

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^[1].
- We're going to start by approximating polymers as straight chains on a lattice.

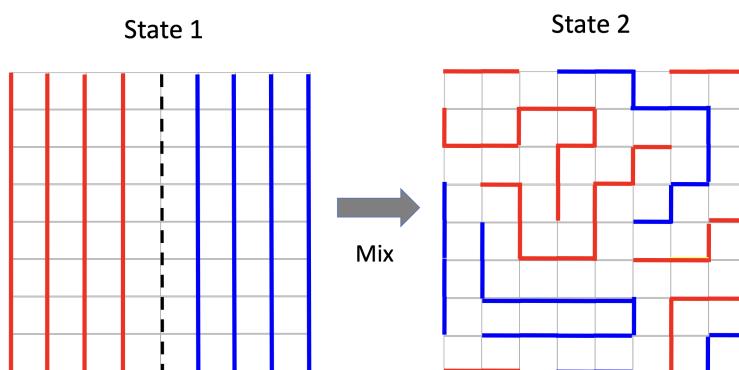


Figure 2.1: Lattice theory for polymer phase behavior.

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

¹"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).

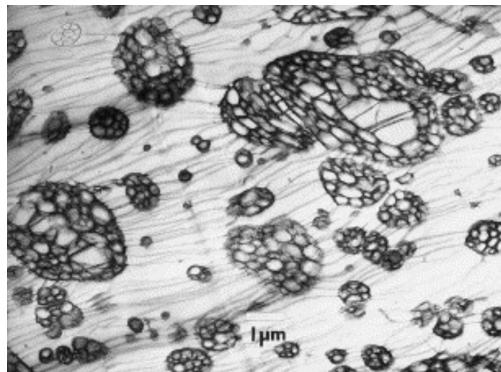


Figure 2.2: Salami phase micrograph in styrene-butadiene mixtures.

- 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

$$V_1 = n_1 N_1 v_1$$

$$V_2 = n_2 N_2 v_2$$

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 ΔV 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 $S = 0$.
 - Mean field lattice theory.

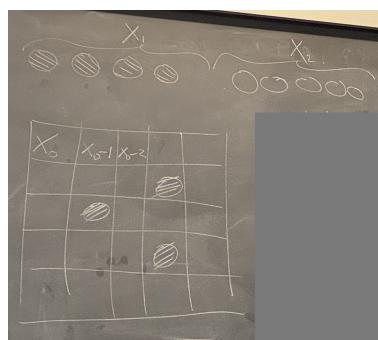


Figure 2.3: Configurations in mean field lattice theory.

- 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.
 - Thus,

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

- It follows that the change entropy ΔS 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

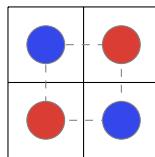
$$\begin{aligned} \frac{\Delta S_M}{k_B X_0} &= \frac{1}{X_0} [(X_1 + X_2) \ln X_0 - X_1 \ln X_1 - X_2 \ln X_2] \\ &= -\frac{X_1}{X_0} (\ln X_1 - \ln X_0) - \frac{X_2}{X_0} (\ln X_2 - \ln X_0) \\ &= -\frac{X_1}{X_0} \ln \frac{X_1}{X_0} - \frac{X_2}{X_0} \ln \frac{X_2}{X_0} \\ &= -\phi_1 \ln \phi_1 -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

where ϕ_i denotes the **volume fraction** of spaces occupied by species i .

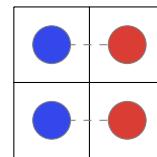
- **Volume fraction** (of i): The fraction of lattice sites occupied by species i . Denoted by ϕ_i . Given by

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

- 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.



(a) Energy E_1 system.



(b) Energy E_2 system.

Figure 2.4: Nearest neighbor interactions.

- Example: Assume nearest neighbor interactions matter.

- Let opposing objects in neighboring cells contribute energy ε_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*.
- 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.

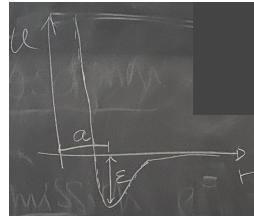


Figure 2.5: Potential well.

- 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 ξ_{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 ϕ_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 ξ_{22} .
- For ξ_{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 ε (see Figure 2.5).
- Let ε_{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 χ denotes the **Flory χ parameter**.

- **Flory χ parameter:** A measure of the degree to which the two species like each other vs. themselves. *Also known as interaction parameter. Denoted by χ . 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 χ determines whether mixing will be enthalpically favorable or not. Moreover, the sign of χ 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), χ will be positive and will be between the middle two lines (we don't know here if it will mix or demix)??
- The χ 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.

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

- How about for polymers?

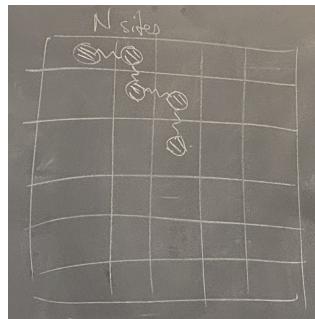
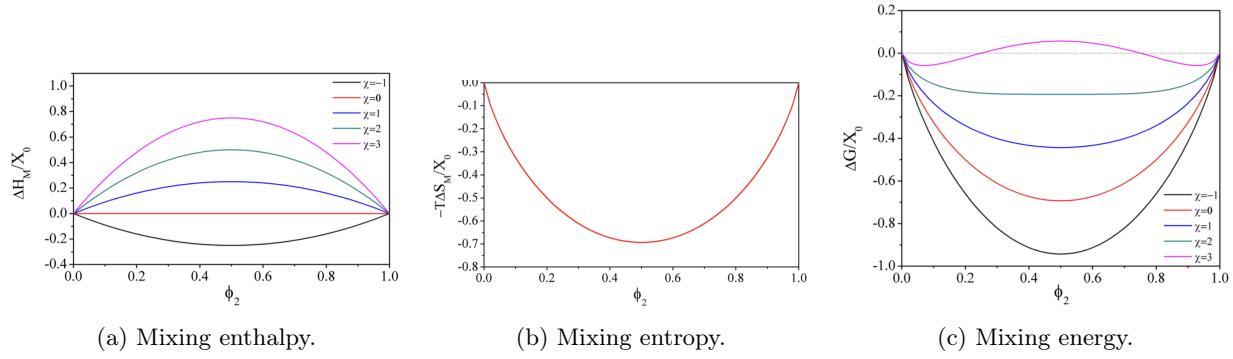


Figure 2.6: Fitting polymers into a square lattice.

- 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, χ, ϕ_i, N_i . Namely, values of these variables that lead to a negative ΔG_M will correspond to mixing, and values of these variables that lead to a positive ΔG_M will correspond to demixing.
 - How do we measure χ experimentally?
 - We will explore this soon.
 - Influence of χ 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 χ reaches the range of 2-3, we get demixing.
 - This is because (at $\chi = 3$, 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 χ 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: χ is pretty good if z is big; if z is small, quadratic and other higher order corrections may be necessary for χ .
- Phase behavior of blends.
 - The critical value χ_c of the Flory χ parameter is the value of χ at which you see phase separation.
 - χ_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.

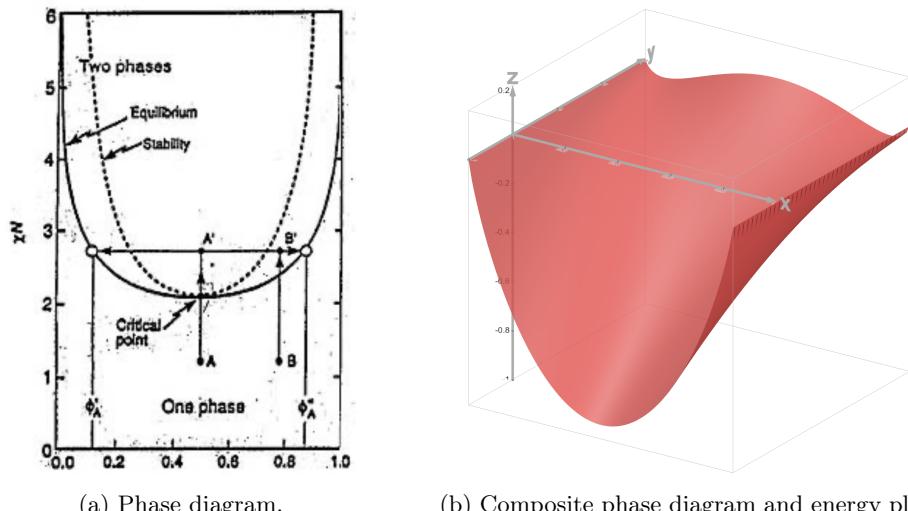


Figure 2.8: Example phase diagram and explanation.

- 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 ϕ_2 and χN as two independent variables that together define a system. A dependent variable of interest in this system is the mixing energy ΔG_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 μ_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 μ_i . This is because we have expressions for ΔG_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.^[2]
- **Spinodal curve:** The set of inflection points along the $\Delta G_M(\phi)$ curves, generated as χ 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 a 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 χ , and the left constraint relates this concentration to the interaction parameter χ_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.

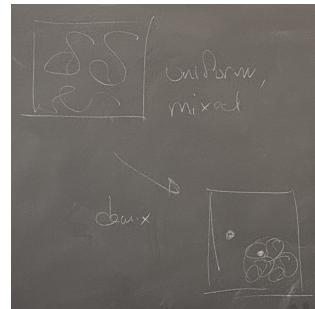


Figure 2.9: Demixing of a polymer-solvent solution.

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

²See 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.

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

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

- 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 x , the following approximation holds.

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

- Moreover, we can choose to use only the first couple of terms for sufficiently small x .
- 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 μ_1 will be less than that of the standard, unmixed state μ_1° . Therefore, to lower chemical potential, hence 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 θ 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 θ condition. It follows that the θ 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 θ 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 θ 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.”

- Does slide 33 imply that 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?? Maybe it’s something to do with the “solvent” becoming more of a swelling additive to the polymer than vice versa?

- 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.

- Solubility parameter and χ .

- How do we estimate χ ?

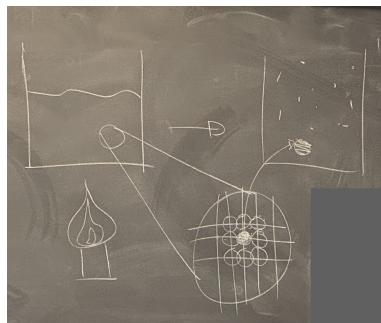


Figure 2.10: Hildebrand's experiment.

- Hildebrand's interesting idea was to use the enthalpy of vaporization ΔH_v .
- Experimental setup.
 - Take your liquid, heat it up, measure how much heat goes into the system, turn it into a gas, and see how the heat has turned into kinetic energy.
 - By the time you have heated an object in a lattice, your are neighborless; you have no potential energy.
 - We now have

$$\delta = \left(\frac{\Delta E}{V} \right)^{1/2}$$

- We'll now calculate δ_1 and δ_2 for species 1 and 2, the **solubility parameters** of the components.

$$\delta_1 = \sqrt{\frac{Z \varepsilon_{11}}{2 v}} \quad \delta_2 = \sqrt{\frac{Z \varepsilon_{22}}{2 v}}$$

- We then use **Berthelot's mixing rule** (which uses the geometric mean) to get ε_{12} :

$$\varepsilon_{12} = \sqrt{\varepsilon_{11} \varepsilon_{22}}$$

- Now imagine two points 1 and 2 separated by a distance r , as in Figure 1.13c.

$$U_{\text{attractive}} = -\frac{\alpha_1 \alpha_2}{r^6}$$

- Scales as $1/r^6$, and also has the **polarizability / polarizability volumes**.
- This is 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."

- Then

$$(\delta_1 - \delta_2)^2 = \frac{1}{v} \left(\frac{z \varepsilon_{11}}{2} + \frac{z \varepsilon_{22}}{2} - z \varepsilon_{12} \right)$$

- Now just multiply by $v/k_B T$ to get the χ parameter.

➢ v is a volume.

- This gets us to the **Hildebrand equation**

$$\Delta H_M = V_m \phi_1 \phi_2 (\delta_1 - \delta_2)^2 \geq 0$$

➢ This works better for nonpolar than polar species.

➢ V_m is the average molar volume of solvent / monomers.

- See Rubinstein and Colby (2003) for an in-depth discussion of this setup.
- Let's now compare the curve with experiments.
 - PS in cyclohexane.
 - Dashed lines are the Flory-Huggins theory, which clearly doesn't look like the experiment at all.
 - This 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.
 - Actual curve is wrong, but scaling is correct (this happens in several of Flory's theories).
 - Reference: Shultz and Flory (1952).
- Phase diagrams of polymer-polymer blends.
 - ϕ for the fraction that a chain occupies is

$$\phi = \frac{Nv}{(N^{1/2}\ell)^3} \approx \frac{v}{\ell^3} N^{-1/2}$$
- Two principal types of phase diagrams.
 - Demixing at higher temperatures, vs. mixing at higher temperatures.
 - Poly(methyl methacrylate) / styrene-*co*-acrylonitrile demixes at increased temperature (because molecules are polar).
 - Polystyrene / polyisoprene mixes at higher temperatures.
 - PEG and PMMA have a negative χ at room temperature. PEG and H₂O is similar (you heat it up, and the polymer comes out of solution).
 - pNIPAM undergoes a transition around 32-34 °C.
 - Attraction gives rise to a low or negative χ .
 - A number of references on polymer blends are included in the slides!
- You can arrest a spinodal decomposition by heating and then cooling very quickly.
- Applications of FH theory.
 - Biocondensates and membrane-free organelles (like the nucleolus and centrioles). Identified another bunch of these after they expanded their definition of organelles! 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).

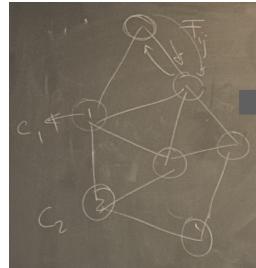


Figure 2.11: Simplified graph of a biochemical network.

- 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.
 - 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 2.11).
 - 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).

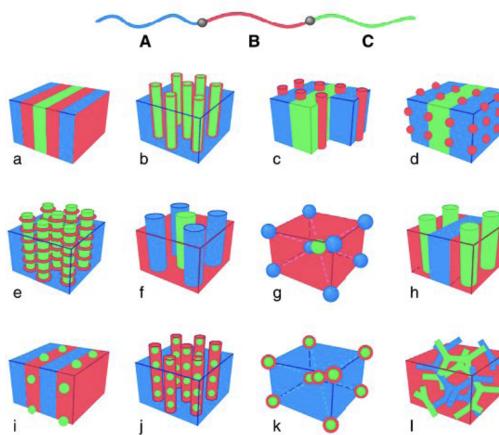


Figure 2.12: Self-assembly of an ABC triblock copolymer.

- What aspects of an ABC triblock copolymer affect its organization?
- There will be **intra interactions** χ_{AB} , χ_{AC} , and χ_{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 2.12, 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 2.12 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 π -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 β -pleated sheet, which will stack vertically with the β -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.

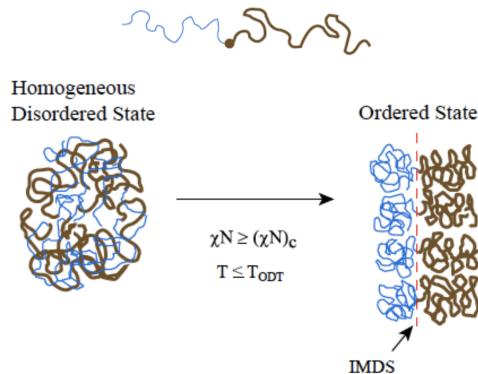


Figure 2.13: Ordering of a diblock copolymer.

- 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 2.13 means "critical."
 - Remember that χN 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.

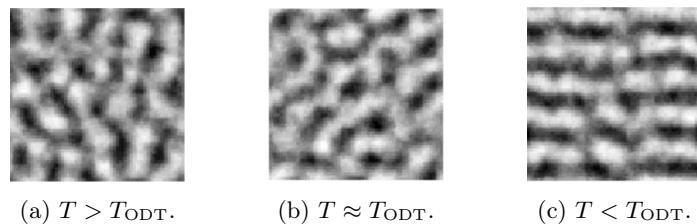


Figure 2.14: Microphase separation in diblock copolymers.

- 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 2.14a-2.14c, you get into a lamellar state.
- Microdomain morphologies: Diblock copolymers.

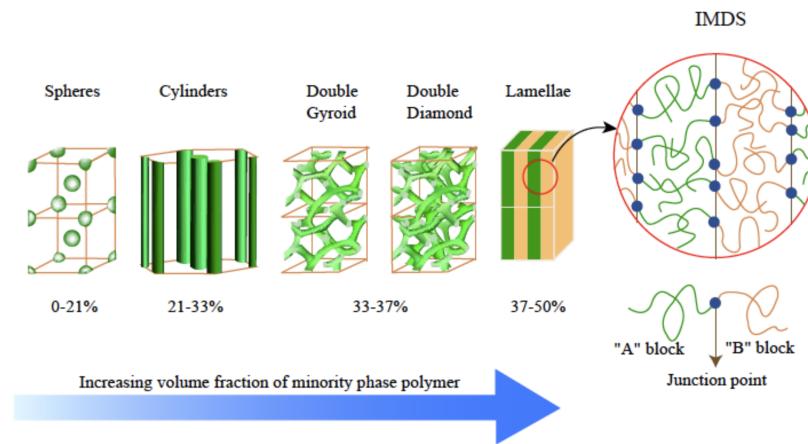


Figure 2.15: Microphase morphologies in diblock copolymers.

- In contrast to Figure 2.15, 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.
 - G is the free energy per chain;
 - $N = N_A + N_B$ is the number of segments per chain.
 - a is the step size.
 - λ is the domain periodicity. *look up definitions!!*
 - Σ is the interfacial area where the chains actually interact.
 - γ_{AB} is the interfacial energy per unit area. It will be computed using Helfand's equation.

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

- a is the Kuhn length or monomer length, varying depending on the context.
- χ_{AB} is the same Flory-Huggins interaction parameter we've been looking at in previous lectures.

- Free energies of these diblock copolymers.

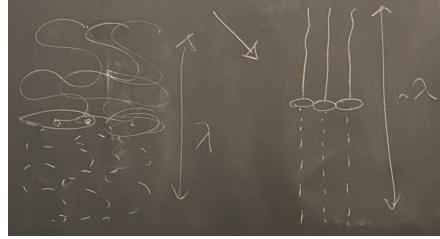


Figure 2.16: Entropy and enthalpy changes as diblock copolymers are stretched.

- We have

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

- The entropic term relates to the springiness of the polymer.
- Note that $Na^3 = \Sigma \cdot \lambda/2$. 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 Σ .
- Important assumption: Chains want to stretch away from the interface.
 - Enthalpy goes way down when you have linear strands (everything is near each other). Entropy goes way up here, though, because we're stretching.
 - In the other regime, though, area is way bigger. This means we get more enthalpy.
 - $\Delta S \approx \lambda^2/a^2 N$.
 - System will try to find the optimal balance between the two; we want to optimize the length λ .
- To find the optimal λ , we'll want to find the minimum Gibbs free energy as a function of λ .

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

- By above definitions and equalities, the first term is the interfacial energy per unit area times the area of the interface.
- Compressing every non- λ variable in the above expression into a constant (termed α , β , const_1 , or 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 optimum period of the lamellae repeat unit is

$$\begin{aligned}0 &= \frac{\partial \Delta G}{\partial \lambda} \\ &= -\frac{\alpha}{\lambda_{\text{opt}}^2} + 2\beta\lambda_{\text{opt}} \\ \lambda_{\text{opt}} &= \sqrt[3]{\frac{\alpha}{2\beta}} = aN^{2/3}\chi_{AB}^{1/6}\end{aligned}$$

- The result that λ_{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 λ_{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 are both much greater than the third term, we neglect it.

- Thus, the sign of ΔG will depend on which of the two remaining terms 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 ($(N\chi)_c$) 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 χN vs. composition phase diagram.

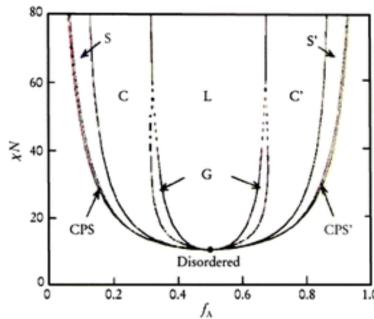


Figure 2.17: Microphase transition diagram.

- Notice as we go in from the outside (homogeneous, disordered mixed melt), we progressively go through spheres (S), cylinders (C), gyroids (G), and lamellae (L).

- Other interfaces: Polymer brushes.
 - Consider a series of polymer strands grown off of a 2D surface.
 - Let each polymer strand be a distance D away from the next nearest strand. In this sense, each polymer strand can be thought to inhabit a volume of diameter D and height H away from the surface.
 - The polymer strands stretch out more (H increases) when they don't want to interact with the 2D interface.
 - What is the energy or enthalpy?
- $\Delta H \approx vc^2 \cdot HD^2$
- H, D are defined as above.
 - v is how many two body interactions there are (counted by mole).
 - c^2 describes how dense the system is.
 - Here, $\Delta S \approx H^2/a^2N$ (as opposed to λ^2/a^2N from earlier).
 - We want to minimize H^2 and $1/H$ on an H vs. Gibbs free energy graph.

2.4 Office Hours (Alexander-Katz)

9/30:

- PSet 2, Q5.

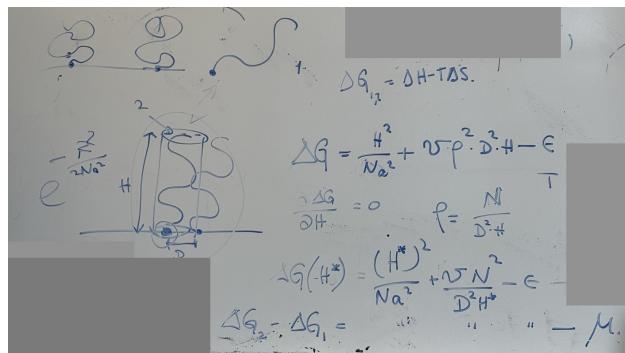


Figure 2.18: PSet 2, Q5 setup.

- 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,

$$\Delta G = \frac{H^2}{Na^2} + V_{\text{ex}} \rho^2 \cdot D^2 H - \epsilon$$

- $D^2 H$ is a volume.
- $\rho = N/D^2 H$ 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 ΔG equation above.
- To find D , we have to evaluate the stability relative to state 1.
 - μ_{bulk} or μ_1 (μ_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

$$\Delta G_2 - \Delta G_1 = \frac{(H^*)^2}{Na^2} + \frac{vN^2}{D^2 H^*} - \varepsilon - \mu_{\text{bulk}}$$
- 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 ε 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 $v\rho^2 \cdot D^2 H$.
 - Balance the two terms H^2/Na^2 and $vN^2/D^2 H$ to find H^* .
 - Then factor in ε .
- Phase diagrams.
 - χN or χ 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 χ_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 χ , 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 χ , 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 2.12 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_∞ .
 - 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^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 θ 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_{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^ν .
 - In a θ 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 χ 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.
- χ 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 χ 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, χN 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 χ to δ , 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 2.17).
 - 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 ϕ 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 Chapter 7: Thermodynamics of Polymer Mixtures

From Lodge and Hiemenz (2020).

- 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⁻¹. 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: $\bar{V}_{\text{H}_2\text{O}}$ 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⁻¹*.
- **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° .*
- **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 ΔS_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 ε_{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 χ parameter.
 - This parameter is equal to the exchange energy per molecule, normalized by the thermal energy $k_B T$.
 - The Flory χ 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 χ 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 ΔS_M equations more rigorously, as alluded to in class.
 - ΔH_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. ΔS_M arises entirely from the ideal combinatorial entropy of mixing.
 3. ΔH_M arises entirely from the internal energy of mixing.
 4. Both ΔS_M and ΔH_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 χ .
- The three features of a phase diagram (in terms of χ).
 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, ϕ_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!
- How does the drawing of tangent lines work for solutions that don't start at $\phi_2 = 0.5??$

- The new free energy is the average of the two “sub” solutions, and can be visually represented as the midpoint of the line connecting the points between the two new solutions.
 - When at a spinodal point, phase separating further by just a bit will result in a line with midpoint *exactly* on the spinodal inflection point, and the system will eventually relax back.
 - There is a good explanation of common tangent construction on Lodge and Hiemenz (2020, pp. 294–95). It appears that this is not part of class material, but would be very helpful in understanding it.
- **Metastable** (system): A system that is stable against small, spontaneous fluctuations, but not globally stable against phase separation.