

3.942 (Polymer Physics) Notes

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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*.
 - 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.



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 basquetbol](#)) 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.

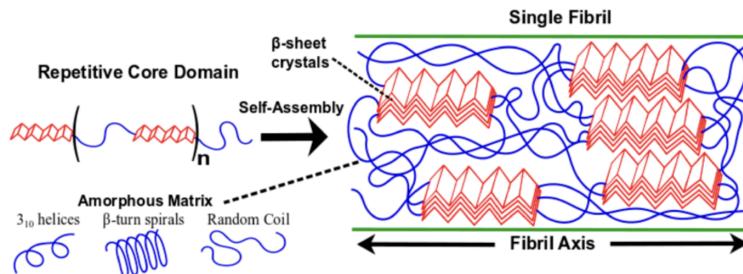


Figure 0.2: Silk.

- 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.

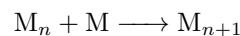
- Vinyl polymers, diene class, vinylidenes.
 - Teflon (polyvinylidene fluoride).
 - Plexiglass: Methacrylics.
 - Acrylics are more liquid; methacrylics are harder and more solid.

- Common classes of step-growth polymers.

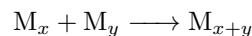
- Silicone.

- 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.

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