

## Topic 2

# Solution Thermodynamics

### 2.1 Flory-Huggins Theory

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

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

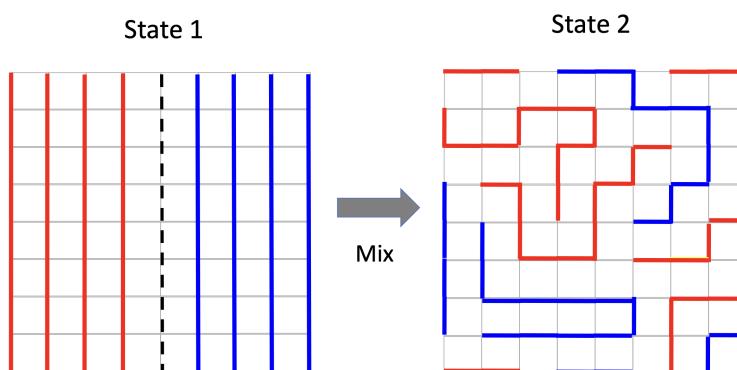


Figure 2.1: Lattice theory for polymer phase behavior.

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

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

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

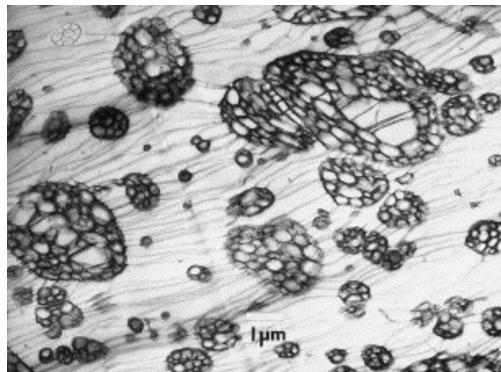


Figure 2.2: Salami phase micrograph in styrene-butadiene mixtures.

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

- Last lecture, we derived a free energy functional for single chains.
  - Today, we're looking at  $G = H - TS$ .
    - What we're really interested in is the free energy of mixing,
- $$\Delta G = G_{1,2} - (G_1 + G_2)$$
- 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  $V_i$ .

- In State 2, we have a mixed phase with total volume

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

- Note that we're assuming that there is no change in volume  $\Delta V$  during mixing.
- Nomenclature: If a system is comprised of a solvent and polymer, name the solvent “1” and the polymer “2”.
- To understand the thermodynamics of mixing, we'll start with the *entropy* of mixing.
  - Comments.
    - In a melt, most chains do not feel themselves because other chains screen the interaction of the original chain with itself.
    - This is great for us, because everything behaves like a truly random walk with scaling relation  $N^{1/2}$ .
      - This realization is what won Flory his Nobel Prize!
  - There is only 1 possible way to arrange a pure component in its volume.
    - This follows from the binomial expression  $\binom{n_i N_i}{n_i N_i}$ .
    - Thus, when phases are separated, each phase has entropy  $S = 0$ .
  - Mean field lattice theory.

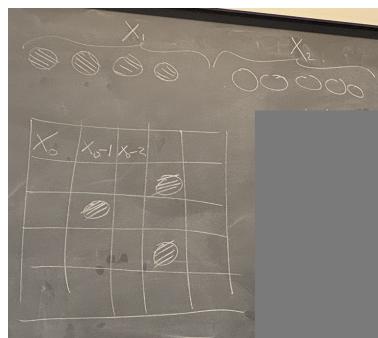


Figure 2.3: Configurations in mean field lattice theory.

- 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  $\Delta S$  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

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

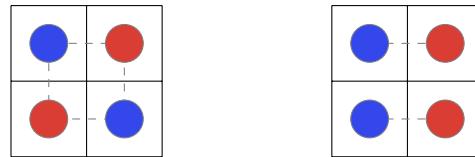
- It follows that the entropy per site  $\Delta S/k_B X_0$  is

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

- Now use the form of the above equation to define the variables  $\phi_i$  ( $i = 1, 2$ ) 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  $\varepsilon_1$  to the total energy of the system. This means that in Figure 2.4,  $E_1 = 4\varepsilon_1$  and  $E_2 = 2\varepsilon_2$ .
- In big systems, the energy won't fluctuate much, though, so Boltzmann equation is more of an approximation, but it's *good enough*.
- 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.

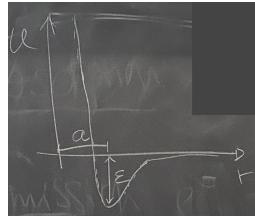


Figure 2.5: Potential well.

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

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

- In a typical attraction well, we have a most probable distance  $a$ , at which the energy depth is  $\varepsilon$  (see Figure 2.5).
- Let  $\varepsilon_{ij}$  refer to how deep the well is between species  $i$  and  $j$ , where  $i, j \in \{1, 2\}$ .
- It follows that in a mixed enthalpic state, the interaction energy is the following.

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

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

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

- 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

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

where

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

is the **Flory  $\chi$  parameter**.

- Implication: If they like themselves more than they like each other (right diagram), chi parameter will be positive and will lie between the middle two lines (we don't know here if it will mix or demix).
- The  $\chi$  parameter is still being debated today; Alfredo is writing a paper on it!
  - The parameter as written is linear, but that's based on a mean field assumption. Should it have a quadratic term? Maybe it does at a (more accurate) higher level of theory.
- At this point, we can assemble everything into the free energy for monomers.
- How about for polymers?

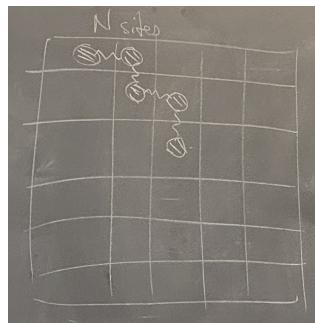


Figure 2.6: Fitting polymers into a square lattice.

- 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.”
- $$\frac{\Delta G_M}{X_0} = k_B T \left( \chi \phi_1 \phi_2 + \frac{\phi_1}{N_1} \ln \phi_1 + \frac{\phi_2}{N_2} \ln \phi_2 \right)$$
- We get this by adding the enthalpic and entropic contributions via the .
  - How do we measure  $\chi$  experimentally?
    - We will explore this soon.
  - Influence of  $\chi$  on phase behavior.
    - When  $\chi$  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:  $\chi$  is pretty good if  $z$  is big; if  $z$  is small, quadratic and other higher order corrections may be necessary for  $\chi$ .
- The  $\chi$  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.