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.
    - Microphase 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.

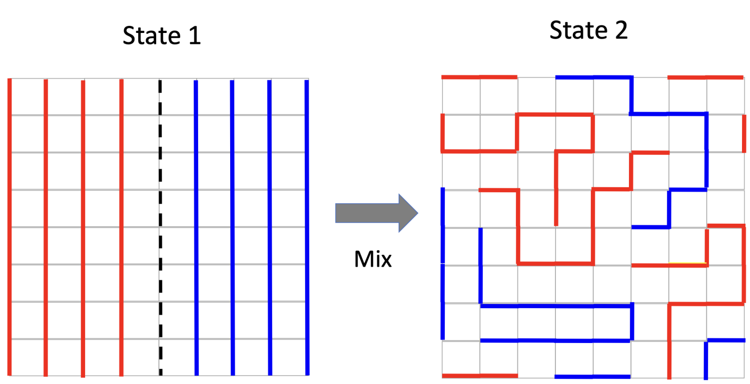


Figure 2.1: Lattice theory for polymer phase behavior.

  - 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).

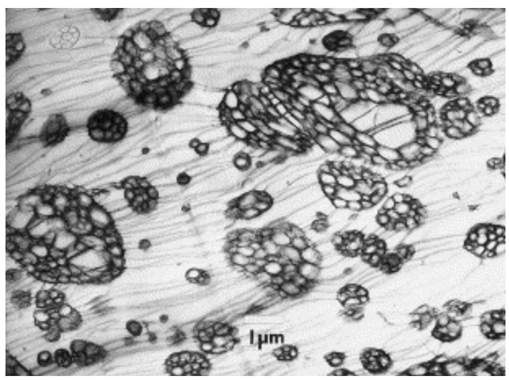


Figure 2.2: Salami phase micrograph in styrene-butadiene mixtures.

  - 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

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

    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.

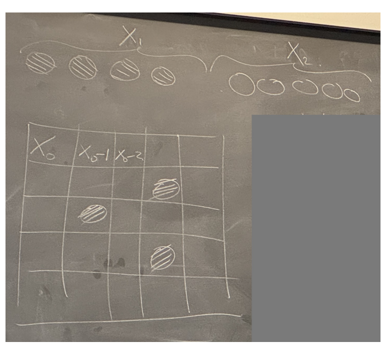


Figure 2.3: Configurations in mean field lattice theory.

- 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
$$\Delta S_M = k_\mathrm{B} \ln \Omega_{1,2} - 0$$
  - Remember that the initial entropy is zero!
- Invoking Stirling's approximation and remembering that $X_1 + X_2 = X_0$, we can then get
$$\begin{aligned}\frac{\Delta S_M}{k_\mathrm{B}} &= X_0 \ln X_0 - X_0 - [X_1 \ln X_1 - X_1 + X_2 \ln X_2 - X_2] \\ &= X_0 \ln X_0 - X_1 \ln X_1 - X_2 \ln X_2\end{aligned}$$
- It follows that the entropy of mixing per site $\Delta S_M / k_\mathrm{B} X_0$ is
$$\begin{aligned}\frac{\Delta S_M}{k_\mathrm{B} X_0} &= \frac{1}{X_0}\left[(X_1 + X_2)\ln X_0 - X_1 \ln X_1 - X_2 \ln X_2\right] \\ &= -\frac{X_1}{X_0}(\ln X_1 - \ln X_0) - \frac{X_2}{X_0}(\ln X_2 - \ln X_0) \\ &= -\frac{X_1}{X_0} \ln \frac{X_1}{X_0} - \frac{X_2}{X_0} \ln \frac{X_2}{X_0} \\ &= -\phi_1 \ln \phi_1 - \phi_2 \ln \phi_2\end{aligned}$$
  - The new variables $\phi_i = X_i / X_0$ are the volume fractions for spaces i.
  - Consequence: $\phi_1 + \phi_2 = 1$.

- 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.

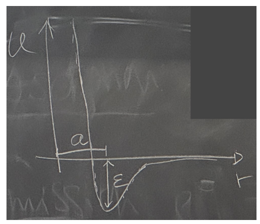


Figure 2.5: Potential well.

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

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

  - 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.

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

- Assuming that volume is constant, energy and enthalpy are the same (we're actually calculating energy but operating under this assumption).
- 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

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

where

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

is the **Flory χ parameter**.

  - 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 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.

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

- How about for polymers?

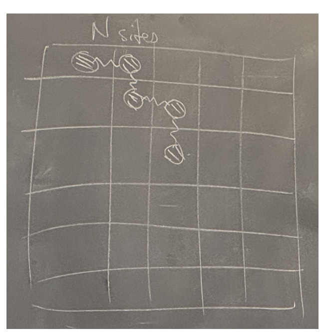


Figure 2.6: Fitting polymers into a square lattice.

- 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

$$\frac{\Delta S_M}{k_{\mathrm{B}} X_0} = -\frac{\phi_1}{N_1}\ln\phi_1 - \frac{\phi_2}{N_2}\ln\phi_2$$

  - 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.

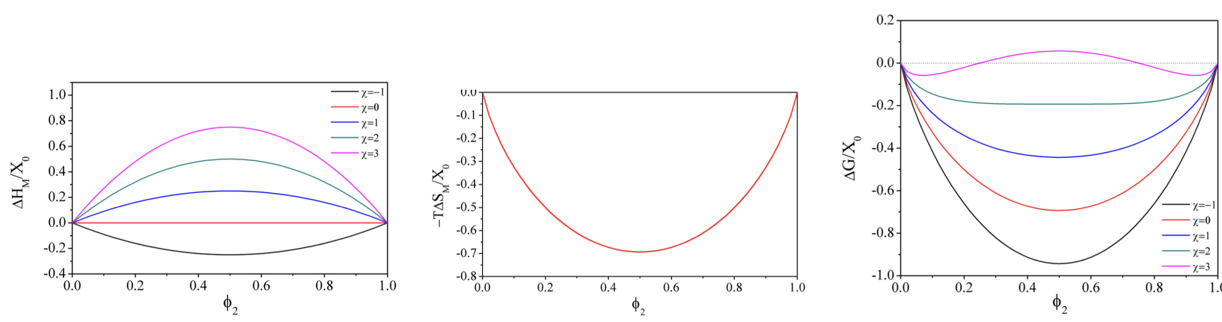
- Using the modified mixing entropy, we can now finally state the "famous Flory-Huggins theory for the free energy of mixing."

$$\frac{\Delta G_M}{X_0} = k_{\mathrm{B}} T\left(\chi\phi_1\phi_2 + \frac{\phi_1}{N_1}\ln\phi_1 + \frac{\phi_2}{N_2}\ln\phi_2\right)$$

  - 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.



(a) Mixing enthalpy. (b) Mixing entropy. (c) Mixing energy.

Figure 2.7: Mixing or demixing based on the Flory χ parameter.

  - 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.

- 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.
  - Construction of phase diagrams.
    - You have a critical point graph that gets flipped??
    - Inside one is binodal line; outside one is spinodal line.
  - Between the two inflection points, the system is unstable.
  - Concave curvature puts sum of two free energies below the points.
  - You will evolve toward the two lowest energy points, phase separating as needed.
  - Demixing 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* $\boldsymbol{\mu_i}$. *Given by*

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

- **Coexistence curve**: The set of points where the chemical potentials are equal. *Also known as* **binodal curve**.
  - The coexistence curve encloses all compositions wherein the mixture demixes into two distinct, coexisting phases.
  - Symbolically, letting the two phases in the mixture be called prime and double prime, we have for each component 1 and 2 that

$$\mu_1' = \mu_1'' \qquad\qquad \mu_2' = \mu_2''$$

  - In PSet 2, we'll derive one of the expressions on this slide.
- Spinodal inflection points are where the 2nd derivative is zero.
  - Critical points has 2nd and 3rd derivatives equal to zero.
  - *equations in slides*
- Polymer-solvent solutions.

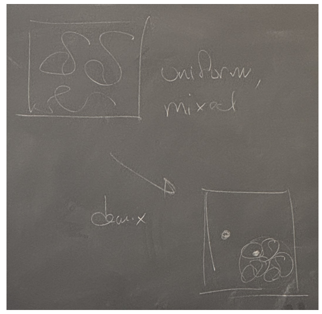


Figure 2.8: Demixing of a polymer-solvent solution.

  - An interesting way of thinking about this: Osmometry.
  - Imagine a uniform, mixed polymer solution.
    - We can demix to a state where the polymer is all clumped together.
    - 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.
  - Important relevant expressions.

$$\mu_1 - \mu_1^\circ = RT\left[\ln\phi_1 + \left(1 - \frac{1}{N_2}\right)\phi_2 + \chi\phi_2^2\right]$$
$$\mu_2 - \mu_2^\circ = RT\left[\ln\phi_2 + (N_2 - 1)\phi_2 + N_2\chi\phi_2^2\right]$$

    - 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 $N_2 = \langle N_2\rangle = M_\mathrm{n}$.
  - We'll now massage the above expressions to get some more mechanistic understanding out of them.
- Chemical potential for a dilute solution.
  - Since we are positing a dilute solution, we may use the approximation that the volume fraction of component 2 is small. This will allow us to expand the expressions.
  - For small x, the following approximation holds.

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

    - We can use fewer terms for quite small x.
  - It also follows from the assumptions that (1) the solution is dilute, i.e., $n_1 \gg n_2N_2$ and (2) that the volume of the monomers is approximately equal, i.e., $v_1 \approx v_2$ that

$$\phi_1 = \frac{n_1v_1}{n_1v_1 + n_2N_2v_2} \qquad\qquad \phi_2 = \frac{n_2N_2v_2}{n_1v_1 + n_2N_2v_2} \approx \frac{n_2N_2}{n_1}$$

– We thus expand

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

– It follows that

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

- Since it's negative, this tells us that the chemical potential μ_1 is always less than μ_1°, which means that the term is always negative, so everything wants to mix.
- In a subsequent course, we describe more results based off of the above equation!

• Phase diagram for a dilute polymer solution.

– The condition where ?? is the θ condition.

– Positive χ means that polymers don't like the solvent as much as they like themselves.

– As N_2 increases, we push to lower fractions.

• It is very difficult to mix high MW polymers because you will need $\chi < 2/N$.

• Solubility parameter and χ.

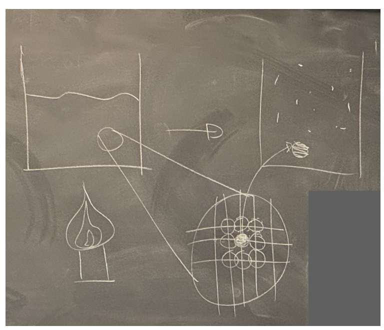


Figure 2.9: Hildebrand's experiment.

– How do we estimate χ?

- 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.

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

- 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 $v/k_{\mathrm{B}}T$ 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 H_2O 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 defintion 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 configuraitonal free energy.
            - This will bring back concepts from Professor Doyle's class.
- A bit more on biocondensates (not testable material).

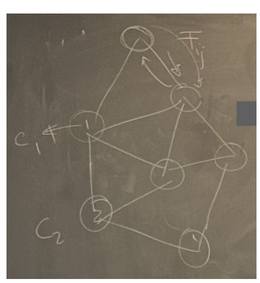


Figure 2.10: Simplified graph of a biochemical network.

- 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 2.10).
  - 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).

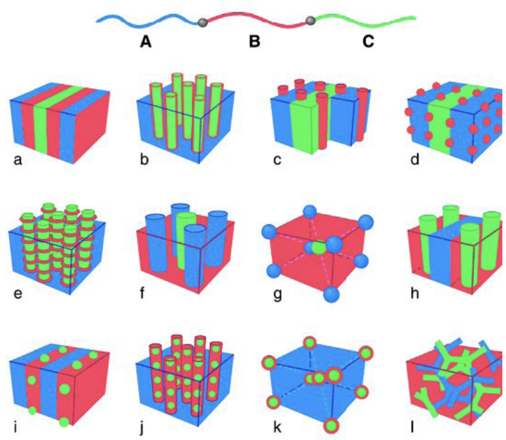


Figure 2.11: Self-assembly of an ABC triblock copolymer.

- 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 2.11, then we probably have $N_A = N_B = N_C$ (becasue 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 2.11 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 substiuent 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.

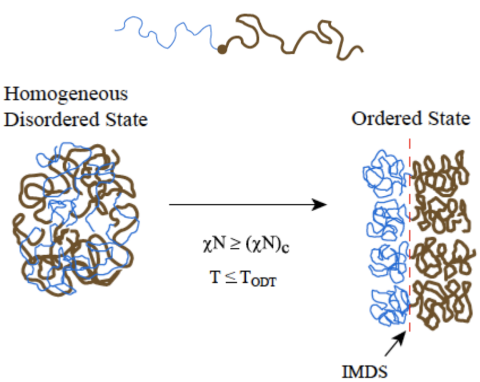
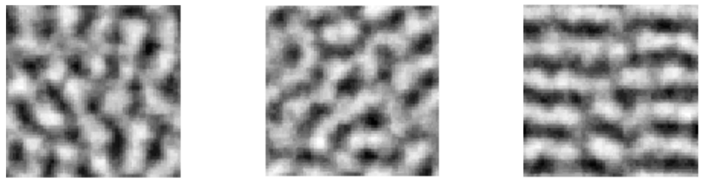


Figure 2.12: Ordering of a diblock copolymer.

  - 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 2.12 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.
  - 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 2.13a-2.13c, you get into a lamellar state.



(a) $T > T_{\text{ODT}}$. (b) $T \approx T_{\text{ODT}}$. (c) $T < T_{\text{ODT}}$.

Figure 2.13: Microphase separation in diblock copolymers.

- Microdomain morphologies: Diblock copolymers.

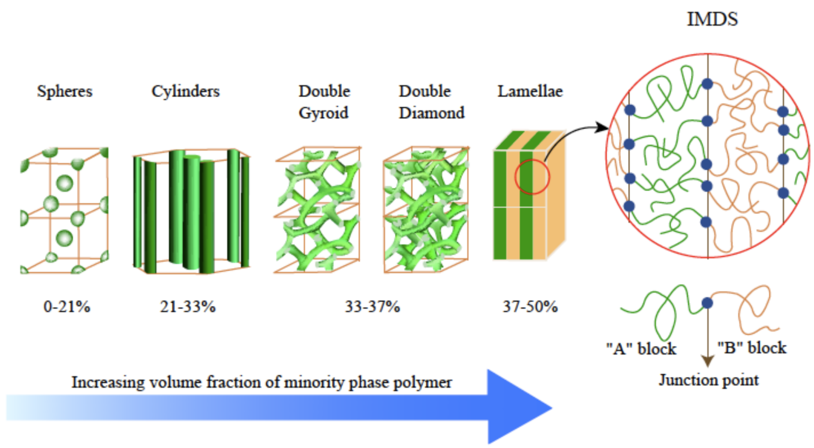


Figure 2.14: Microphase morphologies in diblock copolymers.

  - In contrast to Figure 2.14, 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.

$$\gamma_{\text{AB}} = \frac{k_{\text{B}}T}{a^2}\sqrt{\frac{\chi_{\text{AB}}}{6}}$$

  - 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.

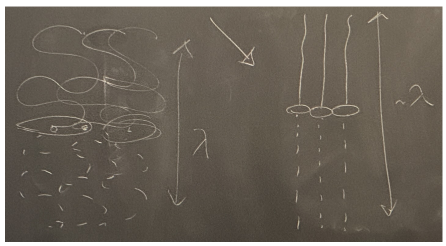


Figure 2.15: Entropy and enthalpy changes as diblock copolymers are stretched.

- We have

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

  - 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.
  - $\Delta S \approx \lambda^2/a^2N$.
  - 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.

$$\Delta G(\lambda) = \underbrace{\frac{k_{\text{B}}T}{a^2}\sqrt{\frac{\chi_{\text{AB}}}{6}}}_{\gamma_{\text{AB}}}\underbrace{\frac{Na^3}{\lambda/2}}_{\Sigma} - N\chi_{\text{AB}}\phi_{\text{A}}\phi_{\text{B}}k_{\text{B}}T + \frac{3}{2}k_{\text{B}}T\left[\frac{(\lambda/2)^2}{Na^2} - 1\right]$$

  - 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

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

  - 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

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

  - Since the first two terms are both much greater than the thrid 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 microdimains, and below which $\Delta G = +$ and we stay in a homogenous melt.
    - In a 50/50 split, $\phi_{\text{A}} = \phi_{\text{B}} = 1/2$. Thus,

$$\phi_{\text{A}}\phi_{\text{B}} = \frac{1}{4}$$

    - 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 homogeneus, mixed melt; and if $N\chi > 10.5$, we'll get demixing into lamellar microdomains.

- 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 diamater 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 tere 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 Chapter 7: Thermodynamics of Polymer Mixtures

From Lodge and Hiemenz (2020).

9/14:

- 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

$$\begin{aligned}\mathrm{d}G &= \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2}\mathrm{d}P + \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2}\mathrm{d}T + \left(\frac{\partial G}{\partial n_1}\right)_{P,T,n_2}\mathrm{d}n_1 + \left(\frac{\partial G}{\partial n_2}\right)_{P,T,n_1}\mathrm{d}n_2\\ &= V\,\mathrm{d}P - S\,\mathrm{d}T + \sum_{i=1}^{2}\mu_i\,\mathrm{d}n_i\end{aligned}$$

- **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* $\bar{\boldsymbol{Y}}_{\boldsymbol{i}}$. *Units* $\mathbf{mol^{-1}}$. *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: $\bar{V}_{\mathrm{H_2O}}$ 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.

$$Y_\mathrm{m} = \sum_i n_i \bar{Y}_i$$

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

$$\frac{Y_\mathrm{m}}{\sum_i n_i} = \sum_i x_i \bar{Y}_i$$

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

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

- **Molar** (quantity Y of substance i): The amount of Y contributed by each mole of a substance i when pure. *Dentoed by* $\boldsymbol{\hat{Y}_i}$. *Units* $\mathbf{mol^{-1}}$.
- **Mole fraction** (of component i): The fraction of moles of component i relative to the total number of moles in the mixture. *Denoted by* $\boldsymbol{x_i}$. *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* $\boldsymbol{Y_i^\circ}$.
- **Activity**: A thermodynamic concentration and measure of the nonideality of solutions. *Denoted by* $\boldsymbol{a_i}$. *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,

$$m_i = N_\mathrm{A} n_i$$

  where $N_\mathrm{A} = 6.022 \times 10^{23}$ 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* $\boldsymbol{z}$.
  - 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.