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# Polymers and Composite Materials

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# POLYMERS AND COMPOSITE MATERIALS

By

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# Polymer and Composite Materials

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**Preface:**

This text serves to cover in more detail polymer physics concepts and specifically how polymers respond from the atomistic to meter length scale. This text spans topics from polymerization chemistry, chain models, Flory-Huggins theory, viscosity, characterization techniques, self assembly, polymer dynamics, viscoelasticity, and mechanics of polymer and composite materials.

## Acknowledgments

For Charles Mansion.....not that one.

The information presented in this OER would not have been possible without the outpouring support from many family members, faculty, colleagues, and friends. In particular I would like to point out Professor Sam Allen, Krystyn Van Vliet, Michael Cima, Alfredo Alexander-Katz, Reid Van Lehn, and Yoda Patta.

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# CHAPTER 1

## INTRODUCTION, BONDING, POLYMER CHAIN STRUCTURE

## 1.1 Key Terms/Definitions:

- **Soft material/soft matter** - molecules that are held together by strong intramolecular bonds, by weak intermolecular bonds with energies on the order of thermal energy kT.
- **Monomer vs Repeat Unit**
- **Thermoplastic, Thermoset, Elastomer**
- **Polymer Structures and Configurations**
- **Inter vs Intra Molecular Interactions**
- **Hydrogen, Hydrophobic, Ionic, Dipole, Van Der Waals**

## 1.2 Soft Matter/Polymers:

Although we will typically focus on polymers in this course, a majority of the concepts that we will discuss will apply to **soft materials/soft matter**. The field of soft matter/materials concerns the class of materials which can include polymers, nanoparticles, organic-inorganic hybrid systems, colloids, and liquid crystals. The study of soft matter is particularly relevant as most **biological systems** are composed primarily if not entirely of soft matter. Thus some of the fundamental principles/physical insights that we will gain into polymers may be applicable more generally to biological systems as well.

Polymers and soft matter have become extremely prevalent everyday life after WWI even though naturally occurring polymers (wood, rubber, silk, cellulose) have existed for centuries. Quick note, the ancient Mayan civilizations not only utilized natural rubbers as materials for sport equipment but also were the first to cross-link rubber as well, long before Charles Goodyear in 1839. Soft materials and polymers are becoming more and more important and are rapidly replacing metallic and other materials in a myriad of applications. We have transitioned from the Stone age to Bronze, Iron, Steel, Silicon (1950), and are currently in the **carbon/polymer/plastic age**.

**Polymers will typically have much lower Young's modulus, strength, temperature use range, and are poor conductors of electricity and heat**. However, polymers are cheap and easy to process, have a lower density, and are more resistant to chemicals that most metals. The are also dynamical at room temperature and are constantly fluctuating and re-configuring bonds which gives rise to self-healing behavior. **For many mechanical applications there is a concerted effort to move to materials with a high strength to density ratio**. This

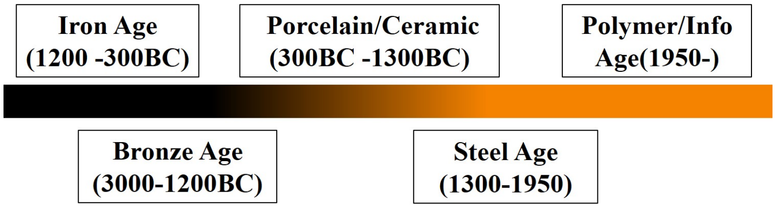


Figure 1-1: Living in the Polymer Age

motivation should be clear for applications in **aerospace and electric vehicles** as replacing dense materials with light weight alternatives will reduce fuel consumption and thus cost. You can see an example of this in the Ashby plot below, named for Michael Ashby who developed a software which plots a scatter plot in a Log-Log scale to compare properties of different.

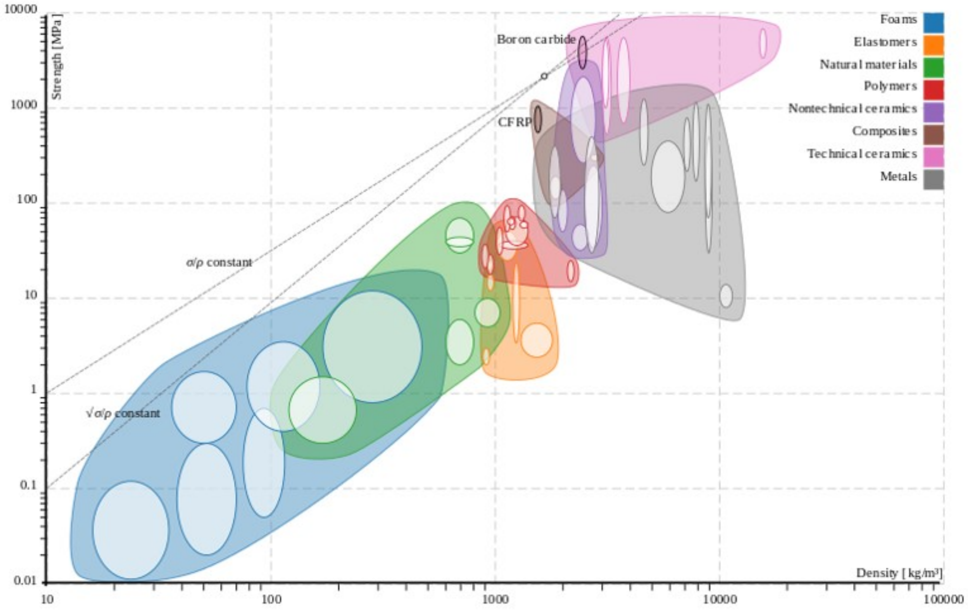


Figure 1-2: Ashby plot of strength vs density.

It is clear from this plot that **polymers and certain natural materials or elastomers can achieve the same strength at an order of magnitude lower density**.

Now polymers microstrucually, mechanically, and in many other aspects are much more complicated and difficult to study than metals or ceramics. You will see in this class over and over again that the basic principles you learned in Materials Science for how to analyze metals and ceramics will often have to be modified or an additional wrinkle will have to be added to study polymeric materials or soft matter. However, once you understand polymers you will find your understanding of metals and ceramics will be much better as well. Once you study polymers you can do anything!

## 1.3 Basic Structure/Configuration of Polymers/Soft Matter:

So let's start with the basics and describe the basic structure of a polymer. In 1920 **Staudinger** first hypothesized that polymers were not composed of many molecules but instead he believed that polymers were composed of **very large molecules containing long sequences of simple chemical units linked by covalent bonds**. Staudinger even gave them a name, **macromolecules**. Macromolecules or polymers are giant chainlike molecules composed of long sequences of one more more species of atoms or groups of atoms (monomer) linked together via covalent bonds. These monomers, also called structural units for protein or peptides, are the basic building blocks of polymer chains as seem below

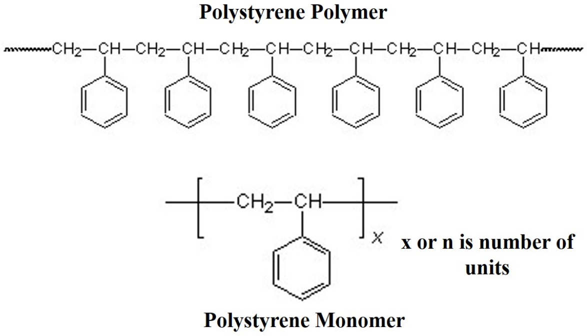


Figure 1-3: Polystyrene monomer and polymer.

These are often confused with a repeat unit which is understandable because in certain cases a repeat unit and a **monomer or structural unit** are the same. A **repeat unit** is a structural unit or combination of structural units that repeat along a chain.

Let's do a quick problem with distinguishing between a repeat unit and a structural unit in the three images below identify the number of structural units and then number of repeat units

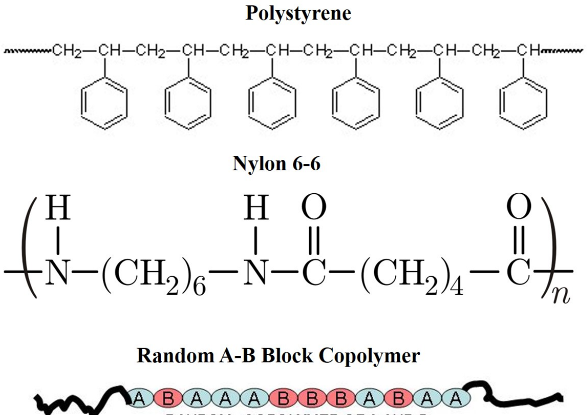


Figure 1-4: Find number of structural and repeat units.

As you can see for polysytrene we have 1 structural unit and 1 repeat unit. This is a typical scenario that you will see for polymers in some polymerization methods. For nylon 6,6 we can actually see two distinct structural units but again only 1 repeat unit. For the random block copolymer we again see 2 structural units but 0 repeat units. Once we get into the polymerization chemistry next lecture you will be able to start distinguishing/recognizing these different structural units. The process by which many monomers are linked together to form a polymer chain is **polymerization.** Much more on polymerization chemistry in the next lecture. You can see an example of polystyrene below

Many monomer units and polymers in general are organic and thus are composed of many hydrocarbons, i.e. molecules composed of hydrogen and carbon. Carbon can form 4 single bonds with hydrogen and this is referred to as a **saturated hydrocarbon**. Here are some common saturated hydrocarbon polymers that you may come across.

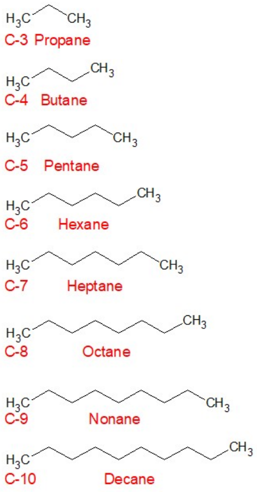


Figure 1-5: Hydrocarbon polymer chains.

If there are **double or triple bonds** then we are dealing with **unsaturated hydrocarbons**, the implications of this will be important when discussing lipid bilayers, $T_g$, and other polymer concepts. A polymer chain can be composed of **less than 100 monomers is referred to as a oligomers** (waxy polymers). However polymers are typically composed of up to **10-100k monomers**. Polytheylene for example is typically composed of $10^4$ monomers. Additionally the monomers may typically be composed of other functional groups or molecules that are a bit more exotic than hydrocarbons and this will imbue some very unique properties to these polymers. Some of the functional groups you may come across can be seen below (no need to memorize them but become a familiar with them to brush up on your chemistry).

Note that R just stands for some arbitrary side group that can be attached, we will discuss this much more in detail next lecture when we discuss polymerization. Additionally here are some common polymers that we will encounter in this class as well as in the real world.

Now we have mentioned the term chain quite a bit when describing the basic structure of a polymer and we will continue to use this description as many of the scenarios that we will

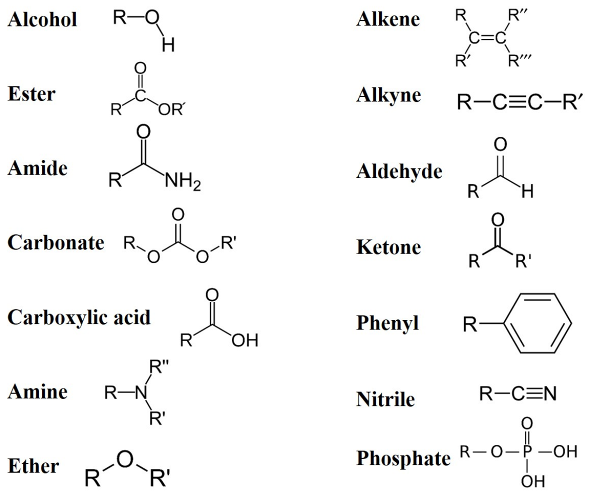


Figure 1-6: Functional groups.

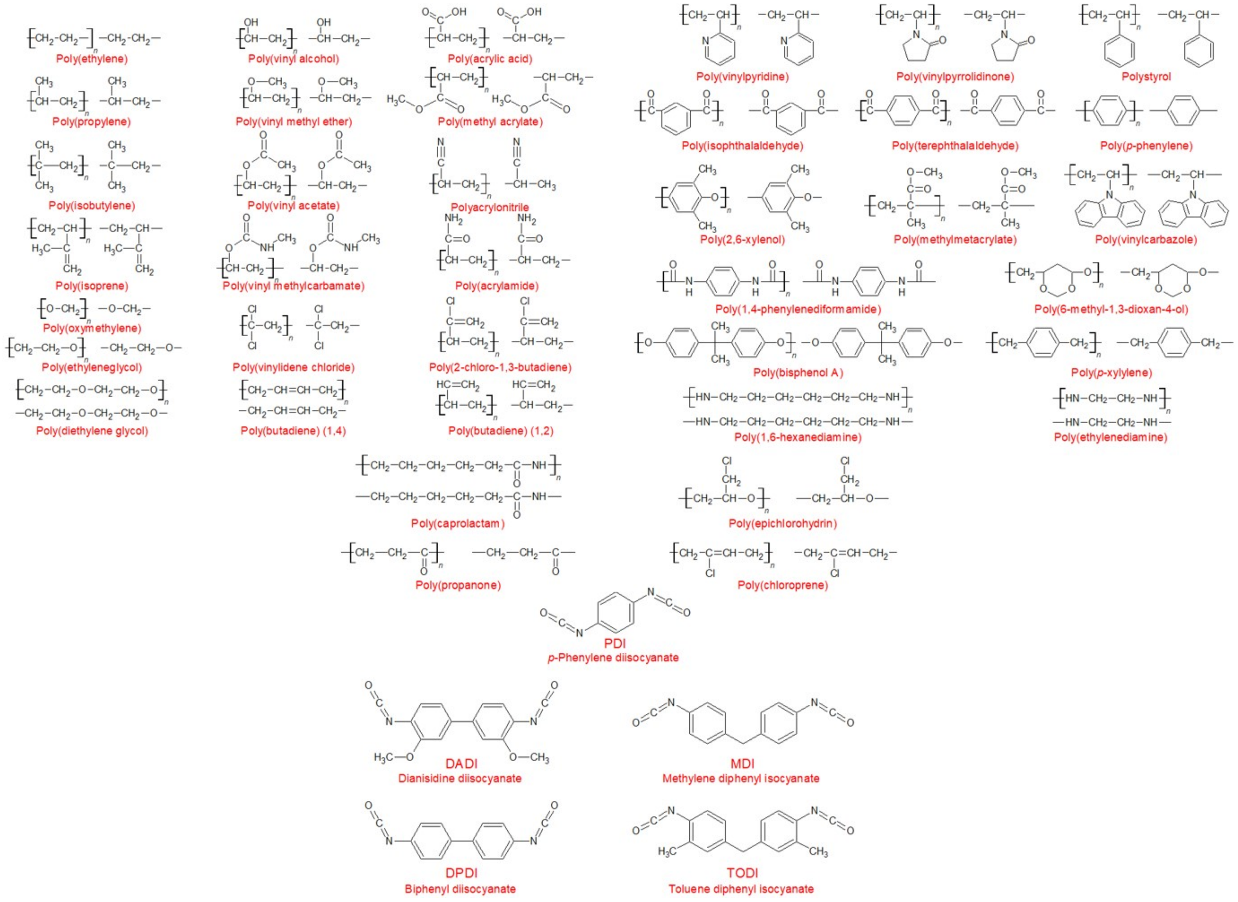


Figure 1-7: Common polymers.

discuss involves treating the **polymer like a random coiled chain, like spaghetti**. However, polymer structure/architecture can vary dramatically and the structure can have implications for the polymer properties. Polymers can be

- **Linear** i.e. polyethylene (PE), polyvinyl chloride (PVC), polymethyl methacrylate (PMMA)
- **Branched**
- **Crosslinked/Network**
- **Ladder**
- **Comb**
- **Star**
- **Dendrimer**
- **Copolymer**

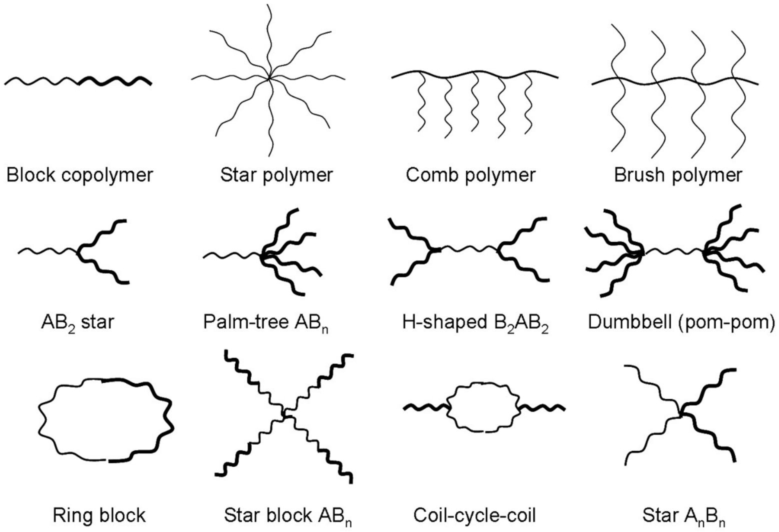


Figure 1-8: Polymer Architecture.

A linear polymer can also be cyclic or closed linear or like a rigid rod. The crosslinked structure will have very different properties (mechanical) depending on type and number of crosslinks. The copolymer structure is one we will return to again later on in the course when we discuss block, random, and graft copolymers.

**Polymer Configurations:**

We have talked about different polymer structures but polymers will also often adopt different configurations depending on a variety of factors like temperature, environment, solvent, and external stimuli. Some of these configurations are listed and seen below

- Random Coil

- Folded Chain
- Extended Chain
- Fringed Micelle

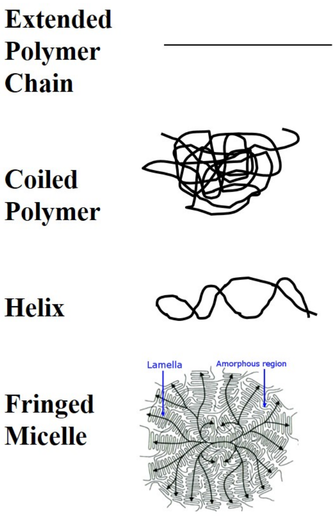


Figure 1-9: Polymer Configurations.

## 1.4 Basic Types/Classification of Polymers:

In addition to structure we can also classify polymers more broadly as being in three distinct groups

1. **Thermoplastics**
2. **Thermosets**
3. **Elastomers**

A **thermoplastic** polymer, the polymer we will discuss most often, can be a linear, branched, comb, star, dendrimer, or copolymer which will **soften or melt upon heating**. **On cooling** they will **harden** and this process of softening and hardening is **reversible** and can be repeated. As the temperature increases the i**nter-molecular bonds are broken**, i.e. the secondary bonds not the covalent bonds. Upon cooling the entire polymer will not crystallize due to the unfavorable energetics of ordering of highly coiled polymer chain. However, some regions of the polymer will form semi-crystalline regions where both crystalline and amorphous regions exist. These semi-crystalline polymers are characterized by their **melting temperature,** $T_m$. However, many polymers are completely amorphous and cannot from any crystalline regions and these polymers are characterized by their **glass transition temperature,** $T_g$, which the temperature which indicated the onset of cooperative segmental mobility. Cooperative segmental mobility refers to the **cooperative motion of 10-100's of polymer repeat units**. You can also think about the glass transition as the transition from a **glassy state (hard) to a more rubbery state (soft)**. Much more on glass transitions later. Thermoplastics can be easily fabricated via extrusion/injection and include polymers such as PE, polystyrene (PS), PET, PVC, PMMA.

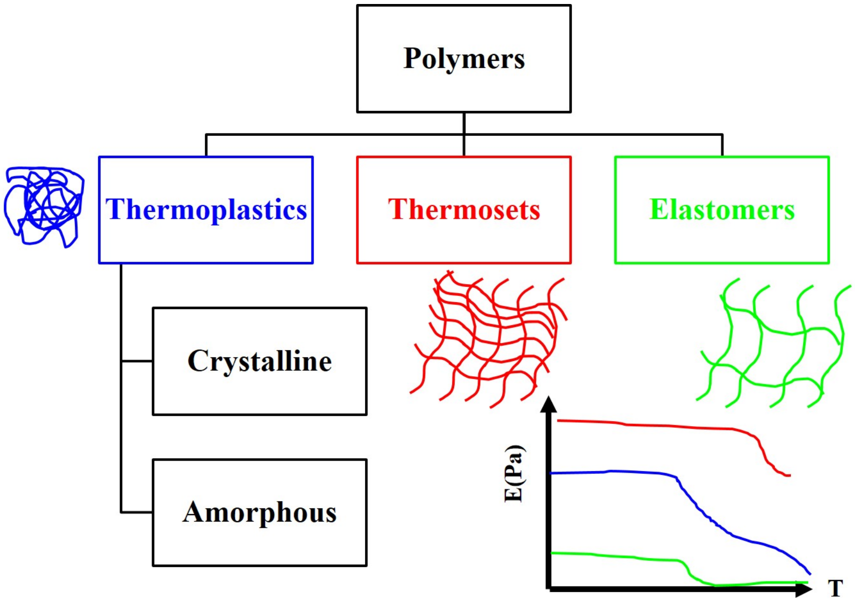


Figure 1-10: Polymer classifications.

A **thermoset** polymer are typically network, crosslinked, or ladder polymers. Due to the **permanent (covalent) crosslinks** between molecular chains they **do not soften upon heating**. Due to the **high degree of crosslinking (10-50%)** the permanent crosslinks resist molecular motion at high temperatures and will eventually d**egrade at extremely high temperatures** due to breaking of crosslinks. This is **not a reversible transition**. Some examples of thermosets are vulcanized rubbers, epoxies, phenolics, and some polyester resins.

An **elastomer** is somewhat similar to a thermoset polymer but has some key distinctions. These polymers are also **crosslinked but not to the degree of thermoset polymers**, much less. Additionally, elastomers can be **stretched very easily up to 10**× their original dimensions and recover once the stress is relieved due to an entropic restoring force. Some examples of elastomers are rubbers like polybutadiene (BR) or styrene-butadiene rubber (SBR).

## 1.5 Bonding/Molecular Interactions: Intra vs Intermolecular Forces

So thus far we have talked a lot about polymer structure and configuration but we have not talked about what makes soft matter unique. **The key to most of the fascinating properties of soft materials lies in intermolecular interactions in soft matter systems**. Here we need to take a step back and define the difference between **intra** and **inter** molecular interactions. **Intra (within)**

**molecular interactions** are interactions that occur within the molecule or polymer chain, i.e. the covalent backbone interactions for polymers (also generally covalent, ionic, or metallic). **Inter (between) molecular interactions** occur between molecules and other types of neighboring particles. These are **typically secondary interactions**, more on this in a bit. These secondary interactions, intermolecular interactions, are t**ypically much weaker than the intramolecular interactions** but these **interactions are critical** for some of the most unique properties of soft matter. In fact **most of the intermolecular interactions in soft matter have energies**, or enthalpies, on the **order of approximately 1 kT**, where k is the Boltzmann constant T is the temperature of the system. The implication here is that soft matter systems are held together by very weak intermolecular interactions and this will lead to **large fluctuations in behavior** because these bonds can be easily broken by applying an external stimulus, like pulling a polymeric material. This is in stark contrast to **hard** materials which are held together by **covalent bonds which are typically 10-200kT**. These weak intermolecular interactions in soft matter also leads to polymers being very **adaptive** and can undergo **large changes in response to fairly weak stimuli**. This behavior is critically important in biological systems where **rapid protein folding** or conformational changes in receptors is critical for biological processes. This is only possible because of these weak interactions. However, don't get it mistaken that all polymers behave like silly putty. These interactions are weak but there are **a very large number of these interactions** and from this you can build up materials like **Kevlar**, which derives much of it's mechanical properties from the structure of the polymer backbone. Again, this will remain the focus of this class which is to relate macroscopic behavior to microscopic properties, or in other words to relate the molecular structure, bonding, and confonformational changes to macroscopic behavior, similar to the Materials Tetrahedron

**Intramolecular Forces/Interactions:**

When it comes to binding and types of intramolecular interactions it is all about the electrons. Elements that have **no valence electrons** or that have a completely filled outer shell are called the **inert or noble gases**. All other elements which do not have a completely filled outer shell have **valence electrons** and these electrons are the ones of **import when it comes to bonding**. Bonding is critically important as **most of the structural, physical, and chemical properties are influenced or determined by the interatomic bonding**.

For intramolecular interactions we will typically deal with

- **Covalent** (5eV or about 200 kT)
- **Ionic** (1-3eV or 80kT)
- **Metallic** (0.5eV or 20kT)

Let's talk a little bit about why bonding occurs. Well it all goes back to Gibbs, the energy of the set of bonded atoms is lower than the isolated atoms. There are forces of attraction and repulsion between electrons and protons. And we remember that the force (F) is related to the potential

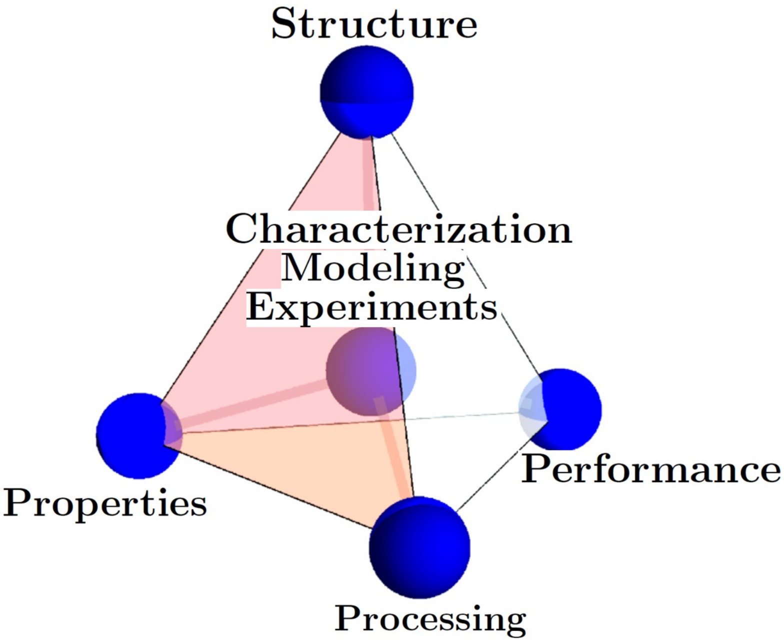


Figure 1-11: Materials Tetrahedron

energy (U) by $F = -\nabla U$. Remember that $\nabla$ is the gradient mathematical operator and will take the partial derivative of the function with respect to the dimensionality of the problem. Now there are many different equations or potentials that describe the interactions between atoms i.e. Morse, Born-Mayer, Van Der Waals, etc. Let's take a look at one of these potentials, the **Lennard-Jones (LJ) Potential** which approximates the **interaction between a pair of neutral atoms** (it is popular due to the computational simplicity)

$$V_{LJ} = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] = \epsilon\left[\left(\frac{r_o}{r}\right)^{12} - 2\left(\frac{r_m}{r}\right)^{6}\right] \tag{1.1}$$

where $\epsilon$ is the depth of the potential well (energy), $\sigma$ is the distance at which the inter-particle potential is zero, $r$ is the distance between particles, and $r_m$ is the distance where the potential is minimized.

We can distinguish between different types of intramolecular interactions and how to distinguish between covalent, ionic, and metallic interactions. Well, the **key to determining which type of bonding occurs is the valence electrons. Specifically if they are gained, lost or shared.**

With **covalent** bonds there are **valence electrons that are shared between adjacent atoms**, which results in a **pairing of electrons into localized orbitals and concentrating the negative charge between the positive nuclei**. For ionic interactions we are typically dealing with atoms that have a different affinity for electrons, different **electronegativities**, a **net transfer of charge** can occur forming **positively** and **negatively charged ions**. These ions can form **networks of ionic bonds** held together by **long-range coulombic interactions**.

**When the electronegativity is similar or the same between atoms the valence elec-**

**trons are shared equally and the bond is purely covalent**. When the **electronegativity is very different** the **more electronegative atom** withdraws nearly **all the valence electrons** and the bond is **purely ionic**. **Thus electronegativity is how we distinguish between Covalent and Ionic interactions!** Now you might ask what happens in the intermediate case of electronegativity differences. Well then you will have bonds that have **both covalent and ionic characteristics**. We call these bonds **polar covalent** and one atom will have a partial positive and negative charge, as in HCl. While there is no universally agreed upon cutoff values **in this class we will define an electronegativity difference of 0-0.4 to be non-polar covalent, 0.5-1.7 to be polar covalent, and greater than 1.7 to be ionic.** In the case of **metallic bonds**, **all atoms share their valence electrons and the nuclei form a positively charged array in a sea of delocalized electrons**.

**For soft matter the most common intramolecular interaction that we will deal with will be covalent interactions.**

**Intermolecular Forces/Interactions:**

As we previously mentioned intermolecular interactions are critical for many soft matter systems and there are several weak intermolecular interactions of interest, which include:

- **Hard sphere potentials** - the ability of atoms to effectively occupy space and repel at short length scales, quantum mechanical in nature
- **Coulombic/electrostatic interactions** - electrostatic attraction/repulsion between charged ions
- **Lennard-Jones (LJ) potentials** - induced dipole interactions between neutral atoms
- **Dipole-dipole interactions** - associated with polar molecules and forces
- **Hydrogen bonding** - net dipole interactions. Typical hydrogen bond donors will be NH groups and possibly OH groups while H-bond acceptors will be electrongative oxygens i.e. -O- or -CO-.
- **Hydrophobic effect** - a largely entropic interaction related to the structuring of water around hydrophobic interfaces.
- **Van der Waals force** - includes London dispersion force, Debye force, and Keesom force which describe attraction and repulsion due to fluctating polarization between nearby atoms/elements/particl quantum mechanical in nature. Van der Waals forces decay as $d^{-6}$
- **Ionic bonding** - ionic bonding mediated by metallic ions between side chains

You can see some of these interactions illustrated here

If you are interested in the origin of these interactions there is an excellent book by Israelsachvili I can recommend but the key thing to focus on is that **all of these interactions have energies on the order of 1kT, so thermal fluctuations can break these bonds potentially**.

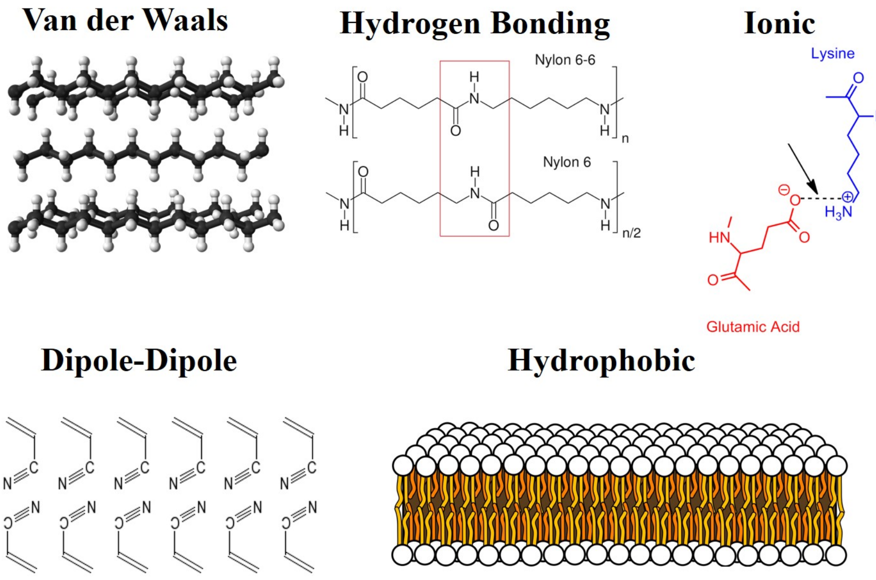


Figure 1-12: Intermolecular bonding in polymers

## 1.6 Isomeric States:

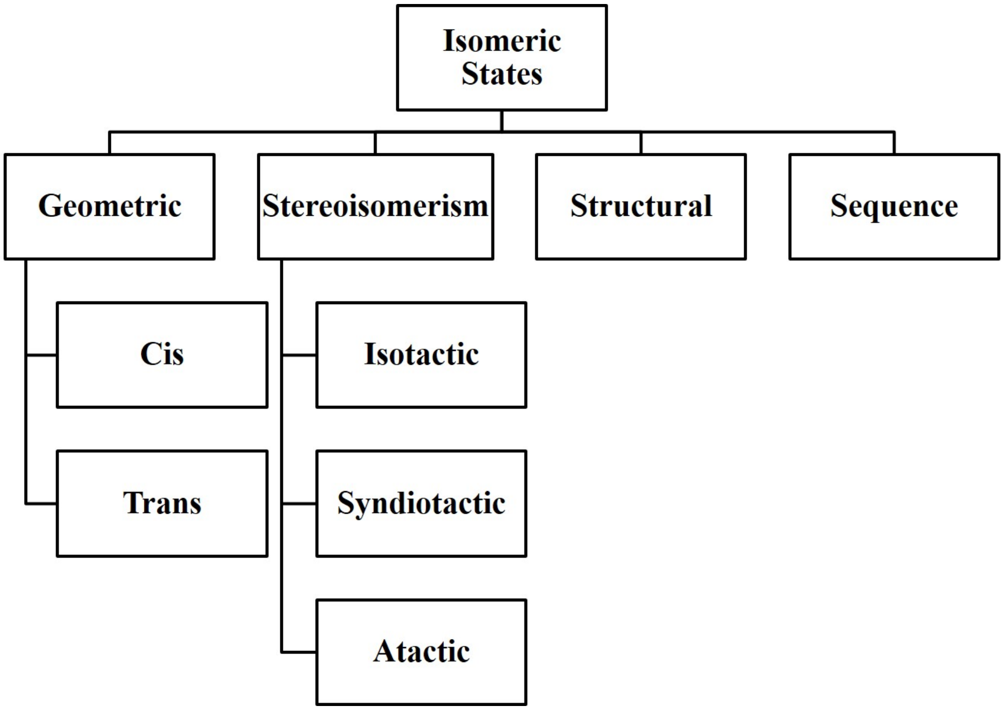


Figure 1-13: Structural, Geometric, Sequence, and Stereoisomerism

Molecules are typically held together by strong covalent bonds with many conformations available via *rotational isomeric states*. In other words, conformations are accessible due to the rotation of atoms around these intramolecular bonds. **Isomers/Isomeric States** are molecules which are **compositionally identical but structurally distinct**. **Conformers/Conformational Isomers** are related by **rotations around single bonds**. Note that **at room temperature thermal rotation around a double or triple bond is essentially zero**. There are **structural isomers, stereoisomers, geometric/configurational, and sequence isomers**. **Structural isomers** occur when certain bonds prohibit rotoconversion of two conformationally distinct states. Let's take a look at an example.

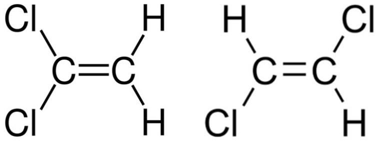


Figure 1-14: Dichloroethene

**Dichlorethene is a structural isomer or a geometric isomer**. We can see the **cis** and **trans** conformations in the figure. Here the **double bond** prevents rotational so they are **structurally distinct**. It is a **structural isomer not a conformer**.

**Stereoisomers** have an **ordered sequence** of linked units but the **substituents pendant to the main backbone of covalent bonds have different arrangements or tacticity**. Specifically they can be **atactic, isotactic, or syndiotactic**.

Stereoisomers are found in many different types of **polymers** and we can see an example of atactic, isotactic, and syndiotactic below:

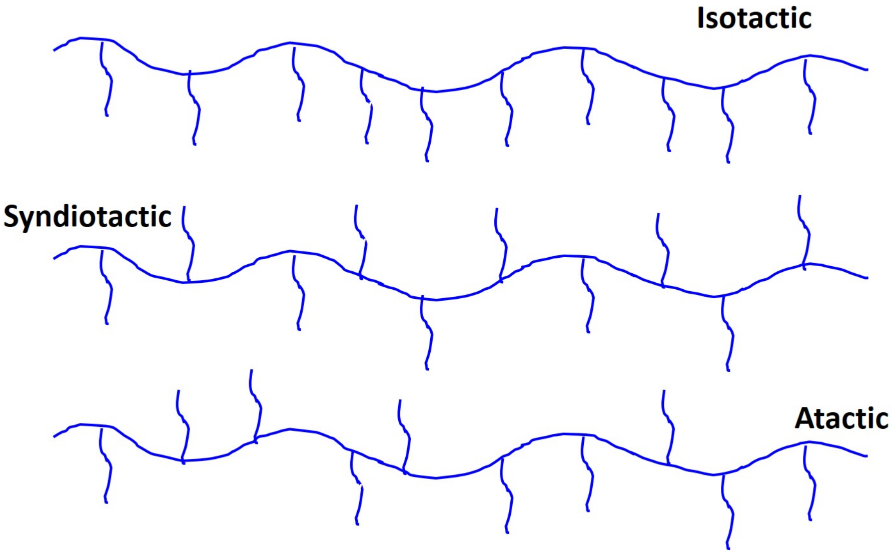


Figure 1-15: Stereoisomers: Isotactic, Syndiotactic, and Atactic

**Isotactic** stereoisomers will have all the side-chains on the **same side**. **Syndiotactic** will have some type of **repeated order** either top and bottom, or top-top, bottom-bottom, etc. **Atactic** is

**completely random**.

A **geometric/configurational/cis-trans isomer** has the same chemical formula but typically the arrangements of the side groups are on different sides of an unsaturated carbon backbone bond. Specifically there will be **cis** and **trans** configurations.

**Sequence isomers** have many linked units like in a polymer but can have a variable sequence. For example think about block co-polymers which can be designed to be ABABABAB or AAAABBBB.

One example of a **conformer** is dichloroethane. This molecule has a single C-C bond so there are several different rotational states that can be accessed. We can actually plot the conformational energies of these different states as a function of the C-C bond torsion angle.

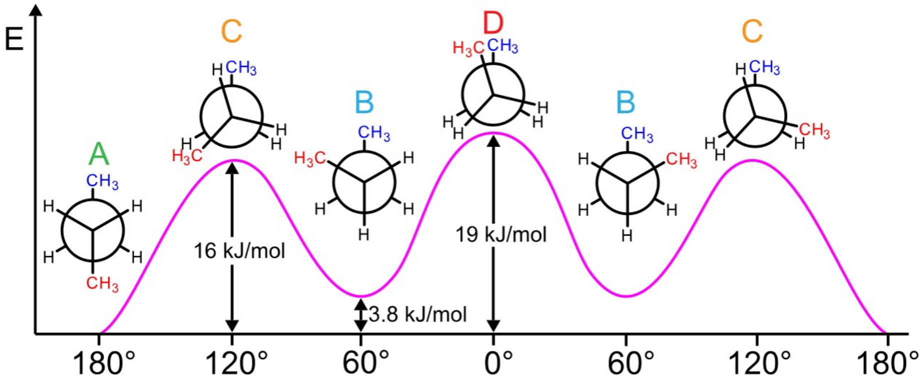


Figure 1-16: Rotational Isomeric States

In the figure we can identify some critical states. The lowest energy states, $A$, is the trans conformation as the methyl groups are the furthest distance apart from each other. The highest energy state, $D$, is the cis conformation and the energy is the largest because the methyl groups are the shortest distance from one another. The other two lower energy states, $B$, are termed **gauche** ± conformations where there is larger amount of distance between the methyl group than in the cis conformation or the final conformation which is called the **eclipsed conformation.** The eclipsed conformation, $C$, where the methyl group is eclipsed by one of the side hydrogens. **Molecules like butane can change conformations up to $10^{10}\times$ depending on the temperature**.

# CHAPTER 2

## POLYMERIZATION

## 2.1 Key Terms/Definitions:

- **Molar Mass**
- $M_n$ **vs** $M_w$
- **Polydispersity Index (PDI)**
- **Extent of reaction/conversion (p)**
- **Reactant Ratio (r)**
- **Step vs Chain Growth Polymerization**
- **Condensation vs Addition Reactions**
- **Reaction Kinetics Equations**
- **Classes of Chain Growth Polymerization**
  - **Radical**
  - **Cationic**
  - **Anionic**
  - **Ring Opening**
  - **Living**
  - **Ziegler-Natta**

## 2.2 Molecular Weights and Degree of Polymerization:

Just a reminder from last time that **polymers** are composed of **monomers**, or **structural units**, and these monomers are repeated approximately **100 times for oligomers** and more typically **10-100k for typical macromolecules/polymers** and we had the following reaction for polyethylene which utilized ethylene as a monomer, or structural unit, and also has ethylene as the repeat unit.

Remember that **n** is the just the number of time we repeat the repeat unit, not trying to repeat myself. We talked last time as well about some of the parameters of polymer chains that we are interested in some of those being chain architecture, isomer states, etc. But one of the key parameters that we also care about is the **molecular weight/molar mass** and the **molecular weight/molar mass distribution** (units in $\frac{g}{mol}$). To be more accurate it is better to use the

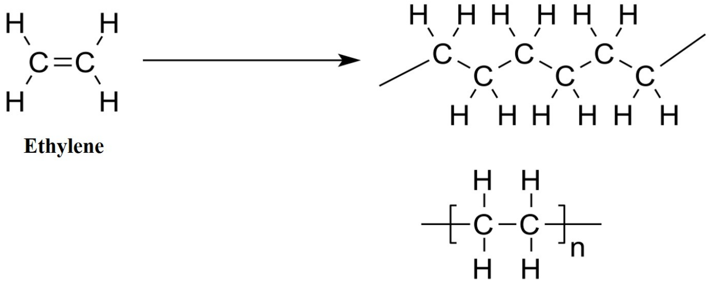


Figure 2-1: Polyethylene

term molar mass but you will typically see the term molecular weight in other literature quite often. These values are critical as at high molar masses the viscosity increases dramatically as does the ultimate tensile strength typicall.

Now let's first talk about how we calculate the molar mass. For a **single homopolymer** (composed of only one polymer unlike co-polymers or block-copolymers), like that for polyethylene above, would simply be:

$$M = nM_r \tag{2.1}$$

where $M$ is the molar mass of the homopolymer, $n$ is the number of times the repeat unit is repeated, and $M_r$ is the molar mass of the repeat unit. However, typically when we synthesize polymers not **all polymers will be of exactly the same length as it is a chemical reaction which polymerizes the monomers**. Thus we are typically concerned with **average molar mass values**, $\overline{M}$. And there are two primary ways we will calculate the average molar mass, those being the **number-average**, $\overline{M}_n$, and **weight-average**, $\overline{M}_w$, molar mass.

The **number-average molar mass** is sum of the products of the molar mass of each fraction multiplied by its mole fraction

$$\overline{M}_n = \sum X_i M_i \tag{2.2}$$

where $X_i$ is the mole fraction corresponding the the molar mass $M_i$. This can also be written as

$$\overline{M}_n = \frac{\sum N_i M_i}{\sum N_i} \tag{2.3}$$

where $N_i$ is the number of polymers with molar mass $M_i$. You'll notice that this is simply the ratio of the total mass divided by the number of chains.

The **weigh-average molar mass** is the sum of the products of the molar mass of each fraction multiplied by it's weight fraction or

$$\overline{M}_w = \sum w_i M_i \tag{2.4}$$

where $w_i$ is the weight fraction. The **weight fraction** is simply the mass of molecules with molar mass $m_i$ divided by the total mass

$$w_i = \frac{N_i M_i}{\sum N_i M_i} \tag{2.5}$$

so we can re-write the weight average molar mass as

$$\overline{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} \tag{2.6}$$

An example of a typical molar mass distribution for polymers can be seen here. Notice that the **weight averaged** is larger than the **umber average.** This must be the case as the larger polymers weight more the weight average is always skewed to the right of the number average.

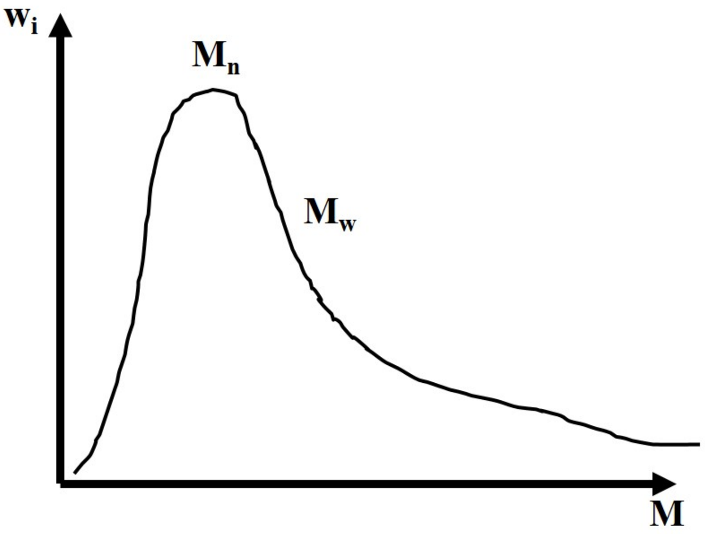


Figure 2-2: Molar Mass Distribution Curve

We can now define another very useful quantity called the **polydispersity index** or **PDI**. This is essentially a measure of the breadth of the molar mass distribution and it is

$$PDI = \frac{\overline{M}_w}{M_n} \tag{2.7}$$

This value typically ranges from **1.5-2.0 for many polymers** but **can range from 1.05-50**. Note that **for a perfectly monodisperse polymer the PDI values would be 1**. We can never be less than 1!

Let's do a quick problem

**Ex. 1:**

Calculate the $M_n, M_w$, and PDI of a polymer sample created by mixing 1 mole of a 50,000 g/mol polymer with 1 moel of a 150,000 g/mol polymer chain.

Finally the last parameter that we have neglected to discuss so far when characterizing the polymerization process is the one that accounts for the chemical nature of polymerization and that is the the **number-average**, $\overline{D}_{p,n}$ and **weight-average**$\overline{D}_{p,w}$ **degree of polymerization**. These values are simply defined as

$$\overline{D}_{p,n} = \frac{\overline{M}_n}{M_r} \tag{2.8}$$

$$\overline{D}_{p,w} = \frac{\overline{M}_w}{M_r} \tag{2.9}$$

notice in the above expressions that these values are a function of the the number or weight of the polymers as expected but they are also functions of $p$ which is a new parameter the **extent of the reaction/conversion**. This quantifies how the extent of the chemical reaction and conversion of monomers to polymers. This value will depend on many factors (temperature, pH, etc.). We will talk more about this and how to relate it to reaction kinetics in just a minute.

Let's do another quick problem

**Ex. 2:**

I have a sample of polyethylene oxide (PEO) where all the chains have number average degree of polymerization of 10,000 and is degraded chemically into equal molar amounts of chains with a $D_{p,n}$ of 7000, 2000, and 500. What is the $M_n, M_w$, and PDI of the polymer sample before and after degradation.

So we now have the tools to characterize our polymer sample after it has been polymerized but how do we go about actually polymerize our polymer? Well I hope everyone is ready for a tiny bit of organic chemistry!! Yeah!

## 2.3 Polymer Chemistry/Polymerization:

As we have discussed previously polymerization in its most basic form is **linking at least two monomers together via a chemical reaction**. So you can imagine there are too many different types of polymerization reactions to cover in this course so we will only highlight a few but I can give you resources to investigate further if you are so inclined to do so. I would also suggest taking an organic chemistry course or two as well if you are interested in polymer synthesis. We can generally classify polymerization into two broad categories distinguished by the underlying polymerization mechanisms. Those two categories are **step-growth** and **chain-growth** polymerization. In **step-growth** polymerization the polymer chains grow by step-wise reactions whereas in **chain-growth** polymerization requires an initial reaction between the monomer and an initiator to start the growth of the chain. This is also expressed below as

$$\text{Chain Growth Polymerization} \quad M_n + M \rightarrow M_{n+1} \tag{2.10}$$

$$\text{Step Growth Polymerization} \quad M_x + M_y \rightarrow M_{x+y} + HCL, H_2O \tag{2.11}$$

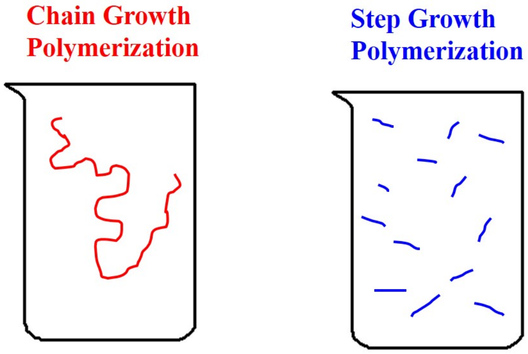


Figure 2-3: Chain vs. Step Growth.

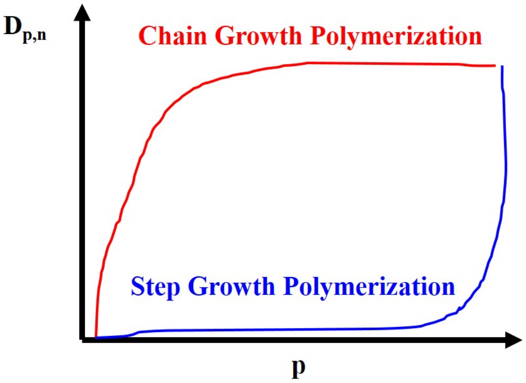


Figure 2-4: Chain vs Step Growth.

Where for chain growth you simply add (sometimes referred to as addition polymerization) a monomer of the same type to grow a polymer chain. For step-growth polymerization you typically utilize two different monomers which will react chemically and produce a new polymer with 2 structural units and 1 repeat unit and there is typically some by product from the reaction typically water or some acid. Additionally the monomer will be present till the end of the reaction for chain growth while the monomer will disappear at very early stages of the reaction. Finally the mechanism by which chain growth occurs is via three steps

1. **Initiation**
2. **Propagation**
3. **Termination**

The step growth mechanism occurs via independent reactions of functional groups at chain ends. We will talk about this more in depth right now!

## 2.4 Step-Growth Polymerization:

For **step-growth polymerization** or simply **step polymerization** the key characteristics of this type of polymerization is that the monomer will typically disappear at the very early stages of the reaction. As the extent of the reaction progress, $p$, the molecular weight is initially very low but at the end of the reaction is increases dramatically. Finally, the mechanism of this type of polymerization is via independent reactions of functional groups at chain ends. Additionally, in order to **have efficient step polymerization**, i.e. high molecular weight, we need to have

- **Exact equivalence of functional groups**
- **Very high degree of conversion**
- **No side reactions**
- **No monofunctional impurities**

Some step growth polymers include esters, amides, carbonates, urethanes, and ureas as seen here as well as some functional groups.

So if we want a high molecular weight how can we achieve this? Well via extent of the reaction and the reactant ratio which we will discuss right now.

**Controlling Molar Mass Via Extent of Reaction and Reactant Ratio: The Carothers Equation**

We can define the **extent of the reaction or conversion** $p$ as simply the ratio of the number of functional groups remaining over the number initially present

$$p = 1 - \frac{N}{N_o} \tag{2.12}$$

where $N$ is the **number of molecules at some time** ,$t$ and $N_o$ is the **number of molecules initially present**. You can also break it down further by the extent to the reaction of functional groups let's say we are trying to polymerize $RA_2$ and $RB_2$, seen here,

then we can write the extent of the reaction for both functional groups

$$p_A = 1 - \frac{N_A}{N_{A,o}} \tag{2.13}$$

$$p_B = 1 - \frac{N_B}{N_{B,o}} \tag{2.14}$$

where $N_{A,o}$ is the number of initial functional groups A and the same for B.

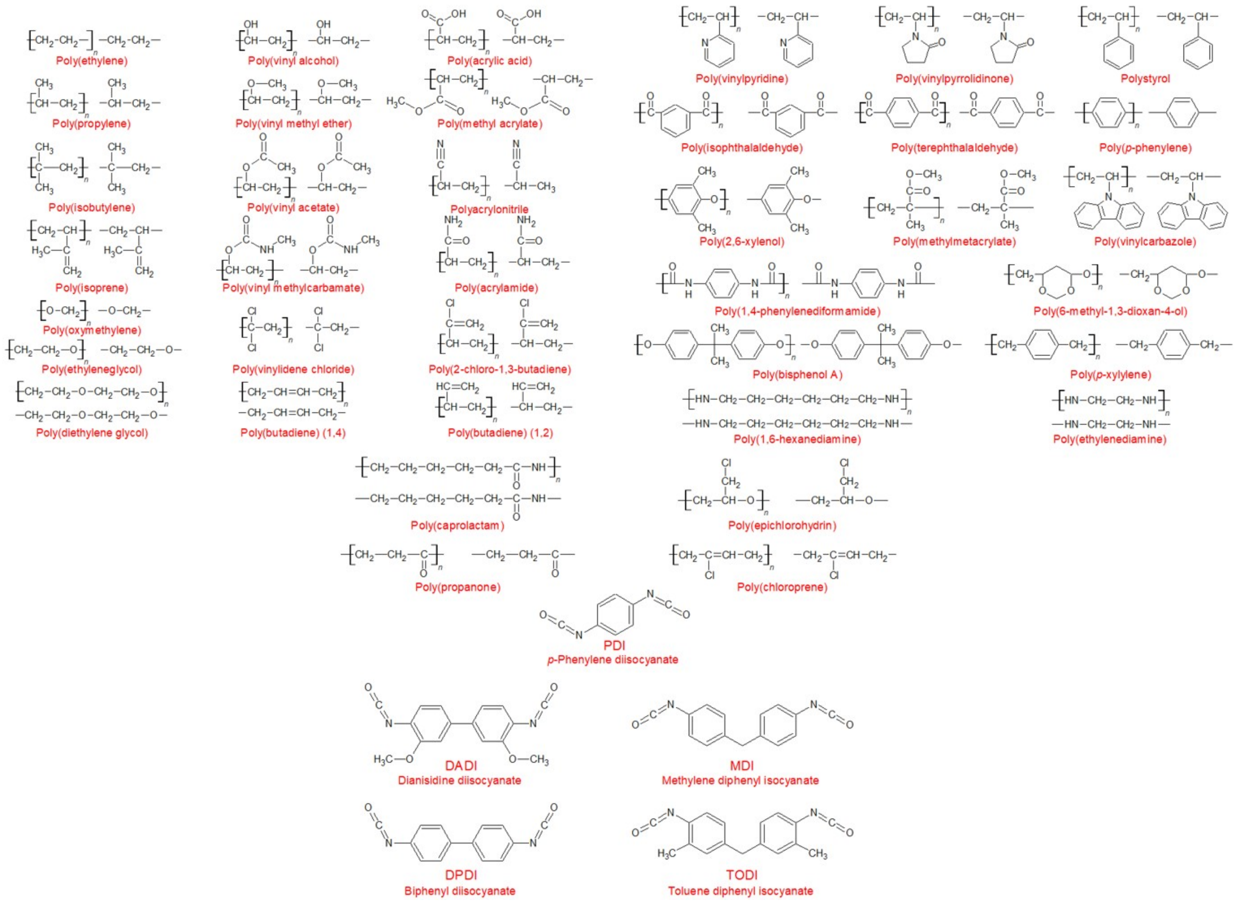


Figure 2-5: Common polymers.

You will notice that we can now re-write this as

$$p = 1 - \frac{1}{\overline{D}_{p,n}} \tag{2.15}$$

As we have hinted at previously in order to achieve the largest molar mass possible we need to have **exact stoichiometric ratios** and we can quantify this using the **reactant ratio** $r$ which is simply

$$r = \frac{N_A}{N_B} \tag{2.16}$$

where $N_A$ is the number of A functional groups and $N_B$ is the number of B functional groups. $r \leq 1$ assuming that B is in excess, one will typically be in excess because it is extremely difficult/impossible to have perfect stoichiometry. Let's consider the polymerization of $RA_2$ and $RB_2$. So initially the number of molecules present initially is

$$N_o = \frac{N_A + N_B}{2} \tag{2.17}$$

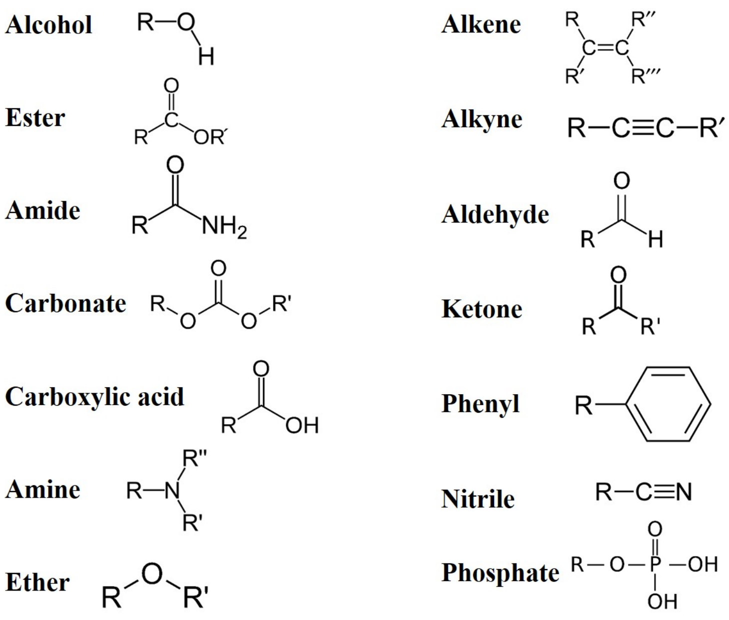


Figure 2-6: Functional groups.

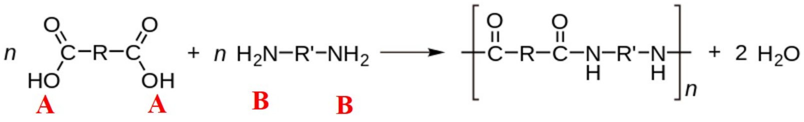


Figure 2-7: $RA_2$ and $RB_2$ polymerization, step growth.

note we divide by 2 because there are two functional groups per molecule. And we can re-write this equation as follows

$$N_o = \frac{N_B(1+r)}{2} \tag{2.18}$$

So we again are working toward an equation that will relate how the number averaged molar mass is controlled by the extent of the reaction and the reactant ratio. Well after some time how many unreacted A and B groups will there be? It should be

$$N_A - pN_A \tag{2.19}$$

$$N_B - pN_A \tag{2.20}$$

Notice that because we have previously indicated that A is in the minority the reaction will obviously stop once we hit our limit of A so we have indicated that above. We can also write the expression above equivalently in terms of the majority component B

$$rN_B(1-p) \tag{2.21}$$

$$N_B - prN_B \tag{2.22}$$

So now we can express the number of molecules remaining at some time $t$ which is

$$N = \frac{N_B(1 + r - 2rp)}{2} \tag{2.23}$$

So now we can relate write an expression for how the **number averaged molar mass is controlled by the extent of the reaction and the reactant ratio**

$$\overline{D}_{p,n} = \frac{N_o}{N} = \frac{1+r}{1+r-2pr} \tag{2.24}$$

This is the most general **Carothers equation** and can also be arrived at using a probabilistic perspective and if you are interested in this you can borrow by Young and Lovell text if you are interested in the derivation. Let's stop one quick moment and appreciate how powerful this equation is. By simply changing the reactant ratio or by waiting for the reaction to proceed via the rate of the reaction we can control the molar mass!! You can see the effects in the Mathematica Demonstration.

**Reaction Kinetics**

We have talked a lot about the extent of the reaction and that it will change as a function of time. So what are the kinetics that control this process? Well let's answer that by returning to our old friends, the equilibrium constants. So let's start by taking a look at a very general and generic step polymerization reaction.

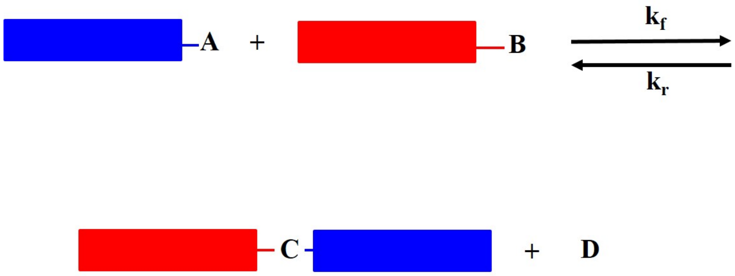


Figure 2-8: Generic Polymer Reaction.

where you can see that the A and B functional groups react to form a new linkage between the two monomers (red and blue), C, and there is an additional byproduct, D. Also since this is a chemical reaction remember that it can proceed in both directions.

For this reaction we know that that equilibrium constant $K_{eq}$ is

$$K_{eq} = \frac{k_f}{k_r} = \frac{[C][D]}{[A][B]} \tag{2.25}$$

where $k_f$ is the forward reaction rate constant, $k_r$ is the backward reaction rate constant, and [ ] denotes concentrations of each respective component. Also it should be noted that at equilibrium the rate of forward reaction, $R_f$, is equal to the rate of the reverse reaction $R_r$. And we have that

$$R_f \approx k_f[A][B] \tag{2.26}$$

$$R_r \approx k_r[C][D] \tag{2.27}$$

Now **for polymerization we want the rate constant to be very high, $10^4$**, because this indicates that we are creating **more products than reactants** which is great because we want to end up with our polymer. If the $K_{eq} \approx 1$ then we will **have to do something externally to bias the reaction forward like removing some of the byproducts of the reaction, i.e. Le Chatlier's principle.** Again this is great but how does this polymerization actually occur.

**Nucleophilic Acyl Substitution:**

One of the most common chemistries/methods of linking monomers together is via **nucelophilic acyl substitution**. A **nucelophile** is an electron rich species that will react with an electron poor species by donating an electron. A nucleophile seeks out electron poor sites. An **electrophile** an electron poor species that will react an electron rich species by accepting a pair of electrons. An electrophile will seek out electron rich sites. So the nucleophile will attack the electrophile, form an intermediate, and then leaving group will depart. Here you can see how the nucleophile attacks the electron poor carbon and then kicks out the leaving group LG.

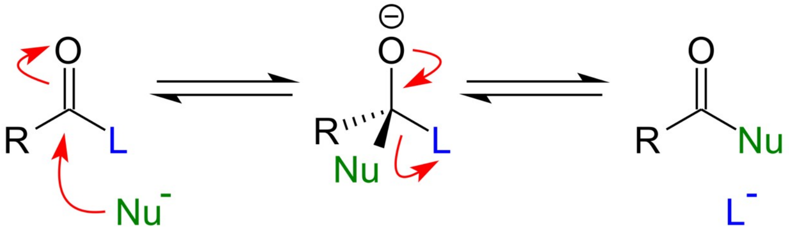


Figure 2-9: Nucleophilic Acyl Substitution.

Or even more generally for a polymer

Let's look at the acyl group. Which is the nucelophile and which is the electrophile? Well O is the nucelophile and C is the electrophile as the C=0 bond is polar and O grabs the electrons, because it is electronegative.

For most of the carboxylic acids that we will deal with in the following polymerization methods it is important to remember the relativity reactivity of the groups which is as follows, with approximate $K_{eq}$.

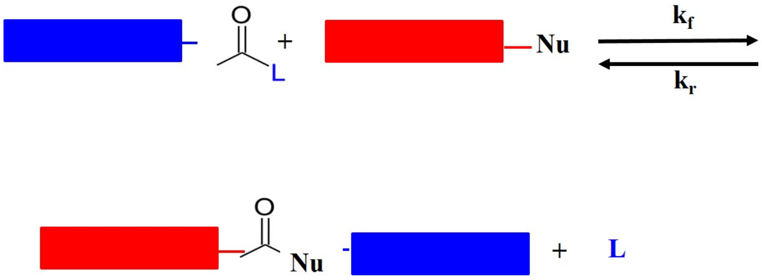


Figure 2-10: General Nucleophilic Acyl Substitution during Polymerization .

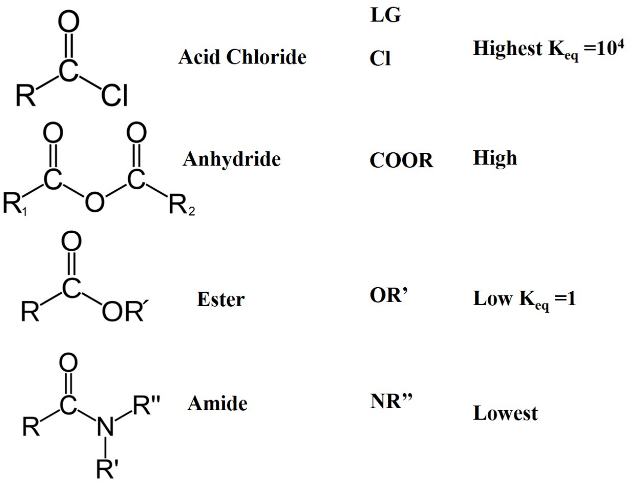


Figure 2-11: Table of Reactivity.

## 2.5 Direct, Exchange, and Acid Chloride Polymerization Methods

With that background let's make our first polymer!!! Some of you are probably wearing it right now, polyester. We will make polyester using three mechanisms

1. **Direct Esterification**
2. **Ester Exchange with Alcohols**
3. **Reactions of Acid Chlorides**

Let's start with **direct esterification** and remember this we are still talking about step-growth polymerization.

**Direct Esterification**

Here we can see a general **direct esterification** reaction and we can see that the byproduct is water. Therefore, this is considered a **condensation reaction** which is a reaction where small molecules are lost as byproducts when forming the larger polymer chain. Now this is an essential point to make here and why we went to the trouble of talk about the different equilibrium constants.

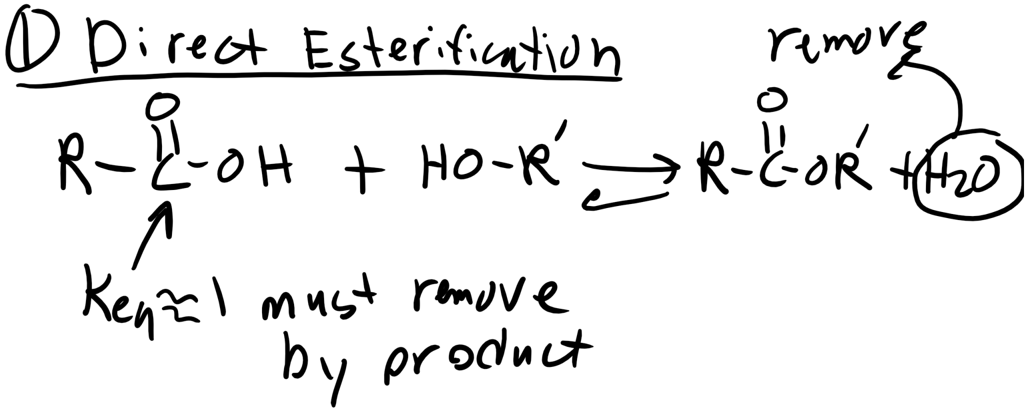


Figure 2-12: Direct Esterification.

If this reaction has a rate constant $K_{eq} \approx 1$ we either need to increase temperature drastically or remove the water to bias the reaction forward. For this reaction we may need to remove water and of course we need to have equal stochiometry.

**Ester Exchange with Alcohols**

For this reaction we also may need to remove alcohol due to the reaction equilibrium constants and we need to have equal stochiometry.

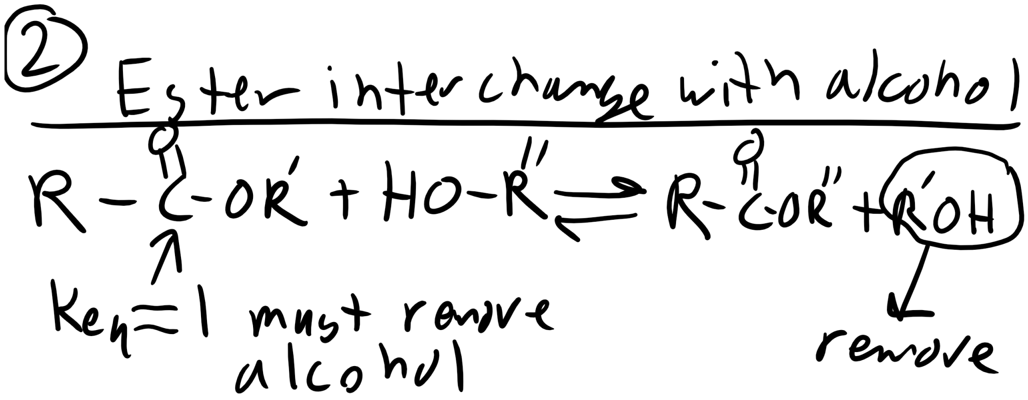


Figure 2-13: Ester Exchange with Alcohols.

**Reactions of Acid Chlorides**

For this reaction luckily we don't have to remove HCL because our reaction equilibrium is much higher as we remember from the table that we introduced earlier. However we will again have to have equal stochiometry and as the reaction proceeds if the solution becomes too acidic you might have to add a base to the solution.

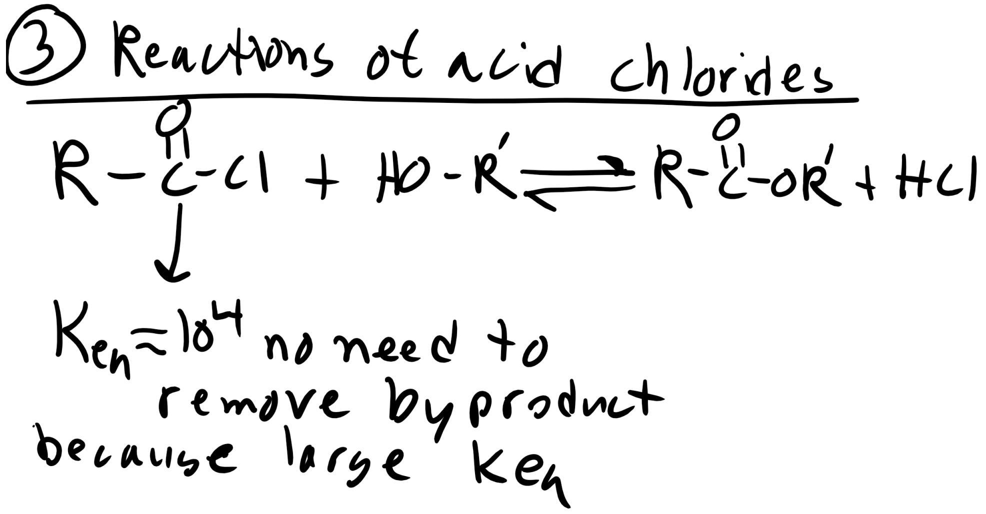


Figure 2-14: Acid Chlorides.

## 2.6 Making Polymers! Finally!

Now that we have seen several general reactions let's start actually making some polymers. Let's start by making polyehtylene adipate from adipic acid and ehtylene glycol using direct esterification.

How about making **polyethylene terephalate (PET)** from terephalic acid and ethylene glycol.

Let's make this polymer another way using ester exchange

Note that in this reaction there are two steps first is our typical exchange and we have to remove the byproduct. By continuing to heat the sample our products from the first step will react with one another producing polythylene which will react with the terephalic acid from the first step.

Now let's make some **polycarbonates (PC)**. We can do so via **reactions with phosgene**

or via our typical **interchange reaction**

Let's make some polyamides as well and we can do so via **direct amidation**. One quick note here is that the reaction that creates the amide linkage can have a $K_{eq} \approx 100 - 1000$ so we may not necessarily have to remove the water in this reaction, as we saw with our Nylon 6,6 demonstration.

or via **reactions with diacid chlorides**

Also take a moment to appreciate the implication of these amide linkages. In a polymer chain these amide linkages can form hydrogen bonds with other polymer chains or even with itself and

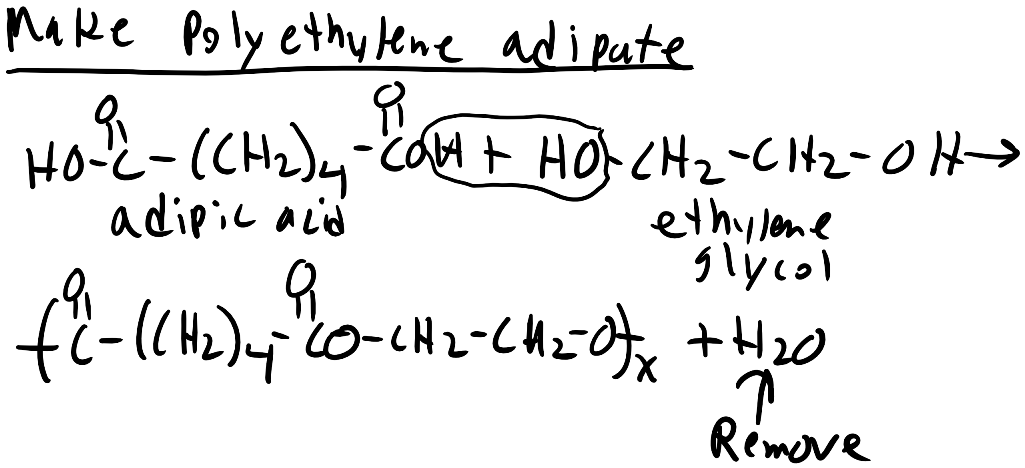


Figure 2-15: Polyethylene adipate.

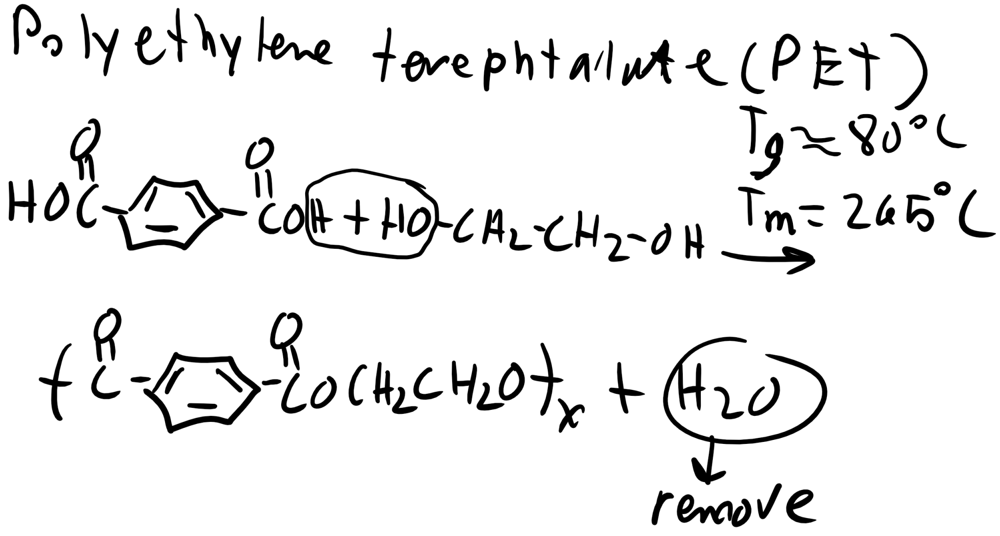


Figure 2-16: Polyethylene terephalate (PET).

this will have vast implication for polyamide mechanical and dynamical properties.

Now let's make some aromatic polyamides, specifically Kevlar which has the ultimate tensile strength of steel at $\frac{1}{5}$ of the weight! When making aromatic polyamides you have to use an acid chloride because the aromatic ring with the $NH_2$ exhibits resonance electron delocalization so it is a weak nucleophile so we need to have the most reactive group for the reaction to proceed. Also typically to increase the yield of this reaction it will typically take place in a solution with catalyzing agents like DMF and LiCl, or even $H_2SO_4$ solutions.

Finally let's talk about synthesizing a very important polymer, polypeptides/proteins (although

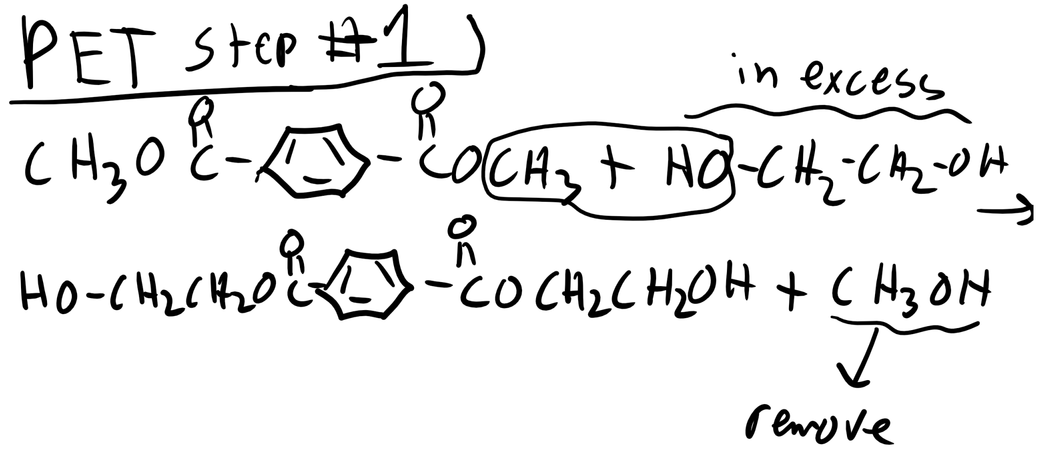


Figure 2-17: Polyethylene terephalate (PET).

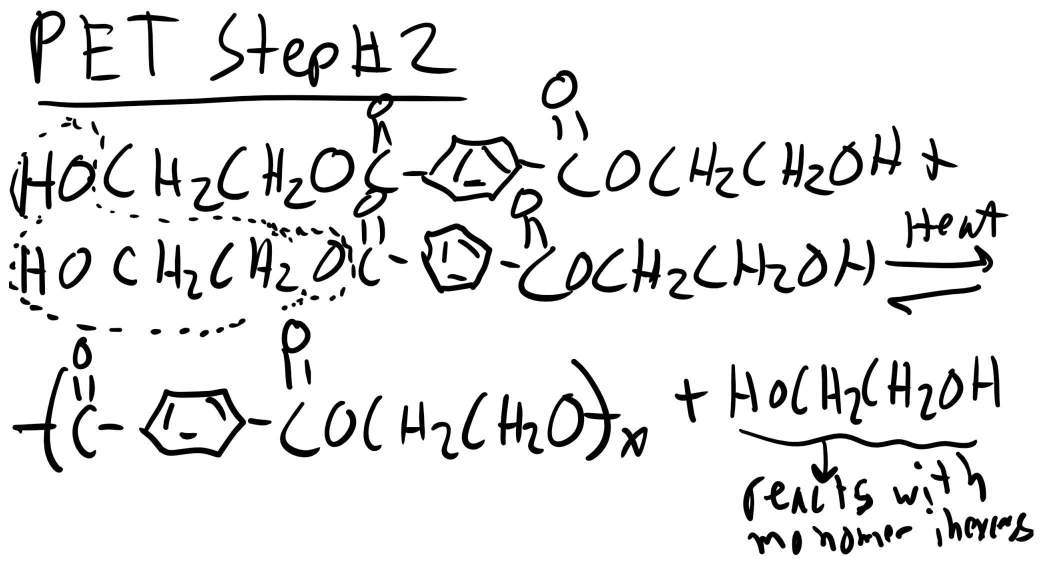


Figure 2-18: Polyethylene terephalate (PET).

proteins will typically have a 3D structure and contains many many peptides). Here we show a general reaction with an R group but it can be any of the 21 amino acids shown in the table here.

In general though you can imagine that if we want to make sure that the reaction proceeds without interacting with these R groups we will most likely have to take steps to protect these R groups. That amount of chemistry is beyond the scope of this class but I can point you to resources if you are interested.

With this we have exhaustively talked about a number of polymerization methods but remember there are many other methods and if you are interested there is some literature or external sources

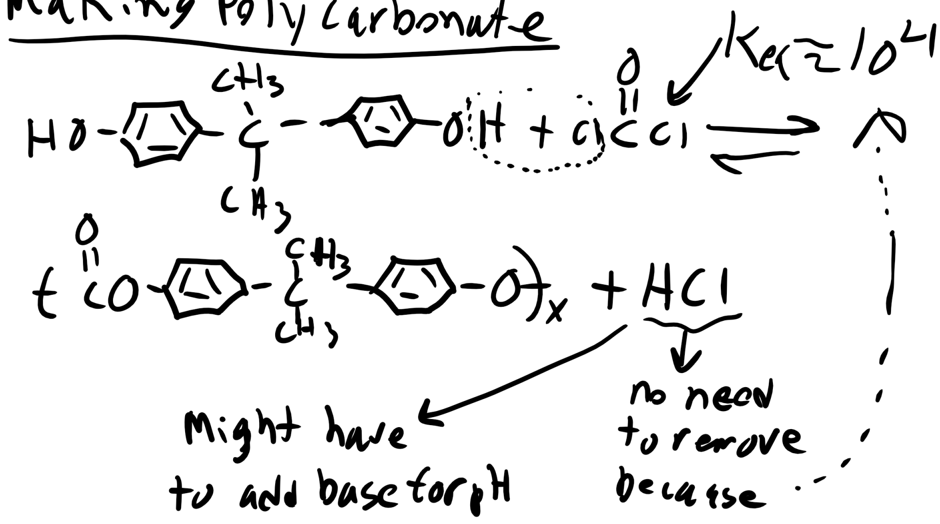


Figure 2-19: Polycarbonate.

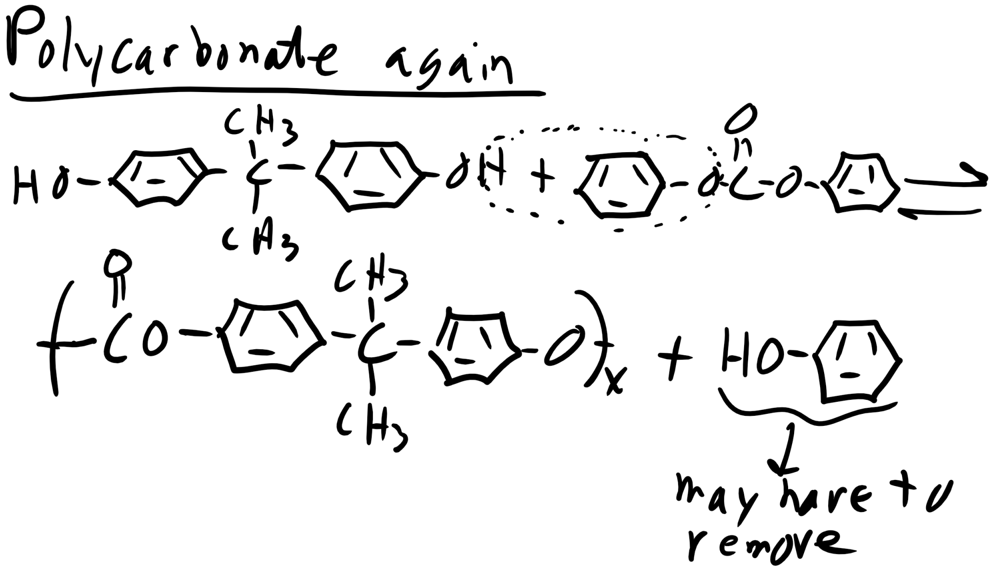


Figure 2-20: Polycarbonate.

of information that might help you find the appropriate mechanism for your material of interest.

## 2.7 Chain-Growth Polymerization:

For **chain-growth polymerization** or more simply **chain polymerization** monomer units are attached one unit at a time to an ever elongating polymer chain. Chain polymerization can catin the following steps

1. **Initiation**

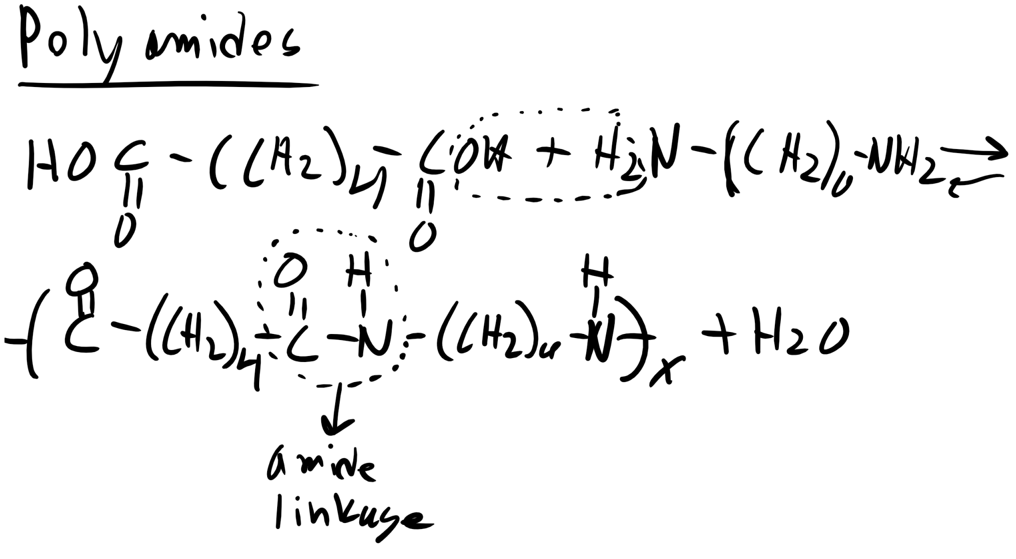


Figure 2-21: Polyamides.

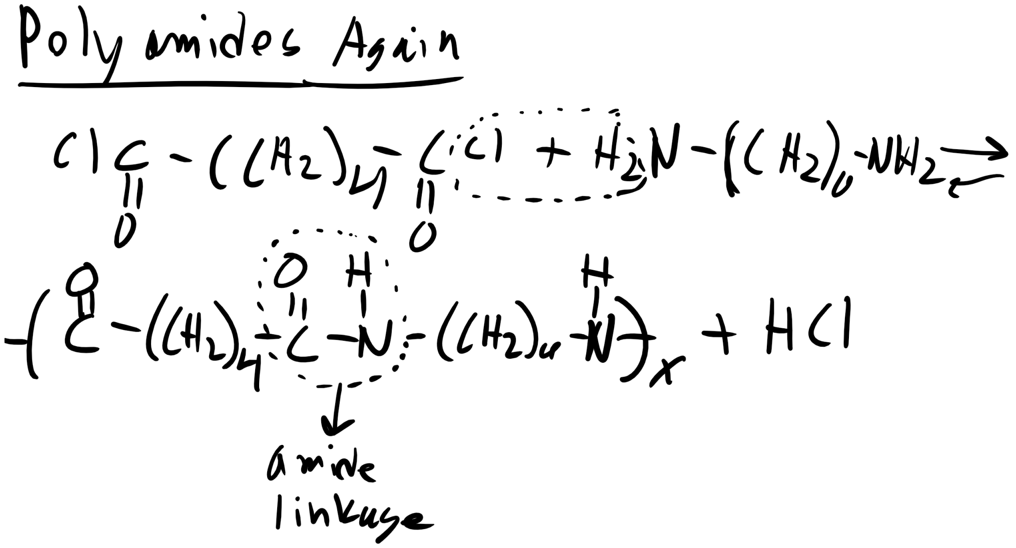


Figure 2-22: Polyamides.

2. **Propagation**

3. **Chain Transfer** - Chain is terminated but the active site is transferred to a new chain and typically results in more branching. This step doesn't always occur.

4. **Termination**

Additionally, the **monomer is present until the end of the reaction**. Also unlike step polymerization, the **molecular weight for chain polymerization initially shoots up and**

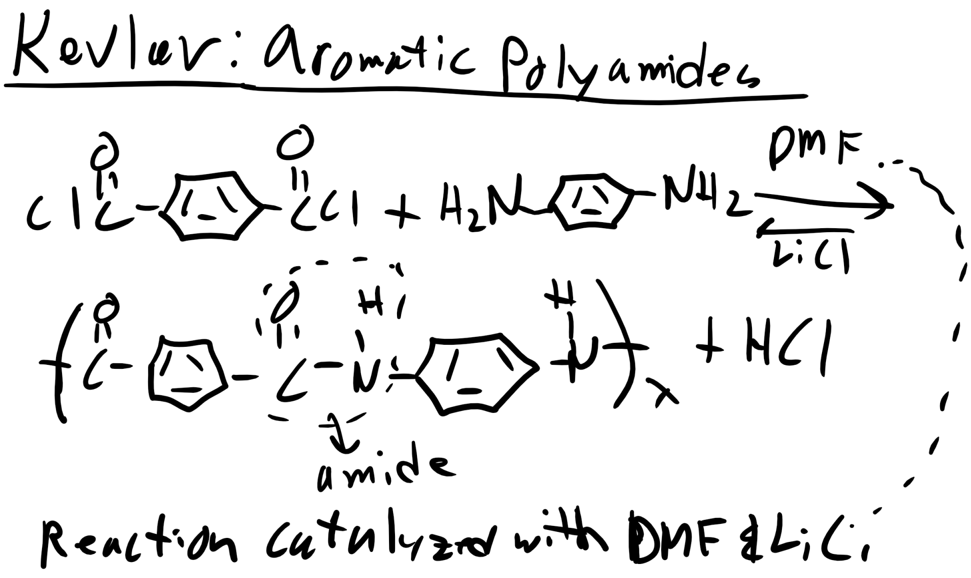


Figure 2-23: Kevlar.

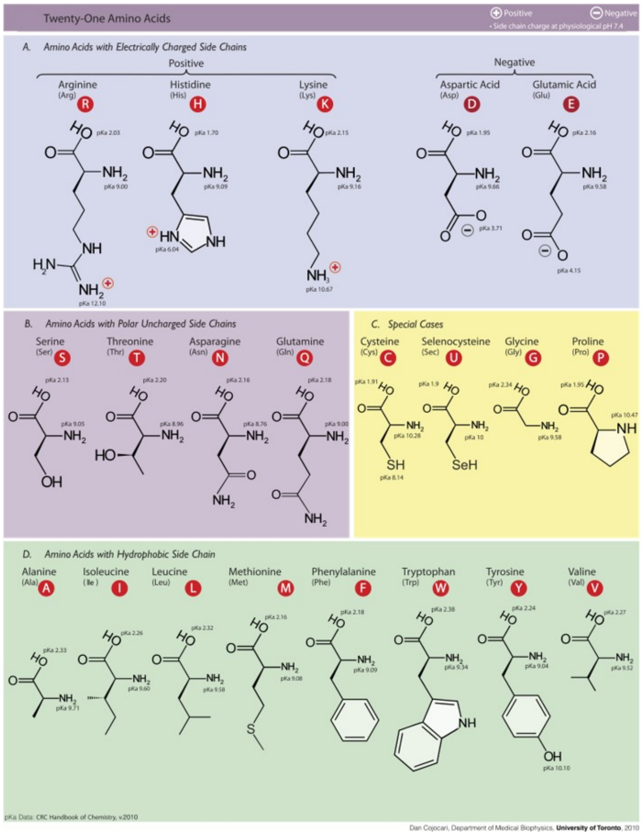
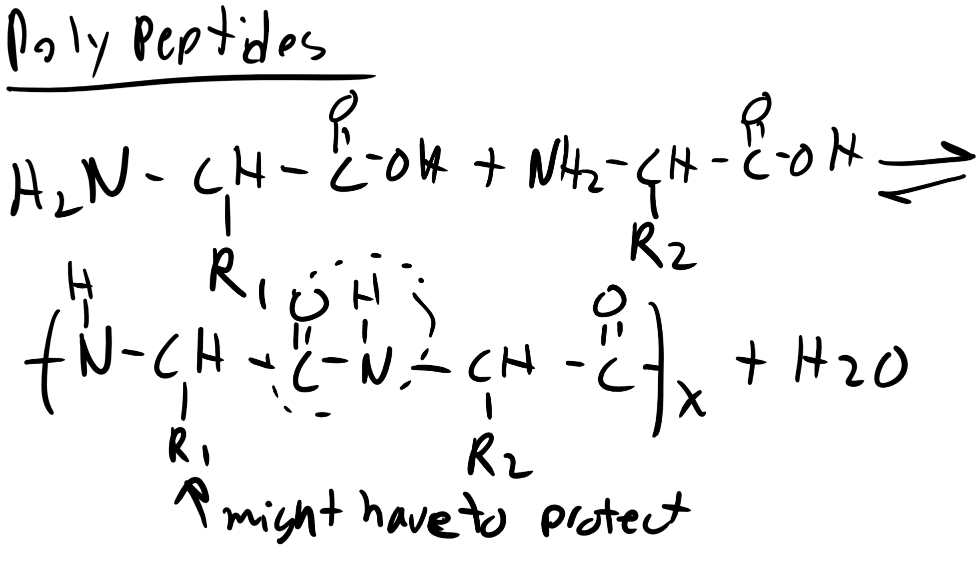


Figure 2-24: Amino Acids.

**then asymptotically increases very slowly** as the extent of the reaction, $p$, increases. Some chain growth polymers include **PVC, PS, and polypropylene (PP).**



$$H_2N-\underset{R_1}{CH}-\overset{O}{C}-OH + NH_2-\underset{R_2}{CH}-\overset{O}{C}-OH \rightleftharpoons \left[\overset{H}{N}-\underset{R_1}{CH}-\overset{O}{C}-\overset{H}{N}-\underset{R_2}{CH}-\overset{O}{C}\right]_x + H_2O$$

Figure 2-25: Kevlar.

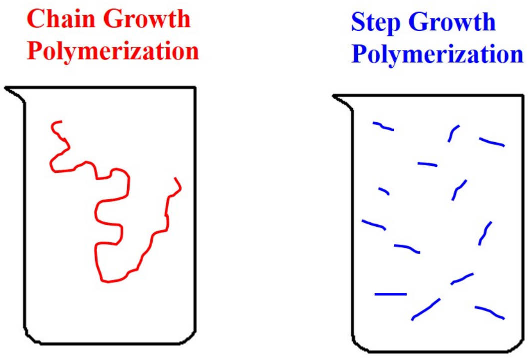


Figure 2-26: Chain vs. Step Growth.

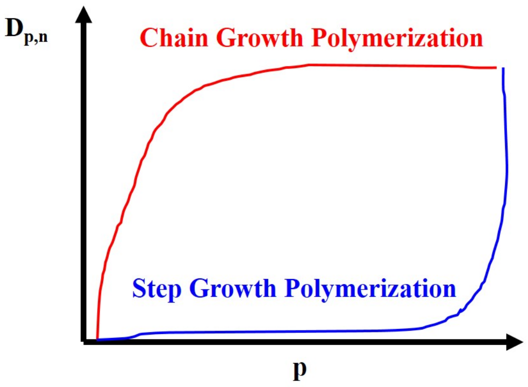


Figure 2-27: Chain vs Step Growth.

Some common **chain growth monomers are vinyl groups, ketones, aldehydes, and heterocyclic ring monomers (strained)**. And some common propagating or active species include **anionic, cationic, and free radicals.**

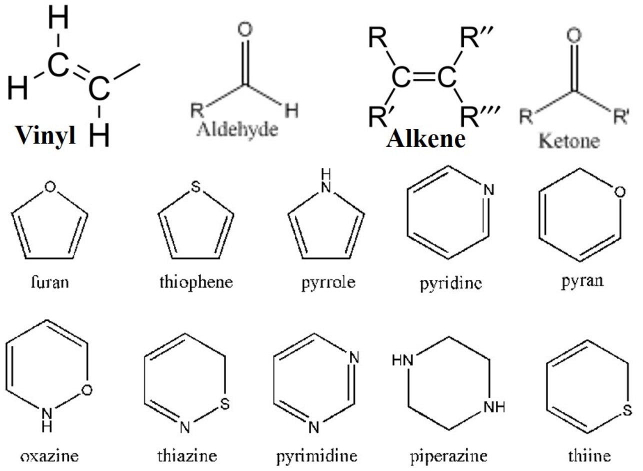


Figure 2-28: Free Radical, Cationic, and Anionic Monomers.

We'll be briefly discuss several key classes of chain-growth polymerization

- Radical Polymerization
- Cationic Polymerization
- Anionic Polymerization
- Ring Opening Polymerization
- Living Polymerization
- Ziegler-Natta Catalytic Polymerization (HDPE)

**Free Radical Chain Polymerization**

So for this method we will need an **initiator** which is typically a **radical** and the **propagating** site is typically a **carbon radical**. Free radical chain polymerization is particularly adept for **polymers** that have **monomers** with **C=C double bonds like vinyl, aldehydes, and ketones**.

Initiation actually has two steps **the creation of free radicals** and then the **radical are transferred to the monomers**. There are a number of different methods to create a free radical including **thermal decomposition, photolysis, redox reactions, electrochemistry, sonication, or even ionizing radiation**. Once the **double bond is broken and the radical is formed the radical initiator will attack the next monomer**. The radical is then **transferred and propagated**. This **process continues until the process is terminated or there**

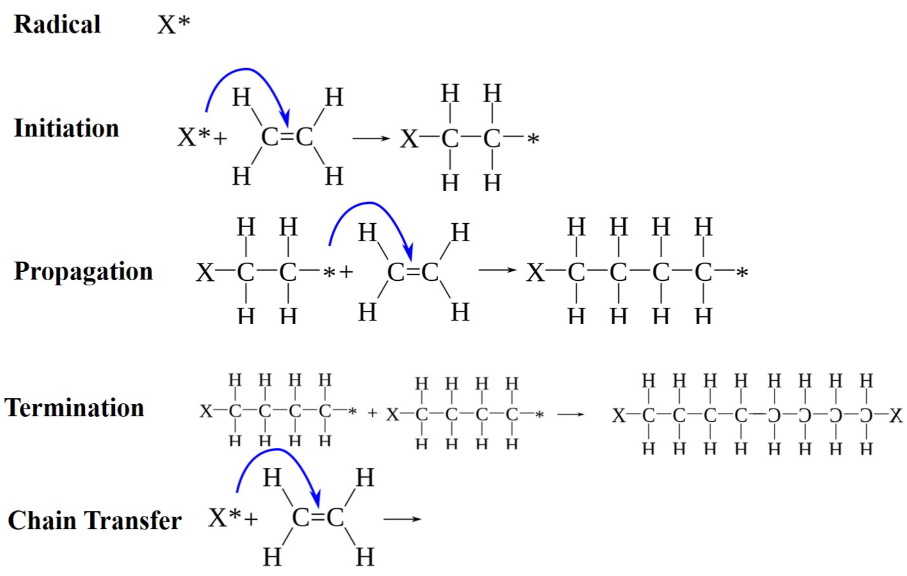


Figure 2-29: Free Radical Polymerization of Polyethylene Steps.

**are no more monomers**. This processes is very dependent on experimental conditions, i.e. **temperature, solvent, environment, reactivity, etc**.

The process is then terminated typically via two methods either **combination** or **radical disproportionality**. **Combination** involves simply the combination of two free radical chains which combine and form a new carbon backbone bond. And **disproportionation** creates a polymer chain with a saturated carbon bond at the end and another polymer chain with an unsaturated carbon bond at the end of the other polymer chain. There are other termination where an active chain can interact with impurities as well. The basic concept is the **radical is converted to a more stable product or products**.

The final method to stop polymerization is via **chain transfer** which involves **moving the radical from the end of the chain** to **another point in the polymer chain**. This will typically create branches which is very common in the production of low density polyethylene, LDPE.

**Cationic Chain Polymerization**

For cationic polymerization the initiator is an acid and the propagating site is a carbocation. The primary monomers for cationic polymerization are olefins and heterocylic monomers (examples). The propagation steps is very similar to the free radical polymerization and the termination step occurs typically via transfer of charge and association with hydrogen or the anion end capping the polymer.

**Anionic Chain Polymerization**

For anionic polymerization the initiator is a nucleophile the propagating site is a carbanion. The typical monomers are vinyl monomers. Again the propagation step is very similar and the termination step occurs typically via impurities like oxygen or water and the polymerization can be stopped manually by adding water or alcohol.

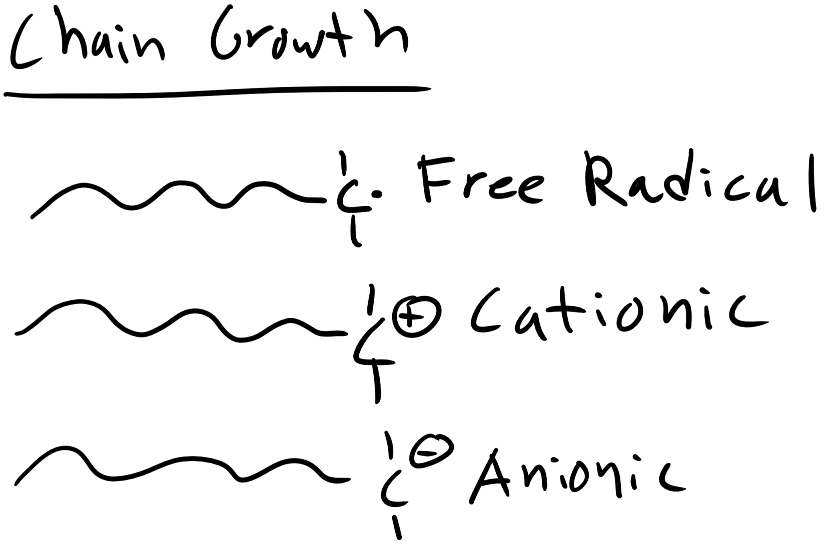


Figure 2-30: Chain Growth Polymerization Methods.

There are also a number of other polymerization methods like **Ring Opening Polymerization**. Or **Ziegler-Natta Catalytic Polymerization** where the initiator is a transition metal complex and the propagating site is a catalytic complex. O**ne additional method to mention is living polymerization where the termination or chain transfer reactions are removed or essentially negligible**. This results in a polymerization rate that is very constant/consistent resulting in a **very low polydispersity index**. This the key difference between HDPE and LDPE.

Again the key thing to take away from this lecture is to understand these different mechanisms, how to produce polymers through a variety of mechanisms and understand via kinetics what reaction will produce the polymer most suited for our application based on PDI and molar mass requirements.

# Chapter 3

## Polymer Chain Models and Scaling Laws

### 3.1 Key Terms/Definitions:

- **Ideal polymer** - an approximation of a linear polymer as having no intramolecular steric interactions such that its conformation can be described by performing a random walk of monomers.
- $\langle r^2 \rangle^{\frac{1}{2}}$ - the root mean squared end-to-end distance of a polymer, measuring the average distance between the ends of the chain; effectively provides a measurement of coil size.
- **Radius of gyration** - the mean squared distance of a polymer segment from its center of mass; provides another method for estimating polymer size, applicable for non-linear polymers.
- **Freely jointed chain model** - a model to estimate the end-to-end distance of an ideal polymer, assuming monomers are able to freely rotate with respect to each other.
- **Freely rotating chain model** - a more accurate model for real polymers incorporating a fixed bond angle into the freely jointed chain model, leading to an increased estimate for coil size
- $C_\infty$ - a parameter to estimate the effect of bond restrictions and steric hindrance on coil size
- $\alpha$ - a parameter to estimate the effect of solvent interactions/solvent quality on coil size
- **Real chain** - a model for a polymer that includes the effect of monomer-monomer interactions along the chain backbone.
- **Entropic spring** - a description of the energy (or force) required to either compress or elongate a polymer from its unperturbed dimensions; the energy is due to a restriction in the conformational entropy of the polymer, and follows the same form as Hooke's law for springs.
- **Excluded volume** - the *effective* volume each monomer in a real chain occupies. Excluded volume interactions tend to expand chains above their ideal sizes due to monomer-monomer overlap interactions. Ideal chains have 0 excluded volume; if excluded volume is negative, chain sizes tend to shrink and are stabilized by 3 body interactions.
- **Self-avoiding random walk** - a random walk in which each move is constrained only to lattice spots which are previously unoccupied; yields estimate for real chain behavior.
- **Mathematician's Ideal Chain**

- **Chemist's Chain in Solution and Melt Model**
- **Physicist's Ideal Chain**

## 3.2 Polymer Chain Conformations:

We now know how to create polymers and we have discussed some of the unique characteristics of polymer chains (inter vs intramolecular bonding). We also have seen some of the different polymer architectures that we will encounter but we haven't really talked much about polymer conformations. I make a distinction here between **architecture** and **conformation**. Polymer **architecture** has a connotation referring to the the structure of the polymer whereas a polymer chain **conformation** has a connotation which refers to the **instantaneous state** of the polymer especially when subjected to an **external stimuli**.

In our discussion of polymer chain conformations we will start simple and build up from a simple **homopolymer** with a very high molecular weight. So this polymer architecture is **simply linear, flexible, chain** or if you like macroscopic analogies **spaghetti**. And the **flexibility** of the chain will be governed by the **intramolecular bonding of the repeat unit**, as well as other factors which we will get into in depth when we discuss the **glass transition temperature**. One of the key ways that we can characterize a polymer chain conformation, just like we did with molar mass in the previous lecture, is by describing the **effective size** of a single polymer chain in solution. Now you might reasonably think that the **size of a linear polymer chain is simply the length of the monomer or repeat unit multiplied by the number of repeat units**. However, this is not the case as we are interested in the **effective** size of the polymer which is the space occupied by the polymer. We will see in this lecture that depending on the **temperature, solvent, and local environment** even this **simple polymer chain** can adopted a **highly coiled collapsed structure, an highly elongated structure, or even in the most extreme circumstances a fully elongated structure**. We also know from our supplemental thermodynamics notes that polymers can adopt a large number of possible conformation, microstates. The conformation and thus the effective size of the polymer can change rapidly. This means that we will also have to develop a metric to measure the size of the polymer which is probabilistic in nature.

You can see this in the embedded video in the PowerPoint slides.

We will describe in detail several different models which will describe the effective size of polymers with increasing complexity

- **Ideal/Freely Jointed Chain Model**
- **Mathematician's Ideal Chain**
- **Chemist's Chain in Solution and Melt Model**
- **Physicist's Ideal Chain**

We will examine the differences in each model and how the **scaling changes** depending on some of the factors mentioned above.

## 3.3 Characterizing Polymer Size: Mean-Squared-Displacement

We have just mentioned that describing the effective size of the polymer can be tricky and it is not just a matter of adding up the monomer lengths. This problem becomes even more complex when we are dealing with polymers with a more **complex architecture, i.e. branched, dendrimer, star polymers, syndiotactic, etc**. How do we characterize the size of a polymer then? Well the tool that we will use is the **root mean squared end to end distance (RMSD)** which is shown below

$$\langle r^2 \rangle^{\frac{1}{2}} \tag{3.1}$$

where $r$ is the vectorial position of the polymer at one end and the other end in 3D, seen in the image below

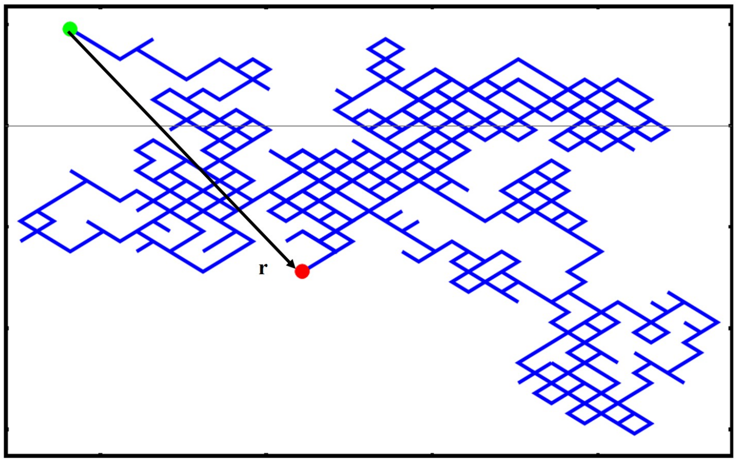


Figure 3-1: End-to-End Distance

We take the square because this will give us a quantity in units of length. Note as well that the $\langle\rangle$ indicates an average quantity as we will typically **average over many microstates and conformations**. You can also see that by squaring the $r$ we will never have negative values. Now there are many ways of calculating a mean square displacement. One method is simply **averaging the end-to-end displacement values of a single polymer chain as it moves and fluctuates over time** or you can **average one snapshot of identical polymer chains which are all under the same external stimuli/experimental conditions**.

To get started let's do a quick couple of extreme example of a linear rigid rod like polymer architecture that is stretched to the fully extended position. This polymer has a monomer length of $l$ and the number of monomers is as always $n$. What is the MSD end-to-end distance?

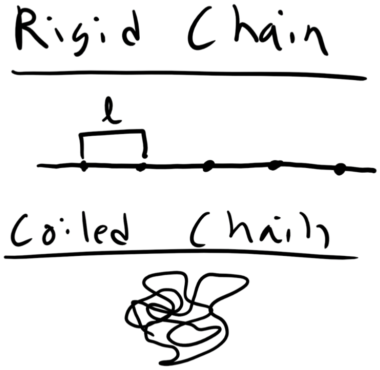


Figure 3-2: Rigid vs Coiled Polymer

Well let's start with the $r$ vector?

It is $nl$! So

$$\langle r^2 \rangle^{\frac{1}{2}} = nl = L \tag{3.2}$$

where $L$ is the contour length of the polymer, the fully extended distance.

What would be the contour length of polyethylene with a $D_{p,n}$ of 10000?

Approximately 1.5$\mu$m.

## 3.4 Ideal/Freely Jointed Chain (FJC)/Gaussian Model

Now the above example is an **very extreme situation**, although an important one to consider. However, polymers are **not typically fully extended** and this is an **energetically unfavorable microstate**. To describe a more typical polymer conformation let's start with a simpler model. Let's consider an **ideal polymer** chain where we assume that there are **no intramolecular steric interactions along the polymer chain**. This means that the polymer can **intersect itself along the backbone without any penalty**. This is the **Ideal/FJC/Gaussian Chain Model.**

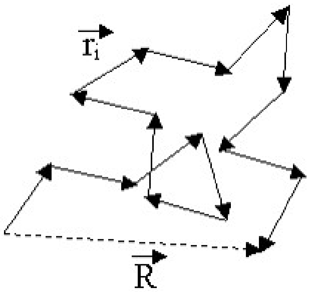


Figure 3-3: Ideal Chain Model

So again here we have a polymer chain with a monomer length, $l$, and a number of monomers, $n$. We also assume that in **addition to the ability of chain to cross over itself** the **monomers can rotate** in **any dimension** with respect to one another. We are essentially **ignoring the constraints that double or triple carbon bonds can place on polymer rotation, steric or repulsive interactions, or intermolecular interactions**. So with all of these assumptions we can describe the polymer as essentially performing a **random walk** through space in time. Or alternatively we can construct a polymer chain by **placing each monomer in a position in space using a stochastic or random algorithm** (Monte Carlo). In this random walk the step size would be fixed at $l$ from the previous step/monomer and would continue until reaching $n$ random steps. Thus the position of monomer $i$ and $i+1$ are completely **uncorrelated**.

Let's start building our polymer chain taking a **probabilistic approach in 1D**. In 1D we can only move left or right and we will indicate that steps to the right are positive + and the left steps are negative −. So our r vector will simply be

$$r = (n_+ - n_-)l \tag{3.3}$$

where $n_+$ is the number of right/positive steps and $n_-$ is the number of left/negative steps. We should also point out that

$$n = n_+ + n_- \tag{3.4}$$

The question now is what is the probability of the polymer chain end to end distance being some arbitrary distance, $x$. Well the distance will be, as we just mentioned above, the probability of getting $n_+$ heads out of a total of $n$ steps. This is valid because in this model the **probability of taking positive and negative steps are equal**, this is a **Markov** process. So the number of ways we can choose $n_+$ steps from a total of $n$ steps which is just

$$\Omega = \frac{n!}{n_+!n_-!} \tag{3.5}$$

or equivalently

$$\Omega = \frac{n!}{n_+!(n! - n_+!)} \tag{3.6}$$

This should look very similar to our supplementary lecture and the discussion about microstates. We should also make a note here that the total number of configurations of this polymer will be $2^n$, as dictated by the **binomial distribution equation** and seen below

$$\Omega_{total} = \sum_{n_+=0}^{n} \frac{n!}{n_+!(n! - n_+!)} = 2^n \tag{3.7}$$

Now to get to the probability of finding a particular configuration or end to end distance of $x$ we have to divide by the total number of combinations which gives us the following expression

$$P_{1D}(x,n) = \frac{n!}{2^n n_+!(n! - n_+!)} \tag{3.8}$$

As $n$ becomes very large we can use Stirling's formula $\ln n! \approx n(\ln n - 1)$ to simplify the equation and we can re-write it, after a lot of math, as seen below

$$\ln P_{1D} = -n \ln 2 + n(\ln n - 1) - n_+(\ln n_+ - 1) - (n - n_+)(\ln(n - n_+) - 1) \tag{3.9}$$

$$\ln P_{1D} = -n \ln 2 + n \ln n - n_+ \ln n_+ - (n - n_+) \ln(n - n_+) \tag{3.10}$$

we also want to re-write this equation in terms of x and we know that the polymer end to end distance x can be expressed as

$$x = n_+ l - (n - n_+) l = l(2n_+ - n) \tag{3.11}$$

so plugging this back into the previous equation we get after much more math we get

$$\ln P_{1D} = \frac{-N}{2}\left[\left(1 - \frac{x}{nl}\right)\ln\left(1 - \frac{x}{nl}\right) + \left(1 + \frac{x}{nl}\right)\ln\left(1 + \frac{x}{nl}\right)\right] \tag{3.12}$$

Now typically polymer are very long and $n$ is very large so the probability is almost zero except at small values of $n$ so we must perform a Taylor expansion up to the second order of $\frac{x}{nl}$ and we get that

$$\ln P_{1D} = -\frac{x^2}{2nl^2} \tag{3.13}$$

And after normalization we finally get our probability distribution which is **Gaussian**, hence the FJC/Ideal/Gaussian model below

$$P_{1D}(x,n) = (\frac{1}{2\pi nl^2})^{\frac{1}{2}} exp(-\frac{x^2}{2nl^2}) \tag{3.14}$$

**Again let's remember the physical nature of what this is telling us.** The **probability** of **finding a polymer** with an **end-to-end distance** $x$ is given by the **probability distribution** above which states that finding **highly elongated polymers** are **extremely rare** which should **make sense intuitively**.

What is the mean of the Gaussian? It is zero.

Also what is the standard deviation of this Guassian? It is $N^{\frac{1}{2}}l$, more on this later.

We can actually confirm this at least qualitatively right now using our Mathematica demonstration. It looks pretty Gaussian to me. We can also fit this quantitatively as well as seen in the Mathematica Notebook.

This is good and all for 1D but typically we operate in 2D or more often 3D. Well since we have a completely uncorrelated random walk we can use the **superposition principle** in order to develop this expression which is

$$P_{3D}(x,y,z,n) = P_{1D}(x,n)P_{1D}(y,n)P_{1D}(z,n) = (\frac{1}{2\pi nl^2})^{\frac{3}{2}} exp(-\frac{3(x^2+y^2+z^2)}{2nl^2}) \tag{3.15}$$

and we can right this a little bit nicer by using our $r$ vector terminology where $r^2 = x^2+y^2+z^2$

$$P(r,n) = (\frac{1}{2\pi nl^2})^{\frac{3}{2}} exp(-\frac{3r^2}{2nl^2}) \tag{3.16}$$

Now everyone who has taken my ENGR110 class for what will be the value of $\int_0^\infty P(r,n)4\pi r^2 dr$? Remember that $4\pi r^2 dr$ is the volume of a thin spherical shell with a thickness $dr$ located at a distance $r$ from one end of the polymer chain. It is simply 1! the **probability of finding a polymer chain with an end-to-end distance from 0 to infinity has to be 1**. From the probability distribution we can also finally get an expression for the MSD which by taking the second moment of the distribution as can be seen below

$$\langle r^2 \rangle = \int_0^\infty r^2 P(r,n) 4\pi r^2 dr = nl^2 \tag{3.17}$$

Again notice above that **this is equivalent to the variance of the Gaussian distribution**. So the **root mean square end-to-end distance** is in effect the width of the end-to-end distance distribution. Can you convince yourself that

$$\langle r \rangle = \int_0^\infty r P(r,n) 4\pi r^2 dr = 0 \tag{3.18}$$

This should make sense intuitively because we have a complete/perfect random walk so on average the end to end distance should be 0! Our physical understanding matches with the math!

**Mathematician's Ideal Chain Derivation for Ideal Chain/FJC Model**

We can derive the MSD of of the FJC Chain model without using a probabilistic perspective as well and this might be a little more intuitive for some people, at least it was for me. Again remember that in the random walk or ideal model we ignore bonding and it is really unphysical in most cases. The end-to-end distance of the Ideal Chain/FJC model can be derived using a different mathematical formalism, sometimes referred to as the **Mathematician's Ideal Chain**. We again assume $n$ monomers with a fixed monomer length $l$ and which is represented as a vector in 3D space $\vec{l_i}$ where this vector refers to monomer i.

So the end to end distance vector is

$$\vec{r} = \vec{l_1} + \vec{l_2} + ... + \vec{l_n} = \sum_{i=1}^{n} \vec{l_i} \tag{3.19}$$

On average what will be the value of $\langle \vec{r} \rangle$? Remember that for the ideal polymer chain each step positive or negative is equally likely, these steps are **uncorrelated**. So on average the value of $\langle \vec{r} \rangle = 0$.

The better question is what will be $\langle \vec{r}^2 \rangle$ and we can write this as the dot product

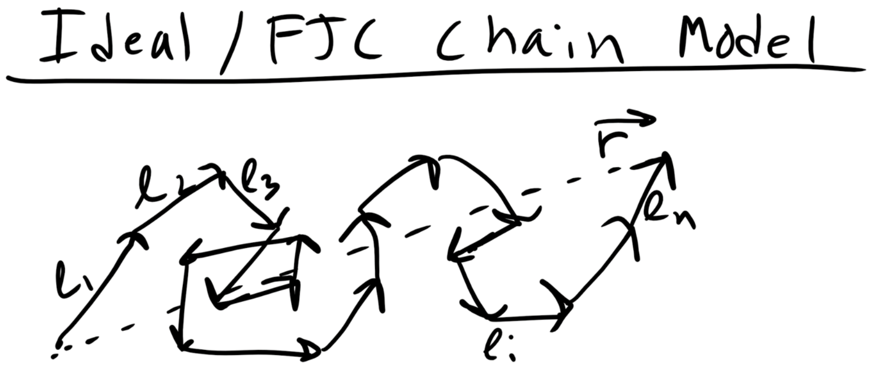


Figure 3-4: Mathematician's Ideal Chain Derivation

$$\langle \vec{r}_i \cdot \vec{r}_j \rangle = \left\langle \sum_{i=1}^{n} \vec{l}_i \cdot \sum_{j=1}^{n} \vec{l}_j \right\rangle \tag{3.20}$$

where $i$ and $j$ refer to monomer $i$ and monomer $j$. Remember that the dot product is

$$\vec{l}_i \cdot \vec{l}_j = |l_i||l_j| \cos \theta_{ij} \tag{3.21}$$

We can show the MSD in matrix notation as well

$$\langle \vec{r}_i \cdot \vec{r}_j \rangle = \begin{bmatrix} \vec{l_1} \cdot \vec{l_1} & \vec{l_1} \cdot \vec{l_2} & \vec{l_1} \cdot \vec{l_3} & \dots & \vec{l_1} \cdot \vec{l_n} \\ \vec{l_2} \cdot \vec{l_1} & \vec{l_2} \cdot \vec{l_2} & \dots & & \\ \vdots & & & \ddots & \\ & & & & \\ \vec{l_n} \cdot \vec{l_1} & \dots & & & \vec{l_n} \cdot \vec{l_n} \end{bmatrix}$$

Now let's think about the value of the dot product on the diagonal component. The **magnitude** will simply be $l^2$ for every component but now we need to think about the $\cos\theta$ between the two vectors. Well for the diagonal component they will always be pointing in the same direction so the angle will be $0^o$ and then $\cos 0^o = 1$.

Now for the off diagonal components. Let's keep it simple and think about the 1D scenario. Well there the value of $\cos theta = 1$ or $= -1$. But remember we are concerned about the averages so since both positive and negative steps are **equally probable (Markov/Monte Carlo) or uncorrelated** so on average the value of $\cos\theta = 0$.

So the matrix reduces to

$$\langle \vec{r_i} \cdot \vec{r_j} \rangle = \begin{bmatrix} l^2 & 0 & 0 & \dots & 0 \\ 0 & l^2 & \dots & & \\ \vdots & & & \ddots & \\ & & & & \\ 0 & \dots & & & l^2 \end{bmatrix}$$

Thus the sum of this matrix becomes

$$\langle r^2 \rangle = nl^2 \tag{3.22}$$

just as we obtained previously with our other probabilistic method!

## 3.5 The Chemist's Polymer Chain Model

So far we have neglected a lot of detail in describing polymer chains that make the previous models a bit unphysical. We have neglected taking into account restrictions in bond angles to to steric hindrance along the backbone chain a well as any solvent effect and how that may affect the end-to-end distance of the polymer chain.

Here, we will introduce two new **effective** parameters, $C_\infty$ and $\alpha$, that can be used to correct for problems in the simple random walk model end-to-end distance based on known bonding constraints and solvent considerations. Note that in a random walk, $C_\infty = \alpha = 1$. The parameter $C_\infty$ is used to take into account restrictions due to bonding and steric hindrance from the polymer chain, while the parameter $\alpha$ takes into account effects from the solvent. This improved models is referred to as the **Chemist's Polymer Chain in Solution and Melt** model. This model is more physically accurate as this model considers bond angle restrictions between adjacent atoms (or monomers) due to chemistry. This governing equation for the Chemist's model is

$$\langle r^2 \rangle = nl^2 C_\infty \alpha^2 \tag{3.23}$$

Let's figure derive where these new values come from starting with going back to the matrix that we developed in the FJC model. So in the **Chemist's Model** we assume that we have a fixed bond angle $\theta$, makes sense thinking of polyethylene. Now the dot product of monomer $i$ and $i+1$ will be

$$\vec{l_i} \cdot \vec{l_{i+m}} = l^2(-\cos\theta)^m \tag{3.24}$$

where $m$ is an integer denoting the number of monomers away from monomer $i$, the $\theta$ keeps getting multiplied because of the projection of the the bond onto the next neighbor. You can see this model schematically here

Now we can adjust our previous matrix and get

# Chemists Chain Model

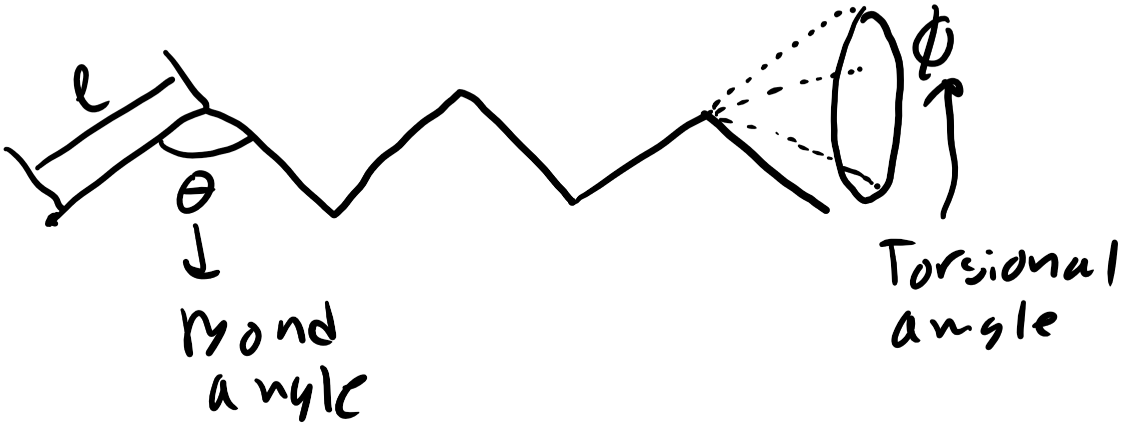


Figure 3-5: Chemist's Chain Model

$$\langle \vec{r}_i \cdot \vec{r}_j \rangle = \begin{bmatrix} l^2 & l^2(-\cos\theta) & l^2(\cos\theta)^2 & \dots & l^2(-\cos\theta)^{n-1} \\ l^2(-\cos\theta) & l^2 & \dots & & \\ \vdots & & & \ddots & \\ & & & & \\ l^2(-\cos\theta)^{n-1} & \dots & & & l^2 \end{bmatrix}$$

And once you sum this matrix we find that

$$\langle r^2 \rangle = nl^2 \left( \frac{1-\cos\theta}{1+\cos\theta} \right) \tag{3.25}$$

This factor of $\frac{1-\cos\theta}{1+\cos\theta}$ is

$$C_\infty = \frac{1-\cos\theta}{1+\cos\theta} \tag{3.26}$$

so we now get that

$$\langle r^2 \rangle = nl^2 C_\infty \tag{3.27}$$

where $C_\infty$ is the **Flory characteristic ratio** can be thought of as a measure of the **stiffness of your monomer unit** or **how hard it is to rotate**. You can look up this ratio for a number of different polymers and we should know that for C-C bonds $\theta = 109.5^o$. Much more on Flory to come.

**Rotational Isomeric States**

Now this is an improvement but we have missed something very important and it is related to our discussion of **conformers vs. isomers**. We have previously briefly mentioned that there are certain molecules with different **isomeric states**, i.e. same chemical formula but distinct structures that can't be related via rotation around a bond. A conformer or conformational isomer can be related different structures via rotations around a single bond and these different rotational states are called **rotational isomeric states (RIS)**. Additionally these different states will each have different potential energies and thus we will find these different RIS states according to the weighted probabilities determined by the rotational potential $V(\phi)$. We can see the different RIS states of a conformer n-butane here

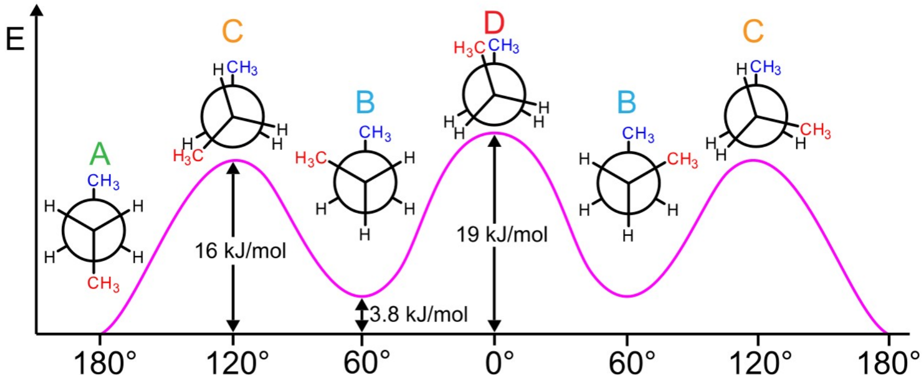


Figure 3-6: Butane RIS States

Here there are clearly high energy states where the bulky methyl groups overlap with either a hydrogen or another methyl group. Then we have our lower energy conformation as seen denoted by **gauche** ± and the lowest energy being the **trans** conformation. I wanted to illustrate this example because we did not treat this case in our derivation of the Chemist's chain model so wee need to take this into account. Luckily we can do so using a very similar train of logic as we did above but instead of simply just using a fixed $\cos theta$ we need to take an **ensemble average** of the R**IS angles based on the number of microstates for each angle** so we will use

$$\langle \cos\phi \rangle = \frac{\int \cos\phi V(\phi) d\phi}{\int V(\phi) d\phi} \tag{3.28}$$

and we eventually end up with (skipping full derivation as it is very very very extremely difficult)

$$\langle r^2 \rangle = nl^2 \left[ \left( \frac{1-\cos\theta}{1+\cos\theta} \right) \left( \frac{1+\langle\cos\phi\rangle}{1-\langle\cos\phi\rangle} \right) \right] \tag{3.29}$$

And now we have our new and improved Flory Characteristic Ratio $C_\infty$ which is

$$C_\infty = \left( \frac{1-\cos\theta}{1+\cos\theta} \right) \left( \frac{1+\langle\cos\phi\rangle}{1-\langle\cos\phi\rangle} \right) \tag{3.30}$$

This derivation is beyond the scope of this course but you can look it up in **Statistical Mechanics of Chain Molecules** if you are interested, which is Flory's text again much more Flory to come. Also some refer to this addition as the Hindered Rotation model.

Let's take a moment here to stop to appreciate what we have just done. By taking into account **bong angles and rotations** we get fairly accurate values of $C_\infty$ compared to experimental measurements and usually this value **varies between 1-20**. It's important to note that $C_\infty$ **must always be at least 1** and this implies that the **FJC/ideal chain is the most coiled conformation**. This makes sense because by **restricting these bond rotations we are inherently expanding our polymer chain**, leading to a **more elongated polymer**.

However our work is not finished yet. We have taken into account bond angles and bond rotation but what else must we consider? Well does this model make any distinction between polymers that might have a large or bulky side chain? No! For these polymers with large bulky side chains we should expect that $C_\infty$ should increase as the rotations are more difficult due to steric interactions. So the increase is not due bonding interactions but due to **excluded volume effects**.

**Excluded Volume**

In order to capture these intramolecular steric interactions between monomers we have to talk about a somewhat initially obtuse concept of **excluded volume**. Excluded volume is the concept that monomers have **some volume around them that other molecules can't cross or move into this sphere**. This takes care of the FJC ability of the chain to self-cross. These **excluded volume interactions usually occur between monomers far apart on the polymer chain** (because they must cross and intersect) and as you might imagine again like the bond angles and rotation this **excluded volume effect will increase the $\langle r^2 \rangle$ of the polymer chain**.

Now this may still be a bit obtuse but you can visualize this excluded volume as a hard, impenetrable sphere that surround a given molecule or monomer. The **size of the sphere must reflect the structure of the monomer**. So a monomer, like **polystyrene** with a large **bulky phenyl group** will have a **larger excluded volume** than **polyethylene** with it's **hydrogen groups and no side chain**. This excluded volume interaction will also depend on the interactions of the monomer with **solvent interactions**. If the monomer **doesn't like to interact with the solvent then the polymer will want to coil and collapse to avoid these interactions and thus the excluded volume will decreases and vice versa**. Remember that the solvent is the majority component and solute is the minority component.

## 3.6 Effect of Solvent on Polymer Chain MSD

Speaking of solvent effect...as we mentioned in our Polymerization lecture there are times when the polymer is immersed in some type of solvent (i.e. water, alcohol, organic solvent, etc.). This solvent can have serious consequences on the dimension of our polymer chain. In **good solvents**, i.e. s**olvents were the polymer likes to interact with the solvent (favorable enthalpic intermolecular interactions)**, the polymer will **extend** in order to **maximize the number of**

**interactions between monomer and solvent**. Conversely, if we are dealing with a **bad solvent** then the polymer **doesn't want to interact with the solvent** and the **polymer chain will fold in on itself** and **coil** in order to **minimize interactions** with the **solvent** and the end-to-end distance will decrease. In the FJC/Ideal model we are in a very special condition with regards to solvent in that we are in a $\theta$ **condition** and thus in a **theta solvent**. In this condition you can imagine that upon mixing a polymer chain and a **solvent the enthalpy of mixing is 0** just like an **ideal solution**. Alternatively you can imagine that **excluded volume of the polymer chain does not change upon adding a $\theta$ solvent**.

The parameter that we use to quantify the effect of **solvent quality** is measured via a factor $\alpha$. Luckily $\alpha$ is a fairly simple quantity to measure and is simply the ratio of the MSD end-to-end distance of the real chain in solution vs the chain in a $\theta$ solvent

$$\alpha^2 = \frac{\langle r^2 \rangle}{\langle r^2 \rangle_\theta} \tag{3.31}$$

where $\langle r^2 \rangle_\theta$ is the MSD of the chain in a $\theta$ solvent. So let's define some values of $\alpha$.

What will be the value of $\alpha$ in a good solvent?

Well $\alpha > 1$ for a good solvent.

What about a bad solvent?

$\alpha < 1$ for a bad solvent

What about a $\theta$ solvent?

$\alpha = 1$ for a $\theta$ solvent

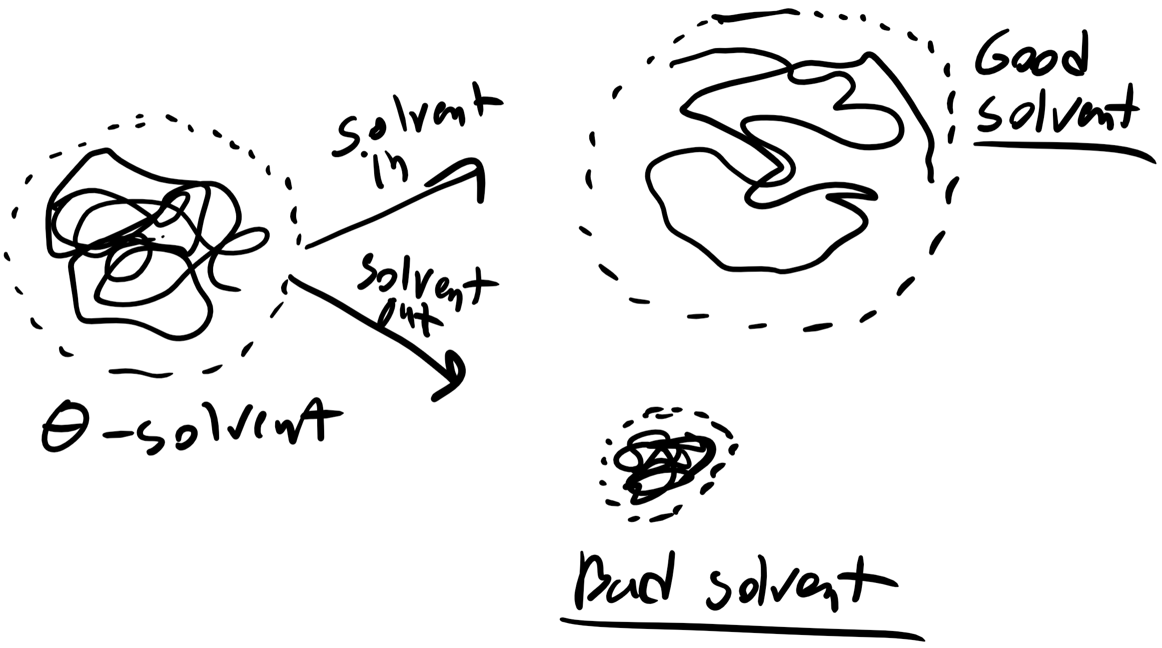


Figure 3-7: Solvent Quality

We will be talking much more about enthalpic interactions when we discuss Flory and whether **enthalpic interactions are good/favorable and whether they are bad/poor/unfavorable interactions**. We will talk about **monomer-monomer interactions** ($\epsilon_{m-m}$), **monomer-solvent interactions** ($\epsilon_{m-s}$), and **solvent-solvent** ($\epsilon_{s-s}$) interactions. Remember from the thermodynamic lecture that we always want lower or negative energies so fo**r a good solvent** $\epsilon_{m-s}$ should be the **lowest energetic interaction** and for **bad solvent** $\epsilon_{m-s}$ **should be larger**. Much more on this when we get to Flory.

## 3.7 Physicist's Ideal Chain

The last model is the **Physicist's Ideal Chain**. Here we take a **coarse-grained approach** and approximate **larger chains as freely jointed chains**. We then change the values of $n$ and $l$ to $N$ and $b$ to reflect a larger length scale, where $b$ is the **Kuhn** length. This model holds for a chain in $\theta$ condition or in the **melt state**, where the polymer chain is not in solvent (again we will discuss this more in depth once we get to Flory). Essentially, all the work that we have just done in defining $C_\infty$ is encapsulated in these terms as seen below

$$N = \frac{n}{C_\infty} \tag{3.32}$$

$$b = C_\infty l \tag{3.33}$$

## 3.8 Radius of Gyration

Now before we move we should consider that polymers are not all simple linear chains. We encounter **star, dendrimers, branched, and many other complex architectures** and it becomes much more complicated to measure the average mean squared end-to-end distance. For these polymers we will typically calculate the **radius of gyration** which is

$$r_g^2 = \frac{1}{n}\sum_{i=1}^{n}(\vec{r}_i - r_{cm})^2 \tag{3.34}$$

where $r_{cm}$ is the center of mass of the polymer as seen below

$$\vec{r}_{cm} = \frac{\sum_{j=1}^{n} M_j \vec{r}_j}{\sum_{j=1}^{n} M_j} \tag{3.35}$$

but typically we know that the monomer mass $M$ will be the same for all monomers so $M_j = M_o$ and we can re-write the position vector of the center of mass as

$$\vec{r}_{cm} = \frac{1}{n}\sum_{j=1}^{n} M_j \vec{r}_j \tag{3.36}$$

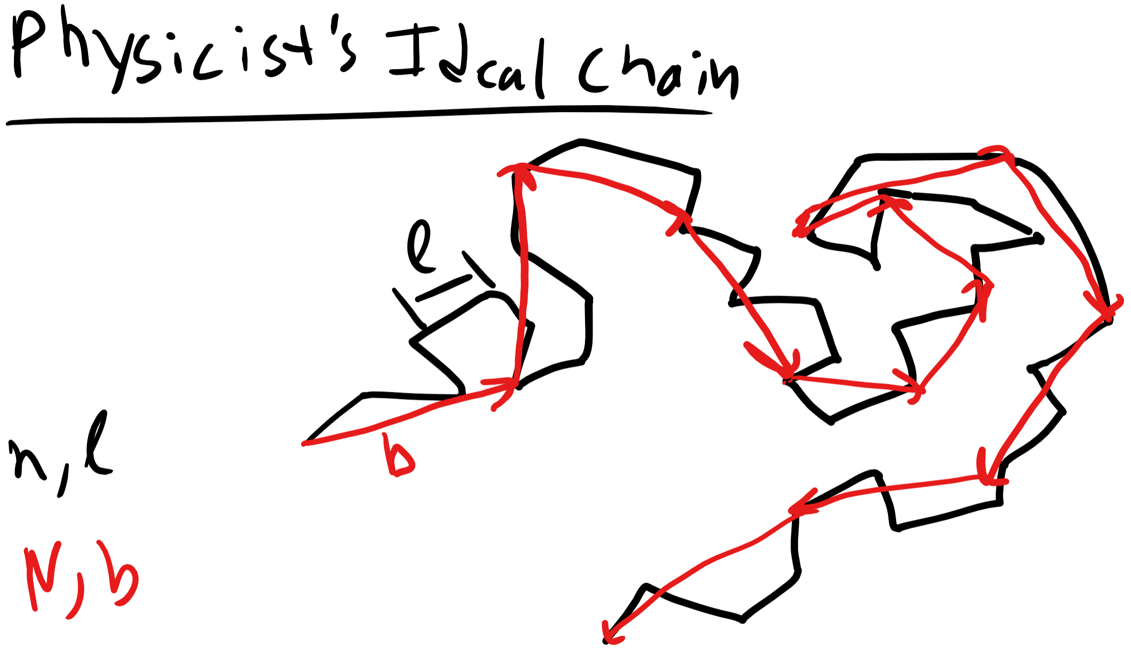


Figure 3-8: Physicist's Ideal Chain

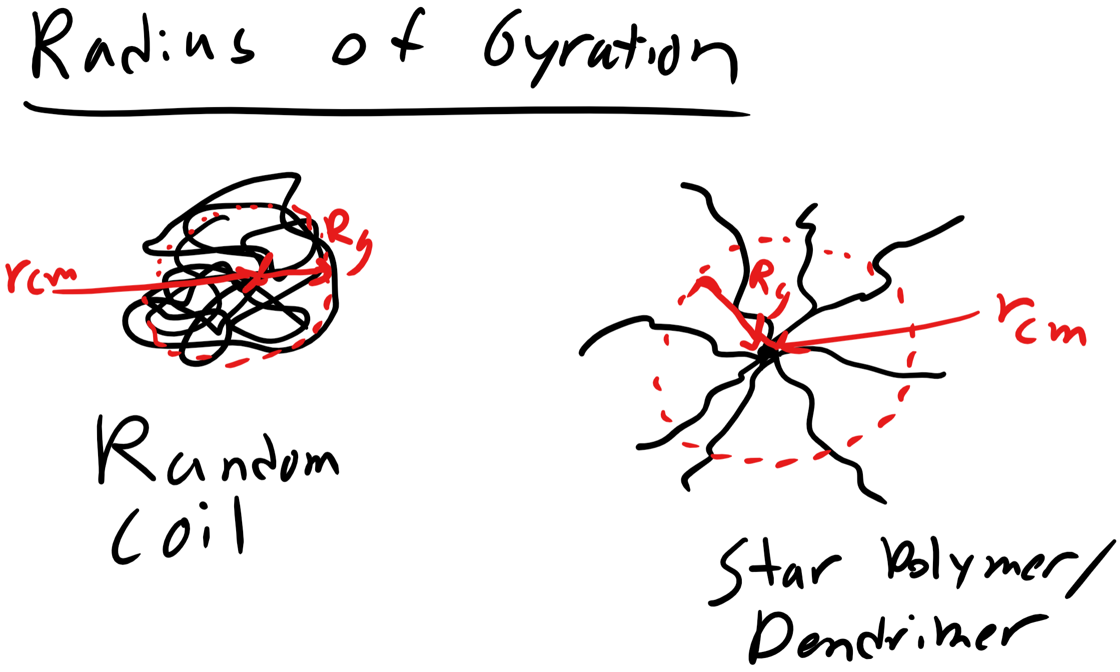


Figure 3-9: Radius of Gyration

This is a very useful parameter because you can calculate this if the polymer is branched, crosslinked, or a comb as well. The **radius of gyration is simply the mean squared end-to-end distance from the center of mass divided by the number of monomers**. This also gives us an idea of the mass density distribution of the polymer as well.

Now you can derive the radius of gyration for all of the polymer chain models that we will discuss in this lecture but one of the most important relationship is **relating the radius of gyration to the ideal linear chain model** which is

$$\langle r_g^2 \rangle = \frac{\langle r^2 \rangle}{6} \tag{3.37}$$

## 3.9 Real Polymer Chains : Swelling and Excluded Volume

We have just given a fairly hand-wavy description of the solvent quality parameter $\alpha$ but we have failed to capture the behavior of **real** chains. Specifically, the **interactions between monomers and between monomers and solvent molecules**. We will now include these interactions and derive $\alpha$ explicitly using theory developed by **Paul Flory a polymer physicist and Nobel Prize winner**. We will also see our **first instance of our never ending battle between entropy and enthalpy**. We will see the different contributions that effect $\alpha$, learn how to control or modify $\alpha$, and the effect it has on properties like viscocity or the end-to-end distance of the chain.

**Contributions to Polymer Swelling: Entropic Spring and Excluded Volume**

So before we jump into the factors that can cause polymer swelling or polymer coiling let's start from the the **initial unperturbed state where** $\alpha = 1$ and move to it's **final swollen state where** $\alpha > 1$. For most polymers we should expect that in reality the polymer end-to-end distance will always be larger than in the $\theta$ solvent case as typically the the monomer-monomer interactions should lead to some **mutual repulsion** (like-like interactions) and **increase the end-to-end distance** of the polymer chain.

When thinking about how to describe the contributions to polymer swelling we will typically have

1. **Entropic (Elastic) Contribution:** Chain wants to compress and coil to maximize number of configurations/microstates
2. **Enthalpic Contribution:** Monomer-monomer interactions (excluded volume) increases chain size, maximize enthalpy

Let's think about these two contributions starting with the **entropic contribution** which is sometimes referred to as the **entropic spring** or **entropic restoring force**. When the polymer chain is extended via swelling or if you take it to the extreme and we pull and stretch a polymer chain we know that the end-to-end distance distribution of polymer chains follows a Gaussian distribution. By **pulling on the polymer chain or swelling a polymer chain we are biasing the distribution and the polymer will adopt much less probable larger end-to-end distances**. Doing this **decreases the number of microstates** and thus **decreases the entropy**

**of the system**. This is not energetically favorable we want to **always increase the entropy of the system**. So this induces an **entropic restoring force** to the undeformed state. You can also call this an **entropic spring** because the functional form of his entropic restoring force will be very similar to Hooke's law. **So when we swell or pull on a polymer we pay a cost in entropy or pay an entropy energy penalty**.

So now what about the **enthalpy contribution.** When we have a polymer in a solvent the effective interactions between monomers is dependent on the interaction between monomers and the monomers with the solvent. As we have mentioned previously in a **good solvent** the monomer-monomer interaction is less favorable (higher energy) than the monomer-solvent interactions and vice versa for the **poor solvent**. In a **theta** solvent the monomer-solvent interaction counter acts the monomer-monomer interaction so that there is no net interaction, i.e. enthalpy of 0, ideal solution.

So with these two contributions we will have the total free energy as being composed of two contributions which sum

$$G = G_{entropic} + G_{enthalpic} \tag{3.38}$$

where $G$ is the system free energy of the polymer and solvent, $G_{entropic}$ is the entropic spring contribution and $G_{enthalpic}$ is the enthalpic contribution. Let's derive these two contributions to free energy.

## 3.10 Entropic Spring

Let's start with the entropic spring contribution. We can remember that the probability distribution of an ideal chain is

$$P(r,n) = (\frac{1}{2\pi n l^2})^{\frac{3}{2}} \exp(-\frac{3r^2}{2nl^2}) \tag{3.39}$$

We want to write an expression for the free energy contribution of the entropic spring, i.e. how the free energy will change as a function of the end-to-end distance of our polymer chain, $r$. Well we know from our thermodynamics and statistical mechanics lecture that we can relate the number of possible configurations $\Omega$ to the entropy

$$S = k \ln \Omega \tag{3.40}$$

When we change the initial end-to-end distance of our initial ideal chain with an end-to-end distance of $r_0$ and a number of monomers $n$ the entropy can be re-written as

$$S(n,r) = k \ln \Omega(n,r) \tag{3.41}$$

where you can see that both the entropy and number of possible configuration will change as a function of the number of monomers and end-to-end distance but typically in the problems that we will work on the **number of monomers will be fixed**, $n$, but the end-to-end distance will change.

Now we can write the probability that a polymer **assumes a given microstate or configuration for a given number of monomers and end-to-end distance** is just as we have described before in our supplementary lecture

$$P(n,r) = \frac{\Omega(n,r)}{\int \Omega(n,r)dr} \tag{3.42}$$

Again quick note that we are working on the assumption that **all configurations are equally probable** i.e. ideal chain. Thus the probability is just the number of configurations with that particular microstate divided by the total number of configurations. So now we can do some math

$$S(n,r) = k \ln \Omega(n,r) \tag{3.43}$$

$$S(n,r) = k \ln \left[ P(n,r) \int \Omega(n,r)dr \right] \tag{3.44}$$

$$S(n,r) = k \ln P(n,r) + k \ln \left[ \int \Omega(n,r)dr \right] \tag{3.45}$$

$$S(n,r) = -\frac{3}{2}k\frac{r^2}{nl^2} + \frac{3}{2}k \ln \left( \frac{3}{2\pi nl^2} \right) + k \ln \left[ \int \Omega(n,r)dr \right] \tag{3.46}$$

$$S(n,r) = -\frac{3}{2}k\frac{r^2}{r_0^2} + S(n) \tag{3.47}$$

We have our entropy expression which **varies as a function of the ratio between the actual end-to-end distance of the chain** $r$ **vs the unperturbed or ideal chain distance** $r_0$ **which should be familiar** $\frac{r^2}{r_0^2} = \alpha^2$ . Now this last term is not a function of $r$ and this will become important in just a bit because we always want to find the state of the system at equilibrium which will involve taking the derivative of the free energy with respect to $r$ so this will eventually disappear. Now we can write

$$G_{entropic}(n,r) = H(n,r) - TS(n,r) = \frac{3}{2}kT\frac{r^2}{r_0^2} + S(n) \tag{3.48}$$

where remember we set $H$ **to 0 as we are working on the ideal chain assumption**. Now you might be concerned about this ratio of distances and at this point we have to state **this expression is valid only in tension**, i.e. $r > r_0$. I won't go into the full derivation but we can modify this expression slightly to include compression and we obtain a more useful equation

$$G(r)_{entropic} = \frac{3kT}{2}\left( \frac{r^2}{nl^2} + \frac{nl^2}{r^2} \right) \tag{3.49}$$

Here we see that in **tension the first term is large** and the **second term goes to 0** and **vice**

**versa for compression**. This make sense as a**ny perturbation from ideal chain conditions** will r**educe the number of possible microstates** and thus **decrease entropy**!

We can derive a similar expression using a statistical mechanics approach by remembering that

$$P(r) \approx \exp\left(-\frac{G(r)}{k_b T}\right) \tag{3.50}$$

Additionally we can also simply our expression for the probability of an ideal chain as follows ignoring the pre-factors. Quick note in this class we will discuss over and over again that scaling behavior is critical when talking about polymer. Prefactors or constants are not critical but scaling behavior is much more important.

$$P(r) \approx \exp\left(-\frac{3r^2}{2nl^2}\right) = \exp\left(-\frac{3r^2}{2r_0^2}\right) \tag{3.51}$$

Note that we have defined $r_0^2 = nl^2$ from the FJC/Ideal chain model. After doing some math we are left with the following expression which is

$$G_{entropic}(n,r) = H(n,r) - TS(n,r) = \frac{3}{2}kT\frac{r^2}{r_0^2} \tag{3.52}$$

where we are missing our additive factor $S(n)$ because of the assumptions and getting rid of our pre-factors. Again we can also relate this expression for the entropic or elastic free energy contribution directly to the solvent quality parameter.

## 3.11 Enthalpic/Excluded Volume Interactions:

Now, we need to write an expression which considers the monomer-monomer interactions. Well to start we can remember back to ENGR045 to our LJ potential and treat the monomers as hard spheres and look at the potential between the spheres as shown below

$$V_{LJ} = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] = \epsilon\left[\left(\frac{r_o}{r}\right)^{12} - 2\left(\frac{r_m}{r}\right)^{6}\right] \tag{3.53}$$

where $\epsilon$ is the depth of the potential well, $\sigma$ is the distance at which the inter-particle potential is zero, $r$ is the distance between particles, and $r_m$ is the distance where the potential is minimized. This is a very specific potential and this expression will change for different interactions but this is a starting point for what we will discuss.

At **short distances the potential will increase** (energetically unfavorable) due to **overlap of electron clouds**. At l**arger distance the potential will be slightly negative but will approach 0 as the monomers are too far away to interact**. At some **equilibrium distance there will either be a well or a hill in the curve and this will depend on the solvent quality**. Lower energy will always denote a more favorable interaction so in **poor solvents where we know that the monomer-monomer interaction is more favorable we will see a well**

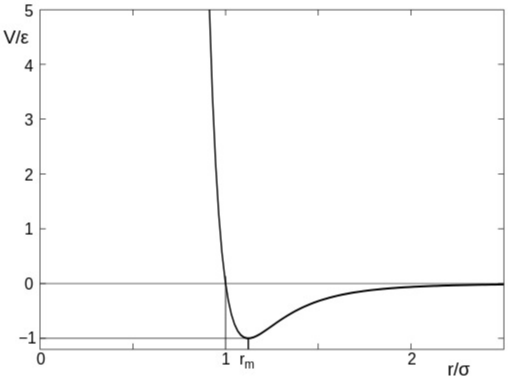


Figure 3-10: Lennard Jones Potential

**and most likely a deep well**. For **good solvent this well will be much more shallow or even become positive and create an energy hill**. The depth of the well or hill is given by $\epsilon$.

Again we can also find the probability of finding two monomers separated by a given distance $r$ is

$$P(r) = \exp\left( -\frac{U(r)}{k_b T}\right) \tag{3.54}$$

which you can see here and we can see that probability matches our discussion above. Note that at very large values of $r$ the energy goes to zero and thus the exponential of 0 is 1.

Now in order to find the excluded volume we have to utilize the **Mayer f-function**, a function that you will work with more often if you take a thermodynamic course which is

$$f(r) = \exp\left( -\frac{U(r)}{k_b T}\right) - 1 \tag{3.55}$$

All this function effectively does is subtract the probability at large $r$ values. What this function effectively does is describe the relative probability of finding two monomers close to one another versus no interaction at all. The excluded volume is then giving by the integral of this curve

$$v = -\int f(r)dr \tag{3.56}$$

which is also shown schematically here

What this graph shows is that the **excluded volume** is related to the **net** probability of finding two monomers close to each other across all space, thus accounting for **net interactions between two monomers**. The **excluded volume** is the **effective** volume occupied by a monomer including interactions with solvent and other monomers as well. We will have $v < 0$ for net attraction (poor solvent), $v = 0$ for no interaction ($\theta$ sovlvent), and $v > 0$ for net repulsion (good solvent).

Let's take a physical look at what this equation is telling us. Let's say think about what will happen if the potential has an energy hill or only a repulsive component, no attraction like in the case for a very good solvent. Well then the excluded volume will only be positive and very large

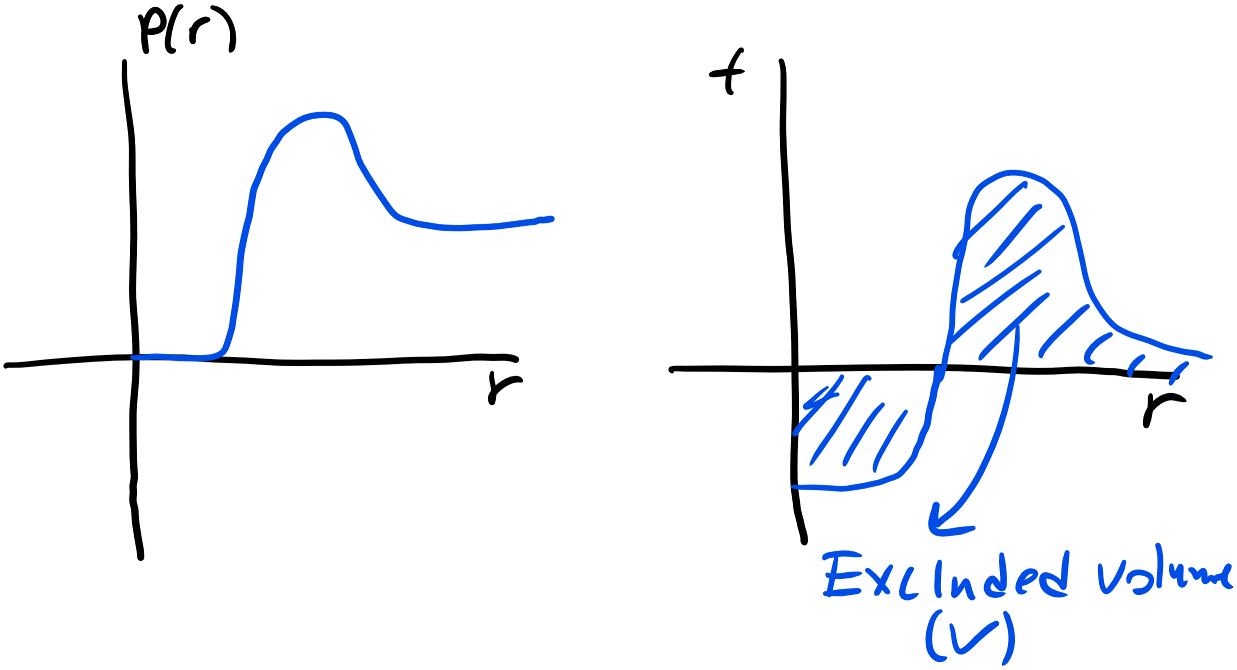


Figure 3-11: Excluded Volume

which leads to swelling as we might expect. As the attraction between monomers increase the excluded volume will still be positive but with a smaller magnitude and less swelling. At some point the attractive part of the potential will be the same magnitude as the repulsive leading to an excluded volume of 0 which is $\theta$ conditions. If the attraction increases further then the excluded volume will become negative the polymer will coil and collapse on itself.

Now that we have defined excluded volume as an interaction between monomers we can **derive an expression for the free energy between all the monomers in the chain**. Let's consider a a single monomer in a polymer chain with an excluded volume $v$ and $n$ other monomers in the polymer chain. Now remember what makes polymers and soft matter unique is that the **polymer chains interaction are on the order of $kT$ and this produces fluctuations of the polymer chain**. So let's consider a scenario where **one of the monomers collides or attempts to occupy the excluded volume of another monomer**. The **interaction energy** between these monomers **increases approximately by an amount of $kT$**. We can then approximate the total interaction based on the number of these collisions.

So let's keep is somewhat simple and say the probability of these interactions will clearly depend one the size of the excluded volume $v$ and the number of monomers $n$. We will also have to divide by the volume of the chain which we will approximate as $V \approx r^3$, as the larger the volume of the chain/end-to-end distance the less likely monomers will collide. So this will give us the interaction for a single monomer but we have $n$ monomers in our chain so we have to multiple again by $n$ and divide by 2 to avoid overcounting.

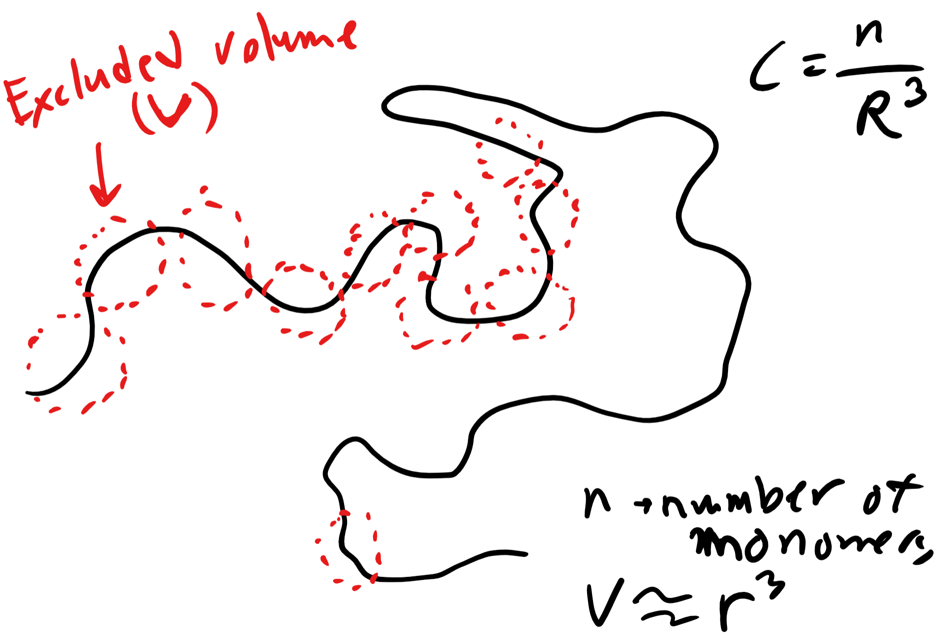


Figure 3-12: Enthalpic Picture

So we can write the free energy density for the enthalpic contribution as

$$\frac{G_{enthalpic}(r)}{V} \approx \frac{kTv}{2}\frac{n^2}{r^6} \tag{3.57}$$

Additionally we can see that the concentration of monomers $c$ as seen below

$$c = \frac{n}{r^3} \tag{3.58}$$

which allows us to write the expression below

$$\frac{G_{enthalpic}(r)}{V} \approx \frac{kTv}{2}c^2 \tag{3.59}$$

Note you can generalize this expression to include many body interactions

$$\frac{G_{enthalpic}}{V} \approx kT\left(\frac{vc^2}{2} + \frac{wc^3}{6} + ...\right) \tag{3.60}$$

We can then simply multiply by volume to get our total free energy

$$G_{enthalpic} \approx kT\frac{vc^2r^3}{2} \tag{3.61}$$

## 3.12 Flory Full Free Energy:

Finally we can now combine our two terms to obtain the full Flory Free Energy

$$G = G_{entropic} + G_{enthalpic} = kT\left(\frac{vc^2r^3}{2} + \frac{wc^3r^3}{6} + ...\right) + \frac{3kT}{2}\left(\frac{r^2}{nl^2} + \frac{nl^2}{r^2}\right) \tag{3.62}$$

We can also re-write this a bit more simply **ignoring the prefactors that are on the order of 1** and we can **ignore interaction terms beyond 3 body interactions**

$$\frac{G}{kT} = vc^2r^3 + wc^3r^3 + \frac{r^2}{nl^2} + \frac{nl^2}{r^2} \tag{3.63}$$

Now we can use our relationship for concentration of polymers and substitute in

$$\frac{G}{kT} = \frac{vn^2}{r^3} + \frac{wn^3}{r^6} + \frac{r^2}{nl^2} + \frac{nl^2}{r^2} \tag{3.64}$$

To obtain free energy we have to take the derivative and set this equal to zero

$$\frac{\partial G/kT}{\partial r} = -\frac{3vn^2}{r^4} - \frac{6wn^3}{r^7} + \frac{2r}{nl^2} - \frac{2nl^2}{r^3} \tag{3.65}$$

$$\frac{\partial G/kT}{\partial r} = -3vn^2 - \frac{6wn^3}{r^3} + \frac{2r^5}{nl^2} - 2nl^2r \tag{3.66}$$

Again **ignoring prefactors on the order of 1** and dividing by $(nl^2)^{3/2}$

$$\frac{\partial G/kT}{\partial r} = -\frac{vn^2}{(nl^2)^{3/2}} - \frac{w}{l^6}\left(\frac{nl^2}{r^2}\right)^{3/2} + \left(\frac{r^2}{nl^2}\right)^{5/2} - \left(\frac{r^2}{nl^2}\right)^{1/2} \tag{3.67}$$

substituting in for $\alpha$ from the Chemists chain model i.e. $\alpha = \left(\frac{r^2}{nl^2}\right)^{1/2}$

$$\frac{\partial G/kT}{\partial r} = -\frac{vn^{1/2}}{l^3} - \frac{w}{l^6}\alpha^{-3} + \alpha^5 - \alpha = 0 \tag{3.68}$$

With this expression in hand we can now explicitly determine the scaling behavior of the end-to-end distance of polymer chains in different solvents.

## 3.13 Scaling Behavior in Solvents:

**Good Solvents:**

Let's first consider the Full Free energy expression for a good solvent where we know that $v >> 0$ and $\alpha >> 0$. In doing so we can re arrange our expression

$$\alpha^5 - \alpha = \frac{vn^{1/2}}{l^3} + \frac{w}{l^6}\alpha^{-3} \tag{3.69}$$

We can see in this expression that the $\alpha^{-3}$ term will be essentially 0 and that $\alpha^5$ will be much greater than the $\alpha$ term so the expression reduces to

$$\alpha^5 = \frac{vn^{1/2}}{l^3} \tag{3.70}$$

We can then again use our Chemist's Chain model definition of $\alpha$ and obtain that

$$\langle r^2 \rangle^{\frac{1}{2}} \approx ln^{3/5} \tag{3.71}$$

This is our **essential finding!** We **quantitatively** prove what we have been discussing for several weeks that the end-to-end distance will scale differently $n^{3/5}$ vs the ideal scenario $n^{1/2}$ and that the polymer will expand and swell. This difference of $n^{1/10}$ may seem small but remember we have $n$ values up to 100,000.

Now we made a lot of assumptions here but when you run computer simulations of **self avoiding random walks (SARW)** where lattice sites can only be occupied by one monomer the scaling exponent is 0.588 so Flory was pretty close, he didn't get a Nobel for no reason.

**Poor Solvent**

We can do the same analysis for a poor solvent knowing that $v < 0$ and $\alpha << 1$. The expression now reduces to

$$\frac{vn^{1/2}}{l^3} = -\frac{w}{l^6}\alpha^{-3} \tag{3.72}$$

and plugging in for again for $\alpha$

$$\alpha^3 = \frac{w}{l^6}\frac{l^3}{vn^{1/2}} \tag{3.73}$$

$$\alpha = \Big(\frac{w}{vn^{1/2}l^3}\Big)^{1/3} \tag{3.74}$$

$$\frac{r}{n^{1/2}l} = \Big(\frac{w}{vn^{1/2}l^3}\Big)^{1/3} \tag{3.75}$$

$$\langle r^2 \rangle^{\frac{1}{2}} \approx \big(\tfrac{w}{v}\big)^{1/3} n^{1/3} \tag{3.76}$$

Here again we care about the scaling behavior so that pre-factor doesn't matter to use and we see that $\langle r^2 \rangle^{\frac{1}{2}} \approx n^{1/3}$ so this scaling is smaller than the ideal polymer chain so this polymer will be more coiled and collapsed and this all matches our intuition.

**Theta Solvent**

In a theta solvent we know that $v = 0$ and the three body parameter $w = 0$. This leads to an $\alpha = 1$ and we obtain our typical scaling for a theta solvent.

This concludes our analysis where we had two competing factors that we had to deal with to reach our thermodynamic state of equilibrium: a compressive elastic contribution that arises from an entropic spring restoring force and an expansive excluded volume effect from enthalpic interactions between polymer segments. Don't worry though we will do a similar analysis many more times in this class.

So to quickly summarize

1. **Mathematician's Ideal Random Walk/Ideal Chain Model** $\langle r^2 \rangle = nl^2$
    - **Assumes freely jointed chain, no bond angles, polymer can cross itself, no RIS states, steric interacitons, or solvent/excluded volume interactions. Captures behavior of** $\theta$ **solvent and melt state fairly well.**
2. **Chemist's Chain Model In Solution and Melt** $\langle r^2 \rangle = nl^2 C_\infty \alpha^2$
    - $\theta$ **Solvent or Melt** $\langle r^2 \rangle \approx nl^2$
    - **Good Solvent** $\alpha > 1$ $\langle r^2 \rangle \approx n^{\frac{6}{5}}$
    - **Poor Solvent** $\alpha < 1$ $\langle r^2 \rangle \approx n^{2/3}$
    - **Takes into account preferred bond angles, steric interactions, RIS states, solvent, and excluded volume interactions.**
3. **Physicist's Universal Chain** $\langle r^2 \rangle = Nb^2$
    - **Simplifies previous the Chemist's chain by incorporating the Flory parameter into the Kuhn length b, accurate for** $\theta$ **solvent and melt.**

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# CHAPTER 4

## FLORY HUGGINS THEORY: MIXING POLYMER BLENDS

## 4.1 Key Terms/Definitions:

- **Entropy of mixing** - the increase in entropy associated with mixing two previously separated species together; the entropy increases due to more possible configurations of the full system.
- **Enthalpy of mixing** - the change in energetic/enthalpic interactions related to contacts between two previously phase separated species; can be positive or negative depending on the nature of these interactions.
- **Bragg-Williams theory** - a description of the enthalpy and entropy of mixing for two small molecule species, predicting a free energy change symmetric around a mole fraction of 0.5 of either species; also known as regular solution theory.
- **Flory-Huggins theory** - an extension of the same conceptual framework as Bragg-Williams theory to include the connectivity of polymers; predicts a free energy change that is not necessarily symmetric around a volume fraction of 0.5.
- **Mean-field approximation** - in general, the approximation that some microscopic property of a system takes on the average value of that property throughout the entire system; in Flory-Huggins theory, the approximation that each lattice point can be treated as representing the average density of a given polymer species.
- **Chemical potential** - the change in free energy of adding one mole of a species to a system; equivalent for all species at equilibrium
- **Excess chemical potential** - in dilute solutions, a term included to account for non-ideal interactions between species; in polymer solutions, equal to 0 when $\chi = 1/2$.

## 4.2 Flory Huggins Theory:

We are now going to get a bit more complex and not only talk about a single polymer but talk about what happens when we mix polymers with other polymers, **polymer blends**, or when we mix polymers with solvents, **polymer solutions**. This requires using **Flory-Huggins** which is an extension of **Bragg-Williams** which should have been covered if you have taken a thermodynamics course but don't panic we will be going over this again for review (yes same Bragg as diffraction, those old scientists always had multiple breakthrough discoveries). The **Flory-Huggins** framework will allow us to **generate phase diagrams, understand fractionization by molecular**

**weight, melting point depression in spherulites, and rubber elasticity**. Additionally it also again will harken back to this idea of **entropic and enthalpic competition**.

Now why are polymer blends important? Well there are a number of critically important polymer blends that you might utilize every day and one such example of this is **High Impact Polystyrene or HIPS**. **HIPS** is a mixture of a very stiff yet brittle **PS** with a more compliant but more ductile **polybutadine (PB)**. This combination leads to a material, **HIPS**, that exhibits a much larger toughness as cracks are blunted by the rubbery PB regions as seen here

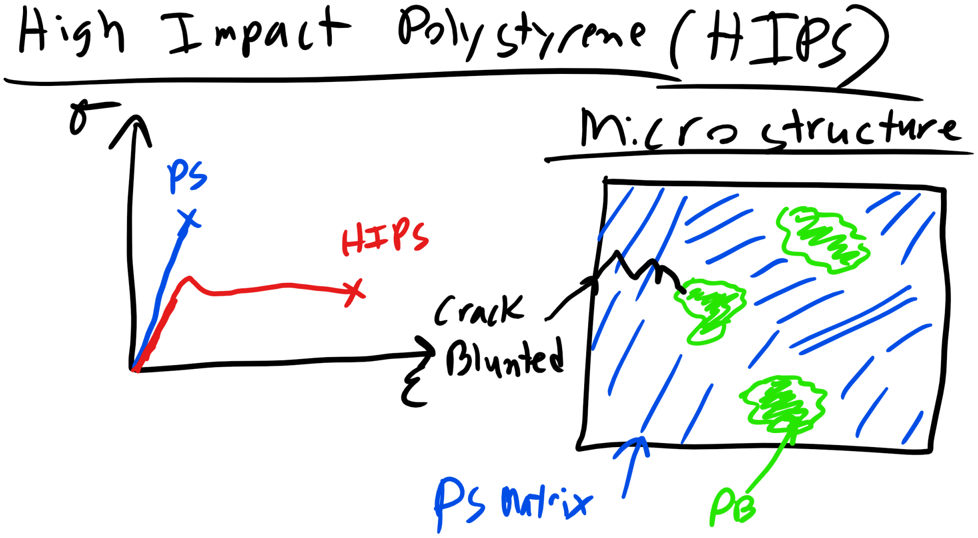

Figure 4-1: HIPS

So if we are dealing with polymer blends and polymer solution this involves **mixing** which is simply starting from a **state with two pure phases** and then these **two pure phases must spontaneously mix**. We know from our supplemental thermodynamics lecture that **spontaneous reactions** can only occur when the **change in free energy of the system upon mixing decreases** and you can guess what are going to be the two competing factors yes once again, say it with me

1. **Entropy:** Two mixed species will have more available configurations than the separated pure phases which increases entropy. Thus we have a entropic driving force that is configuration, combinatorial, or translational in nature as opposed to vibrational, rotational, etc.

2. **Enthalpic:** Two mixed species have some interaction between them. If positive this will avoid mixing, which will often be the case.

We combine these terms to get

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \tag{4.1}$$

We will determine if the **increase in entropy due to more configurations** is enough to **overcome the energy penalty associated with mixing two species with unfavorable enthalpic interactions**. The key idea that drives mixing is that the increase in entropy due to many more available configurations associated with two mixed species is sufficient to overcome the energy associated with bringing two species with unfavorable interactions into contact.

## 4.3 Entropy of Mixing Bragg-Williams:

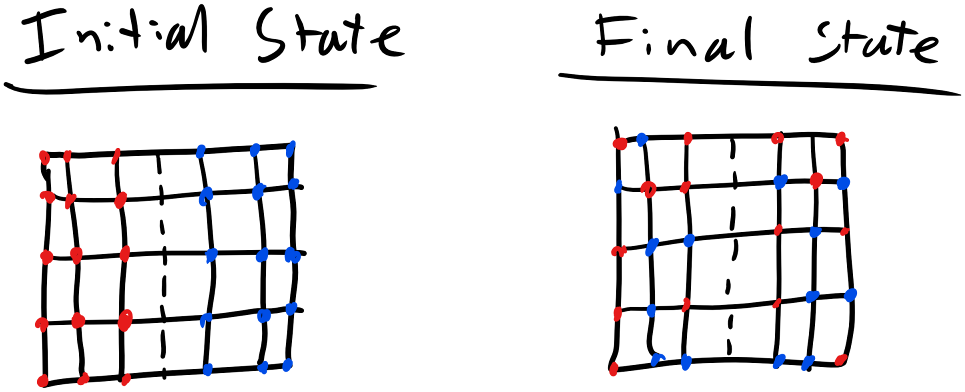

Figure 4-2: Bragg-Williams Mixing Schematic

Before we deal with polymers, which hopefully you appreciate by now is always more complicated than hard or typical materials, we will start off by thinking about the **entropy of mixing for small molecules or even gasses**. Let's consider we have two equally sized molecules, species 1 and 2, that we mix on a lattice or grid with a fixed number of sites $N_0$ where the number of species 1, $N_1$, and the number of species 2, $N_2$, will fill all the points on the lattice or alternatively $N_0 = N_1 + N_2$ as seen schematically here

Well we know that the number of configurations we can arrange species 1 and 2 is

$$\Omega_{12} = \frac{N_0!}{N_1!N_2!} \tag{4.2}$$

and we know entropy is

$$S = k_b \ln(\Omega) \tag{4.3}$$

Now for the initial state of the system prior to mixing how many configurations can we arrange the system? **Just 1! all species 1 on one side and 2 on the other**. So in this case $\Omega = 1$ and thus $S = 0$. So the change in mixing is

$$\Delta S_{mix} = S_{12} - S_{11} - S_{22} = k_b \ln(\Omega_{12}) \tag{4.4}$$

We can use Sterling's approximation $\ln N! \approx N \ln N - N$ to get

$$\Delta S_{mix} = k_b(-N_1 \ln \Phi_1 - N_2 \ln \Phi_2) \tag{4.5}$$

where $\Phi_1 = \frac{N_1}{N_0}$ and $\Phi_1$ is **both** the **mole fraction and volume fraction of species 1**. We have just derived the Bragg-Williams entropy change for small molecules and **we can divide the full expression by $N_0$ to give a molar quantity**

$$\frac{\Delta S_{mix}}{N_0} = k(-\Phi_1 \ln \Phi_1 - \Phi_2 \ln \Phi_2) \tag{4.6}$$

Let's take a quick look at this equation.

Is it every negative?

**No!**

This means that mixing always increases the entropy of the system (**for this ideal case**).

Also when is entropy maximized?

Looking at the equation the curve is symmetric around $\Phi_1 = 0.5$ and maximized at this point.

Now for polymers the mole fraction and volume fractions will typically not be equivalent so from here on out we will say that $\Phi_1$ and $\Phi_2$ refer to the volume fraction of each species.

## 4.4 Enthalpy of Mixing Bragg-Williams:

Now let's take a look at the **enthalpic contribution to free energy** and again we have to think about **interactions between molecules on the lattice**. We can make things a bit easier by using a **mean field theory**. Instead of considering each lattice site discretely and thinking about it's specific interactions with species, we can instead think of the **neighbors of each lattice site** taking on the **average** properties of the **entire lattice based on the volume fraction of the two species**. This is the **mean field approximation**.

We can calculate the enthalpy of mixing by thinking that the probability of finding any species $i$ on any given lattice site is given the by the volume fraction $\Phi_i$ and thus enthalpy of mixing is

$$H_{12} = (\#\text{ 1-2 interactions})(\epsilon_{12}) + (\#\text{ 1-1})(\epsilon_{11}) + (\#\text{ 2-2})(\epsilon_{22}) \tag{4.7}$$

Let's dissect this equation step by step. Well let's think about the number of interactions between species $i$ and $j$

$$\nu_{ij} \tag{4.8}$$

And the number of species 1 and 2 interactions will be

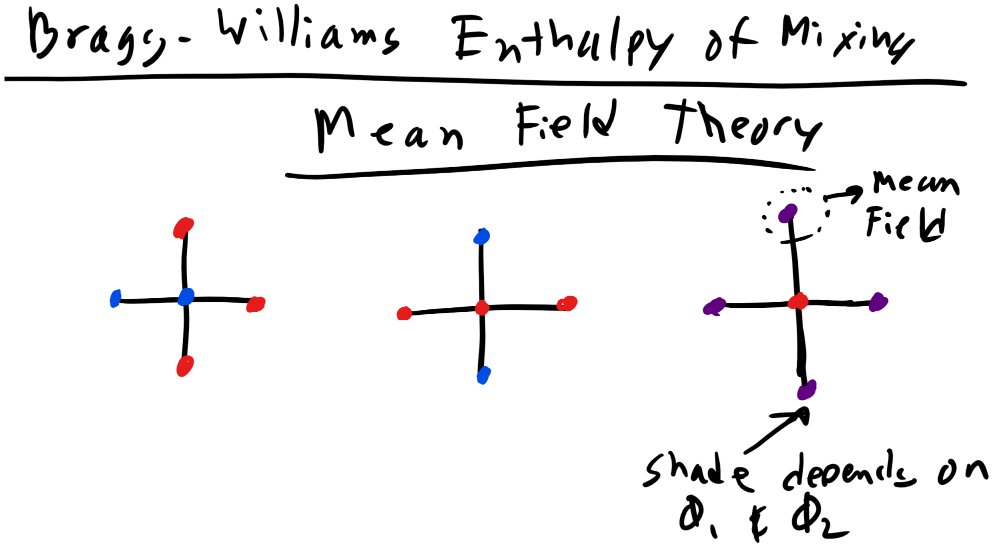

Figure 4-3: Mean Field Approximation

$$\nu_{12} = (\#\text{ num of 1 sites})(\#\text{ nearest neighbors})(\text{Prob. of adj. site being species 2}) \tag{4.9}$$

To keep this general **each lattice site will have $z$ number of nearest neighbors**. The total number of species 1 lattice site is $N_1$ and the probability of the nearest neighbor lattice site being species 2 will be the volume fraction of species 2 so

$$\nu_{12} = N_1 z \Phi_2 \tag{4.10}$$

The same logic can be used to find the number of 1-1 and 2-2 interactions but we have to divide by 2 to avoid overcounting.

$$\nu_{11} = \frac{N_1 z \Phi_1}{2} \tag{4.11}$$

$$\nu_{22} = \frac{N_2 z \Phi_2}{2} \tag{4.12}$$

Then to find total enthalpy of mixing $H_{12}$ is just the **number of interactions multiplied by the energy/strength of the interaction**, $\epsilon_{ij}$,

$$H_{12} = \nu_{12}\epsilon_{12} + \nu_{11}\epsilon_{11} + \nu_{22}\epsilon_{22} \tag{4.13}$$

$$H_{12} = N_1 z \Phi_2 \epsilon_{12} + \frac{N_1 z \Phi_1}{2}\epsilon_{11} + \frac{N_2 z \Phi_2}{2}\epsilon_{22} \tag{4.14}$$

So this is the **enthalpy upon mixing** but we also need the **initial state** which is fairly simple to calculate from the discussion above and doesn't require a mean-field approximation

$$H_{11} = \frac{N_1 z}{2}\epsilon_{11} \tag{4.15}$$

$$H_{22} = \frac{N_2 z}{2}\epsilon_{22} \tag{4.16}$$

So with these expression we can combine everything to obtain the expression for the enthalpy of mixing, remember that $N_0 = N_1 + N_2$.

$$\Delta H_{mix} = H_{12} - H_{11} - H_{22} \tag{4.17}$$

$$\Delta H_{mix} = N_1 z\Phi_2\epsilon_{12} + \frac{N_1 z\Phi_1}{2}\epsilon_{11} + \frac{N_2 z\Phi_2}{2}\epsilon_{22} - \frac{N_1 z}{2}\epsilon_{11} - \frac{N_2 z}{2}\epsilon_{22} \tag{4.18}$$

$$\Delta H_{mix} = z[N_1\Phi_2\epsilon_{12} + \frac{N_1\epsilon_{11}}{2}(\Phi_1 - 1) + \frac{N_2\epsilon_{22}}{2}(\Phi_2 - 1)] \tag{4.19}$$

$$\Delta H_{mix} = zN_0[\epsilon_{12} - \frac{1}{2}(\epsilon_{11} + \epsilon_{22})]\Phi_1\Phi_2 \tag{4.20}$$

To clean up this expression we will introduce a **critical new parameter, the Flory $\chi$ parameter** which is

$$\chi = \frac{z}{kT}(\epsilon_{12} - \frac{1}{2}(\epsilon_{11} + \epsilon_{22})) \tag{4.21}$$

$\chi$ is essentially a measure of the **energy of the interaction between the components mixed**. If the value of $\chi$ is **large and positive** then we know the $\epsilon_{12} >> \frac{1}{2}(\epsilon_{11} + \epsilon_{22})$ and since higher energy is always less favorable this will push towards a **phase separated state** as this is more energetically favorable. This is typically the **more common case** but we can have negative values of $\chi$ like if we have a **very good solvent**. So re-writing our expression in terms of $\chi$

$$\frac{\Delta H_{mix}}{N_0} = kT\chi\Phi_1\Phi_2 \tag{4.22}$$

## 4.5 Full Free Energy Expression: Bragg Williams

Now with this we can write the full free energy expression

$$\frac{\Delta G_{mix}}{N_0} = \Delta H_{mix} - T\Delta S_{mix} \tag{4.23}$$

$$\frac{\Delta G_{mix}}{N_0} = kT\chi\Phi_1\Phi_2 - kT(-\Phi_1\ln\Phi_1 - \Phi_2\ln\Phi_2) \tag{4.24}$$

$$\frac{\Delta G_{mix}}{N_0} = kT[\chi\Phi_1\Phi_2 + \Phi_1\ln\Phi_1 + \Phi_2\ln\Phi_2)] \tag{4.25}$$

Again we can see the for the Bragg-Williams is symmetric around $\Phi_1$ and $\Phi_2$.

## 4.6 Flory-Huggins Free Energy of Mixing for Polymers:

Now **polymers are obviously a bit more complicated** because they are not just simple small molecules on a lattice. Polymers are composed of **connected monomers and this is a complication we must address**. Let's see if we can adjust some parameters and work from there

$$n_1 = \text{Number of molecules/polymers of species 1} \tag{4.26}$$

$$n_2 = \text{Number of molecules/polymers of species 2} \tag{4.27}$$

$$x_1 = \text{Degree of polymerization} \propto \text{molecular weight of 1} \tag{4.28}$$

$$x_2 = \text{Degree of polymerization} \propto \text{molecular weight of 2} \tag{4.29}$$

$$v_1 = \text{Volume of each monomer of species 1} \tag{4.30}$$

$$v_2 = \text{Volume of each monomer of species 2} \tag{4.31}$$

$$V_1 = \text{Total volume of 1} \tag{4.32}$$

$$V_2 = \text{Total volume of 2} \tag{4.33}$$

With these variables redefined let's redefine our lattice model. Let's now assume our **lattice sites have a size commensurate with the monomer size of species 1 and 2 and thus we assume the monomers of each species has the same size** $v_1 = v_2 = v_0$.

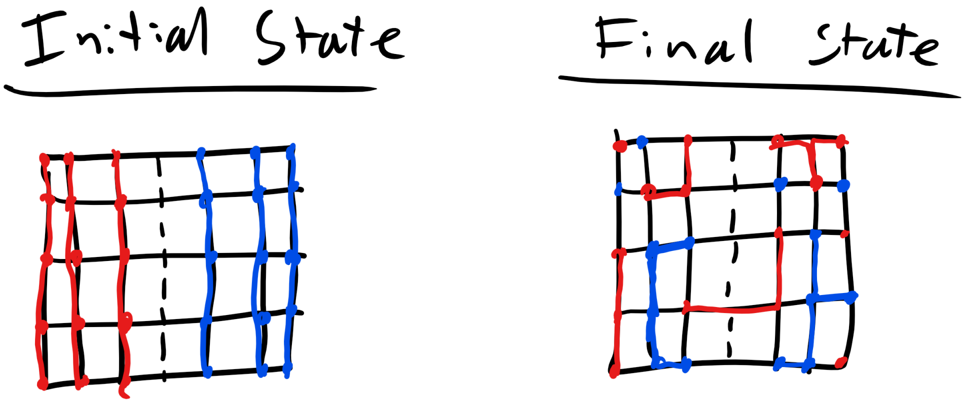

Figure 4-4: Flory-Huggins Mixing Polymer Schematic

With this we know now the **volume of any species** will be

$$V_i = n_i x_i v_0 \tag{4.34}$$

And with that the **volume fraction of a species** is simply defined as

$$\Phi_i = \frac{n_i x_i}{n_1 x_1 + n_2 x_2} \tag{4.35}$$

notice that the total number of lattice sites is $N_0 = n_1x_1 + n_2x_2$ and is **equivalent to the total number** of **monomers**. Because we assume monomers of each species occupy the same volume, we can see that $\Phi_i$ is a **volume fraction** (**and is not equivalent to the mole fraction**, given by $\frac{n_i}{n_1+n_2}$).

## 4.7 Flory Entropy of Mixing for Polymers:

Before we get into the math let's take a step back and think about the **qualitative, physical picture of what will happen when we mix polymers**. So far we have focused on the **configurational entropy** associated with polymer, i.e. when we stretch polymers we reduce the number of available configurations. **This contribution to entropy should not change significantly upon mixing**, assuming chains behave ideally, i.e. if they don't feel the excluded volume from other chains. Whether mixed or separated you can imagine that the **fluctuations around the center of mass will be essentially the same as long** as the center of mass remains constant. And this brings us the major component of entropy that will change significantly for polymers which is **translational** entropy. This refers to the fact that when we mix polymers the **entire** chain can **access more microstates by intermixing with polymers**, **via translation of the center of mass**. Basically **you can treat the entire polymer as a small molecule as was done for Bragg-Williams**.

This means that we might expect that the change in entropy for mixing depends only on the number of polymer molecules and not on the total number of monomers. But we see above that the volume fractions are defined by the number of monomers. So **we should expect that the entropy of mixing will decrease by a factor** of $\frac{1}{x}$ where $x$ **is the degree of polymerization** and $x$ will in general be different for each species. Let's see if this our conceptual understanding hold true for the derivation below

Now the original Flory derivation is extremely complicated as he explicitly counted the number of conformations of monomer on a lattice assuming each monomer was restricted by the position of the previous monomer so we will look at a **simpler derivation developed by Hildebrand**. Let's start by assuming that **polymers are completely ideal** and that their **entropy is equivalent to the entropy of an ideal gas**

$$S_i = k \ln V_i^{n_i} = n_i k \ln V_i \tag{4.36}$$

So for our two polymers we have

$$S_1 = n_1 k \ln V_1 = n_1 k \ln(n_1 x_1 v_0) \tag{4.37}$$

$$S_2 = n_2 k \ln V_2 = n_2 k \ln(n_2 x_2 v_0) \tag{4.38}$$

$$S_{12} = (n_1 + n_2) k \ln V_{12} = (n_1 + n_2) k \ln[(n_1 x_1 + n_2 x_2) v_0] \tag{4.39}$$

then the change in entropy upon mixing is

$$\Delta S_M = S_{12} - S_1 - S_2 \tag{4.40}$$

$$\Delta S_M = -k[n_1 \ln(\frac{n_1 x_1}{n_1 x_1 + n_2 x_2}) + n_2 \ln(\frac{n_2 x_2}{n_1 x_1 + n_2 x_2})] \tag{4.41}$$

$$\Delta S_M = -k[n_1 \ln(\Phi_1) + n_2 \ln(\Phi_2)] \tag{4.42}$$

$$\frac{\Delta S_M}{N_0} = -k[\frac{n_1}{n_1 x_1 + n_2 x_2} \ln(\Phi_1) + \frac{n_2}{n_1 x_1 + n_2 x_2} \ln(\Phi_2)] \tag{4.43}$$

$$\frac{\Delta S_M}{N_0} = -k[\frac{\Phi_1}{x_1} \ln(\Phi_1) + \frac{\Phi_2}{x_2} \ln(\Phi_2)] \tag{4.44}$$

Notice here that we used $N_0 = n_1 x_1 + n_2 x_2$ and the assumption of $v_1 = v_2 = v_0$ which allowed the terms to cancel out nicely and we see that the **term is scaled by the degree of polymerization as we expected**. Also if the degree of polymerization decreases to 1 we recover our small molecule Bragg-Williams theory.

## 4.8 Flory Enthalpy of Mixing for Polymers:

During our last discussion with Bragg-Williams enthalpy we introduced the critical $\chi$ parameter for the small molecules. **Luckily our derivation for enthalpy won't change too much for polymers because we are assuming ideal chains**. If we want to get more **complicated and include details about chain connectivity this will only change $zx_i$ the number of sites around each monomer but again this will be a very small change**. So the enthalpic part of the free energy is identical to the small molecule case, thank goodness!

$$\frac{\Delta H_{mix}}{N_0} = kT\chi\Phi_1\Phi_2 \tag{4.45}$$

## 4.9 Total Flory Free Energy of Mixing for Polymers:

So this gives us a total **Flory Free Energy** of

$$\frac{\Delta G_{mix}}{N_0} = kT[\chi\Phi_1\Phi_2 + \frac{\Phi_1}{x_1} \ln \Phi_1 + \frac{\Phi_2}{x_2} \ln \Phi_2)] \tag{4.46}$$

where $\chi$ is still

$$\chi = \frac{z}{kT}(\epsilon_{12} - \frac{1}{2}(\epsilon_{11} + \epsilon_{22})) \tag{4.47}$$

One quick aside we have defined $x_1$ is the **degree of polymerization of polymer species 1**, and $x_2$ is the **degree of polymerization of polymer species 2**. This allows us to define several systems that we will be working with quite a bit

1. **solvent-solvent** $x_1 = x_2 = 1$
2. **solvent-polymer** $x_1 = 1, x_2 = \text{large}$
3. **polymer-polymer** $x_1 = \text{large}, x_2 = \text{large}$

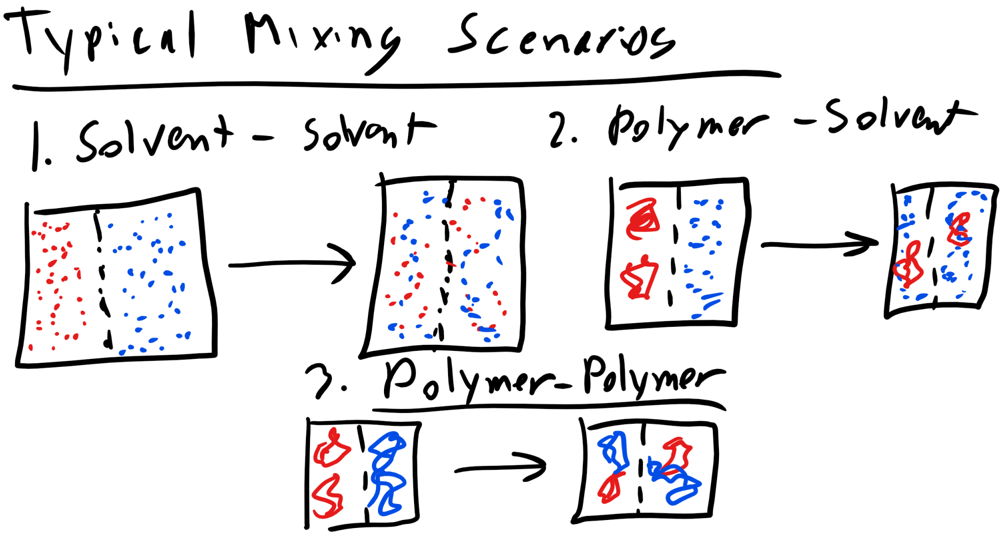

Figure 4-5: Mixing Scenarios

Looking at these systems we see that **solvent-solvent is our small molecule system and the free energy is the same as Bragg-Williams and symmetric around a volume fraction of 0.5**. However for the **solvent-polymer case we will no longer be symmetric around this value** and it will lead to some **interesting phase behavior** which we will get into into right now.

## 4.10 Polymer Phase Behavior

With our free energy of mixing equation complete we can now **create phase diagrams of polymer blends!**. This will look a bit different from the phase diagrams in materials science because we see in the equation above that the **entropy of mixing decreases** as the **degree of polymerization increases** so **high molecular weight polymers are less likely to mix**. So we will develop phase diagrams that are a function of **polymer molecular weight** and $\chi$ which **has temperature built** in as we know that

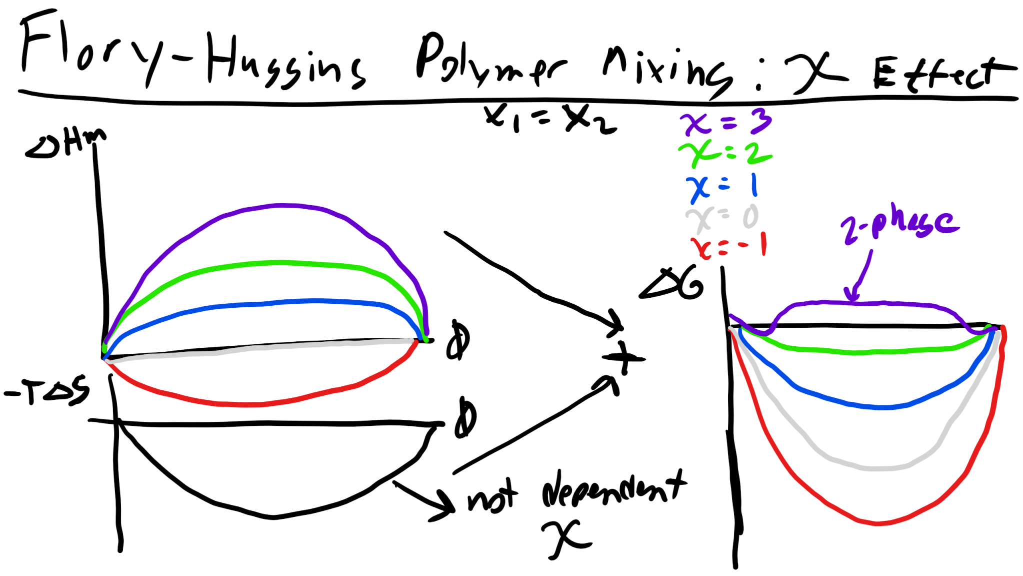

Figure 4-6: $\chi$ Effect on Free Energy for Symmetric Polymer-Polymer Mixing

$$\chi \propto \frac{1}{T} \tag{4.48}$$

So you can see that to **increase the probability of mixing** the $\chi$ value will have to **decrease.** $\chi$ or more typically $\chi N$ will be a critical parameter that will be used to determine when mixing will occur and when the solution will phase separate.

**Polymer-Solvent Solutions:**

To begin our discussion of polymer phase behavior we will discuss **Scenario 2**, which was the polymer-solvent scenario where $x_1 = 1$. Thus, the **solvent is species 1**. And to build up our phase diagram we should remember our conditions from **Gibbs Phase Rule** that the chemical potential $\mu$ of every species in every possible phase must be equivalent at equilibrium where $\mu$ is

$$\mu_i = \left[\frac{\partial G}{\partial n_i}\right]_{T,P,n_j} \tag{4.49}$$

Again physical interpretation time, chemical potential is the change in free energy when we add or remove a molecule of a species and **at equilibrium if we add or remove a molecule of species the change in free energy is 0**. Alternatively **if we can change the number of species and lower free energy then we are not at equilibrium, non-equilibrium**.

Now in the equation (4.46) we derived the change in free energy upon mixing so this is different from the **absolute free energy** but we can still work with this equation by simply changing how we express the chemical potential as a change as well

$$\mu_i - \mu_i^0 = \left(\frac{\partial \Delta G}{\partial n_i}\right)_{T,P,n_j} = RT \ln a_i \tag{4.50}$$

where $\mu_i$ is the chemical potential of species $i$ in the final state, $\mu_i^0$ is the chemical potential in the initial state, and $a$ is the activity.

We can simplify the equation (4.46) by relating $n$ to volume fraction using the chain rule

$$\left(\frac{\partial \Delta G}{\partial n_i}\right)_{T,P,n_j} = \left(\frac{\partial \Delta G}{\partial \Phi_i}\frac{\partial \Phi_i}{\partial n_i}\right)_{T,P,n_j} \tag{4.51}$$

We can now take our free energy equation (4.46) and plug into the derivation above to get

$$\mu_1 - \mu_1^0 = RT\left[\ln \Phi_1 + (1 - \frac{1}{x_2})\Phi_2 + \chi\Phi_2^2\right] \tag{4.52}$$

$$\mu_2 - \mu_2^0 = RT\left[\ln \Phi_2 - (x_2 - 1)\Phi_1 + x_2\chi\Phi_1^2\right] \tag{4.53}$$

where we assumed that $x_1 = 1$ since this species is our solvent.

Now as we have stated previously to build our phase diagram the we have to set the **chemical potential of all the species in the co-existing phases equal to one another or the change must be equal** (assuming same initial state)

$$\mu_1^\alpha = \mu_1^\beta \tag{4.54}$$

$$\mu_1^\alpha - \mu_0 = \mu_1^\beta - \mu_0 \tag{4.55}$$

This requirement for equilibrium is also described by the **common tangent rule** where you find you equilibrium volume fraction of species in each phase via the **common tangents in free energy curves**, i.e.

$$\left(\frac{\partial \Delta G_{mix}}{\partial \phi_2}\right)_{\phi_2=\phi^\alpha} = \left(\frac{\partial \Delta G_{mix}}{\partial \phi_2}\right)_{\phi_2=\phi^\beta} \tag{4.56}$$

You have most likely seen this before in materials science but just as a quick reminder (also read the supplementary notes as well)

For polymers it is a little different since for mixing we already have our full free energy equation so we will typically develop our phase diagram as such

here if we see multiple minimum that indicates a two phase region as we can construct a common tangent. If we only have a single minimum then we are in a single phase region.

This is the same as our equilibrium statement as tangent lines gives the chemical potential of both species in both phases and if the slope is the same then the chemical potentials are equal. We can use the common tangent rule on the plot of $\Delta G_{mix}$ vs $\Phi$ to define the **binodal** curve. **Binodal curves/points** are denoted by

$$\frac{\partial \Delta G}{\partial \Phi_i} = 0 \tag{4.57}$$

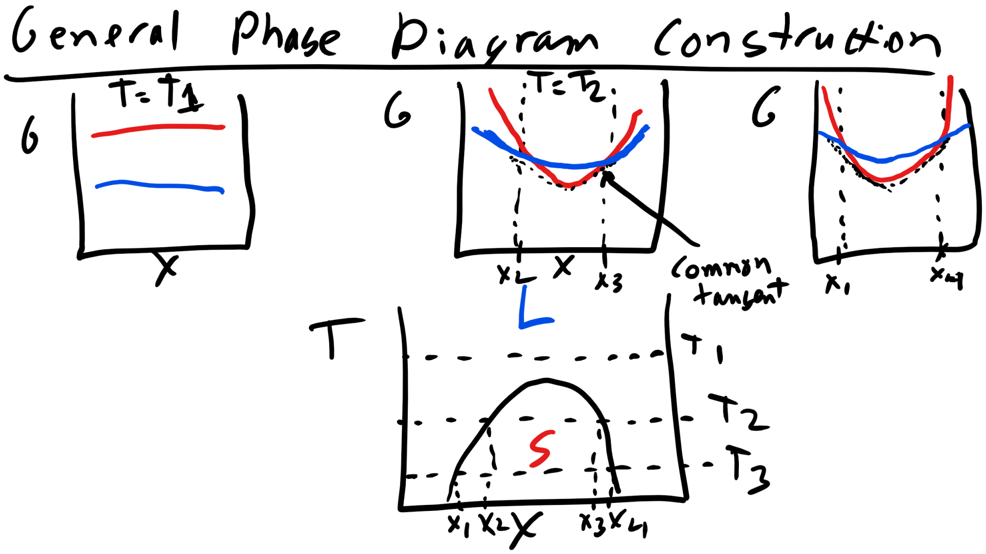

Figure 4-7: Typical Phase Diagram Construction with Common Tangent Line

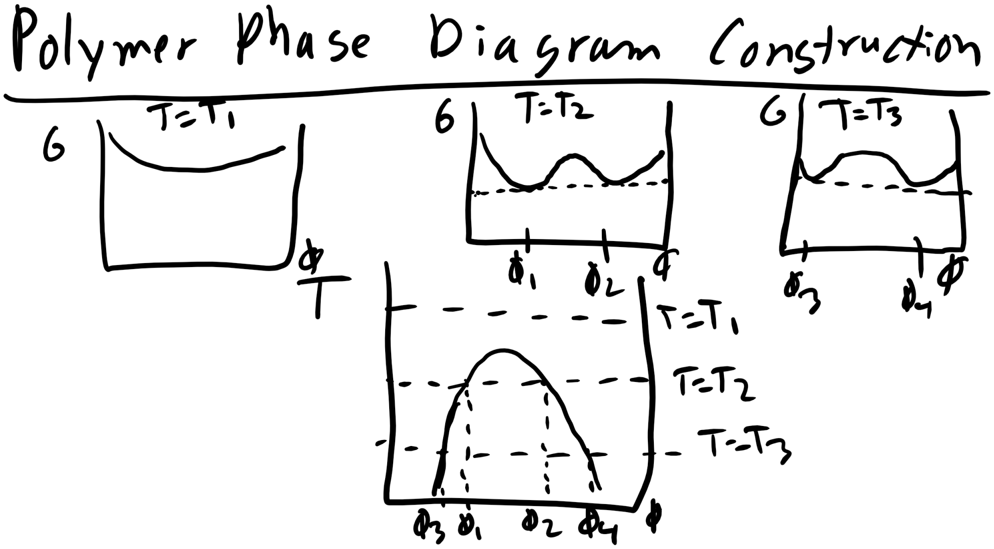

Figure 4-8: Phase Diagram Construction for Polymers

and we can also identify **spinodal curves and points** as well. The **spinodal curve** which determines the **kinetics of phase separation** (**spontaneous or nucleation/growth**) via the inflection point, which denotes the spinodal point.

$$\frac{\partial^2 \Delta G}{\partial \Phi_i^2} = 0 \tag{4.58}$$

You will also notice that the kinetics and mechanism by which the solution phase separates is different in the spinodal and binodal regions. We see that **Spontaneous/Spinodal Decomposi-**

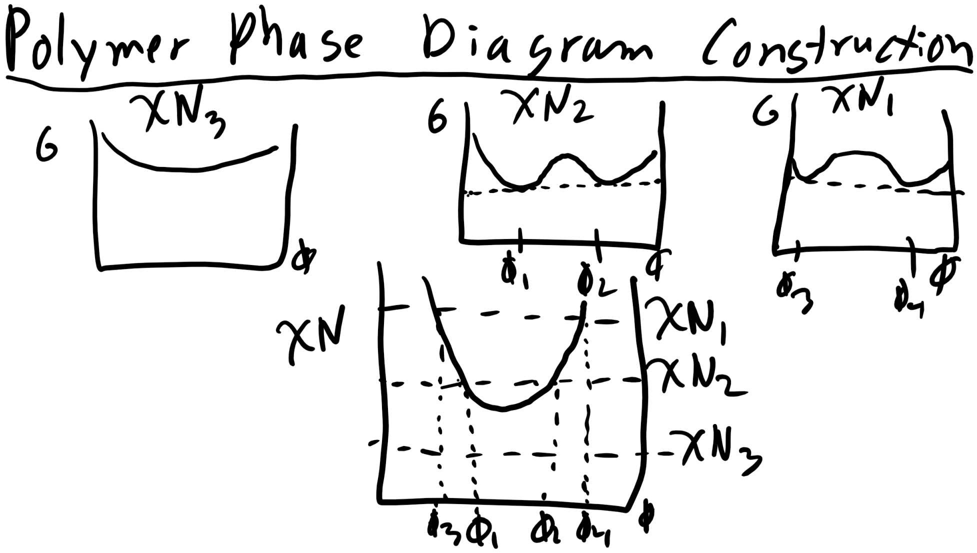

Figure 4-9: Phase Diagram Construction for Polymers Plotted as $\chi$

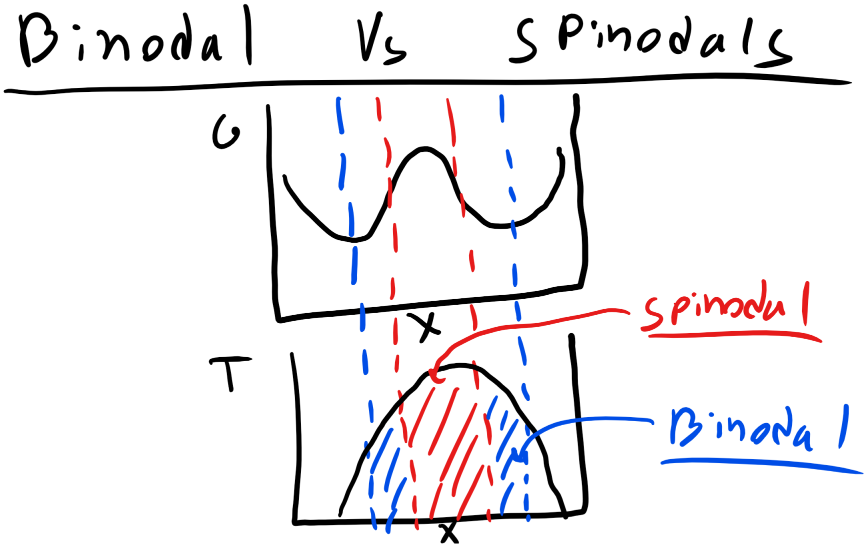

Figure 4-10: Spinodal and Binodal Points

**tion** will occur when one is locally unstable or equivalently when

$$\frac{\partial^2 \Delta G}{\partial \Phi_i^2} < 0 \tag{4.59}$$

Whereas **nucleation and growth** will occur where one is locally stable or equivalently when

$$\frac{\partial^2 \Delta G}{\partial \Phi_i^2} > 0 \tag{4.60}$$

You can see here that **nucleation and growth will occur in the binodal regions** while **spinodal decomposition will occur in the spinodal regions**. With all these key points we can now build our phase diagram. We can then take these key points and build our phase diagram which is plotted as $\chi$ vs. $\Phi$. These points and the interpolated line between them denotes the region of coexistence between phases, back once again to good old **Gibbs Phase Rule**

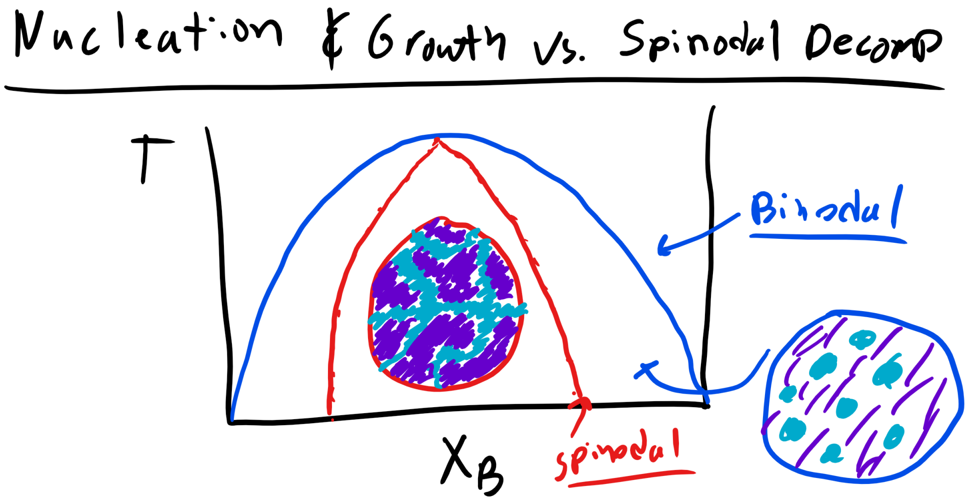

Figure 4-11: Spinodal and Binodal Points

$$D + P = C + 1 \tag{4.61}$$

where $D$ is the degrees of freedom, $P$ is the number of phases, and $C$ is the number of components. As $\chi$ increases, phase separation is the preferred energetic state while at low values mixing is preferred. This should make sense knowing $\chi \frac{1}{T}$.

Finally, we can define several critical points, the first begin $\chi_c$, where the spinodal obtains its lowest value in terms of $\chi$ also the point where the binodal and spinodal intersect.

$$\frac{\partial^2 \Delta G}{\partial \Phi_i^2} = \frac{\partial \Delta G}{\partial \Phi_i} = 0 \tag{4.62}$$

You can also find the **critical composition,** $\phi_c$ associated with $\chi_c$ by solving

$$\frac{\partial \chi}{\partial \phi} = 0 \tag{4.63}$$

There is also a temperature associated with both $\chi_c$ and $\phi_c$ which is either the **Upper Critical Solution Temperature (UCST)** which denotes **the temperature above which the solution will mix** or the **Lower Critical Solution Temperature (LCST)** which **denotes the temperature above which the solution will de-mix**. Atomistically you can understand the appearance of a LCST as there is a **temperature at which you start breaking weak intermolecular**

**interactions that may have promoted mixing which leads to phase separation**. You can see some of these critical points here

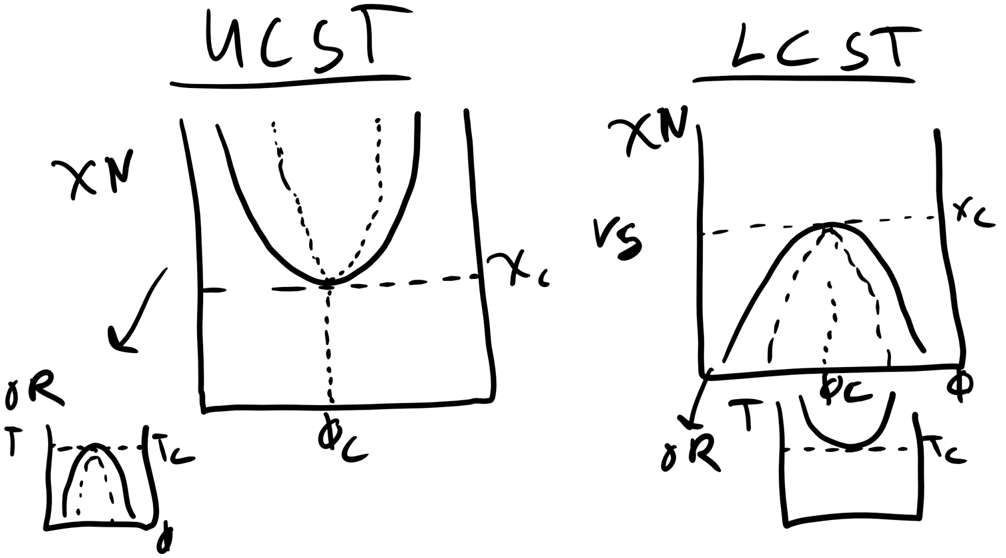

Figure 4-12: Critical Points

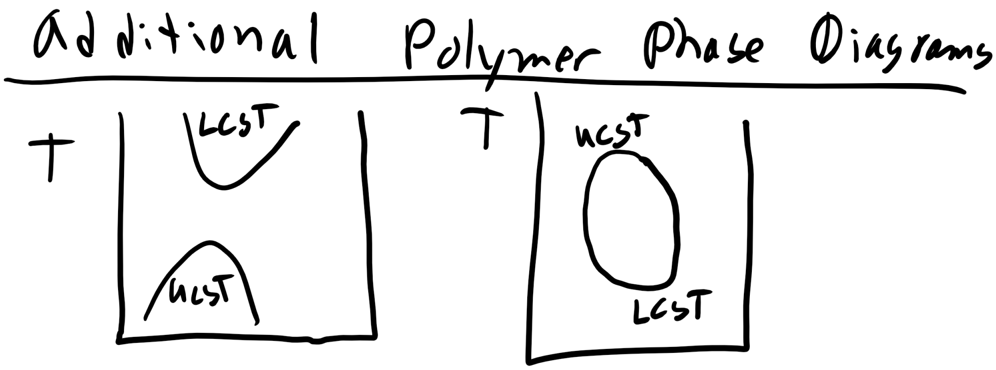

Figure 4-13: Examples of UCST, LCST

You will proves this in the homework but we can actually solve for these critical values here for all the typical scenarios that you may come across

## 4.11 Flory Huggins Polymer Blends Summary:

1. **Solvent-Solvent Scenario** $x_1 = x_2 = 1$**:**

- $\phi_c = 0.5$
- $\chi_c = 2$

2. **Solvent-Polymer Scenario** $x_1 = 1; x_2 = N$**:**
   - $\phi_c = \frac{1}{1+\sqrt{x_2}}$
   - $\chi_c = \frac{1}{2}\left(1 + \frac{1}{\sqrt{x_2}}\right)^2$
3. **Symmetric Polymer-Polymer Scenario** $x_1 = N; x_2 = N$**:**
   - $\phi_c = 0.5$
   - $\chi_c = \frac{2}{N}$
4. **Most General Scenario** $x_1, x_2$**:**
   - $\phi_c = \frac{\sqrt{x_1}}{\sqrt{x_1}+\sqrt{x_2}}$
   - $\chi_c = \frac{1}{2}\left(\frac{1}{\sqrt{x_1}} + \frac{1}{\sqrt{x_2}}\right)^2$

**Dilute Polymer-Solvent Solutions**

You may often encounter scenarios where you are working with a **dilute solution where the moles of solvent is much greater than the number of moles of polymer** (i.e. really anytime working with biological concentrations of proteins/peptides). When you have such a scenario there are a couple of **simplifications** that simplify this derivation the first concerns the volume fraction of polymer

$$\Phi_2 = \frac{n_2 x_2}{n_1 x_1 + n_2 x_2} \approx \frac{n_2 x_2}{n_1} \tag{4.64}$$

Also since $\Phi_1 = 1 - \Phi_2$ and $\Phi_2$ is small in dilute solution we can do an expansion of $\ln \Phi_1$ from our chemical potential above

$$\ln(1 - x) \approx -x - \frac{x^2}{2} - ... \tag{4.65}$$

We can then use these expression and re-write the change in chemical potential of the solvent

$$\mu_1 - \mu_1^0 = RT\left[-\frac{\Phi_2}{x_2} + (\chi - \frac{1}{2})\Phi_2^2\right] \tag{4.66}$$

We previously described that for an **ideal solution, the chemical potential is proportional the log of the activity, which is in turn proportional to the mole fraction of that species in solution ( Henry's law)**. We can use this to

$$\mu_1 - \mu_1^0 = RT\ln a_i = RT\ln X_1 = RT\ln(1 - X_2) \approx -RTX_2 = -RT\frac{\Phi_2}{x_2} \tag{4.67}$$

where $X_i$ is the mole fraction of the species in solution. As you see in the previous expression the first term matches with the ideal solution. But the second term which has $\chi$ and $\Phi_2^2$ **describes the interaction between polymers and is the correction to the purely ideal assumption**. This is sometimes referred to as the **excess chemical potential** because it is an additive term which has two components

1. **Contact interactions (solvent quality)** : $\chi\Phi_2^2 RT$
2. **Chain connectivity (excluded volume effects)**: $-\frac{1}{2}\Phi_2^2 RT$

But there is a an **extremely important** fact in the expression where we see that the **excess chemical potential** disappears if $\chi = \frac{1}{2}$. There is a **balance between the contact interaction and chain connectivity or the solvent quality and excluded volume effects** that can allow for the chain to behave ideally ($\theta$ conditions). So you can **change the value of $\chi$ to obtain ideal solutions**, most typically **via changing temperature!**. We can summarize when/where we obtain $\theta$ conditions for some different scenarios you might encounter

**Limitations of Theory**

As we have mentioned before we are typically **assuming only van der Waals interactions and have ignored hydrogen bonding**. So this framework will only hold for reasonable temperature ranges. We can predict **UCST**, or upper critical solution temperature, behavior where at high temperature we switch from phase-separated solutions to mixed. This is typical when $\chi$ and the solubility parameters are positive. But there are some systems which exhibit **LCST**, or **lower critical solution temperature**, where at a certain temperatures the opposite behavior occurs and the solutions demix. This is **counterintuitive because at high temperatures the entropy of mixing should dominate and encourage mixing however, $\chi$ is also temperature dependent and can switch sign and become negative and encourages phase separation**. Atomistically there is a **temperature at which you start breaking any weak intermolecular interactions that may have promoted mixing which leads to phase separation**. There are also scenarios where you can have **both a LCST and UCST**.

**Determining $\chi$ Parameter**

As we see above $\chi$ is a **critical parameter** for determining the phase behavior of polymer blends so it would be great to calculate it. Luckily **Hildebrand developed a method to estimate $\chi$**. Imagine a liquid on a surface. The surface will have some interaction with the solvent in the liquid and to get **an idea of the strength of these interactions you can heat up and evaporate the liquid**. The amount of energy is the **heat of evaporation, $\Delta H_V$** and if you divide this by the volume for a mole of molecules you get a **cohesive energy density**. And we can relate this to the **solubility parameter $\delta$** which is

$$\delta_i = \sqrt{\frac{\Delta H_V - RT}{V_m}} \tag{4.68}$$

This is essentially the energy required to remove a mole of moles from the bulk to an infinite distance. Hildebrand theorized that the c**ompatibility between two components in a blend could be measured by measuring the difference in the solubility parameters**. We can then relate this to $\chi$. If the intermolecular forces are non-specific in nature like van der Waals interactions, the interaction could act on one species with itself or with the other species and if these interaction strengths are about the same they should be compatible. We can write the energies as we have done previously:

$$-\frac{z\epsilon_{11}}{2} = v_0\frac{\Delta E_1}{V_1} = v_0\delta_1^2 \tag{4.69}$$

$$-\frac{z\epsilon_{22}}{2} = v_0\frac{\Delta E_2}{V_2} = v_0\delta_2^2 \tag{4.70}$$

$$-z\epsilon_{12} = v_0\delta_1\delta_2 \tag{4.71}$$

where $\Delta E$ is the energy change in moving that molecule to infinity. We can then re-write $\chi$ as

$$\chi = \frac{v_0}{kT}(\delta_1 - \delta_2)^2 \tag{4.72}$$

Now there are some problems here as we have discussed previously it is possible to have negative values of $\chi$ but here we can only have positive values. Additionally, polymers will also have other specific intermolecular interactions like hydrogen bonds.

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# CHAPTER 5
## VISCOSITY

## 5.1 Key Terms/Definitions:

- **Viscosity** - the physical property of a fluid that describes the resistance of the fluid to a shear stress; acts as a proportionality constant between shear stress and strain rate (akin to velocity).
- **Newtonian fluid** - a fluid that has a constant viscosity; a non-Newtonian fluid has a viscosity that changes as a function of either total strain or strain rate, leading to a non-linear dependence of shear stress on strain-rate.
- **Non-draining (impenetrable sphere) approximation** - an approximation of a polymer chain as a highly coiled sphere, which is ”seen” by a fluid as an impenetrable hard sphere due to hydrodynamic interactions between monomers in the chain.
- **Freely-draining (penetrable sphere) approximation** - an approximation of a polymer chain as an elongated series of monomers, each of which feels friction from the solvent separately.
- **Hydrodynamic radius** - in the non-draining regime, the effective radius of the (impenetrable) polymer coil as seen by solvent; used to calculate viscosity in solution.
- **Overlap concentration** - the concentration of polymers in solution when chains must first start overlapping, leading to coil-coil interactions.
- **Specific viscosity** - the effective increase in the viscosity of a solution associated with an increase in the polymer concentration.
- **Intrinsic viscosity** - the limit of the specific viscosity as polymer concentration goes to 0; in other words, the infinitesimal increase in solution viscosity when polymer is first added.

## 5.2 Measuring Properties of Polymers:

We have run into several key properties of polymers like molecular weight, end-to-end distance, etc., and there are a number of other key polymer behaviors that depend on some of these key properties like

- **Non-cross linked rubber elasticity**
- **Shear thickening**

- **Elastic modulus of cross linked networks**
- **Electrical conductivity**

The question then becomes if these polymer properties are so critical to behavior how to do we measure them? This question is quite difficult for example it will be important in terms of rubber elasticity to know the distance between cross-links or how do we measure $\chi$? Well we will be talking about several techniques to

- Determine the relationship between the **viscosity of dilute solutions** and the **molecular weight of the polymers**
- Understand the difference between the **free draining** and **non-draining regimes of viscosity**.

## 5.3 Measuring Viscosity:

**Solution and Melt Viscosity $\eta$:**

Most of you are likely familiar with the concept of **viscosity** (peanut butter is more viscous than water) and have likely encountered this in a fluid mechanics class however we will give a very brief review here. We will use $\eta$ to describe **viscosity** and from **mechanics** we know that

$$\tau = \eta \frac{d\gamma}{dt} \tag{5.1}$$

where $\tau$ is shear force, $\eta$ is viscosity, and $\frac{d\gamma}{dt}$ is strain rate. You can think of this equation in the context of a channel filled with some fluid. When you apply a shear force to one plate the plate will apply a shear force to the liquid. You'll notice that this equation has a **very similar form as Hooke's law** but we **replace strain with strain rate and Young's modulus with viscosity**. We see that the **faster the strain rate the larger the resistive shear force** and the **larger the viscosity the larger the shear force**. This makes sense as pulling a plate through water is easier than pulling it through peanut butter. At very slow strain rates the shear force goes to 0 which is a property of liquids whereas solids can be approximated as having infinite viscosity so they will not flow. You can see this scenario schematically here

When the **visocity is independent of strain rate or total strain** as is the case above that material is **Newtonian. Polymers** however, are typically **non-Newtonian**, i.e. **viscosity** is **not** a constant quantity but is **dependent on strain rate or total strain** we can see an example in one of my favorite Youtube Videos in the lecture slides

**Stokes Law and Viscosity Scaling**

So to start with our viscosity discussion let's start with a typical scenario. We have our **polymer** (dry, solid, or lypholized) and **add some liquid solvent**. How will this effect viscosity? We will determine this using **Stokes law** and see how the **viscosity of a solution** will **scale** with **molecular weight** and identify two different scaling regimes

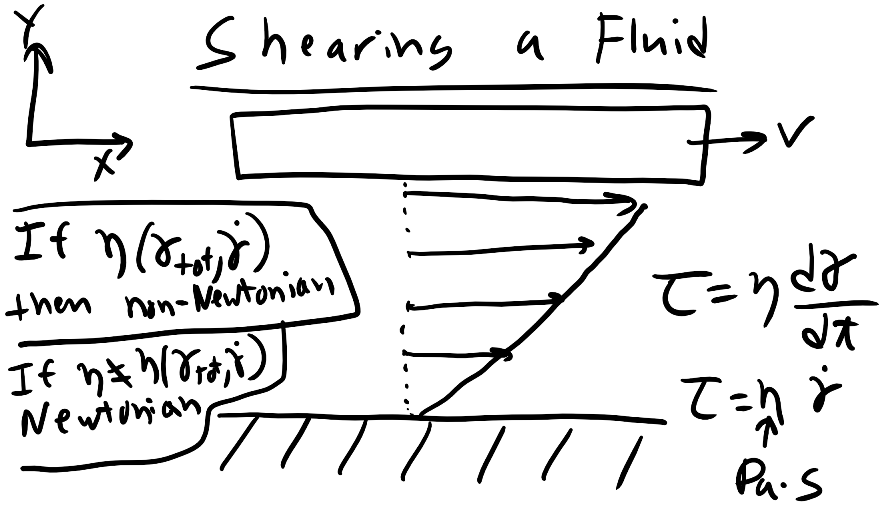

Figure 5-1: Shearing a Fluid.

1. **Freely Draining Regime**
2. **Non-Draining Regime**

and these two regimes lead to the non-Newtonian behavior we saw in the video.

So to start let's think of an idealized scenario that physicists' love, a sphere with radius, $R_s$ falling through a fluid with a viscosity $\eta_0$ at a velocity $v$. The **viscous force** acing on the sphere is simply

$$F_{viscous} = fv \tag{5.2}$$

where $f$ is the **friction factor** of the solution. You can see this equation is very similar to our **shear stress and shear strain relationship** thus we will expect $f \propto \eta$ and the **scaling laws should also scale similarly**. Now you might be asking yourself well what is the expression for the friction factor in terms of the variable in our system. Well luckily Stokes already solved this in 1851 with some fairly complex math and found that

$$f = 6\pi\eta_0 R_s \tag{5.3}$$

You might see in some texts this frictional force denoted as $F_d$ and referred to as **Stokes Drag Force**. Now we have one issue and that is while we can maybe get away with the fact that **we can approximate the shape of a coiled polymer as a sphere we can't always approximate the polymer** as a **solid** sphere. There are two size extremes or regimes we must consider which we mentioned previously. The **non-draining regime** where the polymer is coiled into one impenetrable sphere where fluid cannot pass, hence non-draining. The **freely-draining**

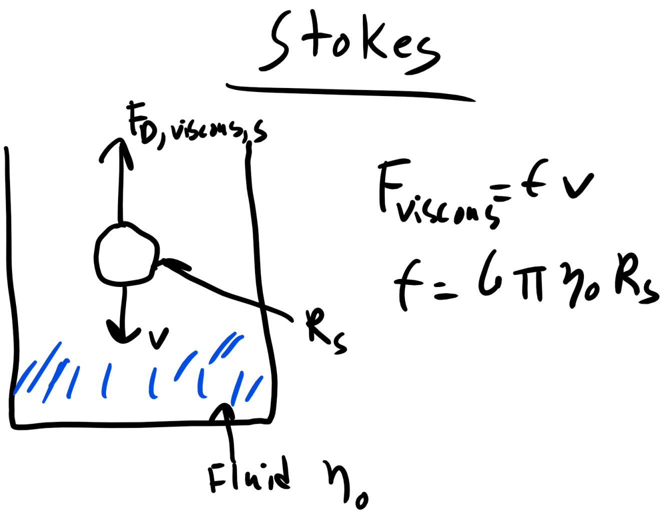

Figure 5-2: Stokes Drag Force.

regime assumes the polymer is permeable to solvent and in this case the polymer is composed of a larger number of small spheres (monomers) and each has some friction factor associated with it. Note: Stokes law is derived from solving the Navier Stokes equation and beyond the scope of the class but again I can provide resources if you are interested.

**Non-Draining Regime:**

Here **each monomer is a solid sphere** drags some solvent and zooming out the **polymer is a highly coiled bunch of monomers** that is **effectively a single large sphere with a radius** that approximates the **radius of gyration**. Now **each monomer will affect the fluid flow and frictional force around the other monomers**, thus the overall friction force applied to the entire coil is lower than for a single similar sized impenetrable sphere. The monomers can only affect or effectively **shielding** neighboring monomers from the **fluid flow effects** (i.e. hydrodynamic interactions) if the neighboring monomer is very close.

Thus this model is **accurate/appropriate for highly coiled polymers**. So in the **non-draining case** the **fluid flow is highly perturbed by the monomers** inside the coiled up polymer so that it **effectively acts as a solid sphere**. Let' go ahead and calculate the **friction factor** for this regimes which is **Stoke's law directly**

$$f = 6\pi\eta_0 R_H \tag{5.4}$$

$$R_H \approx \gamma\langle R_G^2\rangle^{\frac{1}{2}} \tag{5.5}$$

$$f \approx x_2^{\frac{1}{2}} \tag{5.6}$$

You will notice that we simply replaced the radius of the sphere with the **hydrodynamic ra-**

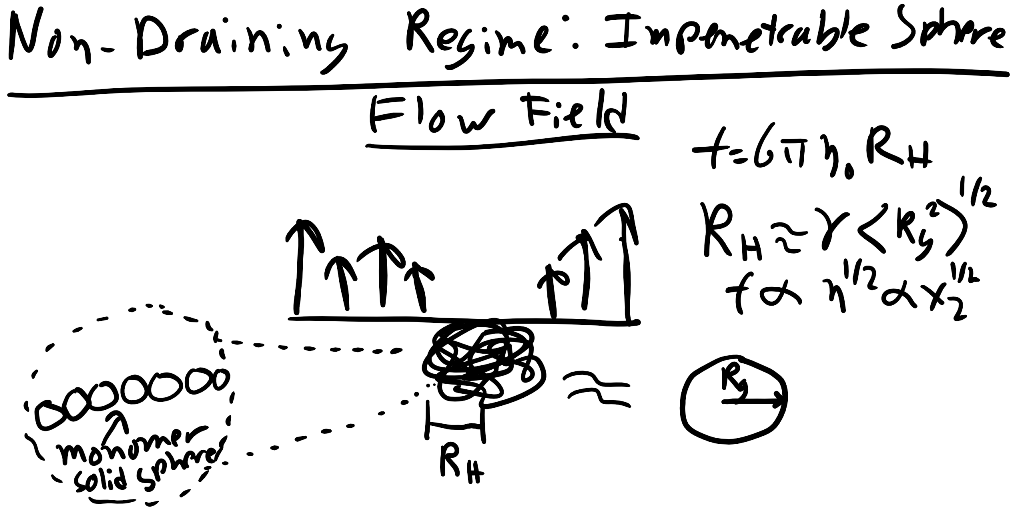

Figure 5-3: Non-Draining Regime.

**dius**, $R_H$, which we can approximate as **radius of gyration** (or the RMSD) with **some constant prefactor** $\gamma$ (typically around 0.85-1). But again we are focused primarily on scaling in this course so we see that the friction will scale as $n^{1/2}$ in **theta solvent** and as $n^{3/5}$ in a **good solvent**.

**Freely Draining Case:**

In the **freely-draining** case the **polymer is idealized as an elongated rod** where **each monomer is a single sphere** and **each monomer/sphere will not effect the fluid flow or effective friction on neighboring monomers**. The total effective friction will be the **sum of the friction force felt by each monomer** and will thus be **larger than the impenetrable sphere** or **non-draining case** as there is no shielding. This model is **appropriate for highly elongated polymers, polymers in good solvents, or polymers at high strain rates**.

To calculate the friction factor for the free draining case we have to account **we have to account for the friction of all the beads** so the friction will be the friction per monomer multiplied by the number of monomers

$$f \approx \zeta x_2 \tag{5.7}$$

where $\zeta$ is the constant monomeric friction factor (assumption). We can clearly see here that in the **non-draining** regime the friction scales with the **square root** of the **number of monomers** while in the **freely draining** regime **scales linear with the number of monomers**. This leads to an **extremely larger friction factor for the freely draining case and thus larger viscosity**!

So if the friction factor differs greatly in these two regimes **we need to understand when each regime is applicable/occurring**. When **we have very high shear forces and shear rates the polymer will elongate and thus it will be described very well by the freely-draining**

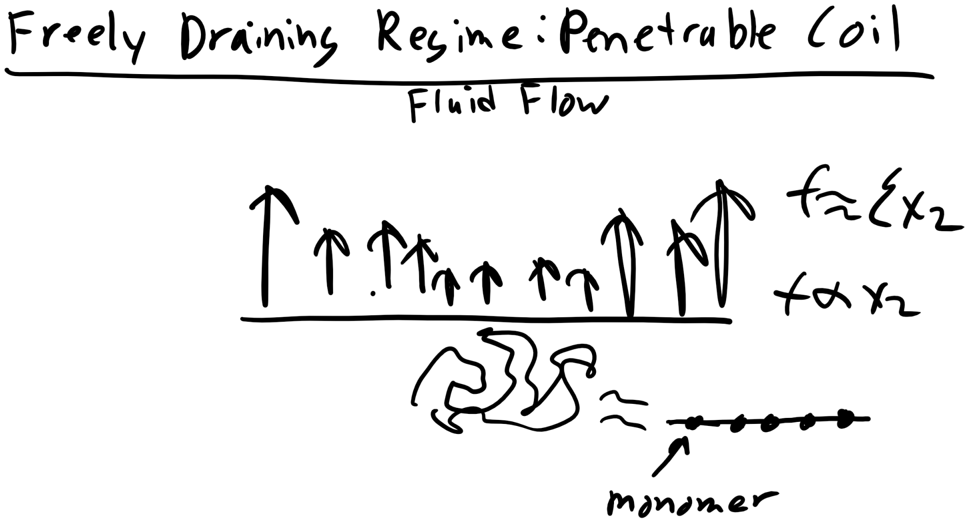

Figure 5-4: Freely Draining Regime.

**model**. The friction factor will increase as will viscosity. This explains the **non-Newtonian behavior of polymers because when we change shear rates the viscosity will change and increase as well**. Alternatively when we have a **high molecular weight flexible chain, that can be highly coiled, the non-draining model is applicable**. So we can start compiling scaling factors below:

1. $f \approx x_2$ - **low MW / rod-like polymers - freely-draining case**
2. $f \approx x_2^{\frac{1}{2}}$ - **theta conditions - Gaussian coil - non-draining**
3. $f \approx x_2^{\frac{3}{5}}$ - **good solvent - also non-draining**

**Intrinsic Viscosity Measurements**

Clearly viscosity and molecular weight are critical parameters and we can measure **intrinsic viscosity** which will then reveal other important polymer properties like **solvent conditions and viscosity-average molecular weight**. To start with this technique we need to introduce the **Einstein equation** for **viscosity** of a **solution containing impenetrable (hard) spheres of volume fraction** $\Phi_{hs}$

$$\eta = \eta_0(1 + 2.5\Phi_{hs} + ...) \tag{5.8}$$

Here $\eta$ is still the **polymer viscosity**, $\eta_0$ is the **solvent viscosity** and $\Phi_{hs}$ is the **hard sphere volume fraction** which can be calculated by

$$\Phi_{hs} = \frac{\text{(number of spheres)(vol. of sphere)}}{\text{Total volume of Polymer}} = \left(\frac{c_2}{M/N_{av}}\right)\left(\frac{4}{3}\pi\gamma^3\langle R_G^2\rangle^{\frac{3}{2}}\right) \tag{5.9}$$

where the total number of spheres is the ratio of the concentration of polymer $c_2$ by the **molecular weight of the polymer** $M$ (scaled by Avogadro). Note that $\Phi_{hs}$ is not equivalent to $\Phi_2$ due to different assumptions in Flory-Huggins and this model. The volume of the sphere is your typical equation for sphere where we substitute the radius of our polymer from the discussions above.

We can now rearrange the Einstein equation to define the **specific viscosity**

$$\eta_{sp} = \frac{\eta}{\eta_0} - 1 = 2.5\Phi_{hs} \tag{5.10}$$

Again the physical meaning in this equation describes that the **specific viscosity is the increase in viscosity beyond that of the solvent due to polymer additives**. Now the **intrinsic viscosity** is **the limit of the specific viscosity as the polymer concentration goes to 0**

$$[\eta] = \lim_{c_2 \to 0} \frac{\eta_{sp}}{c_2} = \lim_{c_2 \to 0} \frac{2.5\Phi_{hs}}{c_2} \tag{5.11}$$

The **intrinsic viscosity is the infinitesimal increase in solution viscosity as you first add the polymer or alternatively the viscosity increase in the limit of an infinitely dilute solution**. So this a **property of a polymer**, **not a property of the solution** and we know that the Chemist's Chain model gives us

$$\langle R_G^2 \rangle^{\frac{1}{2}} \approx \langle r^2 \rangle^{\frac{1}{2}} \approx l C_\infty^{1/2} M^{1/2} \alpha \tag{5.12}$$

Note that I've used $M$ instead of $n$ because I want to represent the **molecular weight of the chain**, which is related to the **length of the chain**. We can now substitute this expression **back into our intrinsic viscosity equation** and get

$$[\eta]_\theta = K_\theta M^{\frac{1}{2}} \tag{5.13}$$

**here all the constants (not dependent on molecular weight) have been encapsulated** into $K_\theta$ for theta conditions and we **see that the intrinsic viscosity scales** with $M^{\frac{1}{2}}$.

We can make this more general if we include the $\alpha$ parameter in the above substitution and get

$$[\eta] = \alpha^3 [\eta]_\theta = K M^a \tag{5.14}$$

where you can see if were are in $\theta$ conditions we get our original $\theta$ expression back but note that $a$ **is how the molecular weight will scale** depending on $\alpha$. This equation is known as **Mark-Houwink equation**. Here we can see that if $a = 0.5$ we are in $\theta$ conditions. This illustrates how important of a parameter **intrinsic viscosity** is as this **parameter relates directly to solvent conditions and molecular weight**.

We know some values of $a$ in previous lectures

1. $a < 0.5$ - **poor solvent**

2. $a = 0.5$ - **theta conditions**

3. $a > 0.5$ - **good solvent**

We thus see that **intrinsic viscosity relates directly to both molecular weight and solvent quality, two important properties we would like to measure**.

## 5.4 Experimentally Determining Intrinsic Viscosity

Now comes the key question you might be asking, well how do we actually perform these measurements in order to obtain these key values. Well first you will typically measure the **specific viscosity** for a series of different concentrations. Typically the way these measurements are taken is by extruding molten polymer and measuring the flow rate and back calculating the specific viscosity. Once you have these measurements you will make a plot of specific viscosity normalized by concentration as a function of concentration and the functional form of the graph is

$$\frac{\eta_{sp}}{c_2} = [\eta] + \text{slope} c_2 \tag{5.15}$$

So once you have this plot the key thing to do will be to extract the y-intercept which will give you the intrinsic viscosity because of our previous relationship that

$$[\eta] = \lim_{c_2 \to 0} \frac{\eta_{sp}}{c_2} \tag{5.16}$$

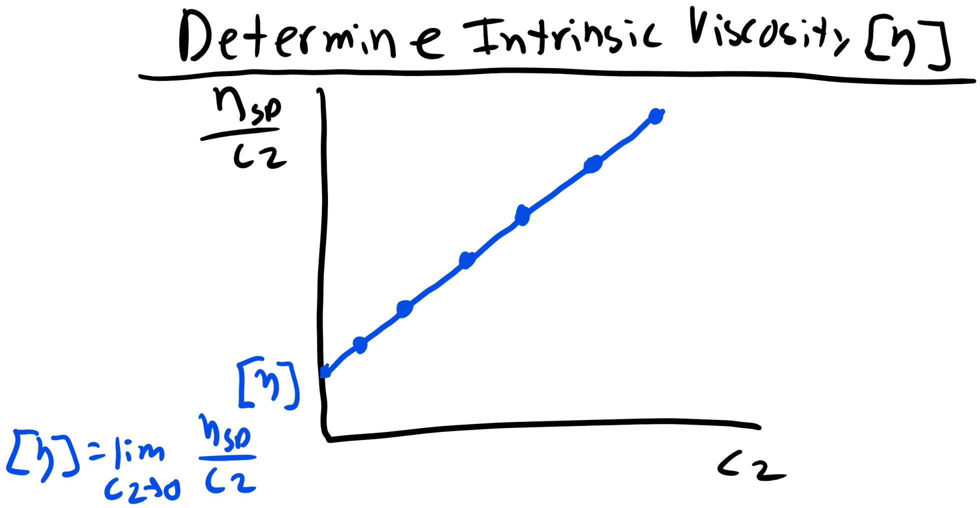

Figure 5-5: Intrinsic Viscosity Measurement.

Nice! But we are not done yet. We can also get information about the solvent quality as well by running this same set of experiments for a series of molecular weights. So you would run the same set of experiments previously for different molecular weights and then you would create a Log-Log plot of intrinsic viscosity as a function of molecular weight remembering we have the following relationship

$$[\eta] = KM^a \tag{5.17}$$

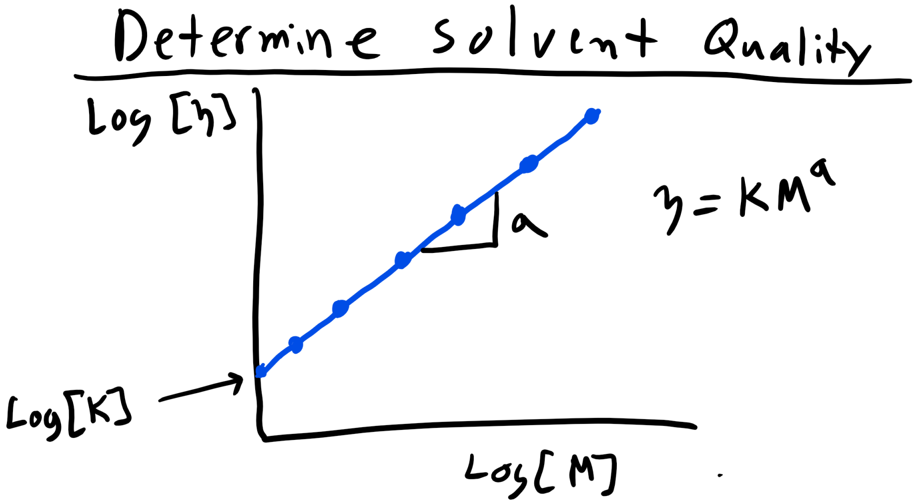

Figure 5-6: Solvent Quality Determination.

So on this Log-Log plot the slope will give us our solvent quality parameter $a$ and we can also find our prefactor term via the y-intercept if that was a parameter of interest.

## 5.5 Summary: Viscosity

We first studied the characterization of polymer solutions by determining the *intrinsic viscosity* of a solution - using the Einstein relation, we could then derive the Mark-Houwink equation, which gives an idea of the viscosity-average molecular weight as well as solvent quality. We also talked about two different regimes of polymer solution viscosity (not to be confused with intrinsic viscosity): the freely-draining regime, where the polymer is treated as an elongated rod with separate, distinct monomers, and the non-draining regime, where the polymer is treated as a single, spherical, coiled up molecule. We identified the different conditions under which these models are applicable, and derived how polymer viscosity scaled with molecular weight in the two regimes.

## 5.6 Intrinsic viscosity

- **Key Ideas:** Einstein relation allows us to determine viscosity of solution based on concentration of additives; relate intrinsic viscosity to size of added polymer; relate size of added polymer to solvent quality, viscosity-average molecular weight.

- **Key Equations:** Mark-Houwink equation - $[\eta] = K\overline{M}_V^a$. $K$ is constant, $\overline{M}_V$ is viscosity average molecular weight, $a$ is scaling exponent that gives solvent quality.

- **Key Experimental Method:** Take two measurements - first plot viscosity of solution vs. polymer concentration, obtain intrinsic viscosity from extrapolation to origin. Next, obtain intrinsic viscosity (again from plot of viscosity vs. concentration) for variety of molecular weights, plot $\log[\eta]$ vs. $\log \overline{M}_V$. Obtain $K$ from intercept, $a$ from slope, and with this can determine $\overline{M}_V$ from any given value of $[\eta]$.

- **Key Insights:** obtaining solvent quality from exponent $a$ - can compare scaling to theta solvent ($a = 0.5$). Can obtain $\overline{M}_V$, which falls between number-average and weight-average molecular weights.

**Viscosity Averaged Molecular Weight**

We have previously discussed both number averaged and weight averaged molecular weight but in measuring intrinsic viscosity we can derive a **viscosity averaged molecular weight** which is given below

$$\overline{M}_V = \left(\frac{\sum_i n_i M_i^{1+a}}{\sum_i n_i M_i}\right)^{1/a} \tag{5.18}$$

You'll notice that the viscosity averaged molecular weight is $\overline{M}_N \leq \overline{M}_V \leq \overline{M}_W$.

**Experimentally Measuring Viscosity**

To determine the intrinsic viscosity experimentally will require two steps:

1. Measure the viscosity of a polymer solution for a series of polymer concentrations.
2. Measure viscosity for a series of molecular weights

So we have the previously relationship for intrinsic viscosity

$$\frac{\eta_{sp}}{c_2} = [\eta] + \text{slope} c_2 \tag{5.19}$$

We can find $[\eta]$ by measuring a number of polymer concentrations and fitting the slope and extrapolating the line back to the origin (finding the intercept). Then, we measure viscosity for a series of molecular weights and plot as a log-log plot

$$\log[\eta] = a \log M + \log K \tag{5.20}$$

where we can find $a$ from the slope of the log-log plot and $K$ from the intercept. We can find these critical parameters which will then allow us to determine the viscosity-averaged molecular weight and our solvent quality $a$.

# CHAPTER 6

## OSMOMETRY

## 6.1 Key Terms/Definitions:

- **Viscosity** - the physical property of a fluid that describes the resistance of the fluid to a shear stress; acts as a proportionality constant between shear stress and strain rate (akin to velocity).
- **Newtonian fluid** - a fluid that has a constant viscosity; a non-Newtonian fluid has a viscosity that changes as a function of either total strain or strain rate, leading to a non-linear dependence of shear stress on strain-rate.
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- **Hydrodynamic radius** - in the non-draining regime, the effective radius of the (impenetrable) polymer coil as seen by solvent; used to calculate viscosity in solution.
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- **Specific viscosity** - the effective increase in the viscosity of a solution associated with an increase in the polymer concentration.
- **Intrinsic viscosity** - the limit of the specific viscosity as polymer concentration goes to 0; in other words, the infinitesimal increase in solution viscosity when polymer is first added.

## 6.2 Measuring Properties of Polymers:

We have run into several key properties of polymers like molecular weight, end-to-end distance, etc., and there are a number of other key polymer behaviors that depend on some of these key properties like

- Non-cross linked rubber elasticity
- Shear thickening

- Elastic modulus of cross linked networks
- Electrical conductivity

The question then becomes if these polymer properties are so critical to behavior how to do we measure them. This question is quite difficult for example it will be important in terms of rubber elasticity to know the distance between cross-links or how do we measure $\chi$? Well we will be talking about several different techniques to understand:

- Understand the origin of osmotic pressure in polymer solutions and relate this to molecular size and polymer-polymer interactions.

## 6.3 Membrane Osmometry

We now know that we can use intrinsic viscosity measurements to determine molecular weight and solvent conditions via our $a$ scaling parameter. We can gain even more insight into a polymer solution using a measurement technique called **membrane osmometry**, which measures the the **osmotic pressure** of a polymer solution.

**Osmotic pressure**, $\pi$, is a **colligative** property of a solution, it depends only on the number of solute molecules in solution. It does not depend on the chemical composition of those solute molecules. For a physical interpretation, **osmotic pressure is a thermodynamic force that arises due to the fact that when species mix the solution tends to maximize entropy via dilution with solvent**. Osmotic pressure is typically measured using an **osmometer** which has two separate containers. One has the solvent and the other the solute. The containers are searated by a semi-permeable membrane which allows only the small solvent molecules to cross, the polymer solute cannot cross the membrane.

So you can imagine that when you put a **polymer solute on one side** the **solvent will tend to flow from the pure solvent side to the polymer side** until the **chemical potential of each side are equal**. Or in other words until **thermodynamic equilibrium has been achieved**. This driving force comes from the **mixing terms** we went over exhaustively from Flory-Huggins, in short the flow of solvent to the polymer side **increases the entropy of the system**. You can imagine this is the case physically because the number of **microstates or configuration states of polymer and solvent increases as opposed to the pure polymer solution**. Additionally this **flow of solvent also increases the volume of the system which further increases the number of microstates**. And the driving force is **thermodynamic in nature** and due to the **osmotic pressure** which pushes the **solvent through the membrane into the increasingly dilute solution of polymer**.

This flow of solvent will increase the volume as we just mentioned and on the polymer solution size you will see the **solution to raise up the vertical tube which extends from the solution side of the chamber**. This **motion in the vertical direction is obviously opposed**

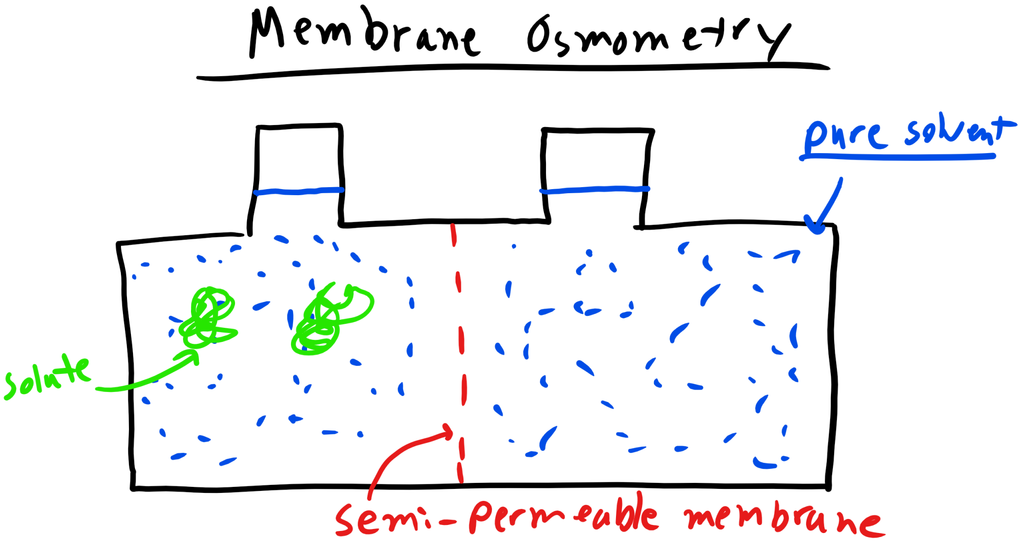

Figure 6-1: Schematic of Membrane Osmometry.

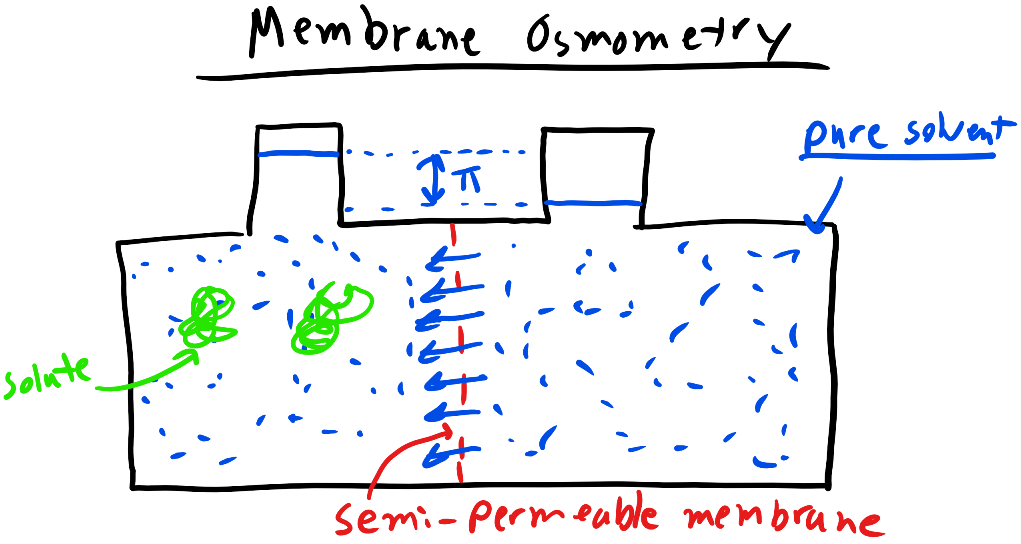

Figure 6-2: Schematic of Membrane Osmometry.

**by gravity** so we have a **mechanical pressure that opposes the osmotic pressure**. At equilibrium, i.e. when the solution stops rising, this **mechanical pressure will be equal to the osmotic pressure**. Once thermodynamic equilibrium is reached we can **measure the osmotic pressure via the final height of the fluid in the solution part of the chamber and we can calculate the mechanical pressure and thus the osmotic pressure**.

Once we have the osmotic pressure we can use this critical quantity to determine other properties of polymers. However, first we have to calculate the osmotic pressure by relating it to the condition of equilibrium which is that the **chemical potential on both sides of the container must be**

**equal**

$$\mu_1^0 = \mu_1 + \int_{P_0}^{P_0+\pi} \frac{\partial \mu_1}{\partial P} dP \tag{6.1}$$

where $\mu_1^0$ is the **chemical potential of the solvent alone (left side)** which has to be equivalent, at equilibrium, to the **chemical potential of the solution**, $\mu_1$, plus the change in the **chemical potential due to the change in pressure**, where the change in pressure is equal to the osmotic pressure $\pi$. To calculate the derivative we can rewrite the chemical potential in terms of its definition as the derivative of the Gibbs free energy:

$$\frac{\partial \mu_1}{\partial P} = \frac{\partial}{\partial P}\left(\frac{\partial G}{\partial n_1}\right) = \frac{\partial}{\partial n_1}\left(\frac{\partial G}{\partial P}\right) \tag{6.2}$$

Here, we have exchanged the order of the partial derivatives so that we can relate the Gibbs free energy to a different and more convenient thermodynamic variable. Remember that $G = U - TS - PV$ so again we have

$$dG = VdP - SdT + \mu dn \tag{6.3}$$

$$\left(\frac{\partial G}{\partial P}\right)_{n,T} = V \tag{6.4}$$

Now we can substitute back in and we get

$$\frac{\partial \mu_1}{\partial P} = \frac{\partial}{\partial n_1}\left(\frac{\partial G}{\partial P}\right) = \frac{\partial V}{\partial n_1} = \overline{V}_1 \tag{6.5}$$

where $\overline{V}_1$ is the **partial molar volume of pure solvent**. This is a **quantity that is constant with pressure**. So we can finish by writing that

$$\mu_1^0 = \mu_1 + \int_{P_0}^{P_0+\pi} \frac{\partial \mu_1}{\partial P} dP \tag{6.6}$$

$$\mu_1^0 = \mu_1 + \int_{P_0}^{P_0+\pi} \overline{V}_1 dP \tag{6.7}$$

$$\mu_1^0 = \mu_1 + \pi \overline{V}_1 \tag{6.8}$$

$$\mu_1 - \mu_1^0 = -\pi \overline{V}_1 \tag{6.9}$$

So the change in chemical potential between the pure and the solution side is simply the **osmotic pressure multiplied by the partial molar volume of the pure solvent**. With this change in chemical potential we can also relate this equation back to Flory-Huggins in the limit of dilute solution

**Dilute Polymer-Solvent Solutions**

You may often encounter scenarios where you are working with a **dilute solution where the moles of solvent is much greater than the number of moles of polymer** (i.e. really anytime working with biological concentrations of proteins/peptides). When you have such a scenario there are a couple of **simplifications** that simplify this derivation the first concerns the volume fraction of polymer

$$\Phi_2 = \frac{n_2 x_2}{n_1 x_1 + n_2 x_2} \approx \frac{n_2 x_2}{n_1} \tag{6.10}$$

Also since $\Phi_1 = 1 - \Phi_2$ and $\Phi_2$ is small in dilute solution we can do an expansion of $\ln \Phi_1$ from our chemical potential above

$$\ln(1-x) \approx -x - \frac{x^2}{2} - ... \tag{6.11}$$

We can then use these expression and re-write the change in chemical potential of the solvent which was previously

$$\mu_1 - \mu_1^0 = RT \left[ \ln \Phi_1 + (1 - \frac{1}{x_2})\Phi_2 + \chi \Phi_2^2 \right] \tag{6.12}$$

to this

$$\mu_1 - \mu_1^0 = RT \left[ -\frac{\Phi_2}{x_2} + (\chi - \frac{1}{2})\Phi_2^2 \right] \tag{6.13}$$

We previously described that for an **ideal solution, the chemical potential is proportional the log of the activity, which is in turn proportional to the mole fraction of that species in solution ( Henry's law)**. We can use this to

$$\mu_1 - \mu_1^0 = RT \ln a_i = RT \ln X_1 = RT \ln(1 - X_2) \approx -RTX_2 = -RT\frac{\Phi_2}{x_2} \tag{6.14}$$

where $X_i$ is the mole fraction of the species in solution. As you see in the previous expression the first term matches with the ideal solution. But the second term which has $\chi$ and $\Phi_2^2$ **describes the interaction between polymers and is the correction to the purely ideal assumption**. This is sometimes referred to as the **excess chemical potential** because it is an additive term which has two components

1. **Contact interactions (solvent quality)** : $\chi \Phi_2^2 RT$
2. **Chain connectivity (excluded volume effects)**: $-\frac{1}{2}\Phi_2^2 RT$

But there is a an **extremely important** fact in the expression where we see that the **excess chemical potential** disappears if $\chi = \frac{1}{2}$. There is a **balance between the contact interaction and chain connectivity or the solvent quality and excluded volume effects** that can allow for the chain to behave ideally ($\theta$ conditions). So you can **change the value of $\chi$ to obtain**

**ideal solutions**, most typically **via changing temperature!**. We can summarize when/where we obtain $\theta$ conditions for some different scenarios you might encounter

$$\mu_1 - \mu_1^0 = RT\left[-\frac{\Phi_2}{x_2} + (\chi - \frac{1}{2})\Phi_2^2\right] \tag{6.15}$$

(Note: Remember when we are dealing with molar quantities the prefactor of $kT$ is replaced by $RT$ and the variables $n_1$ and $n_2$ now refer to the number of moles, not molecules; however, practically speaking this only matters in terms of having the correct units.) This expression is **only valid in the limit of dilute solutions** - that is, $\phi_2 << 1$. We have previously stated above that our experimental set up assumes a dilute solution in the osmometer, so we can again rearrange and get

$$\mu_1 - \mu_1^0 = -\pi\overline{V}_1 \tag{6.16}$$

$$\mu_1 - \mu_1^0 = RT\left[-\frac{\Phi_2}{x_2} + (\chi - \frac{1}{2})\Phi_2^2\right] \tag{6.17}$$

$$\pi = RT\left[\frac{\Phi_2}{\overline{V}_1 x_2} + (\frac{1}{2} - \chi)(\frac{\Phi_2^2}{\overline{V}_1})\right] \tag{6.18}$$

In the limit of **very dilute solutions**, $\Phi_1 >> \Phi_2$, so $\Phi_2 \approx \frac{n_2 x_2}{n_1}$. You can also approximate the total volume of the solution as the volume of the solvent, or $V = n_1 V_1$. This leads to $\overline{V}_1 \approx V_1$. Again physical meaning ... the **increase in volume of the solution due to the addition of solvent is approximately the same as the volume of a single mole of solvent molecules**. When we substitute these approximations into the equation above

$$\pi = RT\left[\frac{n_2}{V} + \left(\frac{1}{2} - \chi\right)\left(\frac{n_2}{V}\right)^2 V_1 x_2^2\right] \tag{6.19}$$

Let's take a **look at the first term and what happens** when $\chi = 1/2$, we get the **ideal gas law** - $\pi V = RTn_2$. This first term is the contribution if we had an ideal solution.

We can simplify the expression a bit more by defining variables in terms of the concentration of polymer $c_2$ instead of the volume fraction $\phi_2$, knowing that

$$c_2 = \frac{\text{Total mass of Polymer}}{\text{Volume}} = \frac{n_2\overline{M}_n}{V} \tag{6.20}$$

remember the total mass is related to the number averaged molecular weight and now we can use this to substitute into the equation above and get:

$$\frac{\pi}{c_2} = RT\left[\frac{1}{\overline{M}_n} + \left(\frac{1}{2} - \chi\right)\frac{V_1 x_2^2}{\overline{M}_n^2}c_2\right] \tag{6.21}$$

**Now we can see how important osmotic pressure is as we can now relate this to the number averaged molecular weight and** $\chi$. You can also see that this equation has the form of a virial expansion (move this to the first instance)

$$P = RT(A_1c + A_2c^2 + A_3c^3 + ...) \tag{6.22}$$

We can match terms with our equation and get that the **first virial coefficient** $A_1 = \frac{1}{\overline{M}_N}$ and the **second virial coefficient** $A_2 = \left(\frac{1}{2} - \chi\right)\frac{V_1 x_2^2}{\overline{M}_n^2}$.

## 6.4 Experimental Membrane Osmometry Technique:

Now how do we utilize this equation. Well now we can measure the $\overline{M}_n$ and $\chi$ from experiments by plotting the **reduced osmotic pressure** $\frac{\pi}{c_2}$ vs. $c_2$.

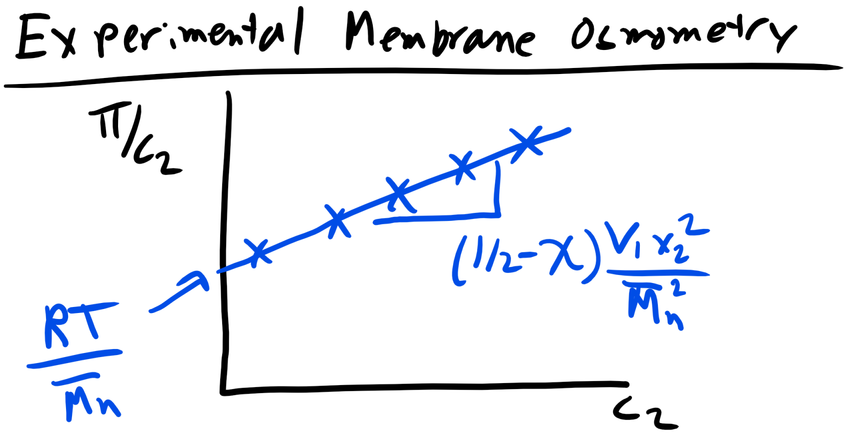

Figure 6-3: Experimentally Determining Key Polymer Parameters via Membrane Osmometry.

This will once again give an y-intercept as

$$\frac{RT}{\overline{M}_n} \tag{6.23}$$

and a slope as

$$\left(\frac{1}{2} - \chi\right)\frac{V_1 x_2^2}{\overline{M}_n^2} c_2 \tag{6.24}$$

So from a single series of measurements we can get both parameters! You can also see that for theta conditions $\chi = 0.5$ and the slope disappears! (write problem with this)

**Key Assumptions in Membrane Osmometry Derivation**

For membrane osmometry, we make two key assumptions:

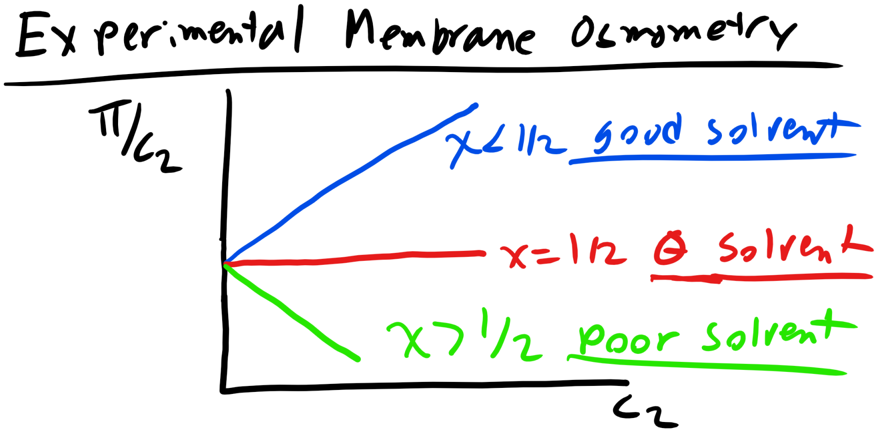

Figure 6-4: Slope Change as a Function of Solvent Quality.

1. We assume **mean-field** conditions - local environments are similar everywhere throughout the polymer solution, we did this in the Flory-Huggins Theory.
2. We assume a **dilute solution** - $\Phi_2 << 1$. We use this assumption to simplify the expression for the chemical potential.

These conditions are somewhat contradictory as mean field conditions break down in dilute solutions so we force experimental conditions to be

1. The system is **thermodynamically concentrated** - $c_2 > c_2^*$
2. The system is **mathematically dilute** - $\Phi_2 << 1$

Our experimental conditions are **very specific** and only valid in the **semi-dilute** condition. The parameter $c_2^*$ is the *overlap* **concentration**, where **polymer coils just begin to overlap in solution**. Around this concentration, polymer coils are **slightly interpenetrating such that the mean-field assumption of equivalent local environments is accurate**; this allows us to apply Flory-Huggins theory. However, there is still enough solvent right at the overlap concentration that the assumption of a dilute solution is accurate, and we can make the assumptions of the limit of $\phi_2 << 1$. We can simply approximate the overlap concentration as

$$c_2^* = \frac{\text{mass of polymer molecule}}{\text{volume of polymer coil}} = \frac{M/N_{av}}{\langle r^2 \rangle^{\frac{3}{2}}} \tag{6.25}$$

We know that $M \propto N^1$ and $\langle r^2 \rangle^{\frac{3}{2}} \propto N^{3/2}$, so the entire expression scales

$$c_2^* \propto N^{-1/2} \tag{6.26}$$

This scaling law is interesting because it says that **at large values of $N$, the overlap concentration actually gets quite small** which should make sense. Additionally, this **implies that the conditions under which our derivation of membrane osmometry apply can be achievable under a broad range of experimental conditions**.

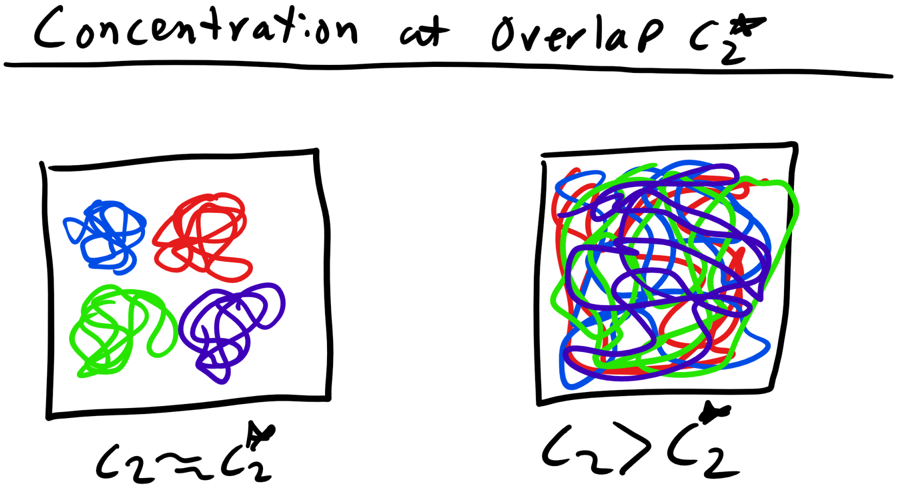

Figure 6-5: Overlap concentration Schematic.

## 6.5 Summary: Membrane Osmometry

We have discussed membrane osmometry, where we place a dilute polymer solution in a container adjoined to a different container filled with only solvent. The two containers are separated by a semi-permeable membrane that permits passage of solvent but not polymer. Due to the free energy gain from the entropy of mixing (characterized as a thermodynamic driving force called the osmotic pressure), solvent will move in the direction of the polymer solution, leading to an increase in competing pressure that opposes the osmotic pressure. When the flow stops, we know the osmotic pressure is directly offset by the pressure from the increased volume of the polymer solution, allowing us to measure the osmotic pressure experimentally. We saw that measuring this quantity led to an estimate of $\chi$ and number-average molecular weight.

## 6.6 Membrane osmometry

- **Key Ideas:** Put polymer solution in container connected to container of pure solvent, separated by semi-permeable membrane. Thermodynamic driving force that wants to further dilute polymer solution (osmotic pressure) will drive solvent across membrane. Competing pressure from volume expansion builds up, allows calculation of osmotic pressure. Can relate osmotic pressure to number-average molecular weight, $\chi$ parameter from Flory-Huggins theory.

- **Key equations:** Osmotic pressure - $\pi/c_2 = RT\left[\frac{1}{\overline{M}_N} + \left(\frac{1}{2} - \chi\right)\frac{V_1 x_2^2}{\overline{M}_N^2}c_2\right]$. $\pi$ is osmotic pressure, $c_2$ is concentration of (dilute) polymer, $\overline{M}_N$ is number-average molecular weight, $\chi$ is Flory-Huggins parameter, $V_1$ is volume of a mole of solvent, and $x_2$ is degree of polymerization of polymer. Combined prefactor in front of $c_2$ is also called second virial coefficient, $A_2$.
- **Key Experimental Method**: Measure osmotic pressure for various polymer concentrations, plot $\pi/c_2$ vs $c_2$. Intercept gives $1/\overline{M}_N$. Slope gives $A_2$, can be related to $\chi$ knowing other parameters and knowing $\overline{M}_N$ from intercept.
- **Key Insights**: obtaining solvent quality and phase behavior from measuring $\chi$; determining degree of deviation from ideality from $A_2$; measuring average molecular weight $\overline{M}_N$.

# Chapter 7

## Size Exclusion/Gel Permeation Chromatography (SEC/GPC)

### 7.1 Measuring Properties of Polymers:

We have run into several key properties of polymers like molecular weight, end-to-end distance, etc., and there are a number of other key polymer behaviors that depend on some of these key properties like

- Non-cross linked rubber elasticity
- Shear thickening
- Elastic modulus of cross linked networks
- Electrical conductivity

The question then becomes if these polymer properties are so critical to behavior how to do we measure them. This question is quite difficult for example it will be important in terms of rubber elasticity to know the distance between cross-links or how do we measure $\chi$? Well we will be talking about several different techniques to understand:

- Utilize fractionation techniques and gel permeation chromatography (also called size-exclusion chromatography) to obtain a complete molecular weight distribution.

### 7.2 Size Exclusion/Gel Permeation Chromatography (SEC/GPC)

**Size exclusion chromatography (SEC)**, also called **gel permeation chromatography (GPC)** allows the measurement of an **entire** m**olecular weight distribution**, which is more favorable than the measurement of a **single molecular weight average** from either **intrinsic viscosity or osmometry measurements**.

The experimental apparatus for SEC consists of a **long column packed with porous polymer beads** of **varying diameters and pore sizes**, typically on the order of 50-100,000 Å. Additionally people will typically utilize multiple columns with different sized beads to increase the resolution. The **beads** themselves are **cross-linked polymers, or gels,** leading to the term **gel permeation chromatography**. A **polymer solution** is then **pushed through the column slowly** (such that the **shear rate is not high enough to bias the polymer conformations**), and as it flows **the solution interacts with the porous beads**. As the solution reaches the bottom of the column, **eluted volume is collected as a function of time and a concentration detector** (which is generally some sort of **light scattering device, UV detector, IR**

**detector, or refractive index (RI) detector**) is used to **determine the concentration of a given sample**. Also the solvent is typically chosen to be a good solvent in order have a different refractive index from the polymer.

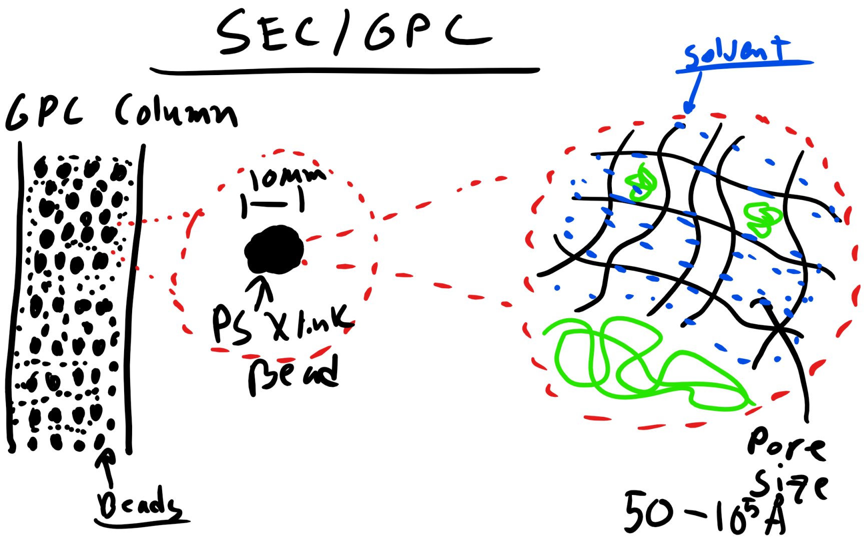

Figure 7-1: SEC/GPC Schematic.

Now the polymers will have a **wide distribution of molecular sizes** and the **beads will also have a distribution of pore sizes**. So the polymers will be able to **penetrate into some of the porous beads depending on the size of the polymers and the size of the pores**. Thus **depending on how many beads each polymer interacts** with (**how many porous beads the polymer can penetrate**) the **time taken to reach the body of the column will change, leading to a difference in polymer sizes eluting at different times**. The **larger polymers will typically elute first** as they will penetrate the smallest number of beads while the **smaller polymers will come out much later**. Thus we are able to separate by size (SEC) based on this **residence time**, the time spent inside the beads. Quick note, this is not an exact technique and really typically only useful as a relative technique that must be calibrated to a reference sample.

**Thermodynamic Principles of SEC:**

SEC is a unique case and will depend on the competition between to **entropic** contributions this time instead of an entropic and enthalpic contribution. The competition is between

1. **Favorable entropy increase** upon **mixing of polymer and solvent inside the pore of the bead**
2. **Unfavorable loss of configurational entropy of large size polymers** when they enter **bead pore size smaller than polymer's unperturbed size**

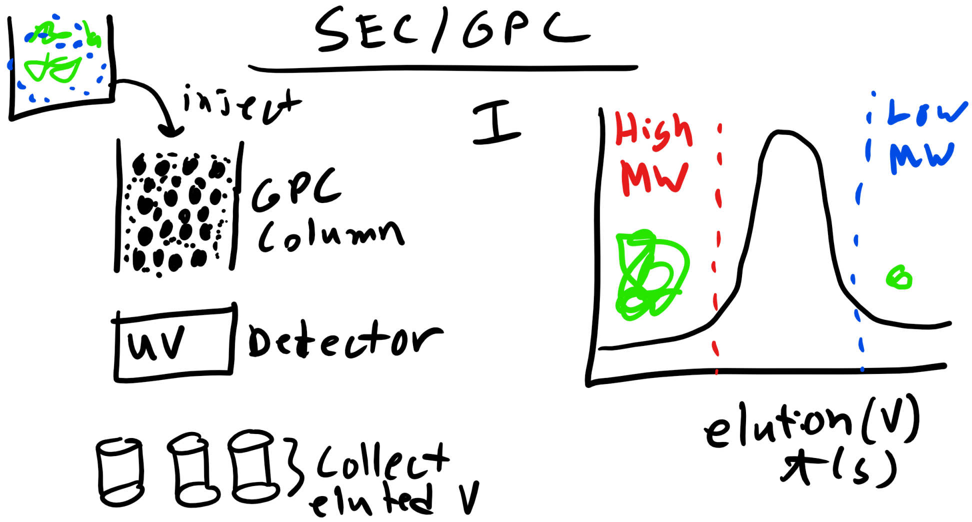

Figure 7-2: SEC/GPC Experimental Method.

For the unfavorable term we remember that for polymer deformation the change in entropy for compression is given by

$$\Delta S \approx \left(\frac{R_0}{R}\right)^2 \tag{7.1}$$

So we can write the change configurational entropy term for larger polymers being compressed when attempting to enter small pores as

$$\Delta S_{conf} \approx \frac{R_{polymer}}{R_{pore}} \tag{7.2}$$

where $R_{pore}$ is approximated as the ratio of the average pore volume to pore surface area. The entropy increase is the same that we have seen previously from Flory (see how important that lecture was). Having identified these two basic entropic considerations, we can now fully flesh out our understanding of SEC in the next section.

**Eluted Volumes of SEC**

We have our physical understanding but now we need to relate this to what will actually happen in the experiment which is **measuring some eluted volume of polymeric materials**. To start let's divide this **volume that is eluted from the column into two parts**

1. $V_o$ the **void volume external to the beads** in the column
2. $V_i$ the **pore volume internal to the beads**

A **polymer will sample some part of this entire volume**, depending on the size of the polymer, but the **solvent will sample the entire volume** so

$$\text{pure solvent eluted volume} = V_{es} = V_o + V_i \tag{7.3}$$

$$\text{polymer solution eluted volume} = V_{ep} = V_o + V_i K_{se} \tag{7.4}$$

The difference between the two eluted volumes lies in the amount of pore volume sampled, which depends on the parameter $K_{se}$, our *size exclusion equilibrium coefficient* which like similar equilibrium constants can be defined by

$$K_{se} = \frac{\text{polymer concentration inside bead}}{\text{polymer concentration outside bead}} = \frac{c_{2i}}{c_{2o}} \tag{7.5}$$

We can relate this to an entropy for pore permeation (just like chemical equilibria constants). Assuming no enthalpy change upon permeation

$$\Delta G_{pp} = -RT \ln K_{se} = -T\Delta S_{pp} \tag{7.6}$$

$$K_{se} = e^{\Delta S_{pp}/R} \tag{7.7}$$

In order to find $K_{se}$ we need to approximate this entropy. Well that will be the expression that we started with **for the change in conformational entropy upon entering the bead which is the size of the unperturbed polymer divided by the size of the pore**. Well pore sizes are difficult to measure so instead we will go with another more easily measured parameter which is $A_s$ is the pore surface area:volume ratio (and hence a characteristic size for the pores). So now the change in entropy is

$$\Delta S_{pp} = -RA_s \langle r^2 \rangle^{\frac{1}{2}} \tag{7.8}$$

Plugging this back in for K

$$V_{ep} = V_o + V_i \exp(-A_s \langle r^2 \rangle^{\frac{1}{2}}) \tag{7.9}$$

Here the **physical insight is that the elution volume is proportional to an exponential relation of the polymer radius**, which we know is related to molecular weight. Thus, we can **relate molecular weight to elution volume**.

Unfortunately, with this technique, as previously mentioned, we first need to determine our constants by utilizing a **known sample with a known molecular weight (calibration)**. Then we can yield a **complete molecular weight distribution and polydispersity index**.

So we have a method for deriving the complete molecular mass distribution based on the relationship derived above between molecular mass and elution volume. We can thus relate the detector response as a function of elution volume (i.e. time) to molecular mass, since a greater detector response corresponds to a higher concentration of polymer at a given volume.

## 7.3 Summary: Viscosity, Membrane Osmometry, and SEC/GPC

We have now studied size exclusion/gel permeation chromatography. In this experimental setup, columns are packed with a dense mixture of porous beads, with differing pore sizes. A polymer sample is then poured through the column. Because of the presence of the beads, polymer coils of different sizes will attempt to either flow directly through the column without interacting with the beads or spend some time permeating into the porous beads themselves. Smaller polymers will be able to get into more pores and thus will spend more time in the column, while larger beads will tend to pass directly through the column without passing through any pores. As a result, we can extract samples from the elution volume of the column as a function of time, assuming that each sample will be relatively monodisperse, and with larger coils emerging from the column earlier. Further characterizing each volume will thus reveal a complete size distribution of the sample.

## 7.4 Gel permeation chromatography

- **Key Ideas:** Fill column with porous beads of varying pore size. Pour solution through column; larger polymer coils will pass through column first since they do not spend time in pores. Can obtain specific molecular weight distribution by measuring elution volume, concentration of polymer as function of time.
- **Key equations:** $V_{ep} = V_o + V_i \exp(-A_s \langle r^2 \rangle^{\frac{1}{2}})$. $V_{ep}$ is elution volume, $V_o$ is volume of solution outside of pores, $V_i$ is volume inside pores, $A_s$ is pore surface:volume ratio, $r^2$ is polymer coil radius. Note that this equation just serves to illustrate that the volume eluted is related to coil size.
- **Key Experimental Method**: First calibrate GPC using known molecular weight sample to obtain elution volumes - in other words obtain molecular weight vs. elution volume curve. Can then add new sample and compare to previously calibrated result to gain molecular weight distribution. Most modern GPCs will be precalibrated and can give size distribution easily. Will generally need some other means (light scattering, viscosity) to obtain polymer concentration.
- **Key Insights**: obtaining full molecular weight distribution of polymer sample, rather than just averages (as obtained from other characterization techniques).

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# CHAPTER 8

## LIGHT SCATTERING

## 8.1 Key Terms/Definitions:

- **Polarizability** - The property of a molecule which determines the ease of distorting its charge distribution in the presence of an external field; determines how strongly a molecule couples to incident electric fields (such as those induced by incident radiation).
- **Light scattering** - The emission of same-intensity light in all directions upon the interaction of an incident light beam with a molecule; in the Rayleigh regime (elastic scattering), the intensity of emitted light varies as a function of the polarizability of the scattering source, the wavelength of the incident radiation, and geometric factors.
- **Point scatterer** - an approximation of a molecule as a single point with no effective volume that emits light upon contact with incident radiation; this approximation is used
- **Rayleigh ratio** - the relative intensity of scattered light compared to incident light, divided by geometric factors; allows relation of measured intensity of scattering to concentration, molecular weight of polymer sample.
- **Zimm plot** - method of double extrapolation for determining the second virial coefficient, radius of gyration, and molecular weight of a polymer solution from measurements of the scattering intensity of a polymer solution (after subtracting the scattering intensity of the pure solvent).

## 8.2 Measuring Properties of Polymers:

We have run into several key properties of polymers like molecular weight, end-to-end distance, etc., and there are a number of other key polymer behaviors that depend on some of these key properties like

- Non-cross linked rubber elasticity
- Shear thickening
- Elastic modulus of cross linked networks
- Electrical conductivity

The question then becomes if these polymer properties are so critical to behavior how to do we measure them. This question is quite difficult for example it will be important in terms of rubber elasticity to know the distance between cross-links or how do we measure $\chi$? Well we will be talking about several different techniques to understand:

- **Light Scattering**
- **Zimm Plots**

## 8.3 Radiation/Light Scattering Techniques:

There are many types of radiation scattering experiments which are used to characterize materials, including small angle light scattering (SALS), small angle x-ray scattering (SAXS), x-ray diffraction (XRD) (more on this when we talk about $T_g$ and semi-crystalline polymers), and small angle neutron scattering (SANS), all of which operate off of the same basic principles but with different types of scattered radiation. Light scatting is based on the principle that an incident beam of radiation will scatter off of a sample in some predictable way as a function of the angle of the scattering detector with respect to the sample, the wavelength of the incident radiation, and the refractive index of the sample.

**Principles of Radiation Scattering**

When a beam of incident light (or other form of electromagnetic radiation) interacts with a molecule, in general the incident radiation can either be **absorbed or scattered**. The latter behavior occurs when the oscillating electric field of the radiation induces an oscillating dipole in the particle, which then acts as a source of additional radiation. Therefore, the **particle then emits light in all directions**, **scattering** the **original incident light beam** in **all directions** (on average). We will be primarily concerned with **Rayleigh scattering**, where it is assumed that the **energy of all emitted light is the same as the incident light** and thus all **emitted light has the same wavelength as the incident light**. The phenomenon of light scattering is responsible for most visible light; for example, when we attribute a color to the sky it is because **incident light from the sun infringes upon gas particles, which then scatter the light in all directions, including toward observers on the Earth's surface**. We will see why the sky appears blue, rather than other colors, in a minute.

Light scattering depends on the geometry, optical properties, and thermodynamics of the system under consideration (in this lecture we mostly discuss polymer-solvent solutions). The geometry is based on the **distance of the detector** from the sample ($r$) and the **angle of the detector with respect to the incident light** ($\theta$). The further away the detector is, the lower the intensity of the incident light. The optical properties of the system are based on the **wavelength of the incident light** ($\lambda$), **index of refraction** $n$ (or polarizability $\alpha$) of the polymer solution and sample, and the **derivative of the index of refraction with respect to solution concentration** $\frac{dn}{dc_2}$. The **important thermodynamic properties** are the **concentration** $c_2$ **of the polymer solution**, the **weight-averaged molecular weight** $\overline{M}_w$, and the **second virial coefficient**, which is again related to $\chi$ from Flory-Huggins.

The basics of light scattering come from the scattering equation, which we will derive in a bit, but physically we should note that **scattering arises from differences in variations in solution properties that differ based on the incident radiation**. For **light scattering**, we measure the difference in **polarizability** $\Delta\alpha$; for **X-ray scattering**, the **difference in electron density** $\Delta\rho$; and for **neutron scattering, the difference in neutron scattering length** $\Delta b$. The choice between which type of scattering to employ depends on what **resolution** you want, and the ease of determining these different properties for different polymer systems. More precisely, **we measure fluctuations in the polarizability of the entire solution (polymer + solvent) that emerge from the difference in polarizability between the solution by itself and the polymer by itself**. In solution, the difference in properties between these two components give rise to d**ifferent scattering behavior** from **different regions of solution corresponding to the relative concentration of polymer throughout the solution**; as polymer diffuses throughout the solution, we can thus **measure fluctuations of the polarizability to gain information about the polymer itself**, knowing the properties of the background solvent.

In essence what we want to achieve with light scattering is to **shine a light on the polymer solution and observe the intensity of the scattered light**. We then want to see if there is a **difference in polarizability between the polymer and the solvent**. If there is a **difference then we can relate the observed scattering intensity to concentration fluctuations of the polymer chain which can then be related to the second virial coefficient due to osmotic pressure build up from those fluctuations**.

## 8.4 Detailed Light Scattering Derivation:

**Theory of Light Scattering from Point Particles:**

To derive the scattering equation, let's first consider a simpler system: a dilute gas in vacuum, filled with small particles. We will call these small particles *point scatterers*, implying that they have no angular dependence on scattering since they have no effective size. To be more precise, the assumption of *no size* just says that the size of the particle is much smaller than the wavelength of the radiation. We start by considering only a single particle.

As discussed before, when a light wave encounters a particle, the oscillating electric field of the radiation forces the electron and nucleus of the particle to move in opposite directions (due to their opposite charges), thereby inducing a dipole that oscillates with the incident wave. The magnitude of this induced dipole is related (by definition) to the polarizability, $\alpha$, of the particle. Since oscillating dipoles emit radiation, the particle thus radiates light away from the particle in all directions with an intensity given by

$$I_\theta = \frac{I_0 8\pi^4(1+\cos^2\theta)}{\lambda^4 r^2}\alpha^2 \tag{8.1}$$

Here, $\theta$ is the angle between the incident radiation and the detector, $\lambda$ is the wavelength of the incident radiation, $\alpha$ is the polarizability of the point particle, and $I_0$ is the initial intensity

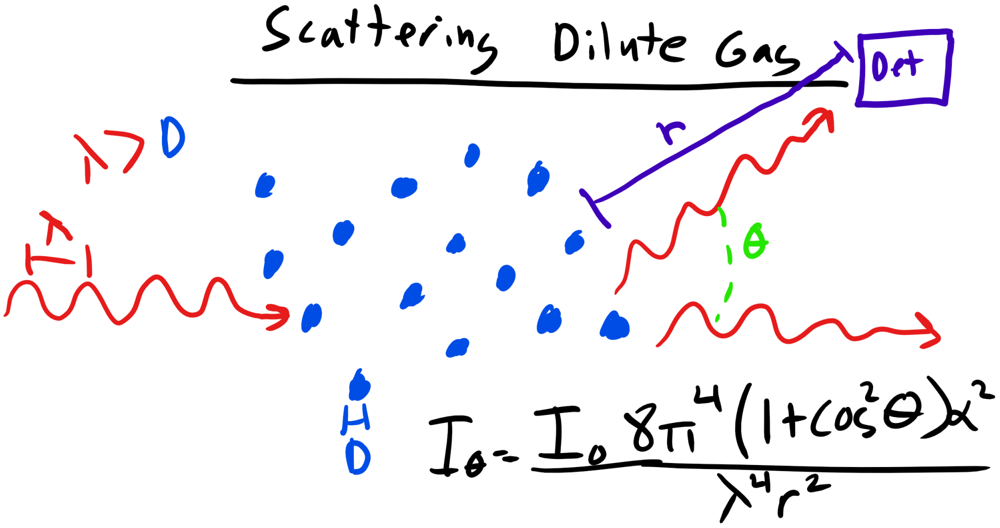


Figure 8-1: Light Scattering for Diluted Gas.

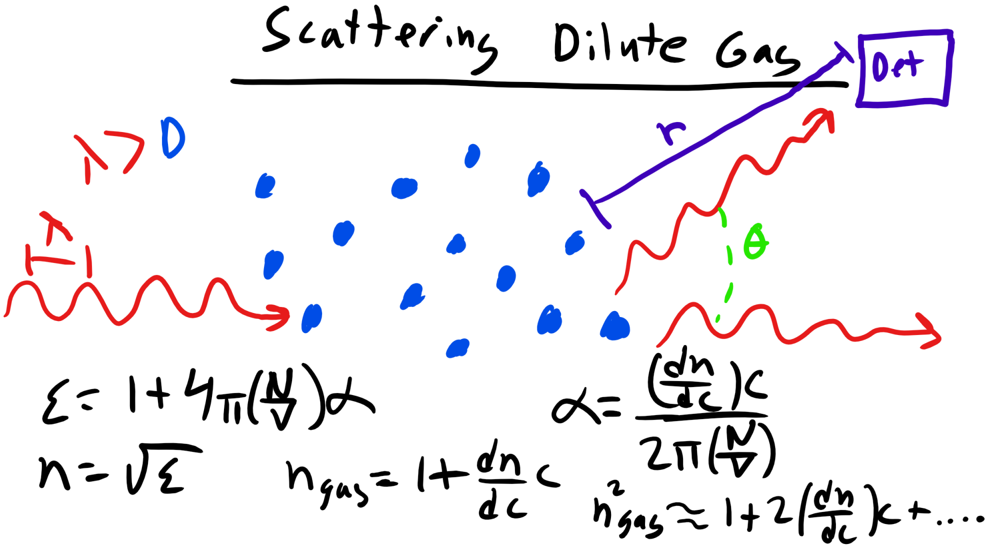


Figure 8-2: Intensity of Scattering.

of the incident radiation. The fourth order dependence on $\frac{1}{\lambda}$ shows that the smallest wavelengths will actually be scattered most (this same relation determines why the sky is blue, since blue is the smallest visible wavelength and hence scatters very strongly from gas particles in the atmosphere, and scattered light is what we primarily observe visibly). By **scatters most** we mean that the intensity at any given $\theta$ will be highest when the wavelength $\lambda$ is lowest. To generalize this equation to many particles, it is only necessary to scale by the density of point scatterers in solution

$$I'_\theta = \frac{N}{V} I_\theta \tag{8.2}$$

Here, $N$ is the number of particles (not to be confused with the degree of polymerization of a polymer), and $V$ is the total volume of the solution. The assumption is effectively that the scattering between different point particles is uncorrelated, and we can simply sum the contributions from all particles in a given volume to get the total intensity (per unit volume). Next, we can relate the polarizability (which is not easily determined) to the dielectric constant of the medium using

$$\epsilon = 1 + 4\pi(\frac{N}{V})\alpha \tag{8.3}$$

Again, we give the effective polarizability of the medium as effectively the concentration of particles times $\alpha$. We also know that the index of refraction is given by

$$n = \sqrt{\epsilon} \tag{8.4}$$

and for a gas is given by the following relationship

$$n_{gas} = 1 + \frac{dn}{dc}c \tag{8.5}$$

which is essentially an expansion of the index around its known value of 1 in a gas. **Note that for polymers, the expression is the same, except that instead of expanding around 1 the value is instead replaced with the solvent index of refraction** $n_0$. In other words, we again make the assumption that we can relate the index of refraction of a solution to the index of refraction of the majority component (vacuum in the gas case, solvent in the polymer-solution case) to the change in index of refraction with concentration multiplied by the concentration. Squaring the index of refraction thus gives an expression for the polarizability

$$\alpha = \frac{(dn/dc)c}{2\pi(N/V)} \tag{8.6}$$

This gives us the polarizability of the sample in terms of quantities that we can measure more easily, specifically the concentration of the (gas/solution) and the change in index of refraction with respect to concentration. It is possible to measure the change in index of refraction with concentration $dn/dc$ directly by increasing the concentration of a solution and measuring the change in the **angle** of refraction for that solution as a result of the change in concentration, since recall that the index of refraction determines the angle of refraction from Snell's law

$$\frac{\sin\theta_2}{\sin\theta_1} = \frac{n_1}{n_2} \tag{8.7}$$

So the relation above provides for a simple way of actually measuring polarizability. The total intensity of the scattered light can now be related to only scattering geometry and measurable optical parameters, and is given by combining equations (8.1), (8.2) and (8.6) to yield the complicated expression

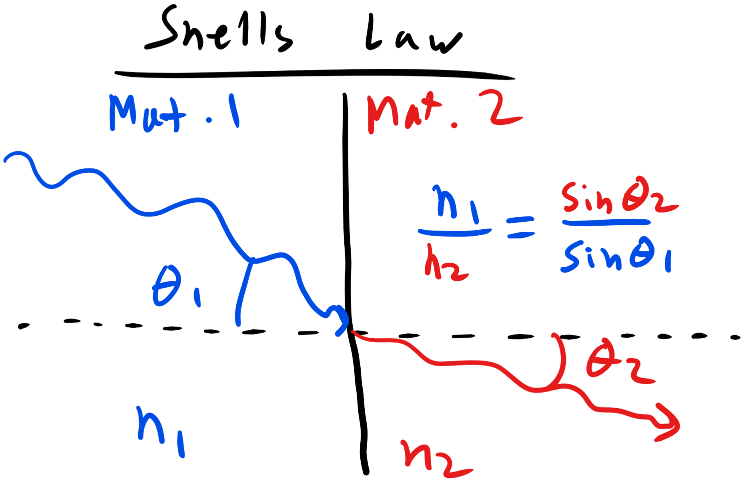


Figure 8-3: Snells Law.

$$I'_\theta = \frac{N}{V}\frac{I_0 8\pi^2(1+\cos^2\theta)}{\lambda^4 r^2}\left(\frac{(dn/dc)c}{2\pi(N/V)}\right)^2 \tag{8.8}$$

Canceling out terms and simplifying

$$I'_\theta = I_0\frac{2\pi^2(dn/dc)^2c^2(1+\cos^2\theta)}{\lambda^4 r^2(N/V)} \tag{8.9}$$

To further simplify the expression, we first relate $N/V$ to concentration via the relation $\frac{N}{V} = \frac{c}{M/N_A}$ and we get

$$I'_\theta = I_0\frac{2\pi^2(dn/dc)^2Mc(1+\cos^2\theta)}{\lambda^4 r^2 N_A} \tag{8.10}$$

This equation alone is called the **Rayleigh Equation for ideal elastic scattering**, and gives the intensity of scattered light as a function of the geometry of the sample ($\theta$, $r$), the characteristics of the solution ($dn/dc$, $M$, $c$) and characteristics of the incident light ($\lambda$, $I_0$). It is also convenient to define the **Rayleigh ratio**:

$$R = \frac{I'_\theta}{I_0(1+\cos^2\theta)/r^2} = \frac{2\pi^2(dn/dc)^2Mc}{\lambda^4 N_A} \tag{8.11}$$

The advantage of looking at the Rayleigh ratio is that the constants related to scattering geometry are incorporated in the left hand side and $R$ is therefore effectively independent of scattering geometry. We can reduce this expression to

$$R = KMc \tag{8.12}$$

where $K$ is the optical constant consisting of the combination of a large number of constants that are properties of a given choice of incident ratio and a given sample choice. Writing out $K$ (for a polymer, with the corresponding inclusion of background index of refraction $n_0$ as measured above) gives:

$$K = \frac{2\pi^2 n_0^2 (dn/dc)^2}{\lambda^4 N_A} \tag{8.13}$$

All of the parameters of the optical constant are either determined from the experimental set up (e.g. $\lambda$) or can be measured from the properties of the sample ($dn/dc$). We also know the concentration $c$ of the polymer sample. Finally, note that the Rayleigh ratio itself can be measured from the scattering intensity measured from a sample. Hence we have a simple (or at least, simplified version) equation relating the relationship between the Rayleigh ratio and the mass of the point scatterers (or polymers for $n_0 > 1$) $M$!

Rayleigh Equation Ideal
Elastic Scattering

$$R = KMc$$

$$R = \frac{I'_\theta}{I_0(1+\cos^2\theta)/r^2} \qquad K = \frac{2\pi^2\left(\frac{dn}{dc}\right)^2}{\lambda^4 N_a}$$

Figure 8-4: Rayleigh Scattering Equation.

**Light Scattering from Polymer Solutions:**

The derivation above assumed a dilute gas (though we made minor corrections to account for a non-vacuum background when using the background index of refraction $n_0$). In a liquid sample, the concentration of molecules will be much greater than in a dilute gas, and as result there will be the potential for interference between scattered light that eliminates any measurable scattering. Thus, in a uniformly dense liquid, we may not expect scattering because of a uniform polarizability - however, in reality, liquids are not uniformly dense! Instead, because of mass fluctuations in an otherwise uniform distribution of liquid particles, at any given instant in time different regions of a liquid will have a different number of molecules, leading to a net scattering if we assume that mass fluctuations are uncorrelated (that is, at any given time any region can have a slightly higher or lower mass independent of other regions). The key idea to remember is that the scattering from any given isolated region of the liquid will depend on that region's density (again referring to equation (8.2)), and in any system with free motion (such as a liquid or gas) there will be local density fluctuations that give rise to net scattering. We can thus measure the Rayleigh ratio from even a uniform liquid, which will be a key idea in analyzing polymer solutions.

In the case of a dilute solution of polymer and solvent, we will find that we can relate the Rayleigh ratio of the polymer alone to properties of that polymer, and we thus want to measure just the scattering of the polymer. However, in practice we will only be able to measure the scattering (and thus the Rayleigh ratio) of the entire solution, so we define the difference in Rayleigh ratios as:

$$\Delta R = R_{solution} - R_{solvent} \tag{8.14}$$

We will now discuss how to calculate this difference in Rayleigh ratios between the solution and solvent alone, yielding what is effectively the change in scattering due to just the polymer molecules. We will find that this light scattering depends on the **difference** in polarizability between the polymer coils and the background solvent; if there were no difference in polarizability we would be unable to distinguish polymer from solvent. We will now discuss dilute polymer solutions in more detail.

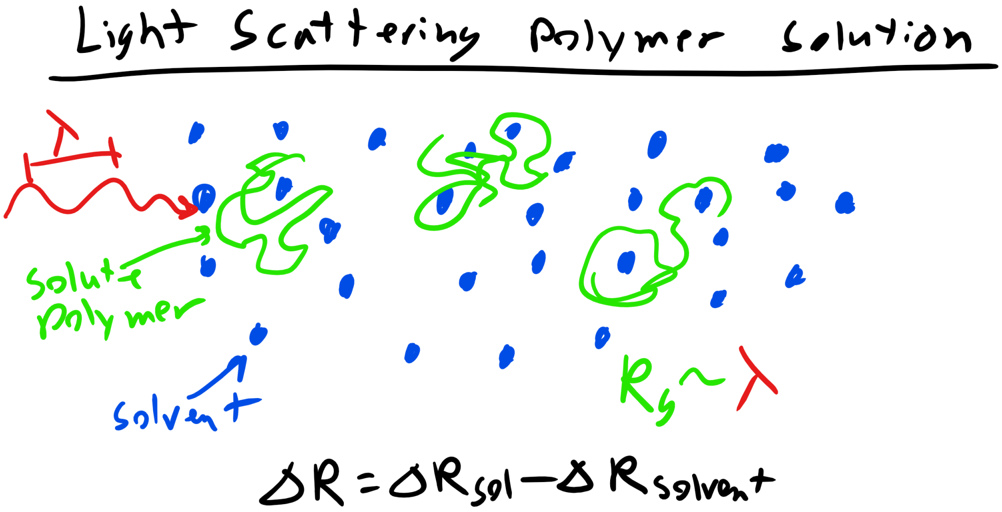


Figure 8-5: Polymer Light Scattering Schematic.

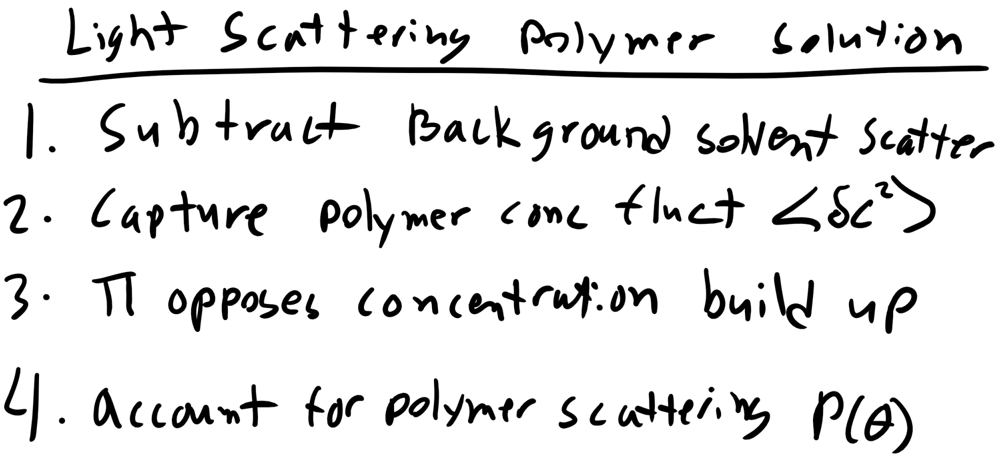
Let's consider a dilute polymer solution. There are four features of this system that need to be considered that were not applicable in the ideal gas system discussed in the previous section.

1. The background solvent will experience density fluctuations and will tend to scatter light on its own. We have to subtract this as background scattering
2. The polymer solution will not be uniformly distributed and will experience concentration fluctuations leading to strong scattering which is amplified by the difference in polarizability

between polymer and background solvent

3. The build up of polymer concentration in a given area is opposed by resulting osmotic pressure. Osmotic pressure will drive uniform polymer distribution and oppose fluctuations.

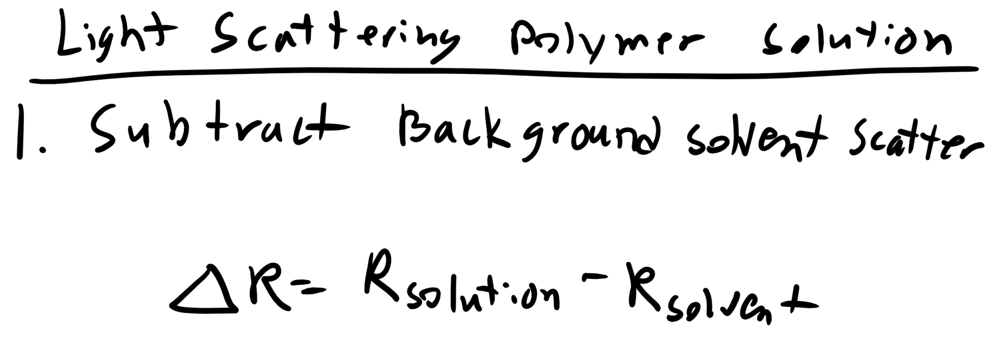
4. We **cannot** treat polymers as simple point scatters as the size of a polymer coil will be on the order of the incoming wavelength. This will lead to interference between the light scattered within the same coil.



Light Scattering Polymer solution

1. Subtract Background solvent Scatter
2. Capture polymer conc fluct $\langle \delta c^2 \rangle$
3. $\Pi$ opposes concentration build up
4. Account for polymer scattering $P(\theta)$

Figure 8-6: Adapting Ralyeigh Light Scattering for Polymers.



Light Scattering Polymer solution

1. Subtract Background solvent Scatter

$$\Delta R = R_{solution} - R_{solvent}$$

Figure 8-7: Subtracting Solvent Scattering.

Let's go ahead and deal with each of these issues. First, we have to get rid of the background effects of the solvent. We already effectively take this into account by considering $\Delta R$ as noted above. Again, $R$ is the Rayleigh ratio as defined in equations (8.11) and (8.12). Next, we note that any remaining scattering, aside from the pure solvent, comes from fluctuations in polarizability throughout the sample, which we will later relate to concentration fluctuations of polymer. If we imagine dividing the entire system in $N$ regions of volume $\delta V$, then $N/V = \delta V$, we can relate the original expression we derived for the intensity of scattering to the Rayleigh ratio using:

$$I'_\theta = \frac{N}{V} I_\theta \tag{8.15}$$

$$= \frac{1}{\delta V} \frac{I_0 8\pi^4 (1+\cos^2\theta)}{\lambda^4 r^2} \alpha^2 \tag{8.16}$$

$$R = \frac{1}{\delta V} \frac{8\pi^4}{\lambda^4} \alpha^2 \tag{8.17}$$

Having related the Rayleigh ratio to polarizability, we now can express the difference in the Rayleigh ratios to the fluctuations in polarizability, recognizing that fluctuations are time-averaged

$$\Delta R = \frac{1}{\delta V} \frac{8\pi^4 \langle (\delta\Delta\alpha)^2 \rangle}{\lambda^4} \tag{8.18}$$

Next, we recognize from equation (8.6) that there is a relation between polarizability and concentration of polymer, so we can also relate their fluctuations

$$\langle (\delta\Delta\alpha)^2 \rangle = \left( \frac{n_0^2 (dn/dc)^2 \delta V^2}{4\pi^2} \right) \langle (\delta c)^2 \rangle \tag{8.19}$$

Finally, we substitute in this expression for polarizability fluctuations into the expression for the difference in Rayleigh ratios to obtain an expression that instead refers to concentration fluctuations:

$$\Delta R = \frac{2\pi^2 n_0^2 (dn/dc)^2 \delta V \langle (\delta c)^2 \rangle}{\lambda^4} \tag{8.20}$$

Recall that concentration fluctuations refer to the fluctuations in concentration of polymer around some equilibrium value (i.e. the overall concentration of polymer in a well-mixed solution), which is characteristic of any system even at equilibrium; however, any fluctuation that drives a system away from its equilibrium value will give rise to a thermodynamic force that drives the system back to equilibrium. In the case of concentration fluctuations, the thermodynamic driving force that drives a system toward an equilibrium concentration is the osmotic pressure. Thus, we can relate the magnitude of concentration fluctuations to the change in the osmotic pressure as the concentration gets farther away from its equilibrium value; an expression for the concentration fluctuations can thus be derived that is called the **Einstein-Smoluchowski relation**

$$\langle (\delta c_2)^2 \rangle = \frac{RTc_2}{\delta V N_A (\partial\pi/\partial c_2)} \tag{8.21}$$

## Light Scattering Polymer solution

2. Relate $\langle \delta \Delta \alpha^2 \rangle$ to $\langle \delta c^2 \rangle$

$$\Delta R = \frac{2\pi^2 n_0^2 (dn/dc)^2 \delta V \langle \delta c^2 \rangle}{\lambda^4}$$

Figure 8-8: Relating Fluctutations in Polarizability to Concentration.

## Light Scattering Polymer solution

3. account for $\pi$ using Einstein-Smoluchowski

$$\langle \delta c^2 \rangle = \frac{RTc_2}{\delta V N_a \left(\frac{d\pi}{dc_2}\right)}$$

$$\frac{d\pi}{dc_2} = RT\left[\frac{1}{M} + 2A_2c_2 + \cdots\right]$$

$$\Delta R = Kc_2\left[\frac{1}{\frac{1}{M} + 2A_2c_2}\right]$$

Figure 8-9: Einstein-Smoluchowski Equation.

**Note that in this equation $R$ is the ideal gas constant, NOT the Rayleigh ratio**. The equation effectively relates the average magnitude of fluctuations (written as $\langle(\delta c_2)^2\rangle$) to the concentration of the solution divided by the change in osmotic pressure with the change in concentration. This derivative is expected since it reflects the rise in osmotic pressure as we are driven away from equilibrium by concentration fluctuations.

This general relation is true for any solution; however, since we know we are dealing with polymer solutions, we can further simplify the **Einstein-Smoluchowski relation** based on the expression for osmotic pressure we developed from Flory-Huggins theory. There, we wrote the osmotic pressure as:

$$\frac{\pi}{c_2} = RT\left[\frac{1}{M} + \left(\frac{1}{2} - \chi\right)\frac{V_1 x_2^2}{M^2}c_2\right] \tag{8.22}$$

$$\pi = RT\left[\frac{c_2}{M} + A_2 c_2^2\right] \tag{8.23}$$

where $A_2 = \left(\frac{1}{2} - \chi\right)\frac{V_1 x_2^2}{M^2}$ is the second virial coefficient, and taking the derivative gives

$$\frac{\partial \pi}{\partial c_2} = RT\left[\frac{1}{M} + 2A_2 c_2 + ...\right] \tag{8.24}$$

Again, in these equations $R$ is the ideal gas constant (it's unfortunate that this notation is confusing by convention). Combining equations (8.20), (8.21) and (8.24) together and simplifying with the same optical constant $K$ defined in equation (8.13) gives:

$$\Delta R = Kc_2\left[\frac{1}{\frac{1}{M} + 2A_2 c_2}\right] \tag{8.25}$$

Here, I have omitted any terms in the expression for osmotic pressure beyond the first order term (with $A_2$ as the prefactor). If we look at this equation, we see that if the second virial coefficient $A_2$ is equal to 0, then we get the expression $\Delta R = KMc_2$ - exactly the expression for the Rayleigh ratio we derived for an ideal gas in a vacuum! This observation is consistent with the knowledge that $A_2 = 0$ occurs when $\chi = 1/2$ and we have a theta solution, where the polymer is ideal. Since $A_2$ is an effective measure of the strength of interactions between polymers in solution, we see that as interactions become stronger (the magnitude of $A_2$ increases) $\Delta R$ becomes smaller; this is consistent with strong interactions reducing fluctuations and thus contributing more order to the solution, *masking* scattering by destructive interference.

Finally, we also have to note that our assumption of *point* scatterers is not accurate for large polymer coils, since in general the size of a coil is on the order of 100-1000 Åand the wavelength of incident light(e.g. lasers) is on the order of 5000 Åas well. When the polymer molecule is at this size, it is possible for light to scatter off of different parts of the same molecule, which could give rise to interference effects (effectively it's like having a uniform concentration of scatterers inside the volume occupied by a single coil).

To take this effect into account, we define an angle-dependent factor $P(\theta)$. This function is basically related to the connectivity of polymer chains, and more specifically related to the fact that fluctuations in polymers are correlated due to connectivity (rather than uncorrelated as assumed earlier in the uniform scatterer case). We then rewrite our definition of the excess Rayleigh ratio as:

$$\Delta R = Kc_2\left[\frac{1}{\frac{1}{M} + 2A_2 c_2}\right]P(\theta) \tag{8.26}$$

Debye showed that for Gaussian polymer coils, $P(\theta)$ is given by:

$$P(\theta) = \frac{2}{u^2}(u - 1 + e^{-u}) \tag{8.27}$$

$$u = \left[\frac{4\pi n_0}{\lambda}\sin\left(\frac{\theta}{2}\right)\right]^2 \langle R_g^2 \rangle \tag{8.28}$$

This allows us to bring in the radius of gyration as a measurable quantity! In the limit of very small $\theta$, we can simplify this equation to:

$$\frac{1}{P(\theta)} \approx 1 + \frac{u}{3} \tag{8.29}$$

Light Scattering Polymer Solution

3. account for $\Pi$ using Einstein-Smoluchowski

$$\langle \delta c^2 \rangle = \frac{RTc_2}{\delta V N_a \left(\frac{d\Pi}{dc_2}\right)}$$

$$\frac{d\Pi}{dc_2} = RT\left[\frac{1}{M} + 2A_2c_2 + \cdots\right]$$

$$\Delta R = Kc_2\left[\frac{1}{\frac{1}{M} + 2A_2c_2}\right]$$

Figure 8-10: Accounting for Polymer Scattering.

Putting this together with the equation for the difference in Rayleigh ratio yields (after slight rearrangement):

$$\boxed{\frac{Kc_2}{\Delta R} = \left[\frac{1}{M} + 2A_2c_2 + ...\right]\left[1 + \left(\frac{16\pi^2 n_0^2 \sin^2(\theta/2)}{3\lambda^2}\right)\langle R_g^2 \rangle\right]} \tag{8.30}$$

While this equation is quite complicated, it shows that we can relate the optical constant, excess Rayleigh ratio and concentration of the polymer solution, all of which are experimentally obtainable, to the second virial coefficient (related to $\chi$), radius of gyration of the polymer coils, and molecular weight of the sample (in reality a molecular weight average but we neglect that here), all of which are important properties we have used repeatedly.

## 8.5 Zimm Plots: Extracting Useful Data From Light Scattering

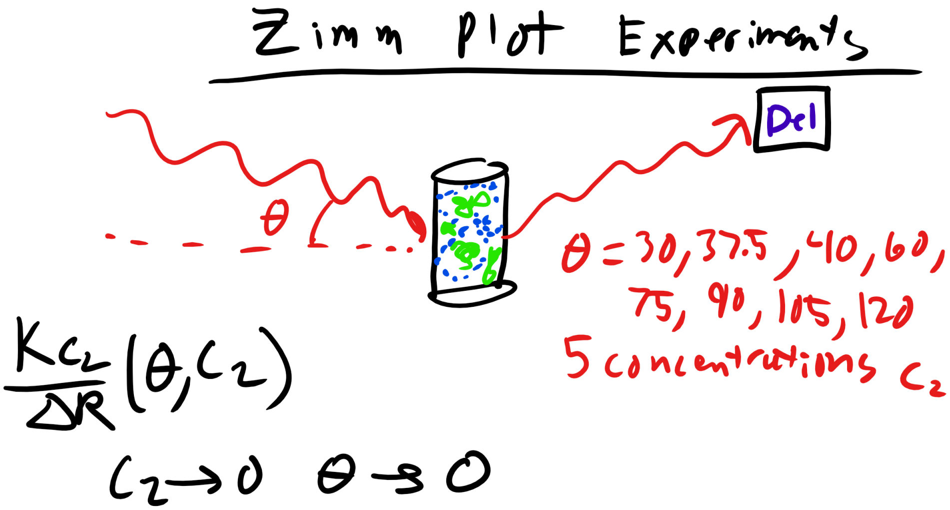


Figure 8-11: Zimm Plots Experimental Method.

The equation for the excess Rayleigh ratio is complicated, but it is possible to extract useful data from it using a *Zimm plot.* The basic idea behind a Zimm plot is to note that $\frac{Kc_2}{\Delta R}$ is a function of effectively two variables: the first term is a linear function of $c_2$ while the second term is a linear function of $\sin^2(\theta/2)$. If we separate out each of these variables by holding the other constant, we can thus derive the 3 useful parameters outlined above ($\chi$, $\langle R_g^2 \rangle$, and $M$). The procedure is to perform a double extrapolation: hold one variable (either $c_2$ or $\theta$) constant while calculating the other variable and extrapolating it to 0, then doing the same for the other variable.

More explicitly, we can see that extrapolating $\theta$ to 0 gives an equation for $c_2$ of:

$$\frac{Kc_2}{\Delta R} = \left[\frac{1}{M} + 2A_2c_2 + ...\right] \tag{8.31}$$

Graphing with respect to $c_2$ thus gives the second virial coefficient from the slope and $\frac{1}{M}$ from the intercept. Conversely, extrapolating $c_2$ to 0 gives:

$$\frac{Kc_2}{\Delta R} = \left[\frac{1}{M}\right]\left[1 + \left(\frac{16\pi^2 n_0^2 \sin^2(\theta/2)}{3\lambda^2}\right)\langle R_g^2\rangle\right] \tag{8.32}$$

Thus, graphing this expression with respect to $\sin^2(\theta/2)$ yields a line with a slope related to $\frac{\langle R_g^2\rangle}{M}$ and an intercept is related to $\frac{1}{M}$.

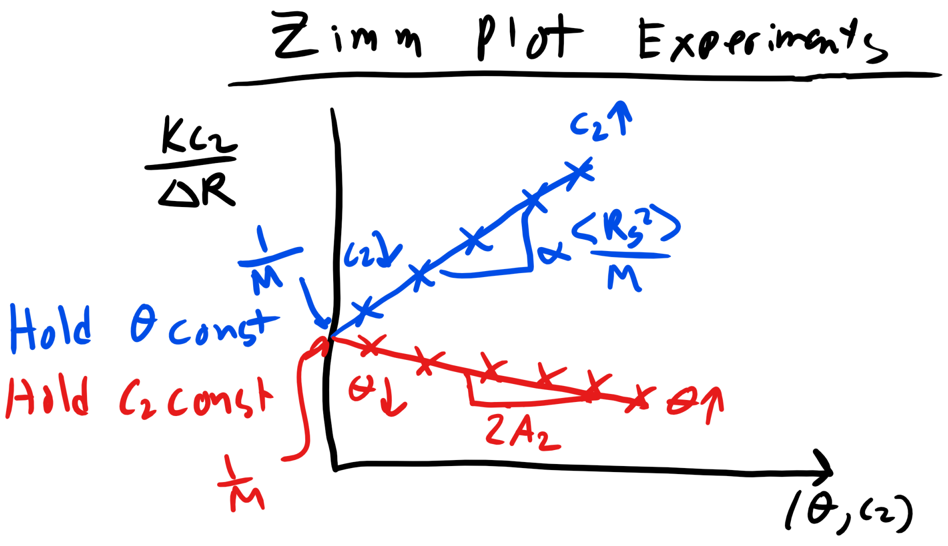


Figure 8-12: Analyzing Zimm Plots.

## 8.6 Light scattering

- **Key Ideas:** Shine light on polymer solution and observe intensity of scattered light. If there is difference in polarizability between polymer and solvent, can relate observed scattering intensity to concentration fluctuations of polymer, which in turn can be related to second virial coefficient due to osmotic pressure build up from fluctuations.

- **Key equations:** Master equation - $\frac{Kc_2}{\Delta R} = \left[\frac{1}{\overline{M}_W} + 2A_2c_2 + ...\right]\left[1 + \left(\frac{16\pi^2 n_0^2 \sin^2(\theta/2)}{3\lambda^2}\right)\langle R_g^2\rangle\right]$. $K$ is optical constant, $c_2$ is concentration of polymer, $\Delta R$ is difference in Rayleigh ratios between solution and solvent, $\overline{M}_W$ is weight-average molecular weight, $A_2$ is second virial coefficient, $n_0$ is index of refraction of background solvent, $\theta$ is angle at which scattering intensity is measured, $\lambda$ is wave length of incident radiation, $R_g$ is radius of gyration of polymer coil.

- **Key Experimental Method**: First measure scattering intensity (Rayleigh ratio) from pure solvent. Next, measure scattering intensity from polymer solution for various values of $\theta$ (with $c_2$ fixed) and $c_2$ (with $\theta$ fixed). Plot both curves on Zimm plot; perform double extrapolation to $\theta = 0$ and $c_2 = 0$ respectively. From new lines, can obtain slopes and intercepts to gain values of $1/\overline{M}_W$, $A_2$, and $R_g$.

- **Key Insights**: obtaining size of polymer coil based on radius of gyration, obtaining solvent information from second virial coefficient, and obtaining weight-average molecular weight of complete sample.

# Part II

# Polymer Self-Assembly, Glass Transition Temperature, and Semi-Crystalline and Amorphous Polymers

# CHAPTER 9

## SELF-ASSEMBLY OF BLOCK COPOLYMERS

## 9.1 Key Terms/Definitions:

- **Order-disorder transition (ODT)** - thermodynamic transition of the system between an ordered state and disordered state in terms of some thermodynamic variable. Order is generally defined via an order parameter, which we will not explicitly discuss in detail here.
- **Interfacial energy** - in ordered systems, the unfavorable interaction energy emerging from the formation of an interface between two separated regions.
- **Min-max principle** - The principle that ordered systems tend to minimize their interfacial energy and maximize their conformational entropy, leading to structures that obey these principles.
- **Intermaterial dividing surface (IMDS)** - the surface dividing microphase separated regions; specifically, the surface created by connecting all of the junction points in a phase-separated block copolymer system.

## 9.2 Self Assembly in Soft Matter: Spontaneous Self Organization

**Self-assembly** refers to the **spontaneous creation of order in a system from a previously disordered state**. Self-assembly is driven or induced by a **change in some environmental variable**. This is similar to lowering temperature of a material that is initially disorder at higher temperatures can induce a **order-disorder transition (ODT)** from a disordered to an ordered state. This is critically important for many systems, particularly magnetic materials. The key point is that self-assembly isn't driven externally by applied stimuli like stress but instead occurs spontaneously driven by the **thermodynamics of the system in response to some external change or stimuli**.

Self-assembly is particularly prevalent and important for soft matter systems. A particularly important example of soft matter **self-assembly occurs in proteins**, which have an unfolded state at high temperatures, consisting of a single polymer chain with only primary structure that then folds and becomes ordered at lower temperatures, leading to secondary/tertiary structure (i.e. formation of helices, beta sheets, etc). Here the **order-disorder transition is driven by the competition** between **favorable enthalpic interactions**, like as hydrogen bonds, in the folded state, versus **favorable entropic considerations** at **higher temperatures** in the unfolded state. Are you sick of entropy vs enthalpy, the answer is no because it is still exciting and interesting. Now although we will talk a lot about temperature being the ODT or self-assembly can also be triggered by **pH changes and other factors.**

Previously we've pretty much only discussed disordered states, like the melt or completely mixed phases, and we only discussed a single macrophase separation process in the context of Flory-Huggins theory where two components either mix or demix. We will now discuss **different ordering transitions**, and the different **morphologies that can exist in block co-polymer systems**. We are particularly interested in understanding the key concepts behind the process of self-assembly, will construct a simple formalism to **understand characteristic length scales** in **ordered copolymer microstructures**, and will identify **factors that enable us to tune the resulting morphology** of diblock copolymers in the ordered state. Finally, self-assembly can lead to structures that are much more complicated than just a demixed or phase-separated state, leading to the rise of **microphase separation**.

Self-assembly is driven by the competition between **enthalpy and entropy**. Several order-forming processes are governed by this competition - **macrosphase separation**, which is what we discussed in the context of Flory-Huggins theory, **microphase separation** (our focus), **mesophase separation**, which is similar to microphase separation but involves **separation over some larger length scale**, **adsorption/complexation**, which involves the interaction of molecules with surfaces and boundaries, and **crystallization**, which involves the creation of order upon cooling below the melting point. The final state of a system after ordering will depend highly on the c**hemical affinities of the different components** of the system and the **architecture of the different species** (e.g. star polymers in general will undergo different ordering processes than linear polymers). Finally, we will also have to consider the **interfacial tension** between any ordered phases that develop in the system, since in general a phase separation process will have some **unfavorable enthalpic interaction between the two distinct phases**. It is also important to consider **kinetic implications** of the self-assembly process, since many of these processes involve multiple energy minima which could lead to the formation of **metastable phases** that are not the desirable final state. These are all considerations that have to be taken into account in designing and studying self-assembled systems.

Soft material systems that undergo ordering processes are vast, and include but are not limited to

- **Liquid crystals** - anisotropic particles with some director vector
- **Polymers and block copolymers**
- **Proteins** via hydrogen bond complexes
- **Nanoparticles** - polymersomes or other particles formed from the assembly of polymers or other soft materials
- **Many other biological systems**
- **Active Matter Systems** (kind of but non-equilibrium so not really)

Structural order may vary across many length scales, from the a**tomistic level up to the level of grains** (100s of $\mu$m) in metallic systems. When thinking about the strategic design of ordered, self-assembled structures, there are a wide variety of factors that must be considered to engineer order at multiple length scales. We need to think about the **structure of our components, their interactions with each other, environmental constraints, the starting state of our system, any bias due to applied stresses, the influence of a substrate or other physical constraints involved in our ordering process, etc**. There is a immense design space for self-assembly that could have implications in some of the most important industries, for example computer chip design.

## 9.3 Microphase Separation in Diblock Copolymers

We are going to tackle the task of develop a **quantitative framework** to understand **microphase separation in diblock copolymers**. To understand microphase separation, we will invoke the so-called **min-max principle**. The **min-max principle** states that ordered polymer systems will want to do 2 things

1. **Minimize Interfacial Energy**-remember back to nucleation and growth i.e. the energy penalty to create surfaces
2. **Maximize conformational entropy of chains**-energetically favorable to increase entropy.

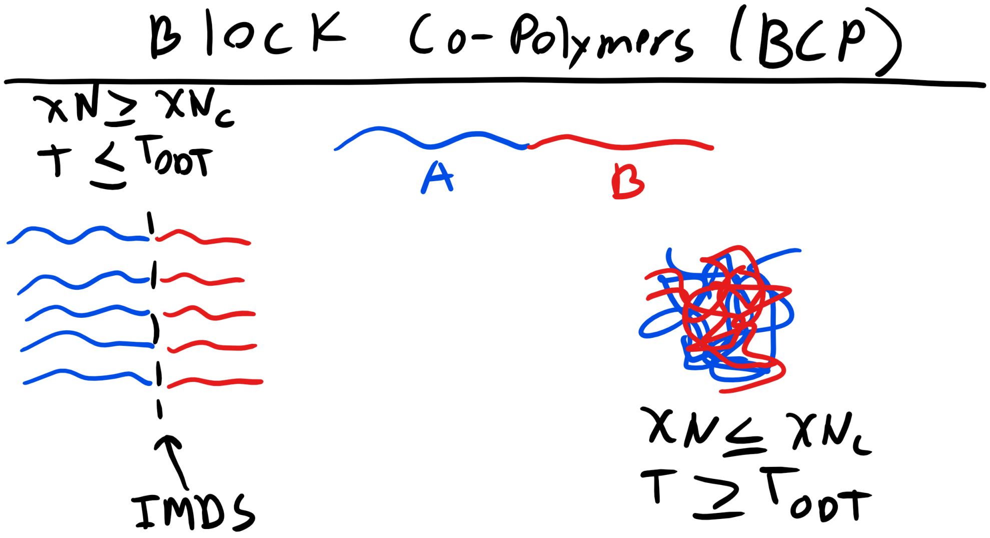


Figure 9-1: Block Co-Polymer Schematic.

Let's keep this general and say that we are working with a diblock copolymer with one block of type A and one block of type B. As we discussed in Flory-Huggins theory, in general **two different polymers will not prefer to mix**, and hence **A-B contacts will tend to be less enthalpicly**

**preferable than A-A or B-B contacts**. Above the **order-disorder temperature (ODT)**, we expect a **homogeneous, disordered mix of copolymers**, where the A and B blocks **freely interpenetrate to maximize conformational entropy of the chains** despite the **unfavorable A-B contacts**. Below the order-disorder temperature, the **copolymers will enter an ordered state such that all the blocks of type A will segregate away from the blocks of type B, maximizing the number of A-A and B-B contacts while minimizing unfavorable A-B contacts**.

Unlike in the case of polymer blends, however, there cannot be separation at the macroscale since the two blocks are **chemically joined**, enforcing a **length scale constraint on the segregation of the two types**. Hence, we establish ordered structures that depend on the **relative proportions of the two blocks**, and in general there will be a **significant interface** between A and B phases that leads to a **large number of unfavorable A-B interactions**. We call the dividing surface between the A phase and B phase the **intermaterial dividing surface**, (**IMDS**), where the IMDS can be thought of as the **surface created by connecting all junction points where A and B blocks are joined**. Since A and B blocks do not want to mix below the ODT, the interface defined by the IMDS wants to be **minimized** since there will be **unfavorable A-B interactions along the IMDS**. Note that in general there will be many IMDSs since the chemical linking of the diblocks limits the extent to which separation can occur this is in contrast to the case of homopolymers, where the amount of interface is effectively limited by the ability of polymers to move throughout the system without constraint. As we change the **relative fraction of blocks A and B we will see different microphase separation behavior ranging form spheres, cylinders, double gyroids, double diamonds, lamellae phases, etc**. The simplest case to study first is the **lamellae** so we will take this first.

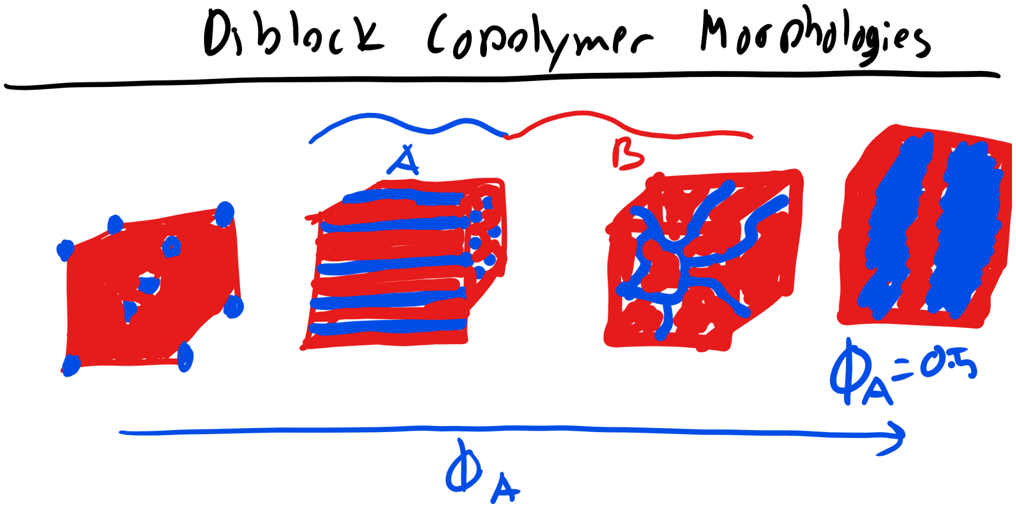


Figure 9-2: BCP Microdomains.

### 50:50 A:B Mixture: Lamellae Microphase Separation

Let's start with a quantitative model for a **flat IMDS** (corresponding to approximately a **50:50 mixture of A:B**), with type A on one side and type B on the other side of the IMDS. The structure thus looks like just a flat interface between **two phase-separated states**. We want to calculate the change in free energy associated with forming this type of structure, since if we find this free energy change to be negative we can expect the formation of the ordered state to be favorable. We must first start with some definitions

- $N$ = **num of segments** $= N_A + N_B$: i.e. total number of segments
- $a$ = **size of one segment**, with $a_a \approx a_b$. The volume of a segment is $\approx a^3$.
- $\lambda$ = **domain periodicity**, i.e. size of lamellae in this case but will be different for different morphologies
- $\sum$ = **Interfacial area per chain**. This can be thought of as the total area of the interface divided by the number of chains, which roughly corresponds to the area of unfavorable overlaps between type A and type B polymers. The interface and IMDS is the same here.
- $\gamma_{AB}$ = **interfacial energy** $= \frac{kT}{a^2}\sqrt{\frac{\chi_{AB}}{6}}$ - note that this calculation to find this scaling is a bit involved, so just take it as fact and put your trust in me or if you are very motivated you can find the derivation in a book by Fredrickson.

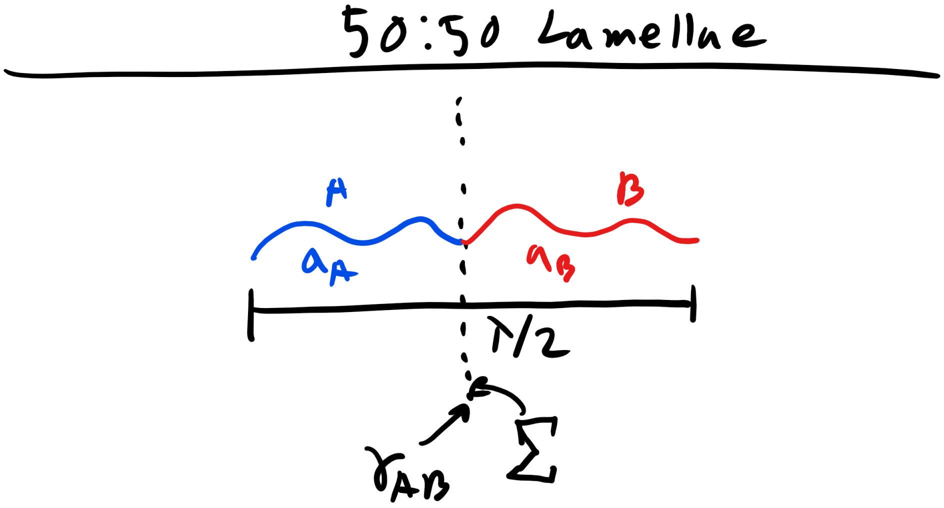


Figure 9-3: 50:50 Schematic.

We will assume we are in the **strong segregation limit**, meaning that the two blocks really do not want to associate, i.e. $\chi_{AB}N$ **is very large and positive**, so that both $\chi_{AB} > 0$ and $N$ is large. In this limit, **there isn't enough entropic drive force to mix and there is a strong**

**enthalpic drive to segregate**. Note that because of this limit, we assume that the ONLY type of phase-separation possible is where **ALL type A goes to one phase and all of type B goes to another**. Practically, this means that looking at the **change in free energy is sufficient to determine ordering**, and we **do not need to look at the chemical potentials of type A/B** in either phase like we previously did with Flory Huggins.

**Qualitative Understanding of Microphase Separation:**

To do this let's think about the free energy components present in this system. Well we know that we have a high positive value of $\chi$ between type A and type B, there is an **unfavorable contribution** to the **enthalpy** due to **interactions along the interface**. Thus the chains want to **minimize their interfacial area** as this scales with the number of A-B contacts. In order to do so, the **chains will thus want to elongate away from the interface**, and effectively **increase their length** to decrease their **projected area onto the IMDS**. What is the penalty in doing so? Remember that we have talked at length the consequences of elongating polymer chains right. To do this we have to pay an **entropy penalty** due to a **decrease in the conformational entropy**. Thus, we can see that **equilibrium** is determined by a **competition** between an **enthalpic desire to minimize interfacial area** and an e**ntropic desire to maximize chain conformations/minimize stretching**.

**Quantitative Understanding of Microphase Separation:**

Now let's calculate the change in free energy. We can start with the disordered state approximated from Flory-Huggins theory:

$$H_D = N\chi_{AB}\phi_A\phi_B kT \tag{9.1}$$

Notice that **we've omitted the entropy of mixing because in general it will be a relatively small contribution**.

This is because we have stated in this case that $N$ **is large** and in Flory Huggins we saw that the **mixing entropy of large polymers is small**. Additionally it will not play a huge factor because we really have a **single component system since the A and B blocks are not truly separate components since they are chemically linked**. This observation helps justify our assumption of strong segregation since the entropy of mixing will in general be much smaller than in macrophase separated mixtures.

In the ordered state, the enthalpy of AA and BB interactions do not contribute as $\chi_{AA} = \chi_{BB} = 0$. Thus **we only care about the interfacial energy**, which is given by the interfacial energy per area times the interfacial area per chain, or $\gamma_{AB}\sum$.

$$\Delta H_O = \gamma_{AB}\sum \tag{9.2}$$

We also need to account for the **conformational entropy of the chains**, which will tend to stretch out in order to minimize the interfacial energy and instead maximize same-block contacts. Luckily we already have this expression remembering back to previous lectures

$$S(r)_{stretching} = -\frac{3k}{2}\frac{r^2}{r_0^2} \tag{9.3}$$

$$\Delta S_{stretching} = S_O - S_D = -\frac{3}{2}k\left[\frac{r^2}{r_0^2} - 1\right] \tag{9.4}$$

Note that the change in stretching free energy is relative to an unstretched state where $r^2 = r_0^2$ which is why we subtract 1. In the case for lamellae, the domain spacing is directly related to the stretching of these coils - specifically, the domain spacing $\lambda/2$ is equal to the total stretched length of both the A and B blocks, so that the total stretched length of any single chain is given by $\lambda/2$. The undeformed length is $Na^2$ from typical chain dimensions. We can thus replace $r^2$ in the entropy expression with $(\lambda/2)^2$ and $r_0^2$ with $Na^2$, and note that in the initial state $r = r_0$ so the entropy is just $-\frac{3k_bT}{2}$. We can thus finally compute the total change in free energy

$$\Delta G = \Delta H - T\Delta S \tag{9.5}$$

$$\Delta G = H_O - H_D - T(S_O - S_D) \tag{9.6}$$

$$\Delta G = \gamma_{AB}\sum -N\chi_{AB}\phi_A\phi_B kT + \frac{3}{2}kT\left[\frac{(\lambda/2)^2}{Na^2} - 1\right] \tag{9.7}$$

The incompressible assumption allows us to write the volume conservation condition as

$$Na^3 = \frac{\lambda}{2}\sum \tag{9.8}$$

where the left term is simply the volume of a segment times the number of segments, while the second term is the size of the resulting domain times the interfacial area, both of which are equivalent when the chain is stretched in the final state. Substituting in this relation and the relation for $\gamma_{AB}$ given above allows us to eliminate $\gamma_{AB}\sum$

$$\Delta G = \frac{kT}{a^2}\sqrt{\frac{\chi_{AB}}{6}}\frac{Na^3}{(\lambda/2)} - N\chi_{AB}\phi_A\phi_B kT + \frac{3}{2}kT\left[\frac{(\lambda/2)^2}{Na^2} - 1\right] \tag{9.9}$$

From this expression, we can find the optimum period of the lamellae repeat unit, $\lambda$, by minimizing the free energy change with respect to $\lambda$.

$$\frac{\partial \Delta G}{\partial \lambda} = 0 \tag{9.10}$$

$$\lambda_{optimal} \approx aN^{2/3}\chi_{AB}^{1/6} \tag{9.11}$$

We can see the dimensions of the lamellae scale as $\lambda \propto N^{2/3}$. It scales with a much larger exponent than expected in either the theta condition ($r \approx N^{1/2}$) or in good solvent ($r \approx N^{3/5}$). Hence, **the chains are very extended** when compared to the melt state.

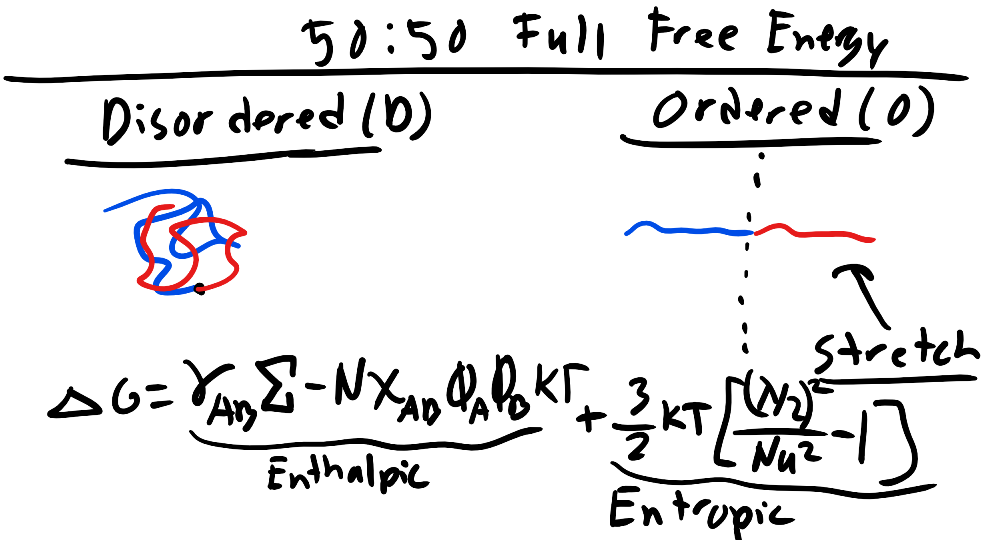


Figure 9-4: 50:50 Full Free Energy.

**Critical $\chi$ Parameter for Phase Separation:** $N\chi_{AB}$

We have established the domain spacing dependence on molecular weight **if** we are in the phase-separated state; however, we have not actually determined **when** phase separation occurs. We can find the critical $\chi_{AB}$ parameter for the order-disorder transition by finding when

$$\Delta G(\lambda_{optimal}) = 0 \tag{9.12}$$

All we have to do is substitute in the optimal value of $\lambda$ which will yield the most negative possible free energy change; if this is less than 0 ordering should occur. Simplifying the expression above for $\Delta G$ and substituting the expression for $\lambda_{opt}$ gives us

$$1.2kTN^{1/3}\chi_{AB}^{1/3} \approx N\chi_{AB}\phi_A\phi_B kT \tag{9.13}$$

where we ignore a factor of $3/2kT$. Again this is small and we care about scaling in this class not prefactors. Solving for $N\chi_{AB}$ for a 50/50 volume fraction thus gives a critical value of 10.5

$$N\chi_{AB} < 10.5 \text{ - } \textbf{Homogeneous, mixed melt} \tag{9.14}$$

$$N\chi_{AB} > 10.5 \text{ - } \textbf{Lamellar, microdomains} \tag{9.15}$$

Take a moment to appreciate that this is a **much greater critical value than we derived for the macrophase separation of polymer blends** ($N\chi \approx 2$)! The major difference here is that **stretching** is required for microphase separation, while in the case of macrophase separation we assumed that chains were ideal and did not stretch. As a result, we need to decrease the temperature **way more** in the case of diblocks to overcome this additional entropy term opposing phase-separation, which is much greater than the mixing entropy present in the macrophase case. Again remember that decreasing temperature is equivalent to raising $\chi N$ so this agrees with our quantitative analysis.

We have seen that there are many more microphases than can occur than just lamellar spacing, but in general the same basic quantitative formalism should apply, i.e. minimizing interfacial area and maximizing conformational entropy.

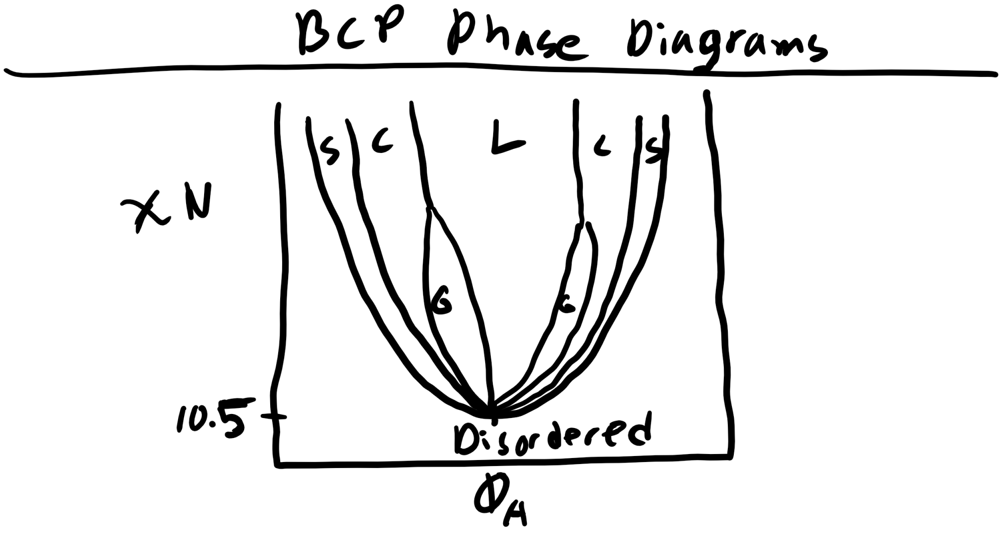


Figure 9-5: BCP Phase Diagram.

**Self-Assembly Isn't Perfect: Defects and Experimental Techniques to Deal with Them**

Now unfortunately for many applications like ligthographic masks, computer chips, optimal and electronic materials, batteries, etc. this self-assembly ordering transition is not perfect and long-ranged. In real systems perfect ordering over long range does not exist due to the presence of defects in the system, just like in we discussed in the Defect lecture in ENGR045. Moreover, block copolymers tend to have the easy onset of defects since there is only a minimal cost for forming them given the relatively low cost of forming interfaces, and as a result we typically see grain boundaries in BCP ordered phases. The origin of these grain boundaries comes from the growth of ordered phases in multiple parts of a sample at once that may not necessarily orient in the same direction, leading to defects when the different ordered regions grow and will eventually impinge upon each other. However hope isn't lost. To minimize and avoid the creation of defects we have some tools at our disposal to bias the growth of ordered phases in a particular direction. Some of these strategies include:

- **Applying bias field** - this involves using some sort of external biasing field, such as applied stress in some direction, an applied electric field, etc., to reduce the energy barrier for growth in some preferred direction.

- **Substrate patterning** - this involves functionalizing the growth substrate with regions of specific chemistry that guide the growth.

- **Substrate constraints** - using physical barriers, such as walls or trenches in the substrate, as guides to growth of ordered phases. To avoid defects it's also important to ensure that the length scale of any physical constraint is compatible with the length scale of the growing BCP - that is, if the growing BCP hits a wall it should make contact at the boundary between phases in order to avoid compression or other effects that may induce defects.

These strategies all fall under the broad classification of applying a biasing field. One of experimental techniques at our disposal to apply a biasing field is via **graphoepitaxy.**

**Graphoepitaxy**

**Epitaxy** refers to the process of patterning some substrate via some lithographic technique. Generally, this pattern will be some chemical monolayer that has regions that interacts preferentially with one of the two blocks in a growing BCP structure. Putting a BCP mixture on this surface in a proportion that would normally form lamellae then would form new morphologies due to the preference for matching the pattern of the chemically modified surface. This process is called surface reconstruction and allows for the fine-tuned control of ordered BCP morphologies with minimal defect formation.

Growing a BCP phase under an **applied stress** can also lead to an anisotropic growth process, as well as providing a means of actually identifying a phase transition since the response to that stress should change dramatically when a transition occurs. The preferred direction of the stress will lead to microstructural growth in a specific direction by biasing the direction of diffusion and thermodynamially decreasing the equilibrium free energy when phases are preferentially aligned with the applied stress. This allows us to create morphologies that are well-aligned, avoiding defects due to the overlap of unaligned domains. The **major issue** with applying a stress versus epitaxy is that stress is typically applied on the macroscale and does not give the nanoscale control that epitaxy does.

A new technique, used heavily by Ross group at MIT and many many others, which combines both chemical and physical constraints is **graphoepitaxy**. This technique consists of coating a surface with both specific chemistries AND some topographical constraints, i.e. roughness, posts, channels, etc. The combination of these two constraints forces the growing microphase to be **commensurate** with the length scale of the physical constraints while also inducing anisotropy from preferential interactions with the chemistries present on the surface. One example is the creation of an array of ordered posts coated with a polymer that mixes preferentially with one of the two BCP blocks. When a BCP blend is added to the array of posts, microphase separation will occur with a long range order imposed by the posts since polymer can only grow in between them. Because the posts are coated with polymer, only one of the two species can interact with them, so the posts serve as **nucleation sites** for an ordered phase, which then sets the length scale for growing additional microphases between the posts. Thus, if the posts are spaced according to the

**same length scale** that would occur if the BCP mixture separated **without** posts, then perfect ordering can be achieved! If the spacing is wrong, however, then there will be some strain energy that may lead to **defect formation**.

Graphoepitaxy also allows complex morphologies - e.g. aligning cylinders, very useful for nanowires. You can basically just change the spacing of posts to orient different cylindrical phases. A problem with this, however, is that there are some rotational directions that are exactly equivalent when assembly cylindrical phases, and there will thus be defects when these different rotationally identical directions overlap. To overcome this, you can elongate posts in one direction to increase surface energy, biasing toward one direction over another. To conclude, the basic idea is use some topology to impose order on the system, inducing the same type of ordering in the resulting BCP matrix, but with some preferential growth direction(s) to ensure perfect order!

## 9.4 BCP-Homopolymer Blends:

## 9.5 Key Definitions/Terms:

- **Micelle** - a spherical aggregate of diblocks (or other two-component molecules) which forms to segregate one component in a **core region** and the second component in a **corona region**. The **corona region** is exposed to **surrounding solvent** (or homopolymer) and thus forms to **"shield" the core from unfavorable interactions with the surrounding solvent**.
- **Critical micelle concentration (CMC)** - the **concentration of diblocks at which micelles first form**; below this, the mixing entropy of the diblocks dominates and prevents aggregation. However, since diblocks tend to be large and thus have minimal mixing entropy, the **CMC tends to occur for small concentrations**.

So far we have been talking about block copolymers alone in solution, but we can also introduce additional phase behavior by **mixing in homopolymer (of one of the two types present in the BCB i.e. A or B) with the BCPs**. In this situation the h**omopolymer should preferentially mix with the corresponding block in the BCP**, assuming that the chemical structure of the homopolymer is identical to the homopolymer of the block and hence their $\chi$ **parameter is roughly 0**. If this the case we will see some new phase behavior which includes the formation of **micelles.**

**Micelle Formation:**

A **micelle** is a a spherical assembly of molecules that have **one region that prefers to mix with solvent** and **one region that tends to avoid mixing with solvent**, leading to the formation of an inner **core** region shielded from solvent and an outer **corona** region that maximizes solvent exposure. On extremely important system that exhibits micelle formation is a **collection lipids**, which have a **hydrophilic head region** and **hydrophobic tail region (amphilic)**.

At very low lipid concentrations, the translational entropy of the lipid mixture tends to be very high and any ordering transition is unfavorable due to the high entropic cost. At a **specific critical**

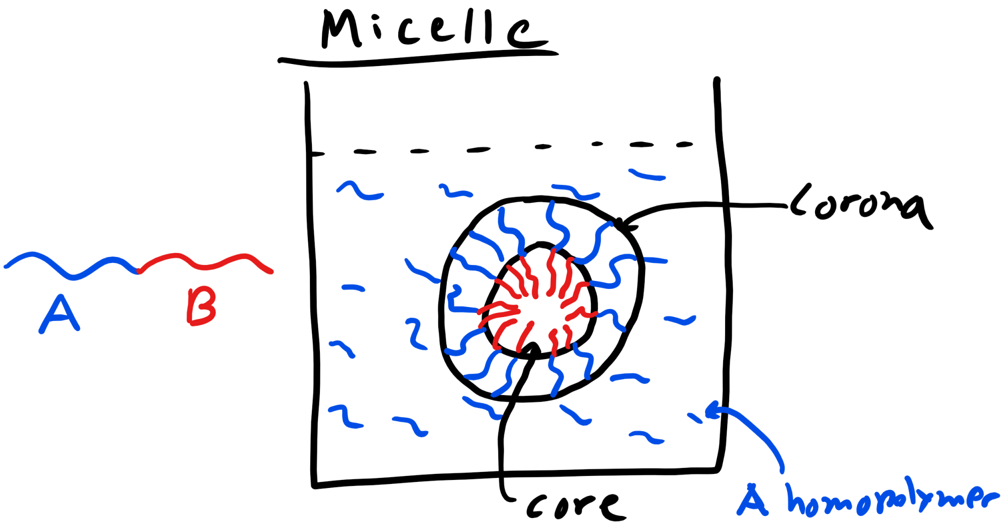


Figure 9-6: Micelle Schematic.

**concentration**, the **cricitical micelle concentration (CMC)**, **ordering is favored in order to reduce the number of unfavorable water-tail contacts**, leading to the **formation of micelles with lipid heads facing outward to mix with water and hydrophobic tails forming an oil-like inner core**. This morphology thus minimizes unfavorable hydrophobic interactions. At even higher concentrations of lipid, more ordered phases can form, including cylinders, bilayers, inverse micelles, etc. You can also add a third component that mixes well with lipid tails (some other hydrophobic component like oil) to yield an even more complicated ternary phase diagram.

In analogy to the small molecule lipid-water system, we can also think of the same ordering process in diblock copolymer - homopolymer mixtures, where we assume the homopolymer mixes perfectly with one of the two blocks (akin to water mixing well with the hydrophilic heads). In this system the **homopolymer is thus the solvent** and the **diblock is the solute**. In a very dilute system, the diblocks will tend to assume a disordered, homogeneous phase, identical to lipids. At the **CMC** the polymers will start interacting, **leading to aggregation of the block that has an unfavorable enthalpic interaction with the surrounding homopolymer medium**. As we increase the concentration of diblock even more, existing **micelles will begin to order with each other to minimize the total amount of unfavorable interfacial interactions with solvent**. Recall that since the diblock alone will tend to microphase separate as the amount of diblock gets larger and larger we will see phases appear that are similar to phases exhibited by block copolymer alone.

We can now use a very simple formalism to understand the concentration at which micelle formation is preferred. As always, here again the **major competition is between enthalpy and entropy**. Forming micelles **costs entropy due to the ordering of diblocks**, but **saves in enthalpy by minimizing unfavorable interactions between the A and B block**, in this case by **sequestering B blocks in the core of the micelle**. Hence the only enthalpic term is the interfacial energy, and the driving force for micelle formation is enthalpic in nature. However, compared to the case of diblocks alone, we must now also consider the influence of the free homopolymer in the system.

**Determining Critical Micelle Concentration:**

We will now develop a model to predict when micelle formation is preferred. We draw upon a lot of the same ideas that we already used to discuss microphase separation but now have to include the influence of the homopolymer component.

Let's start by identifying variables in the system. Just like previously we will have a diblock copolymer consisting of an A block with degree of polymerization $N_A$ and a B block with degree of polymerization $N_B$. The total degree of polymerization is thus $N = N_A + N_B$, and in this example we assume $N_A = N_B = N/2$ for simplicity. We characterize the enthalpic interactions between the two blocks with the Flory-Huggins parameter $\chi_{AB}$, which we assume to be greater than 0 and positive. We also assume to have a homopolymer with degree of polymerization equal to $N$, and also of type A, where $\chi_{AA} = 0$.

**Now what are the initial and final states of the system?**

Initially we have a disordered mixture of copolymer and homopolymer which we can characterize with Flory-Huggins theory in the same way as in the case of diblocks alone.

The final state of micelle formation will occur at some certain diblock volume fraction $\phi_{CMC}$. At this concentration we would expect the **spontaneous formation of a micelle with core radius $R_C$, composed of B type blocks, and corona radius $L_C$, composed of A type blocks since the solvent is homopolymer of type A**. One difference in this case is that we are comparing two systems in which the **number of total molecules** is **not** fixed. This is because the micelle will not occupy all of the block copolymer in the solution in order to reach equilibrium. The condition for equilibrium is that the **chemical potential of diblocks in the disordered state and the micelle state must be equal** - that is, the change in free energy for moving a single diblock from the micelle to disordered solution is 0. Therefore, we want to **calculate the chemical potential of both the micelle and disordered state and set them equal to each other**. For simplicity, we will set the chemical potential equal to the change **in free energy per diblock** (i.e. $\partial G/\partial n \approx \Delta G/\Delta n$).

## 9.6 Free Energy of Disordered DB Solute and Homopolymer Solvent

## 9.7 Free Energy of Disordered State:

We previously described the free energy of the disordered state of diblocks using Flory-Huggins theory and we can do the same here to describe the free energy of mixing (same equation we had way back in Flory-Huggins)

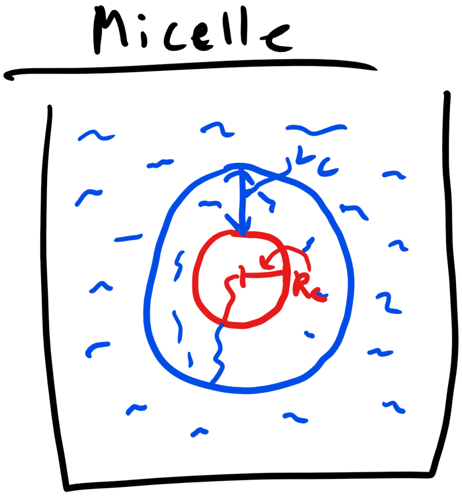


Figure 9-7: Micelle Core and Corona Schematic.

$$\frac{\Delta G_{mix}}{N_0} = kT[\chi\Phi_1\Phi_2 + \frac{\Phi_1}{x_1}\ln\Phi_1 + \frac{\Phi_2}{x_2}\ln\Phi_2] \tag{9.16}$$

Now we need to make a quick notation change since now we are working with BCPs. Here $x_1 = N_A$ and $x_2 = N_B$. Since both of these degrees of polymerization are large for polymers, $\Phi_1/x_1$ and $\Phi_2/x_2$ are very small and we can safely ignore the two mixing terms and concentrate only on the enthalpic term. We also wrote $N_0$ as the total number of lattice sites in the imaginary lattice - in this case, if we instead let $N_0 = N$, **where N is the length of a single diblock in our current formalism**, the expression instead gives the free energy change for **a SINGLE molecule**. Multiplying through thus gives us the **free energy change per polymer** (approx. equal to the chemical potential)

$$\Delta G_{dis} \approx NkT\chi\Phi_A\Phi_B \tag{9.17}$$

where we have now switched notation to the volume fractions of the two types, A and B.

Now, we have to put the **two volume fractions of type A and B into terms of the volume fraction of diblock vs. homopolymer**, since the volume fraction of diblock includes both A and B components but the homopolymer only has type A. We can thus write

$$\phi_A = \phi_A^{homo} + \phi_A^{diblock} \tag{9.18}$$
$$\phi_B = \phi_B^{diblock} \tag{9.19}$$

If we let $\phi = \phi^{diblock}$, then from the condition that $N_A = N_B = N/2$ we can say that

$$\phi_A = (1-\phi) + \phi/2 \tag{9.20}$$

$$\phi_B = \phi/2 \tag{9.21}$$

$$\Delta G_{dis} \quad \approx NkT\chi(1-\phi/2)(\phi/2) \tag{9.22}$$

As a final approximation, we can assume that the volume fraction of the diblock solute is much smaller than that of the homopolymer solvent - that is, $\phi << 1$. hence, we expect that $1 - \phi/2 \approx 1$ and simplify to

$$\Delta G_{dis} \approx \frac{NkT\chi\phi}{2} \tag{9.23}$$

This is our final expression for the free energy **PER POLYMER** in the disordered state.

## 9.8 Free Energy of the Micelle State:

Now we have to calculate the free energy per polymer in the micelle state. Here like there will be three contributions

1. **Energy penalty due to stretching** - stretching blocks in the corona and core of the micelle leads to entropic spring restoring force
2. **Favorable increase in entropy due to mixing**- gain in mixing entropy from mixing homopolymer with blocks in the corona
3. **Energy penalty due to creating interface (IMDS)** - the cost in forming an interface between the unfavorable A and B blocks

$$\Delta G_{micelle} = \Delta G_{stretch} + \Delta G_{mix} + \Delta G_{interface} \tag{9.24}$$

**Stretching Free Energy:**

The **stretching free energy** is something that we have derived previously and we used it in the diblock case as $\Delta G \approx T\Delta S \approx \frac{3kT}{2}\frac{r^2}{r_0^2}$. Here, we recall that in our previous derivation we assume no enthalpy change upon stretching chains, and hence the free energy change is proportional to the final end-to-end distance of the chain squared over the initial squared end to end distance. **In the case of the micelle, we assume the most general possible case - that both the blocks in the corona and core are capable of stretching or compressing**, and that they assume a final length of $R_C$ and $L_C$ respectively. Because it is unclear whether they are elongated or compressed in the free energy minimized state, w**e will leave all 4 terms in the free energy expression**

$$\Delta G_{stretch} \approx \frac{3kT}{2}\left[\frac{R_C^2}{(N/2)b^2} + \frac{L_C^2}{(N/2)b^2} + \frac{(N/2)b^2}{R_C^2} + \frac{(N/2)b^2}{L_C^2} - 4\right] \tag{9.25}$$

Here, the **first two terms correspond to elongation**, where the initial state is given by the unperturbed end-to-end distance of the chain in the core/corona respectively (where $b$ is the monomer size corresponding to the Physicist's Chain model). The **second two terms correspond to compression of the same two regions**. Also note that we have **set unperturbed lengths based on each block having a number of monomers equal** to $N/2$. In principle, we would find at equilibrium that for the core and corona only one of the two terms (i.e. compression or elongation) would apply, respectively, but without performing a full free energy minimization it is unclear whether stretching or compression is preferred. Finally, note that this term is already written **PER POLYMER** since there is no prefactor reflecting the number of polymers in the micelle.

**Mixing Free Energy:**

Next, we can consider the **mixing free energy**. Recall that the species being mixed are type A homopolymer in the type A corona, so no enthalpic term should be present since all enthalpic interactions are 0. The only term then is a **mixing entropy**, but again this is only between really a single component. Given this, let's look at our old Flory Huggins Mixing term

$$\frac{\Delta G_{mix}}{N_0} = kT[\chi\Phi_1\Phi_2 + \frac{\Phi_1}{x_1}\ln\Phi_1 + \frac{\Phi_2}{x_2}\ln\Phi_2] \tag{9.26}$$

But now we can ignore the enthalpy term completely since $\chi_{AA} = 0$. Also here there is only one component so we can ignore the second mixing term. This leaves a single mixing term, which we can write as $\frac{\phi_H}{N_H}\ln\phi_H$, where $\phi_H$ is the volume fraction of homopolymer, which is the same as $1-\phi$ (recall that $\phi$ is the volume fraction of diblock). Similarly, $N_H = N$ is the degree of polymerization of the homopolymer. Since the free energy is divided by $N_0$, which in Flory-Huggins theory is the number of lattice sites and hence an effective volume, we can make this a free energy **PER POLYMER** by **dividing by the density of polymers in the corona**. The density is approximated as the number of polymers in the micelle, $n_M$, divided by the total volume of the corona, $\left((R_C+L_C)^3 - R_C^3\right)$, or the volume of the sphere surrounding corona + core minus the volume of the core. We can now write the free energy change as

$$\Delta G_{mix} \approx \frac{kT}{n_M}\left((R_C+L_C)^3 - R_C^3\right)\frac{\phi_H}{N_H}\ln\phi_H \tag{9.27}$$

**Free Energy of Interface:**

The final free energy change is the **interfacial energy**, which we can derive directly from our treatment of microphase separation and the IMDS. We previously had that the interfacial energy per unit area, $\gamma_{AB}$, is given by

$$\gamma_{AB} = \frac{kT}{b^2}\sqrt{\frac{\chi_{AB}}{6}} \tag{9.28}$$

We then wrote that the the free energy change was a simple function of the interfacial area per chain, $\Sigma$ and $\gamma_{AB}$. The **only distinction now is that the interfacial area per chain is**

**different, and given from the surface area of the spherical core (because the unfavorable interface is between the core of type B and the corona of type A) rather than the area of a flat interface**. This area is

$$\Sigma = \frac{4\pi R_C^2}{n_M} \tag{9.29}$$

where again we have divided by $n_M$, the number of polymer chains in the micelle, to put this as the **interfacial area per chain**. Hence, we can write the total interfacial energy **PER POLYMER** as:

$$\Delta G_{interface} \approx \frac{kT}{b^2}\sqrt{\frac{\chi_{AB}}{6}}\frac{4\pi R_C^2}{n_M} \tag{9.30}$$

## 9.9 Final Total Free Energy:

Now the **final total free energy change in the micelle state PER POLYMER is**

$$\Delta G_{micelle} = \Delta G_{stretch} + \Delta G_{mix} + \Delta G_{interface} \tag{9.31}$$

$$\Delta G_{stretch} \approx \frac{3kT}{2}\left[\frac{R_C^2}{(N/2)b^2} + \frac{L_C^2}{(N/2)b^2} + \frac{(N/2)b^2}{R_C^2} + \frac{(N/2)b^2}{L_C^2} - 4\right] \tag{9.32}$$

$$\Delta G_{mix} \approx \frac{kT}{n_M}\left((R_C + L_C)^3 - R_C^3\right)\frac{\phi_H}{N_H}ln\phi_H \tag{9.33}$$

$$\Delta G_{interface} \approx \frac{kT}{b^2}\sqrt{\frac{\chi_{AB}}{6}}\frac{4\pi R_C^2}{n_M} \tag{9.34}$$

**Simplify Total Free Energy Change in Micelle State:**

The free energy per polymer chain expression for the micelle is very messy, so we can use a variety of simple approximations to reduce the expression considerably.

1. **Assume diblock chains are ideal even in the micelle state-** both blocks in the core and corona are in their unperturbed state. This is a significant assumption but we know that in the bulk this is true for polymers so that will give $\Delta G_{stretch} = 0$

2. $\Delta G_{mix} = 0$ - Because degree of polymerization $N$ is very large and since degree of polymerization of homopolymer is also $N$ the mixing term is close to 0 so $\Delta G_{mix} = 0$. This should make sense as large homopolymers will have trouble penetrating the corona.

With these two assumptions, we have thus shown that the **change in interfacial free energy is the dominant term**, and is the term that **drives aggregation of diblocks into micelles**. We can further simplify this term by assuming an **incompressibility condition** - that is, the volume occupied by chains in the solution is equivalent to the volume occupied in the micelle. We can thus solve for $n_M$ by assuming that the average volume of a B block is given as the number of monomers in a B block, $N/2$, times the average volume of a B type monomer, $b^3$. The total volume occupied by the chains in the core is then

$$n_M \frac{N}{2} b^3 = \frac{4\pi}{3} R_C^3 \tag{9.35}$$

where the right term is the volume of the core in terms of our variable $R_C$. Using this relation to simplify the interfacial energy gives

$$\Delta G_{interface} = \frac{3kT}{2} \sqrt{\frac{\chi_{AB}}{6}} \frac{Nb}{R_C} \tag{9.36}$$

we have eliminated some constants on the order of 1 here. We can make one final simplification by again relating $R_C$ to the unperturbed length of a B block, invoking the same assumption that the chains are in their ideal state. This gives $R_C \approx N^{1/2} b$, and gives a final expression of

$$\Delta G_{interface} = \frac{3kT}{2} \sqrt{\frac{\chi_{AB}}{6}} N^{1/2} \tag{9.37}$$

So we have the **free energy change per chain in the disordered state** as

$$\Delta G_{dis} \approx \frac{NkT\chi\phi}{2} \tag{9.38}$$

The free energy change per chain in the micelle state is given by

$$\begin{aligned} \Delta G_{micelle} &= \Delta G_{stretch} + \Delta G_{mix} + \Delta G_{interface} && (9.39) \\ &\approx \Delta G_{interface} && (9.40) \\ &\approx \frac{3kT}{2} \sqrt{\frac{\chi}{6}} N^{1/2} && (9.41) \end{aligned}$$

So the **critical micelle concentration (CMC)** will be defined as the concentration (or the volume fraction) for which these two chemical potentials are equivalent which is

$$\begin{aligned} \frac{NkT\chi\phi_{CMC}}{2} &= \frac{3kT}{2} \sqrt{\frac{\chi}{6}} N^{1/2} && (9.42) \\ \phi_{CMC} &\approx \frac{1}{\sqrt{\chi N}} && (9.43) \end{aligned}$$

Hence we find via our simple model that the **critical micelle concentration varies inversely with the square root of** $\chi N$, the same parameters ($\chi$ and $N$) we used to describe the phase behavior of both polymer blends and diblock copolymers, so it would make sense that a blend of diblocks with homopolymer would depend on the same parameters. Also we see that **this result makes qualitative sense** - if $\chi N$ is **high, the critical concentration is low** - that is, **as the strength (and number) of unfavorable enthalpic interactions gets higher, it requires**

**less diblock to initiate aggregation into micelles**. This makes sense since the micelle phase minimizes unfavorable enthalpic interactions by clustering together same-type blocks. Finally, note that in the model we employ here, we have effectively ignored the thermodynamic contribution of the homopolymer by ignoring the mixing entropy in the corona - as a result, we see that the **role of the homopolymer is strictly to modify the volume fractions of the two components A and B in the system**; we might expect that this model is also then suitable for describing diblocks with compositional asymmetry.

**Experimentally Observing the CMC**

To determine experimentally when the CMC is reached, micelles can be observed visually via TEM measurements, where the number of micelles per $nm^2$ can be observed. At some point this goes to 0 - this indicates the onset of the critical micelle composition. It's also possible to look at the fraction of free copolymer as a function of total copolymer fraction - at the CMC, micelles will begin to form and the concentration of free diblocks will begin to be used up in micelles, and hence the concentration of FREE copolymer stays constant above the CMC while the total amount of diblocks increases. Changing $N$ as you graph this relation also shows how the onset of the CMC changes.

If you increase the amount of copolymer above the CMC, at some point there will be a large number of micelles in solution that are capable of interacting with each other to generate additional order. At high concentrations, ordered spheres and cylinders can be observed, as these morphologies can again be thought of as minimizing unfavorable interfacial energy interactions. Additional morphologies are also available - as in the case of just diblock copolymers, we again see a wide range of morphologies when mixing diblocks with homopolymers.

**Strategies to Create More Complex Polymer Morphologies:**

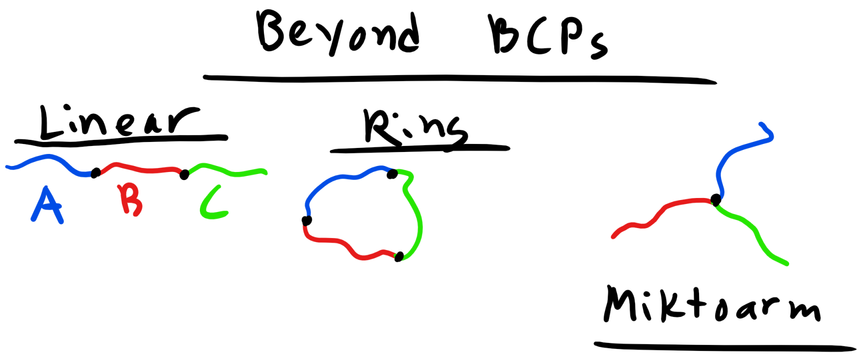


Figure 9-8: Triblock Copolymers.

- **Manipulate the IMDS:** The IMDS will always form to minimize surface area and maximize conformation entropy/polymer deformation or stretching. So we can change the shape of the IMDS by blending polymers or adding assymetric BCP that may have branches or loops.

- **Designer BCPs:** Similar to the last point but you can change the structure of the copolymer to add branches or loops purposefully for applications i.e. use monomers that don't coil but act as rods (very inflexible backbones) to create nanowires. Or disk polymers like graphene. These monomers will have lots of pi-pi bonds which will lead to strong packing and intermolecular interactions between monomers and can lead to interesting electrical/optical behavior

- **Utilize triblock copolymers:** Using polymers that contain 3 different blocks that can have different architectures (linear, ring, or miktoarm, similar to star polymers). By simply adding this 3rd block and assuming all 3 are incompatible there are 64 different morphologies that can be achieved depending on relative volume fractions. You migh also see ordered structures at the interface of two other blocks, like cylinders at the interfaces of lamellae, which occurs in a very similar manner to a heterogeneous nucleation process (formation of one ordered phase lowers interfacial energy between two other phases and forms at the interface)

## 9.10 Summary of Phase Behavior of Different Systems:

- Phase separation for A-B polymer blend (macrophase separation) $\chi N = 2$

- Phase separation for A-B BCP (microphase separation) $\chi N = 10.5$

- Phase separation for homopolymer-BCP mixtures and composition for micelles formation $\phi_{CMC} \approx \frac{1}{\sqrt{\chi N}}$

# Chapter 10

## Semi-Crystalline and Amorphous Polymers

## 10.1 Key Terms/Definitions:

- **Semi-crystalline polymer** - a polymer capable of forming elongated, ordered chains at low temperature that pack against each other to maximize enthalpic interactions. No polymer is fully crystalline, however, due to the entropic cost of elongation, leading to low-temperature amorphous regions mixed with crystalline regions.
- **Degree of crystallinity** - the percentage of a polymer sample that is crystalline vs. amorphous; will depend highly on the degree of undercooling below the crystallization temperature.
- **Chain-folded lamella** - the structure associated with crystalline polymers, consisting of elongated chains that pack against each other with occasional folds. This structure emerges due to the inability of chains to fully elongate spontaneously.
- **Spherulite** - the hierarchical structure of semi-crystalline polymers, consisting of crystalline chain-folded regions surrounded by amorphous regions.
- **Non-crystalline (amorphous) polymer** - a polymer that undergoes a glass transition at low temperatures without first crystallizing.
- **Long-range order** - translational order in a system over a length scale greater than a few molecular diameters; observed as sharp peaks in the radial distribution function; characteristic of crystalline solids.
- **Short-range order** - translational order in a system over short length scales due to weak intermolecular interactions; characteristic of liquids or glassy solids.
- **Characteristic relaxation time** - the time scale over which a material relaxes to equilibrium when a perturbation is applied.
- **Deborah number** - the ratio of the characteristic relaxation time to the experimental time over which a perturbation is applied; low Deborah numbers indicate viscous liquids, high Deborah numbers correspond to elastic solids, intermediate Deborah numbers correspond to viscoelastic materials.
- **Glass** - a phase state exhibiting mechanical properties of a solid (stiff, elastic, etc) but lacking long-range translational order as in crystalline solids; results from large barriers to relaxation.
- **Glass transition temperature** - the temperature at which a liquid transitions to a glass state; not strictly a thermodynamic transition, it instead reflects the kinetics of relaxation.

- **Free volume** - the volume in a sample available for unhindered molecular motion; liquids have high free volume, glasses do not.

- **Plasticizer / anti-plasticizer** - molecules that either increase or decrease the free volume of a polymer when blended together, generally due to modifications to molecular packing.

## 10.2 Review of Crystallization:

Now we are going to zoom about a bit and describe the structure of polymers in terms of **short range and long range order**, hopefully concepts you remember from ENGR045. We will start by talking about **semi-crystalline polymers**, meaning polymers that are capable of obtaining long ranged ordered morphologies at low temperature. As is characteristic of all crystals, **polymers in a crystalline state are highly ordered**, leading to the **alignment of polymer chains** stabilized by **secondary intermolecular bonding interactions**. The ability of a polymer to crystallize is thus highly dependent on the **molecular structure** of its constituent monomers, as we could imagine bulky sidegroups may inhibit ordered chain packing. Hence, we generally distinguish between **amorphous polymers**, which undergo a glass transition (second order transition) at low temperatures and generally only have short-range order, and **semi-crystalline polymers**, which actually crystallize at low temperatures and may have a melting temperature (first order transition). Finally, note that semi-crystalline polymers also undergo a glass transition (just like any material can in principle), but the **glass transition temperature is below the melting temperature** and as a result is only observed when the polymer is cooled down quickly such that crystallization does not have enough time to occur. We will discuss the properties of the glass transition and amorphous polymers in a bit but first we will discuss semi-crystalline polymers as they are a bit simpler to deal with.

In general, crystallization is an ordering process associated with a **loss of entropy** in the system in exchange for **achieving stronger enthalpic interactions**. The crystalline state is favored at low temperatures since the free energy is written as

$$\Delta G = \Delta H - T\Delta S \tag{10.1}$$

so the **penalty for reducing the entropy is less significant at lower temperatures**. In the case of polymers, we know that **stretching out polymer chains** is associated with a significant **decrease in conformational entropy**, but the resulting extended morphology also allows chains to become extremely close to each other on the atomic level, leading to favorable non-specific (van der Waals, dipole interactions) and specific (hydrogen bonding, electrostatic) enthalpic interactions. At a sufficiently low temperature, we can thus imagine that the equilibrium morphology would consist of fully extended polymer chains that are perfectly aligned against each other to maximize bonding (like uncooked spaghetti in its package).

The process of crystallization depends on an interplay between both **kinetics and thermo-**

**dynamics**; the same is true of polymer crystallization. For polymers in the high-temperature melt state the polymer chains will be highly intertwined due to the flexibility of the chains. We can imagine, then, that there would be a significant **kinetic barrier for polymer chains to rearrange these highly intertwined chains into an aligned structure characteristic of a ordered state**. Furthermore, we also discussed that polymers **pay a significant entropic cost to fully extend**, providing a further kinetic barrier against completely ordered chains. Conceptually then, we can imagine a **kinetically trapped state** where some chains or some parts of chains are capable of packing against each other, but overall there are still regions of disorder because the **chains cannot appropriately diffuse** (or more accurately **reptate**, a term we will discuss in future lectures) to an equilibrium ordered state. While this frustrated state is **meta-stable**, it might be stable for a sufficiently long period of time that the **fully-aligned equilibrium state is not reached**. This state is then called **semi-crystalline** because there will be **large regions that are still disordered mixed in between regions of crystalline, well-ordered chains**. Often the crystalline state is thus described in terms of a *degree of crystallinity*, which attempts to measure the fraction of the polymer that is crystalline versus the fraction that is disordered. **In reality there are virtually no polymers that are 100% crystalline they are all either semi-crystalline or amorphous.**

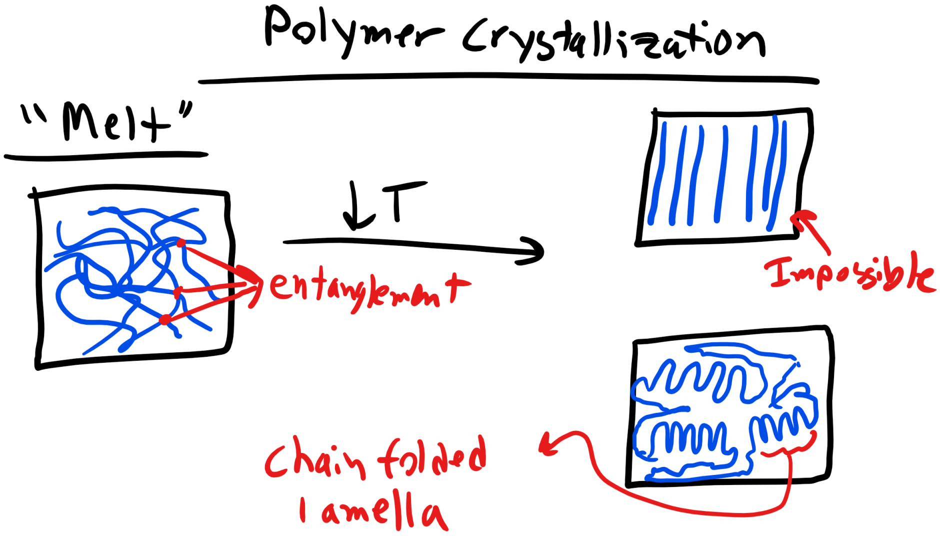


Figure 10-1: Polymer Crystallization Schematic.

**Polymer Crystal Morphology/Structure:**

It is effectively impossible to generate a completely aligned polymer crystal, but there is still a **thermodynamic driving force for the alignment of polymer chains** below the **crystallization temperature** $T_C$. To gain partial crystalline character even in the presence of topological constraints that prevent complete ordering, the chains will tend to form a folded **lamella** structure (not to be confused with the lamellae observed in microphase-separated diblock copolymers). This

**lamella structure** is defined by a series of polymer chains that fold back and forth, such that chains line up and pack against each other but **at a fraction of their fully extend length**, allowing chain ends to still be free and disordered. **The lamella structure allows monomers to interact via non-specific or specific secondary intermolecular bonding**. This state is preferred because for polymers to pack in a completely extended state, the polymer would essentially have to fully extend spontaneously first, then pack next to another fully extended polymer, etc, which is highly unlikely.

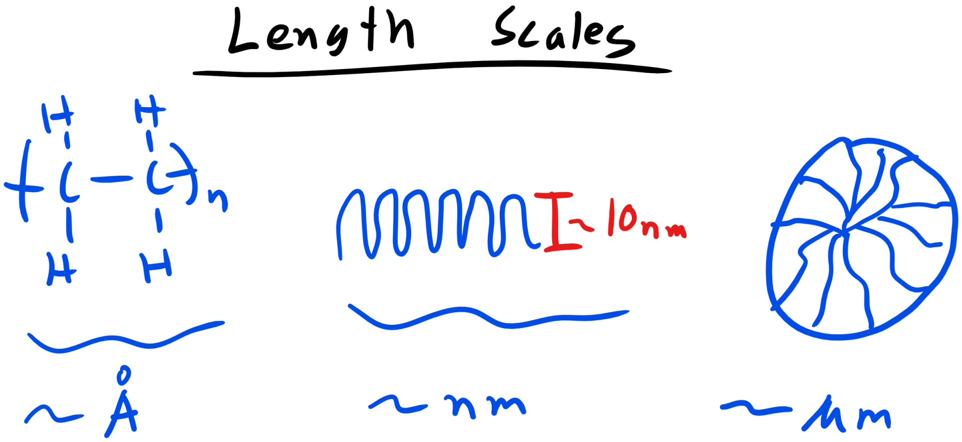


Figure 10-2: Polymer Crystallization Critical Length Scales.

We can then define a crystalline unit cell for the polymer as found in other crystalline materials. Typically, the unit cell appears as a **hexagonally close packed array of cylinders**. The unit cell dimensions can then be derived based on bond lengths, etc, since in the crystalline state the all-trans state will tend to be preferred. As in other materials, the unit cell allows us to understand translational and rotational symmetries of the extended chains.

Finally, note that we described these polymers as semi-crystalline above. The folded, close packed surfaces would thus be the crystalline phase, while **any parts of the chain that extend beyond the folds before repacking would be the disordered phase** (this is a bit easier to see visually than described here, so please look at the lecture slides). Since chains are so long, it is also possible for a **single chain to have multiple regions which are folded and disordered respectively**, allowing different ordered regions to be effectively linked together by a disordered region in between. This will lead to **hierarchical organization of ordered structures**.

**Branching Defects Depress the Melting Temperature:**

The driving force for crystallinity is the ability for chains to pack closely together at the atomic level in order to m**aximize non-specific (and possibly specific) bonding**. As a result, any structural changes in a polymer that would inhibit packing tends to oppose the formation of crystals. For example, **polyethylene (PE) can exist in a branched state, where several alkyl side groups extend away from the main polyethylene backbone**. This branching greatly changes the properties of the PE chain, and actually leads to different engineering applications. When crystallizing, the branches can be handled in two different ways. If the **crystallization process occurs very quickly (fast quench/high undercooling), typically branches will be incorporated/frozen into the crystalline morphology**, leading to the polymer equivalent of **defects in the crystal structure**. If crystallization occurs slowly, then the **branches will be excluded from the perfect crystal structure and tend to form a disordered fringe**. This is again the balance between kinetics and thermodynamics.

If a branches do organize as defects in the crystal structure, we should also note that the **melting point changes as a function of these defect sites**, since these essentially act as an impurity which depresses the melting point. We can write out the change as

$$\frac{1}{T_M(x)} - \frac{1}{T_M^0} = -\frac{R}{\Delta H}\ln(1-x) \tag{10.2}$$

where $x$ is the mole fraction of non-crystallizable units, i.e. the number of branches or defects. $T_M^0$ is the melting point in the limit of no side chains or defects, and $\Delta H$ is the latent heat at the melting point. Qualitatively, this expression says that the melting temperature **decreases** as more branches are introduced ($x$ increases), which makes sense because ordering is more difficult in the presence of branches, leading to a smaller crystallite size, smaller number of secondary intermolecular interactions, and thus a lower temperature is necessary for crystallization. Similarly, **molecular weight should also affect the melting point since chain ends can also act as impurities**.

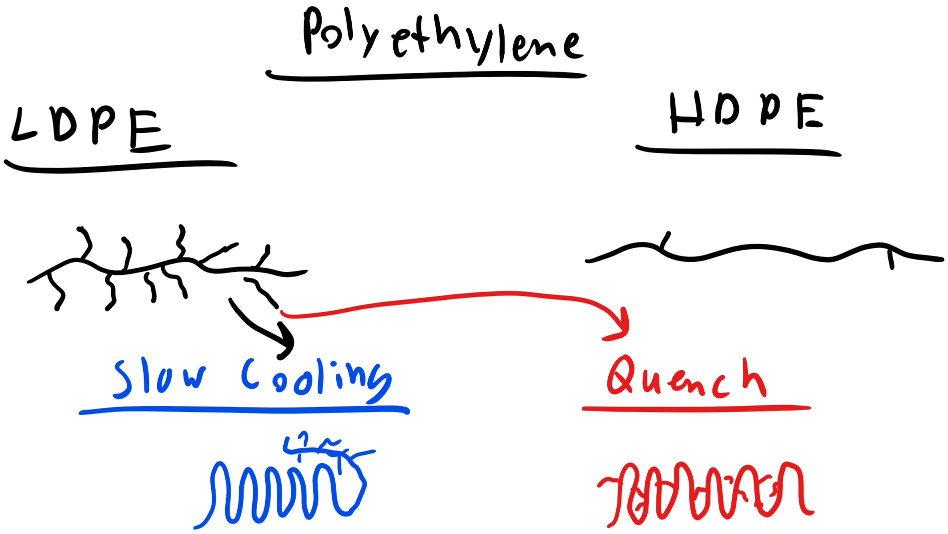


Figure 10-3: LDPE Defect Integration into Lamella Structure.

## 10.3 Spherulites: Hierarchical Structure of Semi-Crystalline Polymers:

We've discussed that a single polymer chain will fold and form lamalla upon crystallization. However, typically we deal with crystallizing a large number of entangled polymer chains at once, and hence have to consider the large scale morphology of the resulting structure. When you crystallize a polymer melt, many polymer chains will tend to **form lamella which has a sandwich like structure with a thickness $l$ defined as the length of the folded polymer chains along the surface of the lamella**. $l$ is typically on the order of 100s of Ås and the **fully extended polymer length is typically thousands** of Ås. Now in the case of a **very dilute polymer solution** the **polymers are typically well separated and are not entangled**. This system will c**rystallize as isolated chain folded single crystals**. As the polymer concentration increases the **chains will overlap and entangle and polymers will fold onto multiple lamella**. This linking of ordered regions disordered amorphous polymer regions creates a structure we call a **spherulite** where multiple lamella grow outward from a **single nucleation site**. In this case, growth consists of chains folding onto the surface of previously crystallized sections of polymer. **Spherulites consist** of **lamella** (ordered region) and **large disordered regions** of **polymer chains** filling space between the growing lamella. Note that the lamella do not necessarily consist of a single chain, but could consist of different polymer chains that also wind through the disordered sections, effectively joining together ordered regions with what are called **tie molecules**. The term spherulite comes from the tendency of growth to proceed outward with **spherical symmetry**. Spherical symmetry is possible because lamella can branch off where chains fold onto a surface at a slightly different angle, allowing lamella to continue growing in a different direction. Thus,**we can think of a complete spherulite as a number of chains folded into the lamella surrounded by a matrix of amorphous chains, some of which act as tie molecules joining the growing lamella together**. The r**elative proportions of the disordered and crystalline regions will determine the degree of crystallinity of the sample**. Finally, it should be noted that due to the presence of an amorphous region, **a semi-crystalline polymer will still undergo a glass transition associated with the glass transition of JUST the amorphous regions**.

In a large melt, many spherulites will nucleate independently, and as a result their **eventual size is restricted by the presence of other spherulites which impinge upon each other**. Effectively spherulites can reach **sizes as large as 100 $\mu$m** if they do not impinge upon each other. The distribution of sizes will depend on **how quickly nucleation occurs which in turn depends on the degree of undercooling of the sample**. Remember that undercooling is the amount of temperature we cool the sample below the melting temperature or

$$\Delta T = T_M - T \tag{10.3}$$

where $\Delta T$ is the amount of undercooling, $T_M$ is the melting temperature, and $T$ is the actual temperature.

At a **high degree of undercooling, nucleation will be strongly preferred thermodynamically so many spherulites will nucleate quickly**. As a result, we can imagine all of the spherulites in a sample nucleating at about the same time and growing at about the same rate, so that when they **begin to impinge upon each other they will be around the same size**. Hence, **high degrees of undercooling lead to an even distribution of spherical sizes**. Physically, the boundaries between spherulites that are about the same size will be flat reflecting identical nucleus sizes and growth rates. Conversely, if the d**egree of undercooling is low, there will be a lower thermodynamic driving force for nucleation and hence nucleation will occur slowly**. We can thus imagine nuclei appearing in a sample sporadically and at different times, such that there will be a **large distribution of sizes when spherulites impinge upon each other**. In this case, the boundaries between spherulites will appear as curved. problem on this

**Melting Temperature for Semi-Crystalline Polymers:**

Now that we have a picture of the structure we can dive back into the thermodynamics of chain folding and crystallization in detail and you can bet that a competition of entropy and enthalpy will be involved. Right now we will start with a simple case and only consider the thermodynamics of melting a chain-folded regime. Let's start by defining a few parameters

- $\sigma$ = surface free energy along the growing edge of the lamella
- $\sigma_E$ = surface free energy along the disordered folded surface of the lamella
- $x$ = edge length of lamella
- $l$ = thickness of lamella
- $T_M^0$ = Melting temperature of infinitely long polymer crystal (i.e. no folds)

The goal here is to **understand the free energy change for forming lamella near the melting temperature as a function of the lamella thickness** $l$. One important thing to keep in mind is that the surface free energy along the well-ordered lamella edges and the surface free energy around the disordered folded surface are different.

The total free energy change will consist of two terms

1. $\Delta G_S$ - which is the **free energy change at the surface of the crystal where the ordered region interacts with the disordered region**. This **contribution should be positive (penalty) as creating a surface where ordered and disordered regions meet is very unfavorable for packing**.
2. $\Delta G_V$ - the **free energy change in the volume or bulk of the crystal**. This contribution should be **negative as at temperatures $T < T_M$ as the bulk will want to order to maximize secondary intermolecular interactions**.

# Semi-Crystalline Polymer $T_m$

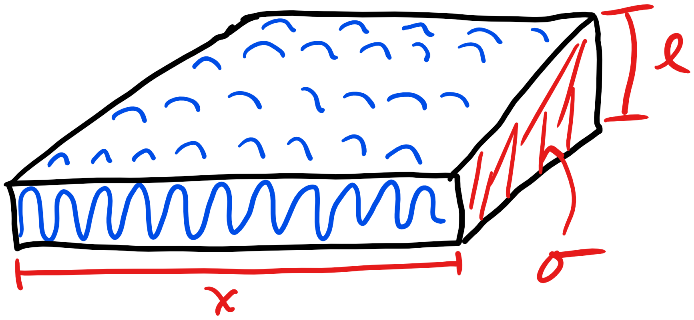


Figure 10-4: Lamella Schematic for Semi-Crystalline Polymer Melting.

Now at the melting temperature, the change in free energy between liquid and solid is 0 so we can write that

$$\Delta G_V = \Delta H - T_M^0 \Delta S = 0 \tag{10.4}$$

$$T_M^0 = \frac{\Delta H}{\Delta S} \tag{10.5}$$

At temperatures near the transition, then, we can approximate the change in entropy using the expression above for the change in entropy at the melting point. So for some general temperature $T$ that is near $T_M^0$, we can write

$$\Delta G_V(T) = \Delta H(T) - T\Delta S(T) \tag{10.6}$$

$$\approx \Delta H(T) - T\frac{\Delta H(T)}{T_M^0} \tag{10.7}$$

$$\approx \Delta H(T)\left(1 - \frac{T}{T_M^0}\right) \tag{10.8}$$

$$\approx \Delta H(T)\left(\frac{T_M^0 - T}{T_M^0}\right) \tag{10.9}$$

We can then rewrite this equation slightly by defining the *degree of undercooling* as $\Delta T = T_m^0 - T$. Rearranging gives:

$$\Delta G_V = \Delta H \Delta T / T_m^0 \tag{10.10}$$

Note that we did not include any terms related to the number of chains, so we can consider this a free energy change per unit volume, assuming $\Delta H$ and $\Delta S$ are also measured per volume.

For the surface free energy

$$\Delta G_S = 2\sigma_E x^2 + 4\sigma x l \tag{10.11}$$

where the first term considers the top and bottom surface and the second term accounts for the four sides. The total free energy for the sample is

$$\Delta G = -\Delta G_V x^2 l + \Delta G_S = -\Delta G_V x^2 l + 2\sigma_E x^2 + 4\sigma x l \tag{10.12}$$

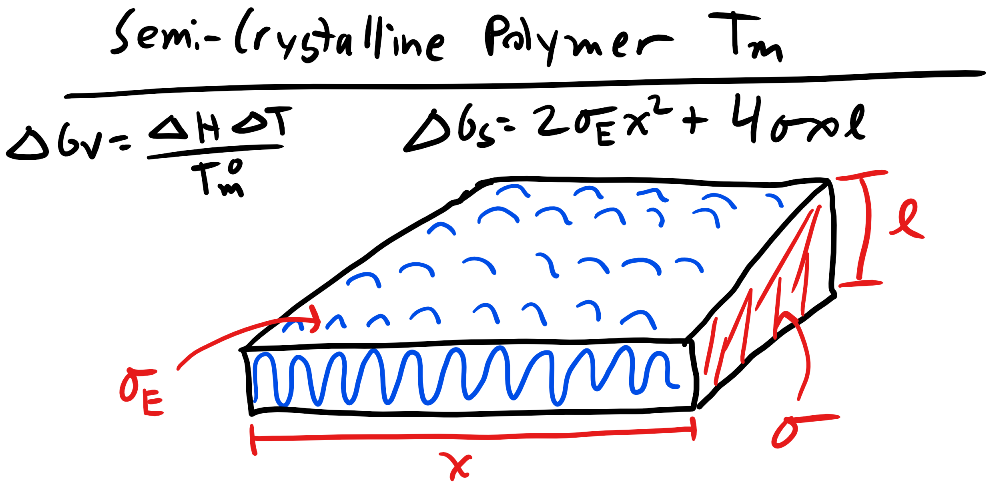


Figure 10-5: Full Free Energy of Crystallization/Melting.

We can simplify this expression by assuming that $x >> l$ as the growing lamalla tend to elongate much more than they thicken. So the second term of the surface free energy is very small and we can ignore the term of $4\sigma x l$. Now, to find the melting point for finite $l$, we can set the free energy change to 0 and solve

$$\Delta G_V x^2 l = 2\sigma_E x^2 \tag{10.13}$$

$$\Delta H(T)\left(\frac{T_M^0 - T}{T_M^0}\right) l = 2\sigma_E \tag{10.14}$$

$$T_m(l) = T_M^0\left(1 - \frac{2\sigma_E}{l\Delta H}\right) \tag{10.15}$$

Hence we see that as the thickness of the lamella, $l$, increases, the resulting **melting temperature also increases to a maximum** of $T_M^0$ when $l = \infty$. This makes sense **since at infinite**

**lamella thickness the chains are maximally elongated and the crystalline state is highly preferred preferred, so as this thickness reduces the temperature necessary to melt the lamella decreases**.

Finally, note that using similar reasoning, this same approach can be employed to find the **critical lamella thickness necessary for stable nucleation at a given temperature**.

## 10.4 Kinetic Consideration of Crystallization: Crystallization Rate

The process of crystallization involves understanding the competition between both **kinetics and thermodynamics**. Qualitatively, we know that at **lower temperatures, the entropic contribution to the total free energy of a system will be lowered**, and as a result **ordered morphologies to maximize enthalpic interactions are preferred**. However, as the temperature of a system is lowered, both **fluctuations and transport in that system will also be reduced**, which may hinder the ability of ordered regions to grow. We thus see that there is a delicate balance between the thermodynamics and kinetics of crystallization. The **rate of crystallization** is defined as the rate at which a sample becomes crystalline, which depends on both the **nucleation** of new spherulites and the **growth** of existing spherulites.

Polymer crystallization proceeds by this two-step process of **nucleation and growth**, which is qualitatively identical to the nucleation and growth of small molecule crystals. In the **nucleation step, a small crystal of polymer spontaneously forms due to thermal fluctuations in the system**. For a polymer, we can imagine this **initial nucleus as simply a section of polymer that is elongated and then folds onto itself (or a neighbor)**. The initial nucleus will have some surface area and some volume; the **surface area will have an associated surface energy which will be due to relatively unfavorable interactions between the surface of the crystal and the surrounding polymers in the bulk**. Conversely, **nucleus formation will be stabilized by favorable interactions between molecules in the volume of the crystal** (i.e. favorable enthalpic interactions from aligned chains). The thermodynamic tendency for a stable nucleus to form will thus depend on the **surface-to-volume ratio of the initial nucleus**. For small nuclei, **the surface-to-volume ratio is high, opposing nucleus formation, but as a nucleus gets bigger the ratio decreases**. At a certain **critical size ($\mathbf{r}^*$)** the free energy change for forming a nucleus achieves a maximum, so that any increase in the nucleus size beyond this point decreases the free energy change.

Thus, once a nucleus of the critical size is achieved, *growth* becomes thermodynamically favorable in order to **continue reducing the free energy of the system**. Furthermore, we can imagine the peak in this curve as something of an **energy barrier for nucleation**, since the formation of a cluster of a given size will depend on the fluctuations in the system that allows for the spontaneous formation of a cluster. For a polymer crystal, the **critical size effectively refers to the elongation of a single chain necessary for nucleation**; since we know that elongation is opposed by an increase in entropy, we can imagine that at high temperatures it is very hard to

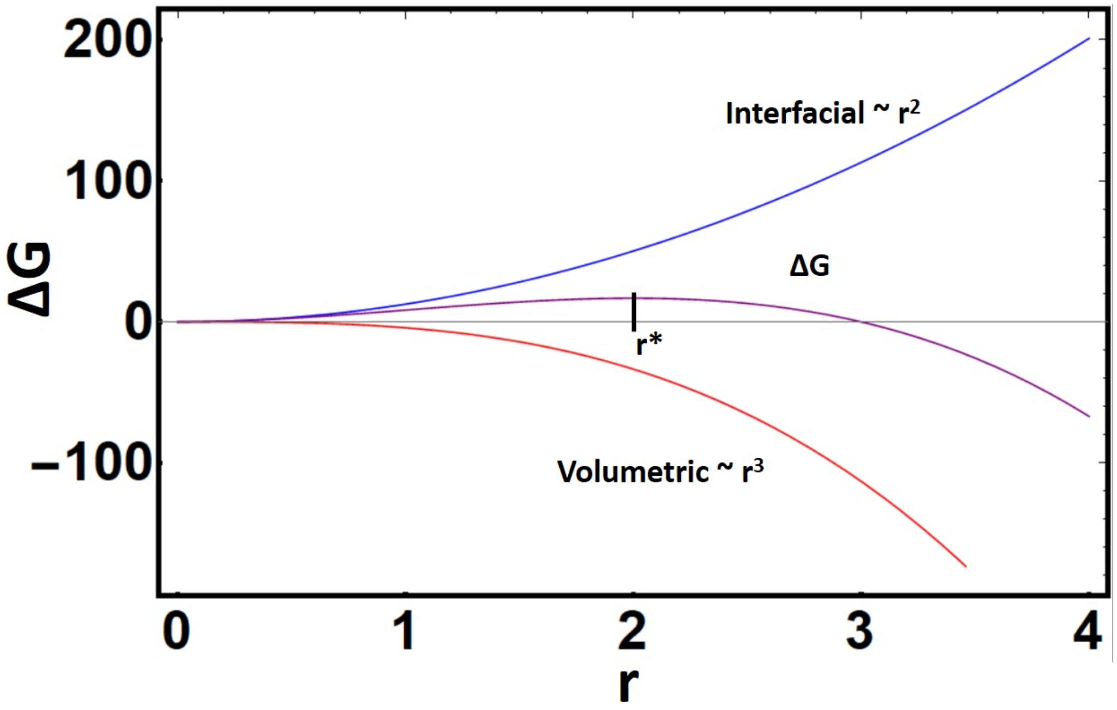


Figure 10-6: Critical Cluster Radius for Growth.

spontaneously elongate a chain to the critical size. Thus, as the temperature of a system is lowered, nucleation becomes easier.

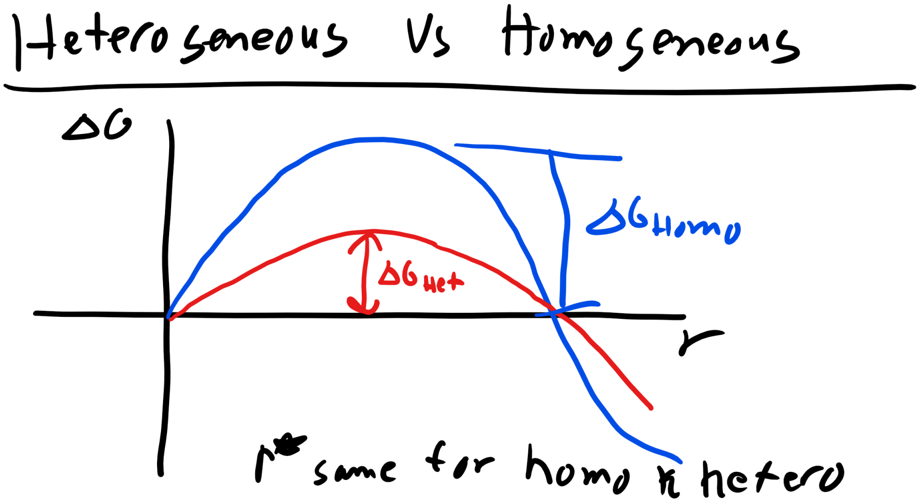


Figure 10-7: Hetergeneous Nucleation Reduces Energy Barrier for Nucleation.

### Growth

First, consider the rate of spherulite **growth**, meaning the rate at which additional polymers pack on the faces of existing lamella leading to their outward expansion. This rate is dependent largely on the amount of time it takes for polymer chains to **diffuse** to the growing face. Qualitatively, diffusion is a temperature-activated process, which can be thought of as a bunch of molecular jumps through space with some activation energy $Q_A$. If we consider diffusion as an Arrhenius process, then we can write the diffusion coefficient as proportional to

$$D \approx \exp\left(-\frac{Q_A}{kT}\right) \tag{10.16}$$

We see that the **lower the temperature - that is, the greater the degree of undercooling - the slower diffusion will occur,** as should be expected. Hence, **lowering the temperature below the melting temperature slows down the transport of polymer to growing spherulites**.

**Nucleation**

Next, though, consider the **rate of nucleation**. In general, we expect nucleation to occur more frequently at lower temperatures, since then nucleation will be **thermodynamically preferred**, and the thermodynamic driving force for nucleation will increase the lower the temperature gets. We can approximate the rate of nucleation as

$$I = \exp\left(\frac{\Delta G}{kT}\right) \tag{10.17}$$

Thus, we expect the rate of nucleation to increase as the temperature lowers. The optimal crystallization rate thus results from some intermediate amount of undercooling to maximize contributions from both nucleation and growth. Near the **melting temperature, the likelihood of forming a nucleus is very small, so the crystallization rate is slow**. Far below the **melting temperature, the rate of diffusion is very low so spherulites nucleate very frequently but are quite small and hardly grow**. **Crystallization rate** is thus **maximized at some small amount of undercooling**, again underlining the importance of both kinetics and thermodynamics in crystallization.

**Modifying Melting Characteristics**

As engineers we want to be able to tune and manipulate the crystallization and melting characteristics of our polymers and other soft materials. And one of the great things about soft matter is that we have a lot of knobs that we can tune and tweak to make sure our soft material is ideal for our particular application of interest. There are a couple of strategies that we can utilize

1. **Add branches:** adding branches will lower the melting point same behavior if you have a lower MW.

2. **Modify the chemical structure of backbone:** stiffer polymers easier to crystallize and bulky groups along the main chain will have higher melting points as rotation will be sterically unfavorable. Highly flexible groups like Si or O will decrease melting point. Any groups that

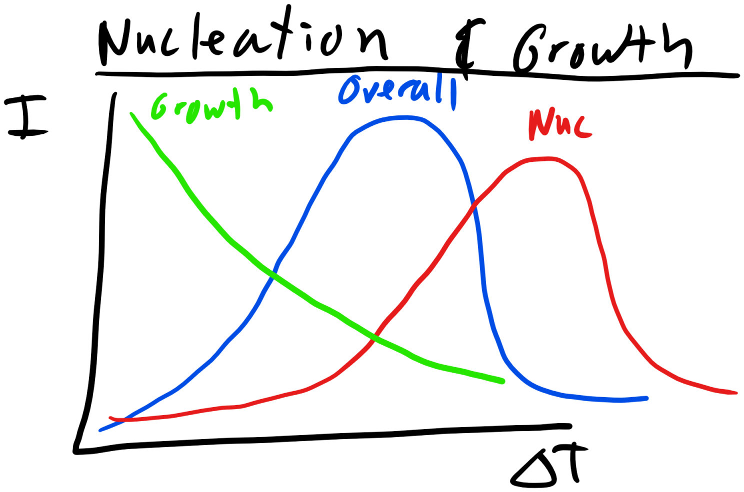


Figure 10-8: Nucleation Rate Maximized at Moderate/Intermediate Undercooling Values.

participate in H-bonding, electrostatic interactions, etc will increase melting point.

3. **Side chains:** Adding long flexible side chains will decrease the melting temperature as they will act as steric barrier to oppose ordered packing while shorter bulky side chains can enhance elongation by restricting the rotation of the main chain.

4. **Environmental conditions:** temperature, applied stress, pressure, MW (small change)

Some of this behavior can be seen below and how it affects melting point and lamella thickness $l$

| **System change** | **Melting point** | $l$ |
|---|---|---|
| Undercooling ↑ | - | ↓ |
| Molar mass ↑ | ↑ | - |
| Pressure ↑ | ↑↑ | ↑↑ |
| Stress | ↑↑ | ↑↑ |
| Add branches | ↓ | - |
| Bulky groups in backbone | ↑↑ | - |
| Flexible groups in backbone | ↓↓ | - |
| Bulky groups in side chain | ↑↑ | - |
| Flexible groups in side chain | ↓↓ | - |
| Specific bonding interactions | ↑↑ | - |

## 10.5 Non-Crystalline/Amorphous Polymers:

Now that we have exhausted our discussion of semi-crystalline polymers we can move on to discussing **non-crystalline/amorphous polymers** which are polymers that do not undergo a melting transition but instead a **glass transition** when the temperature is lowered. These polymers then form amorphous but solid structures that **lack the long range orientational and translational order of crystals**.

**Short Range and Long Range Order**

Non-crystalline materials are characterized as having **short-range order (SRO)** but **not long range orientational or long range translational order (LRO)**. This means that the probability of locating another atom within some distance $r$ is more probable at certain short distances of $r$ than at long distances, where the probability essentially becomes constant. Short-range order (SRO) arises because atoms prefer to pack together is characteristic of liquids in general due to a combination of bonding interactions and weak non-specific bonding. In polymers, **SRO is due to local chemistry (such as polymer connectivity), excluded volume and the restricted conformational states due to the finite rotations of intramolecular covalent bonds**. **Long-range order arises in crystalline solids where the presence of translational symmetry (i.e. a well-defined unit cell) is due to highly specific, strong binding interactions (covalent bonds) or a strong non-specific intermolecular bonding**. Polymers that exhibit short-range order but not long-range order are called amorphous; **non-crystalline polymers are amorphous at all temperatures**, while **semi-crystalline polymers exhibit both amorphous regions and crystalline regions**.

**Pair/Radial Distribution Function:**

One technique that we can utilize to get a quantitative measure of the short and long range order of both semi-crystalline and amorphous polymers is a *pair distribution function* $g(r)$. To calculate $g(r)$, you take a single atom $i$ as a reference and calculate the number of atoms $dn$ in a spherical shell of volume $dv = 4\pi r^2 dr$ centered around atom $i$, where $dr$ is the thickness of the shell and $r$ is the radius of the shell. This counts how many atoms are some distance $r$ from the atom $i$ we are looking at. We can then repeat this measurement for all such atoms $i$ in the sample, and take the average. $g(r)$ is thus defined as:

$$g(r) = \frac{1}{\langle \rho \rangle} \frac{dn(r, r+dr)}{dv(r, r+dr)} \tag{10.18}$$

averaged over all atoms in a system. Note that this equation boils down to counting the number of atoms at some distance $r$, dividing by the size of the shell since this increases as $r$ increases, then normalizing by the average density to make this a dimensionless quantity. You can also think of $g(r)$ as being the **relative** probability of finding an atom at any given distance $r$ - relative meaning that the total integral of $g(r)$ is not 1. Plotting $g(r)$ then provides an illustration of order in different phases of material. In a gas, there is no order inherent to the material, so at any given distance the same relative number of atoms should be expected, and so $g(r)$ is just 1 (i.e. the average number at any distance is uniform and equal to the density). In a crystal, $g(r)$ will have a large number of sharp peaks at different distances, corresponding to the known fixed distances of atoms in the crystalline lattice. In a glass or liquid, we see short range order - there is a broad peak at a characteristic distance slightly larger than the diameter of an atom, implying that atoms tend to cluster close together, and other broad peaks at distances related to probable atomic separations, but sharp peaks at absolutely fixed distances are not observed. In glassy polymers, again, this feature can be related to the excluded volume of the monomers, and hence we expect a peak at some distance corresponding to two times some effective radius that reflects the excluded volume of an individual monomer.

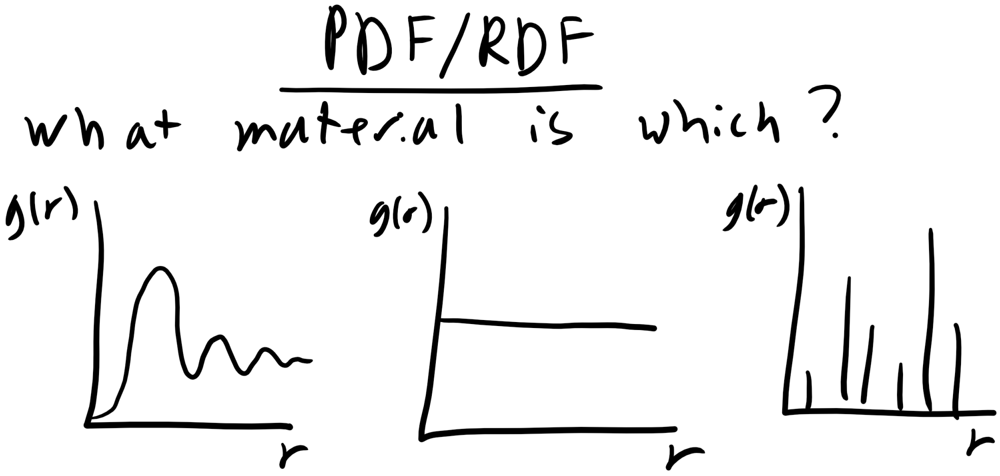


Figure 10-9: RDF/PDF for Different Classes of Materials.

## 10.6 Glass Transition Temperature:

We have just discussed how non-crystalline amorphous polymers can be distinguished from semi-crystalline polymers based on the presence of long range order. However, another critical parameter that is utilized to distinguish/describe amorphous polymers is the **glass transition temperature** ($T_g$. Typically, non-crystalline polymers can be broadly classified as either **rubbery** or **glassy**, both of which exist as highly interpenetrated/entangled Gaussian coils at relatively high temperatures above the glass transition temperature. When we say **interpenetrated, the physical picture is of polymer coils that overlap with each other such that separate coils intertwine with each other**. In this **highly interpenetrated state, without solvent, the polymer acts as if it is unperturbed** - that is, in the **melt state the polymer** is at the $\theta$ condition, and can be treated **as an ideal chain**. You can think of melt polymers as essentially **feeling some pressure due to surrounding polymers that overcomes excluded volume effects,**

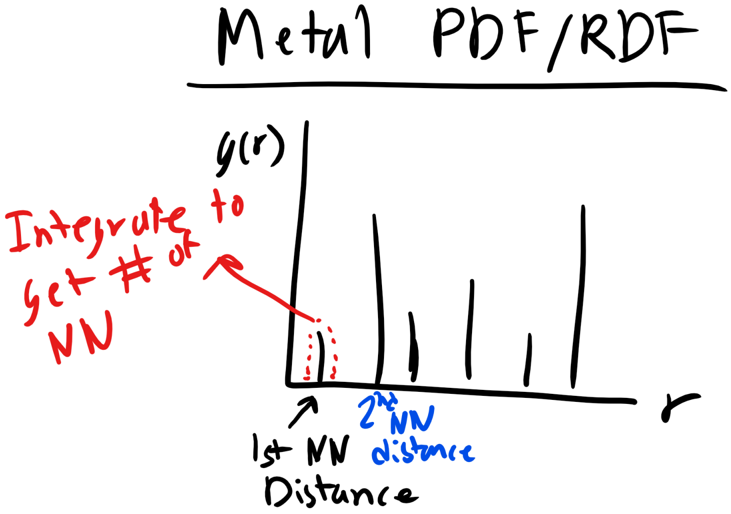


Figure 10-10: RDF/PDF Insight into LRO for Metallic Materials.

**yielding an ideal state**. The ideal nature of polymers in the melt make them much easier to think about theoretically.

The *glass transition temperature* is the temperature at which a polymer transitions from its fluid-like state to a glassy state. When we say a glass, we mean a material with **only short-range order** but **lacking the translational fluctuations** associated with liquids. Hence it is **like a solid, but with randomly positioned atoms rather than ordered ones as we expect in a crystal**. We can identify the physical origin of the glass transition temperature in two different ways - first, you can think of increasing the temperature from below the glass transition, or you can think of decreasing the temperature from above the glass transition temperature. In either case, the **glass transition is a competition between the available thermal energy $kT$ and the strength of intermolecular bonds $\epsilon_{ij}$**.

If we think of **increasing temperature**, then the glass transition temperature is the point at which **thermal energy is sufficient to break local intermolecular bonds, enabling fluid-like motions** - that is, the point where $kT > \epsilon_{ij}$. If we think of **decreasing temperature**, then the glass transition temperature is the point at which the **viscosity of the polymer essentially becomes infinite, eliminating molecular motion**. In either case, the key property of a glass is that the **rearrangement of atoms is hindered**, **limiting the ability of the system to relax to equilibrium when a stress/perturbation is applied**. This is intimately related to the concept of a **characteristic relaxation time** which we will take a quick aside right now to discuss.

**Relaxation Time $\tau^*$:**

The physical properties of amorphous polymers (and materials in general) are influenced by $\tau^*$, the **characteristic relaxation time** of the polymer, and how large this relaxation time is relative to a relevant experimental time (or the interaction time) $t$. The **relaxation time** is essentially a measure of how **long it takes for a material to return to equilibrium after the application of some perturbation**. The ratio between the relaxation time and experimental time is called the **Deborah number** - i.e. $De = \frac{\tau^*}{t}$. It is easiest to think of the importance of the relaxation time in terms of known material behavior.

Let's consider as an example a system consisting of some material in a container such that the material is magically attached to the container walls. We impose a **perturbation on the system consisting of moving the walls of the container apart such that the material in the container is deformed/stretched**. First consider the case that the **relaxation time of a material is much smaller than the experimental time**, such that $\tau^* << t$ and $De << 1$. Because the r**elaxation time is so much lower than the experimental time**, the material **effectively relaxes instantaneously to the new system dimensions as the perturbation is applied**; in other words, the **system adjusts to the new constraint by relaxing to equilibrium immediately**. Physically, we could imagine this as the material rearranging its constituent molecules to instantaneously fill the new volume of the container - we would say that the material **flows**, and call the **material in the container a liquid**.

Now consider the opposite case, where the **relaxation time is much greater than the experimental time** such that $\tau^* >> t$ and $De >> 1$. Now when we adjust the walls of the container, the material effectively **never relaxes to equilibrium as the perturbation occurs**, instead being driven very far from equilibrium into a high energy state. In our physical example, we would imagine the material in the container being stretched but being unable to adjust the positions of its atoms because the relaxation time is so long, so that the material instead **builds up a large amount of strain energy**; we would consider this an **elastic** response and call the material an elastic solid. Note that the only distinction we are drawing here between the liquid and solid case is the experimental time - this implies that if we apply a stress/strain to a solid and wait long enough, it would appear to flow like a liquid (in the case of crystalline solids this would be due to the gradual movement of defects throughout the material to change the solid dimensions). In an intermediate regime where the **relaxation time is roughly the same as the experimental time**, the material will exhibit behavior consistent with both **viscous liquids and elastic solids**; we call these materials *viscoelastic* and will discuss their properties much more in future lectures.

We can **gain some understanding of relaxation times from the molecular structure of a given material**. For example, for small molecules like water, the relatively free motion of water due to its small size would lead to a small relaxation time, and hence water is only solid at low temperatures. Polymers tend to exhibit a **longer relaxation time due to the connectivity monomers**, requiring collective motion to adjust to a perturbation. As we will discuss shortly, **at lower temperatures the energetic cost for this motion is too great to allow the polymer to flow, leading to glassy behavior**. We might also imagine, then, that **polymers with more rigid backbones have longer relaxation times due to the lessened flexibility of the chain**.

Characterizing a polymer as a rubber, liquid, or solid (glass) is impossible without further information on the overall environment, as the response of the polymer depends on the **time scales** involved. We will also see that the relaxation time in polymers is a function of temperature, yielding many of the characteristic mechanical properties which we will discuss in future lectures. To wrap up if the molecular motion is slow/hindered, the relaxation time of the polymer is very long and thus the polymer exhibits solid-like behavior.

**Back to Glass Transition Temperatures:**

A key point about the glass transition temperature is that it is not strictly a thermodynamic transition. The melting temperature, for example, results because there is some specific temperature for materials where the free energy of the liquid phase becomes lower than the free energy of the solid phase, leading to melting behavior (and more specifically there is an abrupt change in thermodynamic quantities reflecting a first-order phase transition). Hence, the melting point is thermodynamic in nature, resulting from the competition between the higher entropy liquid phase and lower enthalpy solid phase. The **glass transition is not strictly thermodynamic**, as a glass is **not a stable thermodynamic phase** but rather a **kinetically-trapped phase resulting** from the large energy barriers faced by a glass when it must adjust to a perturbation. The glass transition thus reflects the kinetics and time scales of a system and as such the transition temperature is not easily defined - in fact,**the exact measurement depends on cooling rate** and typically a range of glass transition temperatures are reported for specific samples.

**Free volume theory of $T_g$**

An explanation for the origin of the glass transition temperature comes from **free volume theory**. **Free volume** (not be confused with excluded volume) is the space in a polymer sample **in excess** of the volume present in a random, *densely packed* glass. Free volume is the **volume that monomers in a particular sample are able to access via thermal fluctuations**. In a **liquid state**, we would imagine that the **free volume is high**, allowing large fluctuations and easy response to perturbations due to the availability of free volume through which monomers can move. By contrast, in the **glassy state** the **free volume is very low** and as a result molecular motion is hindered by steric/excluded volume considerations. The free volume is thus

$$V_F(T) = V(T) - V_0(T) \tag{10.19}$$

where $V_0$ is the volume of a close-packed random glass (0.63), $V$ is the actual volume of the sample, and $V_F$ is the free volume. Note the temperature dependence of each term, which comes from thermal expansion governed by the thermal expansion coefficient

$$\alpha = \frac{1}{V}\frac{\partial V}{\partial T} \tag{10.20}$$

As we gradually increase the temperature the volume available to the system will increase, reflecting increased fluctuations in monomer positions due to more available thermal energy.

Since the thermal expansion coefficient will be different between the glass and fluid states, $V_F$

will increase with increasing temperature because the thermal expansion coefficient in the liquid state $\alpha_l$ is greater than the thermal expansion coefficient $\alpha_g$ in the glassy state (this controls the increase in $V_0$ with T). We can now write

$$V_F(T) = V_F(T_g) + (T - T_g)\frac{dV_F}{dT} \text{ for } T > T_g \tag{10.21}$$

Dividing by $V$ puts the right side in terms of the difference in thermal expansion coefficients, and reduces all volumes to fractions for the total volume

$$f_F(T) = f_F(T_g) + (T - T_g)(\alpha_l - \alpha_g) \tag{10.22}$$

$T_g$ is then defined as the point where this fractional free volume falls below some critical value, and **practically speaking can be found by looking at where the slope of the sample volume changes as a function of temperature** (reflecting the change in expansion coefficient). **Below the critical value**, we can imagine the positions of the monomers are **frozen** due to the low volume available for monomer movements. Note that by this definition, **polymers with greater free volume in the fluid state** will experience a **lower** glass transition temperature, since you will have to **decrease the temperature more to reduce the free volume fraction to the critical threshold**. Qualitatively, this makes sense since if there is **more free volume originally, it requires less thermal energy to access that volume, and so the glass transition temperature will lower**. This observation implies that the **glass transition temperature will depend significantly on the molecular structure of the polymer**, we will talk about this in a second. Finally, it has been shown experimentally that the critical fraction for the glass transition is fairly constant across many different molecules, making this analysis appropriate.

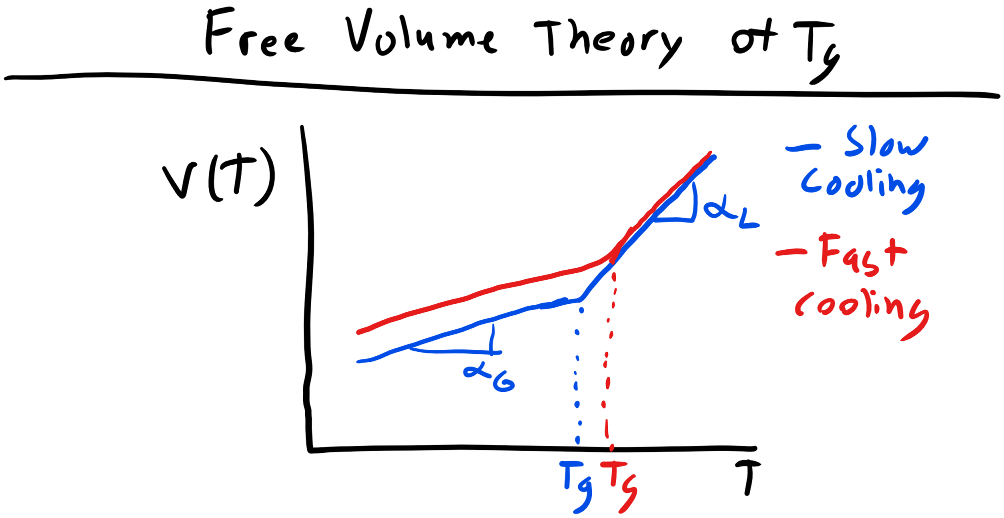


Figure 10-11: Free Volume and $T_g$ as a Functino of Cooling Rate.

The glass transition temperature is also dependent on the **rate of cooling** of the sample. The cooling rate dependence of the glass transition temperature can be explained by what's called **percolation**. If we imagine the polymer sample superimposed on a lattice, and each lattice point can be thought of as either in the glassy state or fluid state, then the **network is percolated when a connected network of glassy points spans the entire lattice**. In other words, it is not necessary for the entire polymer sample to be glassy; it is **only necessary for connected regions that cross the network to be glassy**, since **these connections essentially cut off the fluid parts from each other**, leading to glassy behavior on the macroscale. We can think of each lattice point as transitioning between fluid and glassy with some characteristic probability, and can also imagine some other characteristic probability for the point to transition from glassy back to fluid. **Physically, this reflects the ability of monomers to move through the available free volume**, and hence at **lower temperatures** we expect the probability of a fluid-to-glass transition to increase, and the **probability for a glass-to-fluid transition to decrease** as the **decreasing free volume favors the glassy state**. As we cool the sample, then, the probability of forming a glass progressively becomes higher, and the time taken for glass points to transition back to fluid takes progressively longer. If we **cool at a very fast rate**, lattice points will have **sufficient time to transition from fluid to glass but not back** (since as we cool it takes longer and longer for the glass-to-fluid transition), **leading quickly to a percolated network at a high temperature** since glassy behavior will be observed as soon as connected glassy regions span the sample. If we **cool at a slower rate**, a percolated network is more difficult to form because at **higher temperatures the relatively short time associated with the glass-to-fluid transition** will **disrupt the network** as it forms. This means that the glass transition will be observed at a lower overall temperature.

## 10.7 $T_g$ and Chemical Structure of Monomers:

Trends in $T_g$ can be explained by looking at the chemical structure of monomers due to the influence of monomer structure on both chain flexibility and free volume. Recall that $T_g$ is determined by the onset of long range **cooperative molecular motion**, meaning the motion of 10-30 connected chain monomers at once. The cooperative motion requires both sufficient thermal energy to induce the movement of these monomers and sufficient free volume for the monomers to move into. Both of these requirements are influenced by monomer structure. There are essentially 3 elements of monomer structure that can influence these motions:

1. **Chain interactions** - energetic interactions between monomers
2. **Ease of rotation about main chain bonds** - whether there is significant steric hindrance to rotation
3. **Amount of free volume available** - how densely the monomers pack

We can think of polymers as essentially divided into their backbone and sidechains coming from that backbone. In polymers with flexible backbones, like polyethylene (lots of C-C single bonds) and PDMS (Si-O bonds, which are flexible due to the 4 electrons on the oxygen atoms in place of hydrogens), the hindrance to rotation is low and hence less thermal energy is necessary to induce molecular motion, leading to a low $T_g$. On the other hand, polymers with phenyl molecules along the backbone (e.g. polycarbonate) tend to have a much higher $T_g$, since the bulky phenyl constituent greatly increases the amount of energy necessary for rotation (i.e. the rigidity). Note that we can generally relate $C_\infty$ to the rigidity of a backbone, and hence expect $T_g$ to increase with $C_\infty$.

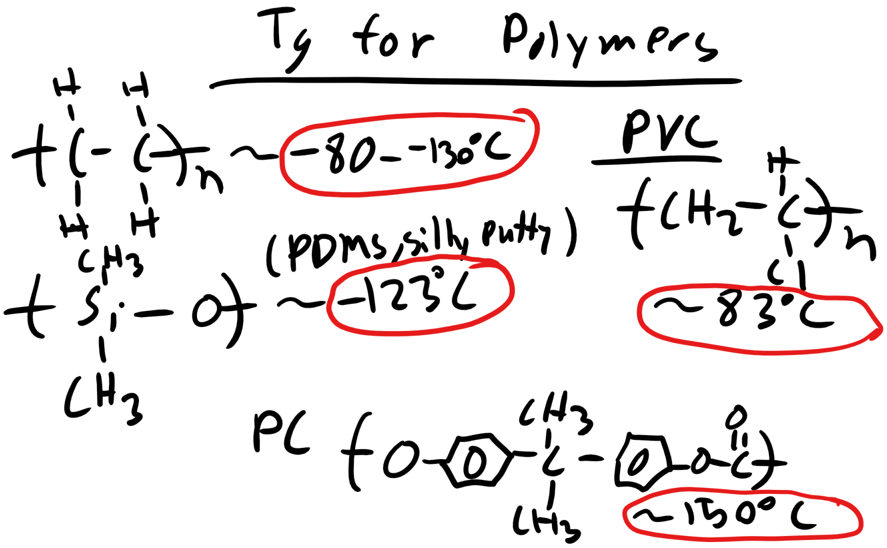


Figure 10-12: T$_g$ for Various Polymers and Influence of Chain Structure.

Similarly, large bulky sidechains, such as phenyl groups, also oppose rotation due to steric hindrance, and in addition decrease the amount of free volume available since they occupy a greater excluded volume, leading to a higher glass transition temperature. Finally, intermolecular interactions, such as hydrogen bonds or ionic interactions, which are typically seen between sidechains, will tend to greatly increase the glass transition temperature since thermal energy will also have to break these bonds to induce rotation. The lecture notes provide some examples of polymers, sidechains, and the related $T_g$s. The main principles to keep in mind are that chain flexibility allows easier cooperative movement of monomers, decreasing the $T_g$, and increased free volume around the chain backbone lowers the barrier to cooperative movement and hence decreases the $T_g$.

**We can also relate these observations back to the idea of crystallinity, as well, as the factors that influence the glass transition temperature will also influence the ability of polymers to crystallize. In fact, there is a correlation between $T_g$ and $T_m$ for semi-crystalline polymers - typically $T_g$ is about 0.5 to 0.8 $T_m$ in Kelvin.**

**Molecular Weight Dependence of $T_g$**

The free volume explanation of the glass transition temperature can also be used to explain an observed molecular weight dependence of $T_g$. In general, the free volume of chain ends should be much greater than the average free volume along the main part of the polymer chain (as expected since the chain ends are only connected to one, rather than two, monomers). As a result, **more chain ends in a sample tend to increase the overall amount of free volume, and hence decrease the glass transition temperature**. In two samples of the same mass, the sample with polymers of lower molecular weight will tend to have more chain ends, and hence a higher free volume and lower glass transition. We can thus write:

$$T_g(\overline{M}_n) = T_g^{\infty} - \frac{c}{\overline{M}_n} \tag{10.23}$$

where $T_g^{\infty}$ is the $T_g$ of a sample with infinite molecular weight and $c$ is the concentration of the sample. This basically says that as the average molecular weight in a sample increases, the glass transition temperature also increases, reflecting the decreasing number of chain ends. Again, note the similarity between this argument and the change in the melting point of semi-crystalline polymers with molecular weight, where chain ends effectively acted as defects in the crystalline matrix.

**$T_g$ of Mixtures**

We can again refer to the free volume concept to approximate the glass transition temperature of mixtures. If it is assumed that both components of a mixture have the same free volume when mixed as they would separately, we can sum the **total free volumes of the mixture based on the weight fraction of each species in the mixture**. Note that to avoid phase separation behavior, the mixture should be either two miscible polymers blended together, or two polymer species that form a random copolymer and hence are "mixed" by the virtue of covalent bonds. Without going through a full derivation, we can find that because free volumes are additive, we can equivalently add glass transition temperatures of the two components to find:

$$T_{g,co} = T_{g,A} w_A + T_{g,B} w_B \tag{10.24}$$

where $w_A$ and $w_B$ are the weight fractions of components A and B.

**Tuning $T_g$ with Small Molecule Additives**

We just saw that the glass transition temperature of a miscible blend can be easily predicted, we can thus figure out ways to arbitrarily increase of decrease the glass transition temperature of a polymer species by adding small molecules. If we wish to decrease the $T_g$, we can add small molecular **plasticizers**, which essentially add free volume to the system. Similarly, if we add small molecules that fit in nicely with the polymer chain of interest and hence decrease the free volume, we can **raise** the $T_g$. These molecules are called **anti-plasticizers**. An interesting example of an anti-plasticizer from biology is **cholesterol**, which induces the formation of a gel phase in lipids by reducing the free volume of lipid chain ends. We can thus use the knowledge of mixtures of polymers and small molecules to control the glass transition temperature of a mixture; this might be useful for decreasing the glass transition temperature of a system to enable better processing control, for example.

## 10.8 XRD Analysis:

We have talked about XRD analysis and have done our XRD lab which included a polymer. We know that the peaks observed in the diffractogram will be more broad than that for metals due to the lack of long range translational and orientational order for polymers[13, 14, 15]. However, we can obtain some key information from XRD analysis of polymers to allow us to deduce some information about the structure of polymers and how they might be arranged. Let's take for example the case of the family of polymethacrylates, specifically PMMA, PPMA, PEMA, and PBMA[13, 14, 15].

When we examine the XRD profile of these polymers we can see that there are some XRD peaks that do not shift for the entire family of polymers. Additionally, the peaks that appear to be consistent between the family are all located at large Bragg angles ($2\theta$)[13, 14, 15]. At lower Bragg angles there appears a considerable amount of peak shifting and perhaps even some creation or destruction of peaks in the XRD curve. How can we explain what is happening here?

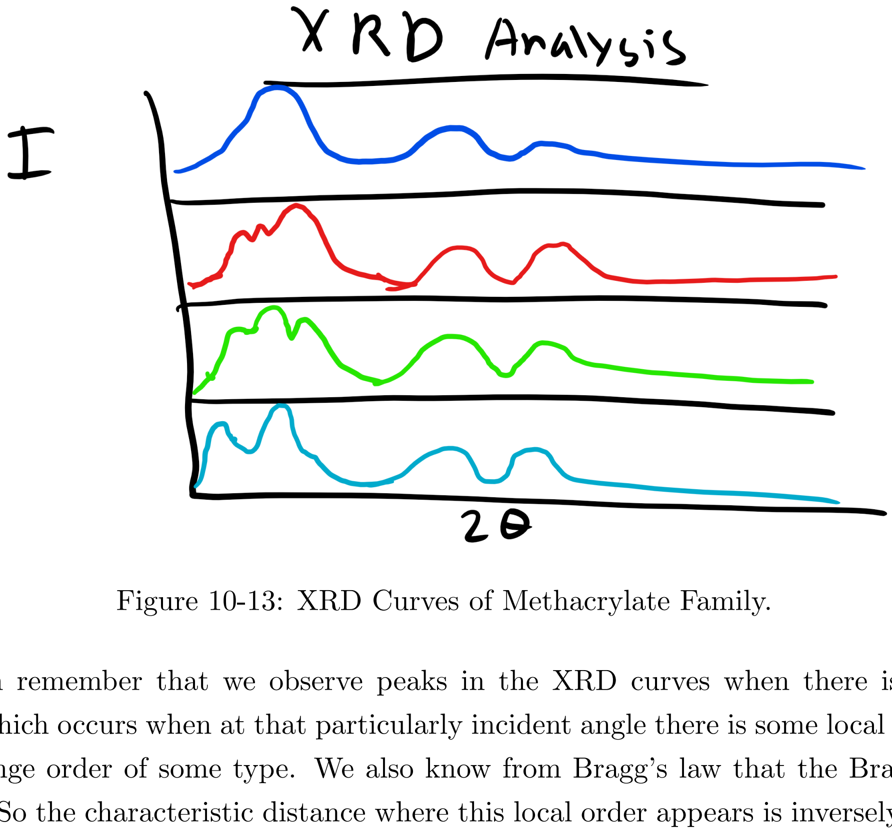


Figure 10-13: XRD Curves of Methacrylate Family.

Well again remember that we observe peaks in the XRD curves when there is constructive interference which occurs when at that particularly incident angle there is some local order perhaps even long-grange order of some type. We also know from Bragg's law that the Bragg Angle $\theta \propto \frac{1}{d}$[13, 14, 15]. So the characteristic distance where this local order appears is inversely proportional to the incident angle. Let's think about the strucure of these polymers at very short distances like the C-C bond distance or the distance between the methyl groups. This distance will not change

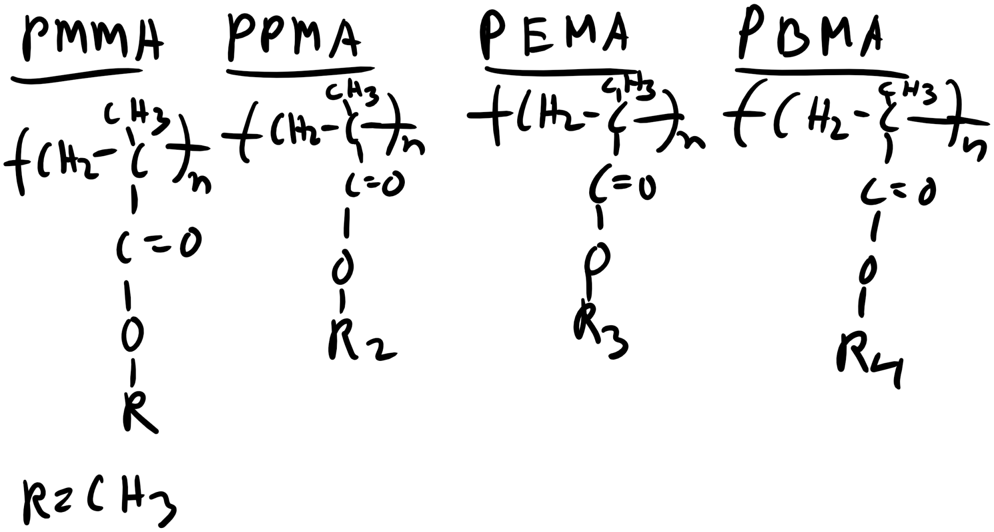


Figure 10-14: Methacrylate Family of Polymers

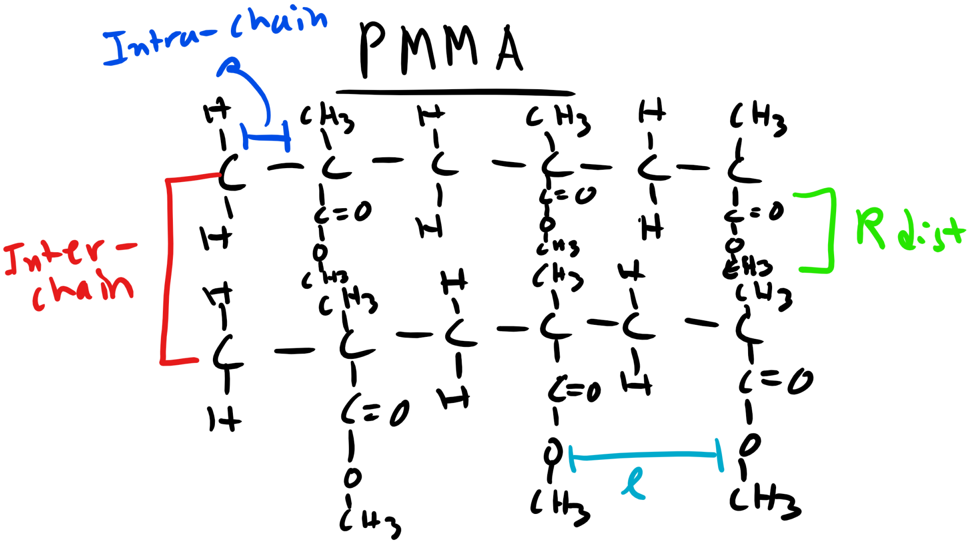


Figure 10-15: PMMA Chain Schematic.

depending on the polymer we are looking at in this family[13, 14, 15]. These small distances correspond to large angles and so this explains why the peaks are conserved for the different polymers.

Now what is happening for the other polymers. Well there are other characteristic distances for these polymers. For example the distance from the chain backbone to the end of the R functional group. Or even the inter-chain distance within the polymer. These distances will change depending on whether the polymer is PMMA, PBMA, etc. If the distance changes there will be a corresponding shift in the location of the peaks[13, 14, 15]. And we see that on average as the side group R increases in length for these polymers the peaks tend to shift to the left which is consistent from what we know about diffraction! This is critical information as it gives us a schematic of the structural characteristics of an unknown polymer chain[13, 14, 15].

## 10.9 DSC Analysis:

Differential Scanning Calorimetry (DSC) is a thermal analysis technique useful for measuring thermodynamic properties of materials such as specific heat, melting point, boiling point, glass transition temperature (in amorphous/semi-crystalline materials), heat of fusion, reaction kinetics, etc. The technique measures the temperature and the heat flow, corresponding to the thermal performance of materials, both as a function of time and temperature.

Typically a DSC will utilize a heat flux type system in which the differential heat flux between a reference (e.g. sealed empty aluminum pan) and a sample (encapsulated in a similar pan) is measured. The reference and the sample pans are placed on separate, but identical, stages on a thermoelectric sensor platform surrounded by a furnace. As the temperature of the furnace is changed (usually by heating at a linear rate), heat is transferred to the sample and reference through the thermoelectric platform. The heat flow difference between the sample and the reference is then measured by measuring the temperature difference between them by using thermocouples attached to the respective stages. The DSC provides qualitative and quantitative information on endothermic heat absorption (e.g. melting) and exothermic heat release (e.g. solidification or fusion). These processes display sharp deviation from the steady state thermal profile, and exhibit peaks and valleys in a DSC thermogram (heat flow vs. temperature profile). The latent heat of melting or fusion can then be obtained from the area enclosed within the peak or valley.

DSC analysis is an extremely critical and useful tool in characterizing the thermodynamic quantities of polymer, specifically in identifying $T_g$ and $T_m$ as well as determining if a polymer is amorphous or crystalline.

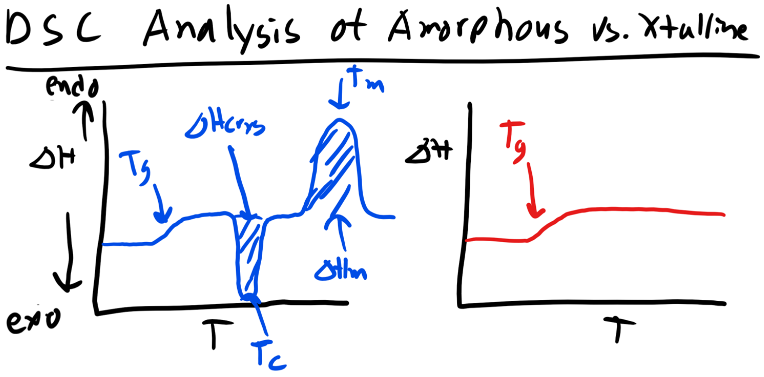


Figure 10-16: Amorphous Vs. Crystalline DSC Curves

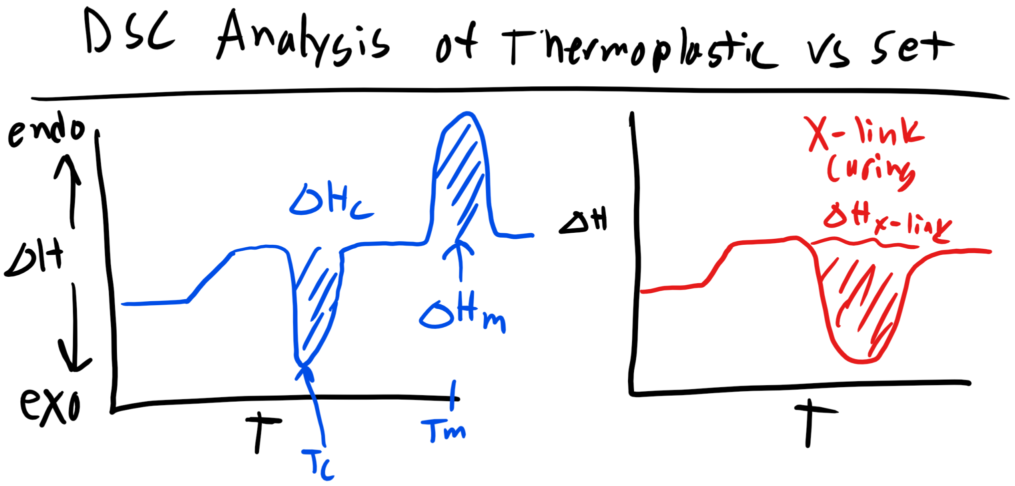


Figure 10-17: Thermoplastic Vs. Thermoset DSC Curves

As you can see below if we are working a polymer that is semi-crystalline we can typically observe 2 peaks in the DSC curve as well as a change in the slope of the curve of heat flow vs temperature. Let's take this analysis step by step. If we remember back to Materials Science we know that a first order phase transition will result in a discontinuity in the first order derivative of the free energy as a function of temperature (at the temperature of the transition). Whereas second order transitions will exhibit a discontinuity in the second derivative of the free energy and will only exhibit a change in slope for the first derivative as a function of temperature. Now the plot that we are looking at is heat flow vs temperature which is essentially $\delta H$ vs $T$ so we are looking at a plot of the first derivative of free energy.

Now the first feature that we come across (increasing in temperature) is a change in slope. Well we know this must be a second order transition. Additionally we know that this transition occurred at fairly low temperatures. Since our sample is a polymer this transition most likely signifies the glass transition temperature, $T_g$. This should make sense as we know the $T_g$ is a second order transition. Now the next feature that we see is an exothermic peak. Well we know that this peak indicates a first order transition and if this is an exothermic reaction this should signify some solidification or re-crystallization, $T_c$. This might at first seem counter-intuitive, why would increasing temperature cause the polymer to crystallize? Well it is because as we increase temperature we increase the mobility of the previously glass amorphous regions. With this increased mobility there is a higher likelihood of encountering other chains the enthalpic interactions accessed here might favor the formation of crystalline regions. This curve might not show up in every polymer. The last peak is an endothermic one and we will recognize this as the melting point, $T_m$. Now remember this does not break the carbon-carbon backbone bonds but instead the secondary intermolecular interactions.

How would this curve change for a purely amorphous polymer? Well we would simply see a change in the slope to indicate the glass transition and the would be it. Now what if you had a thermoset polymer which has to cure and form crosslinks. Well, we would see a $T_g$ as this is still a polymer. Now would you see a melting temperature? No a thermoset does not undergo melting due to the permanent crosslinks! They would exhibit an exothermic peak that would indicate the energy required to cure/crosslink the polymer!

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# CHAPTER 11

## POLYMER DYNAMICS, DIFFUSION, KINETICS

## 11.1 Key Terms/Definitions:

- **Entanglement** - a topological constraint imposed by two polymer chains that intertwine and hence are relatively fixed in place by steric effects.
- **Rouse regime** - low-molecular weight polymer melts are said to be in the Rouse regime, where their diffusive motion is described by the freely-draining model and entanglements do not significantly affect polymer motion.
- **Reptation regime** - high-molecular weight polymer melts are said to be in the reptation regime, where the diffusive motion of each chain is constrained by fixed entanglements. Compared to the Rouse regime, polymer diffusivities are lower and viscosities are higher in the reptation regime.
- **Critical molecular weight** - the molecular weight that marks the transition between the Rouse and reptation regime; typically on the order of $10^4$ g/mol.
- **Reptation** - the snake-like motion of a single polymer chain diffusing through a constraining array of fixed entanglements; often visualized as 1-dimensional diffusive motion through a confining tube that avoids all topological obstacles.
- **Rouse time** - the time taken for a polymer coil to diffuse a distance equal to its own size in the Rouse regime; qualitatively analogous to the characteristic relaxation time.
- **Disengagement time/longest relaxation time/reptation time** - the time taken for a polymer coil to diffuse a length equal to its own size in the reptation regime, analogous to the Rouse time.

**Polymer Dynamics, Diffusion, Kinetics:**

Today we will tackle the concept of polymer *dynamics* in **solution** and in the **melt state**. The general idea to remember is that polymer chains tend to be **highly intertwined** so that a **single polymer chain will interact/overlap/interpenetrate with the volume occupied by other polymer chains**. We can then imagine chains becoming **stuck** on one another. Essentially, a single chain can act as a **topological obstacle** preventing the free motion of a different chain. We call this obstacle an **entanglement**. Again, you have seen this at the macroscale with spaghetti noodles becoming stuck, etc. Since these obstacles are inherently kinetic in nature we will be focusing on polymer properties that reflect system kinetics - specifically, polymer viscosities.

## 11.2 Viscosity and Diffusivity of Polymer Melts:

We will start our discussion on the **viscosity** and **self-diffusion properties of polymers in the melt state (no solvent)**. A perplexing problem that bothered polymer scientists for a long time was the **change in slope of polymer viscosity in the melt as a function of molecular weight**. At some particular molecular weight **the viscosity of the melt changes its scaling exponent with respect to polymer molecular weight**. Since this occurs for **polymers in the melt (only polymer), solvent effects cannot matter**.

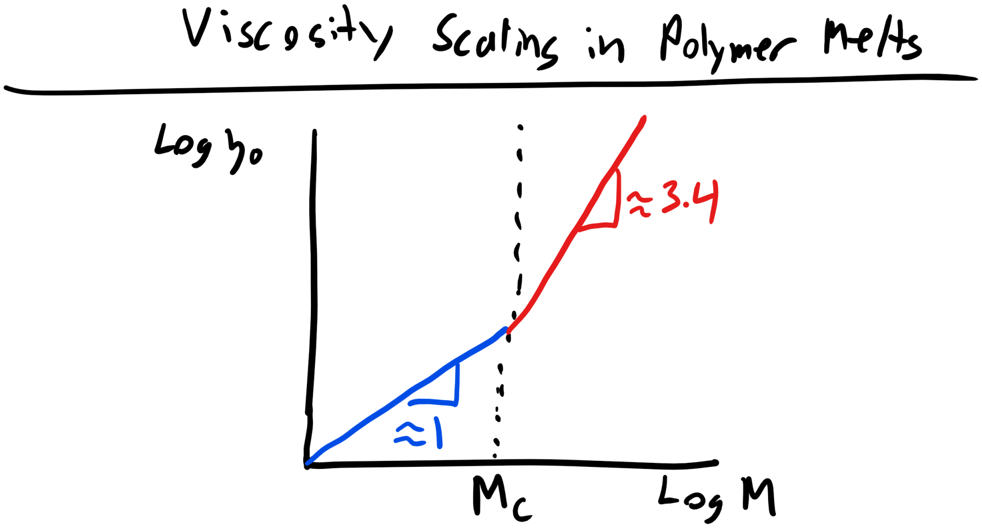

Figure 11-1: Viscosity of Polymer Chains in the Melt State as a Function of Molecular Weight.

Below this **critical molecular weight ($M_c$)** the viscosity tends to scale as

$$\eta_0 \propto M^1 \tag{11.1}$$

however above the $M_c$ the viscosity scales as

$$\eta_0 \propto M^{3.4} \tag{11.2}$$

here the increase in viscosity is dramatically larger as molecular weight increases! The low MW regime is called the **Rouse** regime and the high MW regime is called the **Reptation** regime. As we will see, the critical molecular weight for the crossover between these two regimes will depend on the presence of **entanglements** in the system, which we described above as **topological constraints** due to the tendency of polymers to interpenetrate when concentrated. The critical molecular weight is thus also referred to as the **entanglement molecular weight**.

Typically the $M_c$ is on the order of $10^4$, which **does not correspond to a large number of repeat units per chain** - for example, for polystyrene, only about 200 repeat units are necessary to reach the critical molecular weight. We can look at the structure of the repeat unit to gain

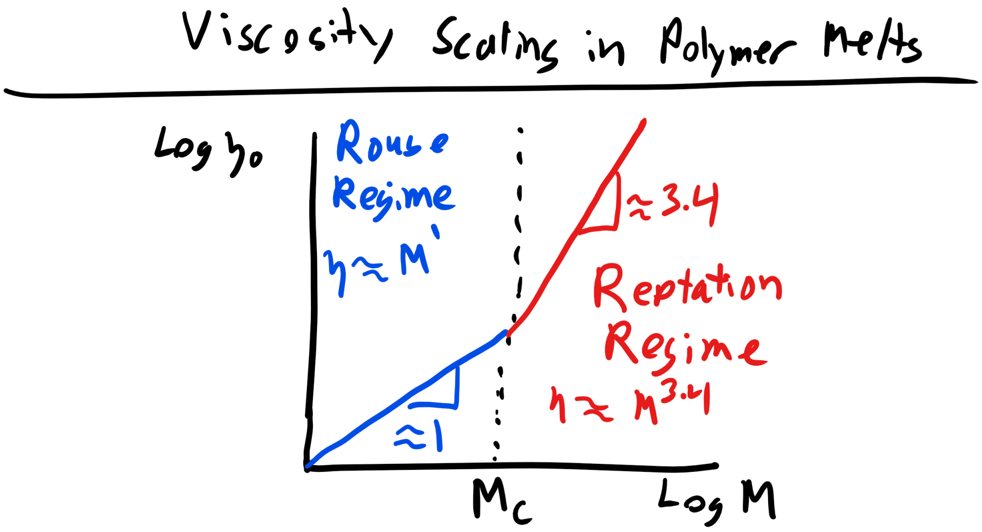

Figure 11-2: Scaling Behavior of the Viscosity of Polymer Chains in the Melt State as a Function of Molecular Weight.

some insight into the critical molecular weight - typically, **more flexible chains will lead to entanglements more easily** or at **lower molecular weight**. Hence, **polyethylene** will probably have a much **smaller critical molecular weight** than **polystyrene**, given that **polystyrene has a large phenyl group which inhibits chain flexibility**.

The **diffusivity of polymer samples** also shows similar molecular weight behavior.

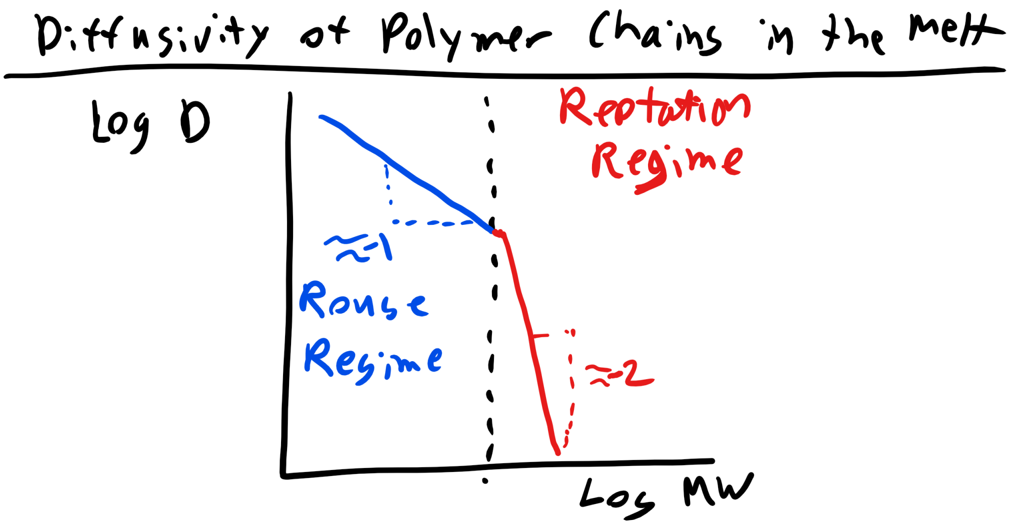

Figure 11-3: Diffusive Scaling Behavior in the Rouse and Reptation Regimes.

In small molecule liquids, **diffusive motion is accomplished via random, stochastic jumps of molecules between adjacent free volume**, similar to **monomer motions through**

**free volume** as described in our discussion of the glass transition temperature. In polymers, however, we observe **much much lower diffusivities than small molecules** - the **diffusion coefficients of small molecules** tend to be on the order of $10^{-5} cm^2/s$, while the **diffusion coefficients of polymers** are usually between $10^{-14}$ and $10^{-18} cm^2/s$, a 9-13 order of magnitude difference! Let's think about what the physical implications of these much smaller diffusion coefficients. Remembering back to ENGR045 the mean-squared displacement from diffusion can be related to diffusivity by:

$$\langle x^2 \rangle = Dt \tag{11.3}$$

This relation is the fundamental equation of **Brownian motion**, and tells us that in a time $t$ the mean-squared displacement of a molecule in 1 dimension is linear with its diffusion coefficient. So if we let $t = 1sec$ we guess that a typical small molecule would move

$$L = \sqrt{\langle x^2 \rangle} \approx \sqrt{D} \approx 10^{-3} cm = 10^{-5} m \tag{11.4}$$

Thus we can say that in one second, small molecules (with a size of about 1 nm) move a distance about $10^4$ times their size! This is incredibly fast, and gives some insight into the fast rearrangement of small molecules when perturbed. Now we can repeat this same exercise for polymers, with their much lower diffusivity

$$L = \sqrt{\langle x^2 \rangle} \approx \sqrt{10^{-14}} \approx 10^{-7} cm = 1nm \tag{11.5}$$

So the polymer tends to move about 1 nm in one second - if we assume that your **average polymer is about 10 nm in size**, then the polymer only displaces 1/10 times its size. Hence, the takeaway is that on average, **polymers move much more slowly than small molecules due to diffusive motion**. If we repeat this calculation for a polymer in the regime where diffusivity is on the order of $10^{-18}$, then this relative motion decreases even more - so **the polymer experiences very little diffusive motion at all**. You can also think instead of how long it would take for a **polymer to diffuse a distance equal to its own size, which would be on the order of hours**. This fact clearly has processing implications, and we also see that we can **tune the diffusion time based on the scaling regime**. So we can get a **very rough estimate of the relaxation time by looking at the time necessary for a polymer to diffuse a length equal to its size/radius of gyration**.

$$\tau^* \propto \frac{\langle R_g^2 \rangle}{D} \tag{11.6}$$

Now we need to understand how to calculate the diffusion coefficient for these two different regimes.

## 11.3 Rouse Regime:

Before we get into talking about the **Rouse Regime** we need to remember back to to the **two regimes that we described when talking about the viscosity of a polymer solution**, additionally let's consider some key equations that we have mentioned throughout this course.

1. $\langle x^2 \rangle = Dt$ – Brownian motion fundamental equation
2. $D = \frac{kT}{\xi}$ – Brownian particle diffusion with a friction factor in host medium
3. $F = \xi v$ – Frictional force for particle moving with velocity $v$ in host medium

The first regime being the **non-draining model** which was appropriate for long, highly coiled polymers, where the polymer coil was thought of as a sphere impenetrable to solvent. The individual monomers on the interior of the coiled polymer experience strong shielding from solvent interactions due to hydrodynamic interactions. Thus, in the non-draining regime these hydrodynamic interactions make the spherical coil appear as a single, impenetrable sphere, and we found that the **viscosity scaled with the size of the sphere**.

The other model, **freely-draining model**, was appropriate for short, highly elongated polymers, where each chain was thought of as a collection of connected monomers that independently interact with solvent. In this regime, **no hydrodynamic interactions are present** as monomers do not see each other due to the elongation of the chain. We thus found that the **viscosity scaled with the number of monomers**.

Both of these models were originally discussed in the context of a polymer in solution with a small molecule solvent. In a **polymer melt**, however, the **polymer is its own solvent**. Because a given monomer cannot distinguish between monomers from the same chain or other chains, in the melt state there will be significant penetration of the solvent into any given polymer coil. Hence, in **the melt state the polymer coils can be described using the freely-draining model**, where we can think of a **single polymer chain as a flexible connected string of particles moving in the presence of a featureless viscous background**. The key here is **featureless**, as the polymer effectively **does not see individual solvent molecules (other chains) other than their influence on the viscosity**; at higher molecular weights (in the reptation regime) we will see that solvent background can no longer be considered featureless due to the presence of entanglements. So in this regime the molecular weight is low enough so the chains are effectively able to move past one another. They can unentangle.

In this **freely-draining model / Rouse regime** the viscosity is given as

$$\eta \approx \xi N \text{ so } \eta \approx M^1 \tag{11.7}$$

We can relate the diffusivity to the friction factor of the entire polymer chain via the Einstein relation recognizing that the friction factor of the entire chain scales as the number of monomers

$$D = \frac{kT}{\xi_{chain}} \approx \frac{kT}{N\xi_{monomer}} \text{ so } D \approx M^{-1} \tag{11.8}$$

This simple model thus correctly obtains the scaling of the diffusion coefficient! Finally, note that we can now obtain the time scale over which a polymer chain diffuses a distance equivalent to its own size, which is called the **Rouse time** in the Rouse regime

$$\begin{aligned} \tau_{Rouse} &= \langle R_G^2 \rangle / D & (11.9) \\ &= \frac{\xi_{monomer}}{kT} N \langle R_G^2 \rangle & (11.10) \end{aligned}$$

This is the time scale over which the polymer coil is able to effectively rearrange, it is **qualitatively the same as the characteristic relaxation time**. Note that the **Rouse time increases with increasing molecular weight**, implying that **higher molecular weight polymers take longer to respond to perturbations**. We can thus correctly explain scaling behavior for the **Rouse regime** ($M < M_c$) using the **freely-draining model**, and recover the scaling exponents of the viscosity and diffusivity observed experimentally.

However, we still need to understand the higher molecular weight regime called the **reptation regime**.

## 11.4 Reptation Regime:

In the **reptation regime**, we imagine a physical picture of a single polymer chain surrounded by **fixed entanglements** which act as **impenetrable obstacles** through which the **chains cannot move**. In the **entanglement regime**, the **distance between these obstacles is much smaller than the length of the chain**, such that the **chain's path of motion is heavily influenced by these obstacles**. Unlike the Rouse regime, where the solvent background was featureless, in the **reptation regime the motion of a single polymer is thus highly constrained by other chains due to the presence of entanglements**, and we might qualitatively expect a **higher viscosity and lower diffusivity** due to the constraints.

We can begin by **imagining the polymer coil as constrained in a tube of free volume that surrounds the polymer chain**. You can imagine the **tube drawn through a sea of topological constraints**, representing the entanglements, such that the **tube is as thick as possible without overlapping any entanglements**. **Within this tube**, the polymer is capable of **freely diffusing**. We know that we can approximate the size of our polymer coil by

$$\langle R^2 \rangle = Nb^2 \tag{11.11}$$

We also know that the contour length of the chain is

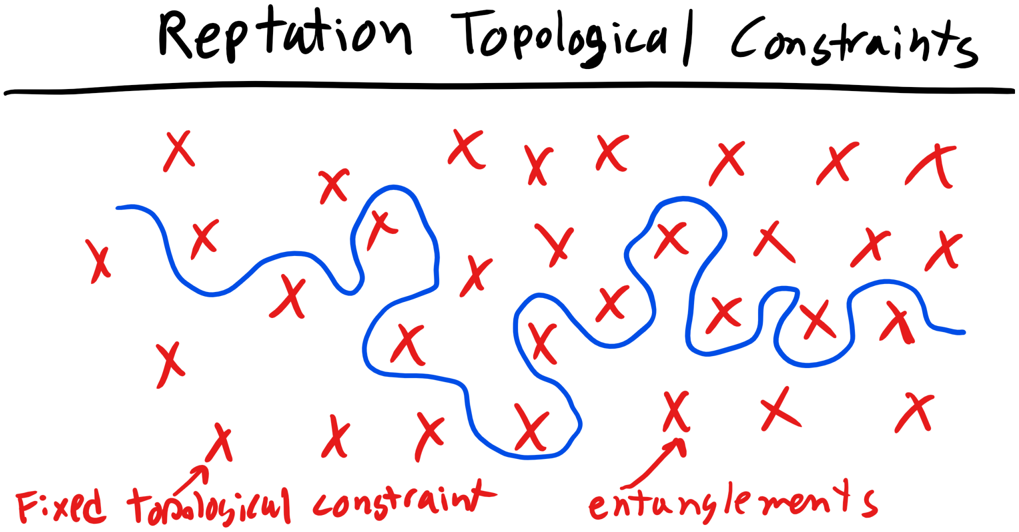

Figure 11-4: Schematic Polymer in Reptation Regime.

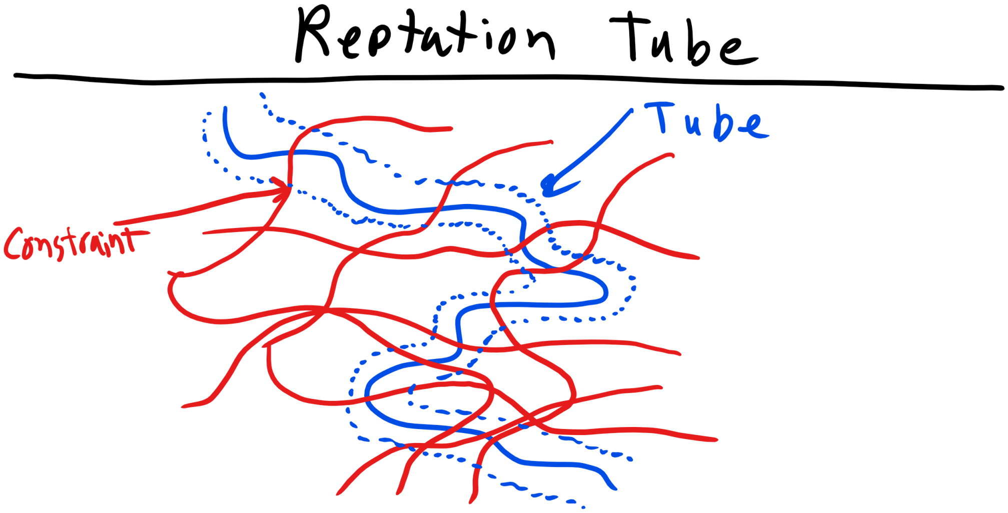

Figure 11-5: Entanglements in Reptation Regime.

$$L = bN \tag{11.12}$$

Since our tube is all around our coil, we can thus say that the **tube contour length is the same as the chain contour length**, and the **tube end-to-end distance is the same as the chain end to end distance**. If we let $Z$ equal the number of tube segments and $a$ equal the length of each tube segment, then we can say that:

$$Za^2 = Nb^2 \tag{11.13}$$

$$Za = Nb \tag{11.14}$$

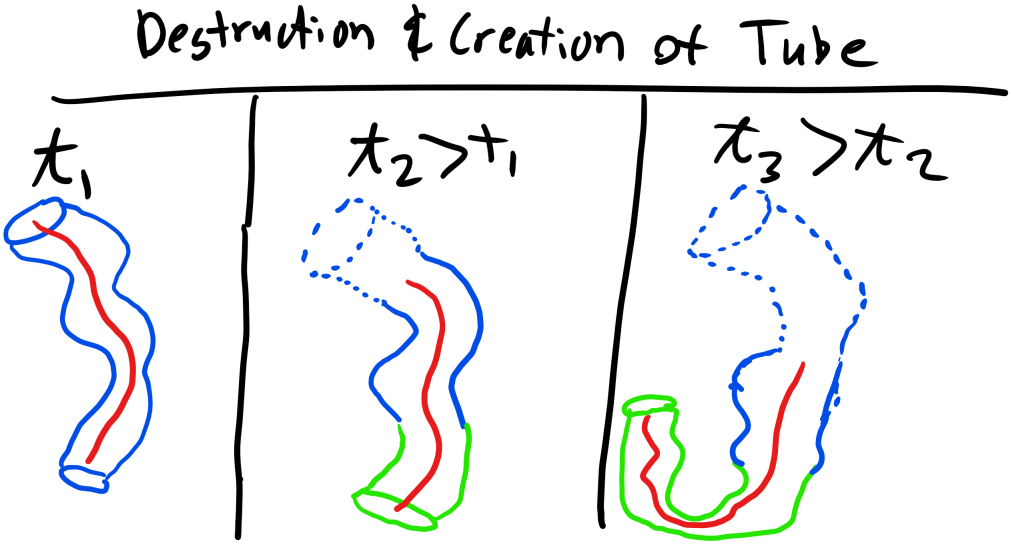

Figure 11-6: Schematic of Tube Creation and Destruction during Reptation Motion.

As the polymer moves, the **front of the tube moves forward into available free volume**, while the **back of the tube is destroyed**, reflecting conservation of volume. We call **this movement reptation** - the name reflects the snake-like motion that we are trying to convey. What we want to find is the **time it takes for a tube at some given instant to be completely destroyed, and replaced by a new tube** - this would correspond to the **time it takes for a polymer coil to diffuse its own length**. We call the time necessary for the formation of a completely new tube the **disengagement time**. Inside the tube, we assume that the chain is free to diffuse within the constraints of the tube walls since the interior of the tube is free of entanglements/obstacles. Hence, **inside the tube the motion is akin to that of the Rouse regime**, since the polymer will tend to be elongated as a result of the tube constraints. We can thus zoom-in on one section of tube and calculate the time necessary for the polymer to diffuse completely out of a tube section - this will give us the time for tube creation/destruction that we described above. Since this is like the Rouse regime we can say

$$D_{tube} = \frac{kT}{N\xi_{monomer}} \tag{11.15}$$

which is the same as Rouse-like polymers with number of monomers N. Note that the physical motion we are picturing is the random 1-dimensional diffusion of the polymer chain back and forth inside the tube (with some radial movement as well within the tube volume). Next, we want to know the **time the coil takes to move its entire contour length**, where motions are given by the **diffusivity of the Rouse regime**

$$\langle x^2 \rangle = L^2 = D_{tube}\tau \tag{11.16}$$

$$\tau = \frac{L^2}{D_{tube}} \approx \frac{\xi_{monomer}}{kT} N L^2 \tag{11.17}$$

$\tau$ is also called the **longest relaxation time in addition to the disengagement time**, and is the time at which the **polymer starts to flow after feeling a stress** - that is, $\tau$ is how l**ong it takes for rearrangement to occur**, qualitatively equivalent to the **characteristic relaxation time in the reptation regime or the reptation time**. We can see from the equations above that

$$L^2 = (bN)^2 \tag{11.18}$$

$$M \propto N \tag{11.19}$$

$$\tau \propto M^3 \tag{11.20}$$

Additionally, we know that viscosity scales linearly with flow time (we will show this in the mechanics section)

$$\eta \propto M^3 \tag{11.21}$$

In the reptation regime, then, our simple derivation gives approximately correct scaling, experimentally it is $M^{3.4}$).

We can derive the diffusion coefficient for entangled chains in the reptation regime as well. We can think that in time $\tau$, the entire polymer coil has moved a distance approximately given by its own size, which we can approximate using the radius of gyration, so

$$R_g^2 = D_{rept}\tau \tag{11.22}$$

$$D_{rept} = \frac{R_g^2}{\tau} \approx \frac{N}{N^3} \approx \frac{1}{N^2} \tag{11.23}$$

Hence, we get the proper scaling of the diffusivity for entangled melts. Note that it is proportional to $1/M^2$ versus the $1/M$ scaling in the Rouse regime

$$D_{rouse} = \frac{kT}{N\xi} \tag{11.24}$$

Our qualitative intuition that in the reptation regime viscosity will be higher ($\propto M^3$ vs $\propto M$) and the diffusivity will be lower ($\propto 1/M^2$ vs $\propto 1/M$) **than in the Rouse regime is correct -**

the t**opological constraints imposed by entanglements slow down polymer dynamics**.

Note carefully the distinction between how we derived $D_{rept}$ and how we derived the longest relaxation time $\tau$. $\tau$ was found based on the assumption of Rouse-like motion in each tube segment, and corresponded to the time necessary for the polymer coil to slide through a tube length equal to the contour length. We then essentially zoomed out and **realized that if the coil moved through a tube equal to the contour length, then the entire center of mass must have moved a distance approximately equal to the radius of gyration** - that is, the **polymer moved a distance approximately equal to its own size**. We used this to find the diffusivity. The **motion of the polymer IN the tube is effectively 1-dimensional along the tube length**, while the **motion of the tube itself is a 3D random walk**. The major contrast between the Rouse regime and the reptation regime is not in the motion of the center of mass of the polymer but rather in the process by which this center of mass moves; in the Rouse regime we can imagine any given segment of the polymer as effectively random walking without constraints, while in the reptation case the fixed entanglements force only limited 1D motion. **These two different views/length scales of the polymer coil's motion - i.e. the motion of individual parts of the polymer vs. motion of the entire polymer coil - are what make reptation a unique form of motion!**

**Polymer-Polymer Diffusion**

So far we have been talking about only the diffusion of a single polymer species, i.e. **self-diffusion**. What happens if we want to think about the diffusion of two different polymer species into each other? What about if the two species have different molecular weights? Hold your horses with all the questions, we can deal with this by thinking about two different scenarios

1. **Fixed obstacles** - you can think of a background matrix of large, **entangled chains** corresponding to the larger of the two polymers. The **shorter of the two polymers then diffuses among these topological constraints**. Since the larger chains have a lower diffusivity, they are apparently **fixed** compared to the faster moving short chains.

2. **Constraint release** - the **small chains act as a featureless background**, and we can envision the **long polymer constraints gradually diffusing against the viscous background without encountering topological obstacles**. The main idea is that because the **short polymers diffuse much more quickly than the large chains**, any **topological constraints associated with the short chain would disentangle more quickly than the large chains could interact with them anyway** and hence would not significant constrain the motion of the large chains.

Note that these same arguments/descriptions may be made for a polydisperse sample of a single species - in either case, the large polymers, with their much slower diffusion times, dominate the overall diffusion process.

However, it should be apparent that the diffusion of either species is going to be different in a blended case than in the self-diffusion case. Specifically, we can recognize that **enthalpic effects**

**can play a large role** - if two polymer species enthalpicly prefer to be mixed (as would be the case if there are some strong intermolecular interactions between the two species), then diffusion will tend to speed up. Recall that the $\chi$ parameter essentially reflects the enthalpic contribution to polymer mixing. If $\chi > 0$, then mixing is not preferred enthalpicly. As a result of this enthalpic barrier, **interdiffusion is slowed down**. In the case of large $\chi$, interdiffusion is stopped completely, as would be expected for immiscible polymer blends.

In the case of $\chi < 0$, where mixing is preferred enthalpicly, we can refer back to Flory-Huggins theory to find the change in free energy of mixing, given by

$$\frac{\Delta G_M}{NkT} = \frac{\Phi_1}{x_1} \ln \Phi_1 + \frac{\Phi_2}{x_2} \ln \Phi_2 + \Phi_1 \Phi_2 \chi_{12} \tag{11.25}$$

When discussing Flory-Huggins theory we only really discussed the $\chi > 0$ case where mixing entropy dominated mixing. If $\chi < 0$, enthalpy dominates and we can assume that:

$$\Delta G_M \approx NkT \Phi_1 \Phi_2 \chi_{12} \tag{11.26}$$

Hence, we can see that the free energy change scales directly with $N$. It was found that this factor of $N$ also then **increases the rate of diffusion** by a factor of $N$ as well, increasing the molecular weight scaling above what would be expected from the simple derivation before. You can think of this in terms of a **driven** motion of the polymer coils into each other due to the free energy difference, which then acts on top of the normal diffusive motion, **leading to a net increase in diffusive speed**.

**Supplemental Qualitative Description of Rouse and Reptation:**

When we discussed viscosity way back we found that that the scaling behavior of a polymer's viscosity was dependent on whether the solvent was able to effectively interact with every monomer in a polymer coil (freely-draining model) or only interact with the coil as a whole (non-draining model). In the non-draining model, we said that hydrodynamic interactions related to some monomers "shielding" others from the influence of the solvent led a coiled-up polymer to look like a single sphere to the solvent; in the freely-draining model, we said that in relatively elongated polymers there were no such hydrodynamic interactions and every monomer interacted with the solvent independently.

In a polymer melt, there is no additional solvent, so we effectively can think of a melt as a single chain dissolved in other chains. In this case, a given monomer has no ability to distinguish monomers along the same chain from monomers in other chains (i.e. "solvent" monomers). As a result, we have described polymers as highly interpenetrating, and thus the "solvent" interacts with all of the monomers in a given chain - i.e. the freely-draining model is appropriate to describe the viscosity of a melt. We called the application of the freely-draining model to the polymer melt the Rouse regime and effectively repeated the derivation from Lecture 5 to find the scaling of the diffusion coefficient and viscosity.

While the Rouse regime makes sense in the context of a single polymer chain moving in a viscous solvent consisting of other chains, an implicit assumption of the model is that the diffusion of this chain is completely unconstrained - that is, other chains only act as viscous solvent but do not otherwise obstruct motion. However, as polymer chains get longer and longer, they will increasingly intertwine and form what are called *entanglements*, or topological constraints where polymer chains are stuck due to steric barriers and effectively cannot move. Since entanglements can be thought of as fixed, any given chain that is diffusing in the presence of entanglements must move to avoid steric hindrance from these fixed points; in other words, the entanglements constrain the motion of other chains. It is analogous to running through a field and then suddenly encountering a forest - the onset of fixed obstacles necessitate that you slow down to avoid intersecting the constraints (my other crazy example is reptation is like a Plinko machine, google it for hilarious Price is Right results). We called diffusion in the presence of entanglements *reptation.* The key point that we recognized was that entanglements are more likely to form when polymer chains are long, and thus the molecular weight is higher; we thus define a reptation regime where the molecular weight of the polymer is above a certain critical threshold and the diffusive motion transitions from being primarily Rouse-like to primarily reptation.

To quantitatively describe reptation, we invoked the idea of a "tube" of free volume surrounding a polymer chain, where the size of the tube reflects the position of constraints with respect to the chain. Inside the tube, we imagined the motion of each section of the chain as relatively unconstrained, and therefore would be described using the Rouse model since the polymer is highly elongated. We thus picture the chain diffusing in 1 dimension, either forward or backward along the tube. As the polymer gradually diffuses forward, we imagine the front of the tube growing into the available free volume between constraints while the back of the tube is "destroyed" to maintain volume conservation. Note that the growth of the tube itself is effectively a random walk - over a large length scale, the tube looks coiled up as it navigates in between obstacles. However, if we zoom-in on the tube and look at the segments of polymer inside the tube itself, there the constraints of the tube restrict the motion to effectively 1D and the polymer looks elongated. We thus have to think of the motion of both the segments of the chain inside the tube and the tube itself separately, as their properties essentially exist over different length scales (and time scales).

We called the time scale over which a given tube is completely reconstructed the longest relaxation time. Note what this time means physically - the polymer chain has travelled a distance inside the tube equivalent to the length of the tube, which is itself equivalent to the contour length of the chain reflecting the 1D motion of the chain inside the tube. If we look at the center of mass of the chain, however, it is has travelled a distance equivalent to its radius of gyration, since the tube itself has moved in a random walk. Therefore, the time necessary to reptate a distance equivalent to the size of the polymer chain can be inferred from the amount of time it takes to diffuse the contour length of the polymer inside the tube. Qualitatively, since the contour length of the tube is much larger than the radius of gyration, this time scale is much longer than the time scale to travel the radius of gyration in the Rouse regime and reptation is much slower than diffusion in the Rouse regime. Finally, we should note that this time scale is also the time scale necessary for entanglements themselves to form and disentangle, so the assumption of fixed constraints is a bit simplistic; however, you can argue that the Rouse motion INSIDE the tube is still very fast compared to the reptation time, so the assumption is justified.

Thus, we are able to relate the amount of time taken for a polymer to diffuse a distance its own size to the molecular weight of that polymer, since at low molecular weights its motion will be described by the Rouse (freely-draining) model while at high molecular weights its motion will be described by reptation. We also related the time necessary to travel this distance to the relaxation time of the polymer, which again as we said above governs the ability of the polymer to return to equilibrium. Connecting these concepts leads to an interesting observation - because this analysis effectively says that the relaxation time is much longer in the reptation regime, and we saw earlier that long relaxation times are characteristic of solids, does this mean that in the reptation regime the polymers act like solids?

The answer to this question is a qualified yes. As the relaxation time of a material increases from a viscous liquid-like state to a solid elastic-like state, it will enter a regime where the material is viscoelastic and demonstrates qualities of both phases. Viscoelastic behavior is highly characteristic of rubbery materials which we will discuss in the next lecture. In the reptation regime, we do indeed observe rubbery behavior even in the absence of physical or chemical cross-links. The molecular reason is that entanglements act as cross-links; however, in the context of time scales, we can also say that the relaxation time of an entangled melt is much higher than an unentangled melt and thus the melt enters the viscoelastic regime.

One final point that bears mention is the idea of the molecular weight of a polydisperse sample. If we say that there is a single critical molecular weight that determines the difference between the Rouse regime and reptation regime, but we have a sample that consists of many polymers of different molecular weights, how do we determine what regime we are in? More specifically, what molecular weight average would be appropriate to describe this sample. We can think of this in the behavior of small and large chains mixed together. Small chains in the Rouse regime will have a much higher diffusion coefficient than the larger chains, and as a result will diffuse effectively instantaneously compared to the large chains. Diffusion of the large chains is thus ”rate-limiting”, and as a result the weight-average molecular weight will provide a better average than the number-average molecular weight because it better characterizes the molecular weight of larger polymers in the sample.

# Part III

# Polymer and Composite Mechanics and Viscoelasticity

# CHAPTER 12

## POLYMER ELASTICITY

## 12.1 Key Terms/Definitions:

- **Elastic deformation** - strain that is recovered upon the removal of an applied stress; strain energy stored in the material.
- **Young's modulus** - a measure of the stiffness of the material; strictly the slope of the stress-strain curve in the linear elastic regime under uniaxial tension.

## 12.2 Review of Material Mechanical Behavior:

Today we will now analyze the mechanical properties of polymers, or more specifically the response of polymers to applied stresses. Polymers are much more complex mechanically than the metals or ceramic materials that were the focus of ENGR045. Polymers can exhibit **liquid (viscous)**, **elastic (glassy/rubbery)**, or **viscoelastic (viscous and elastic)** behavior which we will discuss in a bit. The mechanical response of polymers is intimately related/determined by the timescales of the applied stresses, the temperature, and the structure of the polymer. Before we do this let's take a quick minute to do a nice Mechanics Review.

## 12.3 Overview of Polymer Mechanics:

Typically, **elastomers and gels are the least stiff polymers** (lowest Young's moduli), while **semi-crystalline and glassy polymers tend to be much stiffer**. **Glassy polymers tend to fracture at much lower elongations** than semi-crystalline polymers, which are able to elongate to much larger strains before fracture. In general the Young's moduli of gels and elastomers are lower than metals since deformation is related to the entropic spring response, not actual stretching of bonds. One final note about gels - since they are swollen with lots of solvent, which flows like a liquid, they tend to have the lowest moduli of all. There can be up to a **9 order of magnitude difference in the Young's modulus between polymer gels and polymer crystals**, leading to highly tunable mechanical attributes that are tied to the underlying microstructure of the polymer. For example, you can imagine changing the crosslinking attributes of a polymer to lead to a elastomer, then adding solvent to swell like a gel, leading to many different changes in Young's modulus.

A major difference between polymers and metals is the maximum amount of elongation (strain) possible before yield. Metals are typically restricted to a strain of about 0.1, reflecting the mechanism of bond-stretching associated with strain in metals. Polymers, however, can elongate to much, much longer strains, on the order of 5-10, due to their long-chain microstructure. This is a massive number compared to what is observed in metals, a 3 order of magnitude difference. So, polymers tend to have a **much higher toughness than metals**, which is defined as the total energy necessary to induce fracture.

**Mechanical properties are highly dependent on temperature**. At **very low temperatures, polymers tend to be brittle**, reflecting the glassy state. As the **temperature increases** and the polymer goes through its glass transition temperature, the **modulus of the polymer falls but its maximum possible elongation greatly increases**, reflecting a transition to a rubbery state. The **toughness also increases with temperature**, undergoing a transition at some point between brittle behavior (low fracture strain) to more ductile behavior (large amounts of plastic deformation).

- **Glassy polymers** - high elastic modulus, fail at (relatively) low strains; minimal plastic deformation.
- **Elastomers (rubbers)** - low elastic modulus but high strain to fracture; non-linear elasticity due to strain softening/hardening at high elongation; minimal plastic deformation prior to fracture.
- **Semi-crystalline polymers** - medium elastic modulus; clear onset of yield followed by necking/large amounts of plastic deformation

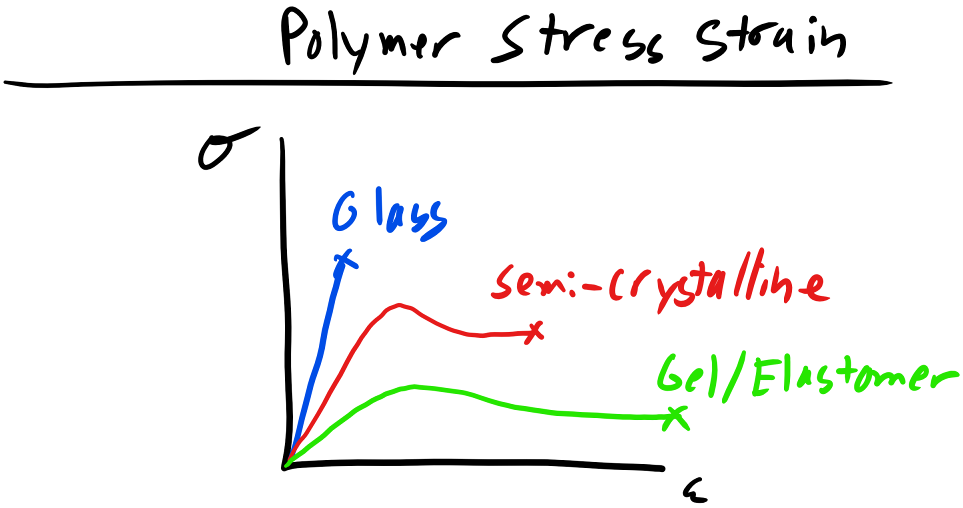

Figure 12-1: Polymer Stress-Strain Curves.

## 12.4 Stress-Strain Curve:

When a material is placed under a stress state we will typically plot a stress-strain curve and that curve typically will have 3 distinct regions: **I) Elastic, II) Plastic, III) Fracture**.

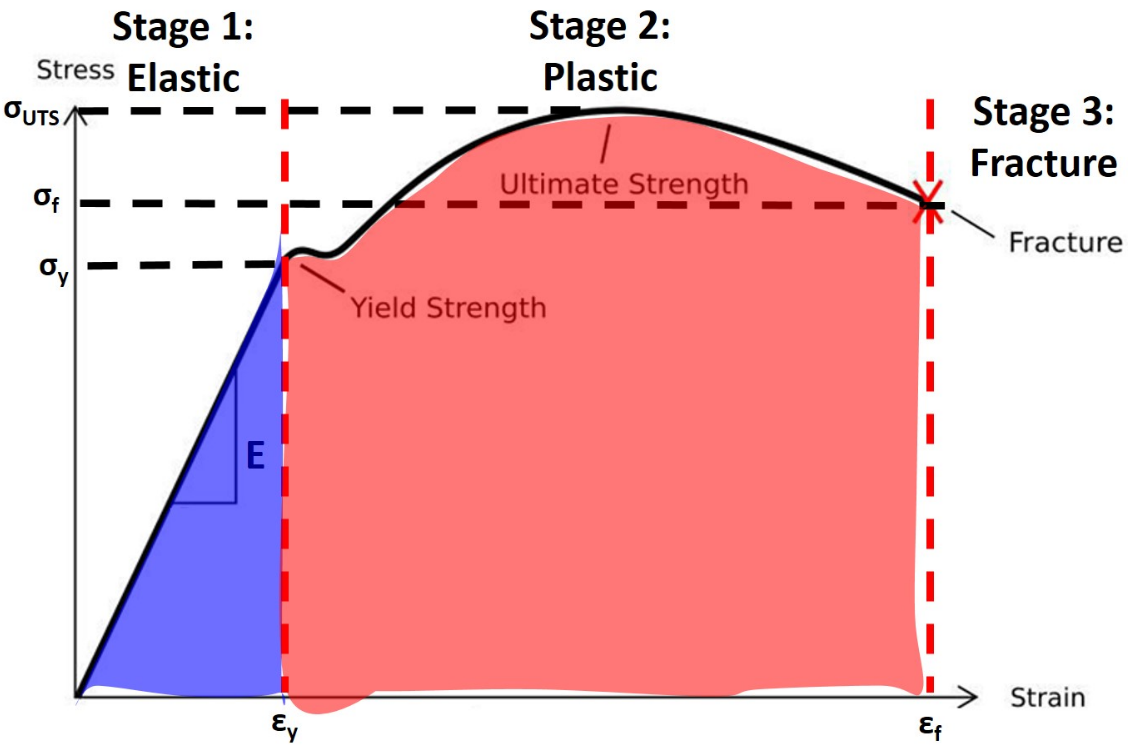

Figure 12-2: Stress Strain Curve.

**I) Elastic Regime:**

In the **elastic regime** the stress strain response is linear and defined by the expression below which should be familiar (Hooke's Law):

$$\sigma = E\epsilon \tag{12.1}$$

where E, sometimes Y, is defined as the **Young's Modulus**. It describes the stiffness of the material and is a material constant. **Metals** are typically in the **100s of GPa**, **ceramics** are high **200's and 300's of GPa**, **polymers** are closer to on the order of **1 GPa**. In the elastic region the strain is **completely reversible**, i.e. **there is no permanent or plastic deformation**. You are just **pulling on the bonds not breaking any bonds**.

**II) Plastic Regime:**

Here you are **plastically** deforming the material and this is signified microstructurally by the **breaking of bonds** and the **movement of dislocations**. Additionally with **plastic dislocation the strain is not reversible**, if you remove the force the strain remains. It is signified to begin on the stress strain curve by $\sigma_y$ which is the **yield stress** and $\epsilon_y$ the **yield strain**. The $\sigma_{UTS}$ is the **ultimate tensile strength** and it denotes the **onset of necking** which is where the instantaneous area is now smaller than the original area.

**III) Fracture:**

As the name denotes this is where the material catastrophically fractures and is denoted by $\sigma_f$ which is the **fracture stress** and the $\epsilon_f$ is the **fracture strain**.

At this point we need to stop and make a clear point about the language that we have to use when discussing the material properties of materials. Word choice is critical here because they mean very different things. When we talk about the **stiffness** of materials we are talking about the **Young's modulus** of the material. The higher the Young's modulus the stiffer the material. When we talk about **strength** we are talking about the **yield strength**, the **ultimate tensile strength**, or the **fracture stress or strength**. We we are talking about how **ductile** a material is we are talking about the **strain at failure**. We also often talk about material resilience and toughness as well.

We define the **elastic strain energy** which is defined as

$$U_r = V \int_0^{\epsilon_y} \sigma_{11} d\epsilon_{11} \tag{12.2}$$

where $V$ is the volume of the sample. This is the blue shaded portion. **Toughness** , $U_t$, is

$$U_t = V \int_0^{\epsilon_f} \sigma_{11} d\epsilon_{11} \tag{12.3}$$

If a material is not as stiff it is called **compliant**, if a material is not strong it is **weak**, and if a material is not **tough** it is termed **brittle**.

## 12.5 Sign Conventions:

To begin let's talk about **units and sign conventions**. We will define any forces, stresses, or strain in **tension as positive** and any forces, stresses, or strain under **compression will be considered negative**[10]. Additionally we will consider moments that are **counter clockwise as positive** and **clockwise as negative**[10].

## 12.6 Stress

**Stress**, $\sigma$, is a force normalized by the area over which it acts and the force is perpendicular to the area:

$$\sigma = \frac{F}{A} = \frac{N}{m^2} = Pa \tag{12.4}$$

where F is force and A is the original area. This is the definition of the **engineering stress** the **true stress** would be **normalized** by the **instantaneous area**[10]. In this class we will use the engineering stress primarily in this class. **Shear stress**, $\tau$, is a force normalized by the area over which it acts and the force is parallel to the area[10].

The shear stress is similarly defined as:

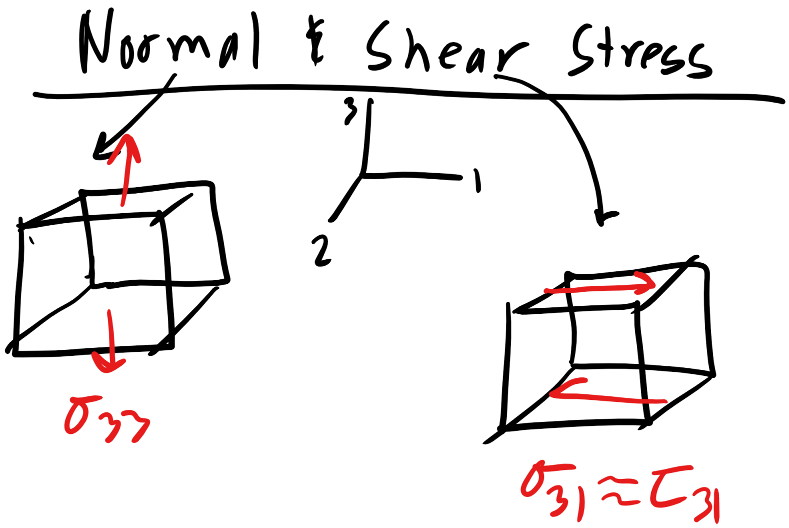

Figure 12-3: Normal and Shear Stress.

$$\tau = \frac{F}{A} \tag{12.5}$$

Now it should be noted here that stress is a second rank tensor, $\sigma_{ij}$, and so is strain, $\epsilon_{ij}$[10]. For stress $i$ denotes the **normal to the plane, on which the force is acting** and $j$ is the **direction of the force**:

$$\sigma_{ij} = \frac{F_j}{A_i} \tag{12.6}$$

So our full stress tensor or our most generic stress state would be:

$$\sigma = \begin{bmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{bmatrix} \tag{12.7}$$

Now this looks like a complex matrix with 9 independent components however they are not completely independent. If we assume that our cube volume element (**representative volume element (RVE)**is in equilibrium (not rotating) then we have the condition that[10]

$$\sigma_{12} = \sigma_{21} \tag{12.8}$$

$$\sigma_{23} = \sigma_{32} \tag{12.9}$$

$$\sigma_{31} = \sigma_{13} \tag{12.10}$$

so our matrix reduces to 6 independent components for our RVE

$$\sigma = \begin{bmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{12} & \sigma_{22} & \sigma_{23} \\ \sigma_{13} & \sigma_{23} & \sigma_{33} \end{bmatrix} \tag{12.11}$$

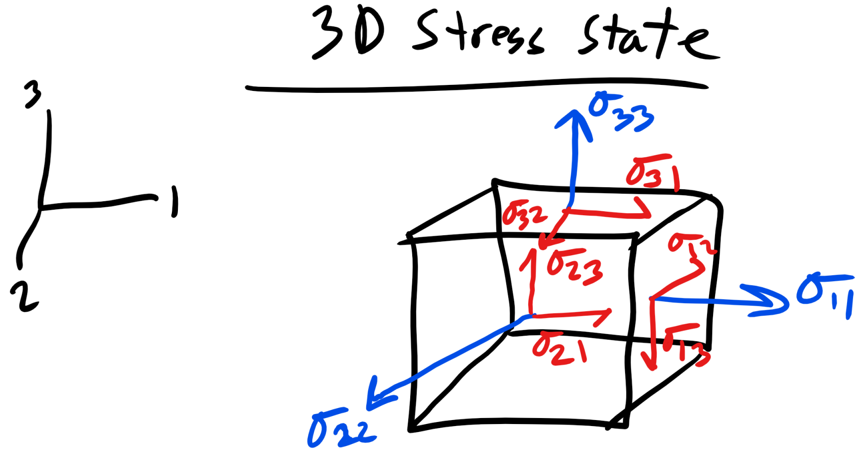

Figure 12-4: 3D Stress State.

Additionally we will encounter several special stress states like Uniaxial stress which gives the following stress state

$$\sigma = \begin{bmatrix} \sigma_{11} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{12.12}$$

and Biaxial stress which gives us

$$\sigma = \begin{bmatrix} \sigma_{11} & \sigma_{12} & 0 \\ \sigma_{12} & \sigma_{22} & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{12.13}$$

but more on those a bit later. Additionally we define the **hydrostatic stress** as

$$P = \frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33}) \tag{12.14}$$

## 12.7 Strain:

All machines, structural members, and materials will deform to some extend when externally loaded by a force or stress. That deformation results in a displacement or **strain**, $\epsilon$[10]:

$$\epsilon = \frac{dL}{L} \tag{12.15}$$

$$\epsilon_t = \int_{L_1}^{L_2} \frac{dL}{L} = ln\frac{L_2}{L_1} \tag{12.16}$$

where $L_1$ is the original length. This is the definition of **true strain**, $\epsilon_t$ but typically we work with a simpler form called the **engineering strain**[10], $\epsilon_e$,

$$\epsilon_e = \frac{L_2 - L_1}{L_1} = \frac{\Delta L}{L_1} \tag{12.17}$$

Typically engineers work with *microstrain* or parts per million. And the shear strain is[10]:

$$\gamma = \frac{dL}{L} = \tan\theta \tag{12.18}$$

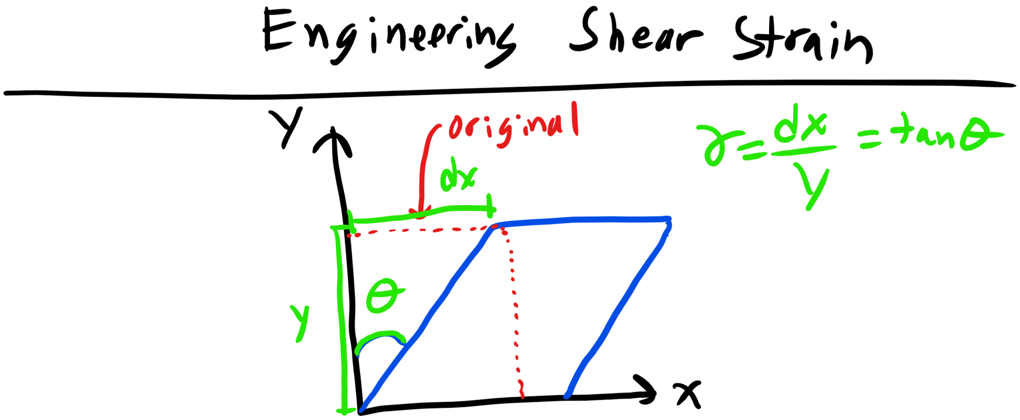

Figure 12-5: Engineering Shear Strain.

This particular case is for **simple shear**. This is going to cause a problem in a second. Also for a material subjected to shear stresses we **observe a proportional relationship between shear stress and strain in the elastic regime**[10] which is defined as:

$$\tau = G\gamma \tag{12.19}$$

where $G$ is the shear modulus.

Now more formally we can define strain using **infinitesimal strain theory** (if you are interested please read in Chapter 5 of Young and Lovell Introduction to polymers)[10]. The essential idea is that you take an infinitesimally small representative volume element and displace the points. This can be most easily observed for

$$\epsilon_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right) \tag{12.20}$$

where $x$ is an axis dimension and $u$ is the displacement we also have from this theory that

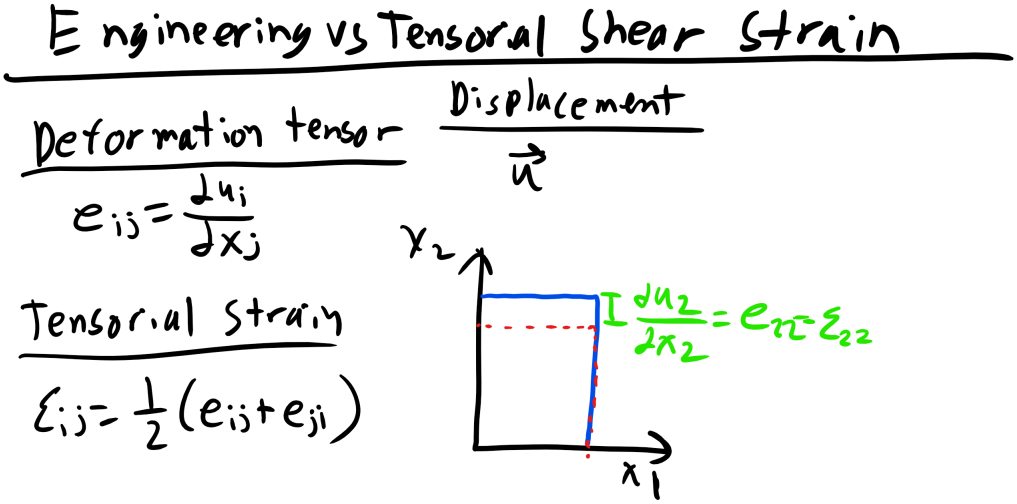

Figure 12-6: Infinitesimal Strain Theory.

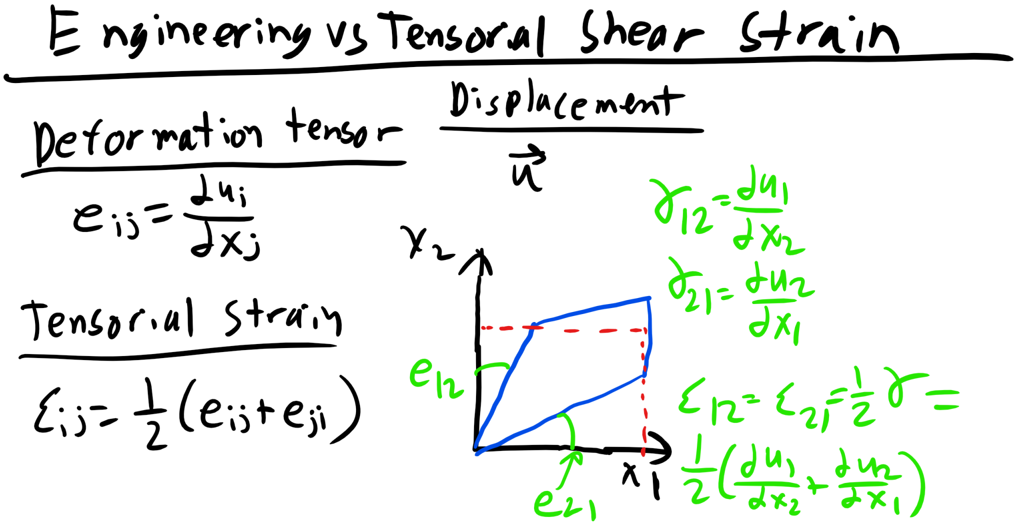

Figure 12-7: Infinitesimal Strain Theory.

$$\epsilon_{11} = \frac{\partial u_1}{\partial x_1} \tag{12.21}$$

$$\epsilon_{22} = \frac{\partial u_2}{\partial x_2} \tag{12.22}$$

$$\epsilon_{33} = \frac{\partial u_3}{\partial x_3} \tag{12.23}$$

$$\epsilon_{12} = \epsilon_{21} = \frac{1}{2}\left(\frac{\partial u_1}{\partial x_2} + \frac{\partial u_2}{\partial x_1}\right) \tag{12.24}$$

$$\epsilon_{23} = \epsilon_{32} = \frac{1}{2}\left(\frac{\partial u_2}{\partial x_3} + \frac{\partial u_3}{\partial x_2}\right) \tag{12.25}$$

$$\epsilon_{31} = \epsilon_{13} = \frac{1}{2}\left(\frac{\partial u_3}{\partial x_1} + \frac{\partial u_1}{\partial x_3}\right) \tag{12.26}$$

$$\gamma_{12} = \gamma_{21} = \left(\frac{\partial u_1}{\partial x_2} + \frac{\partial u_2}{\partial x_1}\right) \tag{12.27}$$

$$\gamma_{23} = \gamma_{32} = \left(\frac{\partial u_2}{\partial x_3} + \frac{\partial u_3}{\partial x_2}\right) \tag{12.28}$$

$$\gamma_{31} = \gamma_{13} = \left(\frac{\partial u_3}{\partial x_1} + \frac{\partial u_1}{\partial x_3}\right) \tag{12.29}$$

with all this we can now create our strain matrix and seeing from the definitions above we know that $\epsilon_{12} = \epsilon_{21}$ and $\epsilon_{23} = \epsilon_{32}$ and finally $\epsilon_{13} = \epsilon_{31}$[10] so that now our strain matrix has 6 independent components and can be written as

$$\epsilon = \begin{bmatrix} \epsilon_{11} & \epsilon_{12} & \epsilon_{13} \\ \epsilon_{12} & \epsilon_{22} & \epsilon_{23} \\ \epsilon_{13} & \epsilon_{23} & \epsilon_{33} \end{bmatrix} \tag{12.30}$$

or equivalently

$$\epsilon = \begin{bmatrix} \epsilon_{11} & \frac{\gamma_{12}}{2} & \frac{\gamma_{13}}{2} \\ \frac{\gamma_{12}}{2} & \epsilon_{22} & \frac{\gamma_{23}}{2} \\ \frac{\gamma_{13}}{2} & \frac{\gamma_{23}}{2} & \epsilon_{33} \end{bmatrix} \tag{12.31}$$

## 12.8 Poisson's Ratio:

Now what happens to the dimensions perpendicular to the direction of applied force when a the material is subjected to uniaxial tension? We know from experience that a **body begin pulled in tension will contract laterally**[10]. This **lateral strain** is described by the **Poisson's Ratio**[10]:

$$\nu = -\frac{\epsilon_L}{\epsilon_A} \tag{12.32}$$

where $\epsilon_L$ is the lateral strain and $\epsilon_A$ is the axial strain. Note the **negative sign which signifies a decrease in length**. The Poisson's ratio is typically around **0.3 for metals**, **0.5 for rubber**, **0.4-0.5 for polymeric materials or biomaterials**, and **0.2 for cork, cellular materials, or ceramics**[10].

## 12.9 Biaxial and Complex Stress States:

What happens when we have a **more complex stress state** and we are interested in the **stress state of a particular plane of orientation angle $\theta$?** Well we do this the same way we resolve force vectors onto a new axes of interest. Let's look at a case of **plane stress** which is a case when all the stress is contained in one plane[10].

So far we have been dealing with simple uniaxial stress along the principal testing direction however often materials can also be subjected to shear stress or strain.

With this information let us move on to more **complex stress states**, specifically one that typically exists on a **free**, not constrained, surface of a stressed material[10].

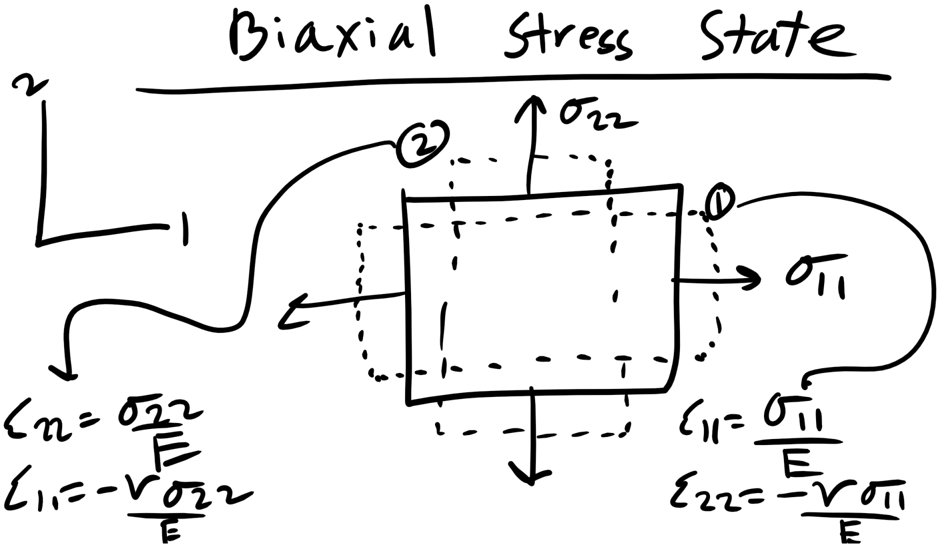

Figure 12-8: Biaxial stress condition

Consider the element which is initially stressed in the $x$ direction by applying $\sigma_x$[10]. There will be a resultant strain:

$$\epsilon_x = \frac{\sigma_x}{E} \tag{12.33}$$

$$\epsilon_y = \frac{-\nu\sigma_x}{E} \tag{12.34}$$

The element is **then stressed in the $y$ direction** by applying $\sigma_y$. The resultant strain will be:

$$\epsilon_y = \frac{\sigma_y}{E} \tag{12.35}$$

$$\epsilon_x = \frac{-\nu\sigma_y}{E} \tag{12.36}$$

therefore the **total strain** in $x$ and $y$ directions will be:

$$\epsilon_x = \frac{\sigma_x - \nu\sigma_y}{E} \tag{12.37}$$

$$\epsilon_y = \frac{\sigma_y - \nu\sigma_x}{E} \tag{12.38}$$

We can solve these two equations (two unknowns and two equations) to find the **total stress** in the $x$ and $y$ directions[10]:

$$\sigma_x = \frac{E(\epsilon_x + \nu\epsilon_y)}{1-\nu^2} \tag{12.39}$$

$$\sigma_y = \frac{E(\epsilon_y + \nu\epsilon_x)}{1-\nu^2} \tag{12.40}$$

## 12.10 3D Stress State

We can extend this even further to find the total strain if there is another stress applied, $\sigma_z$, in the $z$ direction[10]:

$$\epsilon_x = \frac{1}{E}[\sigma_x - \nu(\sigma_y + \sigma_z)] \tag{12.41}$$

$$\epsilon_y = \frac{1}{E}[\sigma_y - \nu(\sigma_z + \sigma_x)] \tag{12.42}$$

$$\epsilon_z = \frac{1}{E}[\sigma_z - \nu(\sigma_x + \sigma_y)] \tag{12.43}$$

We can similarly write the stress as well:

$$\sigma_x = \frac{E}{(1+\nu)(1-2\nu)}\Big[(1-\nu)\epsilon_x + \nu(\epsilon_y + \epsilon_z)\Big] \tag{12.44}$$

$$\sigma_y = \frac{E}{(1+\nu)(1-2\nu)}\Big[(1-\nu)\epsilon_y + \nu(\epsilon_z + \epsilon_x)\Big] \tag{12.45}$$

$$\sigma_z = \frac{E}{(1+\nu)(1-2\nu)}\Big[(1-\nu)\epsilon_z + \nu(\epsilon_x + \epsilon_y)\Big] \tag{12.46}$$

Or for a nicer notation we can write stress for an isotropic linear elastic material as

$$\epsilon_{ij} = \frac{1}{E}\Big[\sigma_{ij}(1+\nu) - \nu\delta_{ij}\sigma kk\Big] \tag{12.47}$$

where $\delta_{ij}$ is the Kronecker delta and will be 1 when $i = j$ and 0 when $i \neq j$.

## 12.11 Anisotropic Linear Elasticity:

Now let's stop for just a second and look at these expressions. We have really been looking how to write expressions looking at matrices with primarily normal stresses but if both **stress** and **strain** are **second rank tensors** if we want a general relationship we need to introduce a **fourth rank tensor** to stand in for E in the Hooke's law expression[10]. So instead of our Hookes Law

$$\sigma = E\epsilon \tag{12.48}$$

We will have

$$\sigma_{ij} = C_{ijkl}\epsilon_{ij} \tag{12.49}$$

$$\epsilon_{ij} = S_{ijkl}\sigma_{ij} \tag{12.50}$$

where $C$ is the stiffness matrix and $S$ is the compliance matrix and we have the relationship that $S = C^{-1}$. As you can see this will get very, very messy quickly[10]. Instead of our nice and simple stress tensor that we were working with previously that we assumed to be isotropic and cubic and having only 6 independent components the full anisotropic fourth rank stiffness and compliance tensor has **81!** independent elastic components[10]. Now typically for almost every material this will not be the case there will be symmetries that reduce this number drastically and we can also reduce it further right now remembering the convenient relationships that reduced the number of independent components in our stress and strain second rank tensors to 6[10]. Remembering this we can make a quick change in notation where we have

$$\sigma_1 = \sigma_{11} \tag{12.51}$$

$$\sigma_2 = \sigma_{22} \tag{12.52}$$

$$\sigma_3 = \sigma_{33} \tag{12.53}$$

$$\sigma_4 = \sigma_{23} \tag{12.54}$$

$$\sigma_5 = \sigma_{13} \tag{12.55}$$

$$\sigma_6 = \sigma_{12} \tag{12.56}$$

$$\epsilon_1 = \epsilon_{11} \tag{12.57}$$

$$\epsilon_2 = \epsilon_{22} \tag{12.58}$$

$$\epsilon_3 = \epsilon_{33} \tag{12.59}$$

$$\epsilon_4 = 2\epsilon_{23} = \gamma_{23} \tag{12.60}$$

$$\epsilon_5 = 2\epsilon_{13} = \gamma_{13} \tag{12.61}$$

$$\epsilon_6 = 2\epsilon_{12} = \gamma_{12} \tag{12.62}$$

Again notice the problem due to the definition of engineering vs tensoral strain[10]. We can then re-write our expression as

$$\sigma_i = C_{ij}\epsilon_j \tag{12.63}$$

where now you should note that $C_{ij}$ is $6 \times 6$ matrix not a tensor so we went from 81 to 36 components[10] as seen below

$$\begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} \\ C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} \\ C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66} \end{bmatrix} \begin{bmatrix} \epsilon_1 \\ \epsilon_2 \\ \epsilon_3 \\ \epsilon_4 \\ \epsilon_5 \\ \epsilon_6 \end{bmatrix} \tag{12.64}$$

Here we see there are 36 components but we can reduce these components[10]. The strain energy density (area under stress strain curve in the elastic regime) does note depend on the direction of strain (compression or tension) so this implies that our stiffness, compliance, strain, and stress matrices must be symmetric, i.e. $C_{ij} = C_{ji}$ so this reduces our number of independent components to 21[10]. We are making progress!!!

But we can reduce this even more by envoking **Onsager's theorem:** which states that materials cannot exhibit properties of higher symmetry other than that of the material itself[10]. In other words, depending on the symmetry of the material some of these constants could disappear. Note: for a more complete discussion of Onsager read Sam Allen's Kinetics of Materials, best description that I have come across. For example:

- **Triclinic Materials:** Have all 21 independent coefficients
- **Monoclinic Materials:** Have 13 independent coefficients
- **Orthorhombic Materials:** Have 9 independent components, some examples of these are wood, composite laminate, polyethylene (semi-crystalline), etc.
- **Tetragonal Materials:** Have 7 independent components
- **Cubic Materials:** Have 3 independent components can be reduced to 2 if material is isotropic.

Remember for cubic materials (a=b=c and $\alpha = \beta = \gamma = 90^o$ for cubic) you will find that there are only **3 independent elastic constants** $C_{11}, C_{12}$, and $C_{44}$ and all others are 0 (proof beyond scope here)[10]. And if we assume elastically isotropic (same properties in all directions) then this reduces to just two where we have the relationship that

$$C_{44} = \frac{C_{11} - C_{12}}{2} \tag{12.65}$$

this proof is arduous and beyond the scope of the class. There is also a useful parameter called the Zener anisotropy ratio (same from light scattering)[10]

$$A = \frac{2C_{44}}{C_{11} - C_{12}} \tag{12.66}$$

A perfect isotropic material will have a value of 1 while materials that are more anisotropic will have larger values[10].

So the stiffness matrix for isotropic cubic linear elastic materials is thus

$$\begin{bmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{C_{11}-C_{12}}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{C_{11}-C_{12}}{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{C_{11}-C_{12}}{2} \end{bmatrix} \tag{12.67}$$

and the compliance matrix is

$$\begin{bmatrix} S_{11} & S_{12} & S_{12} & 0 & 0 & 0 \\ S_{12} & S_{11} & S_{12} & 0 & 0 & 0 \\ S_{12} & S_{12} & S_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & 2(S_{11} - S_{12}) & 0 & 0 \\ 0 & 0 & 0 & 0 & 2(S_{11} - S_{12}) & 0 \\ 0 & 0 & 0 & 0 & 0 & 2(S_{11} - S_{12}) \end{bmatrix} \tag{12.68}$$

Do you understand how/why the value of $S_{44}$ changed? Well remember we have the relationship that $C = S^{-1}$! Now this is good but again we want to put this in terms of material constants instead of these arbitrary compliance or stiffness notations[10]. Let's write out that first top line which gives us

$$\epsilon_1 = S_{11}\sigma_1 + S_{12}\sigma_2 + S_{12}\sigma_3 \tag{12.69}$$

Well we know previously we had an expression that looked very similar for strain in the 1 direction with only normal stress components right

$$\epsilon_1 = \frac{1}{E}\bigg[\sigma_1 - \nu(\sigma_2 + \sigma_3)\bigg] \tag{12.70}$$

Well with these two expression we can know begin to put these values in terms of what we already know the full matrix for only normal stresses will then be

$$\epsilon_1 = \frac{1}{E}\bigg[\sigma_1 - \nu(\sigma_2 + \sigma_3)\bigg] \tag{12.71}$$

$$\epsilon_2 = \frac{1}{E}\bigg[\sigma_2 - \nu(\sigma_1 + \sigma_3)\bigg] \tag{12.72}$$

$$\epsilon_3 = \frac{1}{E}\bigg[\sigma_3 - \nu(\sigma_1 + \sigma_2)\bigg] \tag{12.73}$$

So can you see any relationship pop up immediately? How about focus on $S_{11}$ well we see that

$$S_{11} = \frac{1}{E} \tag{12.74}$$

and we can see for the other components that

$$S_{12} = -\frac{\nu}{E} \tag{12.75}$$

We can also introduce here a more general way to write strain where

$$\epsilon_{ij} = \frac{1}{E}\bigg[(1+\nu)\sigma_{ij} - \nu\sigma_{kk}\delta_{ij}\bigg] \tag{12.76}$$

where $\delta_{ij}$ is the **Kronecker Delta** which will be 1 when $i = j$ and 0 when $i \neq j$[10].

Let's keep this relationship in mind as we move on to the 4-6 rows of the compliance matrix. Well those equations are pretty straight forward

$$\epsilon_4 = 2(S_{11} - S_{12})\sigma_4 \tag{12.77}$$

$$\epsilon_5 = 2(S_{11} - S_{12})\sigma_5 \tag{12.78}$$

$$\epsilon_6 = 2(S_{11} - S_{12})\sigma_6 \tag{12.79}$$

We can alternatively write an expression for strain using the equation above and noting that the 4th row of our matrix we have only a shear stress component so we would have that

$$\epsilon_{12} = \frac{1+\nu}{E}\sigma_{12} \tag{12.80}$$

$$\gamma_{12} = 2\epsilon_{12} \tag{12.81}$$

$$\gamma_{12} = \frac{2(1+\nu)}{E}\sigma_{12} \tag{12.82}$$

$$\tag{12.83}$$

now look at that last expression and remember that we had the general relationship for to relate shear stress and strain that

$$\tau = G\gamma \tag{12.84}$$

so now we can see that

$$G = \frac{E}{2(1+\nu)} = \frac{1}{2(S_{11} - S_{12})} \tag{12.85}$$

We can find the **Poisson's ratio** as well since we know that in general

$$\nu_{ij} = -\frac{\epsilon_j}{\epsilon_i} \tag{12.86}$$

so we can find that for this system (assuming uniaxial tension only)

$$\nu_{12} = -\frac{S_{12}}{S_{11}} \tag{12.87}$$

with all these values now defined we can re-write our compliance matrix as

$$\begin{bmatrix} \epsilon_1 \\ \epsilon_2 \\ \epsilon_3 \\ \epsilon_4 \\ \epsilon_5 \\ \epsilon_6 \end{bmatrix} = \begin{bmatrix} \frac{1}{E} & -\frac{\nu}{E} & -\frac{\nu}{E} & 0 & 0 & 0 \\ -\frac{\nu}{E} & \frac{1}{E} & -\frac{\nu}{E} & 0 & 0 & 0 \\ -\frac{\nu}{E} & -\frac{\nu}{E} & \frac{1}{E} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{G} & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{G} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{G} \end{bmatrix} \begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{bmatrix} \tag{12.88}$$

This is a very nice result and you can convince yourself why I neglected putting the notation on the Poisson's ratio. Now you will additionally see some further constants utilized to bundle these elastic constants like the **Lame's** constants[10]:

$$\mu = G \tag{12.89}$$

$$\lambda = C_{12} \tag{12.90}$$

This is just another way to represent the matrix seen above in another notation that is common.

## 12.12 Ex. Jewelry Maker: Strain Without Stress?

A jewelry maker creates a die to form a new cufflink made of steel. We need to know how much stress to apply to the metal slab to reduce the thickness to 3mm. The die is a simple channel that does not constrain the metal in the x-direction and the channel is well lubricated so that all frictional forces and stresses along the channel walls can be ignored[10].

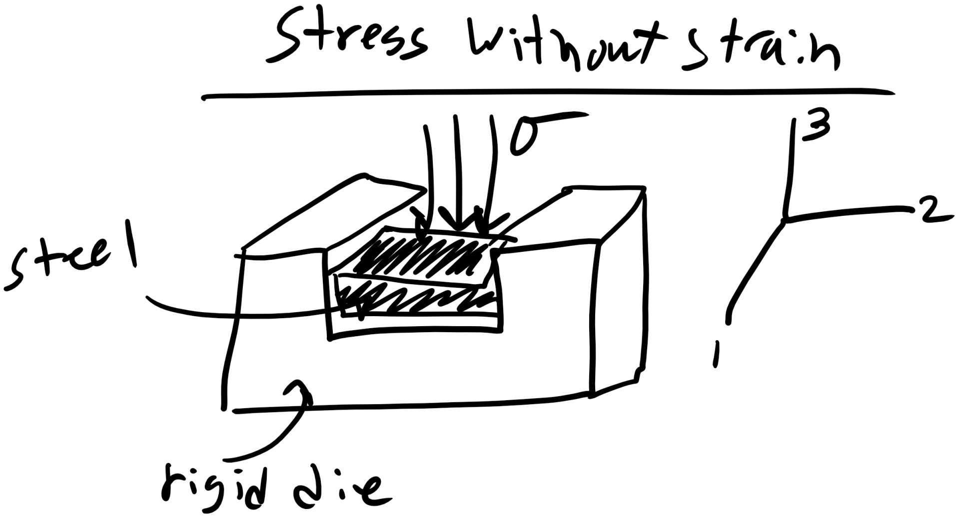

Figure 12-9: Die in which steel of initial thickness 6mm will be subjected to normal stress $\sigma_{zz}$.

**a.) State all the components of the stress tensor under the applied stress.**

Well there is clearly a stress in the z direction. What about x and y?

**b.) Which normal strain components are zero and why?**

**c.) Use your answers in part a) and b) to express the relationship between the non-zero stresses in this system.**

## 12.13 Pressure Vessels: A Special Stress State

Finally let's consider a very common scenario, a **thin walled pressure vessel**. The thin walled vessel has an applied **pressure difference** $\Delta P$ between the internal pressure and the environment[10]. The **wall thickness is sufficiently small** where we can say $t << R$ or that $\frac{R}{t} \geq 10$[10]. **What is the stress state?** It is **plane stress state** due to symmetry considerations. Therefore we need to find $\sigma_1$ and $\sigma_2$ which we will accomplish by **drawing free body diagrams**[10].

Let us first **consider the longitudinal direction**. Remember that the **forces must sum to zero**.

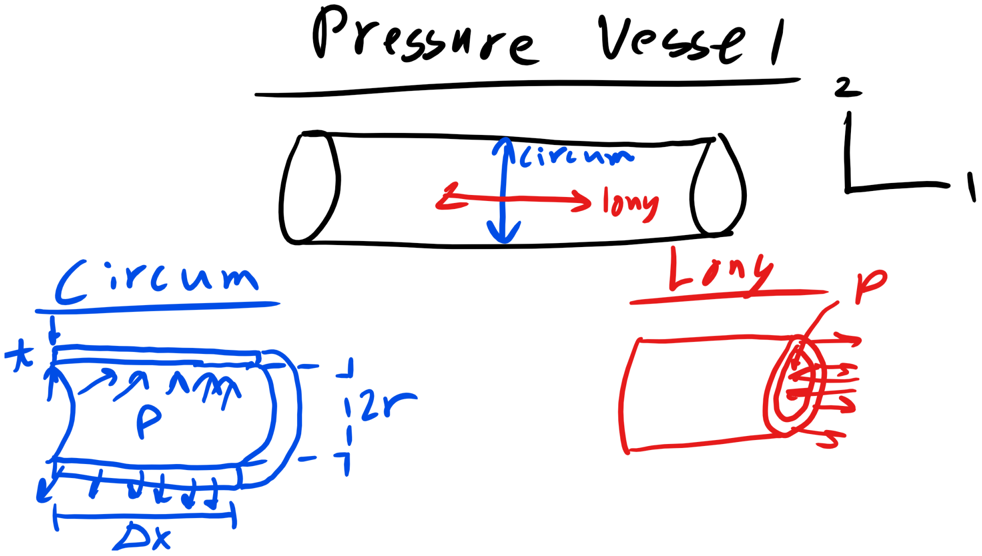

Figure 12-10: Pressure Vessel.

$$\sum F_1 = 0 = \Delta P \pi r^2 - \sigma_{11} 2\pi r t \tag{12.91}$$

$$\sigma_{11} = \sigma_{Longitudinal} = \frac{\Delta P r}{2t} \tag{12.92}$$

We have the longitudinal stress so now let us look at the other direction, **circumferential or hoop**, and again the forces must sum to equal zero:

$$\sum F_2 = 0 = -\Delta P \Delta x 2R + \sigma_{22} \Delta x t 2 \tag{12.93}$$

$$\sigma_{22} = \sigma_{Hoop} = \frac{\Delta P R}{t} \tag{12.94}$$

As you can see the **hoop stress is twice as large as the longitudinal stress** so you should expect the material to fail in such a manner, unless there are extenuating conditions, i.e. defects, corrosion, different processing, etc. The **strain ratio for hoop to longitudinal strain is nearly 4 : 1.**[10]

## 12.14 Resolving Stress on Plane of Interest:

First we must define a new coordinate system that aligns with the plane of interest, i.e. we must rotate our old coordinate axes $(x, y)$ to align with our new coordinate axes $(x', y')$[10].

Then we balance out the forces assuming **static equilibrium**[10]:

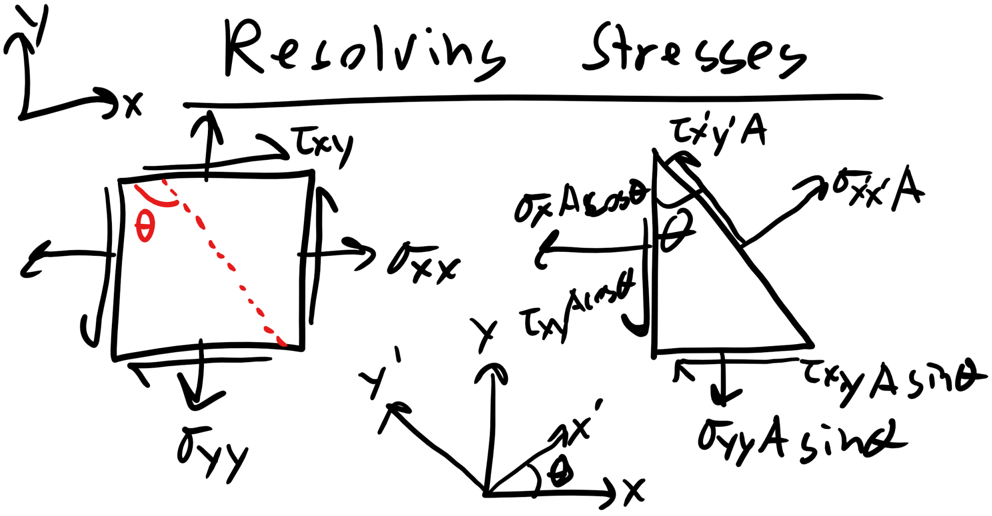

Figure 12-11: Biaxial stress condition and investigating stress state in an arbitrary plane.

$$\sum F_{x'} = 0 = \sigma_{x'x'}A' - (\tau_{xy}A'\sin\theta)\cos\theta - (\sigma_{yy}A'\sin\theta)\sin\theta - (\tau_{xy}A'\cos\theta)\sin\theta - (\sigma_{xx}A'\cos\theta)\cos\theta \tag{12.95}$$

After some rearranging and trig transformations:

$$\sigma_{x'x'}(\theta) = \frac{\sigma_{xx}+\sigma_{yy}}{2} + \frac{\sigma_{xx}-\sigma_{yy}}{2}\cos 2\theta + \tau_{xy}\sin 2\theta \tag{12.96}$$

$$\sigma_{y'y'}(\theta) = \frac{\sigma_{xx}+\sigma_{yy}}{2} - \frac{\sigma_{xx}-\sigma_{yy}}{2}\cos 2\theta - \tau_{xy}\sin 2\theta \tag{12.97}$$

$$\tau_{x'y'}(\theta) = -\left(\frac{\sigma_{xx}-\sigma_{yy}}{2}\right)\sin 2\theta + \tau_{xy}\cos 2\theta \tag{12.98}$$

You can also do this transformation a bit easier using a transformation matrix $T$ where

$$\Big[T\Big] = \begin{bmatrix} c^2 & s^2 & 2sc \\ s^2 & c^2 & -2sc \\ -sc & sc & c^2-s^2 \end{bmatrix} \tag{12.99}$$

where $c = \cos\theta$ and $s = \sin\theta$.

So we now write that

$$\sigma^{'} = T\sigma \tag{12.100}$$

or similarly

$$\begin{bmatrix}\sigma_{xx'} \\ \sigma_{yy'} \\ \tau_{xy'}\end{bmatrix} = \begin{bmatrix} c^2 & s^2 & 2sc \\ s^2 & c^2 & -2sc \\ -sc & sc & c^2 - s^2 \end{bmatrix} \begin{bmatrix}\sigma_{xx} \\ \sigma_{yy} \\ \tau_{xy}\end{bmatrix} \tag{12.101}$$

We can almost do the same for strain but for the following complication that we have the definition that $\epsilon_{xy} = \frac{1}{2}\gamma_{xy}$ so we have to account for this in our transformation specifically via the introduction of the **Reuter's Matrix**[10]

$$\begin{bmatrix}R\end{bmatrix} = \begin{bmatrix}1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 2\end{bmatrix} \tag{12.102}$$

So to transform to new coordinate systems for strain we have to do the following

$$\epsilon^{'} = RTR^{-1}\epsilon \tag{12.103}$$

or similarly

$$\begin{bmatrix}\epsilon_{xx'} \\ \epsilon_{yy'} \\ \gamma_{xy'}\end{bmatrix} = \begin{bmatrix}1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 2\end{bmatrix} \begin{bmatrix} c^2 & s^2 & 2sc \\ s^2 & c^2 & -2sc \\ -sc & sc & c^2 - s^2 \end{bmatrix} \begin{bmatrix}1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \frac{1}{2}\end{bmatrix} \begin{bmatrix}\epsilon_{xx} \\ \epsilon_{yy} \\ \gamma_{xy}\end{bmatrix} \tag{12.104}$$

Note that we have to use the Reuter's matrix because we have resolved the stresses and strain or created the transformation matrix using the tensorial definition of stress and strain. So first we need to transform from our engineering strain to tensorial strain and then back again.

**Principal Stresses**

We have successfully transformed the stress state to our new coordinate system! But as engineers we recognize that typically materials will **fail** at locations of **maximum stress**[10]. Typically **ceramics, brittle oxides, glassy polymers will fail at maximum normal stress** and **metals or composites will fail at maximum shear stress**[10]. In order to find the **maximum stress state** or **principal** stress state we simply **differentiate** with respect to $\theta$ and **set equal to zero** and find that[10]:

$$\tan 2\theta = \frac{\tau_{xy}}{\frac{\sigma_{xx}-\sigma_{yy}}{2}} \tag{12.105}$$

We can then substitute this back into the above equations and get:

$$\sigma_1 = \frac{\sigma_{xx} + \sigma_{yy}}{2} + \sqrt{\left(\frac{\sigma_{xx} - \sigma_{yy}}{2}\right)^2 + \tau_{xy}^2} \tag{12.106}$$

$$\sigma_2 = \frac{\sigma_{xx} + \sigma_{yy}}{2} - \sqrt{\left(\frac{\sigma_{xx} - \sigma_{yy}}{2}\right)^2 + \tau_{xy}^2} \tag{12.107}$$

$\sigma_1$ and $\sigma_2$ are the **principal maximum normal stresses** and you can see by definition that $\sigma_1 > \sigma_2$[10]. We can do the same for the **maximum shear stress** and find that:

$$\tau_{xy,max} = \sqrt{\left(\frac{\sigma_{xx} - \sigma_{yy}}{2}\right)^2 + \tau_{xy}^2} \tag{12.108}$$

## 12.15 Mohr's Circle Construction

Otto Mohr, a German engineer in the 1800's, recognized that we can **represent the principal stress state graphically**[10]. We can re-write the equations above and sum the square of Eq.12.96 and Eq.12.98 to give us:

$$\left[\sigma_1 - \left(\frac{\sigma_{xx} + \sigma_{yy}}{2}\right)\right]^2 + \tau_{xy,max}^2 = \left(\frac{\sigma_{xx} - \sigma_{yy}}{2}\right)^2 + \tau_{xy}^2 \tag{12.109}$$

You should notice that this form has a similar form to the equation of a circle, i.e.

$$(x - c)^2 + y^2 = r^2 \tag{12.110}$$

where the center of the circle is $\frac{\sigma_{xx}+\sigma_{yy}}{2}$ and the radius of the circle is $\sqrt{(\frac{\sigma_{xx}-\sigma_{yy}}{2})^2 + \tau_{xy}^2}$[10]. We can **plot Mohr's circle for an arbitrary initial stress state.**

## 12.16 Ex. Plane Stress States

Consider a material initially under a strain state where $\sigma_{xx} = 22$ MPa, $\sigma_{yy} = 10$ MPa and $\tau_{xy} = 6$ MPa.

**What is the stress state of a plane inclined at 30° CCW?**

**Draw Mohr's circle to find the principal stress state.**

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# CHAPTER 13

## VISCOELASTICITY

### 13.1 Key Terms/Definitions:

- **Elastic deformation** - strain that is recovered upon the removal of an applied stress; strain energy stored in the material.
- **Young's modulus** - a measure of the stiffness of the material; strictly the slope of the stress-strain curve in the linear elastic regime under uniaxial tension.

### 13.2 Linear Viscoelasticity (LVE):

So far we have dealt with **continuum isotropic linear elasticity** and **anisotropic linear elasticity**. All these modes of deformation are **independent of time, rate, and temperature**. However, we know that polymer properties are intemately related to time, rate, and temperature. So we will now discuss linear viscoelasticity whose deformation is governed by time, rate, and temperature. **Linear viscoelasticity** is the deformation between that of an **elastic solid and a viscous fluid.** We can actually see this in the name linear viscoelasticity. There is still a linear relationship between stress and strain for a given time and temperature. The **visco** term denotes a **time component** and **elasticity denotes reversibility**. Polymers are typically though of behaving elastically at low temperatures and high rates of strain whereas at high temperatures and low strain rates they behave more like a viscous fluid. The **elastic solid** will again behave Hookean with the relationship

$$\sigma = E\epsilon \tag{13.1}$$

and the **viscous fluid** will be governed by a familiar equation, **Newtons law**

$$\sigma = \eta\dot{\epsilon} \tag{13.2}$$

Linear Viscoelasticity is typically used to describe the **mechanical response for polymers, glasses, tissues, and cells**.

When a **viscous fluid** is deformed under an applied shear stress there is **no recovery when the shear stress is removed** so our equation for shear stress becomes

$$\tau = \eta\dot{\gamma} \tag{13.3}$$

where $\eta$ is the **fluid viscosity** (units of Pa s) and $\dot{\gamma}$ is the **shear strain rate** (units of inverse seconds). Again this is linear because there is a proportional increase in $\sigma$ and $\epsilon$ for some time or temperature.

We can make a couple of linear viscoelastic (LVE) models which describe some LVE behavior phenomonolgically as combinations of **springs and dashpots**.

**Maxwell Model:**

Let's take a look at the **Maxwell model** which is a combination of a **spring in series with a dashpot** that contains a Newtonian fluid.

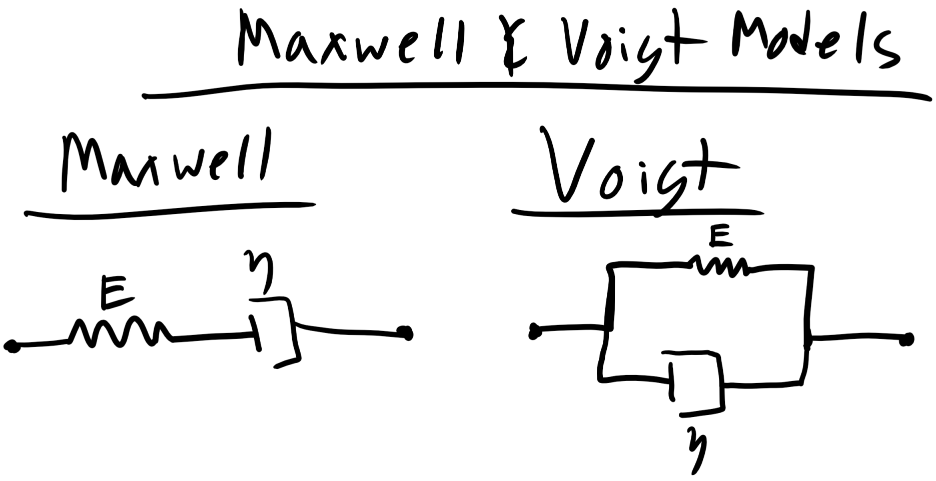

Figure 13-1: Maxwell and Kelvin-Voigt Models for Viscoelasticity

The spring is described by the following equation:

$$\sigma_s = E_s \epsilon_s \tag{13.4}$$

where $\sigma_s$ is the stress in the spring, $E_s$ is the stiffness of the spring, and $\epsilon_s$ is the strain in the spring.

The dashpot is described by:

$$\sigma_d = \eta_d \dot{\epsilon_d} \tag{13.5}$$

where $\sigma_d$ is the stress in the dashpot, $\eta_d$ is the viscosity of the dashpot, and $\dot{\epsilon_d}$ is the strain rate of the dashpot.

Now let's say that I stress the system with some applied stress $\sigma_M$. In this configuration the **stresses will be the same for the spring and the dashpot** as they are arranged in series however the **strains in the dashpot and the spring will be different** which gives us the following relationships:

$$\sigma_M = \sigma_s = \sigma_d \tag{13.6}$$

$$\epsilon_M = \epsilon_s + \epsilon_d \tag{13.7}$$

$$\dot{\epsilon_M} = \dot{\epsilon_s} + \dot{\epsilon_d} \tag{13.8}$$

$$\dot{\epsilon_M} = \frac{\dot{\sigma_M}}{E} + \frac{\sigma_M}{\eta} \tag{13.9}$$

With this system we can do two types of experiments: **stress relaxation** ($\epsilon = \epsilon_0$ i.e. constant strain) and **creep** ($\sigma = \sigma_0$, i.e. constant stress).

For **stress relaxation** we can plug into our equation and solve for how the stress in our Maxwell model should vary over time:

$$0 = \frac{1}{E}\frac{d\sigma}{dt} + \frac{\sigma}{\eta} \tag{13.10}$$

$$\int_{\sigma_0}^{\sigma} \frac{d\sigma}{\sigma} = \int_0^t \frac{-E}{\eta} dt \tag{13.11}$$

$$\sigma(t) = \sigma_0 \exp\left(\frac{-Et}{\eta}\right) \tag{13.12}$$

$$\sigma(t) = \sigma_0 \exp\left(\frac{-t}{\tau}\right) \tag{13.13}$$

where $\tau = \frac{\eta}{E}$ is the **relaxation time**. Similarly for **creep**:

$$\frac{d\epsilon}{dt} = 0 + \frac{\sigma_0}{\eta} \tag{13.14}$$

$$\int_{\epsilon_0}^{\epsilon} d\epsilon = \int_0^t \frac{\sigma_0}{\eta} dt \tag{13.15}$$

$$\epsilon(t) = \epsilon_0 + \frac{\sigma_0 t}{\eta} \tag{13.16}$$

**Kelvin-Voigt Model:**

There is also the **Kelvin-Voigt (KV) model** has the **spring and dashpot series in parallel**.

In this case now the **strain is the same**, because they are in parallel, but now the **stresses are different** so we get:

$$\epsilon_{KV} = \epsilon_s = \epsilon_d \tag{13.17}$$

$$\sigma_{KV} = \sigma_s + \sigma_d \tag{13.18}$$

$$\sigma_{KV} = E_s \epsilon_s + \eta_d \dot{\epsilon_d} \tag{13.19}$$

$$\dot{\epsilon_{KV}} = \frac{\sigma_{KV}}{\eta_d} - \frac{E_s}{\eta_d} \epsilon_{KV} \tag{13.20}$$

Now for **stress relaxation** we get the final equation for stress vs time as:

$$\sigma(t) = E\epsilon_0 \tag{13.21}$$

and for **creep** we get:

$$\epsilon(t) = \frac{\sigma_0}{E}\left[1 - \exp\left(-\frac{t}{\tau}\right)\right] \tag{13.22}$$

You can now build even more complex combinations to model viscoelastic properties like the **Standard Linear Solid Model or Maxwell-Zener Model** which combines both models to better capture the behavior of viscous materials and there are many more complex models as well to represent the behavior of materials.

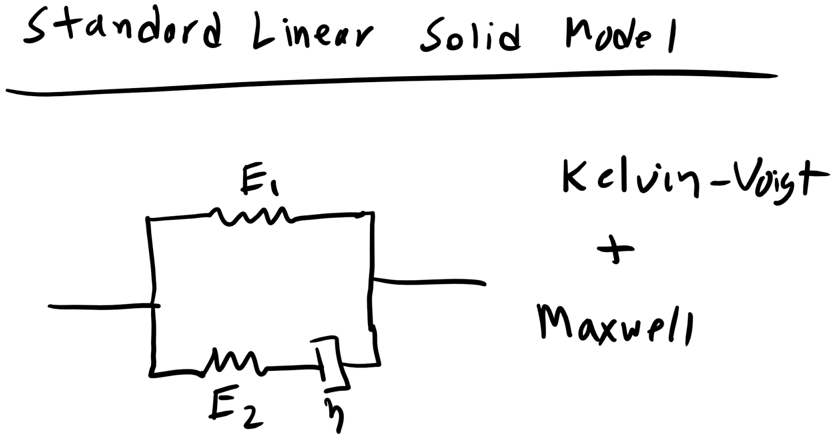

Figure 13-2: Standard Linear Solid Model

You can also describe the stress and strain as a function of time for this model as well by making a couple of assumptions like that at small times/high frequencies the dashpots can be treated as rigid links and that long times/small frequencies the dashpots are essentially disconnected.

You can also use the **Boltmzann superposition principle** to determine the stress by summing the strain during multiple deformation steps and defining a parameter called the **creep compliance**

**J(t)** which relates strain to stress as a function of time

$$\epsilon(t) = J(t)\sigma \tag{13.23}$$

You can do the same procedure for stress relaxation but you have to define the **stress relaxation modulus G(t)**.

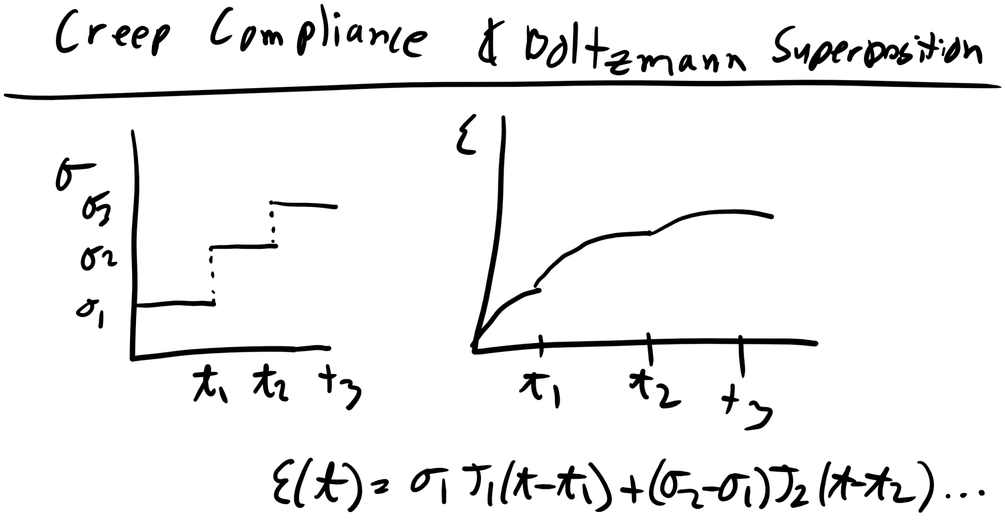

Figure 13-3: Modeling Strain Using Boltzmann Superposition Principle and the Creep Compliance.

## 13.3 Dynamic Mechanical Testing:

The more utilized characterization technique is **dynamic mechanical testing** to probe the viscoelastic behavior of materials. In this experiment the polymer is subjected of a sinusoidal loading at variable frequencies which can be described as such as

$$\sigma_{applied} = \sigma_o \sin \omega t \tag{13.24}$$

This is the applied stress but remember we are dealing with a viscoelastic material so there will be a phase lag, $\delta$, in the strain behavior which will also be sinusoidal

$$\epsilon = \epsilon_o \sin \omega t \tag{13.25}$$

So what we will end up with is that the material will actually experience a stress that contains the phase lag as shown below

$$\sigma = \sigma_o \sin(\omega t + \delta) \tag{13.26}$$

$$\sigma = \sigma_o \sin \omega t \cos \delta + \sigma_o \cos \omega t \sin \delta \tag{13.27}$$

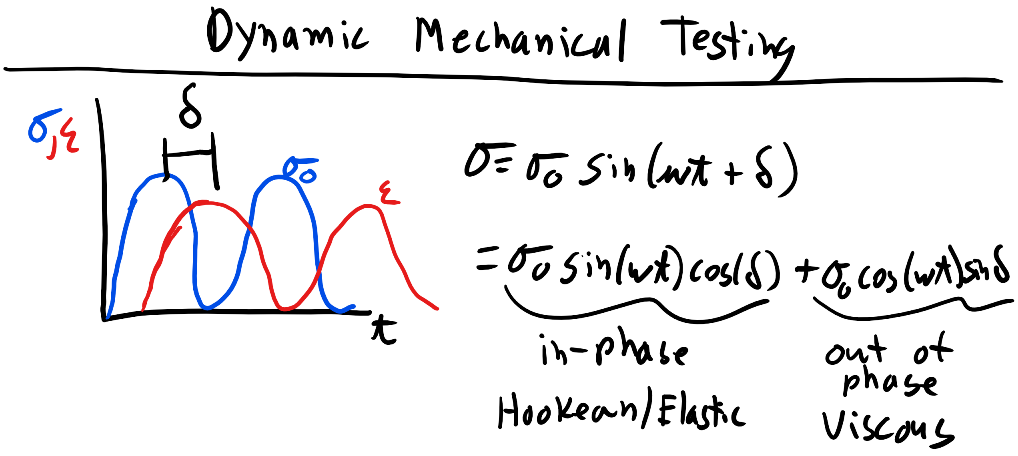

Figure 13-4: Dynamic Mechanical Testing.

where in the equation above we just expanded our trig functions. Notice here that the first term represents the component that is in phase with the strain or the elastic response while the second term represents the out of phase behavior or the viscous response. We can then define two elastic moduli to describe the in-phase and out of phase behavior. The **storage** or elastic modulus is the in-phase contribution and defined as

$$E' = \frac{\sigma_o \cos \delta}{\epsilon_o} \tag{13.28}$$

and the **loss** modulus is the out of phase component is

$$E'' = \frac{\sigma_o \sin \delta}{\epsilon_o} \tag{13.29}$$

We can now re-write our expression for the stress in the material as

$$\sigma = E' \sin \omega t + E'' \cos \omega t \tag{13.30}$$

then by definition we have that

$$\tan \delta = \frac{E''}{E'} \tag{13.31}$$

This is sometimes called the **loss tangent** and essentially represents the amount of energy lost over the energy stored. You might also see these expressions written using complex variables like so

$$\epsilon = \epsilon_o \exp i\omega t \tag{13.32}$$

$$\sigma = \sigma \exp i\omega t + \delta \tag{13.33}$$

$$E = \frac{\sigma_o}{\epsilon_o} \exp i\delta = \frac{\sigma_o}{\epsilon_o}(\cos\delta + i\sin\delta) = E' + E'' \tag{13.34}$$

**Analysis of Dynamic Mechanical Testing Experiments:**

Typically you will find, at a fixed temperature that the **loss tangent** and the loss modulus are typically very small at very low and and very high frequencies and they will typically peak at intermediate frequencies. The storage modulus is high at high frequencies (short times) which should make sense intuitively as polymers will typically behave glassy or elastic at high frequencies and short times (strain rate is faster than relaxation time of polymer) and at low frequencies (long time longer than relaxation time) the polymer will behave more like a vicious fluid.

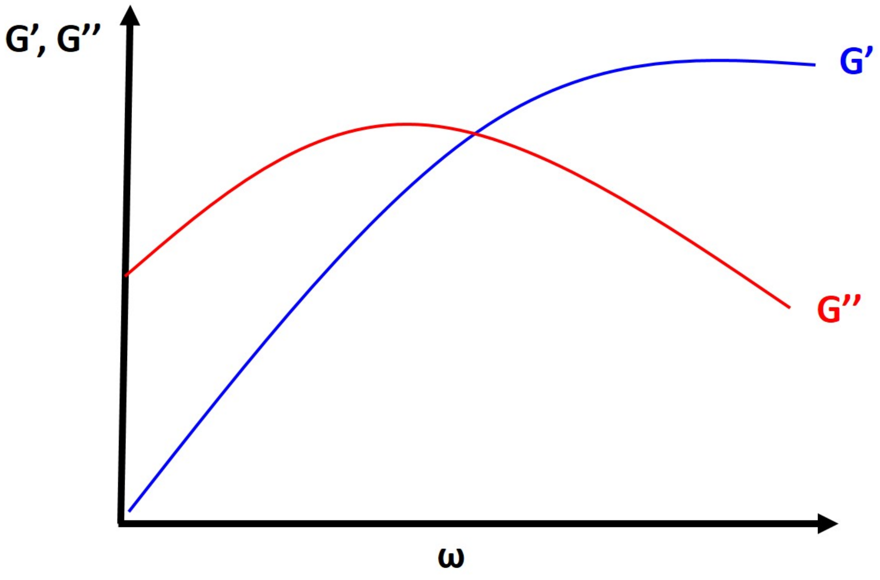

Figure 13-5: Viscoelastic Behavior of Polymers.

More importantly from this analysis we can determine experimentally the **characteristic relaxation time** from the point where G' and G" intersect.

More often we will find that typical DMA experiments where G', G", and tan $\delta$ are plotted as a function of temperature. Here you will typically see larger peaks and changes in these parameters as we have already seen that the modulus of polymers is temperature dependent. Alternatively, as we have already discussed at length the temperature will affect the amount of molecular motion and free volume will increase and this will affect these properties, particularly the loss tangent. So you will expect to see large changes at the glass transition temperature and melting temperature but you also might expect to see other small peaks associated with **secondary transitions** (note this is not referring to second order thermodynamic transitions like $T_g$ this is just referring to the magnitude of the peaks) associated with molecular motion of the polymer such as the temperature at which backbone side group rotation is accessible.

As you can see in the figure the primary observable and measurable change in the storage modulus occurs when you pass through $T_g$. However, the more subtle difference in behavior can be found in the variation of the **loss tangent** as a function of temperature. Here we can see multiple different peaks at different temperatures with varying amplitudes. In these plots each peak is typically labeled $\alpha, \beta, \gamma$, etc in order of descending temperature. In this graph the $\alpha$ peak or relaxation corresponds to the $T_g$ in an amorphous polymer or it could be $T_m$ for a semi-crystalline polymer. The $\beta$ peak here for cooperative motion of segments of the main chain. The $\gamma$ peak is due the phenyl group rotation around the backbone and the $\delta$ peak has been linked to some *wiggling* of the phenyl group most likely due to defects/tacticity differences.

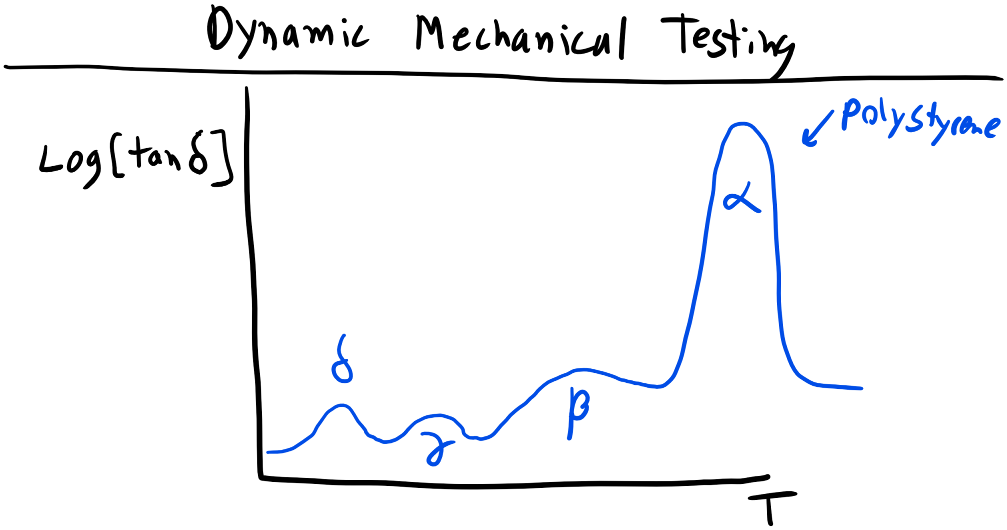

Figure 13-6: DMT Transition Analysis in Polystyrene.

For semi-crystalline polymers this analysis can become even more difficult because of the microstructure of spherulites. This makes it very difficult to separate the amorphous and crystalline behavior. One example of this can be seen for LDPE and HDPE you can see some similar transitions (i.e. $\gamma$) but other stark differences. First, the primary difference between LDPE and HDPE is the amount of branching is much larger in LDPE than in HDPE. Here the $\alpha$ and $\alpha'$ peaks are associated with motion in the crystalline regions while the $\gamma$ peak is associated with the amorphous region. Finally, the $\beta$ relaxation is associated with the motion of the branches. Now the analysis of these peaks in polymers are a great source of debate but when analyzing them just make a reasoned argument thinking about the thermal energy required for a particular type of motion .

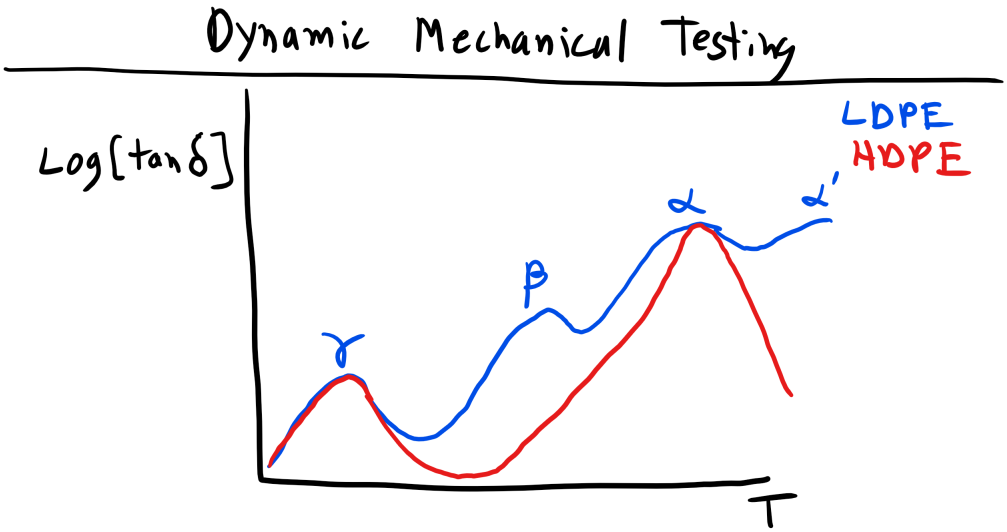

Figure 13-7: DMT Transition Analysis in HDPE and LDPE.

## 13.4 Time-Temperature Equivalence of Polymeric Materials

There is a well-defined difference in the Young's modulus between glassy, amorphous polymers and rubbery elastic polymers. Furthermore, we know that there is a temperature dependence for the Young's modulus. Below the $T_g$ the modulus is very high, while at higher temperatures the modulus falls to that of a rubber. This relationship is typically drawn on a log (E) vs. log (T) plot where the several order of magnitude difference between the glassy and rubbery moduli is clear.

One other thing that must be noted is that at high temperatures, strictly amorphous polymers will have moduli that fall to zero; only crosslinked rubbers will maintain a non-zero modulus at high temperatures that is relatively invariant compared to the change between the amorphous and rubbery moduli. If there are no crosslinks, the polymer will simply flow irreversibly.

Now, if we remember back to the discussion of the glass transition, we said that the onset of glassy behavior is really due to the change in the characteristic relaxation time of a polymer, and how that relaxation time compares to the experimental time associated with a given stress effect. The glass transition would then be interpreted as changing the relaxation time with temperature, which molecularly could be understood as providing more (or less) thermal energy to overcome barriers to flow. However, we also said that if you change the timescale of the perturbation (e.g. deform a polymer really really fast) you could obtain glassy behavior even without changing the temperature. This information leads us to believe that the modulus of a polymer is also time dependent, a fact that is born out empirically. In fact, the graph of log (E) vs log (T) is qualitatively the same as the plot of log (E) vs. log (time), reflecting the origin of the glass transition.

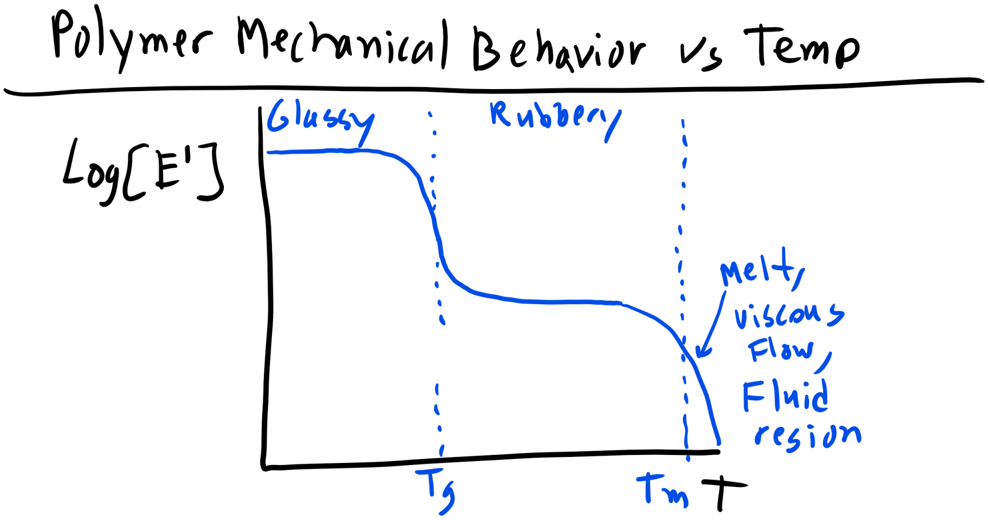

Figure 13-8: Polymer Stiffness vs. Temperature.

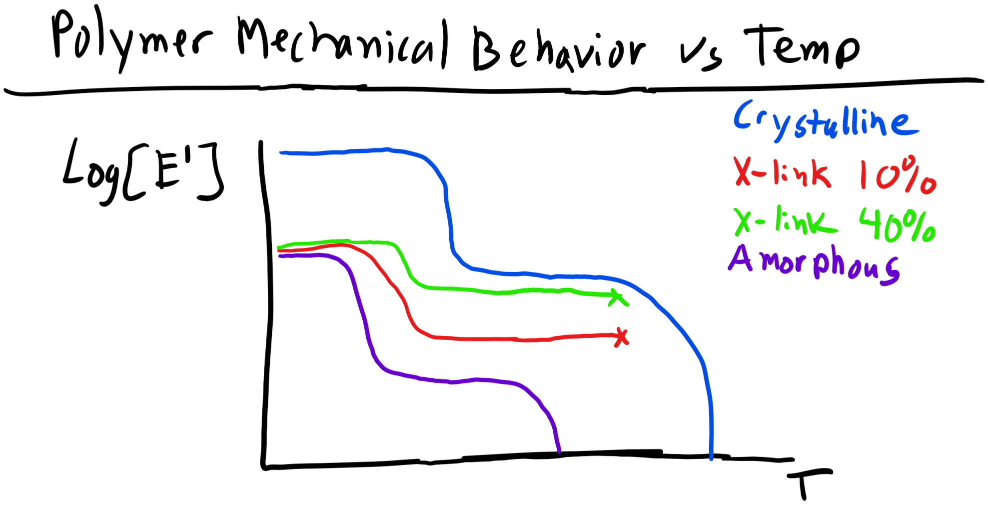

Figure 13-9: Crystalline, Amorphous, and Cross-Linked Polymeric Stiffness vs. Temperature.

In addition to changing the value of the Young's modulus, changing the timescale or temperature of an experiment can qualitatively change the shape of a stress-strain curve, as well. For example, heating up a brittle, glassy polymer sample will decrease the Young's modulus but also increase the ductility of the sample, allowing longer elongations and more plastic deformation. There is thus a **ductile-to-brittle** transition where the polymer switches from undergoing stable plastic deformation (necking) to brittle failure; the exact temperature depends on the rate of testing and vice versa.

Finally, note that semi-crystalline polymers are characterized by a degree of crystallinity, which reflects the relative proportion of amorphous to crystalline regions. We would imagine that these regions could have very different moduli, especially above the glass transition temperature, and thus would expect the modulus depends highly on the degree of crystallinity. This is indeed the case, and the modulus of semi-crystalline polymers has been observed to increase by a factor of over 100 as the degree of crystallinity increases. At low degrees of crystallinity, this change can be regarded as an increase in an effective crosslinking density for the amorphous regions, as the crystalline regions will likely bear very little load themselves. However,as the degree of crystallinity gets higher the material can be more accurately regarded as a composite of a low modulus material and high modulus material, a problem that is often treated in materials science.

## 13.5 Time-temperature Equivalence

For viscoelastic polymers there is a **theoretical equivalence of time and temperature**. We have seen previously that a polymer can behave glassy or rubbery behavior by changing either the temperature or the strain rate, i.e. time. So we can establish the principle of **time-temperature superposition**, or the theoretical equivalence between changing the timescale or temperature of an experiment. An **experimentally-derived equation** relating these two quantities, known as the WLF equation was found by noticing that you can s**uperpose curves by keeping one curve fixed and shifting all the others by different amounts horizontally parallel to the logarithmic time axis**. We can take a reference temperature point, $T_s$, and a temperature point, $\tau_s$, in order to fix one curve. We then have to find the $\tau$ for a new curve with the same compliance as our reference curve at $T_s$. The amount of shift will then simply be $\log \tau_s - \log \tau$ which we will define as our **shift factor**

$$\log a_T = \log \tau_s - \log \tau = \log \frac{\omega_s}{\omega} \tag{13.35}$$

Well with this **Williams-Landel-Ferry (WLF)** empirically fit these polymer curves and found the following empirical equation:

$$\log a_T = \frac{-C_1(T - T_s)}{C_2 + (T - T_s)} \tag{13.36}$$

where $C_1$ and $C_2$ are empirical fitting constants, 17.44 and 51.6K respectively for the two constants if one chooses $T_s = T_g$. This equation was later re-derived using theory based on free volume, akin to the theory for the glass transition, reflecting similar physical origins. The derivation is beyond the scope (and you all are probably sick of derivations at this point but you can read in Young and Lovell Chapter 5) so the resulting equation is

$$\log a_T = \frac{-(B/2.303 f_g)(T - T_g)}{f_g/\alpha + (T - T_g)} \tag{13.37}$$

where $f_g$ is the fractional free volume at the glass transition temperature and $\alpha$ is the volumetric thermal expansion coefficient. Typically for polymers $f_g = 0. - 25$ and $\alpha = 4.8 \times 10^{-4} K^{-1}$. And

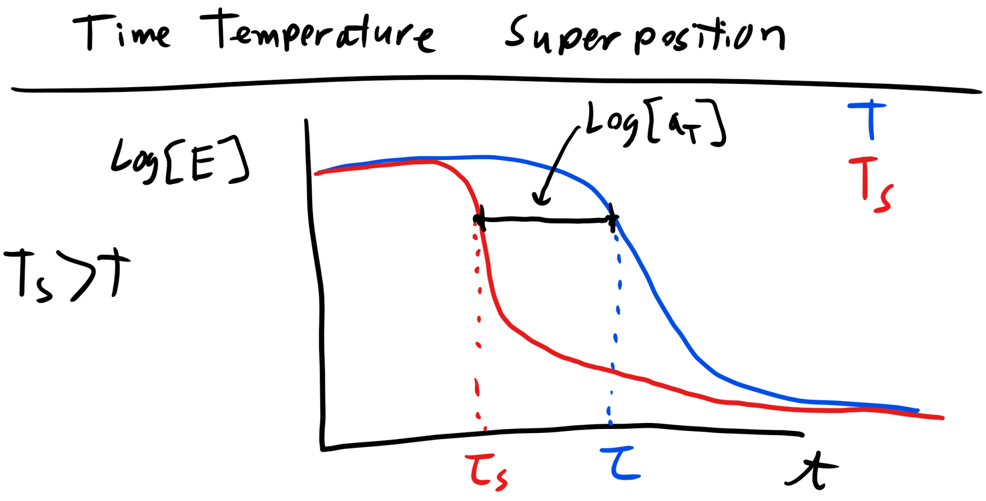

Figure 13-10: WLF Time-Temperature Superposition.

$B$ is another fitting constant.

**Limitations of WLF**

The **WLF equation** is applicable to homogeneous, linear viscoelastic materials, that are isotropic and amorphous. They must be in the temperature range $T_g - T_g + 100^oC$.

# CHAPTER 14

## COMPOSITES

### 14.1 Key Terms/Definitions:

- **Elastic deformation** - strain that is recovered upon the removal of an applied stress; strain energy stored in the material.

- **Young's modulus** - a measure of the stiffness of the material; strictly the slope of the stress-strain curve in the linear elastic regime under uniaxial tension.

### 14.2 Composite Mechanics:

So far we have been talking about the mechanics of primarily polymers but we haven't really touched on composite mechanics. **Composites materials are materials that contain typically more than one type of material combined**. This typically involves a **material matrix** which is the **major component** in terms of **volume fraction**. This matrix material is reinforced by an additional material typically one that is **stiffer or tougher than matrix material**. The material that reinforces the matrix can be in **particle form, fibers, or precipitates**. A composite can also be a porous material like metal foams, concrete, ECM, etc.

Let's take a look at a **particle reinforced composite** that is composed of a matrix which has some elastic modulus, $E_m$, and volume fraction, $f_m$. There is also the particle reinforcement in this case which again has an associated elastic modulus, $E_p$, and volume fraction $f_p$. Thus the **total composite modulus**, $E_{composite}$ is

$$E_{composite} = E_m f_m + E_p f_p \tag{14.1}$$

empirically there is typically a constant that is less than 1 for the particle reinforcement contribution but again that constant can only be found empirically.

Let's now look at a **fiber reinforced composite** that is pulled or stressed in the **transverse direction** with respect the the **longitudinal or axial direction of the fibers**. The **stresses are the same on the matrix and the fibers**. However the **strains of the fiber and matrix will be different**. With these constraints:

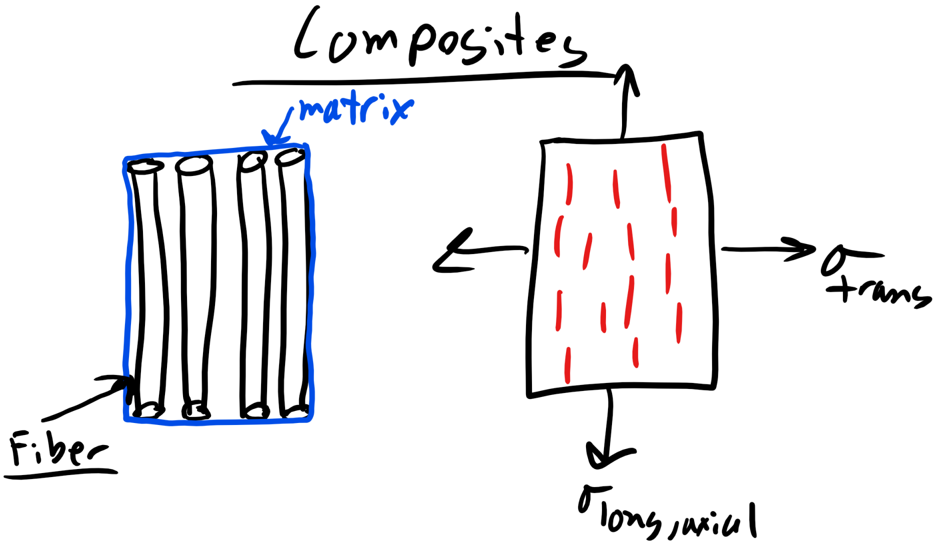

Figure 14-1: Composites pulled in the transverse or longitudinal/axial direction.

$$\sigma_m = \sigma_f = \sigma \tag{14.2}$$

$$\epsilon_c = \epsilon_m f_m + \epsilon_f f_f \tag{14.3}$$

$$\epsilon_c = \sigma\left(\frac{f_m}{E_m} + \frac{f_f}{E_f}\right) \tag{14.4}$$

$$\frac{1}{E_c} = \frac{f_f}{E_f} + \frac{f_m}{E_m} \tag{14.5}$$

If we instead **pull parallel to the fiber longitudinal or axial direction**. Here the **strain is the same** but now the **stresses will be different** for the fibers and the matrix. So with those constraints we get

$$\sigma_c = \sigma_f f_f + \sigma_m f_m \tag{14.6}$$

$$\epsilon_c = \epsilon_m = \epsilon_f \tag{14.7}$$

$$\sigma_c = E_f \epsilon f_f + E_m \epsilon f_m \tag{14.8}$$

$$E_c = E_f f_f + E_m f_m \tag{14.9}$$

We can see the difference in the Young's modulus in both of these directions as function of volume fraction in the plot below:

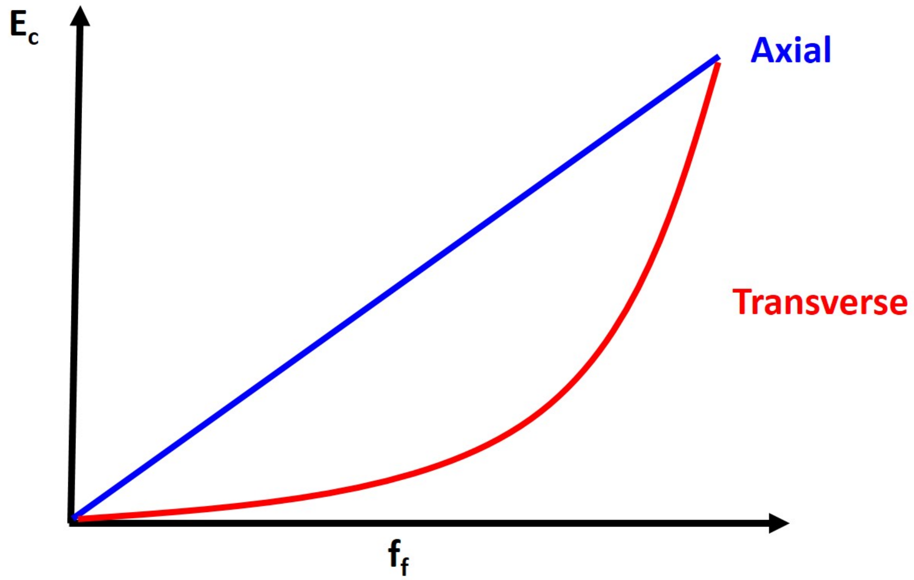

Figure 14-2: Composite modulus as a function of fiber fraction.

## 14.3 Transversely Isotropic Composite

Let's go a bit further and do an example of a composite or laminate that is transversely isotropic (i.e. $E_{33} = E_{22} \neq E_{11}$).

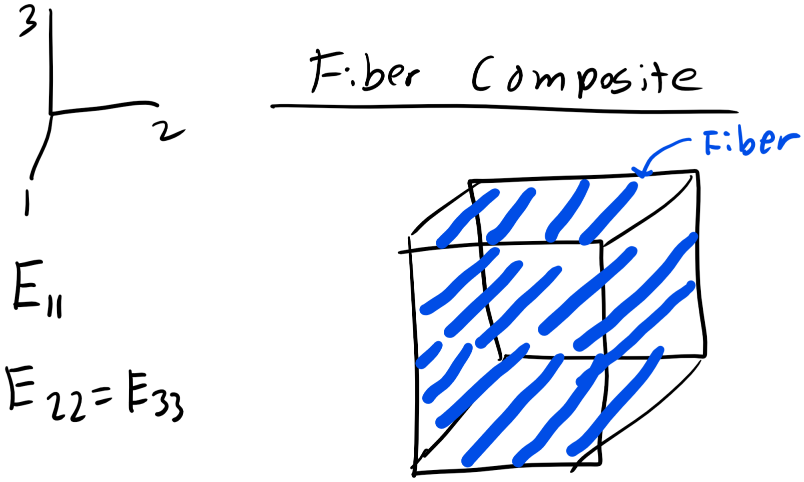

Figure 14-3: Schematic of a fiber composite.

In this scenario our compliance and stiffness matrices would like like this

$$\begin{bmatrix}\sigma_1\\\sigma_2\\\sigma_3\\\sigma_4\\\sigma_5\\\sigma_6\end{bmatrix}=\begin{bmatrix}C_{11}&C_{12}&C_{13}&0&0&0\\C_{12}&C_{22}&C_{13}&0&0&0\\C_{13}&C_{13}&C_{33}&0&0&0\\0&0&0&C_{44}&0&0\\0&0&0&0&C_{44}&0\\0&0&0&0&0&\frac{C_{11}-C_{12}}{2}\end{bmatrix}\begin{bmatrix}\epsilon_1\\\epsilon_2\\\epsilon_3\\\epsilon_4\\\epsilon_5\\\epsilon_6\end{bmatrix} \tag{14.10}$$

or equivalently

$$\begin{bmatrix}\epsilon_1\\\epsilon_2\\\epsilon_3\\\epsilon_4\\\epsilon_5\\\epsilon_6\end{bmatrix}=\begin{bmatrix}\frac{1}{E_1}&-\frac{\nu_{21}}{E_2}&-\frac{\nu_{31}}{E_2}&0&0&0\\-\frac{\nu_{12}}{E_1}&\frac{1}{E_2}&-\frac{\nu_{32}}{E_2}&0&0&0\\-\frac{\nu_{13}}{E_1}&-\frac{\nu_{23}}{E_2}&\frac{1}{E_2}&0&0&0\\0&0&0&\frac{1}{G_{12}}&0&0\\0&0&0&0&\frac{1}{G_{23}}&0\\0&0&0&0&0&\frac{1}{G_{13}}\end{bmatrix}\begin{bmatrix}\sigma_1\\\sigma_2\\\sigma_3\\\sigma_4\\\sigma_5\\\sigma_6\end{bmatrix} \tag{14.11}$$

We can see from this that as a result we will have that $\epsilon_4 = \epsilon_5 = 0$. We also know that from our conditions of tensor symmetry that

$$\frac{\nu_{21}}{E_2}=\frac{\nu_{12}}{E_1} \tag{14.12}$$

$$\frac{\nu_{13}}{E_1}=\frac{\nu_{31}}{E_2} \tag{14.13}$$

$$\frac{\nu_{23}}{E_2}=\frac{\nu_{32}}{E_2} \tag{14.14}$$

Now a typical scenario for composites will be when they are placed under plane stress conditions and we can then simplify our matrix and only focus on the **in-plane** stress and strains where we now have

$$\begin{bmatrix}\epsilon_1\\\epsilon_2\\0\\0\\0\\\epsilon_6\end{bmatrix}=\begin{bmatrix}\frac{1}{E_1}&-\frac{\nu_{21}}{E_2}&-\frac{\nu_{31}}{E_2}&0&0&0\\-\frac{\nu_{12}}{E_1}&\frac{1}{E_2}&-\frac{\nu_{32}}{E_2}&0&0&0\\-\frac{\nu_{13}}{E_1}&-\frac{\nu_{23}}{E_2}&\frac{1}{E_2}&0&0&0\\0&0&0&\frac{1}{G_{12}}&0&0\\0&0&0&0&\frac{1}{G_{23}}&0\\0&0&0&0&0&\frac{1}{G_{13}}\end{bmatrix}\begin{bmatrix}\sigma_1\\\sigma_2\\\sigma_3\\\sigma_4\\\sigma_5\\\sigma_6\end{bmatrix} \tag{14.15}$$

or more visually appealing

$$\begin{bmatrix}\epsilon_{11}\\\epsilon_{22}\\\epsilon_{12}\end{bmatrix}=\begin{bmatrix}\frac{1}{E_1}&\frac{-\nu_{21}}{E_2}&0\\\frac{-\nu_{12}}{E_1}&\frac{1}{E_2}&0\\0&0&\frac{1}{G_{12}}\end{bmatrix}\begin{bmatrix}\sigma_1\\\sigma_2\\\sigma_{12}\end{bmatrix} \tag{14.16}$$

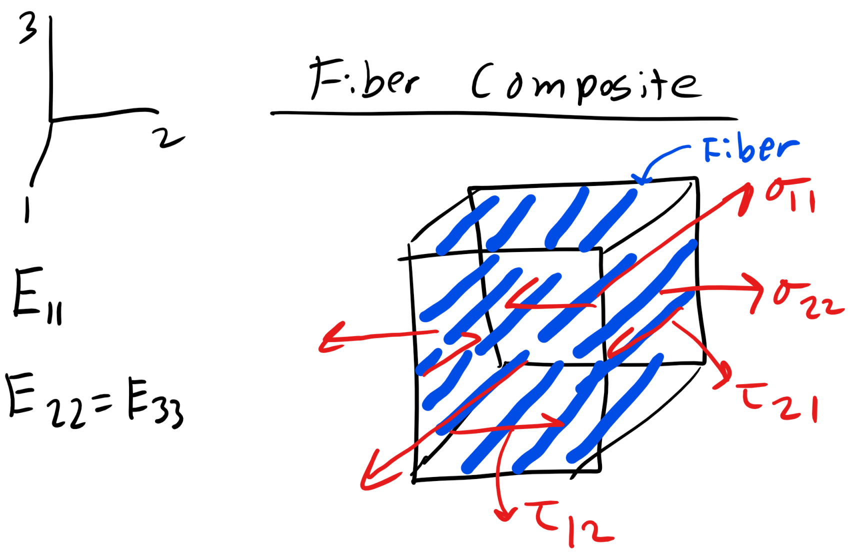

Figure 14-4: Plane Stress Conditions of Composite.

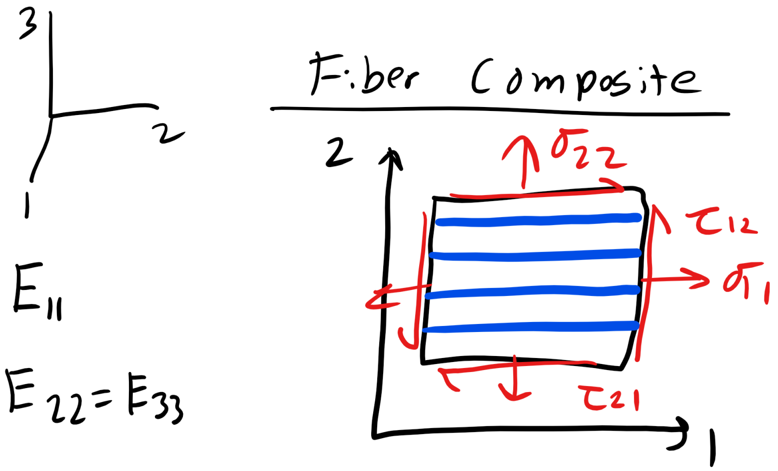

Figure 14-5: Plane Stress Conditions of Composite.

This great but this is only applies if we are pulling along the principal axes. How can we express the properties of this material when stressed along arbitrary directions with regards to the principal axes. Well we will use linear algebra!

We have previously seen in the elasticity lecture how to rotate stresses and strains in relation to Mohr's circle and we can do the same thing here. We will use our same rotation matrices, **transformation matrix (T)**, as previously defined and we can obtain stress after an arbitrary rotation

$$\begin{bmatrix} \sigma_{x'} \\ \sigma_{y'} \\ \sigma_{xy'} \end{bmatrix} = \begin{bmatrix} T \end{bmatrix} \begin{bmatrix} \sigma_x \\ \sigma_y \\ \sigma_{xy} \end{bmatrix} \tag{14.17}$$

For strain again we have to deal with this factor of 2 in relating shear strain so first we have to account for $\epsilon_{12} = \frac{\gamma_{12}}{2}$ so we have to introduce another matrix, the **Reuter Matrix (R)** as previously defined. So to convert to

$$\begin{bmatrix} \epsilon_{x'} \\ \epsilon_{y'} \\ \gamma_{xy'} \end{bmatrix} = RTR^{-1} \begin{bmatrix} \epsilon_x \\ \epsilon_y \\ \gamma_{xy} \end{bmatrix} \tag{14.18}$$

Now we can finally determine the strain at an arbitrary rotation for a transverse isotropic polymer composite or laminate which can be seen below when we combine these expressions

$$\begin{bmatrix} \epsilon_{x'} \\ \epsilon_{y'} \\ \gamma_{xy'} \end{bmatrix} = RTR^{-1}ST^{-1} \begin{bmatrix} \sigma_{x'} \\ \sigma_{y'} \\ \sigma_{xy'} \end{bmatrix} \tag{14.19}$$

**Case Study: Block Copolymers Composite Mechanics**

In BCPs, we saw a variety of different morphologies based on the phase fraction and temperature of the system. In principal, the anisotropy of these systems gives rise to anisotropy in the mechanical properties as well, since pulling along the axis of a cylinder, for example, will yield a different modulus than pulling perpendicular to the axis.

Let's consider an example of triblock copolymers forming lamellae, with glassy domains forming one lamella and rubbery domains forming the other. This would occur if two of the blocks in the triblock have very different glass transition temperatures, such that one would be glassy while the other rubbery. We can now treat the mechanical properties in much the same way as we would treat compositics . Pulling along the axis of the lamellae (that is, along the long edge) leads to pulling on actual glassy domains, since in order to deform in this direction both rubbery and glassy lamellae have to elongate by an equal amount. Since the modulus of the glassy domain is much higher, the glassy modulus will essentially be the only contributor to the measured modulus in this direction.

If you pull at $90^o$ to the axis (i.e. in the direction that intersects each face of the lamellae), then the rubbery regions will preferentially deform first since their modulus is much lower, and the glassy domains will not deform at all. The modulus in this direction is dominated by the rubbery modulus, though higher because of the constraints of maintaining a lamellar geometry.

The surprising result, though, is that when pulling at $45^o$, the modulus is lowest - this is because the material is being sheared at constant volume. At $90^o$, the uniaxial deformation leads to necking which attempts to change the volume of the sample locally - think of the rubbery polymers stretching out and thinning the sample while still aggregating laterally, which leads to bowing. Pulling at $45^o$, however, applies stress along the axis of maximum shear stress, leading to shear at constant volume and minimizing the modulus felt.

In the limit of high strains, all of the moduli tend to converge together. The explanation behind this behavior is the onset of kinks - independent of what direction you are applying the stress, eventually the material will reorient to a lowest-energy configuration, which can result in lamellae "kinking" such that they are at $45^o$ to the pulling direction, which as noted above has the lowest modulus (and hence lowest energy for a given strain). Some strain energy is thus localized to each kinking point, but overall the morphology can sustain much greater energy by putting energy into shearing the lamellae at $45^o$, the preferred direction.

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# CHAPTER 15

## POLYMER YIELDING

## 15.1 Key Terms/Definitions:

- **Plastic deformation** - strain that is permanent upon removal of an applied stress; strain energy dissipated from the system.
- **Yield stress** - the stress at which strain switches from elastic to plastic.
- **Toughness** - the amount of strain energy necessary to bring a material to fracture.
- **Ductile materials** - materials with a high toughness, usually due to the ability to plastically deform to high strains.
- **Brittle materials** - materials that fracture at low strains; low toughness.
- **Fracture** - the catastrophic failure of a material such that it can no longer hold a load.
- **Shear yielding** - the plastic deformation of amorphous or semi-crystalline polymers due to the flow of material at locations of high shear stress
- **Crazing** - the formation of crack faces joined by polymer tendrils that open under an applied tension
- **Necking** - the formation of a region of an elongated sample with a smaller cross-sectional area due to the increase in the true stress in excess of strain hardening
- **Strain hardening** - the increase in the stress required for elongation; in polymers, arises due to the orientation of polymer chains in the direction of pulling.
- **Strain softening** - the decrease in the stress required for elongation; in semi-crystalline polymers, related to the conversion of crystalline regions to amorphous regions.

## 15.2 Yielding Criterion:

So far we have just been talking about stress and strain up to the yield point. However what happens beyond the elastic limit of materials? Well we have already discussed that the **yield point** denotes that the deformation is now permanent or **plastic** and we have initiated **dislocation or defect motion**. But as engineers perhaps the better or more useful question to ask is can we predict whether yielding will occur for materials that are not just simply loaded uniaxially. There are multiple yielding criterion that we will discuss, specifically: **Rankine, Tresca, and von Mises Yield Criterion**.

## 15.3 Rankine:

**Rankine** criterion also known as the **maximum normal stress** criterion states the a material will fail or yield when the maximal principal (normal) stress ($\sigma_1$) reaches the value where the material yields in uniaxial tension or compression so the material will yield when:

$$\sigma_1 \geq \sigma_y \tag{15.1}$$

**IMPORTANT NOTATION NOTE:** Once again these mechanics people utilize some confusing notation. This $\sigma_1$ is not equivalent to $\sigma_{11}$ this $\sigma_1$ is referring to the maximum principal normal stress. Rankine doesn't accurately describe material yielding, it is **missing shear stress.**

## 15.4 Tresca:

So let's take a look at the **Tresca criterion** or the **max shear stress criterion** which states that the material yields when the $\tau_{max} = \frac{\sigma_1 - \sigma_3}{2} = \sigma_y$ reaches the value it does when material yields under uniaxial loading which is described below:

$$\sigma_1 - \sigma_3 \geq \sigma_y \tag{15.2}$$

Again here it should be noted that $\sigma_3$ is the minimum principal normal stress. This is better, but in 1913 for WWI/WWII subs because they found that the Tresca criterion was a poor predictor for yielding.

## 15.5 Von Mises:

So we developed the **Von Mises criterion** is also called the **maximum shear deformation energy (SDE) criterion** and states the material will yield when the SDE reaches the yield stress value under uniaxial loading which is:

$$\sigma_{eff} = \sqrt{\frac{1}{2}[(\sigma_{11} - \sigma_{22})^2 + (\sigma_{22} - \sigma_{33})^2 + (\sigma_{33} - \sigma_{11})^2 + 6(\sigma_{23}^2 + \sigma_{31}^2 + \sigma_{12}^2)]} \geq \sigma_y \tag{15.3}$$

or in terms of the principal stresses:

$$\sigma_{eff} = \sqrt{\frac{1}{2}[(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2} \geq \sigma_y \tag{15.4}$$

You can see by drawing the yield loci of these different criterion that Rankine is the most conservative yield criterion.

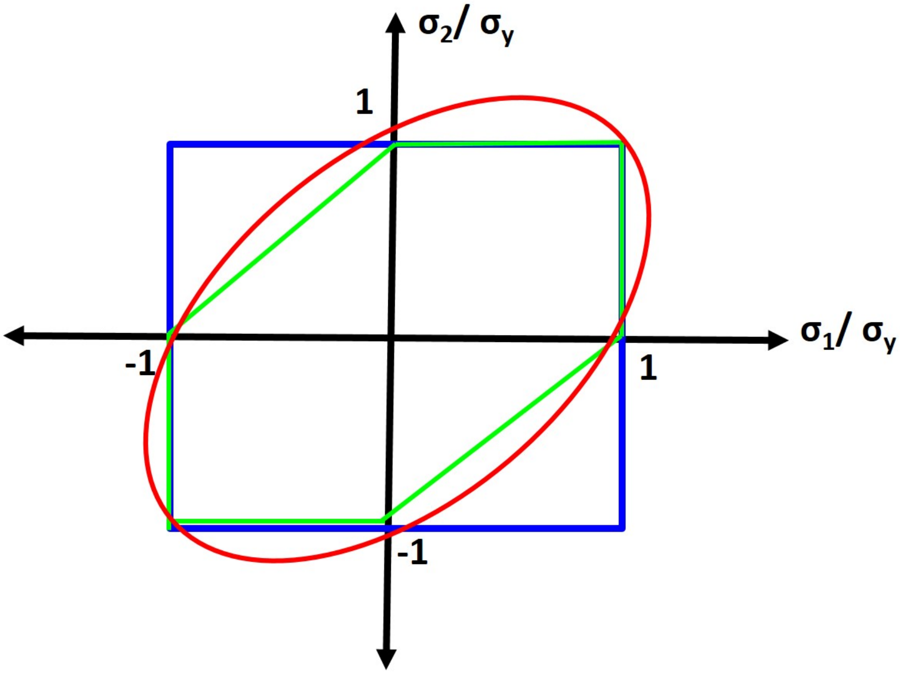

Figure 15-1: Yield Criterion. Rankine (blue), Tresca (green), Von Mises (red).

## 15.6 Polymer Yielding Mechanisms:

Upon application of a stress in excess of the yield stress the sample permanently deforms and any additional plastic strain is not recoverable once stress is removed. In metals, the origin of plastic deformation is the introduction and movement of dislocations in a lattice, resulting in shear banding on the macroscale; similar mechanism also apply for single-crystal polymer fibers.

In amorphous and semi-crystalline polymers, there are two observed yield behaviors: **crazing** and **shear banding**. Both can appear in the same material at the same time, or one can be observed and not the other. **Crazes are observed as the opening of a crack with strands of polymer that extend between the crack faces**, and leads to a change in volume (called dilational deformation). A **shear band in polymers is essentially the same as shear banding in other materials**, and is caused by a movement of material along directions of **maximum shear stress** (typically ± $45^o$ under uniaxial tension) if the stress is above the yield point. **Shear bands lead to the formation of necking** and the **reduction in cross-sectional area** at the neck, versus in the bulk; however, volume is still conserved in the sample overall.

## 15.7 Shear Banding:

Shear yielding in glassy, amorphous polymers (or semi-crystalline polymers) looks at the macroscale very similar to the shear yielding in non-polymeric materials. Above a critical yield stress, the strain will begin to increase at a roughly constant plateau stress as the material undergoes **necking**. Upon reaching high strains, the stress for continued elongation again begins to increase in a process called **strain hardening** until eventually the material fails.

As the material is elongated due to strain, it undergoes a process called **strain hardening**, which means that the **amount of stress required to continue straining the material increases**. In polymers, the molecular mechanism for strain hardening **is the alignment of polymer chains with the stress**; at **high strains we can imagine the polymers become aligned with the stress and require further straining the sample requires pulling on bonds**. Regardless of the molecular mechanism, as the material strain hardens more and more stress is necessary to continue elongation. However, to maintain volume conservation, elongating the material along the direction of pulling necessarily reduces the cross-sectional area in the other dimensions; since stress is measured as a force divided by an area, the **true stress** felt by the sample thus increases as elongation increases even if the actual force applied to the sample is held constant. Typically, stress-strain curves are drawn to show the engineering stress applied, since this is directly controllable experimentally. Above the yielding point, the **decrease in the cross-sectional area upon elongation leads to an increase in the true stress felt by the sample even if the engineering stress is held constant**. However, at the same time the amount of stress necessary to induce further strain is also increasing due to strain hardening. The onset of necking is thus a competition between the strain hardening and the decrease in the cross-sectional area.

When **the material's cross-section decreases by a greater amount than the material strain hardens**, the true stress will be sufficient to drive further elongation of the sample even **without an increase in the engineering stress**. As a result, the material will **continuously elongate at a plateau in the engineering stress until it strain hardens enough to prevent this unstable elongation and force other parts of the material to harden instead**. This **unstable propagation** is called **necking** because physically the strain will concentrate in **one section of the sample** (**typically where there is some fluctuation in the microstructure that leads to a stress concentrator**) which will then preferentially elongate and form the neck. In polymers, because the **stiffness of an aligned polymer is highly anisotropic**, there is a huge amount of strain hardening at high elongations **once the sample becomes aligned with the applied engineering stress**. This **leads to stable necking because upon neck formation the neck will unstably reduce to a small cross-sectional area consistent with full alignment**, at which point the highly strain-hardened neck region will stop elongating, and the other **softer** regions will deform instead to increase the volume of the necked region. Hence, the polymers tend to form very stable necks. Again, this entire process appears to occur at constant stress because the stress in a stress-strain curve is the engineering stress, but **the true stress felt in the material increases as the cross-sectional area decreases**.

Finally, it is possible to observe the morphological transitions behind strain hardening. As necking occurs, x-ray scattering patterns can be used to observe the alignment of chains. Prior to necking, there is some isotropy to the polymer sample, which is then oriented by the application of stress. Upon elongation of a long neck, almost all chains tend to be elongated, leading to the high

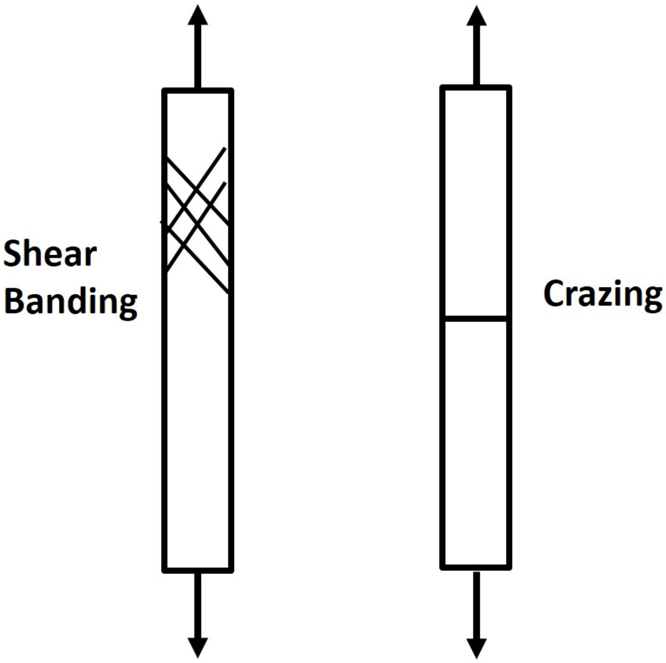

Figure 15-2: Shear Banding vs. Crazing

degree of strain hardening as just noted.

**Shear bands** are zones of material alignment that are **1000s of nm wide** and **nucleate at stresses** that are approximately $\frac{G}{10}$ (theoretical yield stress) and continue to grow as stress exceeds. **Shear band deformation is highly nonuniform.** They are also not regions of high defect density but instead they are regions of **chain alignment**. Shear banding nucleation is also highly temperature dependent. Typically for uniaxial tension **shear bands will form at 45$^o$ relative to the applied stress** at the locations of maximum shear stress.

## 15.8 Crazing:

**Crazes** regions of **highly localized deformation** and they are **distinct from a crack**. **Fibrils will span the craze**. Crazes will form **perpendicular to the loading axis** with fibrils aligned with the loading axis. Crazing will **not occur under compressive stress**. You can **modify the von Mises criterion when considering shear banding and Tresca when considering crazing**.

**Crazes** are also regions of **highly localized deformation** which is distinct from both a crack and a void but very similar to both. A craze occurs when a void is formed between two faces of a polymer and some polymer chains, **fibrils/tendrils**, will span the void and connect the two faces. Crazes **occur in tension only**, and look and act very similarly to cracks, though they are not identical. A crack is essentially the same **but without the polymer tendrils connecting faces**; crazes are thus unique to polymer samples because they have the long molecules necessary to cross across the void volume. Note that **metals cannot form crazes because they do not have long chains in their microstructure that form these tendrils**. Due to the formation of the void area between the two faces, the volume of the polymer increases, unlike the case of shear yielding where volume is conserved. Typically the fibrils are on the order of 20-50Å, and about 50% of the void is filled with fibrils. Crazes are very visible in samples because they **scatter light due to a large change in the index of refraction between the bulk sample and the void**, and the void is sufficiently wide that this scattering is visible. The **craze will open such that the void is oriented perpendicular to the applied tensile stress**, and will continue to grow/open in the perpendicular direction, essentially growing in width. Craze formation is favored by the inclusion of agents that lower the surface energy of the faces, essentially leading to nucleation points in the bulk where crazes can first grow.

We can understand the formation of crazes, and especially the formation of fibrils, by thinking about the **surface free energy of the exposed craze face**. As the craze grows, the polymer at the edge of the growing craze will have a large surface area, which is unfavorable given some positive surface energy (since polymer prefers to be in bulk, and the lack of neighboring polymers when facing a void effectively is an energetic penalty). At some point, **it is more favorable for fibrils to break off from the bulk in order to exist independently in order to minimize their surface area**. This is called the **Taylor meniscus instability**, and explains why fibrils form as the craze grows. As the craze continues to grow, the fibrils will elongate (since the faces essentially move farther apart), leading to some crystallization which will oppose the further growth of the craze.

The **maximum stretching we can get is the length of polymer between entanglements, assuming entanglements are fixed over the timescale of craze formation. We can approximate the contour length between entanglements in terms of the entanglement molecular weight divided by the molecular weight of a monomer.**

**Asymmetry in Yield Criterion:**

Unlike metals, **polymers have a significant response to hydrostatic pressure**, which **changes the yield criteria considerably**. The influence of pressure can be thought of as packing the sample together if the pressure is compressive. In metals the sample typically may not respond because the influence of pressure should not significantly change the metallic bonding in metals, which develop from the sharing of electrons, not favorable packing. In polymers, however, **non-specific, relatively weak van der Waals interactions stabilize the crystalline state, interactions that are highly dependent on the distance in between polymer molecules**. These interactions are weak enough that pressure can significantly influence the local packing of polymer chains. Hence, applying a compressive pressure improves the packing of the polymer which then requires more stress to yield the polymer crystal, while an outward pressure decreases the amount of energy required to deform the material. This means that the **yield criterion for polymers is not symmetric as is the case for metals**!

For amorphous polymers, the yield surface has **two additional effects**

1. **Crazing Yield Line:** Onset of crazing, which can only occur under tension, leads to a separate yield line above which crazing is preferred to shear banding

2. **Asymmetry in Yield Surface Under Compression:** Yield occurs at higher stress when a polymer is under compression than under tension. The yield surface is distorted from the typical ellipse as a result.

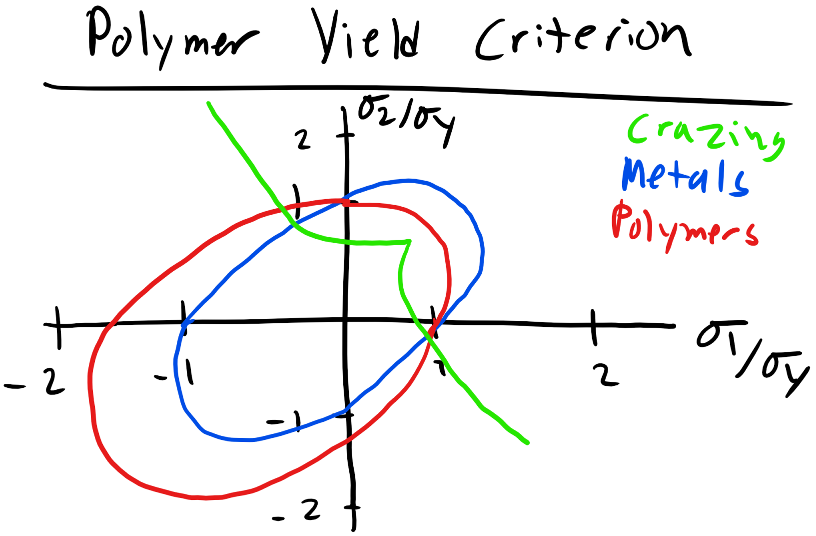

Figure 15-3: Shear Banding Yield Curve

Finally, it should again be noted that the onset of yield will be temperature and time dependent, with the yield stress dropping to 0 at either $T_M$ or $T_G$ depending on the type of polymer.

**Atomistic Perspective of Polymer Yielding:**

At the atomistic level, plastic flow for semi-crystalline polymers can be explained by the **slip of polymer chains past each other**, where the aligned lamella deform as chains move past each other. This process is qualitatively **analogous to the slip of metallic materials in a crystalline lattice**, which makes sense since crystalline regions of polymer are also characterized by a crystalline lattice. However, how does plastic deformation occur for glassy polymers?

Well in a glassy state, we can think of **polymer molecules as frozen in place in an amorphous state**. This frozen state is due to a low temperature and minimal free volume, meaning that molecules have insufficient thermal energy to jump past near-neighbors due to a large barrier to this motion. We can think of the application of stress, then, as **modifying the energy barrier to jumping**, and can use an **effective activated jumping model**, which in this case is called the **Eyring Theory of viscous flow**. In Eyring theory, we imagine the molecules of the glass as largely confined to some lattice, where there is an energy barrier associated with hopping from one site on the lattice to the other. Under stress-free conditions, this energy barrier is prohibitively high, but **we can imagine that applying a stress reduces the barrier for**

**hopping in the direction at which the stress is applied**. **Under compression**, then, we can imagine squeezing the polymer **sample by reducing the barrier for flow in the directions orthogonal to the compression**. Since we are assuming that all molecular motion is due to a series of jumps, the total strain rate should thus be related to the effective jumping rate after the application of stress. Let's call the jumping rate in the absence of stress $\nu_0$, and assume it is given by an Arrhenius type equation:

$$\nu_0 = B \exp(-\Delta G^*/kT) \tag{15.5}$$

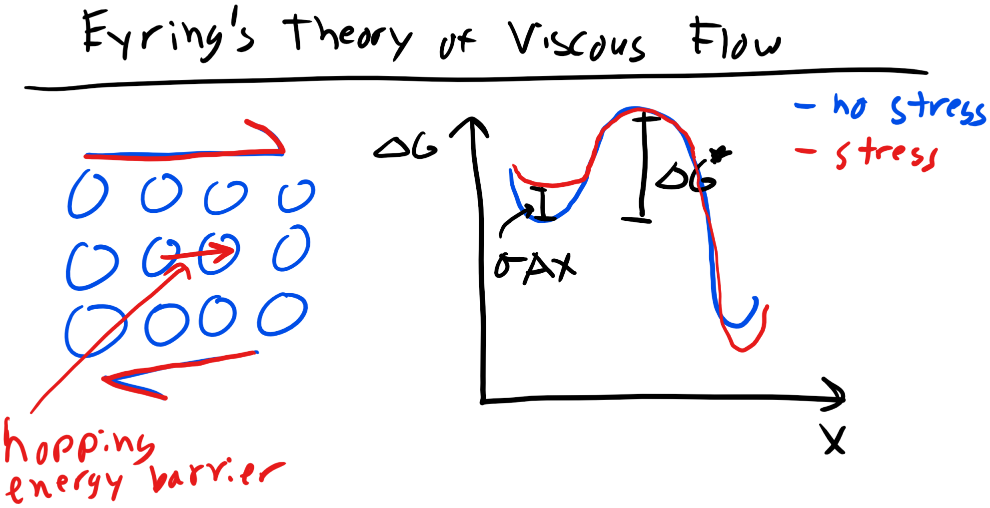

Figure 15-4: Shear reduces energy barrier for hopping.

This expression gives the jump rate for a glassy molecule in the absence of stress, where $B$ is some constant and $\Delta G^*$ is the energy barrier for jumping. Now consider applying some stress $\sigma$ across and area $A$ acting over a jump distance of $x$. The application of this stress changes the energy barrier by an amount of $\sigma Ax$, **since this is a work term**. We expect the barrier to be lowered in the direction in which the stress is applied, giving a new forward jumping rate $\nu_f$

$$\nu_f = B \exp[(-\Delta G^* - \sigma Ax)/kT] = \nu_0 \exp(\sigma Ax/kT) \tag{15.6}$$

Note that we rewrote the **final forward jumping rate in terms of the initial jumping rate**. Similarly, the **backwards jumping rate**, that is, the **rate at which molecules jump in a direction opposed to the stress, should be significantly lower since the energy barrier to jumping backwards is higher by the same factor** of $\sigma Ax$. The backwards jumping rate $\nu_b$ is thus

$$\nu_b = \nu_0 \exp(-\sigma Ax/kT) \tag{15.7}$$

Note the sign change as the only difference - this rate is much lower than the initial jumping rate $\nu_0$. We can thus **express the strain rate as proportional to the difference between the forward and backwards jump rates**, since this difference is essentially some net flow in the forward direction. We thus write the strain rate as

$$\frac{d\epsilon}{dt} = \nu_f - \nu_b = \nu_0 \left[\exp(\sigma Ax/kT) - \exp(-\sigma Ax/kT)\right] = K \sinh\left(\frac{\sigma V}{kT}\right) \tag{15.8}$$

Note that the term on the left is equivalent to the sinh function with **new prefactor $K$ as a lumped constant**, and replacing $Ax = V$, reflecting the fact that the cross sectional area A times the distance x is a volume, called the **activation volume**. Physically, the **activation volume is the volume of polymer material that must move to yield shear flow**.

If $\sigma V$ is comparable to $\Delta G^*$, then the **jump rate starts to become very high, and we would expect very high strain rates, which we can think of as essentially a liquid state**. This would then mark the onset of yield, since now it is much easier for the glassy molecules to move past each other.

**Plastic Strain Recovery in Polymeric Materials:**

One extremely unique property of polymers is the ability of polymers to recover plastic deformation at long times and elevated temperatures. Polymers that undergo plastic deformation, can recover plastic strain due to the ability of polymers to flow at long times/elevated temperatures. This behavior is also techically accessible to metals but the conditions are very extreme to achieve this behavior. For polymers heating to near $T_g$ can result in significant recovery depending on the material, processing history, and loading history.

**Polymer Self-Healing:**

Polymers also have the unique ability to exhibit self-healing behavior. Certain polymers when damaged can intrinsically self heal and repair cracks via cross-linking or some type of triggered polymerization. Also for some materials like silly putty which are above $T_g$ at room temperature this material can self heal at reasonable time scales due to polymer interdiffusion. Alternatively you can make **extrinsic** self-healing polymers that will self heal when a crack triggers some type of microcapsules that will polymerize and fill the crack gap.

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# Bibliography

[1] Callister. *Materials Science and Engineering: An Introduction, Tenth Edition.* John Wiley & Sons, Incorporated, December 2017.

[2] Sam Allen and Edwin L. Thomas. *The Structure of Materials.* Wiley, February 1999. Google-Books-ID: JgtpQgAACAAJ.

[3] Keministi. English: Newman projections of butane conformations & their relative energy differences (not total energies). Conformations form when butane rotates about one of its single covalent bond. Torsional/dihedral angle is shown on x-axis., September 2018.

[4] Original: DornelfVector:DePiep. English: Hexagonal close packed crystal structure (vectorised from png), July 2012.

[5] Ficheiro:Empilement compact.svg.

[6] Zureks. Polski: Schematyczne przedstawienie dyslokacji krystalicznej - dyslokacja śrubowa, 2008.

[7] Javier Bartolomé Vílchez. English: Scheme of the Burgers‘ vector in edge and screw dislocations, July 2008.

[8] Robert W. Balluffi, Sam Allen, and W. Craig Carter. *Kinetics of Materials.* Wiley, December 2005. Google-Books-ID: i9jPjwEACAAJ.

[9] Darrel J. Irvine. Thermodynamics., September 2009.

[10] Krystn Van Vliet and John M. Maloney. Mechanical behavior of materials., September 2010.

[11] 2D_geometric_strain png: Sanpazderivative work: Mircalla22. English: Deformation of an infinitesimal rectangular material element., August 2009.

[12] Yet-Ming Chiang. *Physical Ceramics.* John Wiley Sons, 1997. Google-Books-ID: aBYtswEACAAJ.

[13] Reid Van Lehn and Alfredo Alexander-Katz. Polymer physics., September 2011.

[14] Robert J. Young and Peter A. Lovell. *Introduction to Polymers, Third Edition.* CRC Press, June 2011. Google-Books-ID: ImQg2MK8NtkC.

[15] Michael Rubinstein and Ralph H. Colby. *Polymer Physics.* OUP Oxford, June 2003. Google-Books-ID: RHksknEQYsYC.

[16] 718 Bot at English Wikipedia. English: personal production. Diffusion and usage unrestricted, July 2008.

[17] Stephen Blundell. *Magnetism in Condensed Matter*. OUP Oxford, October 2001. Google-Books-ID: OGhGmgEACAAJ.

[18] Kittel. *INTRODUCTION TO SOLID STATE PHYSICS, 7TH ED*. Wiley India Pvt. Limited, 2007. Google-Books-ID: F9Qu5c_hUaUC.

[19] Anthony Mark Fox and Department of Physics and Astronomy Mark Fox. *Optical Properties of Solids*. Oxford University Press, 2001.

[20] Reid Van Lehn, Alfredo Alexander-Katz. Polymer physics., September 2012.