

3.942 (Polymer Physics) Notes

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September 29, 2025

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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 ε between atoms is much greater than $10^{-21}k_{\text{B}}T$.
- 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 $100k_{\text{B}}T$.
- **Soft matter:** Polymers, organics, liquid crystals, gels, foods, life!
 - $\varepsilon \approx k_{\text{B}}T$.
- 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.*

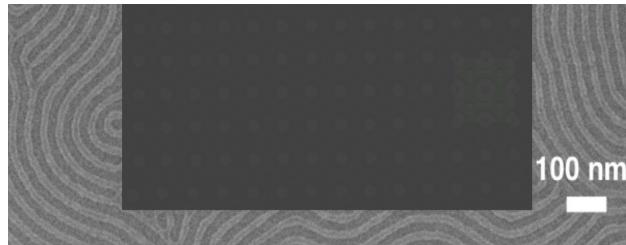


Figure 0.1: Short range order in PS-*b*-PDMS.

- 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.

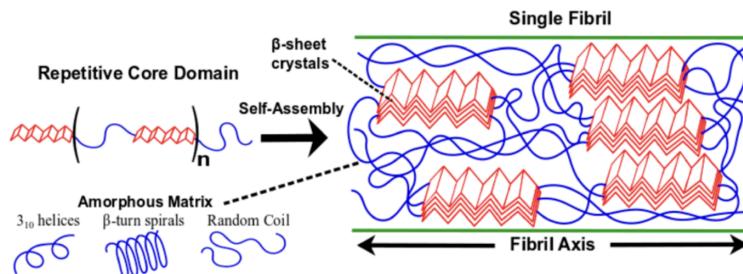


Figure 0.2: Silk.

- Made out of proteins with amorphous and crystalline (β -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.

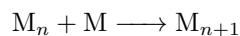
- Vinyl polymers, diene class, vinylidenes.
 - Teflon (polyvinylidene fluoride).
 - Plexiglass: Methacrylics.
 - Acrylics are more liquid; methacrylics are harder and more solid.

- Common classes of step-growth polymers.

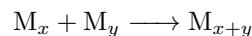
- Silicone.

- 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. Ω_{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 CH_2CH_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.

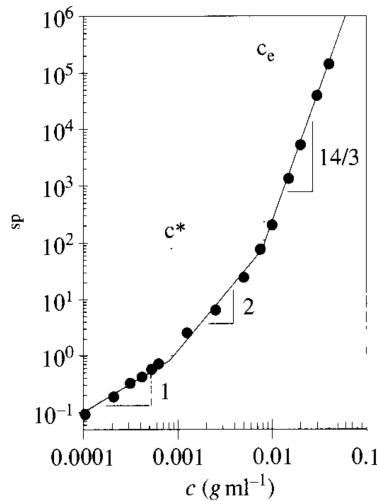


Figure 1.1: Polymer viscosity scales universally by power laws.

- 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) _n	- <i>alt</i> -	poly[(ethylene glycol) ^a - <i>alt</i> -(terephthalic acid)]
periodic	periodic with respect to at least three monomeric units	(ABC) _n (ABB) _n (AABB) _n (ABAC) _n	- <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 ^b	-AAAAAAAAAA- B B B B B 	- <i>graft</i> -	polybutadiene- <i>graft</i> -polystyrene

^a ethane-1,2-diol, ^b 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_i*:** The molecular weight of the *i*-mer. *Given by*

$$M_i := iM_0$$

- ***M₀*:** The molecular weight of the repeat unit in a polymer chain.
- ***n_i*:** 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_i*. 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 weight fraction. Denoted by *w_i*. 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_i* 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_n*. 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 σ^2 . Given by*

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

- **Schultz-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.

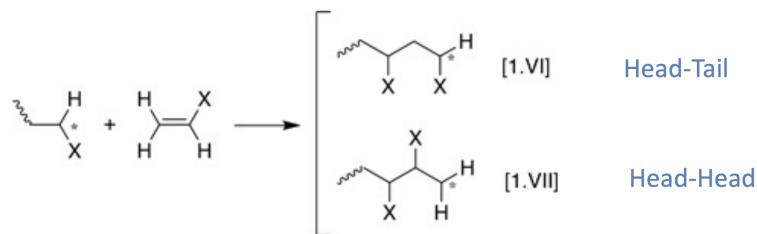


Figure 1.2: Head-head and head-tail monomer addition.

- **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**.

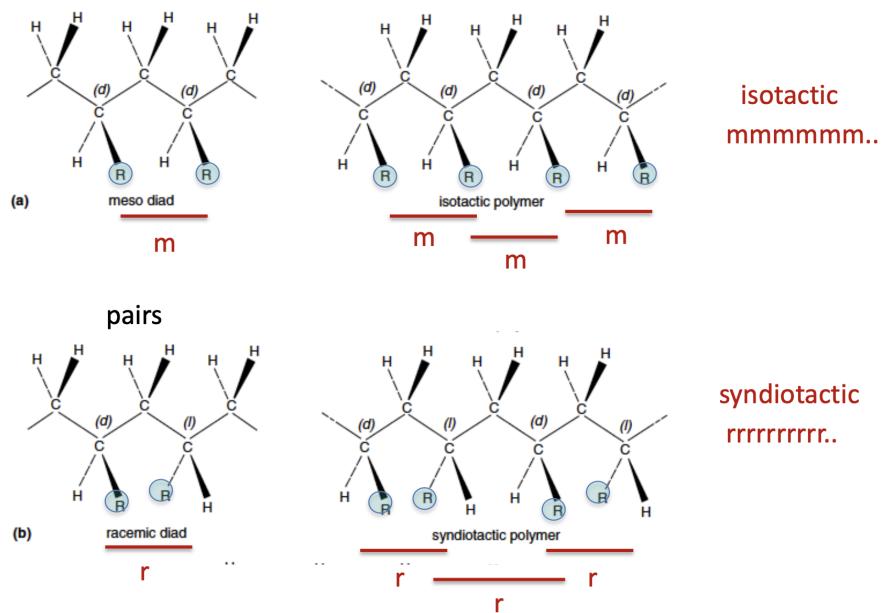


Figure 1.3: Tacticity.

- 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 ^1H 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}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° .
 - Eclipsed configuration then starts at 60° .
 - 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 θ .
 - 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^{47000} 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.

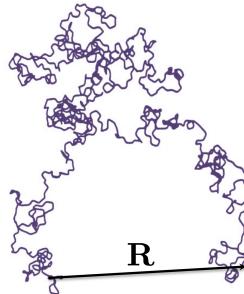


Figure 1.4: End-to-end polymer vector.

- 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.

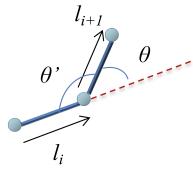


Figure 1.5: A joint in a polymer chain.

- 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 θ 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 θ , but there is no energy penalty to rotate in ϕ .
 - 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 ϕ but not in θ .

- 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 ϕ 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_∞ 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 θ and ϕ in different texts!

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

Polymer	Structure	C_∞
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_∞ values for common polymers at 413 K.

- C_∞ 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 (CH_2CH_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.

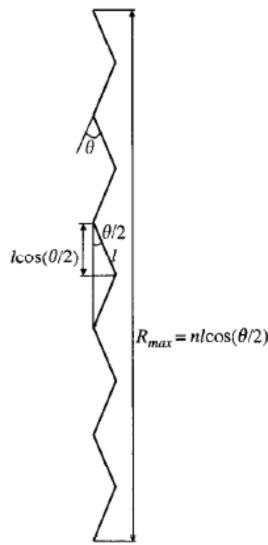


Figure 1.6: Straight chain estimation of a polyolefin.

- 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.

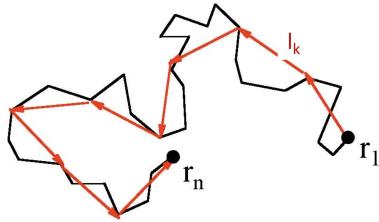


Figure 1.7: Kuhn steps.

- 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_∞ 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).

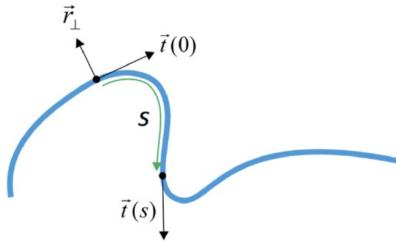


Figure 1.8: Worm-like chain.

- 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 κ_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 1000s 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. *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 . Given by*

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

- 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. *Denoted by c^* .*

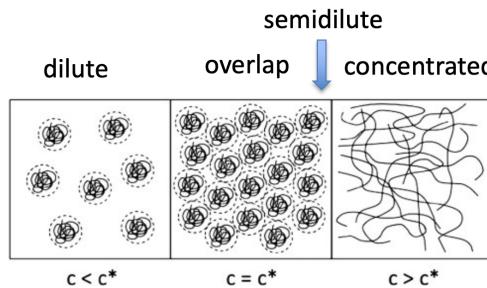


Figure 1.10: Concentration regimes.

- 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 α .
- 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}_{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.

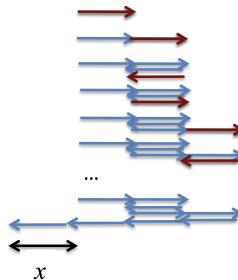


Figure 1.11: Progression of a 1D random walk over time.

- 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 Ω of ways (microstates) in which you can move a distance x is

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

- Ω 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 Ω 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 Ω 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 Ω 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 Ω_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!^[1]
- 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).

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

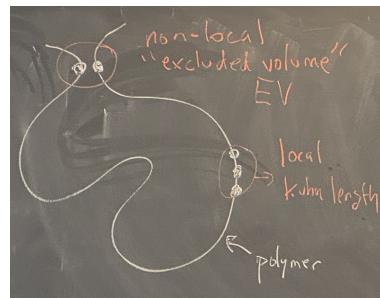


Figure 1.12: Local and non-local interactions in a polymer.

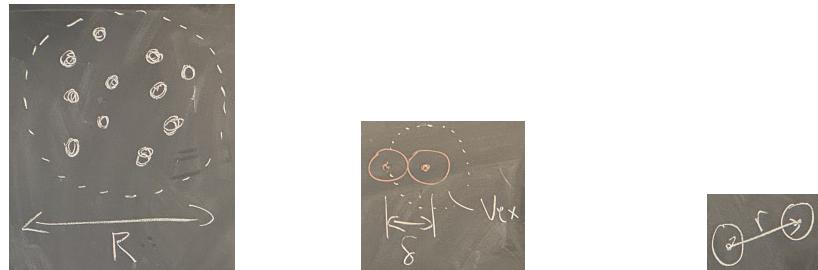
(a) Gas in a volume R . (b) Excluded volume. (c) Distance between monomers.

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 δ , 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

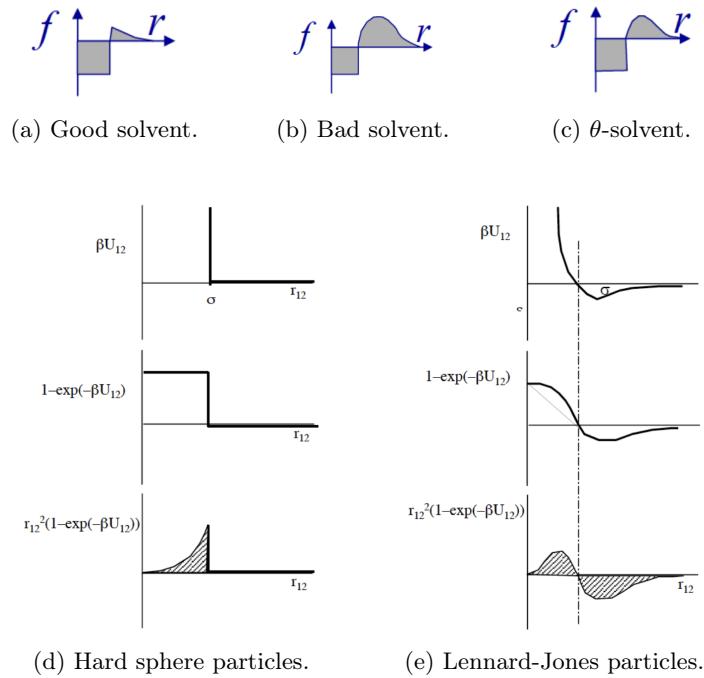
$$f(r) = \exp\left(-\frac{U(r)}{k_B T}\right) - 1$$

- $f(r)$ 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 θ -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 θ -temperature or θ -solvent.
 - In contrast, for the Lennard-Jones potential (Figure 1.14e), there are both repulsive and attractive contributions. Thus, there *will* be a θ -temperature in each θ -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_{ex} and T more explicitly!
- The heart of polymer physics is Flory mean-field approximations.

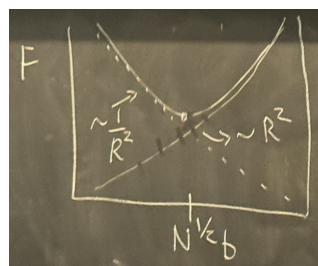


Figure 1.15: A post-facto compression penalty.

- In a θ -solvent, $F = -TS$ (because $U = 0$).
- As we derived above, for this situation, the entropic free energy F_{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.
 - This gives us a term for binary interactions, ternary interactions, etc.
 - We say concentration is approximately equal to the number of monomers divided by R^3 (throwing out prefactors like $4/3$ and π).
- In a good solvent, $R > Nb^2$ because the polymer swells due to V_{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

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

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

- The full Flory free energy has many terms that all balance; you play with the ingredients to see what fits.

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

- 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 θ -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** α 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_2O 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.^[2]
- **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**.

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

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 reactions 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.
 - 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 positoin 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.

Topic 2

Solution Thermodynamics

2.1 Flory-Huggins Theory

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

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

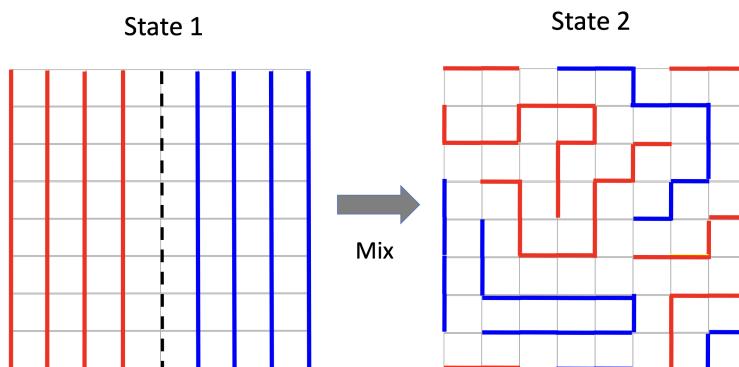


Figure 2.1: Lattice theory for polymer phase behavior.

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

¹“HOY-gins”

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

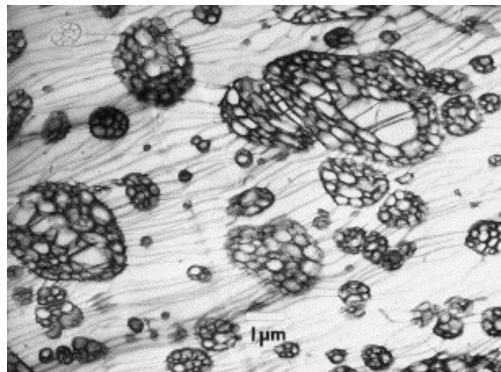


Figure 2.2: Salami phase micrograph in styrene-butadiene mixtures.

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

- Last lecture, we derived a free energy functional for single chains.
 - Today, we're looking at $G = H - TS$.
 - What we're really interested in is the free energy of mixing,
- $$\Delta G = G_{1,2} - (G_1 + G_2)$$
- In multicomponent systems — besides the typical parameters of excluded volume, etc. — we need to know...
 - How many chains we have of each type;
 - What their degree of polymerization is;
 - What total volume do they occupy.
 - Thus, in State 1, we have

$$V_1 = n_1 N_1 v_1$$

$$V_2 = n_2 N_2 v_2$$

which describes two separate phases...

- Containing n_i moles of species i ;
- With degree of polymerization N_i ;
- Each occupying a total volume V_i .

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

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

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

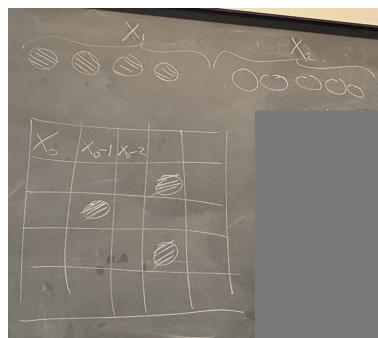


Figure 2.3: Configurations in mean field lattice theory.

- We get another binomial because we're adjacent to a random walk where we have 1 or 2 in each adjacent cell as we go along.
- As we fill up the grid, we first have access to all X_0 of the objects. Then we have 1 less, then we have 2 less, etc.
 - But since all the objects in group 1 or group 2 are the same, we need to divide out by the number of objects X_1 in category 1. We need to do the same because all objects in X_2 are the same.
 - Thus,

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

- It follows that the change entropy ΔS upon mixing is

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

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

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

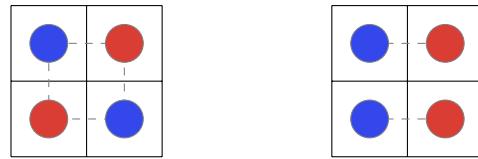
- It follows that the entropy per site $\Delta S/k_B X_0$ is

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

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

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

- It follows that $\phi_i = X_i/X_0$ is the volume fractions for spaces i .
- Consequence: $\phi_1 + \phi_2 = 1$.
- Note: An assumption underlying the use of the Boltzmann equation is that all microstates have equal energy. This isn't strictly true, but it's a good enough approximation.



(a) Energy E_1 system. (b) Energy E_2 system.

Figure 2.4: Nearest neighbor interactions.

- Example: Assume nearest neighbor interactions matter.
- Let opposing objects in neighboring cells contribute energy ε_1 to the total energy of the system. This means that in Figure 2.4, $E_1 = 4\varepsilon_1$ and $E_2 = 2\varepsilon_2$.
- In big systems, the energy won't fluctuate much, though, so Boltzmann equation is more of an approximation, but it's *good enough*.
- Mean field mixing enthalpy.

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

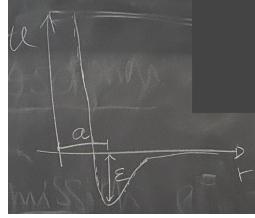


Figure 2.5: Potential well.

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

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

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

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

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

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

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

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

and hence

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

where

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

is the **Flory χ parameter**.

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

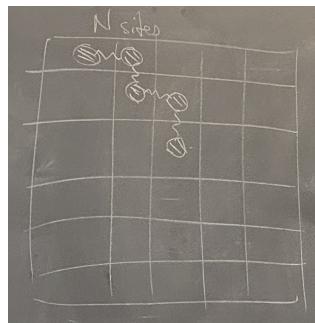


Figure 2.6: Fitting polymers into a square lattice.

- We have to pick N adjacent sites.
 - Then the next time we pick is the number of sites minus $N!$ And on and on.
 - This essentially reduces the number of sites by N_1 and N_2 .
 - When N is very big, this equation tells us that entropy doesn't play a huge role (because N_1, N_2 in the denominator). Thus, enthalpy matters more for polymers.
 - Finally, we have gotten to the “famous Flory-Huggins theory of free energy.”
- $$\frac{\Delta G_M}{X_0} = k_B T \left(\chi \phi_1 \phi_2 + \frac{\phi_1}{N_1} \ln \phi_1 + \frac{\phi_2}{N_2} \ln \phi_2 \right)$$
- We get this by adding the enthalpic and entropic contributions via the .
 - How do we measure χ experimentally?
 - We will explore this soon.
 - Influence of χ on phase behavior.
 - When χ reaches 2-3, we get demixing.
 - When $\chi = 2$, free energy is largely flat. Thus, very different compositions have similar free energy, which means that the system will “undergo a 2nd order transition where all length scales are viable.”
 - A parameter that has gained more importance in recent years: The coordination number z .
 - It turns out that the more neighbors you have, the better mean-field behavior you get.

- This is essentially because you're averaging over more values.
- Recent finding: χ is pretty good if z is big; if z is small, quadratic and other higher order corrections may be necessary for χ .
- The χ at which you see phase separation decreases exponentially with increasing $N_A = N_B = N$.
 - N is just how long the chains are!
- Preliminaries to next class.
 - Construction of phase diagrams.
 - You have a critical point graph that gets flipped??
 - Inside one is binodal line; outside one is spinodal line.
 - Between the two inflection points, the system is unstable.
 - Concave curvature puts sum of two free energies below the points.
 - You will evolve toward the two lowest energy points, phase separating as needed.
 - Demixing occurs by nucleation and growth.

2.2 The Theta State

9/23:

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

$$\mu_i := \left(\frac{\partial G}{\partial n_i} \right)_{T, P, N, n_j} \quad (j \neq i)$$
- **Coexistence curve:** The set of points where the chemical potentials are equal. *Also known as binodal curve.*
 - The coexistence curve encloses all compositions wherein the mixture demixes into two distinct, coexisting phases.
 - Symbolically, letting the two phases in the mixture be called prime and double prime, we have for each component 1 and 2 that
$$\mu'_1 = \mu''_1 \quad \mu'_2 = \mu''_2$$
 - In PSet 2, we'll derive one of the expressions on this slide.
- Spinodal inflection points are where the 2nd derivative is zero.
 - Critical points has 2nd and 3rd derivatives equal to zero.
 - *equations in slides*
- Polymer-solvent solutions.
 - An interesting way of thinking about this: Osmometry.
 - Imagine a uniform, mixed polymer solution.

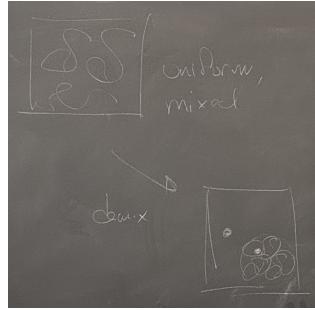


Figure 2.7: Demixing of a polymer-solvent solution.

- We can demix to a state where the polymer is all clumped together.
- The clumps still have some solvent in them though.
- The phase separation stops when a solvent molecule *inside* and *outside* the polymer clump has the same chemical potential.
- Important relevant expressions.

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

- Remember that by convention, phase 1 is the solvent and phase 2 is the polymer.
- Notice the multiplying vs. dividing of N_2 .
- For a polydisperse system of polymer chains, let $N_2 = \langle N_2 \rangle = M_n$.
- We'll now massage the above expressions to get some more mechanistic understanding out of them.
- Chemical potential for a dilute solution.

- Since we are positing a dilute solution, we may use the approximation that the volume fraction of component 2 is small. This will allow us to expand the expressions.
- For small x , the following approximation holds.

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

- We can use fewer terms for quite small x .
- It also follows from the assumptions that (1) the solution is dilute, i.e., $n_1 \gg n_2 N_2$ and (2) that the volume of the monomers is approximately equal, i.e., $v_1 \approx v_2$ that

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

- We thus expand

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

- It follows that

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

- Since it's negative, this tells us that the chemical potential μ_1 is always less than μ_1° , which means that the term is always negative, so everything wants to mix.
- In a subsequent course, we describe more results based off of the above equation!
- Phase diagram for a dilute polymer solution.
 - The condition where ?? is the θ condition.
 - Positive χ means that polymers don't like the solvent as much as they like themselves.
 - As N_2 increases, we push to lower fractions.
- It is very difficult to mix high MW polymers because you will need $\chi < 2/N$.
- Solubility parameter and χ .

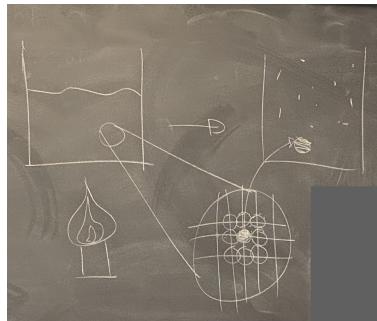


Figure 2.8: Hildebrand's experiment.

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

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

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

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

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

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

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

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

➤ Scales as $1/r^6$, and also has the **polarizability / polarizability volumes**.

➤ This is related to dipole-induced dipole attractions; when you average over all possible combinations, this relation falls out. And that's what Lennard and Jones based their use of $1/r^6$ as the attractive term on!

➤ In PSet 2, we will prove that this attraction rule is "like likes like."

- Then

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

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

➤ v is a volume.

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

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

➤ This works better for nonpolar than polar species.

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

- See Rubinstein and Colby (2003) for an in-depth discussion of this setup.

- Let's now compare the curve with experiments.

- PS in cyclohexane.
- Dashed lines are the Flory-Huggins theory, which clearly doesn't look like the experiment at all.
 - This is because of Flory's mean field assumption, which doesn't hold here. Indeed, as you heat up, you will be more likely to have the same neighbor.
 - Actual curve is wrong, but scaling is correct (this happens in several of Flory's theories).
- Reference: Shultz and Flory (1952).

- Phase diagrams of polymer-polymer blends.

- ϕ for the fraction that a chain occupies is

$$\phi = \frac{Nv}{(N^{1/2}\ell)^3} \approx \frac{v}{\ell^3} N^{-1/2}$$

- Two principal types of phase diagrams.

- Demixing at higher temperatures, vs. mixing at higher temperatures.
- Poly(methyl methacrylate) / styrene-*co*-acrylonitrile demixes at increased temperature (because molecules are polar).
- Polystyrene / polyisoprene mixes at higher temperatures.
- PEG and PMMA have a negative χ at room temperature. PEG and H₂O is similar (you heat it up, and the polymer comes out of solution).
- pNIPAM undergoes a transition around 32-34 °C.
- Attraction gives rise to a low or negative χ .
- A number of references on polymer blends are included in the slides!

- You can arrest a spinodal decomposition by heating and then cooling very quickly.

- Applications of FH theory.

- Biocondensates and membrane-free organelles (like the nucleolus and centrioles). Identified another bunch of these after they expanded their definition of organelles! These things come together because of FH theory.

- Next time.

- Self-assembly.

- The PSet 2 might be a bit long, so start early! We should currently be able to do every problem up to 3, and after Thursday, we should be able to do every problem.

2.3 Phase Behavior, Melting Point Depression, Osmometry, and Microphase Separation

9/25:

- Last time.
 - Entities that are not covalently bonded.
- Today.
 - Entities that *are* connected together.
 - You cannot get rigid phase separation here.
 - Self-assembly is a thing.
- Lecture outline.
 - Copolymers.
 - Microphase separation.
 - Interfacial free energy.
 - Chain stretching and configurational free energy.
 - This will bring back concepts from Professor Doyle's class.
- A bit more on biocondensates (not testable material).

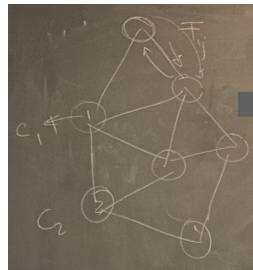


Figure 2.9: Simplified graph of a biochemical network.

- Correction: The protein discussed last time goes into solution if you *add* salt.
- Principle in biology: At some point, it gets better to have things that do multiple tasks poorly than one task really well.
 - This is because it takes energy to produce proteins.
 - Example: In computer science, engineers used to spend a lot of time to make 1 really nice transistor. But now, they go for a lot of transistors that are almost all the same and you connect them in different ways. Now you can do basically any task, but not all of them are great. In D. E. Shaw, they have a computer that *only* runs molecular dynamics (1000 times faster than Nvidia GPUs), but that's the only thing it does.
 - So since we need a lot of functions in a cell and we don't want to produce a lot of very specialized proteins, it's better to be a bit more general.
- Suppose you have a (biochemical) network, and we control each transition between nodes locally (Figure 2.9).
 - 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).

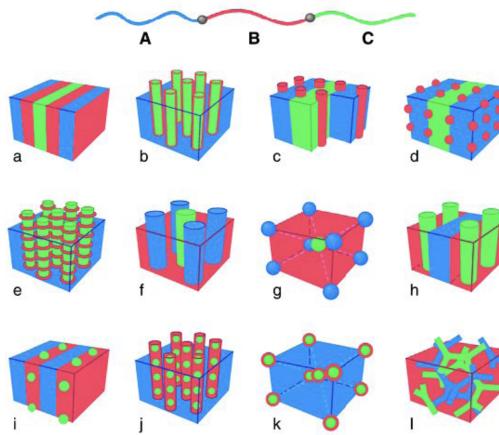


Figure 2.10: Self-assembly of an ABC triblock copolymer.

- What aspects of an ABC triblock copolymer affect its organization?
- There will be **intra interactions** χ_{AB} , χ_{AC} , and χ_{BC} between the various components of the chain.
- Let the chain have total length N , and let each of the three segments have length N_i .
 - Then we have N_A , N_B , and $N_C = N - N_A - N_B$.
 - If we have something like (a) of Figure 2.10, 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 2.10 with 3 things, imagine how much we can do with the 20 amino acids!
 - Note on the “hydrophobic” amino acids: They have branching (see valine, leucine, isoleucine)! Nature doesn’t just use n -alkyl chains of different length because the methyl groups sticking off have partial charges of 0.4 (40% the charge of an electron), which makes them still pretty polar.
 - Tyrosine can use its phenolic substituent to *enhance* its π -cation non-covalent interactions relative to phenylalanine.
- Key question: How can a homogeneous state go to a semiordered state, to an even more ordered state?
 - Example: Unfolded protein, to good prions, to rogue prions.
 - Aside: In rogue prions, there is an exposed β -pleated sheet, which will stack vertically with the β -pleated sheets of other prions. This stacking is what causes the brain to shut down in Mad Cow Disease.
- Goals for self-assembly.
 - Understand the key concepts behind the process of self-assembly, in particular for the case of block copolymers.
 - Construct a simple formalism to determine which variables contribute more relative to other ones.
 - Recent stuff on how to control self-assembly using external methods.
- **Min-max principle:** Phases are most stable when we (1) minimize interfacial energy and (2) maximize the conformational entropy of the chains.

- The min-max principle governs self-assembly.

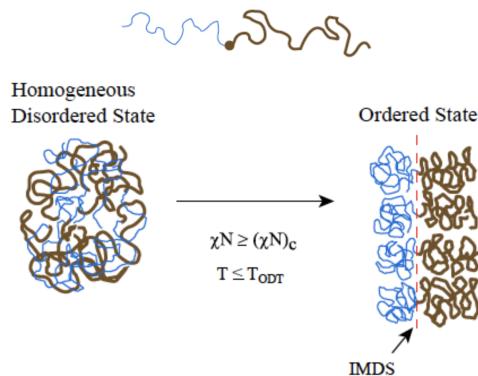


Figure 2.11: Ordering of a diblock copolymer.

- 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 2.11 means "critical."
 - Remember that χN controls whether or not we develop microdomains (more on this below). We will investigate this in PSet 2, too.
- Principles of self-assembly: Microphase separation in diblock copolymers.

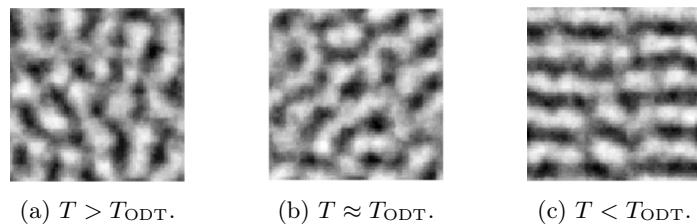


Figure 2.12: Microphase separation in diblock copolymers.

- 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 2.12a-2.12c, you get into a lamellar state.
- Microdomain morphologies: Diblock copolymers.

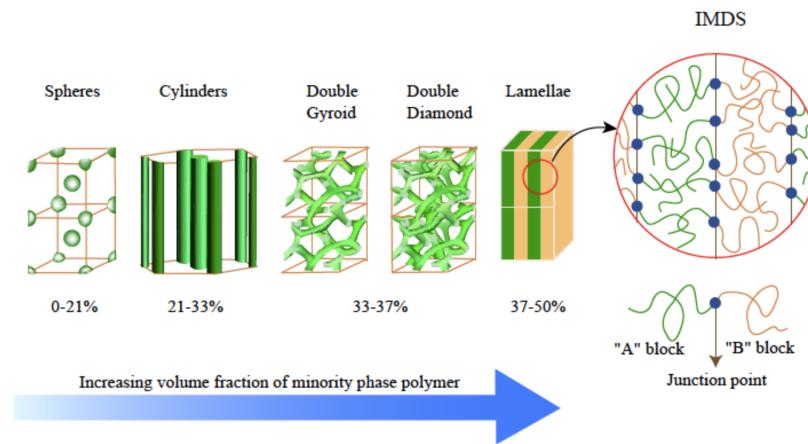


Figure 2.13: Microphase morphologies in diblock copolymers.

- In contrast to Figure 2.13, 40-60% gets you a lamellar state. This accounts for the fact that going on either side of 50% is equivalent.
- On the outskirts of this, you get **bicontinuous phases**.
 - The Double Diamond is heavily sought after in optics.
 - Double Gyroid is more common.
 - Difference is tri- vs. tetracoordination at the nodes.
- Then cylinders.
- And an even smaller amount of green gets you spheres.
- **Bicontinuous** (phases): Two demixed phases such that for any two points in a single phase, there exists a path between them that never crosses a phase boundary.
- Where are the above morphologies used?
 - Example: Krayton's / green rubbers.
 - This is a PS-*block*-PB-*block*-PS polymer, with a big PB domain.
 - The PS ends either land in another domain, or come back to the same domain.
 - Good for high-performance applications, like the rubber in an F1 track.
- We now investigate microdomain spacing for diblock copolymers.
- Variables to be aware of.
 - G is the free energy per chain;
 - $N = N_A + N_B$ is the number of segments per chain.
 - a is the step size.
 - λ is the domain periodicity. *look up definitions!!*
 - Σ is the interfacial area where the chains actually interact.
 - γ_{AB} is the interfacial energy per unit area. It will be computed using Helfand's equation.

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

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

- Free energies of these diblock copolymers.

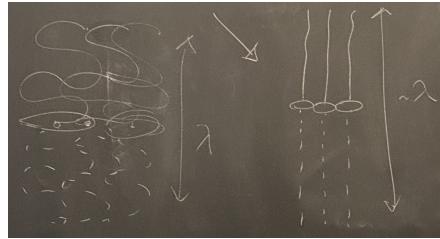


Figure 2.14: Entropy and enthalpy changes as diblock copolymers are stretched.

- We have

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

- The entropic term relates to the springiness of the polymer.
- Note that $Na^3 = \Sigma \cdot \lambda/2$. This essentially equates (1) the total volume occupied by N monomers each of volume a^3 and (2) the volume of the cylinder bounding said monomers, a cylinder having height $\lambda/2$ and base area Σ .
- Important assumption: Chains want to stretch away from the interface.
 - Enthalpy goes way down when you have linear strands (everything is near each other). Entropy goes way up here, though, because we're stretching.
 - In the other regime, though, area is way bigger. This means we get more enthalpy.
 - $\Delta S \approx \lambda^2/a^2 N$.
 - System will try to find the optimal balance between the two; we want to optimize the length λ .
- To find the optimal λ , we'll want to find the minimum Gibbs free energy as a function of λ .

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

- By above definitions and equalities, the first term is the interfacial energy per unit area times the area of the interface.
- Compressing every non- λ variable in the above expression into a constant (termed α , β , const_1 , or const_2) reveals that the above equation is of the following general form.

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

- Thus, the optimum period of the lamellae repeat unit is

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

- The result that λ_{opt} scales as $N^{2/3}$ is important! It implies that chains in microdomains are stretched compared to the homogeneous melt state (in which scaling is the smaller $N^{1/2}$).

- Let's now investigate the order-disorder transition temperature.

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

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

- Since the first two terms are both much greater than the third term, we neglect it.

- Thus, the sign of ΔG will depend on which of the two remaining terms is bigger.

- Let's analyze the case of a 50/50 volume fraction of components A and B. Specifically, we want to know what the critical $N\chi$ value is above which $\Delta G = -$ and we form lamellar microdomains, and below which $\Delta G = +$ and we stay in a homogenous melt.

- In a 50/50 split, $\phi_A = \phi_B = 1/2$. Thus,

$$\phi_A \phi_B = \frac{1}{4}$$

- It follows that the critical $N\chi$ value ($(N\chi)_c$) is

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

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

- 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, $\Delta S \approx H^2/a^2 N$ (as opposed to $\lambda^2/a^2 N$ from earlier).

- We want to minimize H^2 and $1/H$ on an H vs. Gibbs free energy graph.

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