

# 3.942 (Polymer Physics) Notes

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# Topics

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# Topic 0

## Introduction

### 0.1 Introduction

9/4:

- Starts at MIT time.
- Alexander-Katz begins.
- Extra notes on the syllabus.
  - All of the numbered courses were combined recently because offerings were almost identical.
  - Alexander-Katz is a DMSE prof; Doyle is a ChemE prof.
  - On textbooks.
    - He used to send us to the library, and we'd sort out which text was easiest for us to understand.
    - He recommends we buy Lodge and Hiemenz (2020), but the chapters will also be posted.
      - The first chapters in the book are chemistry, and the later ones are physics.
    - Strobl (1997) will give us more information about some areas. Good if you're interested in mechanics, solid states, and plastics.
    - Young and Lovell (1991) is similar to Lodge and Hiemenz (2020).
    - Rubinstein and Colby (2003) is advanced undergrad to grad, and has lots of examples. Good for understanding scaling concepts. Doesn't have any hard phases. Has a bit on characterization methods.
    - de Gennes (1979) is widely hated because it was written very colloquially, but the ideas are really interesting. The man himself had a very straight mind, and thought about problems in a very interesting manner.
  - There will be about 6 homeworks, 1-2 per quiz.
    - They will give us a key, and we will have to grade our own homework.
    - We will then have to turn in a second homework, which is revised and has a grade on it.
    - In Alexander-Katz's experience, this method gives a 10% increase in quiz scores on average. This is because going through your homework in depth is very beneficial!
    - Also, the last few times they had a grader, (s)he usually knew nothing about polymer physics.
  - There will be 3 quizzes.
    - Each counts for 20%; they're not cumulative.
    - Alexander-Katz and Doyle will be grading our quizzes themselves.
  - Make sure to participate! Don't stay quiet; ask questions, etc.
  - You may work together; just note your collaborators' names on your assignments.
  - Don't trust ChatGPT and generative AI 100%. You won't be able to use them for the quizzes, but they may be useful for searching.

- Lecture now begins.
- **Hard matter:** Metals, ceramics, and semiconductors, which are typically highly crystalline.
  - For hard matter, the binding energy  $\varepsilon$  between atoms is much greater than  $10^{-21}k_B T$ .
- In this course, we're going to be working with materials of  $\varepsilon \approx 1 \text{ eV} \approx 10^{-19} \text{ J}$ .
  - So to break these bonds, it takes about  $100k_B T$ .
- **Soft matter:** Polymers, organics, liquid crystals, gels, foods, life!
  - $\varepsilon \approx k_B T$ .
- A good mental picture for the barrier dividing small molecules and soft matter is the following.
  - Ethane is a gas. Very little forces between molecules.
  - When we make polyethylene, it can become extremely strong. This is because of the **multivalent effect**. When the chains are long enough, we get a solid.
- **Multivalent effect:** The observation that multiple copies of a weakly binding molecule — when arranged on a common scaffold — exhibit a significantly stronger and more specific binding response than a single, isolated molecule.
- A fundamental idea: As the **degree of polymerization  $n = N$**  grows, a lot of interesting behavior appears.
  - In this course, most of the behavior we're concerned with will be *qualitative*.
  - For example, we don't care about *exact* numerical properties if  $n = 64$ , but we do want to answer questions like, “if  $n$  doubles, what will happen?”
- Topics to understand in this class (the key origins of soft matter behavior).
  - Relatively weak forces between molecules.
    - We'll discuss this today.
  - Various types of bonding.
  - Molecular shapes and sizes.
  - What chemistries are relevant.
  - Fluctuating molecular conformations/positions.
  - Influence of solvent, diluent, particles, surfaces.
  - Entanglement.
    - Alexander-Katz gives the pasta analogy.
    - Entanglement gives interesting rheological properties, dramatic increases in viscosity (much higher than you'd expect from simple arguments), etc.
  - Many types of entropy.
  - What architectures and structural hierarchies exist over several length scales (nano, micro, etc.).
- We'll also discuss some characterization methods for harder and softer materials.
  - We'll do the theory first, and then figure out what to measure to figure out what's in the materials.
- Lastly, we'll talk about some opportunities to exploit the properties of soft matter in diverse applications.
- Aside: They used to have a final project on how to make contact lenses comfortable.
  - They are semisoft and silicone-based nowadays!

- Two types of interactions in soft matter: **Intramolecular** and **intermolecular** interactions.
- **Intramolecular** (interactions): (Macro)molecules are predominantly held together by strong covalent bonds with many conformations accessible via rotational isomeric states.
  - Think Newman projections. These reduce the possible conformational states substantially.
  - The allowed conformations are **gauche plus**, **gauche minus**, and **trans**. This reduces the polymer entropy a lot.
  - We will talk about how this tacticity affects polymer size and other quantities.
- **Intermolecular** (interactions): Hard sphere, Coulombic (including stacking; usually just a  $1/r$ ), Lennard-Jones (induced dipoles, such as van der Waals forces), or hydrogen bonding (net dipoles; polar interactions will definitely be important).
  - We think of polyethylene as not that polar, but it is kind of polar (especially if you put a methyl group at every other position, as in polypropylene).
  - The PE vs. PP  $T_g$ 's vary *dramatically*.
- **Short range order:** When you turn molecules into polymers, other length scales start to matter. *Also known as SRO.*



Figure 0.1: Short range order in PS-*b*-PDMS.

- Consider a block copolymer of polystyrene and PDMS. When you put it all together, it forms a fingerprint-like pattern (PDMS light, PS dark).
- The chains look random at the nanoscale, but they phase-separate when you zoom out a bit.
- Think of this as spaghetti on a surface.
- SRO is always present in condensed phases.
- **Long range order:** Visible in perforation lamellae, for example. *Also known as LRO.*
  - LRO is sometimes present in condensed phases.
- Example: If a material is ordered by *layer* from bottom to top, defects can assemble and give you color control. This happens in some soft matter films.
  - In the specific example in the slides, P2VP keeps a charge always, and polystyrene does not.
  - Defects allow swelling to happen much faster, and swelling changes length scales which changes color (almost like in quantum dots, where size affects color).
- Overall, the goal of soft matter studies is the manipulation of structures, orientation, and defects. We seek to develop methods to process polymers and soft solids, so as to create controlled structures and hierarchies.
- Mantra: Whatever we want to do with polymers, nature has done it first.
  - Indeed, the color changing thing above is the same principle as color-changing octopi!

- History of polymers.

- First users were in Mesoamerica (around 1600 BC). They harvested natural latex (polyisoprene) from trees. As soon as it comes out, it hardens. They used this polymer to make a game ([prehispanic basquethol](#)) and shoe soles.
  - If you don't crosslink latex, it will be like silly putty, going everywhere.
  - They crosslinked it with the juice of a cactus that they had chewed.
- 300 years after the Spanish invaded (around 1850 AD) and crosslinking was forgotten, Goodyear figured out once again how to crosslink natural rubber (he did so with very strong acids, sulfuric acid and such).
- Aside: Humans tend to find uses for materials far before they understand what it's made of, how to process it, etc.
- Pretty much all of biology is made out of polymers: DNA, RNA, proteins, cells, etc.
- People only discovered polymers (in the modern sense) in the 1920s, when H. Staudinger put forth the **macromolecular hypothesis**.
- After Staudinger, people started thinking about what they would *like* to make.
- 1930s: Silk was the highly desired textile of the time.

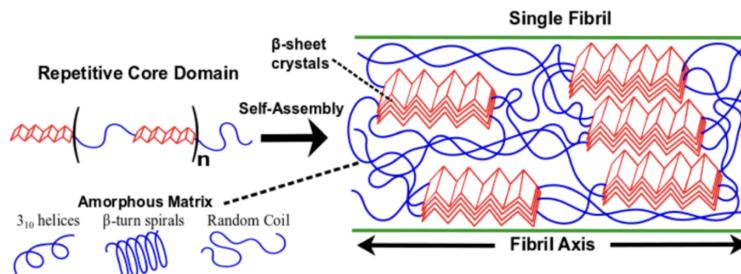


Figure 0.2: Silk.

- Made out of proteins with amorphous and crystalline ( $\beta$ -pleated sheets) regions (Sarkar et al., 2019).
- So they thought about repeating a peptide (polyglycine). Even more similarly, though, Carothers (really talented chemist who went to Dupont) made nylon out of alternating aliphatic segments and hydrogen-bonded amides!
  - Nylon is made via **step-growth polymerization**; Alexander-Katz diagrams this out on the blackboard.
  - Nylon has very nice properties and is even stronger than silk. Nicer properties than silk.
  - Changing the number of carbons in the chain varies the melting temperature!
  - Note that members of the nylon family are named by counting the number of carbon atoms in the backbone between nitrogen atoms.
- 1965: Stephanie Kwolek (also Dupont) develops Kevlar.
  - Better hydrogen bonding, much stiffer.
  - Same number of carbons as nylon 6! It really does matter how you arrange the carbons.
- Common polymers.
- **Polyethylene:** *Also known as PE.*
  - Invented 1933.
  - One of the biggest polymers on the market today.

- Polyester.

- Invented 1941.
  - You can make many different kinds of these; defined by the ester linkage.
  - Nature is full of polyesters, all very different.
    - If you change one carbon on an oligoester, it can go from tangarine-sented to very bad.
  - Used for lubrication, since the polar carbonyl moiety gives interesting properties.
  - These don't have the N–H moiety of polyamides, but can still be assembled by condensation.
  - These melt very easily.
  - Example: Polyethyleneterephthalate, PET.

- Common classes of polyolefins.

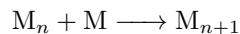
- Vinyl polymers, diene class, vinylidenes.
  - Teflon (polyvinylidene fluoride).
  - Plexiglass: Methacrylics.
    - Acrylics are more liquid; methacrylics are harder and more solid.

- Common classes of step-growth polymers.

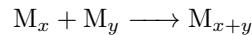
- Silicone.

- Polymer nomenclature.

- Addition reactions.



- Condensation reactions.



- **Monomer:** Small molecule.
  - **Oligomer:**  $n < 100$ .
  - **Polymer:**  $n \in [100, 10000]$ .

- Characteristic properties of polymers (depend on the chemistry, *and* how everything is arranged).

- Insulating or conducting.
  - Light-emitting.
  - Photovoltaic, piezoelectric.
  - Soft elastic (really large reversible deformations, often temperature dependent like the PGS rubber band example) or very stiff.
  - Zero/few crystals or highly crystalline.

- Polymers are in everything now.

- About 50% of a plane is made out of composites (like carbon fiber; very strong and very light).
  - It's really expensive to cure the polymers that hold all the carbon fibers, so they're looking for new ways to do that (this is like REMAT stuff!).

- Biggest shares of the polymer market.

- PE (plastic bags), PP, PET (clothes and garments), PVC (pipes), and polyamides.
  - They are trying to make the polymer market “look” better now by calling it the “*circular* polymers market.” Alexander-Katz doesn't believe properties are the same in recycled polymers.

- Thermodynamics refresher.
  - Given your state variables ( $T$ ,  $P$ ,  $E$ ,  $s$ , etc.), some states are allowed to a system and some are not.
  - We usually work with the **Helmholtz free energy** in this class, not the **Gibbs free energy**. Alexander-Katz doesn't care about the difference; Doyle will.
  - If you start in an out-of-equilibrium state, thermodynamic forces will push you down into an equilibrium state. We will think of forces as the derivative of the slope of the energy hypersurface.
- Statistical mechanics primer.
  - We will use Boltzmann's law,  $S = k \ln(\Omega_{\text{tot}}[U])$ , a lot.
  - Because suicide is so stigmatized, his tomb (in Vienna, Austria) is very hidden away.
  - In the nineteenth century, there was a big debate over whether the world was molecular or continuous. Chemists (who tend to be right) said molecular, and physicists said that we didn't need to worry about that. Boltzmann tried to reconcile these two philosophies.
  - He eventually discovered the following.  $\Omega_{\text{tot}}$  is all the possible ways you can arrange the system. Technically,  $\Omega_{\text{tot}}[U]$  is the total number of equivalent microstates at constant energy,  $U$ . If you take the natural log and multiply by a constant, we get the entropy.
  - Recall that Boltzmann's discovery can be related to the pressure of ideal gases.
- Next Tuesday, Prof. Doyle will begin on single chains.

# Topic 1

## The Macromolecule

### 1.1 The Macromolecule

9/9:

- Pat Doyle begins; he will teach the next three lectures.
  - They've broken the class up into modules taught alternatingly.
  - Aside: Alfredo has taught this course 10 times; Doyle never has (he's replacing Greg Rutledge this year).
- Announcements.
  - Slides and homework 1 have been posted.
  - Slides should be posted before lecture, but may not be posted much before.
- Lecture outline.
  - Connectivity: Thermodynamic limit, architecture, and molecular weight.
  - Configurations: Structural, chemical, stereo, and geometrical isomerism.
  - Conformations: Rotational isomeric states.
- **Connectivity:** The joining of small parts (monomers) into larger molecules (polymers).
- **Degree of polymerization:** The number of repeat units in a polymer. *Denoted by  $N$ .*
  - Derivable from the molecular weight(s).
- Example: Polyethylene.
  - In this course, vinyl examples will be our workhorses, but we will “riff off of them” to other polymer types.
  - The **repeat unit** here is  $\text{CH}_2\text{CH}_2$ , consistent with the IUPAC nomenclature of polyethylene.
  - Ethylene is also the monomer.
  - The end groups do look different, but the **thermodynamic limit** addresses them.
- **Repeat unit:** A part of a polymer whose repetition would produce the complete polymer chain (except for the end groups) by linking the repeat units together successively along a chain.
- **Thermodynamic limit:** The finding that as  $N \rightarrow \infty$ , the end group chemistry matters less. *Also known as polymer limit.*
  - The thermodynamic limit is also sometimes discussed in the context of statistical mechanics, where collective behavior also matters more than individual or picoscale.

- **Glass transition temperature:** The temperature at which a substance will go from brittle to kind of rubbery. *Denoted by  $T_g$ .*
- **Flory-Fox correlation:** The simple model that the  $T_g$  of a polymer asymptotically approaches a limit  $T_g(M \rightarrow \infty)$  for higher and higher molecular weights at some empirically derived rate  $A$ . *Given by*

$$T_g(M_n) := T_g(M \rightarrow \infty) - \frac{A}{M_n}$$

- Alkane series often obey this simple  $1/x$  relation.
- Another example of thermodynamic limits: Regardless of polymer structure, a power law defines polymer viscosity.

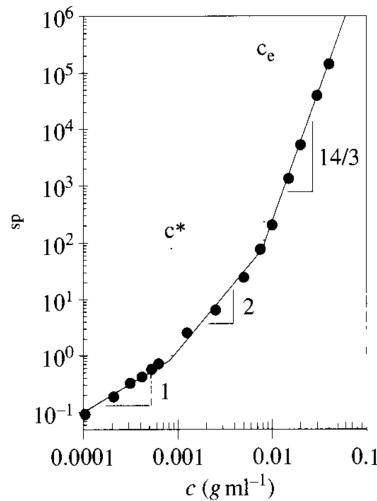


Figure 1.1: Polymer viscosity scales universally by power laws.

- Namely, polymer viscosity increases up to a critical concentration  $c^*$  at a slope of 1, then to an entanglement concentration  $c_e$  at a slope of 2, and then at a slope of  $14/3$  past that.
- Thus, there are three universal scaling regimes.
- A log-log plot is used to show power-law scalings, like in high school trigonometry!
- Aside: Power laws are present everywhere once you get big enough, down to the volume of our lungs relative to our bodies in bigger and bigger animals.
- This class isn't super stringent on nomenclature, but it's good to know terms for when we read papers (Table 1.1).
  - Alfredo will talk about block copolymers a good bit!
- Polymer architectures.
  - Linear polymers.
    - Polyrotaxanes and other supramolecular assemblies can have interesting properties. Example: Catenated DNA!
  - Cross-linked systems (nice gelation).
  - Branched polymers can have a single monomer, or multiple as in graft (Table 1.1).
  - Dendritic polymers have different generations with regular branching for very dense structures.
  - There are a few more classes, as well.

Copolymer type	Arrangement of monomeric units	Representation	Connective	Example
unspecified	unknown or unspecified	(A- <i>co</i> -B)	- <i>co</i> -	poly[styrene- <i>co</i> -(methyl methacrylate)]
statistical	obeys known statistical laws	(A- <i>stat</i> -B- <i>stat</i> -C)	- <i>stat</i> -	poly(styrene- <i>stat</i> -acrylonitrile- <i>stat</i> -butadiene)
random	obeys Bernoullian statistics	(A- <i>ran</i> -B)	- <i>ran</i> -	poly[ethene- <i>ran</i> -(vinyl acetate)]
alternating	alternating	(AB) <sub>n</sub>	- <i>alt</i> -	poly[(ethylene glycol) <sup>a</sup> - <i>alt</i> -(terephthalic acid)]
periodic	periodic with respect to at least three monomeric units	(ABC) <sub>n</sub> (ABB) <sub>n</sub> (AABB) <sub>n</sub> (ABAC) <sub>n</sub>	- <i>per</i> -	poly[formaldehyde- <i>per</i> -(ethene oxide)- <i>per</i> -(ethene oxide)]
block	linear arrangement of blocks	-AAAAA-BBBBB-	- <i>block</i> -	polystyrene- <i>block</i> -polybutadiene
graft	polymeric side chain different from main chain <sup>b</sup>	-AAAAAAAAAA-   B B B B B 	- <i>graft</i> -	polybutadiene- <i>graft</i> -polystyrene

<sup>a</sup> ethane-1,2-diol, <sup>b</sup> main chain (backbone) is specified first in the name.

Table 1.1: IUPAC nomenclature of copolymers.

- We'll now discuss some nomenclature on molecular weight.
- Aside: Other than nature, synthetic chemists cannot make dispersity 1 polymers; “polymer chemists aren’t gods, despite some thinking they are.”
- ***i*-mer:** A segment of a polymer with degree of polymeriation *i*.
- ***M<sub>i</sub>*:** The molecular weight of the *i*-mer. *Given by*

$$M_i := iM_0$$

- ***M<sub>0</sub>*:** The molecular weight of the repeat unit in a polymer chain.
- ***n<sub>i</sub>*:** The number of *i*-mers.
- **Number fraction** (of an *i*-mer): The probability of picking an *i*-mer out of solution when picking a chain. *Denoted by *x<sub>i</sub>*. Given by*

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

- **Weight fraction** (of an *i*-mer): The probability that a repeat unit picked out of solution belongs to an *i*-mer. *Also known as mass fraction. Denoted by *w<sub>i</sub>*. Given by*

$$w_i := \frac{n_i M_i}{\sum_i n_i M_i} = \frac{n_i (iM_0)}{\sum_i n_i (iM_0)} = \frac{i n_i}{\sum_i i n_i}$$

- Note that *i n<sub>i</sub>* is the total number of monomers in the *i*-mer, and  $\sum_i i n_i$  is the total number of monomers in solution.
- **Number-average molecular weight:** The arithmetic mean of the molecular masses of the individual macromolecules. *Denoted by *M<sub>n</sub>*. Given by*

$$M_n := \sum_i x_i M_i = M_0 \cdot \frac{\sum_i i n_i}{\sum_i n_i}$$

- **Weight average molecular weight:** A measurement of molecular weight that gives more contribution to higher-weight molecules. *Denoted by  $M_w$ . Given by*

$$M_w := \sum_i w_i M_i = M_0 \cdot \frac{\sum_i i^2 n_i}{\sum_i i n_i}$$

- Both  $M_n$  and  $M_w$  look like moments of a distribution (i.e., first and second moment).
  - We could generalize even more, but we don't need to.
  - However, to figure out if we have a tight or wide distribution, we often look at ratios of our moments. This leads to the following definition.
- **Dispersity:** A measure of the breadth of the distribution of fragment molecular weights in a polymer sample. *Also known as polydispersity index, PDI. Denoted by  $D$ . Given by*

$$D := \frac{M_w}{M_n} = \frac{\text{second moment}}{\text{first moment}}$$

- In Lodge and Hiemenz (2020), they also derive the **variance**. You don't need to worry about the math, though.
- **Variance:** Another measure of the breadth of the distribution of fragment molecular weights. *Denoted by  $\sigma^2$ . Given by*

$$\sigma^2 := M_n^2[D - 1]$$

- **Schulz-Zimm distribution:** An idealized mathematical model for polymer molecular weight distribution.
- With these definitions, we can now do homework problem number 1!
- Experimental techniques to measure molecular weight.
  - Size exclusion chromatography.
  - Osmotic pressure.
  - End group analysis.
  - Light scattering techniques.
    - More sensitive to higher moments.
- We now move onto polymer configurations.

- **Configurations:** The way things are connected or bonded together.
  - Physicists and chemists have many competing definitions of “configurations,” but the one above is what we'll use in this class. Essentially, think of it as a synonym for constitutional isomerism.
  - Under this definition, you have to *break bonds* to create a new configuration.
  - We are *not* yet talking about rotamers (what we'll call **conformations**). As you make your polymers longer and longer, the conformational space you can explore gets bigger.
- There are 3 main types of structural isomers (i.e., configurations): **Positional, stereo, and geometric** isomers.
- **Positional** (isomers): Changing connectivity.
- **Stereoisomers:** Related to chiral centers.
- **Geometric** (isomers): Related to double bonds.

- More on positional isomers.

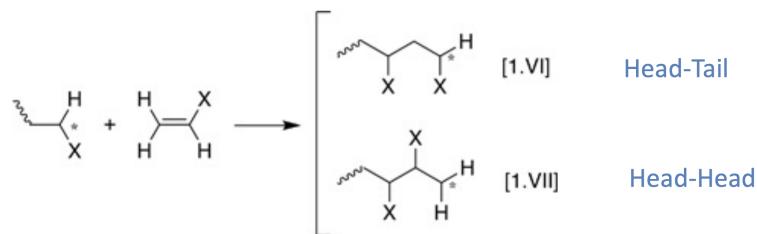


Figure 1.2: Head-head and head-tail monomer addition.

- **Head-head** vs. **head-tail** bonding in vinyl monomers.
- Head-tail is more common, and differences can change the  $T_g$  substantially.
- **Head-head** (orientation): Monomer addition wherein the substituted carbon attaches to the growing chain end. *Also known as head-to-head*.
- **Head-tail** (orientation): Monomer addition wherein the unsubstituted carbon attaches to the growing chain end. *Also known as head-to-tail*.
- More on stereoisomers.
- Doyle reviews **chirality**, **rectus** vs. **sinister**, and the **Cahn-Ingold-Prelog nomenclature**.
- **Pseudochiral** (center): A chiral center where two of the substituents are identical *except* for chirality.
  - In this case, CIP nomenclature gives priority to the branch with more R chiral centers.
- Chiral centers in polymers give rise to **tacticity**.

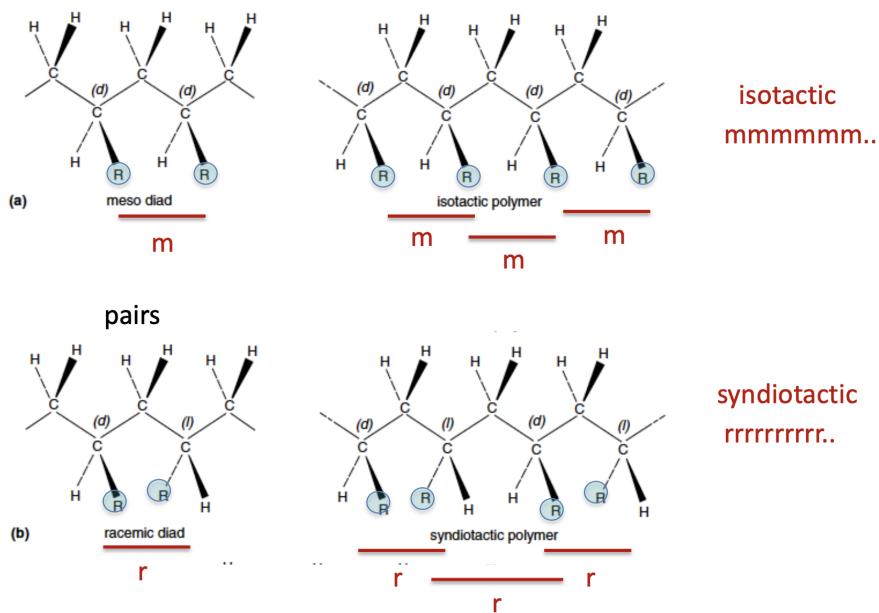


Figure 1.3: Tacticity.

- There are **meso diads** and **racemic diads**; which ones you have determine if the polymer is **isotactic**, **syndiotactic**, or **atactic**.

- **Meso** (diad): Two adjacent chiral centers with a local plane of symmetry halfway between them.
- **Racemic** (diad): Two adjacent chiral centers *without* a local plane of symmetry halfway between them.
- **Isotactic** (polymer): A polymer containing only meso diads.
- **Syndiotactic** (polymer): A polymer containing only racemic diads.
- **Atactic** (polymer): A polymer containing both meso and racemic diads.
- Example: Atactic polystyrene tends to be more amorphous than syndiotactic or isotactic polymers, which can be semicrystalline.
  - Nobel prize (1963) to Ziegler and Natta for a catalyst generating isotactic polystyrene (PS-it).
    - Note that the initial Ziegler-Natta catalysts weren't metallocenes! The introduction of these types only came later.
  - Syndiotactic polystyrene (PS-st) came later in 1986 and had superior properties.
    - PS-st crystallizes an order of magnitude faster than PS-it; has half the entanglement molecular weight; and is commonly used today in auto parts, electronics, and medical equipment.
- Tacticity is often measured by certain splittings (or their absence) in  $^1\text{H}$  NMR.
  - Isotactic polymers put the geminal methylene protons into distinct chemical environments; syndiotactic polymers do not. Atactic polymers will have a mix of both, and the mix can be quantified with integration.
  - $^{13}\text{C}$  NMR can be used, too.
- More on geometric isomers.
  - Example: Polybutadiene can be formed *trans* or *cis*, as guided by a catalyst.
  - Natural rubber is *cis*-1,4-polyisoprene. Other types of tree sap can give *trans*-1,4-polyisoprene.
- We now move onto polymer conformations.
- **Conformations:** The spacial arrangements possible (or “probable,” taking energy into account) for a polymer.
  - No bonds are *broken* here, just rotated.
- Reviews **Newman projections**.
  - Staggered configuration is defined as  $0^\circ$ .
  - Eclipsed configuration then starts at  $60^\circ$ .
  - There are energy penalties to being in different conformations.
    - As one example, eclipsed is higher energy than staggered due to sterics.
    - Generally sinusoidal relation in a plot of potential energy  $V$  against dihedral angle  $\theta$ .
    - The energy difference between rotamers is approximately  $3k_{\text{B}}T$ , which is not huge but big enough that the system will spend most of its time in the valleys. Each “valley” is a **conformer**.
    - So then since probability is proportional to  $e^{-V/k_{\text{B}}T}$ , the probability that a molecule will be staggered is greater than that it will be eclipsed.
  - In molecules longer than ethane, we break degeneracy of the valleys.
  - The rapid growth of conformers: Ethane has 3 conformers. Propane has  $3^2$ . Butane has  $3^3$ . Decane has  $3^{10}$ . Polyethylene with  $N = 10^5$  already has on the order of  $10^{47\,000}$  possible conformers, a huge conformational space.

- This is because each bond has 3 valleys!
- Many of the models we'll develop are ways of enumerating these conformations in relation to some higher-order measurement of the polymer, such as the **n-band difference**.
- Polymers are indeed often moderately sized coils rather than fully stretched out rods.
- Example: 166 kbp DNA (approximately 684 **Kuhn steps**, discussed next lecture) can be videotaped moving around, and it never fully elongates.
- Stretched out polymers shrink back over some characteristic time.
- Polymers with high degrees of polymerization result in many possible conformations without breaking bonds — this is what we'll discuss in the next two lectures!
- A good conversions to keep in mind:  $2.5 \text{ kJ/mol} \approx 1k_B T$ .
- Today is probably the most jampacked bits and pieces day; other lectures will be more focused, but this is important background.

## 1.2 Conformation: Ideal Chains

9/11:

- Lecture outline.
  - Conformation (degrees of freedom).
  - Ideal chain models.
  - Entropic elasticity.
- Many material properties we care about are correlated with the size of the polymer.
- This size is measured by a vector **R** that goes from one end of the polymer to the other.

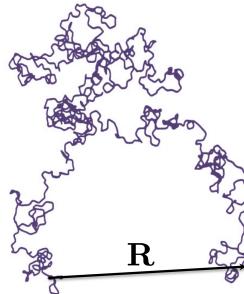


Figure 1.4: End-to-end polymer vector.

- We define **R** as the sum of all constituent bond vectors **l** (end-to-end of each chemical bond along the backbone). Symbolically,

$$\mathbf{R} := \sum_{i=1}^n \mathbf{l}_i$$

- Note that **R** has length  $|\mathbf{R}| = R$ .
- Today, we will look at several models that can be used to calculate the expected length of this vector,  $\langle R \rangle$ .

- Freely Jointed Chain (FJC) model.

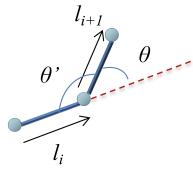


Figure 1.5: A joint in a polymer chain.

- In this model, there are no restrictions on how adjacent bonds rotate relative to each other. Rather, this is just a random walk. In effect, this means that there are no energy barriers and no excluded volume.
  - It follows that  $\langle R \rangle = 0$ .
  - However, while  $\langle R \rangle = 0$ , we have

$$\begin{aligned} \langle R^2 \rangle &= \left\langle \sum_{i=1}^n \mathbf{l}_i \cdot \sum_{j=1}^n \mathbf{l}_j \right\rangle \\ &= \sum_{i=1}^n \sum_{j=1}^n \langle \mathbf{l}_i \cdot \mathbf{l}_j \rangle \\ &= \sum_{i=1}^n \langle \mathbf{l}_i \cdot \mathbf{l}_i \rangle + \sum_{i=1}^n \sum_{j=1, j \neq i}^n \langle \mathbf{l}_i \cdot \mathbf{l}_j \rangle \\ &= nl^2 + 0 \end{aligned}$$

- The second term goes to zero as  $n \rightarrow \infty$  because there is no correlation among segments (i.e., they are randomly oriented).
- This gives us the following important scaling law.

$$\langle R^2 \rangle^{1/2} \propto n^{1/2}$$

- This means that scaling is consistent with the polymer taking a “coil-like” conformation.
- This combined with the fact that the polymer’s fully stretched length is  $nl$  gives us the following expression for the number of backbone bonds in a polymer.

$$\frac{(\text{fully stretched length})^2}{\langle R^2 \rangle} = n$$

- Note that Lodge and Hiemenz (2020) uses  $\theta$  for the *complement* of bond angle, as in Figure 1.5. Other texts may use a different convention.
- Now, let’s refine the FJC by accounting for nearest neighbor correlations.
- First, we’ll look at a polymer with only two segments (i.e.,  $n = 2$ )
  - Suppose every joint is *fixed* at complementary angle  $\theta$ , but there is no energy penalty to rotate in  $\phi$ .
  - From Figure 1.5, trigonometry tells us that

$$\mathbf{l}_i \cdot \mathbf{l}_{i+1} = l^2 \cos \theta$$

- Thus, under the conditions of this model,

$$\begin{aligned}\langle R^2 \rangle &= 2l^2 + \sum_{i=1}^2 \sum_{\substack{j=1 \\ j \neq i}}^2 \langle \mathbf{l}_i \cdot \mathbf{l}_j \rangle \\ &= 2l^2 + 2 \langle l^2 \cos \theta \rangle \\ &= nl^2(1 + \cos \theta)\end{aligned}$$

- The important takeaway is that with this chemical realism, the chain is bigger than in the previous model!

■ It is also noteworthy that the  $nl^2$  scaling relation is retained.

- This is a precursor to the freely rotating chain, where we can rotate in  $\phi$  but not in  $\theta$ .

- Let's now look at the full Freely Rotating Chain (FRC) model.

- As we elongate the chain, there is a slow decay of “memory of correlation” since  $\phi$  rotates freely. Eventually (see Lodge and Hiemenz (2020, pp. 239–40) for the derivation), we asymptote to

$$\langle R^2 \rangle = nl^2 \underbrace{\left( \frac{1 + \cos \theta}{1 - \cos \theta} \right)}_{C_n}$$

where  $C_n$  may be an empirically derived **characteristic ratio**.

- Model 3: Symmetric hindered rotations.

- Recall from last class that certain rotational conformations have lower energies than others.
- As such, we can give a Boltzman weighting to the energetic valleys.
- Thus, we reevaluate our hindered rotations with a Boltzmann weighting and the following expression crashes out of the math.

$$\langle R^2 \rangle = nl^2 \underbrace{\left( \frac{1 + \cos \theta}{1 - \cos \theta} \right) \left( \frac{1 + \langle \cos \phi \rangle}{1 - \langle \cos \phi \rangle} \right)}_{C_\infty}$$

■ Note that it's still just  $nl^2$  times a constant!

- The **characteristic ratio**  $C_\infty$  can be calculated for models or obtained from experiments. The following rearranged definition is also important.

$$C_\infty := \frac{\langle R^2 \rangle_0}{nl^2}$$

- Alert: Be aware of sign changes due to different conventions for  $\theta$  and  $\phi$  in different texts!

- There are tables of characteristic ratios in both Lodge and Hiemenz (2020) and Rubinstein and Colby (2003).

Polymer	Structure	$C_\infty$
1,4-Polyisoprene (PI)	$-(\text{CH}_2\text{CH}=\text{CHCH}(\text{CH}_3))-$	4.7
1,4-Polybutadiene (PB)	$-(\text{CH}_2\text{CH}=\text{CHCH}_2)-$	5.5
Polypropylene (PP)	$-(\text{CH}_2\text{CH}_2(\text{CH}_3))-$	6.0
Poly(ethylene oxide) (PEO)	$-(\text{CH}_2\text{CH}_2\text{O})-$	6.7
Poly(dimethyl siloxane) (PDMS)	$-(\text{OSi}(\text{CH}_3)_2)-$	6.8
Polyethylene (PE)	$-(\text{CH}_2\text{CH}_2)-$	7.4
Poly(methyl methacrylate) (PMMA)	$-(\text{CH}_2\text{C}(\text{CH}_3)(\text{COOCH}_3))-$	8.2
Atactic polystyrene (PS)	$-(\text{CH}_2\text{CHC}_6\text{H}_5)-$	9.5

Table 1.2:  $C_\infty$  values for common polymers at 413 K.

- $C_\infty$  gets bigger with bigger side chains.
- Typical range is 5-10; can go up to 20 or higher, though.
- Example: What is the size of a polyethylene molecule at 413 K and having molecular weight  $10^4$  g/mol?
  - Approach: We want to find  $\langle R^2 \rangle$  and take its square root; that will be our answer.
  - We can look up that the length  $l$  of a typical C–C bond is 0.154 nm.
  - Based on the molecular weight and the known weight of the ethylene ( $\text{CH}_2\text{CH}_2$ ) repeat unit,

$$N = \frac{10^4 \text{ g/mol}}{28 \text{ g/mol}} \approx 357.1$$

- Because there are two carbon-carbon bonds per repeat unit,  $n = 2N$ .
- Thus,

$$\begin{aligned} \langle R \rangle &= \langle R^2 \rangle^{1/2} \\ &= [nl^2 C_\infty]^{1/2} \\ &= [(2 \cdot 357.1)(0.154 \text{ nm})^2(7.4)]^{1/2} \\ \langle R \rangle &\approx 11 \text{ nm} \end{aligned}$$

- Let's compare the answer in the above example to the straight chain estimation.

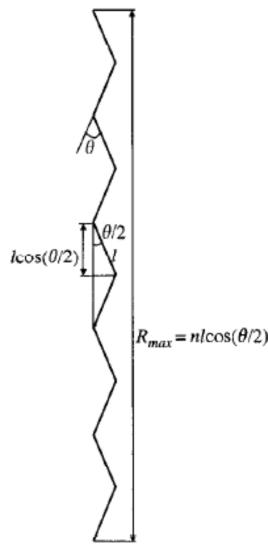


Figure 1.6: Straight chain estimation of a polyolefin.

- In this case,

$$R_{\max} = nl \cos(\theta/2)$$

- We can look up that for a typical C–C bond,  $\theta = 180^\circ - 109.5^\circ = 70.5^\circ$ .
- Thus,

$$\begin{aligned} R_{\max} &= nl \cos(\theta/2) \\ &= (2 \cdot 357.1)(0.154 \text{ nm}) \cos(70.5/2) \\ R_{\max} &\approx 90 \text{ nm} \end{aligned}$$

- This calculation is a bit tedious, so Kuhn refined the coarse grained FJC model to be computationally simpler.
- Model 4: Kuhn's Equivalent Chain.

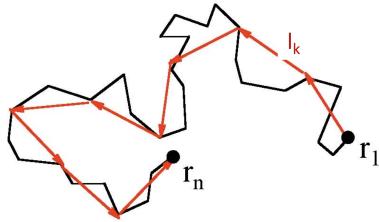


Figure 1.7: Kuhn steps.

- Building off of models 3 and 1, let's postulate the existence of an FJC along our polymer. This FJC will have  $N$  steps of length  $l_k$ , where  $l_k$  is a Kuhn step.
- This gives us two variables to define. We thus need two equations by which to define them.

- Equation 1: By the universal scaling law,

$$Nl_k^2 = \langle R^2 \rangle = C_\infty nl^2$$

- Equation 2: If the total length of the chain is  $R_{\max}$ , and the chain is being broken up into  $N$  Kuhn steps each of length  $l_k$ , then

$$R_{\max} = Nl_k$$

- By solving this system of equations, we can then define  $N$  and  $l_k$  purely in terms of previously derived variables.

- **Kuhn step:** A subsegment of a polymer chain with length defined as follows. *Denoted by  $l_k$ . Given by*

$$l_k := \frac{\langle R^2 \rangle}{R_{\max}} = \frac{C_\infty nl^2}{R_{\max}}$$

- **Number of Kuhn steps:** The number of Kuhn steps in a polymer chain. *Denoted by  $N$ . Given by*

$$N := \frac{R_{\max}}{l_k} = \frac{R_{\max}^2}{C_\infty nl^2}$$

- Example: In the case of a fully elongated carbon-carbon chain (Figure 1.6), the number of Kuhn steps is

$$l_k = \frac{C_\infty nl^2}{R_{\max}} = \frac{C_\infty nl^2}{nl \cos(\theta/2)} = \frac{C_\infty l}{\cos(\theta/2)}$$

- Note that the symbols  $R_{\max}$  and  $L$  will be used interchangeably for the straight-chain length of a polymer.
- $R_{\max}$  largely depends on the chemistry of the polymer (e.g., specific atoms' bond angles).
- We'll now look at some models for "stiff" chains, such as dsDNA or microtubules.
  - These tend to have even higher  $C_\infty$  values.
  - Note that twists in the chain are *much* bigger than individual nucleobases.
  - Molecular simulations of 75 bp dsDNA shows barely any bending. Indeed, there is a high correlation between end vectors even though they are very far away.

- A model for very stiff polymers: The Worm-Like Chain (WLC).

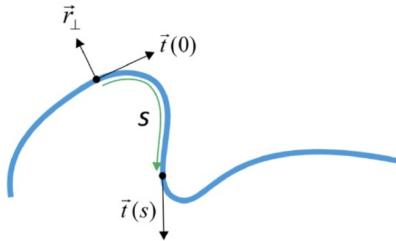


Figure 1.8: Worm-like chain.

- Represent a segment as an infinitesimal elastic rod.
- This rod has a contour you can be some point  $s$  along, where  $s \in [0, L]$ .
- The direction of the rod is defined by a tangent vector  $\mathbf{t}(s)$ .
- We also give the rod some bending energy  $U_b$ , related to how the tangent changes as we go along  $s$ . But physically, this is just curvature squared. To get the right units, we throw in a bending stiffness parameter  $\kappa_b$ , which incorporates some chemical / molecular details. Throw in a  $1/2$  from mechanics definitions, and we get

$$U_b = \frac{1}{2} \kappa_b \int_0^L \left( \frac{\partial \mathbf{t}}{\partial s} \right)^2 ds$$

- An implication of this is that correlation decays exponentially per

$$\langle \mathbf{t}(0) \cdot \mathbf{t}(s) \rangle = e^{-sk_B T/\kappa_b}$$

- I.e., you use memory of how oriented you are in one part of the chain when you get farther away from that point.
- Since  $\kappa_b/k_B T$  has units of length by dimensional analysis, we can define it to be the **persistence length**.
- From this tangent correlation function, we can calculate many interesting properties — including the mean squared end-to-end distance!

$$\langle R^2 \rangle = 2aL \left[ 1 - \frac{a}{L} \left( 1 - e^{-L/a} \right) \right]$$

- The calculation is complicated, so Dolye skips it.
- This equation reveals some interesting polymer behavior in two limits: That of *long* and *short* stiff polymers.
  - When the polymer gets long,  $a/L \rightarrow 0$  and  $\langle R^2 \rangle \rightarrow 2aL$ .
  - When the polymer gets short,  $a/L \rightarrow \infty$  and  $\langle R^2 \rangle \rightarrow L^2$ .
    - This makes intuitive sense as if it's short, it should be roughly straight and have end-to-end distance approximately equal to its length!
    - Note that in real life, there *are* polymers where the persistence length is longer than the length of the polymer! These behave like rigid rods.
- Lastly, it follows from definition of Kuhn steps that

$$2aL = \langle R^2 \rangle = Nl_k^2 = \frac{R_{\max}}{l_k} \cdot l_k^2 = Ll_k$$

- Thus, the Kuhn length is twice the persistence length! Symbolically,

$$2a = l_k$$

- **Persistence length:** A characteristic length over which a stiff polymer loses memory of its orientation along other parts of the chain. *Denoted by  $a$ . Given by*

$$a := \frac{\kappa_b}{k_B T}$$

- In conclusion, two biggest models to remember: Kuhn model (rigid steps) and WLC (continuum approximation with persistence length for semi-rigid chains).
- Example: Actin has a persistence length of  $10\text{ }\mu\text{m}$ ; since most cells are smaller than this, actin is functionally a rigid rod within a cellular context.
- Example: Measuring persistence length of dsDNA.
  - Adsorb DNA onto a surface that loosely binds it, so that it can still move around but won't fall off.
  - Then look at thousands of strands next to each other and calculate tangent lengths!
  - Reference: Kundukad et al. (2014).
- Example: Bottlebrush polymers in cartilage.
  - These have highly charged side chains, but fewer with age.
  - This causes more bending.
  - We can observe this with atomic force microscopy.
- Example: As you increase the concentration of salt in solution, you shrink the **Debye length** and also the persistence length.
  - This modifies the effect of charges on dsDNA.
- Example: Actin cytoskeleton filaments.
  - Made out of polymerized protein subunits.
  - A very thin polymer, biologically speaking.
  - Very long persistence length, as mentioned earlier.
  - As cells move, they push actin against the cell membrane to distort it! This works because actin is a very rigid rod, so rigid that it can overcome the membrane pressure.
- Example: Conjugated polymers.
  - They calculated the persistence length using DFT, and then measured it experimentally.
  - Some of their polymers are stiffer than dsDNA!
  - Rotation around one particular engineered bond is used to estimate persistence length.
- **Flexible** (polymer): A polymer for which chain length is much greater than persistence length.
- **Semi-flexible** (polymer): A polymer for which chain length is approximately equal to persistence length.
- **Rod-like** (polymer): A polymer for which chain length is much shorter than persistence length.
- Summary of ideal chains.
  - All chains show a similar, universal scaling relation that  $R \approx N^{1/2}$ .
  - For ideal chains, local interactions set the rigidity length scale and excluded volume is not significant.
  - This approximation is ok for dilute solutions at **theta conditions** and polymer **melts**.

- **Theta condition:** When you've essentially turned off excluded volume for the chain.
- **Polymer melt:** A condition in which the polymer is essentially in a solution of itself.
- Nomenclature for polymer solution regimes.



Figure 1.9: The volume occupied by polymers.

- **Hard volume** (of a polymer): The volume occupied by the chain, where each repeat unit is considered to occupy a sphere with radius equal to the bond length and the polymer is the sum of these “beads” touching each other. *Also known as occupied volume. Denoted by  $v$ . Given by*

$$v \propto nl^3$$

- The volume of each bead is thus on the order of the bond length.
- **Pervaded volume** (of a polymer): The sphere encapsulating the volume in which the polymer chain is *expected* to move around. *Denoted by  $V$ ,  $V_p$ . Given by*

$$V \propto \langle R^2 \rangle^{3/2} \propto n^{3/2} l^3$$

- From this, we can see that

$$\frac{v}{V} \propto n^{-1/2}$$

- It follows that the pervaded volume is mostly empty as  $n$  becomes large.
- **Critical concentration:** The concentration at which all polymers in solution can “see” each other. *Also known as coil overlap concentration. Denoted by  $c^*$ .*

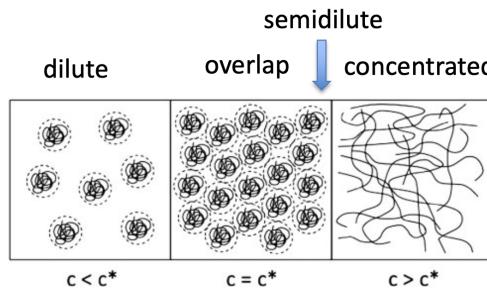


Figure 1.10: Concentration regimes.

- In dilute solutions, polymers will all be coiled up within their own pervaded volume and will not interact.
- When they reach the critical concentration, all of the pervaded volumes are essentially touching each other.
- Past the critical concentration, we get entanglement and no longer see individual polymer coils in their own pervaded volume.

- This is the same  $c^*$  as in Figure 1.1!
- Unifying implication: These concentrations are related to pervaded volume, which is related to expected size.
- Next time.
  - Adding in excluded volume, which will wrap up our discussion on chains.
  - Then Alfredo on thermodynamics of interactions.

### 1.3 Conformation: Real Chains

9/16:

- Announcements.
  - PSet 1 due Thursday. We can do 1-2 right now; 3-4 will be possible after today.
  - Reach out if we have questions!
- Lecture outline.
  - Ideal chains.
    - Gaussian chains.
    - Entropic elasticity.
  - Real chains.
    - Excluded volume.
    - Solvent quality.
    - Expansion factor  $\alpha$ .
- Review from last lecture.
  - Our workhorse model for polymer chain length is Kuhn's equivalent chain, which is in turn based on the FJC random walk.
  - This is a coarse-grained model because atoms don't matter, and we're neglecting to consider excluded volume and energy.
- Aside: Another measure of polymer size worth being aware of is the Radius of Gyration.
  - The radius of gyration  $R_g$  is defined as the 2nd moment of the monomers relative to their center of mass  $\mathbf{R}_{\text{cm}}$ .

$$R_g^2 = \frac{1}{N} \sum_{i=1}^N (\mathbf{R}_i - \mathbf{R}_{\text{cm}})^2$$

- Since the center of mass is defined as

$$\mathbf{R}_{\text{cm}} = \frac{1}{N} \sum_{j=1}^N \mathbf{R}_j$$

we can do some algebra to learn that

$$\langle R_g^2 \rangle = \frac{1}{6} \langle R^2 \rangle$$

- Covered in the lecture reading.
- Question: How many monomers before Kuhn steps have statistical meaning?
  - About 100 before you converge to a Gaussian distribution.

- We'll derive the “easy force response of a freely jointed chain.”
- Before we relate Kuhn's equivalent chain (a 3D model) to polymer size, let's look at the 1D analog: The full probability distribution of a 1D random walk.

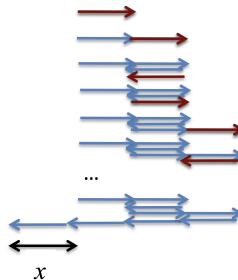


Figure 1.11: Progression of a 1D random walk over time.

- In 1D, you can either go in the positive or negative direction by a distance  $b$ .
- Imagine you keep doing this for  $n$  steps, after which we'll say you've gone a distance  $x$  from your starting point.
- If  $n_1$  is the number of steps right and  $n_2$  is the number of steps left, then

$$x = b(n_1 - n_2)$$

- Let's now analyze this problem statistically.
- From the perspective of statistics, the 1D random walk is equivalent to the coin flipping problem. Specifically, the total number  $\Omega$  of ways (microstates) in which you can move a distance  $x$  is

$$\Omega = \frac{n!}{n_1!n_2!} = \binom{n}{n_1} = \binom{n}{n_2}$$

- $\Omega$  is then a binomial, and as such is maximized when  $n_1$  is close to  $n_2$ . But when  $n_1 \approx n_2$ ,  $x = b(n_1 - n_2)$  is small.
- The overall implication is that you are most likely to end up back where you started!
- Aside: Why is  $\Omega$  a binomial?
  - Binomials mathematically originate from “ $n$  choose  $k$ ” counting of unordered *combinations*. For example, if you have 4 objects A, B, C, and D, there are  $\binom{4}{2} = \frac{4!}{(4-2)!2!} = 6$  ways you can choose two of them: AB, AC, AD, BC, BD, and CD. Note that choosing AB is the same as choosing BA, i.e., order does not matter. This situation is related to a binomial because the “first” time we choose an object out of ABCD, we have 4 options. Suppose we choose B. Then when we go back to choose a second object, we have 3 remaining choices: ACD. Thus, there are  $4 \cdot 3 = 12 = \frac{4!}{(4-2)!}$  paths to two objects (aka *permutations*). But choosing A then B is the same as choosing B then A when it comes to combinations, so we have overcounted by exactly the number of ways there are to arrange 2 objects, which is  $2!$ . Thus, we must divide by  $2!$  again to get  $\frac{4!}{(4-2)!2!} = 6$ .

- This established, where in the context of the 1D random walk are we “choosing” objects, and what objects are we choosing?
- Suppose we are taking  $n = 4$  steps, and we want to identify the total number  $\Omega$  of ways we can move a distance  $x = 0$ . By solving the system of equations  $4 = n_1 + n_2$  and  $0 = b(n_1 - n_2)$ , we can learn that  $n_1 = n_2 = 2$ . This means that we must take  $n_1 = 2$  steps to the right, and  $n_2 = 2$  steps to the left in order to end up back at zero. But when do we take these steps? Diagramming this out, there are four timeslots at which we can take a step (\_\_\_\_\_), and two of those must eventually be filled by steps to the right R. The

first time we *choose* a timeslot, we have 4 options: R\_\_\_\_, \_R\_\_\_, \_\_R\_, and \_\_\_R. Then the second time we choose, we have three remaining options; moreover, if we fill (for example) the first and then the second timeslot, that's equivalent to filling the second and then the first! This is how we relate the 1D random walk to “ $n$  choose  $k$ ” probability.

- Now that we know the number of ways we can move a distance  $x$ , we can calculate the probability  $P(x)$  of moving a distance  $x$  by dividing by the total number of possible paths (which is just  $\Omega_{\text{tot}} = 2^n$ ).

$$P(x) = \frac{\Omega}{\Omega_{\text{tot}}} = \frac{n!}{n_1! n_2! 2^n}$$

- Moreover, because  $\Omega$  is a *binomial*,  $P(x)$  is a *binomial distribution*.
- **Stirling’s approximation** allows us to expand the factorials for large  $n$ , and subsequently prove that the above binomial distribution converges to the following Gaussian distribution.

$$P(x, n) = \left( \frac{1}{2\pi nb^2} \right)^{1/2} \exp\left( \frac{-x^2}{2nb^2} \right)$$

- This allows us to then get back to the following familiar expression.

$$\langle x^2 \rangle = nb^2$$

- From this 1D model, we can generalize to the Gaussian distribution of an end-to-end vector in 3D.

$$P(\mathbf{R}, N) = \left( \frac{3}{2\pi Nb^2} \right)^{3/2} \exp\left( -\frac{3R^2}{2Nb^2} \right)$$

- Note the units of reciprocal volume, as we’d expect for a spatial probability.
- Using spherical coordinates gets us to a familiar expression again, as follows.

$$\langle R^2 \rangle = \int_0^\infty R^2 P(\mathbf{R}, N) 4\pi R^2 dR = Nb^2$$

- Note that  $R^2$  appears twice. The first time, it is because  $R^2$  is what we’re taking the expected value of over all space. The second time, it is because an easy way to take the integral of a radial probability distribution is in spherical coordinates.
- $P(\mathbf{R}, N)$  is radial because the random walk does not have a particular direction in mind in 3D space; you are equally likely to end up  $x$  units from the origin in the  $+x$  direction, as you are in the  $-x$  direction,  $-z$  direction, or any other direction you can imagine.

- This concludes our discussion of Gaussian chains.
- We’ll now discuss entropic elasticity.

- Recall from thermodynamics that

$$F = U - TS$$

- $F$  is free energy;
- $U$  is internal potential energy;
- $T$  is temperature;
- $S$  is entropy.
- For an FJC,  $U = 0$  (by definition) and  $S$  is the only thing we have to consider.
- Recall from Boltzmann that

$$S = k_B \ln[\Omega(\mathbf{R}, N)]$$

- The generalization of our above definition of probability is the following.

$$P(\mathbf{R}, N) = \frac{\Omega(\mathbf{R}, N)}{\int_{\mathbb{R}^3} \Omega(\mathbf{R}, N) d\mathbf{R}}$$

- We'll denote the denominator by  $\Omega_N$  going forward, representing the fact that it is a function of  $N$  and not  $\mathbf{R}$ .
- Then substituting and bashing out the math, we get

$$\begin{aligned} S(\mathbf{R}, N) &= k_B \ln[P(\mathbf{R}, N)] + k_B \ln(\Omega_N) \\ &= -\frac{3k_B R^2}{2Nb^2} + k_B \ln\left(\frac{3}{2\pi Nb^2}\right)^{3/2} + k_B \ln(\Omega_N) \\ &= -\frac{3k_B R^2}{2Nb^2} + S_N \end{aligned}$$

- We will call the second two terms  $S_N$  because they're less interesting, and they only depend on  $N$  (not  $\mathbf{R}$ ).
- By substituting the above back into  $F = U - TS$ , it follows that our entropic free energy for the FJC is

$$F = \frac{3k_B T R^2}{2Nb^2} + S_N$$

- In this context, we can think of  $S_N$  as an additive normalization constant.
- With this result, we can determine how to minimize  $F$  relative to  $R$ .
- Minimizing  $F$  relative to  $R$  is a goal because the radius at which the free energy is minimal will be the radius of polymer coils in solution (everything wants to minimize energy).
- Using this (FJC) model, we can calculate an entropic spring force  $\mathbf{F}(\mathbf{R}, N)$ .

- We know that

$$\mathbf{F}(\mathbf{R}, N) = \frac{\partial F}{\partial \mathbf{R}} = \frac{\partial F}{\partial R} \hat{\mathbf{R}} + \frac{\partial F}{\partial \theta} \hat{\theta} + \frac{\partial F}{\partial \phi} \hat{\phi} = \frac{3k_B T}{Nb^2} \hat{\mathbf{R}}$$

- It follows that at a molecular level, a polymer constitutes a linear Hookean spring ( $F = kx$ ), where the whole prefactor to  $\hat{\mathbf{R}}$  is our spring constant  $k$ .
- Rearranging, we can express the above equation with a relative extension.

$$\mathbf{F}(\mathbf{R}, N) = \frac{3k_B T}{b} \left( \frac{\hat{\mathbf{R}}}{Nb} \right)$$

- $Nb$  is the length of the fully extended freely jointed chain, and  $\hat{\mathbf{R}}$  is a partial extension. Thus, their the fraction is a **relative extension**.
- It has been experimentally shown that up to about 30% extension, these force laws hold!<sup>[1]</sup>
- We'll now begin discussing **real chains**.
  - Up to now, we've been discussing **ideal chains**, which occur at Theta conditions and in melts.
  - Real chains.
    - Local chemistry is coarse-grained out by Kuhn lengths.
    - Non-local elements are related by excluded volume. Essentially, monomers may have some interaction (favorable or unfavorable) when they float near each other in solution.
  - In ideal chains...
    - There are only local effects;
    - Ideal is synonymous with either theta conditions or melts.
  - To ground our mathematical/physical analysis, we will approximate monomers in a polymer as an ideal “gas” of monomers in a volume  $R$  (Figure 1.13a).

<sup>1</sup>Thus, Kuhn steps are like a higher level of theory to rationalize an experimentally observed result!

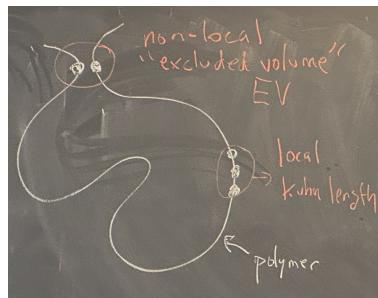


Figure 1.12: Local and non-local interactions in a polymer.

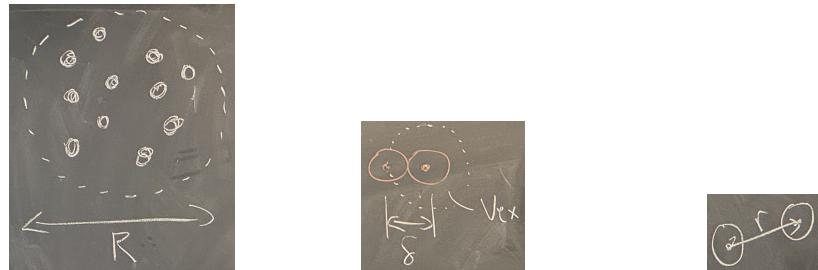
(a) Gas in a volume  $R$ . (b) Excluded volume. (c) Distance between monomers.

Figure 1.13: Monomer gas model of a polymer's excluded volume.

– For nonlocal interactions, we will consider “hard sphere” monomers.

- In particular, for two hard-sphere monomers with center-to-center distance  $\delta$ , Figure 1.13b tells us that excluded volume  $V_{\text{ex}} = v$  is

$$V_{\text{ex}} = \frac{4}{3}\pi\delta^3$$

– Let’s generalize: The Boltzmann weighting for the probability of finding two monomers at a distance  $r$  from each other is

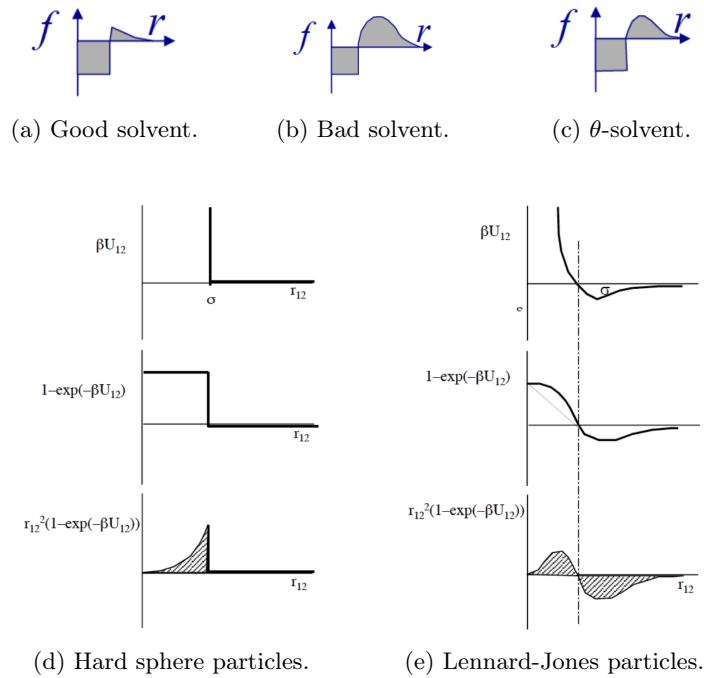
$$f(r) = \exp\left(-\frac{U(r)}{k_B T}\right) - 1$$

- $f(r)$  is called the **Mayer- $f$  function**.
- It is equal to zero when there is no interaction (i.e.,  $U = 0$ ) because when  $U = 0$ , all  $r$  are equally probable.

– It follows through some math — see Rubinstein and Colby (2003) — that the excluded volume is equal to

$$V_{\text{ex}} = -4\pi \int_0^\infty r^2 f(r) dr$$

- Notice that we’re in polar coordinates.
- What is going on here?? Why is excluded volume related to the probability of finding monomers near each other?
- Note that  $U(r)$  (which is the monomer interaction) also incorporates the solvent since the energy is not that of two bare monomers, but those monomers with a medium between them (e.g., two styrene monomers in a sea of toluene).
- The excluded volume is a way of quantifying interactions.
- The Mayer- $f$  function can be visualized through plots and integrals.
  - Depending on  $U$ , we have three possibilities.

Figure 1.14: Visualizing the Mayer- $f$  function.

- In a good solvent, the coils unwind and the volume expands. Repulsion dominates (Figure 1.14a).
- In a bad solvent, the coils bunch up. Attraction dominates (Figure 1.14b).
- In a  $\theta$ -solvent, repulsion balances attraction (Figure 1.14c).
  - We can also plot out precursors to and variants of the Mayer- $f$  function for specific potentials of interest.
    - Thus, we can see that in the hard-sphere potential (Figure 1.14d), there is only a repulsive contribution and thus no  $\theta$ -temperature or  $\theta$ -solvent.
    - In contrast, for the Lennard-Jones potential (Figure 1.14e), there are both repulsive and attractive contributions. Thus, there *will* be a  $\theta$ -temperature in each  $\theta$ -solvent.
  - In a theta solvent,  $V_{\text{ex}}(T) = 0$ .
    - The temperature  $T$  at which  $V_{\text{ex}} = 0$  is called the **Boyle temperature**; it is the temperature at which excluded volume is zero. Basically, you always have excluded volume, but if that excluded volume is balanced by a bit of attraction, you can have something that looks ideal.
    - PSet 1, Q5 explores the relation between  $V_{\text{ex}}$  and  $T$  more explicitly!
  - The heart of polymer physics is Flory mean-field approximations.

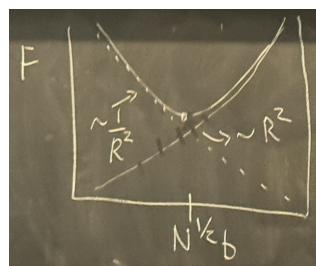


Figure 1.15: A post-facto compression penalty.

- In a  $\theta$ -solvent,  $F = -TS$  (because  $U = 0$ ).
- As we derived above, for this situation, the entropic free energy  $F_{\text{ent}}$  is

$$F_{\text{ent}} = \frac{3k_{\text{B}}T}{2} \frac{R^2}{Nb^2}$$

and

$$\frac{\partial F}{\partial R} = \frac{3k_{\text{B}}TR}{Nb^2}$$

- At equilibrium,  $\partial F/\partial R = 0$ . It follows that

$$\begin{aligned} \frac{3k_{\text{B}}TR}{Nb^2} &= 0 \\ R &= 0 \end{aligned}$$

- But this is inconsistent with the finding that  $\langle R^2 \rangle = Nb^2$ .
- We will address this with a post facto compression penalty. Indeed, if we set

$$F_{\text{ent}} = \frac{3k_{\text{B}}T}{2} \left( \frac{R^2}{Nb^2} + \frac{Nb^2}{R^2} \right)$$

then  $\partial F/\partial R = 0$  implies

$$\begin{aligned} R &= N^{1/2}b \\ R^2 &= Nb^2 \end{aligned}$$

- The nice thing about this compression penalty is that the graph of  $1/R^2 + R^2$  forms a nice energy well, dictated by the rates at which one or the other increases. See Figure 1.15.

- Now analogously to a **Virial expansion** (from thermodynamics), we are going to do another expansion.

$$\frac{F_{\text{int}}}{V k_{\text{B}} T} = \frac{1}{2!} v c^2 + \frac{1}{3!} w c^3 + \dots$$

- This takes the perspective that we disregard monomer connectivity, and evaluate the enthalpic interaction energy  $F_{\text{int}}$  as if it was a gas of monomers in a spherical container of radius  $R$ .
- $c = N/R^3$  is the concentration of the monomers, and  $V \propto R^3$ .
- We are throwing out prefactors like  $4/3$  and  $\pi$ .
- This gives us a term for binary interactions, ternary interactions, etc.

- In a good solvent,  $R > Nb^2$  because the polymer swells due to  $V_{\text{ex}}$ .

- Free energy is then

$$F = \frac{3k_{\text{B}}TR^2}{2Nb^2} + \frac{1}{2} V_{\text{ex}} \frac{N^2}{R^3} k_{\text{B}} T$$

- Then  $\partial F/\partial R = 0$  implies

$$\begin{aligned} 0 &= \frac{k_{\text{B}}TR}{Nb^2} - \frac{3V_{\text{ex}}N^2k_{\text{B}}T}{2R^4} \\ R^5 &= \frac{1}{2} N^3 b^2 V_{\text{ex}} \\ R &\approx b^{2/5} V_{\text{ex}}^{1/5} N^{3/5} \end{aligned}$$

- Taking everything into account with renormalized group theory yields something pretty close!
- This stands in contrast to the ideal  $R \approx N^{1/2}b$ .

- In a bad solvent, enthalpic interactions matter more than entropic interactions because the polymer is compressed into a globule regardless.

– Thus, we have to balance the first two terms in  $F_{\text{int}}$  to determine the scaling.

$$\begin{aligned} 0 &= \frac{\partial F_{\text{int}}}{\partial R} \\ &= \frac{\partial}{\partial R} \left\{ k_{\text{B}} T R^3 \left[ \frac{1}{2} v \left( \frac{N}{R^3} \right)^2 + \frac{1}{6} w \left( \frac{N}{R^3} \right)^3 \right] \right\} \\ &= k_{\text{B}} T \frac{\partial}{\partial R} \left( \frac{v N^2}{2 R^3} + \frac{w N^3}{6 R^6} \right) \\ 0 &= -\frac{3vN^2}{2R^4} - \frac{wN^3}{R^7} \\ R^3 &= -\frac{2wN}{3v} \\ R &\propto \left( \frac{w}{-v} \right)^{1/3} N^{1/3} \end{aligned}$$

- Combining the enthalpic and entropic terms, the full Flory free energy has many terms that all balance; you play with the ingredients to see what fits.

$$\frac{F}{k_{\text{B}} T} = \frac{V_{\text{ex}} N^2}{2 R^3} + \frac{w N^3}{6 R^6} + \frac{3 R^2}{2 N b^2} + \frac{3 N b^2}{2 R^2}$$

- The chain or polymer must be long enough for excluded volume to factor in.
  - In  $F_{\text{ev}} \geq k_{\text{B}} T$ , we have a good solvent.
  - We then do some more math and get

$$z = \frac{V_{\text{ex}} N^{1/2}}{b^3} < 1$$

- There is additional material in the slides.
  - Importantly, as you go away from  $\theta$ -conditions, you still have an  $N^{1/2}$  relation.
  - $1 - \theta/T$  is related to the homework; it's a perturbation of a Taylor series.
- The **expansion factor**  $\alpha$  is just the ratio of the real volume to the ideal.

## 1.4 Chapter 1: Introduction to Chain Molecules

*From Lodge and Hiemenz (2020).*

9/14:

- Begins with the uses and history of polymers.
- **Macromolecule:** A large or long molecule.
- **Polymer:** A macromolecule made by repeating one (or a few) chemical units many times.
  - All polymers are macromolecules, but not all macromolecules are polymers.
- Lodge and Hiemenz (2020) will often write molecular weights without the unit “g/mol,” but we should write them with this unit.
- Some types of polymerization involve only the joining of monomers; others involve this joining, but with the elimination of a small molecule byproduct (like H<sub>2</sub>O or HCl).

- Figure 1.6's derivation uses the **law of cosines** from high school trigonometry.
- Polyolefin size: Based on typical C–C bond angles and lengths...
  - The straight-chain length is approximately  $N \cdot 0.25 \text{ nm}$ ;
  - The actual end-to-end distance is approximately  $N^{1/2} \cdot 0.25 \text{ nm}$ .
- **Oligomer:** A molecule made of repeat units but for which  $N < 10$ .
- Note that *polymers* typically have  $M \geq 1000 \text{ g/mol}$ , but this cutoff is arbitrary (and probably on the low side).
- Polymer architectures.
- **Branched** (polymer): A linear molecule with additional polymeric chains issuing from its (linear) backbone.
- **Short-chain branch:** A small substituent (such as a methyl or phenyl group) on the repeat unit.
  - These are generally not considered branches.
- Branching can occur *by design, adventitiously, or through grafting*.
  - By design, we may introduce polyfunctional junctions into the formulation.
  - Adventitiously, “an atom [may be] abstracted from the original linear molecule, with chain growth occurring from the resulting active site” (Lodge & Hiemenz, 2020, p. 7).
    - This commonly happens with polyethylene!
- **Graft to** (polymerization): Pre-formed but still reactive polymer chains can be added to sites along an existing backbone.
- **Graft from** (polymerization): Multiple initiation sites along a chain can be exposed to monomer.
- Note: **Graft through** polymerization is not covered.
- For simple branching (no loops), a molecule with  $v$  branches has  $v + 2$  chain ends.
- **Comb** (polymer): A polymer in which a series of relatively uniform branches emanate from along the length of a common backbone.
- **Star** (polymer): A polymer in which all branches radiate from a central junction.
- **Cross-linked** (polymer): A polymer with such extensive branching that the macroscopic object may be considered to consist of essentially one molecule.
  - These polymers are given cohesiveness by covalent bonds instead of intermolecular forces, and thus have very different properties from non-cross-linked polymers.
- **Hyperbranched** (polymer): A polymer that is highly branched, but in which the components remain as discrete entities.
- **Dendrimer:** A class of hyperbranched polymers that are tree-like, in that they have completely regular structures formed by successive condensation of branched monomers.
  - Start with a  $B_3$  junction (generation 0), condense on three  $AB'_2$  monomers and deprotect (generation 1), condense on six  $AB'_2$  monomers and deprotect (generation 2), etc.
  - At generation 6 or 7, the surface of the molecule becomes so congested that adding further complete generations is impossible.
- **Cycle** (polymer): A polymer in which the two chain ends react to close the loop. *Also known as ring.*

- **Homopolymer:** A polymer with only a single kind of repeat unit.
  - Note that polymers made with two different monomers can still be homopolymers. For example, a polyester condensed from diacid and diol *monomers* still only has one kind of *repeat unit*.
- **Copolymer:** A polymer with two kinds of repeat units.
- **Terpolymer:** A polymer with three kinds of repeat units.
- **Multicomponent** (polymer): A polymer with four or more kinds of repeat units.
- **Random** (copolymer): A copolymer in which the A-B sequence is governed strictly by chance, subject only to the relative abundances of repeat units.
- **Statistical** (copolymer): A copolymer in which monomer addition at a growing chain end may depend on the preceding monomer(s), according to a statistical law.<sup>[2]</sup>
- **Alternating** (copolymer): A copolymer containing a regular pattern of alternating repeat units.
- **Block** (copolymer): A copolymer containing long, uninterrupted sequences of each monomer.
- ***n*-block** (copolymer): A block copolymer containing *n* uninterrupted sequences of each monomer.
  - For small *n*, the terms **diblock**, **triblock**, and **tetrablock** are commonly used.
  - If a triblock copolymer consists of a sequence of monomer A, followed by monomer B, followed by monomer A, we may call it an **ABA triblock copolymer**.

9/16:

- In addition to classifying polymers by architecture, we can classify them by the reactions used to make them.
- **Addition and condensation** polymerization are the most common, but there are more.
- **Addition** (polymerization): A polymerization for which the following three statements apply. *Also known as chain-growth. Defined by*
  1. The repeat unit in the polymer and monomer have the same composition (although bonding is different in each).
  2. The polymerization proceeds through a **chain reaction** mechanism, with either free radicals or ionic groups responsible for propagating the chain reaction.
  3. The product molecules *often* have an all C–C backbone, with pendant substituent groups.
- **Condensation** (polymerization): A polymerization for which the following three statements apply. *Also known as step-growth. Defined by*
  1. The polymer repeat unit arises from the reaction of two different functional groups, which *usually* originate on different monomers. In this case, the repeat unit is different from either monomer. In addition, small molecules are *often* eliminated during the condensation reaction.
  2. Mechanistically, the reactions occur in steps; in other words, the formation of the linkage functional group between two small molecules is not essentially different from that between one of these growing polymers and a monomer.
  3. The product molecules have the functional groups formed by the condensation reactins interspersed regularly along the backbone of the polymer molecule.
- Properties of condensation polymerizations.
  - Either two difunctional monomers with different functional groups, or one difunctional monomer with a functional group of each kind.

<sup>2</sup>The copolymers we make with CCs are all statistical, since addition is governed by probability-based reactivity ratios.

- Beware the creation of loops!
  - Very sensitive to impurities.
    - Example: Trace methanol in a polyester condensation could cap some carbonyl derivatives as methyl esters, preventing them from reacting further.
    - Functionality greater than 2 can introduce branching.
    - Introduction of reagents with varying functionalities in carefully controlled amounts affords control over polymer size and geometry.
  - The physics in this text apply equally well to organic and inorganic (e.g., PDMS) polymers.
  - Biopolymers are briefly introduced.
  - Polymer nomenclature.
  - IUPAC recommendation.
    - Polymers formed from a single monomer.
      - Take the IUPAC name of the monomer, enclose it in parentheses, and add the prefix “poly”.
      - Example: poly(1-chloroethylene) for PVC.
      - Polymers need not be synthesized from the monomer named. For example, poly(1-hydroxyethylene) is synthesized from the hydrolysis of poly(1-acetoxyethylene).
    - Polymers formed from multiple monomers.
      - Apply the preceding rules to the repeat unit.
      - Example: poly(hexamethylene adipamide) is nylon-6,6.
    - Commercially important cross-linked polymers.
      - Typically go without names, or at best, by specifying the monomers that go into it.
      - Example: “Phenol-formaldehyde resin” for bakelite.
  - Notes on common names.
    - Many polymers have a common/outdated chemical name, a trade name, and/or an acronym.
    - Examples: polyethylene glycol, Teflon, PVC.
  - On positional isomerism.
    - Head-to-head addition is more common (1) at higher temperatures and (2) with halogenated monomers.
    - Head-to-tail is dominant because of (1) resonance stabilization at the head position and (2) steric exposure of the tail.
    - Polymer cleavage can provide information about head-head vs. head-tail polymerization: Since diols are cleavable by periodate, poly(vinyl alcohol) can have its weight measured, be subject to cleavage conditions, and have the resultant fragments' weight remeasured to calculate the average frequency of diols.
  - Stereoisomerism reviewed.
  - On geometric isomerism.
    - Not only can you have *cis*- or *trans*-backbones, but isoprene (for example) can polymerize through either — or both! — of its double bonds.

- **Mass concentration** (of an  $i$ -mer): The number of grams per mole of  $i$ -mer per unit volume. *Denoted by  $c_i$ . Given by*

$$c_i := \frac{n_i M_i}{V}$$

- $M_n$  and  $M_w$  are by far the most important and most common measurements of polymer average weight, but there are also others such as the  **$z$ -average molecular weight**.

- **$z$ -average molecular weight**: The third moment of the weight distribution. *Denoted by  $M_z$ . Given by*

$$M_z := M_0 \frac{\sum_i i^3 n_i}{\sum_i i^2 n_i}$$

- **Monodisperse** (sample): A polymer sample for which  $D = 1$ .
- **Narrow** (distribution): A polymer weight distribution for which  $D < 1.5$ .
- **Broad** (distribution): A polymer weight distribution for which  $D > 2$ .
- Lodge and Hiemenz (2020) derive the variance expression given in class.
- **Mean** (of a distribution  $i$ ): The numerical average of the distribution. *Denoted by  $\langle i \rangle$ . Given by*

$$\langle i \rangle := \frac{\sum_i i n_i}{\sum_i n_i} = \sum_i i x_i \quad \langle i \rangle := \int_0^\infty i P(i) di$$

- **Normalized** (distribution): A discrete distribution  $x_i$  or continuous distribution  $P(i)$  satisfying the following respective criterion. *Constraints*

$$\sum_i x_i = 1 \quad \int_0^\infty P(i) di = 1$$

- **$k$ -th moment** (of a normalized distribution): The number defined as follows. *Denoted by  $\mu_k$ . Given by*

$$\mu_k := \sum_i x_i i^k \quad \mu_k := \int_0^\infty i^k P(i) di$$

- The mean is therefore the first moment of a distribution!
- $M_w$  and  $M_z$  are proportional to the ratios of the 2nd to the 1st moment and the 3rd to the 2nd moment, respectively.
- **$k$ -th moment about the mean** (of a normalized distribution): The number defined as follows. *Denoted by  $v_k$ . Given by*

$$v_k := \sum_i x_i (i - \langle i \rangle)^k$$

- It follows that the variance is the second moment about the mean.
- **Schulz-Zimm distribution**: A one-parameter mathematical model for polymer weight distributions, where varying the one parameter affords reasonable descriptions for typical narrow or moderately broad samples. *Given by*

$$P(M_i) := \frac{z^{z+1}}{\Gamma(z+1)} \frac{M_i^{z-1}}{M_n^z} e^{-zM_i/M_n}$$

- $\Gamma$  denotes the **gamma function**, a popular extension of the factorial function.
- Lodge and Hiemenz (2020) extend their discussion of this distribution quite a bit and graph some examples of it. One such graph is included in the lecture 2 slides.

- Measurement of molecular weight.
- **Size exclusion chromatography:** A method of measuring polymer molecular weight that can provide information about the full distribution of weights. *Also known as SEC.*
  - Benefits.
    - The dominant method today; almost all polymer chemistry laboratories have SEC capabilities.
    - Automated analysis of a few milligrams of sample in a good solvent can be achieved in half an hour.
  - Limitations.
    - Poor resolution.
    - Reliance on standards.
- **Matrix-assisted laser desorption/ionization mass spectrometry:** A method of measuring polymer molecular weight that can provide information about the full distribution of weights. *Also known as MALDI.*
  - Benefits.
    - High resolution.
  - Limitations.
    - Relatively new and still being expanded in scope.
    - Resolution is diminished as  $M$  increases.
    - Sensitivity is diminished as  $M$  increases: Higher MW polymers are just harder to get into the gas phase.
      - Sensitivity is also a heretofore unknown function of molecular weight, so extracting  $M_n$  and  $M_w$  quantitatively is unreliable.
      - Microscopic differences in drops and their structure add further uncertainty.
    - Works better for more polar polymers (PE is almost impossible).
    - More highly charged species confound data.
  - Section 1.8.3 covers the basics of how MALDI works.
    - “A great deal remains to be learned about both the desorption and ionization processes, and standard practice is to follow particular recipes (matrix and salt) that have been found to be successful for a given polymer” (Lodge & Hiemenz, 2020, p. 35).
- If SEC and MALDI can be done reliably, accurately, and conveniently, then there is little need for any other technique.
- **Colligative** (property): A property of a solution that depends on the *the number* of solute particles alone, with no consideration of their nature.
- Some techniques provide information on *only*  $M_n$  by measuring colligative properties.
  - Osmotic pressure (most common), freezing point depression, boiling point elevation, light scattering, end group analysis, etc.
  - Osmotic pressure is based on equilibrium thermodynamics, and thus affords absolute measurements *without* calibration!
  - End group analysis relies on the fact that if a molecule only has two ends, counting the number of ends is equivalent to counting the number of molecules.
    - Common techniques: Acid-base titration (acidic or basic end groups), NMR (esp.  $^1\text{H}$  qNMR).
- Some techniques provide information on *only*  $M_w$ .

- Light scattering is also based on equilibrium thermodynamics (so absolute and no calibration needed).
- Misc. techniques: Sedimentation, gel electrophoresis, and intrinsic viscosity.
- End group analysis principles.
  1. “The chemical structure of the end group must be sufficiently different from that of the repeat unit for the chosen analytical technique to resolve the two clearly” (Lodge & Hiemenz, 2020, p. 32).
  2. “There must be a well-defined number of end groups per polymer, at least on average. For a linear polymer, there will be two and only two end groups per molecule, which may or may not be distinct from each other. For branched polymers, the relation of the number of end groups to the number of polymers is ambiguous, unless the total number of branching points is also known” (Lodge & Hiemenz, 2020, p. 32).
  3. “The technique is limited to relatively low molecular weights, as the end groups become more and more dilute as  $N$  increases... As a general rule end groups present at the 1% level (corresponding to degrees of polymerization of 100 for a single end group, 200 for both end groups) can be reliably determined; those at the 0.1% level cannot” (Lodge & Hiemenz, 2020, pp. 32–33).

## 1.5 Chapter 6: Polymer Conformations

*From Lodge and Hiemenz (2020).*

- **Globule:** A compressed conformation of a polymer similar to a dense ball.
- **Random coil:** A conformation of a polyemter where the monomer subunits are oriented randomly while still being bonded to adjacent units.
- The approximately  $0.7k_B T$  ( $3k_B T$  from class appears to be wrong) energy difference between the trans and either gauche state implies that the gauche states will be about  $e^{-0.7} \approx 0.5$  times as populated as the trans states.
- **Ergodic** (system): A system for which the time average of its states is equivalent to the ensemble average.
  - For example, polymer conformations are ergodic because the end-to-end distance of a polymer averaged over time as it wiggles around is the same as its end-to-end distance averaged over a large collection of structurally identical chains at a given instant in time.
- **Isotropic** (quantity): A quantity that is not biased in any particular direction.
  - For example, the polymer end-to-end vector should not orient in any particular direction in the absence of external bias. This is why  $\langle \mathbf{R} \rangle = 0$ , as discussed in class.
- A more rigorous basis for why the cross terms in the FJC expansion of  $\langle R^2 \rangle$  equal zero.
  - For any two vectors  $\mathbf{l}_i, \mathbf{l}_j$ , we have
 
$$\langle \mathbf{l}_i \cdot \mathbf{l}_j \rangle = l^2 \langle \cos \theta \rangle$$
 where  $\theta$  is the angle between them when translated through space to be tail-to-tail.
  - Since we are assuming lack of correlation,  $\theta$  is equally likely to be anywhere along its principle branch of  $[0, \pi]$ . Thus,
 
$$\langle \cos \theta \rangle = \int_0^\pi \cos \theta \cdot \frac{d\theta}{\pi - 0} = 0$$
  - This zeroes out the cross term.
- Lodge and Hiemenz (2020, pp. 239–40) explicitly derive the full FRC result for  $\langle R^2 \rangle$ .

- It is an exact, analytical derivation; the only assumptions are that  $n \rightarrow \infty$  (generally justified within measurement error for  $n > 100$ ) and  $\theta \neq 0$  (generally justified because most bonds are not straight from one to the next).
- Lessons from the FRC.
  - $\langle R^2 \rangle$  grows relative to the FJC approximation. This is reasonable because we have less doubling back.
  - We still have  $\langle R^2 \rangle \propto nl^2$ , despite the increase in complexity of the model.
  - When  $\theta \approx 70.5^\circ$  (as for a C–C bond),  $\langle R^2 \rangle \approx 2nl^2$  under this model.
- Flory (1969) derives  $\langle R^2 \rangle$  for the symmetric hindered rotations model.
- Theorem: Under the assumptions that  $n \rightarrow \infty$  and polymer chains can freely pass through themselves,  $\langle R^2 \rangle = Cnl^2$  where  $C$  is a numerical constant that depends only on local constraints and not on  $n$ .
- The principle of Kuhn's equivalent chain follows from this theorem: Memory of orientation is lost at a far enough distance away from the original link, making it so that “for any chain of  $n$  links whose relative orientations are constrained, we can always generate an equivalent chain with a new (bigger) link that is freely jointed, so that the original chain and the new chain have the same [ $\langle R^2 \rangle$ ]” (Lodge & Hiemenz, 2020, p. 241).
- Common backbone bond lengths.

Bond Type	C–C	C=C	C–O	C–N	Si–O
Bond Length (Å)	1.53	1.34	1.43	1.47	1.6

Table 1.3: Common polymer backbone bond lengths.

- For polymers with multiple backbone bonds, add  $n_1 l_1^2 + n_2 l_2^2 + \dots$  for each type of backbone bond.
- Larger  $C_\infty$  implies stiffer chains.
- Characteristic ratio terminology.
  - $C_n$  describes the characteristic ratio for a type of chain with *exactly*  $n$  bonds.
  - $C_\infty$  is  $C_n$ , but specifically in the large  $n$  limit where  $n \rightarrow \infty$ .
- Common monomer parameters ( $C_\infty$ , Kuhn length, monomer volume, etc.) are compiled in a table on Lodge and Hiemenz (2020, p. 243), sourced from Fetters et al. (1994). This significantly extends Table 1.2.
- Although the Kuhn length varies monotonically with  $C_\infty$ , it is not as good a measure of flexibility.
  - Example: The Kuhn length for polystyrene is just a bit longer than for polyisoprene, but polystyrene is much stiffer (as reflected by a  $C_\infty$  more than double polyisoprene's).
  - See Problem 6.4 for more.
- **Monomer volume:** The volume of a single monomer of interest. Denoted by  $v_0$ .
- A good visual for semiflexible, worm-like chains: A garden hose ( $a$  is approximately 1 foot).
- The persistence length is equal to the end-to-end vector onto the direction of the first bond??  $a = \langle \hat{\mathbf{l}}_1 \cdot \mathbf{R} \rangle$ ? See Lodge and Hiemenz (2020, p. 246).
  - It seems that all subsequent results about the WLC differ significantly from our treatment in class.

- Radius of gyration content and derivations of the in-class equation, as well as relation to the textbook's definition of persistence length.
- The distribution of most probable sizes is Gaussian.
  - Derivation of the binomial is *exactly* as I rationalized!
  - Lodge and Hiemenz (2020, pp. 255–56) also derives the 3D Gaussian from the binomial using only first principles.
  - Problem 6.20 shows that the Gaussian is useful for  $N$  as small as 10.
  - It is important to keep in mind that the Gaussian is a continuous approximation for a discrete function; thus, its values can never be *exactly* accurate, and some (e.g., finite probabilities at lengths greater than the contour length) may be meaningless.
  - The pure Gaussian tells us that the most probable *vector* value  $\mathbf{R}$  is 0, but multiplying by  $4\pi R^2$  reveals that the most probable *scalar* value  $R$  is finite.
    - Analogous to normalization of the  $s$  electrons in the hydrogen atom and molecular speeds in the Maxwell-Boltzmann distribution.
- **Dilute** (solution): A solution for which the concentration  $c$  is much less than the critical concentration  $c^*$ .
- A note on excluded volume.
  - Tends to *expand* the coil, because the polymer feels like it has less space available to it.
  - Two cases where excluded volume disappears: Polymer melt and  $\theta$  solvent.
    - Polymer melt: Two monomers still cannot occupy the same space, but there is no benefit to expanding the coil because the adjacent space is *already* surrounded by monomers.
      - Conjectured by Flory long ago, and confirmed by SANS in the 1970s.
    - $\theta$  solvent: A non-very-good solvent that makes monomers prefer to be near each other than far away.

## 1.6 Chapter 7: Thermodynamics of Polymer Mixtures

*From Lodge and Hiemenz (2020).*

- 10/12:
- Lodge and Hiemenz (2020, pp. 310–14) has some additional information on the derivation of the full Flory free energy and its four constituent terms.

## Topic 2

# Solution Thermodynamics

### 2.1 Flory-Huggins Theory

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

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

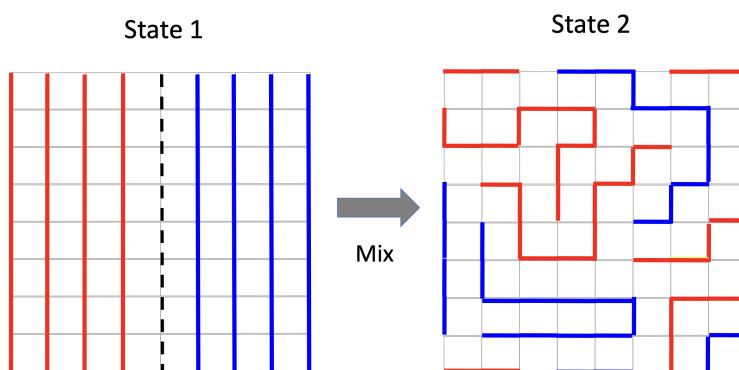


Figure 2.1: Lattice theory for polymer phase behavior.

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

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<sup>1</sup>“HOY-gins”

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

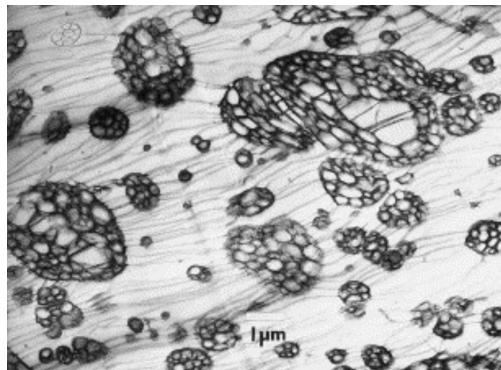


Figure 2.2: Salami phase micrograph in styrene-butadiene mixtures.

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

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

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

– In multicomponent systems — besides the typical parameters of excluded volume, etc. — we need to know...

- How many chains we have of each type;
- What their degree of polymerization is;
- What total volume do they occupy.

– Thus, in State 1, we have

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

which describes two separate phases...

- Containing  $n_i$  moles of species  $i$ ;
- With degree of polymerization  $N_i$ ;
- Each occupying a total volume  $V_i$ ;
- Where the volume of each monomer/solvent molecule is given by  $v_i$ .

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

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

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

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

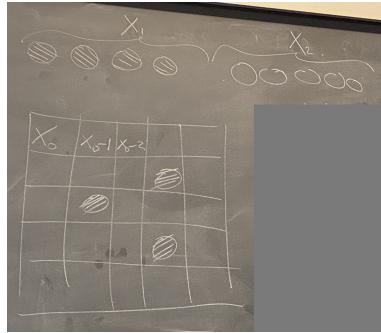


Figure 2.3: Configurations in mean field lattice theory.

■ Thus,

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

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

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

■ Remember that the initial entropy is zero!

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

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

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

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

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

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

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

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

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

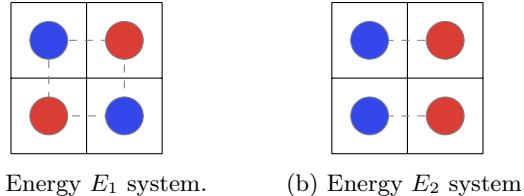


Figure 2.4: Nearest neighbor interactions.

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

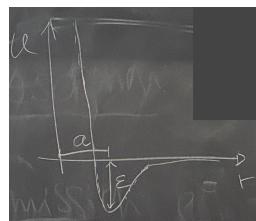


Figure 2.5: Potential well.

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

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

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

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

- In a typical attraction well, we have a most probable distance  $a$ , at which the energy depth is  $\varepsilon$  (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.

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

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

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

and hence

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

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

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

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

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

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

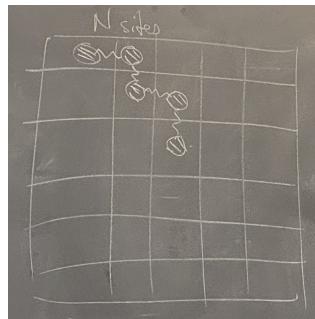
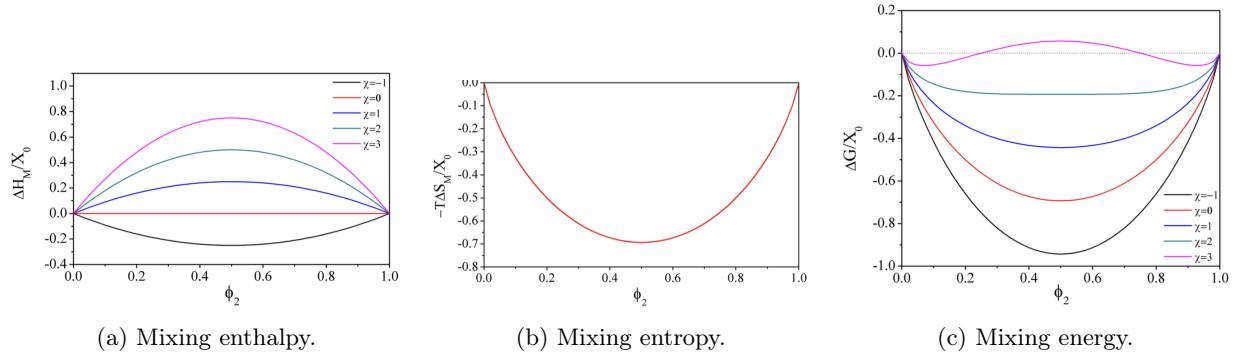


Figure 2.6: Fitting polymers into a square lattice.

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

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

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

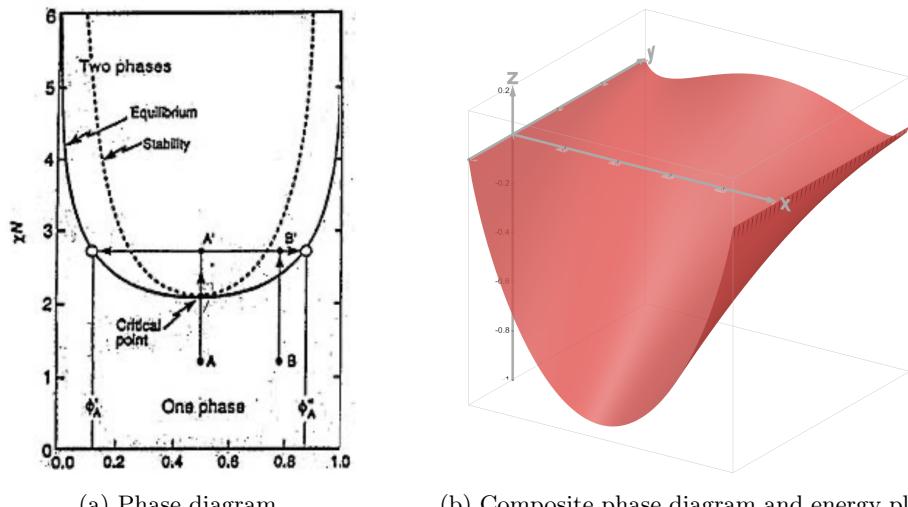


Figure 2.8: Example phase diagram and explanation.

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

## 2.2 The Theta State

9/23:

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

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

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

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

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

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

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

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

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

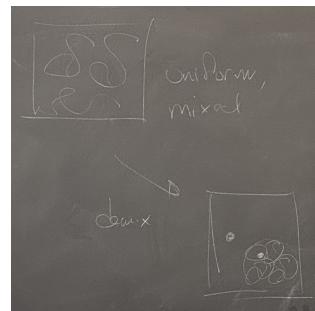


Figure 2.9: Demixing of a polymer-solvent solution.

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

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

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

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

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

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

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

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

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

- We thus expand

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

- It follows that

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

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

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

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

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

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

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

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

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

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

- The excess chemical potential describes...

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

$$\chi \phi_2^2 RT$$

- Excluded volume as follows.

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

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

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

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

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

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

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

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

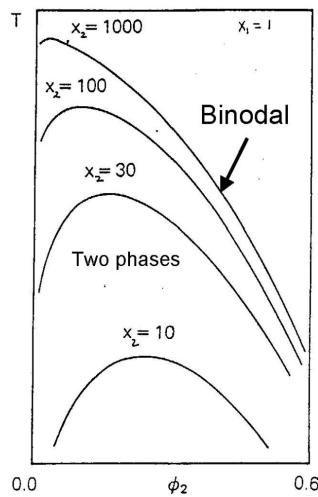
- Recall that a polymer-solvent solution occurs when component 1 is a solvent ( $N_1 = 1$ ), component 2 is a polymer ( $N_2 \gg 1$ ), and the solution is dilute ( $n_1 \gg n_2 N_2$ ).

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

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

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

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

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

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

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

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

$$N_1 = N = N_2$$

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

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

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

- In the specific case of vaporization,

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

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

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

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

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

- Hildebrand's experimental setup and derivation.

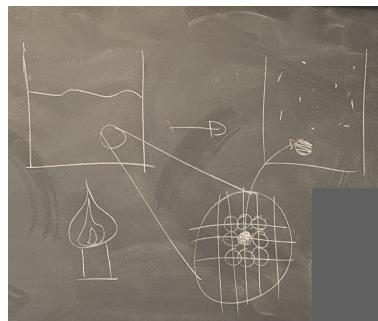


Figure 2.11: Hildebrand's experiment.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

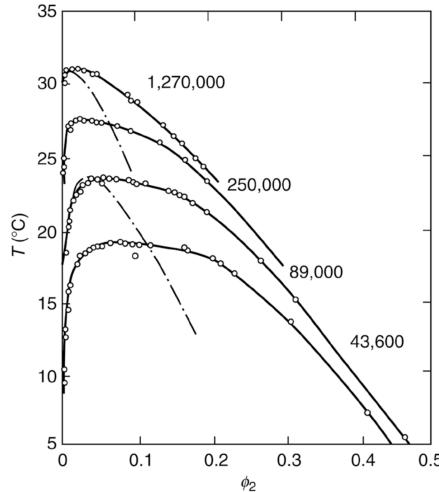


Figure 2.12: Flory-Huggins theory vs. experiment.

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

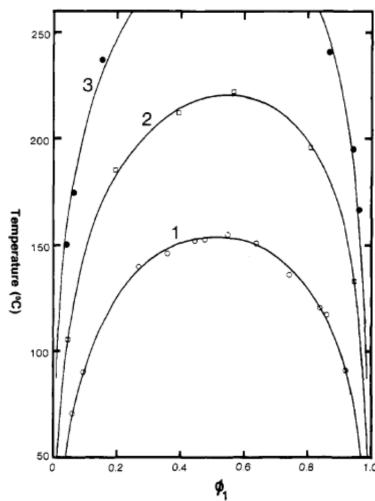


Figure 2.13: Binodal curves for PS-PB blends at almost symmetric compositions.

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

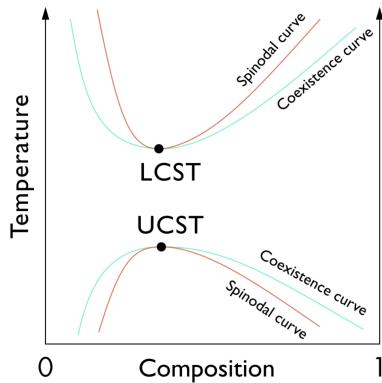


Figure 2.14: The upper and lower critical solution temperatures.

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

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

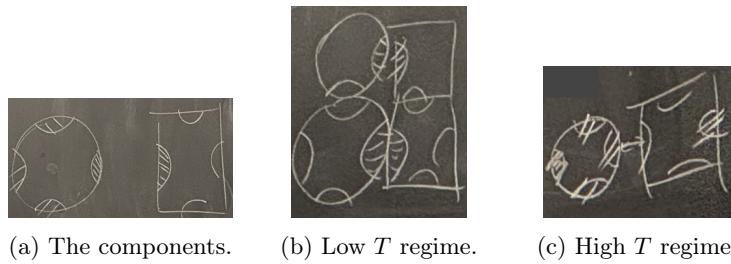


Figure 2.15: Systems with negative Flory  $\chi$  parameters.

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

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

## 2.3 Phase Behavior, Melting Point Depression, Osmometry, and Microparticle 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.
    - Microparticle separation.
    - Interfacial free energy.
    - Chain stretching and configurational free energy.
      - This will bring back concepts from Professor Doyle's class.
- A bit more on biocondensates (not testable material).
  - Correction: The protein discussed last time goes into solution if you *add* salt.
  - Principle in biology: At some point, it gets better to have things that do multiple tasks poorly than one task really well.

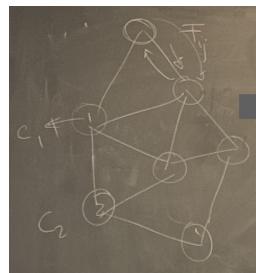


Figure 2.16: Simplified graph of a biochemical network.

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

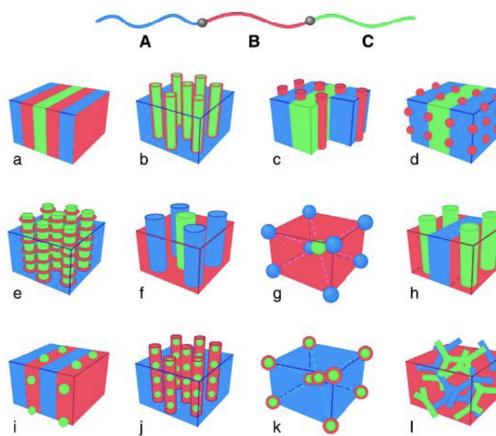


Figure 2.17: Self-assembly of an ABC triblock copolymer.

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

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

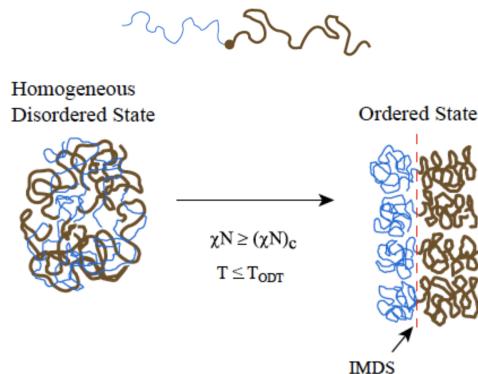


Figure 2.18: Ordering of a diblock copolymer.

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

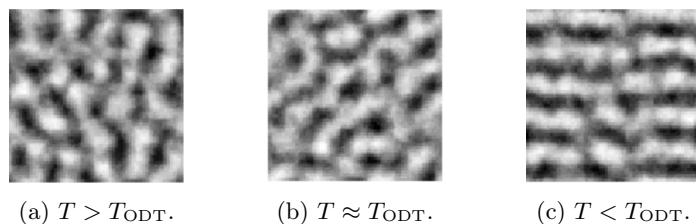


Figure 2.19: Microphase separation in diblock copolymers.

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

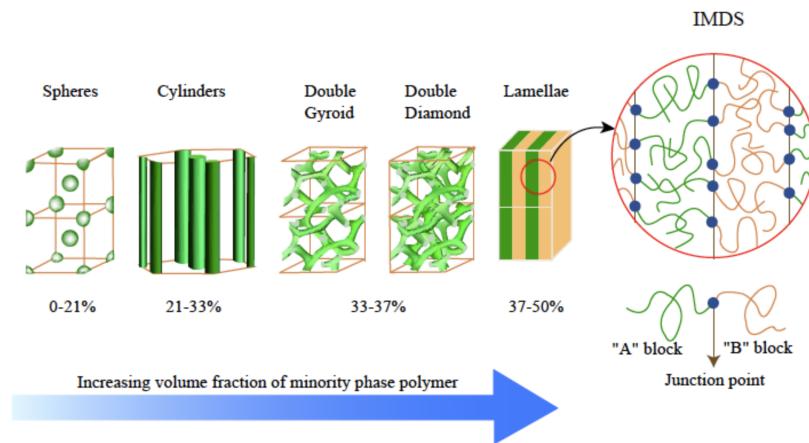


Figure 2.20: Microphase morphologies in diblock copolymers.

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

- The PS ends either land in another domain, or come back to the same domain.
- Good for high-performance applications, like the rubber in an F1 track.
- We now investigate microdomain spacing for diblock copolymers.
- Variables to be aware of.
  - $G$  is the free energy per chain;
  - $N = N_A + N_B$  is the number of segments per chain.
  - $a$  is the step size.
  - $\lambda$  is the domain periodicity. *look up definitions!!*
  - $\Sigma$  is the interfacial area where the chains actually interact.
  - $\gamma_{AB}$  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.
- $\chi_{AB}$  is the same Flory-Huggins interaction parameter we've been looking at in previous lectures.
- Free energies of these diblock copolymers.

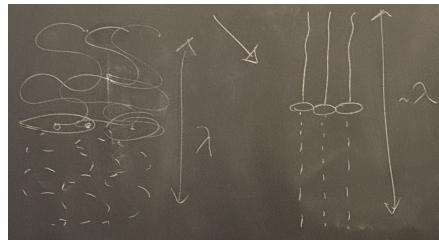


Figure 2.21: Entropy and enthalpy changes as diblock copolymers are stretched.

- We have

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

- 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  $\Sigma$ .
- 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  $\lambda$ .

- To find the optimal  $\lambda$ , we'll want to find the minimum Gibbs free energy as a function of  $\lambda$ .

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

- By above definitions and equalities, the first term is the interfacial energy per unit area times the area of the interface.
- Compressing every non- $\lambda$  variable in the above expression into a constant (termed  $\alpha$ ,  $\beta$ ,  $\text{const}_1$ , or  $\text{const}_2$ ) reveals that the above equation is of the following general form.

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

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

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

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

- Since the first two terms are both much greater than the third term, we neglect it.
- Thus, the sign of  $\Delta G$  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

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

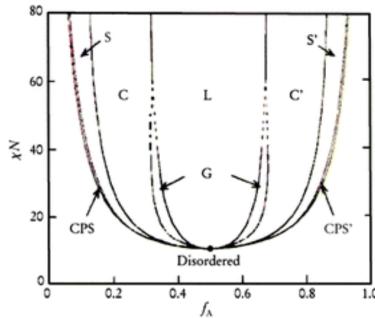


Figure 2.22: Microphase transition diagram.

- Therefore, if  $N\chi < 10.5$ , we'll get a homogeneous, mixed melt; and if  $N\chi > 10.5$ , we'll get demixing into lamellar microdomains.
  - Phase transitions between different microstructures can also be represented on a  $\chi N$  vs. composition phase diagram.
    - 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  $\lambda^2/a^2N$  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.

- 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,

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

- $D^2H$  is a volume.

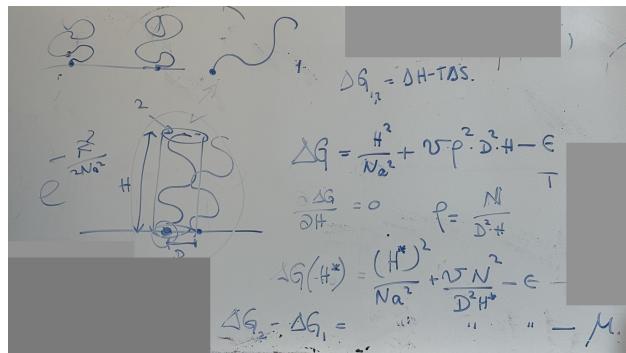


Figure 2.23: PSet 2, Q5 setup.

- $\rho = N/D^2 H$  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  $\Delta G$  equation above.
  - To find  $D$ , we have to evaluate the stability relative to state 1.
    - $\mu_{\text{bulk}}$  or  $\mu_1$  ( $\mu_1$  seems to be the notation Alexander-Katz used most consistently) can be the chemical potential / energy of state 1. We will have to define this variable.
    - We consider this because we need the energy to take a chain out of state 1 (and into state 2), but changes in state relative to concentration is chemical potential.
  - Then the last thing is
 
$$\Delta G_2 - \Delta G_1 = \frac{(H^*)^2}{Na^2} + \frac{vN^2}{D^2 H^*} - \epsilon - \mu_{\text{bulk}}$$
    - 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  $\epsilon$  and not  $N\epsilon$  (which would be for the whole system).
  - You need to account for the entropy of stretching, the enthalpy of sticking, and excluded volume.
    - $vN^2/H D^2$ .
    - 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  $\epsilon$ .
- Phase diagrams.
  - $\chi N$  or  $\chi$  on the  $y$ -axis.
    - This is approximately  $1/T$ , so going up is low  $T$ .
  - Inner dashed line is **spinodal** or **stability** curve.
    - The inflection points on the pink curve in Figure 2.7c defines the spinodal curve.
    - Flat bottomed curve defines critical point!
  - Outer solid line is **binodal** or **equilibrium** or **coexistence** curve.
    - Lowest point where the two curves touch is the **critical** point.
    - Real phase separation is at the binodal line.
      - If we wait a long time.

- For a symmetric system, we get flat bottomed tangents.
- Why does the spinodal matter? Won't we just get to the lowest energies?
  - Free energy is the sum of the two states. Downhill from the middle to the spinodal points.
  - Splitting our system in two past the spinodal is not downhill. The way we go beyond this is **nucleation**. You will end up at a higher energy until the nucleating thing is big enough.
- Nucleation between the curves, spinodal decomposition (to the spinodals) in the middle.
- Example of utility: QDot synthesis.
  - They first jump into the spinodal zone that will phase separate, creating a bunch of little dots.
  - Then we quickly move the solution (once we have similarly sized nuclei) into the intercurve region. Here we no longer have spontaneous nucleation, but we have growth. And everything will grow at the same rate.
  - People who do nanoparticles play this game all the time. Heterogeneous nucleation: Dumping some trash in to nucleate other stuff, e.g., gold nanoparticles to nucleate silicon-oil phase separation.
- PSet 2, Q3b: When we need to determine  $A$ ? Finding  $\chi_c$  based on other problems, but then how do we get  $A$ ?
  - Critical temperature in the thousands of kelvins? Should be  $A = 45$  and  $\chi_c \approx 8000$  K.
  - We're not accounting for the entropic term in  $\chi$ , so we get an unreasonable value.
- $\Sigma\gamma_{AB}$  is the interfacial energy, which is kind of like the surface tension.
- Helfand parameter.
  - For a particular  $\chi$ , what will be the expected loop crossing the interface into the region of the other polymer.
- PSet 2, Q4 for the star polymer. Is the setup a B cylinder surrounded by AC mixed region?
  - Yes, something like that.
- Aside: It is really hard to get away from the phases in Figure 2.17 and get into new ones.
  - Stadler's goldmine.
- nVT vs. nPT constant regimes.
  - Lowest common energy is the *tangent* line, not the line connecting the two minima.
  - For the calculation for a real phase diagram, the math gets dicey because we have to deal with tangent lines.
  - Implication: The combination of the two unequal wells will give you the total lowest energy, rather than the lowest and the lowest. Moreover, we need to not be at the bottom of the wells, but slightly to the side so we get the tangent line rather than the line connecting the minima.

## 2.5 Review for Quiz 1

- Quiz 1 details.
  - Starts at 3:05 PM sharp.
  - 80 minutes to take it.
  - They're not here to fail us; they will put things appropriate for us to do in 80 minutes.

- Open book (bring Kwangwook's textbook), notes (print out notes!!), cheat sheets (“you'll probably want one of these”), but no electronic except for the occasional use of a calculator (check TI-84 batteries!! Phone calculator allowed, though).
- Undergrads need to answer 3/4 questions; grad students must answer all of them.
- Quiz is based on the HW, so make sure you know how to do it!
- Announcements.
  - 2nd HW solutions will be posted tomorrow.
  - A pre-test has been posted.
- Review starts now.
- Topic 1 (ideal chains) topics to know.
  - General characteristics of polymers: Degree of polymerization  $N$ , tacticity, bond length, etc.
  - Properties of polymer systems:  $M_w$ ,  $M_n$ , architecture.
  - Different models for polymers: Freely jointed chain (FJC), freely rotating chain (FRC), symmetric hindered rotations (and rotational isomeric states).
    - Things that come out of these models: End-to-end distances  $\mathbf{R}$  (with  $\langle R^2 \rangle = C_\infty Nl^2$ ), characteristic ratio  $C_\infty$ .
  - An important model for polymers: Kuhn's equivalent chain (with its effective bond length  $l_k$  and degree of polymerization  $N_k$ ).
    - This is the only model we've used since we introduced it, as we've increasingly neglected the *chemistry* involved to focus on the thermodynamics.
  - The end-to-end distribution is a Gaussian.
    - Since the probability  $p \propto e^{-\Delta G/k_B T}$  and  $\Delta G = F = 3k_B T R^2 / 2Nb^2$ , we get  $\Delta S/k_B T \propto R^2/Nb^2$ .
    - Spring constant in our Hookean spring is  $3k_B T/Nb^2$ .
  - Crossover concentrations (Figure 1.10).
    - The chain inhabits a sphere of volume  $R^3$ , and the volume per chain is  $V_c \propto R_e^3$ .
    - The number density in the bead is  $c = N/R_e^3$ . When  $c$  is greater than the critical concentration  $N/R_e^3$ , we start to get overlap.
- Topic 2 (real chains) things to know.
  - Excluded volume  $v$  comes from a hard core and the attractive part of the potential.
  - The Mayer- $f$  function is
 
$$f = e^{-U/k_B T} - 1$$
    - The excluded volume is the integral of  $f$  over all space.
    - Intuition for why the integral is excluded volume?
      - The Mayer- $f$  function gives the probability of finding two things close to each other.
      - It essentially tells us how this probability relates to that of an ideal gas where there is no interaction.
      - The attractive component raises the probability that things are close together.
      - The entropic component compensates for this, and doing the integral takes both into account. It measures the effective volume a particle feels like it has when in a sea of other particles.
      - If the interaction is only repulsive, a given particle will feel the volume of the box minus the volume of other monomers.

- If an attractive component exists, you can eventually balance out repulsion. It's not that the volume has been reduced; it's just that negative excluded volumes mean you don't care about repulsion, you just want to be closer together. So negative excluded volumes effectively reduce the volume the polymer wants to occupy.
- The  $\theta$  condition for a chain is where excluded volume is zero.
- Solvent quality.
  - A polymer in a vacuum attracts to itself because of van der Waals forces; it doesn't just float around.
- Interaction energies.

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

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

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

- There is a handwavey and a formal way to come up with the compression term.
- First two terms are the “entropic terms,” in contrast to the latter two “enthalpic terms.”
- Scaling of polymer chains.
  - The size  $R$  will be proportional to  $b$  (the segment length, commonly Kuhn length) times  $N^\nu$ .
  - In a  $\theta$  solvent,  $\nu = 1/2$ . For a good solvent,  $\nu = 3/5$ . For a bad solvent,  $\nu = 1/3$ .
  - We don't use all terms when we're minimizing things; we use the ones that matter. If the chain is going to expand, we get rid of the compression term. If one of them is negative, we use the last term. Know when to use which terms!!
- Dimensionality matters.
  - $\nu_{\text{good}} = 1, 2, 3, 4$  for  $\nu = 1, 3/4, 3/5, 1/2$ .

- Topic 3 (Flory-Huggins) things to know.

- Blends and solutions of polymers and (sometimes) solvents.
- We're interested in the free energy of mixing  $\Delta G_M = \Delta H_M - T\Delta S_M$ .
  - An entropic term and enthalpic term come together to make

$$\frac{\Delta G_M}{k_B T X_0} = \frac{\phi_1}{N_1} \ln \phi_1 + \frac{\phi_2}{N_2} \ln \phi_2 + \chi \phi_1 \phi_2$$

- The Flory  $\chi$  parameter quantifies interactions.

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

- Take the coordination number, divide by your units of energy, and then compare the interphase attractive energy to the average of the two intraphase attraction energies.
- $\chi$  scales as  $A/T$ , for some number  $A$ . To make the real world fit the system, we often add another term  $B$  as the “entropic contribution.” Symbolically,

$$\chi = \frac{A}{T} + B$$

- The above equation allows us to interconvert between  $\chi$  and  $T$ , which we often do in phase diagrams, etc.
- Phase diagrams.
  - 3 systems of interest.
    - Polymer-polymer systems.
    - Monomer-monomer systems.
    - Polymer-monomer systems.
  - For polymer-polymer and polymer-monomer systems,  $\chi N$  really controls things.
  - Outside the coexistence / equilibrium / binodal curve, you mix into 1 phase.
    - Inside both, you demix to the spinodal. Then with nucleation over a long period of time, you demix to the binodal.
  - Solubility parameters: Interconverting from  $\chi$  to  $\delta$ , as in PSet 2.
  - UCST and LCST transitions. Heating it up goes into an LCST regime, and cooling it down goes into a UCST regime.
- Topic 4 (self-assembly).
  - Be familiar with the min-max principle of (1) minimizing energy and (2) maximizing entropy.
  - Phases of diblock copolymers.
    - Spheres (BCC), cylinders (hexagonal; 20% – 35%), bicontinuous ( $35\% \pm 2\%$ ; gyroid, double diamond, and perforated lamellae), lamellae (40-60%).
  - Aside: There is no excluded volume in self-assembly.
  - Be familiar with diagrams like the binodal/spinodal one but with many nested curves, each one for a different phase transition (Figure 2.22).
    - Not binodal and spinodal but actual different phases where you have spheres, cylinders, gyroids, lamellae. Happens theoretically around  $(\chi N)_c = 10.5$ ; experimentally around 20.
    - $f$  on the  $x$ -axis; the fraction of one thing relative to the other, which accounts for polymer structure instead of just  $\phi$  for monomers.
- Should we know the polymer names and monomer repeat units?
  - Print this!!
- For the scaling of polymer chains, is this the same as the radius of gyration?
  - Slight difference in prefactor, but for linear chains, it's very close.
  - There's a  $\sqrt{6}$  term in the radius of gyration.

## 2.6 Office Hours (Alexander-Katz)

10/7:

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

- Rubinstein and Colby (2003) has some good information on brushes.
- Strobl (1997) has some good information on block copolymers.
- Bates and Fredrickson (1999) — which was also referenced in the slides, though not cited in full
  - has some good overview of the concepts as well.

## 2.7 Chapter 7: Thermodynamics of Polymer Mixtures

*From Lodge and Hiemenz (2020).*

- 9/30:
- Goals for this chapter.
    - Thermodynamically analyze a solution of a polymer in a low molecular weight solvent.
    - Determine the phase equilibria relevant to this situation.
  - **Polymer blend:** A mixture of two polymers.
  - **Pure** (thermodynamics): The purely phenomenological study of observable thermodynamic quantities and the relationships among them.
  - **Statistical** (thermodynamics): The atomistic model justifying purely thermodynamic observations.
    - “*Doing* thermodynamics does not even require knowledge that molecules exist... whereas *understanding* thermodynamics benefits considerably from the molecular point of view” (Lodge & Hiemenz, 2020, p. 271).
  - In this chapter, we are concerned with the state of a two-component system at equilibrium. The Gibbs free energy relates to this equilibrium, and in this case, it is given by

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

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

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

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

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

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

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

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

- Examples:

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

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

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

- **Standard state** (value of  $Y_i$ ): The value of  $Y_i$  when the substance  $i$  is pure. *Denoted by  $Y_i^\circ$ .*
- **Activity**: A thermodynamic concentration and measure of the nonideality of solutions. *Denoted by  $a_i$ . Given by*

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

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

$$m_i = N_A n_i$$

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

- This is also equal to  $X_i$  from class!
- **Coordination number**: The number of nearest neighbors that surround a central lattice point. *Denoted by  $z$ .*
  - Example: A cell in a 2D square lattice has  $z = 4$ .
- Regular solution theory: A simple statistical model that provides a useful expression for the free energy of mixing for a binary solution of two components.
  - Assume that the two molecules in the mixture have equal volumes.
  - Assume that the two components have equal (and concentration-independent) partial molar volumes, i.e.,  $\bar{V}_1 = \bar{V}_2$ .
  - Imagine each molecule occupying a cell in a lattice with volume equal to the molecular volume.
  - Let the lattice have coordination number  $z$ .

- 10/2:
- Lodge and Hiemenz (2020, p. 275) presents the entropy of mixing in the four useful forms: Original, with  $R$  and number of moles, per site, and per mole of sites.
    - This really helps clarify some of the rearrangements in PSet 2, Q1a.
  - Comments on the entropy of mixing.

- $\phi_i < 1$  always, so  $\ln \phi_i < 0$  always. This implies that  $\Delta S_M$  is always positive, so configurational entropy always favors spontaneous mixing!
- The expression derived is symmetric with respect to exchange of 1 and 2. Such symmetry comes from the assumption that both mixing molecules are the same size, and is difficult to satisfy in real situations.
- We are assuming that all configurations are equally probable (i.e., that 1 is equally likely to be next to 1 as it is to 2 and vice versa). But if there was an energetic preference, each configuration would need to be weighted by the appropriate Boltzmann factor.
- Lodge and Hiemenz (2020, p. 276) take the perspective that each  $\varepsilon_{ij}$  is negative, rather than being the absolute value of the depth of the well in Figure 2.5.
  - It is unclear which perspective we take in class. However, it does make sense for these terms to be negative, as every type of molecule attracts at least a bit to every other type due to London dispersion forces at minimum.
- **Exchange energy:** The difference between the attractive cross-interaction of 1 and 2 and the average self-interaction of 1 with 1 and 2 with 2. *Denoted by  $\Delta\varepsilon$ . Given by*

$$\Delta\varepsilon := \varepsilon_{12} - \frac{1}{2}(\varepsilon_{11} + \varepsilon_{22})$$
- When only London dispersion forces are present, we preferentially have  $\Delta\varepsilon \geq 0$  because “like dissolves like.”
- On the Flory  $\chi$  parameter.
  - This parameter is equal to the exchange energy per molecule, normalized by the thermal energy  $k_B T$ .
  - The Flory  $\chi$  parameter is the energy penalty you must pay (as a fraction of  $k_B T$ ) in order to lift one molecule of type 1 out of a beaker of pure 1, one molecule of type 2 out of a beaker of pure 2, and exchange them. See Lodge and Hiemenz (2020, p. 277). This is because when we do this in a typical square lattice, four things happen.
    1. First, removing a molecule of 1 from a lattice of pure 1 disrupts its interaction with each of its  $z = 4$  nearest neighbors. But as established earlier, each nearest neighbor interaction only contributes  $\varepsilon_{11}/2$  to the total energy/enthalpy of the pure state because we ‘see’ the interaction from the perspective of each molecule involved. Thus, the energy penalty of this removal is  $4 \cdot \varepsilon_{11}/2 = 2\varepsilon_{11}$ .
    2. Removing a molecule of 2 is analogous, and costs  $2\varepsilon_{22}$ .
    3. Adding a molecule of 2 to the now-empty space in a beaker of pure 1 *rewards* you  $2\varepsilon_{12}$ .
    4. Analogously, adding a molecule of 1 to the now-empty space in a beaker of pure 2 rewards you  $2\varepsilon_{12}$ .
  - Adding up all of these contributions gives  $\chi k_B T$ .
  - Then finally dividing by  $k_B T$  makes  $\chi$  unitless, by expressing the energy summed above as a numerical fraction of a known reference energy (namely,  $k_B T$ ).
- **Mean field** (theory): A theory that assumes that the local interactions are determined solely by the bulk average composition.
- On volume fractions.
  - For solvent-solvent systems, volume fractions are equal to mole fractions.

- For polymer-solvent and polymer-polymer systems, volume fractions are easier to use because calculating them only requires measuring the mass of each component and comparing it against known densities. Measuring mole fractions, on the other hand, requires precise knowledge of the full molecular weight distribution. Therefore, although mole fractions and volume fractions are mathematically equivalent, expressing our results in terms of volume fractions provides an empirically easier to use equation.
  - Lodge and Hiemenz (2020, pp. 279–82) derives the  $1/N$  prefactors in the  $\Delta S_M$  equations more rigorously, as alluded to in class.
    - $\Delta H_M$  would also change a bit in the polymer cases, but this complication is ignored.
  - Note that because monomers are not equally dispersed in dilute solutions (see Figure 1.10, left), the mean field approximation is not as good here.
    - It follows that the mean-field approximation (and hence Flory-Huggins theory) should get better as  $c \rightarrow c^*$ . This turns out to be the case!
  - A summary of the assumptions used in Flory-Huggins theory (Lodge & Hiemenz, 2020, p. 283).
    1. There is no volume change on mixing, and  $\bar{V}_i = \hat{V}_i$  is independent of concentration.
    2.  $\Delta S_M$  arises entirely from the ideal combinatorial entropy of mixing.
    3.  $\Delta H_M$  arises entirely from the internal energy of mixing.
    4. Both  $\Delta S_M$  and  $\Delta H_M$  are computed assuming random mixing.
    5. The interactions are short-ranged (nearest neighbors only), isotropic, and pairwise additive.
    6. The local concentration is always given by the bulk average composition (the mean-field assumption).
  - Lodge and Hiemenz (2020, pp. 283–89) covers some good osmotic pressure content that may be useful someday. Reviewing activity, activity coefficient, osmotic pressure, and Virial expansion info from Thermo will be necessary before delving into this.
  - **Phase diagram:** A mapping of the temperature-composition plane of a solution at fixed pressure, divided into regions wherein we find different phases.
  - Lodge and Hiemenz (2020, p. 291) view a phase diagram in terms of temperature, not  $\chi$ .
  - The three features of a phase diagram (in terms of  $\chi$ ).
    1. A **critical point** below which a one-phase solution is formed in all compositions.
    2. A **binodal** describing the composition of the two phases that coexist at equilibrium, after liquid-liquid separation at some fixed  $\chi > \chi_c$ . Any solution prepared such that  $(T, \phi_1)$  lies above the binodal will be out of equilibrium until it has undergone phase separation into two phases with compositions along the binodal.
    3. A **spinodal** dividing the two-phase region into a **metastable** window between the binodal and spinodal, and an **unstable** region above the spinodal.
  - An additional consequence of Figure 2.7c is that even on the pink curve, *some* mixing is still favorable. Thus,  $\Delta G_M < 0$  here, too!
- 10/6:
- Postulate: “Phase separation will occur whenever the system can lower its total free energy by dividing into two phases” (Lodge & Hiemenz, 2020, p. 293).
  - Let’s discuss when exactly phase separation will or will not occur.

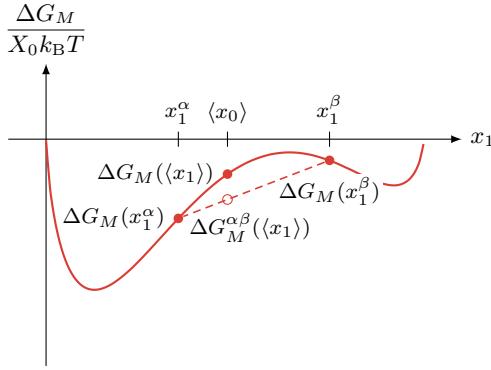


Figure 2.24: Tie lines predict the favorability of demixing.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

- Let's interpret these two expressions graphically.  $\Delta G_M(\langle x_1 \rangle)$  will just be a point on the  $\Delta G_M$  curve. If we plot  $\Delta G_M^{\alpha\beta}$  as a function of  $x_1$ , it will be the tie line between  $\Delta G_M(x_1^\alpha)$  and  $\Delta G_M(x_1^\beta)$ !
- Therefore, if the tie line lies above the curve, demixing will raise the energy of the system and will not occur. If the tie line lies below the curve, demixing will lower the energy of the system and will occur. As such, with the choices of  $\langle x_1 \rangle$ ,  $x_1^\alpha$ , and  $x_1^\beta$  in Figure 2.24, mixing will occur.
- An important consequence of the tie-line finding is that — since tie lines are an alternate way of defining concavity — concave up is the criterion for **stability** of a phase.
- Stable (phase):** A phase such that any spontaneous, small local fluctuation in concentration will increase the free energy, and hence these out-of-equilibrium fluctuations will relax back to the expected composition.
- Some personal thoughts and thought experiments on *how* a solution demixes into two phases.
  - A spinodal decomposition is an iterative process.

- From the initial concentration  $\langle x_1 \rangle$ , we will demix into two phases with compositions only slightly higher and slightly lower than  $\langle x_1 \rangle$ . These new phases then act as their own starting points, and must determine if demixing is higher or lower in energy.
- Demixing will continue as long as each little phase can decrease its energy by demixing, and this process will stop when the two phases lie along the spinodal.
  - Indeed, regardless of the exact starting composition  $\langle x_1 \rangle$ , if our starting solution is in the unstable region, it will undergo a spontaneous spinodal decomposition to two phases (of possibly different volumes) with compositions equal to the spinodal ones.
- Once a phase lies at the spinodal, any choice of new phases that includes one phase outside the unstable region will correspond to a tie line above the curve (unless the other phase is *vastly* different in composition).
- This is where nucleation must come along to ‘remove’ some particles from the system and into a more stable nucleus.

- Phase separation *raises* entropy, always, as we are creating order. But it may decrease enthalpy. (Think of the enthalpy and entropy graphs separately, as in Figure 2.7a-2.7b, and their respective tie lines.) Phase separation thus occurs when the gain in enthalpy outweighs the loss in entropy.
  - Temperature decreasing causes  $\chi$  to increase. But by the definition of the Flory  $\chi$  parameter, a decrease in temperature is mathematically equivalent to temperature staying the same and things starting to like themselves more than they like each other ( $\varepsilon_{12}$  getting more negative).
- An important characteristic of a metastable system at the spinodal points is that the two phases are in a *dynamic* equilibrium.
  - A certain amount of component  $i$  can move out of one phase and into the second, just so long as the flow is balanced by an equal amount of component  $i$  moving from the second phase into the first.
  - Demixing can also be thought of as a dynamic transfer of matter that is *not* in equilibrium; that is, the exodus of component 1 from a phase may be greater than the flow of component 1 into that phase, resulting in that phase decreasing in its  $\phi_1$ .
  - This flow of matter is driven by the change in free energy of the system with the number of moles in it. But this is exactly the chemical potential! That's why the chemical potential is the perfect tool with which to visualize the flow of matter in demixing.
    - Spinodal decomposition: The flow of matter from one phase to the other at a rate governed by the chemical potential until we have a dynamic equilibrium of matter flowing from one phase to the other that balances out.
    - Matter will “roll downhill” until it gets to the bottom of the chemical potential, which occurs at the spinodal points.
- Nucleation of ‘stable’ nuclei.
  - Suppose ideal stability occurs for  $\phi_1 = 0.7$ . Then take 7 molecules of 1 and 3 molecules of 2 as a nucleus. It will be energetically favorable for another 7 molecules of 1 and 3 molecules of 2 to come out of the phase they are in and join the growing nucleus; the remaining phases can then reequilibrate their distribution of molecules to reach stability with a smaller amount of matter.
- Lattice theory can be an instructive way to visualize phases and separations.
  - For example, model a beaker containing a mixture as a  $4 \times 4$  lattice with 8 black circles and 8 white circle randomly arranged. This could represent a homogeneous solution at high temperature.
  - As temperature is lowered (or  $\chi$  increases), there will come a point where demixing occurs into a denser, bottom phase and a lighter, top phase. Perhaps first, the top phase will gain an extra white circle on average and the bottom phase will gain an extra black circle on average.
  - As the decomposition continues, eventually we will reach a stable point (perhaps 6 black circles and 2 white circles at bottom, and 2 black circles and 6 white circles at top). The particles still move around, as long as this general trend is maintained.
  - Lattice theory also provides a good backdrop for visualizing the importance of energy *per site*, as we can only obtain the total energy through multiplying the energy per site by each site in each region and dividing by the total number of sites.
- Finding the binodal.
  - There are infinitely many pairs  $x_1^\alpha, x_1^\beta$  of phases to which an unstable system can demix, so how do we determine which pair corresponds to the most energetically stable system?
  - Well, a phase equilibrium is established when  $T, P$  are equal in both phases, and the chemical potentials are, too. Symbolically, our criteria are

$$\mu_1(x_1^\alpha) = \mu_1(x_1^\beta)$$

$$\mu_2(x_1^\alpha) = \mu_2(x_1^\beta)$$

- Warning: While the chemical potential of component 1 must be equal in both phases (and likewise for component 2), the chemical potential of component 1 *does not* need to equal the chemical potential of component 2.
- We will now show that finding the phases  $x_1^\alpha, x_1^\beta$  which satisfy the above criteria is equivalent to finding the lowest possible tangent line graphically.
- Since the chemical potential is a partial molar free energy, we can write the total free energy of mixing as the mole-weighted sum of the chemical potentials, as follows.

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

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

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

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

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

as desired.

- Note that we could also use the two original constraints and our known expressions for the chemical potentials to find  $x_1^\alpha, x_1^\beta$  analytically, but the algebra would get a bit hairy.

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

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

- Lodge and Hiemenz (2020, p. 303) covers several possible definitions of a reference volume for one monomer.

- One possibility is a geometric mean of the molar volumes of the repeat units. Why the geometric mean??
  - Another is to take  $100 \text{ \AA}^3$  as a generally good number.
  - Lodge and Hiemenz (2020, p. 306) has a table of solubility parameters, but in non-SI units.
- 10/12:
- For the specific case of polymer-solvent solutions, solubility parameter-based formulations of  $\chi$  differ significantly from experimental results.
    - A related model that is empirically more accurate is

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

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

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

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

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

- $\chi_h = \alpha/T$  is the enthalpic contribution to  $\chi_{\text{eff}}$ .
- $\chi_s = \beta$  is the entropic contribution to  $\chi_{\text{eff}}$ .
- $\alpha, \beta \in \mathbb{R}$ .
  - $\alpha < 0$  implies an attractive interaction between the components, e.g., hydrogen bonding.
  - The sign of  $\beta$  reflects the details of molecular packing. For example, if molecules pack very efficiently into real space (as opposed to the idealized equal volume of lattice cells), then there is probably *more* entropy of mixing than lattice theory would predict and  $\beta < 0$ .
- The signs of the various components give us insight into the phase diagram.

- Consider the case of  $\alpha < 0$  and  $\beta > 0$ . Herein, molecules of different components enthalpically attract to each other, and fit less well into space when they're around each other than we might ideally expect. Thus, there should be a temperature at which we rupture the enthalpic bonds and allow the components to pack more efficiently (i.e., with themselves). Thus, we may expect an LCST on the phase diagram.
  - Last note:  $\chi_{\text{eff}}$  often depends on concentration  $\phi_i$ .
    - This can lead to asymmetry in the  $\Delta G_M(\phi_i)$  curves.
    - It can also complicate experimental measurement of  $\chi_{\text{eff}}$ .

# Topic 3

## Dilute Solutions

### 3.1 Intrinsic Viscosity - 1

10/7:

- Announcements.
  - Grade our HWs on Canvas.
  - The profs are grading the first quiz.
  - PSet 3 will be posted tomorrow morning.
  - After today's lecture, we'll have a lot of fodder to get going on it!
- Overview of Topic 3.
  - We've built up a lot of theory, but now we want to discuss how we measure the parameters we've introduced.
    - Example: Measuring polymer size and conformation.
  - We'll also touch on why such parameters are important for various material properties.
    - Examples of where polymer size and conformation are important: Non-entangled rubber elasticity, shear thickeners, elastic modulus of crosslinked networks, and electrical conductivity.
- Upcoming lectures by day.
  - Today: Viscometry. What is the viscosity, intrinsic viscosity, etc. of a polymer? How rheology tells us stuff about a polymer sample.
    - Specifically, we'll relate the viscosity of a dilute polymer-solvent solution to the polymer molecular weight.
  - Thursday: Standard through state-of-the-art ways to measure the viscosity of a polymer solution.
  - Next Tuesday: Fractionation (e.g., via GPC), and how it works (based on our theory). Also osmotic pressure.
    - Fractionation techniques can provide us the full molecular weight distribution of a polymer sample.
    - Osmotic pressure can provide information on molecular size and polymer-polymer interactions.
  - Next Thursday: A high-level discussion of light scattering. Different power sources (e.g., NMR), and how scattering tells us something about the polymer size.
- Outline of today's lecture.
  - Drag coefficient of a polymer.
    - Also referred to (e.g., by the textbook) as the "friction factor."

- This number is related to a polymer's conformation.
- Draining and free draining models.
- The diffusion coefficient, and how molecules randomly move in a solution due to thermal energy.
- Intrinsic viscosity.
- This is key, and the first three topics all build up to it.
- The intrinsic viscosity has a scaling with the diffusion coefficient?? Did we cover this today?
- Mark-Houwink-Sakurada model.
- Before we get to the viscosity of dilute solutions of polymers, let's introduce some basic concepts around just plain viscosity. This will basically serve as a "fluid dynamics 101."
- To help visualize the following definitions, consider this thought experiment.

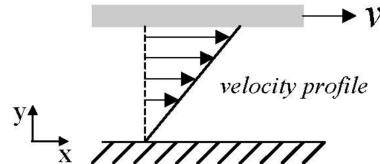


Figure 3.1: Viscosity visualization.

- Put a liquid between two plates, and move the top one.
- You can show (via the fluid equation or **Navier-Stokes equations**) that you will quickly develop a velocity profile. Molecular friction exerts a force, and the force is related to the **viscosity**.
- Consideration of the viscosity leads us to the other definitions below.
- **Navier-Stokes equations:** The governing equations of fluids.
- **Viscosity:** A relationship which tells us something about when we exert stresses on surfaces as a result of flow, and the relation to how fast we're moving a fluid. *Also known as coefficient of viscosity, shear viscosity. Units Pas. Denoted by  $\eta$ . Given by*
$$\eta := \frac{\text{shear stress}}{\text{rate of shear}}$$
- **Shear rate:** How fast we move the plates relative to each other, normalized by the distance between the plates. *Also known as velocity gradient, rate of shear. Units s<sup>-1</sup>. Denoted by  $\dot{\gamma}$ .<sup>[1]</sup> Given by*
$$\dot{\gamma} := \frac{U}{H}$$
- $U$  is the difference in velocity between the top and bottom plates.
- $H$  is the distance between the top and bottom plates.
- **Shear stress:** The pressure resulting from the viscous force applied over the area of the moving plate. *Units Pa. Denoted by  $\tau$ ,  $\tau_{yx}$ . Given by*
$$\tau := \frac{\text{viscous force}}{\text{area}} = \eta \dot{\gamma}$$
- The  $\tau_{yx}$  notation comes from the fact that stress is a tensor, and the  $yx$  element of this tensor is the shear stress.

<sup>1</sup>"gamma dot"

- However, we are not concerned with tensors in this class, so we may think of shear stress as nothing more than a scalar with units of pressure.

- **Newtonian** (fluid): A fluid that satisfies the following condition. *Constraint*

$$\eta \neq \eta(\gamma_{\text{tot}}, \dot{\gamma})$$

- The above constraint states that for a Newtonian fluid, the viscosity  $\eta$  is a constant. In particular, viscosity is *not* a function of the shear strain  $\gamma$  or the shear rate  $\dot{\gamma}$  (as is the case for some non-Newtonian fluids).

- **Non-Newtonian** (fluid): Any fluid that is not Newtonian.

- This encompasses a *broad* range of fluid properties.
- Polymers are very non-Newtonian.

- This concludes our introduction to the terminology of fluid mechanics.

- We now address today's focus, the behavior of dilute ( $\phi_2 \ll 1$ ) polymer-solvent solutions at small shear rates ( $\dot{\gamma} \ll 1$ ).

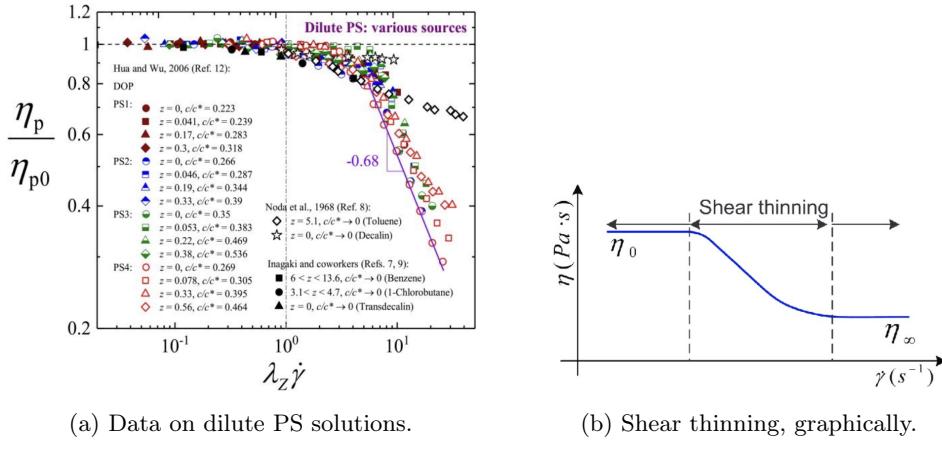


Figure 3.2: Polymer viscosity at varying shear rates.

- Figure 3.2a compiles a bunch of data from the literature on viscosity vs. shear rates.
  - The *y*-axis is the viscosity  $\eta_p$  of the polymer-solvent solution, normalized by said solution's asymptotic viscosity  $\eta_{p0}$  as you go to very small shear rates.
  - The *x*-axis is the shear rate, again normalized by some constant  $\lambda_Z$ . Here, we have picked a scaling  $\lambda_Z$  that makes our data dimensionless (i.e., 1 on the *x*-axis) and reveals the two important trends that...
    - Faster shearing ( $\lambda_Z \dot{\gamma} > 1$ ) leads to a decrease in viscosity known as **shear thinning**;
    - Lower shearing ( $\lambda_Z \dot{\gamma} < 1$ ) leads to the asymptotic viscosity.
  - Below a certain shear rate, we observe Newtonian behavior and “zero shear viscosity.”
- Figure 3.2b sketches the idea of shear thinning.
  - **Zero shear viscosity** occurs at left.
    - Note that this regime would more aptly be termed the “low shear viscosity” regime, since we're only asymptotically approaching zero shear.
    - However, “zero shear viscosity” is what's in the lexicon.
  - Shear thinning occurs in the middle.

- At right, we enter the asymptotic regime wherein most viscosity comes from the solvent, not the polymer.
- Reference: Pan et al. (2018).
- **Shear thinning:** A property of certain fluids wherein viscosity decreases the faster the fluid is sheared (i.e., as the shear rate  $\dot{\gamma}$  increases).
- **Zero shear viscosity:** The viscosity under a shear rate sufficiently low that the fluid behaves as if its Newtonian. Denoted by  $\eta_0$ . Given by

$$\eta_0 := \lim_{\dot{\gamma} \rightarrow 0} \eta$$

- **Weissenberg number:** A dimensionless shear rate. Denoted by  $Wi$ . Given by

$$Wi := \dot{\gamma} \tau_{\text{polymer}}$$

- Before we dive deeper, we should state an important assumption about shear rate underpinning our analysis.

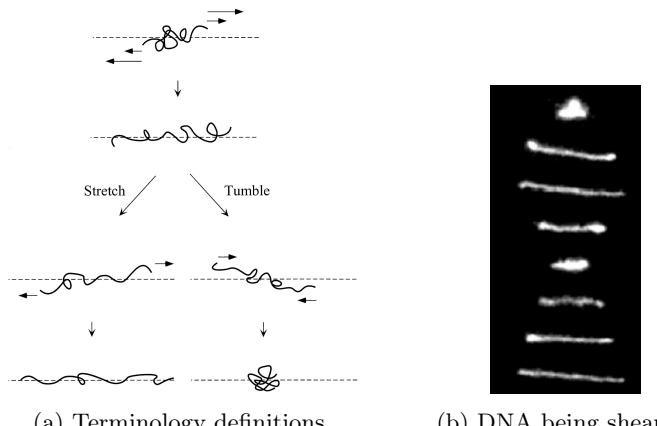


Figure 3.3: Stretching and tumbling upon shearing.

- In this class, we will assume that polymer coils are *not* deformed by the flow (i.e.,  $Wi < 1$ ).
- Typically, polymers **stretch** and **tumble** when  $Wi > 0$  (Figure 3.3a).
- For example, DNA has been micrographed stretching and tumbling at higher shear rates and Weissenberg numbers (Figure 3.3b).
- Reference: Smith et al. (1999).
- **Stretch:** A behavior of a sheared polymer in which a usually flexible coil is elongated by shear forces.
- **Tumble:** A behavior of a sheared polymer in which a stretched coil is compressed with rotation by shear forces.
- We now describe how the Navier-Stokes equations treat viscosity.
  - Consider a hard sphere of size  $r_s$  falling through a fluid of viscosity  $\eta_0$  with velocity  $v$ .
  - By Newton's laws, the fluid will exert a viscous force  $F_{\text{viscous}}$  on the sphere. Moreover, this force will be given by the following.

$$F_{\text{viscous}} = fv$$

- $v$  is the velocity with which the sphere is moving.

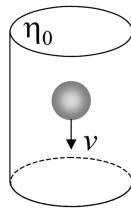


Figure 3.4: Drag coefficient on a hard sphere in a viscous fluid.

- $f$  is the drag coefficient or friction factor. It can be thought of as the proportionality factor between the velocity and viscous force.
  - Solving the Navier-Stokes equations for this scenario, we obtain **Stokes' law**.
  - How, then, can we treat a polymer molecule moving through a viscous fluid? There are two limiting cases.
    1. The polymer coil acts as an impenetrable sphere with dimensions given by the pervaded volume.
    2. The polymer coil is entirely penetrable, with only individual monomers interacting with the viscous fluid.
  - **Stokes' law:** The Navier-Stokes equations' relation between the drag coefficient  $f$  on a sphere of size  $r_s$  falling through a fluid, and the fluid's viscosity  $\eta_0$ . *Given by*
- $$f = 6\pi\eta_0 r_s$$
- The  $6\pi$  falls out of the math when solving the Navier-Stokes equations.
  - It makes intuitive sense that  $f \propto \eta_0$  and  $f \propto r_s$ , so it is not hard to rationalize or visualize that such proportionality manifests itself as a bilinear relation.
  - Let's now extend our investigation into the possible behaviors of a polymer molecule in shear flow.

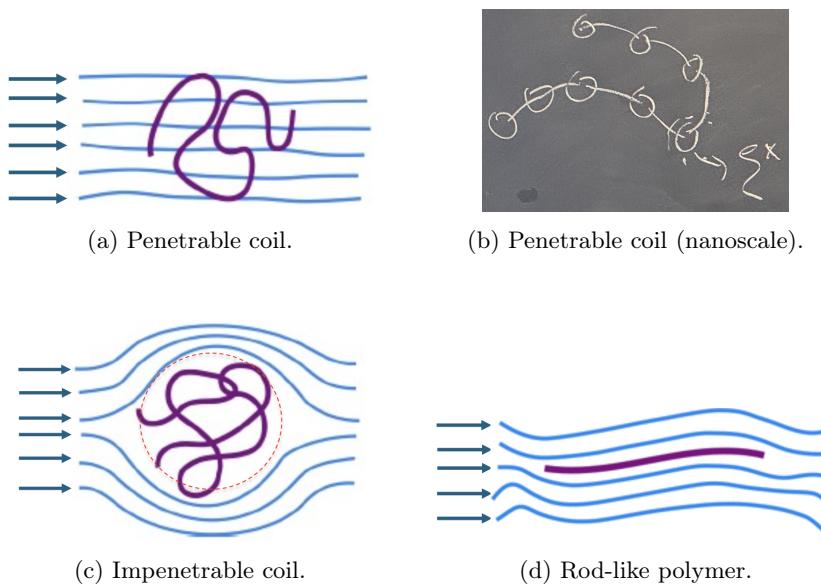


Figure 3.5: Modeling a polymer in a viscous fluid.

1. Penetrable coil, i.e., Rouse's free draining model.

$$f \propto N_2 \xi^*$$

- Notation.
  - We still let  $N_2$  be the number of segments per chain (e.g., number of Kuhn steps).
  - $\xi^*$  is the **monomeric friction factor**.
- Globally, the fluid passes through the coil freely (Figure 3.5a).
- However, very locally (Figure 3.5b), there is no slip. In other words, each monomer contributes a small amount  $\xi^*$  to the total friction factor. It follows that in this case, the friction factor scales linearly with the number of units  $N_2$  in the polymer!
- 2. Impenetrable sphere, i.e., Zimm's non-free draining model (Figure 3.5c).
 
$$f = 6\pi\eta_0 R_H \quad R_H \propto \langle R_g^2 \rangle^{1/2} \quad f \propto N_2^\nu$$
  - $R_H$  denotes the sphere's **hydrodynamic radius**.
  - The rightmost relation follows from transitivity and the scaling of  $R_g$ .
    - $\nu$  is the same measure of solvent quality (e.g., 1/2, 3/5, or 1/3) discussed previously.
  - There is a strong hydrodynamic interaction (HI), or coupling, of the motion of monomers in dilute solution.
    - Essentially, when one monomer moves somewhere along a polymer chain, it yanks others in the chain along with it.
    - HI  $\propto 1/r$ , where  $r$  is the relative separation of monomers (like the bond length??).
    - Additional equation for  $\mathbf{v}(\mathbf{r})$ ??
  - This model is appropriate for a (1) high molecular weight and (2) flexible polymer.
  - Is  $2R_H$  the radius or diameter of the hydrodynamic sphere?? See the slides.
- 3. A rod-like molecule (Figure 3.5d).

$$f = 6\pi\eta_0 R_H \quad R_H \propto R_{\max} = L \quad f \propto N_2$$

- This is one more commonly encountered possibility.
- The above relations should be fairly self-explanatory.
- When choosing which of the above three models to use for a given situation, remember that the one that is most appropriate depends on the size and concentration of the polymers.
- How might we measure the friction factor  $f$ ?

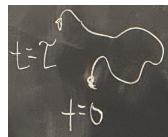


Figure 3.6: A diffusing molecule.

- Consider the Stokes-Einstein diffusivity / diffusion coefficient

$$D_t = \frac{k_B T}{\xi}$$

- $\xi = f$  is the drag coefficient / friction factor.
- We are taking this to be of a tracer molecule, i.e., some molecule in solution far from everything else.
- $k_B T$  is an energy (i.e., a force times a length), and the friction factor has been defined as the quotient of (the viscous) force divided by a velocity. Thus, the units cancel out to length squared per time for  $D$ .

- We have a flux  $J$  satisfying **Fick's law**.
  - This is a continuum view of diffusion.
- The average squared displacement of a molecule as it moves around over a period of time  $\tau$  is

$$\langle \Delta x^2 + \Delta y^2 + \Delta z^2 \rangle_\tau = 6D\tau$$

- This is a molecular view of diffusion, from time  $t = 0$  to time  $t = \tau$  (Figure 3.6).
- $D$  has units of length squared over time here, as well!
- Thus, to actually get the diffusion coefficient, we could track molecules, e.g., by taking movies of them.
  - Take movies of everywhere it goes, break up the path into segments  $\tau$ , and then take the ensemble or time average

$$\langle \Delta r^2 \rangle = 6D\tau$$

- It follows by combining several of the above equations that

$$R_H = \frac{k_B T}{6\pi\eta D}$$

- Additionally, it is important that

$$R_H \propto R_g \propto R$$

- **Fick's law:** A relationship between flux, diffusivity, concentration, and distance. *Given by*

$$J = -D \frac{\partial c}{\partial x}$$

- $J$  is the flux.
- $c$  is the concentration.
- $x$  is the distance.

- How long does a polymer have to be to obey Zimm scaling?

- For most systems in which we are interested, we will use Zimm's non-draining sphere.
- However, there is still significant debate in the literature about when this non-draining sphere assumption is ok to use.
- Smith et al. (1996) posits that once  $N > 10$ , we can use this model.
- Wang et al. (2023) — published just two years ago — posits that we need to wait until  $N > 30$ .
- Many polymers we have are well into the hundreds or thousands, though. Above  $N = 100$  is a generally solid cutoff for this behavior, so we can think of these as very good and very non-draining.

- Scaling behavior of the friction factor.

- $\nu$  values reviewed again.
- For high MW flexible chains, the correct model is non-draining impenetrable units (Zimm-like).
  - As discussed above, this model obeys  $\xi = f = 6\pi\eta_s R_H$ , where  $R_H \propto R_g$ .

- $R_H$  vs.  $R_g$  vs.  $R$ .

- The prefactor  $\gamma$  in

$$R_H = \gamma R_g$$

is on the order of 1.

- The above equation is really important! We will use it later today.
- Recall that  $R_H$  is related to a hydrodynamic interaction tensor??

Polymer structure	Solvent	$R_g/R_h$ Zimm theory	$R_g/R_h$ experiment
Randomly branched	Good	—	2.0
Linear monodisperse	Good	1.6	1.5
Randomly branched	$\theta$	1.7	—
Linear $M_w/M_n = 2$	$\theta$	1.7	—
Linear monodisperse	$\theta$	1.5	1.3
3-Arm star	$\theta$	1.4	1.2
4-Arm star	$\theta$	1.3	1.05
12-Arm star	$\theta$	1.17	0.93
18-Arm star	$\theta$	1.14	0.82
270-Arm star	$\theta$	1.08	0.77
Hard sphere	—	0.77	0.77

Table 3.1: Ratio of radius of gyration and hydrodynamic radius for different polymer architectures.

- Note that  $\gamma = R_g/R_H$  converges to 1 (middle-right column in Table 3.1) as the number of arms on a polymer increases because, as you get more arms, you do just start to look like a sphere.
- Rubinstein and Colby (2003) has some good explanations on this; Table 3.1 is also lifted from “Table 8.4” in this textbook.
- For the rest of class, we focus on viscosity. We’ll get as far into this topic as we can today, and then we’ll carry on next time.
- Einstein model for viscosity.
  - Simulating viscosity in full is a computationally intensive process.
  - On pen and paper, we will focus on what we can do for idealized hard spheres in a Newtonian fluid. This is the setup Einstein considered.
  - Let the hard spheres be of volume fraction  $\phi_{hs}$  in the solution.
  - Einstein did his calculation in the dilute limit, obtaining

$$\eta(\phi_{hs}) = \eta_s(1 + 2.5\phi_{hs} + \dots)$$

- Einstein’s detailed calculation got 2.5 as the linear correction.
- The power series continues, but in the dilute limit ( $\phi_2 \ll 1$  and  $c_2 \ll c_2^*$ , where  $c_2^*$  is the overlap concentration), we only need the linear correction.
- This solution will have a viscosity  $\eta$ , composed of a linear contribution from the solvent  $\eta_s$ , and then an added contribution from the polymer in the form of a **specific viscosity**  $\eta_{sp}$ . This gives us the following.

$$\eta = \eta_s + \eta_s \eta_{sp}$$

- Thus, from the above by transitivity,

$$\frac{\eta}{\eta_s} - 1 = \eta_{sp} = \underbrace{2.5\phi_{hs}}_{\text{for hard spheres}} + \dots$$

- From the specific viscosity, we can define the **intrinsic viscosity**  $[\eta]$ .
- It follows that in general, our solution has a viscosity

$$\eta = \eta_s (1 + c \cdot [\eta] + K_H c^2 [\eta]^2 + \dots)$$

- This equation represents viscosity as a perturbation in concentration  $c$ .
- The first prefactor is the intrinsic viscosity.
- $K_H$  denotes the **Huggins coefficient**.

- We now want to relate the intrinsic viscosity to our polymer models.
- Let's go back to hard spheres.
- The volume fraction of hard spheres is the number of spheres times the sphere volume  $V_{hs}$  divided by the total volume.
- To get it in terms of concentration so as to bridge this model over to our new concentration-based model, we obtain

$$\phi_{hs} = \frac{(\# \text{ spheres})(\text{vol sphere})}{\text{total volume}} = \frac{cN_A V_{hs}}{M}$$

- We measure concentration in g/L.
- We measure molar mass in g/mol.
- The units of Avogadro's number  $N_A$  is mol<sup>-1</sup>.
- Thus, in the above expression, the units do work out correctly to number times volume divided by volume!

- Thus, we can now put everything together.

- The Einstein model's correction is

$$2.5\phi_{hs} = \frac{2.5cN_A V_{hs}}{M}$$

- We can relate the hard sphere volume back to polymer radius with

$$V_{hs} = \frac{4}{3}\pi R_{hs}^3$$

- The specific viscosity is then equal to  $2.5\phi_{hs}$  by definition, so

$$\eta_{sp} = \frac{2.5 \cdot 4\pi R_H^3 c N_A}{3M}$$

where we have replaced the hard sphere radius with the polymer's hydrodynamic radius.

- Now  $R_H = \gamma R_g$ , as mentioned earlier today. Additionally, we can divide through by concentration to turn the specific viscosity into an intrinsic viscosity. Therefore,

$$[\eta] = \frac{10\pi N_A \gamma^3 \langle R_g^2 \rangle^{3/2}}{3M}$$

- The above result is our final theory — a very commonly used theory.
- It follows that for our polymer-solvent solution, we have the following scaling.

$$[\eta] \propto \frac{R_g^3}{M} \propto M^{3\nu-1} \propto N^{3\nu-1}$$

- We still have  $\nu$  dependent on the solvent type exactly as discussed repeatedly above.
- Thus, for a  $\theta$  solvent, scaling of the intrinsic viscosity is  $3(1/2) - 1 = 1/2$ . For a good solvent,  $3(3/5) - 1 = 4/5$ .
- Note that we get the scaling because  $R_g \propto R \propto N^\nu$ , and  $N \propto M$ .
- **Specific viscosity:** A dimensionless quantity describing how much more viscous a solution becomes as polymers are introduced. *Denoted by  $\eta_{sp}$ . Given by*

$$\eta_{sp} := \frac{\eta}{\eta_s} - 1$$

- From the definition, we can see that for a pure solution (only solvent), the specific viscosity is zero. As the viscosity of the solution increases with increasing solute,  $\eta_{sp}$  will obtain a value greater than zero (and likewise for decreases in viscosity).

- **Intrinsic viscosity:** A measure of a solute's contribution to the viscosity of a solution. *Units conc<sup>-1</sup>.*  
*Denoted by  $[\eta]$ . Given by*

$$[\eta] := \lim_{c \rightarrow 0} \left( \frac{\eta_{sp}}{c} \right) = \lim_{c \rightarrow 0} \left( \frac{\eta - \eta_s}{c\eta_s} \right)$$

- **Huggins coefficient:** The viscometric equivalent of a Virial coefficient. *Denoted by  $K_H$ .*
- Implicit assumptions used today.
  - We are in a dilute solution.
  - If we use this viscosity in a real flow, our Weissenberg number must be much less than one ( $Wi \ll 1$ , where  $Wi := \tau_p \dot{\gamma}$ ).
  - The Zimm/non-draining argument is essential.
- Do we need to know anything else about the radius of gyration?
  - We will not be doing any detailed calculations, so no.
  - Just know that all of the different radii are applicable in different circumstances, and all related by order 1 coefficients. Thus, we can convert between all of them as needed.
- **Mark-Houwink-Sakurada model:** A scaling of the intrinsic viscosity derived above. *Given by*

$$[\eta] = KM^a$$

- $K, a$  depend on solvent quality and polymer.
- Exponent scaling.
  - $a < 1/2$  implies a poor solvent.
  - $a = 1/2$  implies a  $\theta$  solvent.
  - $4/5 > a > 1/2$  implies a good solvent.
- There's lots of data for various polymer types.

## 3.2 Intrinsic Viscosity - 2

10/9:

- Review of last lecture (various terms introduced last time).
- To begin, we'll wrap up some concepts from last time.
- More types of viscosity.
  - **Relative, reduced, and inherent** viscosity.
  - These exist, but we don't need to know much about them.
- **Relative viscosity:** The overall viscosity normalized by that of the solvent. *Denoted by  $\eta_r$ . Given by*

$$\eta_r := \frac{\eta}{\eta_s}$$

- **Reduced viscosity:** The increase in viscosity, normalized by the concentration of the added solute. *Denoted by  $\eta_{red}$ . Given by*

$$\eta_{red} := \frac{1}{c} \left( \frac{\eta}{\eta_s} - 1 \right)$$

- **Inherent viscosity:** The measure of viscosity defined as follows. *Denoted by  $\eta_{inh}$ . Given by*

$$\eta_{inh} := \frac{1}{c} \ln \left( \frac{\eta}{\eta_s} \right)$$

- On the scaling of the intrinsic viscosity with the polymer molecular weight.
  - Doyle provides the justification I thought up for the  $3\nu - 1$  proportionality discussed last time!
  - The Mark-Houwink-Sakurada model's benefit is that it allows us to fit our data to a more general law that doesn't depend on "good" or "bad" solvents so explicitly, but rather allows you to interpolate between them.
- Doyle skips the slide on Mark-Houwink parameters, but know that these are tabulated.
- Last class, we built a lot of theory around viscosity. But is that theory consistent with our theory from Topics 1-2?
- Let's show that it is in one example: Intrinsic viscosity and  $c^*$ .
  - Recall Figure 1.10.
  - Recall the geometric argument that

$$c^* = \left( \frac{M}{N_A} \right) \frac{1}{V_p} = \frac{3M}{4\pi N_A R_g^3}$$

- $M$  is the mass of 1 mole of polymers.
- Thus,  $M/N_A$  is the mass of a single polymer and  $M/N_A V_p$  is the concentration of polymer within the excluded volume.
- But this is equal to the concentration of  $n$  polymers within  $n$  of their excluded volumes, or of a whole solution at the critical concentration!
- $V_p$  is related to the radius of gyration by the equation for the volume of a sphere.
- Alternatively, the critical concentration occurs when the effective volume fraction  $\phi_{\text{eff}} = \phi_{hs} = 1$ . Thus, substituting in the values at the critical moment,

$$\begin{aligned} [\eta] &= \frac{2.5\phi_{hs}}{c_2} \\ [\eta]_c &= \frac{2.5 \cdot 1}{c^*} \\ c^* &= \frac{2.5}{[\eta]} = \frac{3M}{4\pi N_A R_g^3 \gamma^3} \end{aligned}$$

- The second line above is a *very* famous equation that shows up in many research articles.
- The two definitions of  $c^*$  are very similar!
  - This provides a good "sanity check" for our theory.
  - We can rest easy about the  $\gamma^3$  difference because  $\gamma$  is an order 1 term, so it doesn't change the value of the expression much.
- Determination of the intrinsic viscosity.
  - Let's start with a derivation.
  - Recall that for  $c < c^*$ ,

$$\eta \approx \eta_s (1 + c \cdot [\eta] + K_H c^2 [\eta]^2) \quad \eta_{sp} = \frac{\eta}{\eta_s} - 1$$

- Thus, we can divide the right equation through by concentration and the solvent viscosity, rearrange, and relate it to the intrinsic viscosity, as follows.

$$\begin{aligned} \frac{\eta}{\eta_s c} &= \frac{1}{c} + [\eta] + K_H [\eta]^2 c \\ \underbrace{\frac{\eta/\eta_s - 1}{c}}_{\eta_{sp}/c} &= [\eta] + \underbrace{K_H [\eta]^2 c}_{\text{constant}} \end{aligned}$$

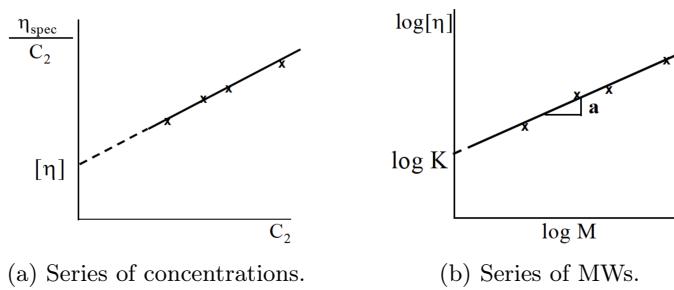


Figure 3.7: Determination of intrinsic viscosity.

- The equation above tells us that given a series of concentrations, we can plot  $\eta_{sp}/c$  vs.  $c$  and get a linear plot, the  $y$ -intercept of which will be the intrinsic viscosity and the slope of which could give us the Huggins coefficient (Figure 3.7a).
- Notice that in the limit of  $c \rightarrow 0$ , the above equation reduces to the definition of intrinsic viscosity!
- Now that we have the intrinsic viscosity, we can do even more.
  - The Mark-Houwink model tells us that given a series of molecular weights and their intrinsic viscosities, we can make a log-log plot to measure  $K$  and  $a$  (Figure 3.7b).
  - The data on the next slide shows agreement with the theoretical expectation.
- Doyle is skipping the Intrinsic Viscosity - Key Idea & Viscosity-Average Molecular Weight derivations.
  - Key result: Each of our species  $i$  in solution obeys its own Mark-Houwink equation.
  - The **viscosity-averaged molecular weight** tends to lie between the number- and weight-averaged MW; it's what you use for  $M$  in the Mark-Houwink plot analysis.
- Example of the above method of measuring intrinsic velocity, from a recent article in Nature.
  - The authors were interested in the degradation of cellulose.
  - They measured the decrease in molecular weight by Mark-Houwink analysis, but in reverse! They knew  $K, a$ , measured  $[\eta]$ , and found  $M$  for each sample.
  - Reference: Maraghechi et al. (2023).
- We now move into today's lecture content in earnest: Measuring intrinsic viscosity, from classic methods to the state-of-the-art ones people are currently researching.
- Challenges to the measurement of intrinsic viscosity.
  - Low concentrations of polymer.
    - This implies that the viscosity of the polymer solution is very close to that of the solvent, so we need very accurate instruments.
  - Need to operate in the  $Wi < 1$  regime.
    - This is because we need the polymer to not be deformed, so we can't shear *too* fast (or we'll get into stretching and tumbling regimes that throw off our calculations, as in Figure 3.3).
    - Since the shear stress  $\tau = \eta \dot{\gamma}$ ,
$$Wi = \tau \dot{\gamma} = \eta \dot{\gamma}^2$$

and so we need  $\eta \dot{\gamma}^2$  less than one.
- We may not have much of our sample to commit to this experiment, especially in the case of precious materials.

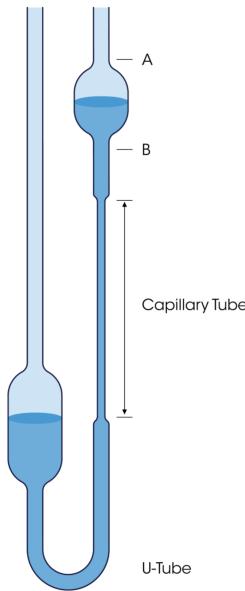


Figure 3.8: Capillary viscometer.

- This is especially challenging because relatively large volumes of solutions are typically needed for viscosity measurements.
- Classic method: Capillary viscometer.
  - From the 1800s.
  - We suck some liquid up into a straw.
  - Gravity will then want to equilibrate the chambers, and we measure the time that the equilibration takes.
  - All you need is the set up, a means to draw your liquid up, and a stopwatch.
- Basic (without Navier-Stokes) physics for the why a capillary viscometer works.

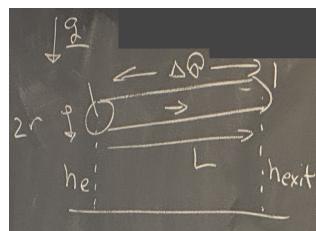


Figure 3.9: Hagen-Poiseuille derivation.

- Hagen and Poiseuille<sup>[2]</sup> solved a nice problem for a Newtonian fluid (constant viscosity  $\eta$ ) traveling through a straight tube of diameter  $2r$  and length  $L = h_{\text{entrance}} - h_{\text{exit}}$  at pressure  $\Delta P$ .
  - The flow  $Q$  is assumed to be sufficiently slow so as not to be **turbulent**. In other words, the flow is **laminar**.
    - Specifically, they wanted the flow to have **Reynolds number**  $\text{Re} \leq 2000$ .
    - Note that  $Q$  is measured in units of volume per second (e.g.,  $\text{m}^3/\text{s}$ ).

<sup>2</sup>“POY-say”

- The result of the derivation is that the flow is

$$Q = \frac{\pi r^4}{8\eta L} \Delta P$$

➤  $\Delta P = P + \rho gh$  is a dynamic pressure, which is equal to the regular pressure  $P$  plus  $\rho gh$ . It is the pressure difference between the two ends of the pipe.

- It follows that — in the context of a capillary viscometer — the time to drain a volume  $V$  is going to be

$$\frac{V}{Q} \propto \underbrace{\frac{VL}{r^4 g \Delta h}}_{\text{constant}} \cdot \frac{\eta}{\rho}$$

- Thus, we have a relation between our observable ( $V/Q$ ), the desired quantity ( $\eta$ ), and parameters baked into our system.
- Note that the parameters baked into the system can be broken down into two classes. The first is the contents of the constant, which are all specific to a given capillary viscometer. The second is the density of the fluid, which we can experimentally measure independently of our capillary viscometer (e.g., with a micropipette and a balance) for any fluid whose viscosity we seek to determine.
- A convenient rewrite of the above equation (in the specific case of water, a common solvent) is

$$t_{\text{H}_2\text{O}} = \text{constant} \cdot \frac{\eta_{\text{H}_2\text{O}}}{\rho_{\text{H}_2\text{O}}}$$

- Water is very extensively studied, so we can look up the right terms above in a handbook.
- Doing the same for our polymer solution and combining the two equations, we get the following result. This result will give us our material properties.

$$\frac{t_{\text{H}_2\text{O}}}{t_{\text{polymer}}} = \frac{\eta_{\text{H}_2\text{O}}}{\rho_{\text{H}_2\text{O}}} \cdot \frac{\rho_{\text{polymer}}}{\eta_{\text{polymer}}}$$

- We measure  $t_{\text{H}_2\text{O}}$  in our specific viscometer, either measure or look up the right term above, determine the density of our polymer-water solution, and then can obtain the viscosity of our polymer!
  - This equation eliminates the need to measure the constant for our specific viscometer.
  - Basically, it replaces measuring a constant with calibrating the viscometer against a known solvent.
- Note that every term subscripted “polymer” refers to a property of the polymer-solvent solution. This is because we want to measure quantities at the conditions under which we’re running the experiment.
- We can also use the approximation for  $c \ll c^*$  that  $\rho_{\text{polymer}} \approx \rho_{\text{solvent}}$ .
- We need about 5-10 mL of solution to run this experiment.
- These instruments are \$200-\$400 from Sigma today!

- **Reynolds number:** A dimensionless quantity that helps predict fluid flow patterns (e.g., laminar vs. turbulent). Denoted by **Re**. Given by

$$\text{Re} := \frac{2rU\rho}{\eta}$$

- **Kinematic viscosity:** A measure of the viscosity of a solution that is directly proportional to the time the solution takes to flow under certain conditions. Given by

$$\frac{\eta}{\rho}$$

- We now begin discussing **rheology**.
- **Rheology:** The study of the flow of matter. *Etymology* from Greek “rhei” (to flow or stream) and “logos” (the study of).
- History of rheology.
  - Plato (400 BC): “All things move and nothing stands still.”
  - Simplicius (500 AD): “Panta rhei.”
    - Translation: Everything flows.
    - This is true! Some things just appear not to because we’re looking at them at too short of a timescale.
  - Prof. Bingham (1920s): Coins the term “rheology.”
  - Influence of the idea that everything flows: The **Deborah number**.
    - Named after Deborah in the Bible’s Book of Judges, who famously said, “the mountains flowed before the Lord.”
    - The idea is that on the scale of observation of God (which is infinite), even mountains will flow.
- **Deborah number:** A dimensionless number used to characterize the fluidity of materials over a given timescale. *Denoted by De. Given by*

$$\text{De} := \frac{\tau}{\tau_{\text{flow}}}$$
  - $\tau$  is the time it takes for a material to react to a stimulus.
  - $\tau_{\text{flow}}$  is the time over which the change is observed.
  - Thus, low Deborah numbers correspond to fast-flowing substances, and high Deborah numbers correspond to more immutable substances (e.g., the proverbial mountains).
- What is a rheometer?
  - A rheometer applies a controlled flow or stress via a specific geometry.
  - Many geometries to do this.
  - A spinaret is common. It’s a moving boundary, you put your sample inside, you get your force.
- Intrinsic viscosity is measured via a co-centric cylinder rheometer.

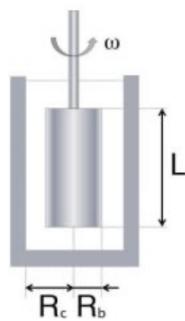


Figure 3.10: Co-centric cylinder rheometer.

- The gap is very small relative to the size of the central bob. Thus, the surface looks flat locally.
- A bit of geometry gets you your shear rate and shear stress, from which we know viscosity  $\eta = \tau/\dot{\gamma}$ .

$$\dot{\gamma} = \frac{2\omega R_c^2}{R_c^2 - R_b^2} \quad \tau = \frac{M}{2\pi R_b^2 L}$$

- Typical sample volume: 1-50 mL.
- People like these because you put your sample in, press a button, and get your result.
- Aside: Just how sensitive are rheometers?
  - Gareth McKinley (in MechE) will tell you that rheometers can typically measure 6 orders of magnitude dynamic range.
  - Modern rheometers are about an order of magnitude more sensitive than the capillary rheometer.
- Microfluidics approaches to rheometry.
  - Still pretty similar to Hagen-Poiseuille.
  - Advantages.
    - Help when you only have very little sample (as is often the case in pharma).
    - Subject fluids to variety of flows in a single device.
    - Etc.
  - Challenges.
    - No moving surface, so no direct analog to Figure 3.10.
      - Thus more similar to the capillary viscometer, fundamentally speaking.
    - Key challenge: We have to extrapolate to zero concentration to take the limit in the definition of intrinsic viscosity.
- Microrheometry overview.
  - Many types.
  - Rheometry on a chip (a device you can buy now).
  - Microrheology, also a thing we'll discuss.
- Measuring intrinsic viscosity on a chip.
  - More benefits and challenges.
- Theory for an intrinsic viscometer.

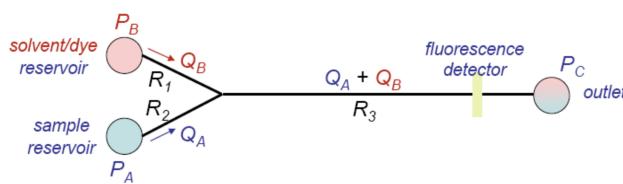


Figure 3.11: Intrinsic viscometer schematic.

- Black lines are very small; width on the order of our hair (100  $\mu\text{m}$ ).
- The rightmost circle is just an outlet; that's trash.
- One reservoir has our sample, of which we'd like to take a measurement.
- The other reservoir has just the solvent in which the sample is dissolved, and a dye!
- Flow rates are given by volumetric resistances. Then the flows combine with conservation of mass.
- You create a dilution series with optically detectable concentration.
- How an intrinsic viscometer works.
  - Recall that  $\Delta P = QR_H$ , where  $R_H = 8\eta L/\pi r^4$  is the **hydrodynamic resistance**.

- Some of  $R_H$  is geometric, and some is the viscosity.
- The geometric terms we denote  $\tilde{R}_H = 8L/\pi r^4$ .
- Hydrodynamic resistance is analogous to electrical resistance and Ohm's law  $V = IR$ .
- Four equations.

$$\Delta P = P_A - P^* = \tilde{R}_1 \eta_p Q_1 \quad (1)$$

$$P_B - P^* = \tilde{R}_2 \eta_s Q_2 \quad (2)$$

$$P^* - P^{**} = \tilde{R}_3 \eta (Q_1 + Q_2) \quad (3)$$

$$P^{**} - P^* = \tilde{R}_4 \eta (Q_1 + Q_2) \quad (4)$$

- $P^*$  is the pressure right where the two flows meet.
- $P^{**}$  is the pressure once the two flows have equilibrated.
  - We don't know what either of these are, hence why we use placeholder variables for them.
- $\eta_p$  is the viscosity of the polymer solution.
- Suppose  $P_A = P_B$ .
- Then the lefthand sides of equations 1 and 2 are the same, so

$$\begin{aligned} \tilde{R}_1 \eta_p Q_1 &= \tilde{R}_2 \eta_s Q_2 \\ \eta_p &= \underbrace{\frac{\tilde{R}_2 \eta_s}{\tilde{R}_1}}_{\text{known}} \cdot \frac{Q_2}{Q_1} \end{aligned}$$

- Pressure and flow are related in a dependent/independent relation; we can control one of them or the other, but not both. Thus, the one that we're not controlling will have to be measured.
- In this case, we're applying pressures, so we don't know the flows  $Q_1, Q_2$ .
- The detector signal divided by the max signal gives

$$Y = \frac{Q_2}{Q_1 + Q_2}$$

- The remaining math is hard and not worth our time. Using all four allows us to get rid of the unknowns  $P^*, P^{**}$  and fully analyze the system.
- Intrinsic viscometer: Device performance.
  - Lee and Tripathi (2005) showed that it worked pretty well, even with a tiny sample volume of 5  $\mu\text{L}$ .
    - Recall that a traditional viscometer requires closer to 5 mL.
  - The authors did both kinds of measurements in Figure 3.7 successfully.
  - Design calculations: The authors wanted this to be a device that everyone could use, so they defined an operating range.
    - The Deborah or Weissenberg number must be less than 1.
    - Assuming a good solvent,  $\lambda$  should scale as molecular weight to the 1.8 power.
    - We need very fast diffusion laterally across the channel so that the two fluids merge into one. This is the Pe calculation. The ratio cancelling out with fast diffusion time implies that **Peclet number** is greater than 1.
- Commercial realization: Formulaction.
  - Dye might interact with polymer; initial device was too complicated for commercialization.

- Now we let the fluids *not* mix quickly and look at the index of refraction for them flowing next to each other.
- Hydrodynamic resistance is related to the width.
- Microrheology.
  - Spherical bead probes act like constant stress rheometers.
  - Look at variations in Brownian motion!
  - We can ensemble average the trajectories (as in Figure 3.6), plot against  $\tau$ , and get  $2D$  as the parameter.
  - By Einstein,  $D = k_B T / 6\pi a \eta$ , so we can back out viscosity!
  - Can do this with a few microliters, can do this inside living objects, etc.
  - Developed by Doyle's lab!
  - Here,  $\tau$  is time, not the shear stress.
  - $k_B T$  divided by a length is a force (the way the units work out). Thus,  $k_B T$  divided by a volume ( $L^3$ ) is a force over length squared, which is a pressure. This pressure is what we call the **thermal stress**.
- High throughput microrheology.
  - By one of Doyle's old UROPs who's now doing a PhD w/ Eric Furst.
  - Each drop is a microliter experiment.
- More on Figure 1.1.
  - Doyle recapitulates what he said when he originally showed the figure.
- Expectations for PSet 3 and the Quiz: We're not gonna have to solve a pipe flow problem or anything, but the diffusivity relation to mean squared displacement is well within our wheelhouse.
- Class next Tuesday confirmed!
- Exam.
  - Average 80, standard deviation of 10.

### 3.3 Chapter 9: Dynamics of Dilute Polymer Solutions

*From Lodge and Hiemenz (2020).*

- What relates “the viscosity of polymer solutions, the diffusion of polymer molecules, the technique of dynamic light scattering, the phenomenon of hydrodynamic interaction, and the separation and analysis of polymers by size exclusion chromatography” (Lodge & Hiemenz, 2020, p. 377)? They all help determine polymer molecular weight, and they all depend on the spatial extent of polymer coils.
- We have studied *static* properties of polymer up to this point. Now, we will discuss *time-dependent* dynamics.
  - We begin our study of dynamics with dilute solutions, so as to highlight the properties of individual polymer molecules.
- **Molecular friction factor:** The proportionality factor between the force  $\mathbf{F}$  directionally applied to a polymer in a solvent, and the polymer's equilibrium velocity  $\mathbf{v}$  after accelerating to the point where drag counterbalances  $\mathbf{F}$ . *Units kg/s. Denoted by  $f$ . Given by*

$$f = \frac{|\mathbf{F}|}{|\mathbf{v}|}$$

- Figure 3.4 may be helpful in visualizing this definition.
- The textbook uses the units of g/s.
- Typical values of  $f$  for a polymer in water fall between  $10^{-7}$ - $10^{-6}$  g/s.
- Two questions we will focus on answering.
  - How can we experimentally measure  $f$ ?
  - What can  $f$  tell us about polymers?
- First model we will use: The impenetrable sphere.
  - Surprisingly accurate for certain polymers (e.g., floppy random coils, as discussed in class).
  - Allows us to use the computationally simple ideal solution model to underpin our analysis!
- Defining the viscosity of a fluid, and related terms (see Figure 3.1).
  - A *fluid* is preliminarily defined to be “a set of infinitesimally thin layers moving parallel to each other, each with a characteristic velocity” (Lodge & Hiemenz, 2020, p. 377).
  - We postulate that our fluid has no **slip** at the interface between the stationary and flowing phases.
    - This is a good approximation for the systems in which we are interested.
    - This leads our fluid to behave as a **steady flow**.
- **Slip:** Any difference in velocity between those fluid layers that are adjacent to nonflowing surfaces and the nonflowing surfaces themselves.
- **Steady flow:** The time-independent velocity profile developed when the upper plate (Figure 3.1) is moving at a constant velocity.
- We now build up to justifying the notation “ $\dot{\gamma}$ ” for the shear rate.
- **Shear displacement:** The distance  $\Delta x$  that the top layer in the velocity profile moves relative to the bottom layer during a short time interval  $\Delta t$ .
- **Shear strain:** The shear displacement per unit distance  $H$  between the two plates. *Denoted by  $\gamma$ . Given by*

$$\gamma := \frac{\Delta x}{H}$$
- Thus, the shear rate (i.e., the rate at which the shear strain develops) is given by the first time derivative of the shear strain  $d\gamma/dt$ . But in Newton’s notation, first derivatives are represented by putting a single dot over the variable being differentiated. Thus, we represent the shear rate as  $\dot{\gamma}$ .
- **Shear force:** The force applied to the top plate (Figure 3.1) to develop a velocity profile. *Also known as viscous force. Denoted by  $\mathbf{F}$ .*
- **Newton’s law of viscosity:** The statement that the shear stress  $\tau$  depends bilinearly on the viscosity  $\eta$  and shear rate  $\dot{\gamma}$  with no proportionality constant. *Given by*

$$\tau = \eta \dot{\gamma}$$
- **Newtonian (fluid):** A fluid that satisfies Newton’s law of viscosity, i.e., for which the viscosity  $\eta$  is independent of the shear rate  $\dot{\gamma}$ .
  - Liquids of low molecular weight compounds are generally Newtonian.
  - Newtonian fluids are characterized by a single viscosity.
- Any liquid that undergoes shear thinning is non-Newtonian, as a Newtonian liquid would have a straight line on the graphs in Figure 3.2 ( $\eta$  independent of  $\dot{\gamma}$ ).

- Shear thinning is often observed for polymer solutions or melts.
- Most viscometers can determine if a fluid is Newtonian by varying the shear rate  $\dot{\gamma}$  and measuring whether or not the viscosity stays constant.
- Lodge and Hiemenz (2020, pp. 379–80) covers **viscous heating**, which was not mentioned in class.

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