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.
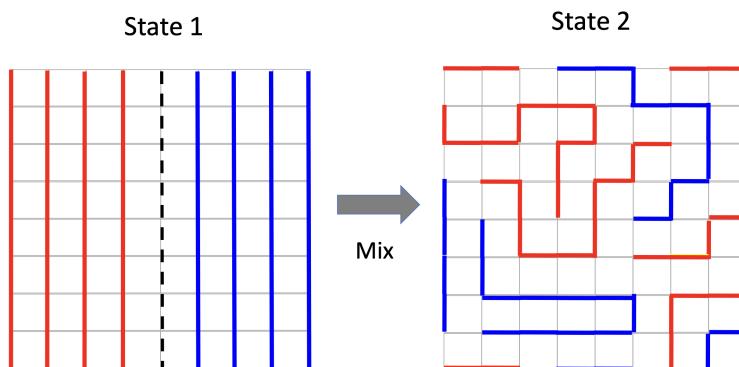
Figure 2.1: Lattice theory for polymer phase behavior.

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

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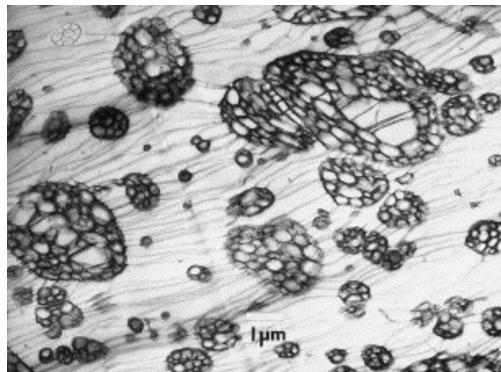
Figure 2.2: Salami phase micrograph in styrene-butadiene mixtures.

  – 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,

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

  - 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.
  - 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.
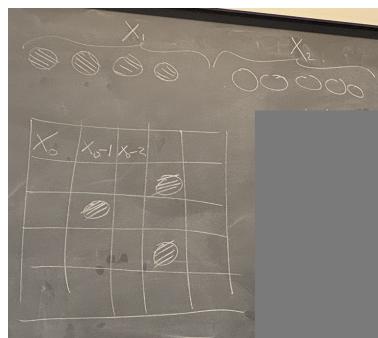
Figure 2.3: Configurations in mean field lattice theory.

- – 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

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

  - ■ Remember that the initial entropy is zero!
- – Invoking Stirling's approximation and remembering that $X_1 + X_2 = X_0$, we can then get

$$\frac{\Delta S}{k_B} = X_0 \ln X_0 - X_0 - [X_1 \ln X_1 - X_1 + X_2 \ln X_2 - X_2]$$

$$= X_0 \ln X_0 - X_1 \ln X_1 - X_2 \ln X_2$$
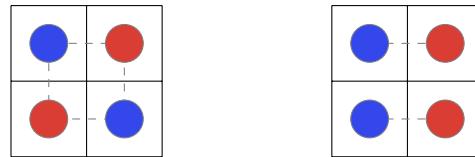
- – It follows that the entropy per site $\Delta S/k_B X_0$ is

$$\frac{\Delta S}{k_B X_0} = \frac{1}{X_0} \left[(X_1 + X_2) \ln X_0 - X_1 \ln X_1 - X_2 \ln X_2 \right]$$

- – Now use the form of the above equation to define the variables ϕ_i ($i = 1, 2$) as follows.

$$-\frac{X_1}{X_0} \ln \frac{X_1}{X_0} - \frac{X_2}{X_0} \ln \frac{X_2}{X_0} = -\phi_1 \ln \phi_1 - \phi_2 \ln \phi_2$$

  - ■ It follows that $\phi_i = X_i/X_0$ is 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 has z nearest-neighbor cells.
  - 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.
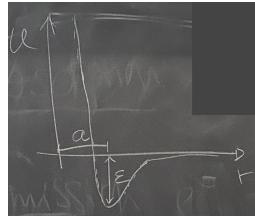
Figure 2.5: Potential well.

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

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

  - 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.

$$H_{1,2} = \xi_{12}\varepsilon_{12} + \xi_{11}\varepsilon_{11} + \xi_{22}\varepsilon_{22}$$

$$= z X_1 \phi_2 \varepsilon_{12} + \frac{z X_1 \phi_1 \varepsilon_{11}}{2} + \frac{z X_2 \phi_2 \varepsilon_{22}}{2}$$

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

$$H_1 = \frac{z X_1 \varepsilon_{11}}{2} \qquad\qquad H_2 = \frac{z X_2 \varepsilon_{22}}{2}$$

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

$$\Delta H_M = H_{1,2} - (H_1 + H_2)$$

$$= z \left[X_1 \phi_2 \varepsilon_{12} + \frac{X_1 \varepsilon_{11}}{2}(\phi_1 - 1) + \frac{X_2 \varepsilon_{22}}{2}(\phi_2 - 1) \right]$$

and hence

$$\frac{\Delta H_M}{X_0} = z \left[\phi_1 \phi_2 \varepsilon_{12} + \frac{\phi_1 \varepsilon_{11}}{2}(-\phi_2) + \frac{\phi_2 \varepsilon_{22}}{2}(-\phi_1) \right]$$

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

$$= \phi_1 \phi_2 \chi$$

where

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

is the **Flory χ parameter**.

– Implication: If they like themselves more than they like each other (right diagram), chi parameter 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 for monomers.

- How about for polymers?
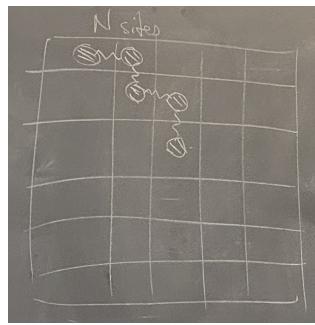
Figure 2.6: Fitting polymers into a square lattice.

  – We have to pick N adjacent sites.
  – Then the next time we pick is the number of sites minus N! And on and on.
  – This essentially reduces the number of sites by N_1 and N_2.
  – When N is very big, this equation tells us that entropy doesn't play a huge role (because N_1, N_2 in the denominator). Thus, enthalpy matters more for polymers.

- Finally, we have gotten to the "famous Flory-Huggins theory of free energy."

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

  – We get this by adding the enthalpic and entropic contributions via the .

- How do we measure χ experimentally?

  – We will explore this soon.

- Influence of χ on phase behavior.

  – When χ reaches 2-3, we get demixing.
  – 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.

- The χ at which you see phase separation decreases exponentially with increasing $N_A = N_B = N$.

  - N is just how long the chains are!

- 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

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

  - 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.

  - An interesting way of thinking about this: Osmometry.
 - Imagine a uniform, mixed polymer solution.
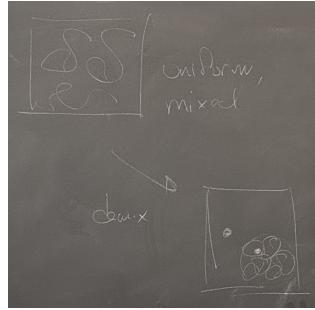
Figure 2.7: Demixing of a polymer-solvent solution.

- ■ 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 $N_2 = \langle N_2 \rangle = M_n$.
  - – 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., $n_1 \gg n_2 N_2$ and (2) that the volume of the monomers is approximately equal, i.e., $v_1 \approx v_2$ that

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

- – We thus expand

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

- – It follows that

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

$$= -\phi_2 - \frac{1}{2}\phi_2^2 + \phi_2 - \frac{\phi_2}{N_2} + \chi \phi_2^2$$

$$= -\frac{\phi_2}{N_2} + \left(\chi - \frac{1}{2} \right) \phi_2^2$$

■ 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.
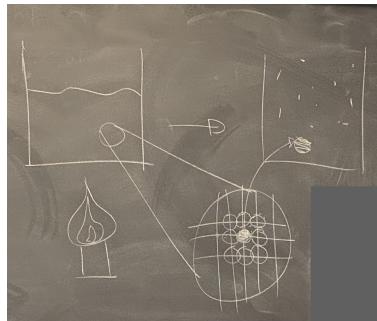
Figure 2.8: Hildebrand's experiment.

– 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.

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

■ 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.