hiemenz (2020, pp. 279–82) derives the  $1/N$  prefactors in the  $\Delta S_M$  equations more rigorously, as alluded to in class.
  - $\Delta H_M$  would also change a bit in the polymer cases, but this complication is ignored.
- Note that because monomers are not equally dispersed in dilute solutions (see Figure 1.10, left), the mean field approximation is not as good here.
  - It follows that the mean-field approximation (and hence Flory-Huggins theory) should get better as  $c \rightarrow c^*$ . This turns out to be the case!
- A summary of the assumptions used in Flory-Huggins theory (Lodge & Hiemenz, 2020, p. 283).
  1. There is no volume change on mixing, and  $\bar{V}_i = \hat{V}_i$  is independent of concentration.
  2.  $\Delta S_M$  arises entirely from the ideal combinatorial entropy of mixing.
  3.  $\Delta H_M$  arises entirely from the internal energy of mixing.
  4. Both  $\Delta S_M$  and  $\Delta H_M$  are computed assuming random mixing.
  5. The interactions are short-ranged (nearest neighbors only), isotropic, and pairwise additive.

6. The local concentration is always given by the bulk average composition (the mean-field assumption).
- Lodge and Hiemenz (2020, pp. 283–89) covers some good osmotic pressure content that may be useful someday. Reviewing activity, activity coefficient, osmotic pressure, and Virial expansion info from Thermo will be necessary before delving into this.
  - **Phase diagram:** A mapping of the temperature-composition plane of a solution at fixed pressure, divided into regions wherein we find different phases.
  - Lodge and Hiemenz (2020, p. 291) view a phase diagram in terms of temperature, not  $\chi$ .
  - The three features of a phase diagram (in terms of  $\chi$ ).
    1. A **critical point** below which a one-phase solution is formed in all compositions.
    2. A **binodal** describing the composition of the two phases that coexist at equilibrium, after liquid-liquid separation at some fixed  $\chi > \chi_c$ . Any solution prepared such that  $(T, \phi_1)$  lies above the binodal will be out of equilibrium until it has undergone phase separation into two phases with compositions along the binodal.
    3. A **spinodal** dividing the two-phase region into a **metastable** window between the binodal and spinodal, and an **unstable** region above the spinodal.
  - An additional consequence of Figure 2.7c is that even on the pink curve, *some* mixing is still favorable. Thus,  $\Delta G_M < 0$  here, too!
- 10/6: • Postulate: “Phase separation will occur whenever the system can lower its total free energy by dividing into two phases” (Lodge & Hiemenz, 2020, p. 293).
- Let’s discuss when exactly phase separation will or will not occur.

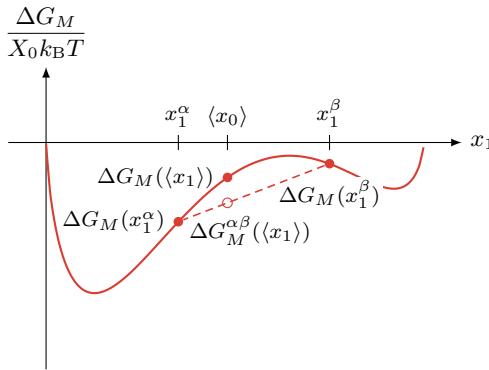


Figure 2.26: Tie lines predict the favorability of demixing.

- Suppose we have a two-component solution with overall composition

$$\langle x_1 \rangle = \frac{n_1}{n_1 + n_2}$$

where  $n_i$  is the total number of moles of component  $i$  present in the solution.

- We will justify the notation “ $\langle x_1 \rangle$ ” shortly.
- Let  $x_1^\alpha$  and  $x_1^\beta$  two compositions such that  $x_1^\alpha \leq \langle x_1 \rangle \leq x_1^\beta$ . We want to determine if it will be energetically favorable for our solution to divide into two phases  $\alpha$  and  $\beta$  with respective compositions  $x_1^\alpha$  and  $x_1^\beta$ .
- First, we would like to determine — based on our choice of  $x_1^\alpha$  and  $x_1^\beta$  — how many moles will be in each phase.

- Let  $n_i^j$  be the number of moles of component  $i$  in phase  $j$ . Then by definition, we may write the following expressions.

$$x_1^\alpha = \frac{n_1^\alpha}{n_1^\alpha + n_2^\alpha} \quad x_1^\beta = \frac{n_1^\beta}{n_1^\beta + n_2^\beta} \quad n_1^\alpha + n_1^\beta = n_1$$

- Now is also a good time to mention that — as the notation suggests — we have

$$\langle x_1 \rangle = x_1^\alpha x_1^\alpha + x_1^\beta x_1^\beta$$

where  $x^j$  is the mole fraction of the total solution in phase  $j$ .

➤ Equality holds between this “intuitive” definition of  $\langle x_1 \rangle$  and the original definition since

$$\underbrace{\frac{n_1^\alpha + n_2^\alpha}{n_1 + n_2}}_{x_1^\alpha} \cdot \underbrace{\frac{n_1^\alpha}{n_1^\alpha + n_2^\alpha}}_{x_1^\alpha} + \underbrace{\frac{n_1^\beta + n_2^\beta}{n_1 + n_2}}_{x_1^\beta} \cdot \underbrace{\frac{n_1^\beta}{n_1^\beta + n_2^\beta}}_{x_1^\beta} = \frac{n_1^\alpha + n_1^\beta}{n_1 + n_2} = \frac{n_1}{n_1 + n_2}$$

- With these definitions, we may derive the following **lever rule**. See my Thermo notes for more on lever rules.

$$\begin{aligned} n_1^\alpha + n_1^\beta &= n_1 \\ x_1^\alpha(n_1^\alpha + n_2^\alpha) + x_1^\beta(n_1^\beta + n_2^\beta) &= \langle x_1 \rangle \cdot (n_1 + n_2) \\ &= \langle x_1 \rangle \cdot (n_1^\alpha + n_2^\alpha) + \langle x_1 \rangle \cdot (n_1^\beta + n_2^\beta) \\ \frac{n_1^\alpha + n_2^\alpha}{n_1^\beta + n_2^\beta} \cdot x_1^\alpha + x_1^\beta &= \frac{n_1^\alpha + n_2^\alpha}{n_1^\beta + n_2^\beta} \cdot \langle x_1 \rangle + \langle x_1 \rangle \\ \underbrace{\frac{n_1^\alpha + n_2^\alpha}{n_1^\beta + n_2^\beta}}_{n^\alpha/n^\beta} &= \frac{\langle x_1 \rangle - x_1^\beta}{x_1^\alpha - \langle x_1 \rangle} \end{aligned}$$

- With the lever rule and the fact that  $n^\alpha + n^\beta = n$ , we can derive the following expressions for  $n^\alpha, n^\beta$ .

$$n^\alpha = \frac{n(\langle x_1 \rangle - x_1^\beta)}{x_1^\alpha - x_1^\beta} \quad n^\beta = \frac{n(x_1^\alpha - \langle x_1 \rangle)}{x_1^\alpha - x_1^\beta}$$

➤ Notice that we have two variables and two equations, so we can solve the system of equations!  
 ➤ If we care to, we can also use this result to derive expressions for any of the variables  $n_1^\alpha, n_2^\alpha, n_1^\beta, n_2^\beta$  in terms of the givens. For example,

$$n_1^\alpha = n^\alpha x_1^\alpha = \frac{n x_1^\alpha (\langle x_1 \rangle - x_1^\beta)}{x_1^\alpha - x_1^\beta}$$

- We can now compare the mixing energy of the initial uniform phase with composition  $\langle x_1 \rangle$  to the total mixing energy of the two new phases with compositions  $x_1^\alpha$  and  $x_1^\beta$ .
- The mixing energy of the initial uniform phase is just  $\Delta G_M(\langle x_1 \rangle)$ , but the total mixing energy of the two new phases is

$$\begin{aligned} \Delta G_M^{\alpha\beta}(\langle x_1 \rangle) &= x^\alpha \cdot \Delta G_M(x_1^\alpha) + x^\beta \cdot \Delta G_M(x_1^\beta) \\ &= \frac{1}{x_1^\alpha - x_1^\beta} \left[ (\langle x_1 \rangle - x_1^\beta) \cdot \Delta G_M(x_1^\alpha) + (x_1^\alpha - \langle x_1 \rangle) \cdot \Delta G_M(x_1^\beta) \right] \end{aligned}$$

- Let's interpret these two expressions graphically.  $\Delta G_M(\langle x_1 \rangle)$  will just be a point on the  $\Delta G_M$  curve. If we plot  $\Delta G_M^{\alpha\beta}$  as a function of  $x_1$ , it will be the tie line between  $\Delta G_M(x_1^\alpha)$  and  $\Delta G_M(x_1^\beta)$ !
- Therefore, if the tie line lies above the curve, demixing will raise the energy of the system and will not occur. If the tie line lies below the curve, demixing will lower the energy of the system and will occur. As such, with the choices of  $\langle x_1 \rangle$ ,  $x_1^\alpha$ , and  $x_1^\beta$  in Figure 2.26, mixing will occur.
  - An important consequence of the tie-line finding is that — since tie lines are an alternate way of defining concavity — concave up is the criterion for **stability** of a phase.
- **Stable** (phase): A phase such that any spontaneous, small local fluctuation in concentration will increase the free energy, and hence these out-of-equilibrium fluctuations will relax back to the expected composition.
- Some personal thoughts and thought experiments on *how* a solution demixes into two phases.
  - A spinodal decomposition is an iterative process.
    - From the initial concentration  $\langle x_1 \rangle$ , we will demix into two phases with compositions only slightly higher and slightly lower than  $\langle x_1 \rangle$ . These new phases then act as their own starting points, and must determine if demixing is higher or lower in energy.
    - Demixing will continue as long as each little phase can decrease its energy by demixing, and this process will stop when the two phases lie along the spinodal.
      - Indeed, regardless of the exact starting composition  $\langle x_1 \rangle$ , if our starting solution is in the unstable region, it will undergo a spontaneous spinodal decomposition to two phases (of possibly different volumes) with compositions equal to the spinodal ones.
    - Once a phase lies at the spinodal, any choice of new phases that includes one phase outside the unstable region will correspond to a tie line above the curve (unless the other phase is *vastly* different in composition).
    - This is where nucleation must come along to ‘remove’ some particles from the system and into a more stable nucleus.
  - Phase separation *raises* entropy, always, as we are creating order. But it may decrease enthalpy. (Think of the enthalpy and entropy graphs separately, as in Figure 2.7a-2.7b, and their respective tie lines.) Phase separation thus occurs when the gain in enthalpy outweighs the loss in entropy.
    - Temperature decreasing causes  $\chi$  to increase. But by the definition of the Flory  $\chi$  parameter, a decrease in temperature is mathematically equivalent to temperature staying the same and things starting to like themselves more than they like each other ( $\epsilon_{12}$  getting more negative).
  - An important characteristic of a metastable system at the spinodal points is that the two phases are in a *dynamic* equilibrium.
    - A certain amount of component  $i$  can move out of one phase and into the second, just so long as the flow is balanced by an equal amount of component  $i$  moving from the second phase into the first.
    - Demixing can also be thought of as a dynamic transfer of matter that is *not* in equilibrium; that is, the exodus of component 1 from a phase may be greater than the flow of component 1 into that phase, resulting in that phase decreasing in its  $\phi_1$ .
    - This flow of matter is driven by the change in free energy of the system with the number of moles in it. But this is exactly the chemical potential! That's why the chemical potential is the perfect tool with which to visualize the flow of matter in demixing.
      - Spinodal decomposition: The flow of matter from one phase to the other at a rate governed by the chemical potential until we have a dynamic equilibrium of matter flowing from one phase to the other that balances out.
      - Matter will “roll downhill” until it gets to the bottom of the chemical potential, which occurs at the spinodal points.

- Nucleation of ‘stable’ nuclei.
- Suppose ideal stability occurs for  $\phi_1 = 0.7$ . Then take 7 molecules of 1 and 3 molecules of 2 as a nucleus. It will be energetically favorable for another 7 molecules of 1 and 3 molecules of 2 to come out of the phase they are in and join the growing nucleus; the remaining phases can then reequilibrate their distribution of molecules to reach stability with a smaller amount of matter.
- Lattice theory can be an instructive way to visualize phases and separations.
  - For example, model a beaker containing a mixture as a  $4 \times 4$  lattice with 8 black circles and 8 white circle randomly arranged. This could represent a homogeneous solution at high temperature.
  - As temperature is lowered (or  $\chi$  increases), there will come a point where demixing occurs into a denser, bottom phase and a lighter, top phase. Perhaps first, the top phase will gain an extra white circle on average and the bottom phase will gain an extra black circle on average.
  - As the decomposition continues, eventually we will reach a stable point (perhaps 6 black circles and 2 white circles at bottom, and 2 black circles and 6 white circles at top). The particles still move around, as long as this general trend is maintained.
  - Lattice theory also provides a good backdrop for visualizing the importance of energy *per site*, as we can only obtain the total energy through multiplying the energy per site by each site in each region and dividing by the total number of sites.
- Finding the binodal.
  - There are infinitely many pairs  $x_1^\alpha, x_1^\beta$  of phases to which an unstable system can demix, so how do we determine which pair corresponds to the most energetically stable system?
  - Well, a phase equilibrium is established when  $T, P$  are equal in both phases, and the chemical potentials are, too. Symbolically, our criteria are
 
$$\mu_1(x_1^\alpha) = \mu_1(x_1^\beta) \quad \mu_2(x_1^\alpha) = \mu_2(x_1^\beta)$$
  - Warning: While the chemical potential of component 1 must be equal in both phases (and likewise for component 2), the chemical potential of component 1 *does not* need to equal the chemical potential of component 2.
  - We will now show that finding the phases  $x_1^\alpha, x_1^\beta$  which satisfy the above criteria is equivalent to finding the lowest possible tangent line graphically.
    - Since the chemical potential is a partial molar free energy, we can write the total free energy of mixing as the mole-weighted sum of the chemical potentials, as follows.

$$\Delta G_M = n_1 \Delta \mu_1 + n_2 \Delta \mu_2$$

- It follows that the free energy of mixing per mole of solution is

$$\Delta G_M = x_1 \Delta \mu_1 + (1 - x_1) \Delta \mu_2 = \Delta \mu_2 + x_1 (\Delta \mu_1 - \Delta \mu_2)$$

- This equation corresponds to a line of the form  $y = mx + b$  across an energy-composition plot and tangent to the  $\Delta G_M$  curve at  $x_1$ . In fact, this line’s  $y$ -intercept will be  $\Delta \mu_2(x_1)$  and its intercept with the line  $x_1 = 1$  will be  $\Delta \mu_1(x_1)$ ! This is the key.
- In particular, if we have a  $\Delta G_M$  curve with a bump, we can draw exactly one straight line that is tangent to the curve at *two* points. We take these points to be  $x_1^\alpha, x_1^\beta$  for the following reason: By the above argument, the line being tangent to  $x_1^j$  (for  $j = \alpha, \beta$ ) means that the  $y$ -intercept is  $\Delta \mu_2(x_1^j)$  and the other intercept is  $\Delta \mu_1(x_1^j)$ . But since a single line can only have one of each intercept, we know that

$$\begin{array}{ll} \Delta \mu_1(x_1^\alpha) = \Delta \mu_1(x_1^\beta) & \Delta \mu_2(x_1^\alpha) = \Delta \mu_2(x_1^\beta) \\ \mu_1(x_1^\alpha) - \mu_1^\circ = \mu_1(x_1^\beta) - \mu_1^\circ & \mu_2(x_1^\alpha) - \mu_2^\circ = \mu_2(x_1^\beta) - \mu_2^\circ \\ \mu_1(x_1^\alpha) = \mu_1(x_1^\beta) & \mu_2(x_1^\alpha) = \mu_2(x_1^\beta) \end{array}$$

as desired.

- Note that we could also use the two original constraints and our known expressions for the chemical potentials to find  $x_1^\alpha, x_1^\beta$  analytically, but the algebra would get a bit hairy.
- **Metastable** (system): A system that is stable against small, spontaneous fluctuations, but not globally stable against phase separation.
- An alternate way of finding the spinodal points is by (1) differentiating  $\Delta G_M$  with respect to  $n_1$  to find the chemical potential  $\mu_1$  of component 1 and then (2) setting the derivative of  $\mu_1$  with respect to composition  $x_1$  equal to zero to find the minimum chemical potential. This chemical potential minimum corresponds to a region of stability for the phase dominated by component 1, and hence exactly the spinodal point.
- On the critical point.
  - In the context of the exchange energy: If it costs any more than  $\chi_c k_B T$  to exchange a pair of molecules of different components, there will be phase separation.
- “As a disperse polymer solution is cooled below the theta point, the higher molecular weight chains will tend to phase separate first, a feature which can be used to advantage in fractionation” (Lodge & Hiemenz, 2020, p. 299).
- The free energy of mixing when an arbitrary number of components  $i$  are included is

$$\Delta G_M = \sum_i \frac{\phi_i}{N_i} \ln \phi_i + \sum_{i < j} \chi_{ij} \phi_i \phi_j$$

- 10/10:
- Lodge and Hiemenz (2020, p. 303) covers several possible definitions of a reference volume for one monomer.
    - One possibility is a geometric mean of the molar volumes of the repeat units. Why the geometric mean??
    - Another is to take  $100 \text{ \AA}^3$  as a generally good number.

- Lodge and Hiemenz (2020, p. 306) has a table of solubility parameters, but in non-SI units.
- For the specific case of polymer-solvent solutions, solubility parameter-based formulations of  $\chi$  differ significantly from experimental results.
  - A related model that is empirically more accurate is

$$\chi \approx 0.34 + \frac{v}{k_B T} (\delta_1 - \delta_2)^2$$

- In particular, our theory often *underestimates*  $\chi$  for polymer-solvent solutions, so we need to add a temperature-independent correction.
  - This means that in reality, each component likes itself more (and the other component less) than regular solution theory would predict.
- This correction reflects the finding that the entropy of mixing in polymer-solvent solutions is smaller than regular solution theory would suggest, since it implies that

$$\begin{aligned} \frac{\Delta G_M}{X_0} &= k_B T (\chi_{\text{corrected}} \phi_1 \phi_2 + \phi_1 \ln \phi_1 + \phi_2 \ln \phi_2) \\ &= k_B T \underbrace{(\chi_{\text{RST}} \phi_1 \phi_2)}_{\text{enthalpic}} + \underbrace{0.34 \phi_1 \phi_2 + \phi_1 \ln \phi_1 + \phi_2 \ln \phi_2}_{\text{entropic}} \end{aligned}$$

- $\chi_{\text{corrected}}$  is the new empirical formula for  $\chi$ , and  $\chi_{\text{RST}}$  is the value expected from Hildebrand's derivation using only regular solution theory.

- As we can see, the new (strictly positive) entropic term makes the overall entropy of mixing less negative than when only the former (strictly negative) terms were present.
- Additional empirical issues with the regular solution theory approach to polymer-solvent solutions.
  - Some behavior is wildly different than just having a single LCST and/or UCST.
  - Some mixtures contain polar species, which do not satisfy the purely combinatorial assumptions of regular solution theory.
- One commonly used theoretical solution to the polymer-solvent solution conundrum: The **effective interaction parameter**.
- **Effective interaction parameter:** An interaction parameter that quantifies a solution's deviation from ideality. *Denoted by  $\chi_{\text{eff}}$ . Given by*

$$\chi_{\text{eff}} := \frac{\alpha}{T} + \beta = \chi_h + \chi_s$$

- $\chi_h = \alpha/T$  is the enthalpic contribution to  $\chi_{\text{eff}}$ .
- $\chi_s = \beta$  is the entropic contribution to  $\chi_{\text{eff}}$ .
- $\alpha, \beta \in \mathbb{R}$ .
  - $\alpha < 0$  implies an attractive interaction between the components, e.g., hydrogen bonding.
  - The sign of  $\beta$  reflects the details of molecular packing. For example, if molecules pack very efficiently into real space (as opposed to the idealized equal volume of lattice cells), then there is probably *more* entropy of mixing than lattice theory would predict and  $\beta < 0$ .
- The signs of the various components give us insight into the phase diagram.
  - Consider the case of  $\alpha < 0$  and  $\beta > 0$ . Herein, molecules of different components enthalpically attract to each other, and fit less well into space when they're around each other than we might ideally expect. Thus, there should be a temperature at which we rupture the enthalpic bonds and allow the components to pack more efficiently (i.e., with themselves). Thus, we may expect an LCST on the phase diagram.
  - Last note:  $\chi_{\text{eff}}$  often depends on concentration  $\phi_i$ .
    - This can lead to asymmetry in the  $\Delta G_M(\phi_i)$  curves.
    - It can also complicate experimental measurement of  $\chi_{\text{eff}}$ .