

MECHANICS AND SCIENCE OF MATERIALS



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Mechanics and Science of Materials

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Chapter 1: Introduction to Materials, X-Ray Diffraction, and Inter and Intramolecular Bonding

1.1 Topics Covered in this Book

- **Part I: Bonding, Structure, Defects, and Phase Diagrams**
- **Part II: Mechanics of Materials**
- **Part III: Electrochemistry, Electrical, and Optical**

I have recorded a series of recorded video lectures to supplement this text which can be viewed in the playlist here:

<https://www.youtube.com/playlist?list=PL5J4dxGKE5Wgkrk>

1.2 The Materials Tetrahedron

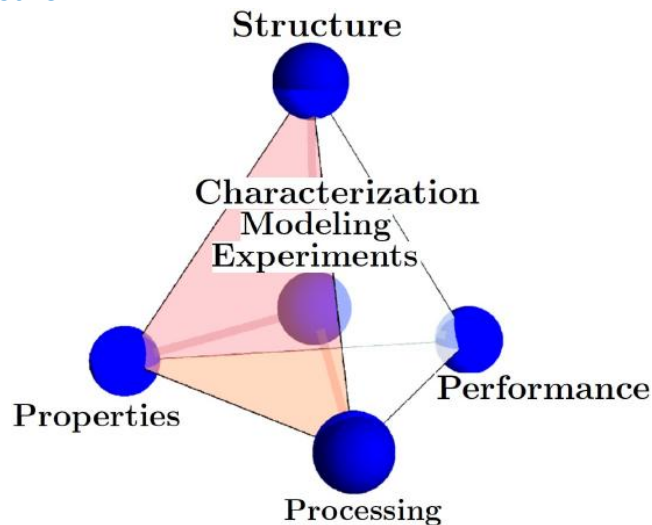


Figure Chapter1.1: Materials Tetrahedron

The four corners of the Materials Science and Engineering Tetrahedron are: **Structure, Processing, Properties, Performance**. At the center is a combination of **Charact/Modeling/Exp.**

A couple of quick examples if you **process** sheet metal by cold rolling you change the **structure** and induce more dislocations in the material. This in turn will change the yield strength (**property**) and thus the **performance** of that sheet metal in the application of interest. As materials scientists at the core of what we do is try to characterize material with **experimentation and simulation** to better understand this materials tetrahedron and to eventually reach a point where we can begin to predict some material responses.

Any other examples where we can apply this materials tetrahedron?

- Lead Titanate
- Cold Rolling Titanium Sheet
- Cross-Linked Rubber or Kevlar

Different Types or Classifications of Materials:

- Metals
- Polymers
- Ceramics
- Composites
- Active Matter
- Piezoelectric
- Shape Memory Alloys
- Ferromagnetic Materials

Material Properties:

- Mechanical
- Thermal
- Magnetic
- Optical
- Electrical
- Structure

1.3 Atomic Structure and Bonding:

Before diving into materials structure, we need to start at the basics and build up from the subatomic to atomic, nano, micro, and then macrostructure. So hopefully we all remember from our chemistry classes...

An atom is composed of a nucleus of protons and neutrons. A cloud of electrons surrounds the nucleus. The atomic number of an element is denoted by the number of protons in the nucleus. Atomic mass is the sum of the masses of proton and neutrons. Atomic weight of an element is the weighted average of the atomic masses. The atomic mass unit (amu) is defined as $\frac{1}{12}$ the atomic mass of Carbon 12.

When we discuss the different types of bonding we are typically interested in the electronic structure of an element or a material. In particular, we are interested in the valence electrons or the outermost electrons. Now electrons have particle-wave duality, i.e. electrons are governed by quantum mechanics. The classical example being the double slit experiment. It was conducted by Thomas Young in 1801 where he showed that light and later Davisson and Germer demonstrated that electrons display an interference pattern when shot at a double slit. This is because electrons can behave like particles and waves and when a wave passes through a double slit there will be constructive and destructive interference of the waves.

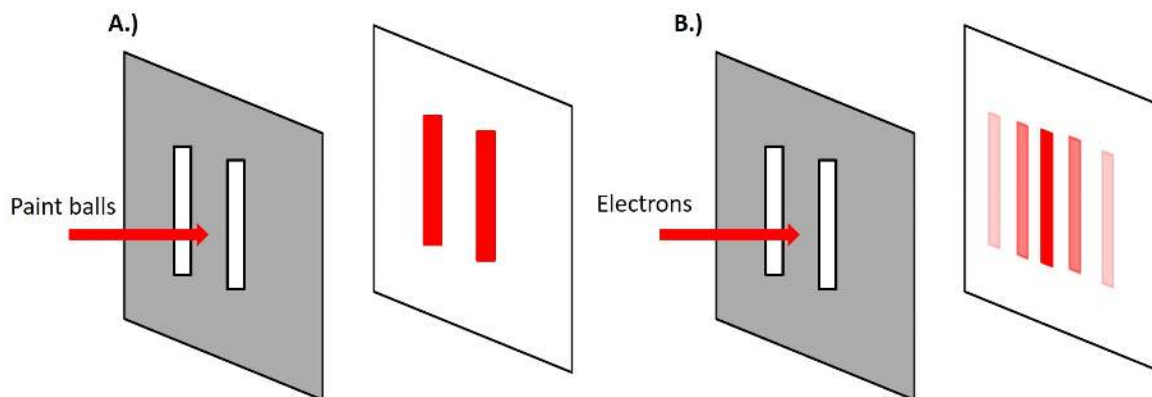


Figure Chapter1.2: Double Slit Experiment. A) Particle pattern and B) Electron pattern.

This phenomenon is particularly relevant to X-Ray Diffraction (XRD). This is a technique we will use in our first lab to investigate the atomic structures of several different materials. In general, diffraction will occur when a wave encounters a series of regularly spaced obstacles or slits that are capable of scattering the wave and have spacings that are comparable to the magnitude of the wavelength of the incident wave.

Let's look at an example of constructive vs. destructive interference as seen below. Consider the first set of waves that are incident to the scattering event. After they pass through the scattering event you see that the waves are still in phase so the resultant waves constructively interfere with each other and produce the resultant diffracted wave that is now twice the amplitude. We previously assumed that the two incident waves were both of the same magnitude and wavelength. Conversely for destructive interference after the waves encounter the scattering event they are out of phase which results in the waves canceling each other out or in other words destruction.

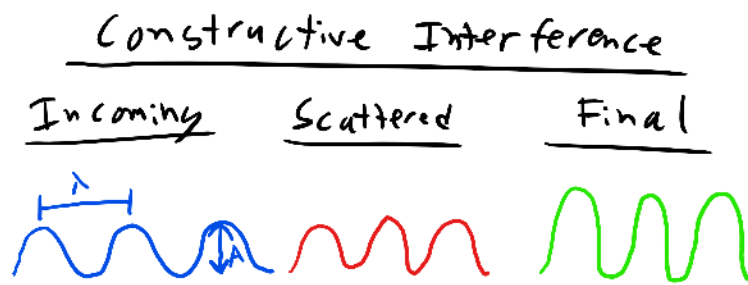


Figure Chapter1.3: Constructive Interference

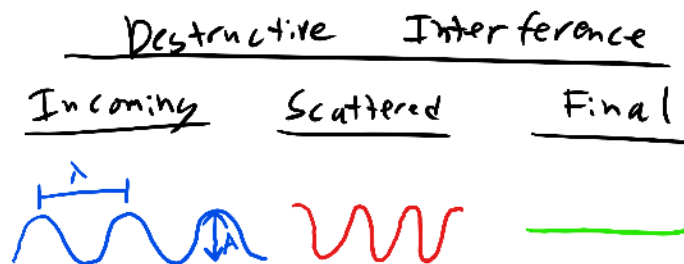


Figure Chapter1.4: Destructive Interference

1.3.1 Bragg Diffraction

Sir William Lawrence Bragg was a very brilliant scientist and he won the Nobel Prize for Bragg Diffraction when he was 25 and he won it with his father. Bragg realized that if we want to deduce material structure we can actually investigate this with X-rays. Cu-K_α radiation has a wavelength of $1.542\text{\AA}$. This is on the order of the spacing of atomic structures which meets one of our criterion for diffraction and crystal structures are made of regularly spaced obstacles for which a beam of X-rays can scatter. Bragg saw that in doing so it would be possible deduce the inter-atomic or inter-planar spacing between atoms for a given incident wavelength. Look at 2D schematic below

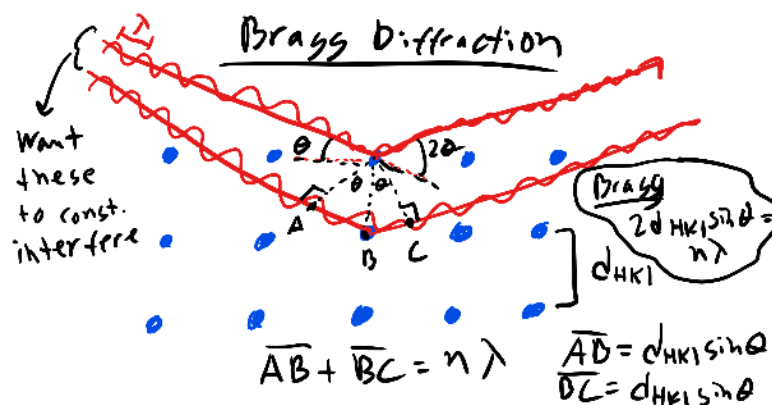


Figure Chapter1.5: Bragg Diffraction

We again have two incident beams that will interact with two planes of atoms each at an angle of incidence θ_B which is the Bragg angle or the condition for diffraction. So what is the condition for diffraction in the example? Well we have to have constructive

interference so the extra path length traveled by the lower incident wave must be equal to an integer number of wavelengths as the upper incident wave and that equivalence gives us Bragg's Law

$$n\lambda = 2d_{hkl} \sin \theta_B \quad (\text{Chapter 1.1})$$

where n is an integer number which denotes the order of reflection, λ is the wavelength, θ_B is the Bragg angle, and d_{hkl} is the interplanar spacing.

The interplanar spacing for cubic materials is defined as

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (\text{Chapter 1.2})$$

where a is the lattice parameter of the unit cell, and h, k , and l are the miller indices. More on these much later in the Structure Lecture.

But now back to electrons... Electrons are described by quantum numbers, specifically 4 quantum numbers. The principal quantum number, n , specifies the electron shell which takes on integer values, sometimes designed by K, L, M, N, O which corresponds to $n = 1, 2, 3, 4, 5, \dots$. Remember back to chemistry that these shells correspond to the Bohr atomic model where electrons revolve around discrete orbitals and that the electrons are quantized in discrete energy states. In reality it is not a discrete orbital but instead electrons reside within some cloud according to a probability distribution. The second quantum number sometimes referred to as the azimuthal quantum number, l , designates the subshell. l is an integer value as well and defined as $l = 0$ to $l = (n-1)$. The letter designation is s, p, d, and f respectively. The orbital shapes depends on l .

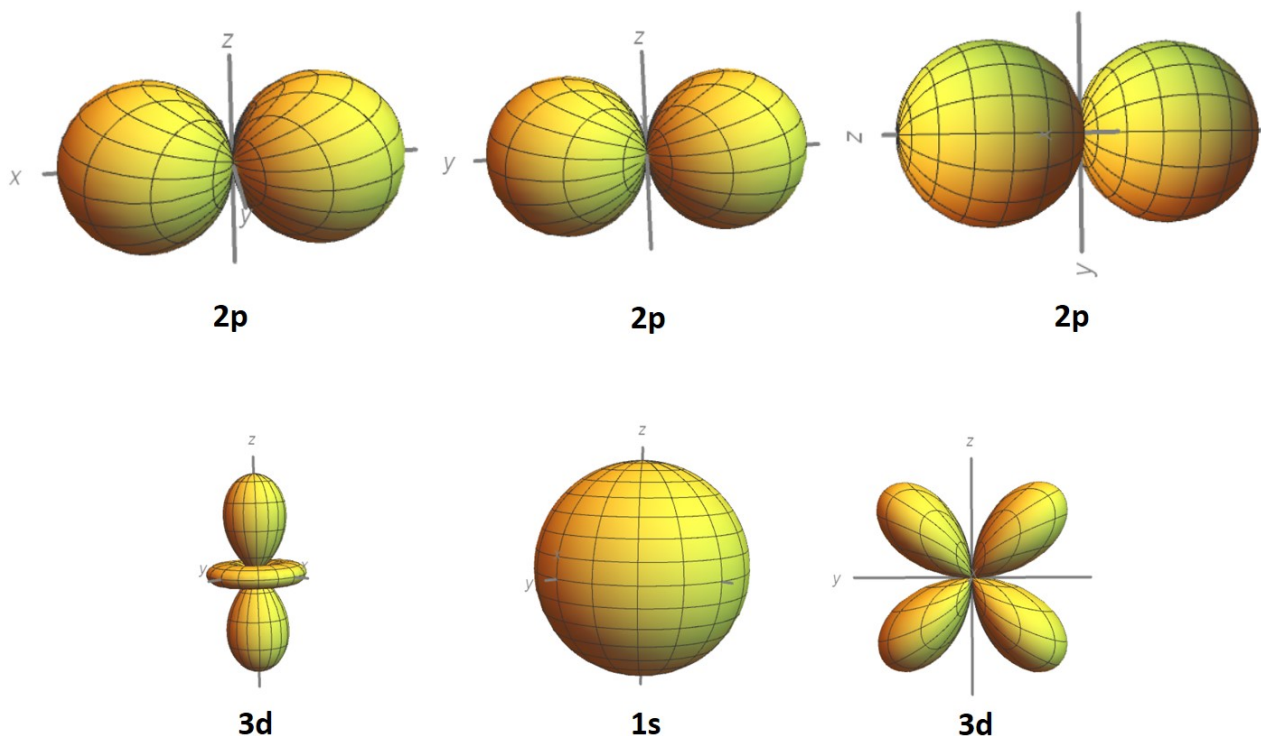


Figure Chapter1.6: Electron orbitals

The number of electron orbitals for each subshell is determined by the third quantum number sometimes called the magnetic quantum number, m_l . m_l can take on integer values between $-l$ and $+l$. Additionally with each electron there is a spin moment which must be oriented either up or down and this is captured by the fourth and final quantum number m_s .

We fill electron orbitals or states using the Pauli exclusion principle, each electron state can hold no more than two electrons and just have opposite spins. When electrons are occupying states such that the energy is minimized they are in the ground states but there are times when the electrons can become excited and transition to higher states.

1.4 Types of Bonding: Covalent, Ionic, Metallic, and Van Der Waals

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. And typically we are concerned with four types of bond.

1. **Covalent (5eV or about 200 kT)**
2. **Ionic (1-3eV or 80kT)**
3. **Metallic (0.5eV or 20kT)**
4. **Van Der Waals (0.001-0.1eV or 0.2kT)**

First question why do we even need bonding? Or a better question why does bonding occur?

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 energy (U) by $F = -\nabla U$. Remember that ∇ 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)

$$V_{LJ} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] = \epsilon \left[\left(\frac{r_o}{r} \right)^{12} - 2 \left(\frac{r_m}{r} \right)^6 \right] \quad (\text{Chapter 1.3})$$

where ϵ is the depth of the potential well, σ 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..

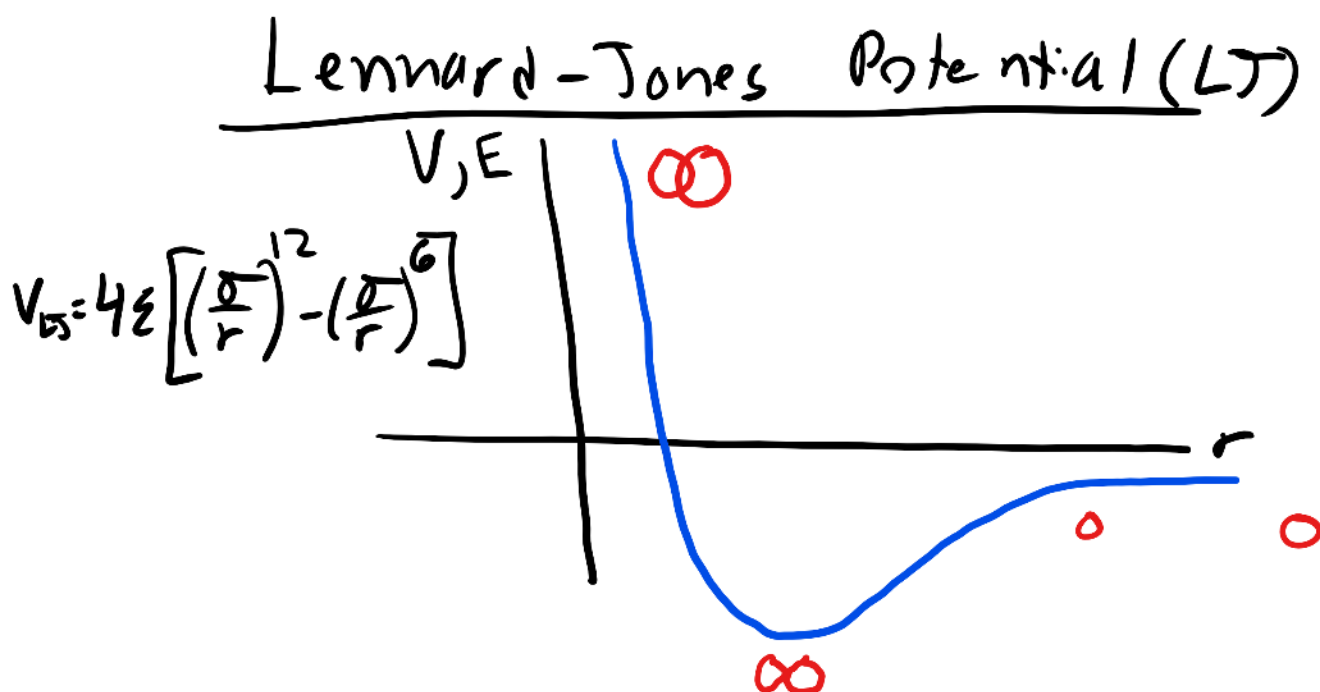


Figure Chapter1.7: Lennard-Jones Potential

1.4.1 Distinguishing Between Types of Bonding By Electronegativity

However, again the key to determining which type of bonding occurs is the valence electrons. Specifically if they are gained, lost or shared.

For Van der Waals interactions there is no charge transfer. Instead we have induced electric dipoles or permanent dipoles from weak attractive bonds. 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.

Now when atoms 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 electrons 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. Van der Waals form between covalently bonded molecules which have net or induced dipoles. These are very short-range force bonds and therefore localized between neighboring molecules. While these bonds are typically very weak and short range these interactions are critical to a number of unique phenomenon, in particular Gecko pads, graphite sheets, water, polymers, and proteins.

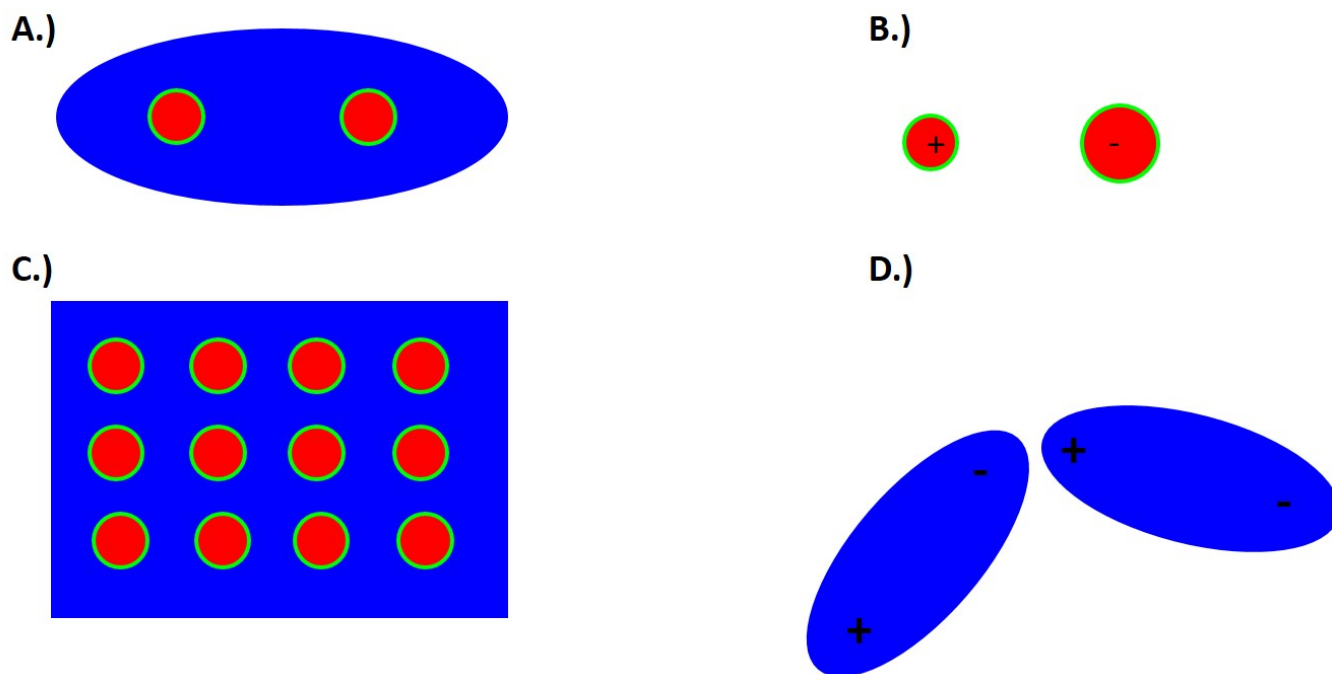


Figure Chapter 1.8: Bond Schematic

1.4.2 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 interactions** - electrostatic attraction/repulsion between charged ions
- **Lennard-Jones (LJ) potentials** - induced dipole interactions between neutral atoms

- **Hydrogen bonding** - net dipole interactions
- **The 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 fluctuating polarization between nearby atoms/elements/particle, quantum mechanical in nature. Van der Waals forces decay as d^{-6} .

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.

1.4.3 Structural Descriptors of Bonding

We also have structural descriptors of bonded materials particularly bond length, bond angles, and the size of atoms or ions. The bond length is simply the distance between two bonds. The distance between a Carbon-Carbon bonds is $1.54\text{\AA}$ for reference. Bond length can change depending on whether the bond is covalent or ionic. Bond angles are defined by the relative location of three atoms. In CO_2 , this molecule is planar so the angle is 180° . For trigonal planar molecules like BF_3 the bond angle is 120° . What is the bond angle for our Materials Tetrahedra? It is 109.28° .

The size of an atom is determined by the distance the electron distribution extends from the nucleus. However, this definition is problematic as the type of bonding and bonding in general will change the shape of the electron distribution. So the better value to look for is the covalent, ionic, metallic, and van der Waals radii of the atom. For metals we simply use metallic radii. Covalent radii is one half the covalent bond length. Ionic radii can vary and depends on how many electrons are transferred and the electronegativity difference. The van der Waals radii is the distance of closest approach or approximately the nearest neighbor distance. We will be talking a lot more about the nearest neighbor distances in the next lecture.

The 3D shapes of molecules can be predicted using electron-domain theory which focuses on the 3D distribution of the outermost electrons about a given atom and how these electrons will pair with other electrons from bonding atoms allen_structure_1999}. This theory distinguishes between bonding and non-bonding domains. The bonding domain is the shared electrons and the non-bonding domain belongs to a particular atom. Nonbonding domains occupies a larger space than the bonding domains. This leads to preferred angles for example for two domains they will be 180° apart, for 3 it will be 120° , and for 4 it will be 109.28° .

1.4.4 Isomeric States

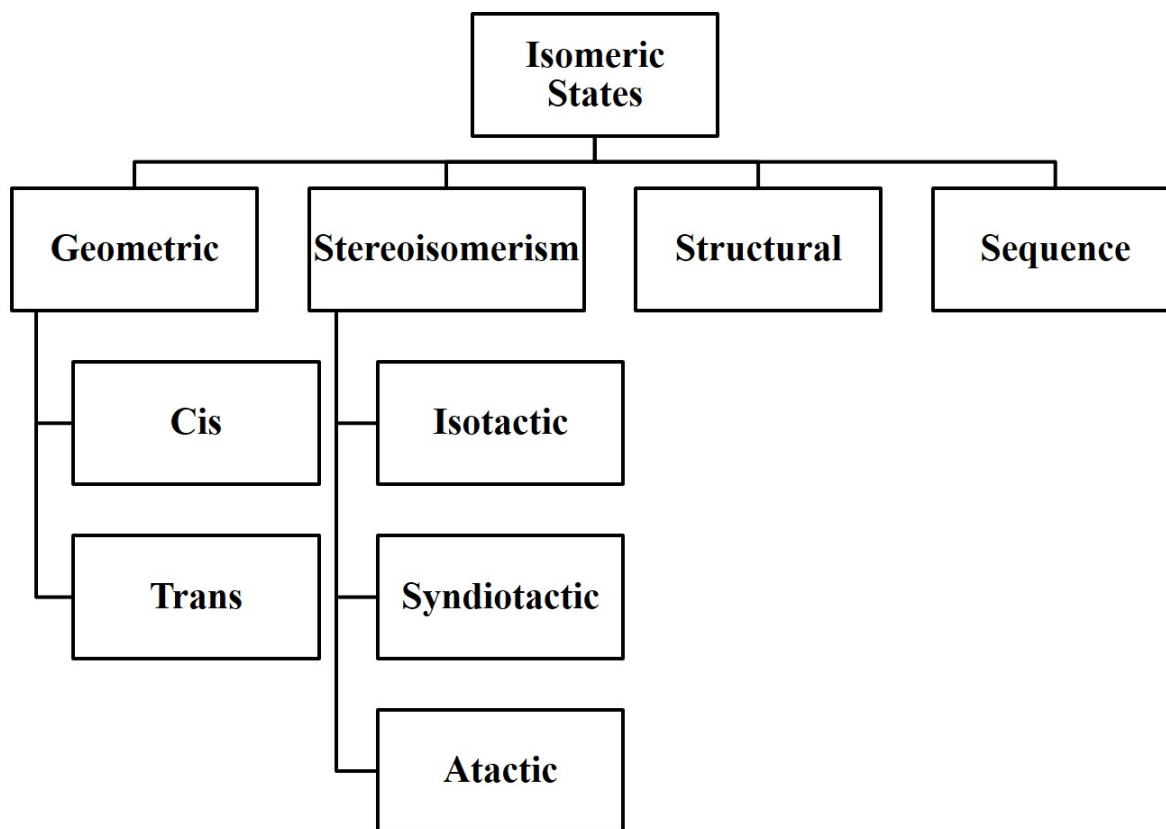


Figure Chapter1.9: Types of Isomers

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.

ichlorethene 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:

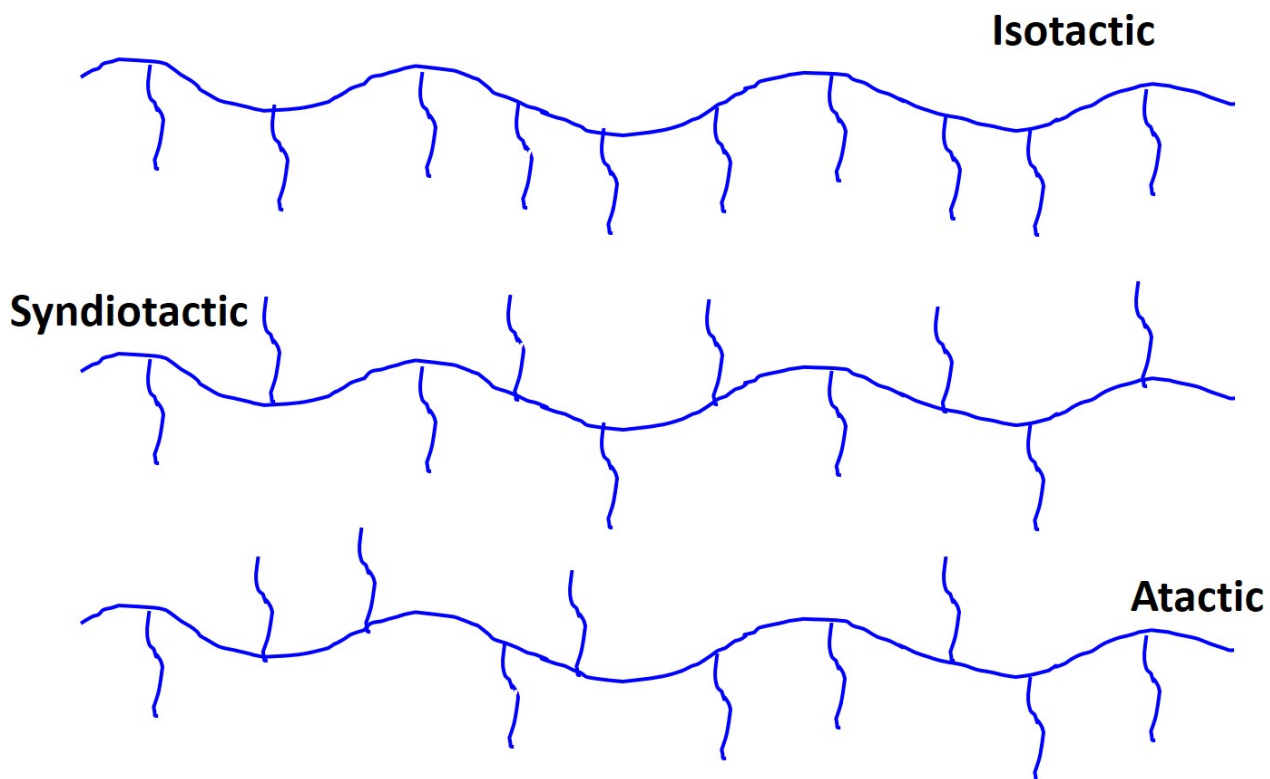


Figure Chapter1.10: Stereoisomers

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 copolymers which can be designed to be ABABABAB or AAAABBBB.

1.4.5 Coordination Number (CN)

The coordination number (CN) is the number of nearest neighbors (NN). There are a number of coordination shells like the nearest neighbors and the next nearest neighbors (NNN). For liquids and amorphous materials it will typically be an average number of nearest neighbors in a predefined shell of a particular distance or length or Voronoi Tessalation. We will also define and discuss the packing fraction V_v which is the ratio of the total occupied volume to the total volume. For gases this should be very low, almost zero. Fluids or glasses should be about 0.5 and we will see this is much higher for metals and ceramics.

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Chapter 2: Structure: Crystalline, Amorphous, Non-Crystalline, and Liquid Crystal Materials

2.1 Crystal Structures

We will eventually talk about **crystalline materials**, **amorphous materials**, **liquid crystals**, **short range order**, **long range order**, etc. But to start we are going to deal with the most ideal case of perfect crystalline materials.

Do we ever have a perfect crystal? **No!** Why? Well maybe at 0K but even then still probably not. **There are always defects in materials** but let's start with the simple case where we assume everything is perfect.

A **crystal structure** is a **periodic array of atoms that repeats over large distances**. There is **long-range periodic order both long range translational and orientational order in addition to short range order**. So before we start to run off and analyze crystal structures we have to first start off with a **primitive lattice**, **lattice constants**, **interaxial angles**, **symmetries**, **point groups**, **Bravais lattices**....

I have recorded a series of videos to supplement this text which can be found in the playlist here:

https://www.youtube.com/playlist?list=K6ucyYrAKh-v_z

2.2 Lattice, Primitive Unit Cell, Basis Vectors, Lattice Constants

A **lattice** is a periodic array of points (atoms) in 1,2 or 3D. Those points are lattice points. Let's start with the 2D case. A 2D lattice can be described by a primitive or unit cell which in turn is described by **two lattice constants** (a, b), two **basis vectors** (a_1 and a_2) **an interaxial angle** γ . Once we have defined this we can pick any point in our 2D lattice as an origin and we can describe any point in our lattice with the previous values. That is the beauty of crystallography!

Now when we pick our basis vectors we pick the shortest lattice translation as a_1 and the second to shortest translation is a_2 . The lattice constants are then just given by $a = |a_1|$ and $b = |a_2|$. The interaxial angle γ is then simply defined. This also defines our primitive cell which will only contain a single lattice point. **Let's do a couple of examples looking at the parallelogram cell below:**

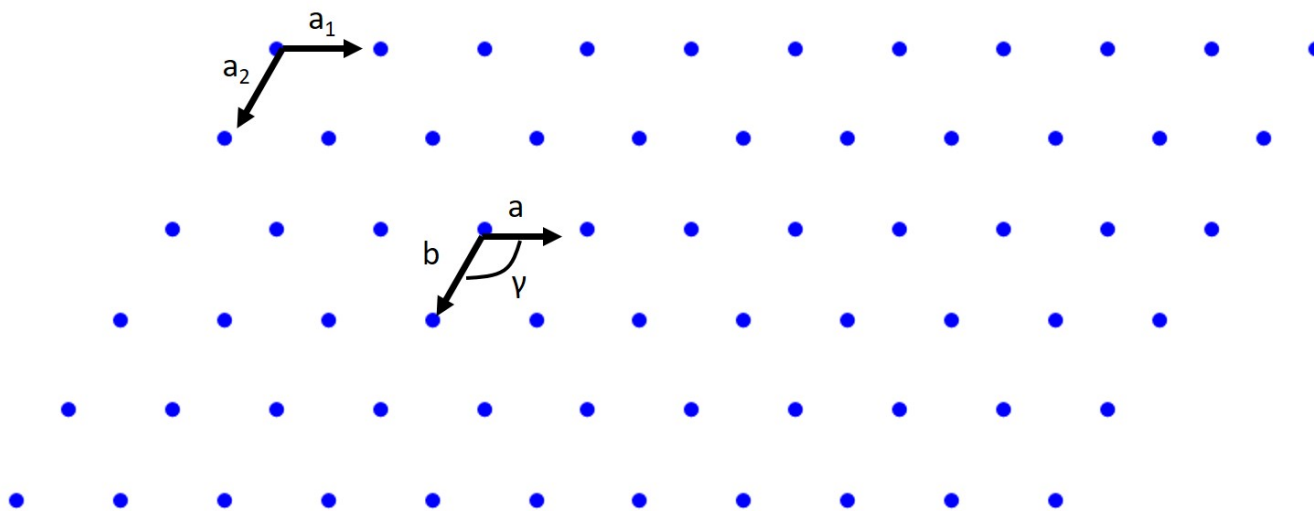


Figure Chapter2.1: Lattice with Parallelogram Primitive Cell

How about a Rectangular lattice?

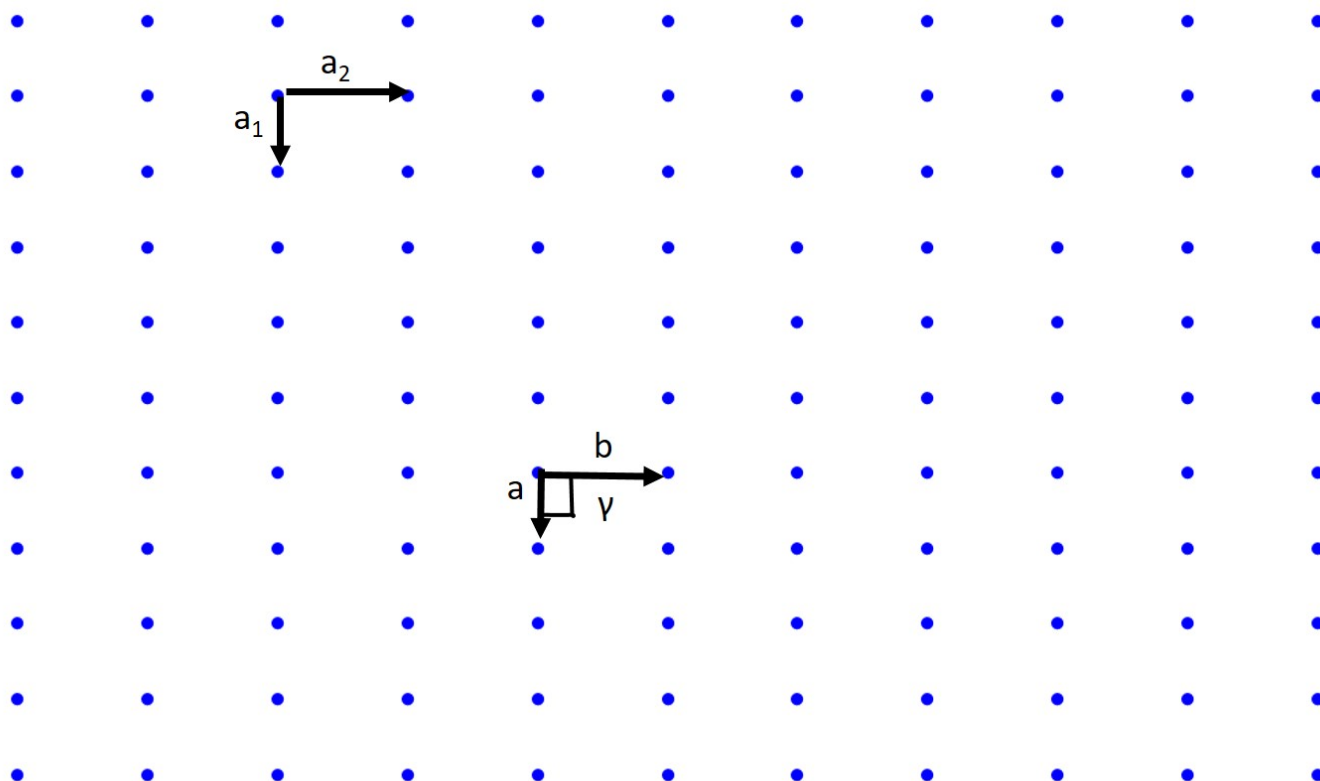


Figure Chapter2.2: Lattice with Rectangular Primitive Cell

Associated with crystallography is a myriad of **symmetry operations** and we have actually just dealt with **translational symmetry just now**. There are also reflection or **mirror symmetry**, **glide symmetry**, **rotational symmetry**, etc. These topics are all important but we are not a crystallography class so we will not be covering this in detail but you should know these concepts exist. **There are also 230 space groups, 32 crystallographic point groups, 14 Bravais lattices (we will discuss these), and 6 crystal systems (will discuss these as well).**

2.3 Crystal Systems: Simple Cubic, BCC, FCC, HCP

We are going to focus on the 6 crystal systems: **triclinic, monoclinic, orthorhombic, tetragonal, hexagonal, and cubic** and how to describe the unit cell, the primitive lattice vectors, and interaxial angles.

2.3.1 Crystallographic Directions:

When discussing crystals we will also have to specify crystallographic directions and planes. In order to refer to specific crystallographic planes or direction we need a labeling system to index these directions or planes. Luckily such an index has already been developed, **Miller indices**. A crystallographic direction is a vector denoted by $[uvw]$. u, v , and w are integers which correspond to the reduced projections along the x, y , and z axes, respectively. Note we will always use $[]$ for vectors. Let's do a couple of examples.

Let start simple and draw the $[100]$ direction.

To draw the direction of a vector it is pretty straight forward. Pick an origin for the vector tail (side without arrow) then pick the ending point for the vector (arrow) and subtract the arrow point from the tail point and the resultant vector must coincide with the direction that you are trying to draw. Typically try to pick the origin as your origin.

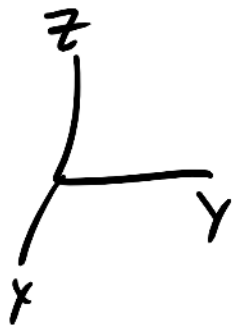
How about the $[111]$ direction?

What about $[100]$?

Little more complicated what about $[110]$?

What about drawing $[222]$?

Now a little more complicated what is the vector I am drawing below?



What direction?

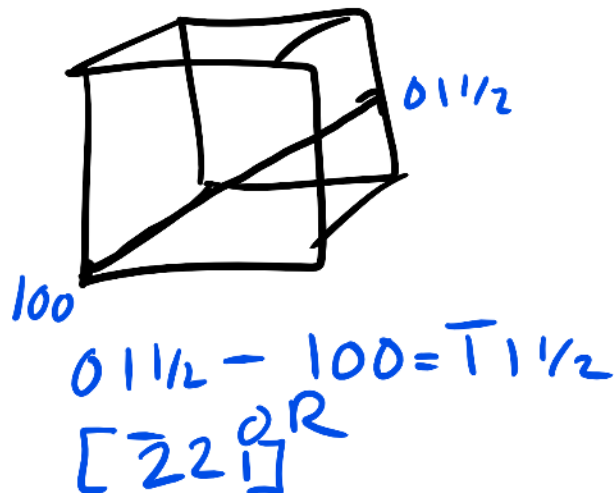


Figure Chapter2.3: What direction is this?

Now for a number of crystal structures there are **several nonparallel directions** with different indices that are **crystallographically equivalent**. This means that the spacing and number of atoms along each direction is the same! In cubic crystals $[100]$, $[\bar{1}00]$, $[010]$, $[0\bar{1}0]$, $[001]$, and $[00\bar{1}]$ are all crystallographically equivalent so we group them in a family which is denoted by angled brackets $\langle 100 \rangle$.

2.3.2 Crystallographic Planes:

Now for crystallographic planes we utilize the Miller indices (hkl) which corresponds to the x , y , and z axes respectively. Notice again that we use $()$ for planes and $[]$ for directions. $\langle \rangle$ is for family of directions. We will denote families of planes in $\{ \}$.

Now the question becomes how do we draw planes. Well we first must determine if the intercepts. The intercepts will be the inverse of the Miller indices. Let's take a look at a relatively straightforward example of the (111) .

(111) Plane
Intercepts $\rightarrow x = 1 \ y = 1 \ z = 1$

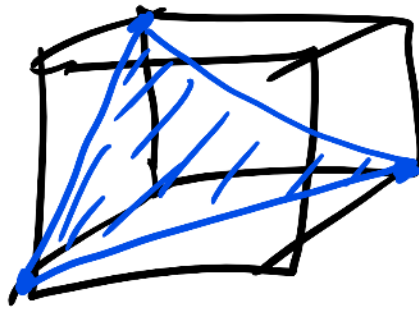


Figure Chapter2.4: (111) Crystallographic Plane

Now what happens in the case of (110) for example. Well if you run into this problem an inverse that gives you an infinite number means that the plane will not intersect that coordinate axes and will instead be parallel to that axis. So the plane should look like this:

(110) Plane
Intercepts $\rightarrow x = 1 \ y = 1 \ (z = \frac{1}{0} = \infty \text{ Parallel!!})$

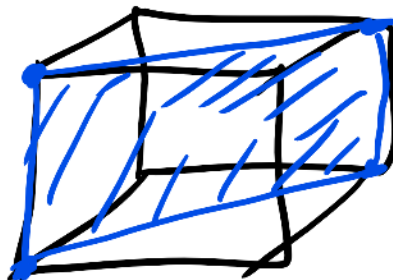
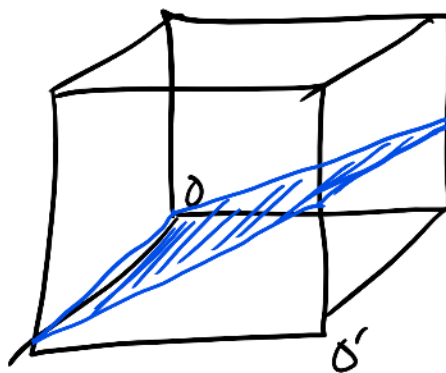


Figure Chapter2.5: (110) Crystallographic Plane.

How about another tricky problem like below when we have the plane passing through our origin?



What is the Plane?



Intercepts origin!
Redefine $0'$

Intercepts
 $X = \text{none}$ $Y = -1$
 $Z = 1/2$

$(0\bar{1}2)$

Figure Chapter2.6: Crystallographic Planes.

Here all the axes appear to be intersected, there are no parallel planes. True but this is actually misleading. When you have a plane that intersects the origin you need to choose a different origin and go through the same procedure to determine where the plane intercepts and then we can find the Miller indices of the plane.

The plane intercepts are again the inverse of the Miller indices and families of planes are denote in curly brackets hkl .

Here is a nice demonstration to visualize the Crystallographic Planes:

<https://demonstrations.wolfram.com/PlanarDensityOfCrystallographicPlanesInSCBCCAndFCCCrystals/>

2.3.3 Anisotropy

Now it's important to mention that we have been assuming until now that material properties are the same in every direction however this is not actually the case. Often many materials are **anisotropic**, meaning that some materials properties (mechanical, optical, kinetic, etc.) are different depending on the crystallographic direction you are investigating. For example titanium exhibits a larger modulus along the z-axis in the HCP structure than in the basal plane. This presents a significant problem when trying to superplastically form very thin foil made of titanium. A similar issue arises with magnetic properties of HCP materials as well. You should always remember as well that materials are not one perfect single crystal instead they are made of multiple crystalline grains, i.e. they are polycrystalline.

2.4 Simple Cubic

So let's start **simple with the simple cubic** to begin. So the simple cubic (SC) is also sometimes called primitive cubic and it is the crystal structure for Oxygen, Fluorine, etc. **As you can see below it is described by the primitive lattice vectors a_1 , a_2 , and a_3 and interaxial angles α (angle between a_2 and a_3), β (angle between a_1 and a_3), and γ (angle between a_1 and a_2).**

Notice the figure on the right is how the structure actually looks with the atoms touching. Here $\alpha = \beta = \gamma = 90^\circ$. **For simple cubic structures $a_1 = a[100]$, $a_2 = [010]$, and $a_3 = [001]$.** Right now I want to point that this is going to be the vector notation we use to signify a direction in a crystal lattice, more on this a bit later. **And for this case the lattice constants are all equal $a = b = c = a = 2R$ where R is the atomic radius of our element.**

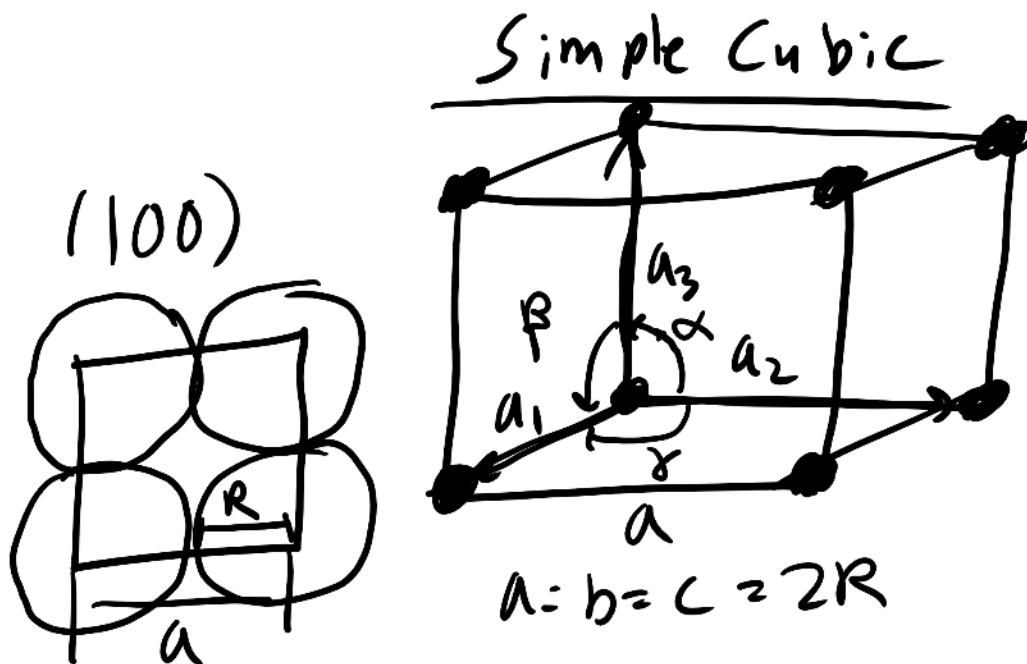


Figure Chapter2.7: Simple cubic unit cell.

How many atoms are contained in our simple cubic cell?

Well it is simply 1 because the all the corner atoms are shared by 8 other unit cells so

How many nearest neighbors (NN) does each atom have?

6.

How many second nearest neighbors?

12.

What is the NN distance?

$2R$

What about the NNN distance?

$2R\sqrt{2}$

What about the atomic packing factor?

To calculate this we must calculate the volume of atoms in a unit cell by the total unit cell volume. Well for simple cubic we know that the volume of our conventional unit cell is a^3 . Additionally with the simple cubic lattice we only have 1 atom so that volume is simply $\frac{4}{3}\pi R^3$ so plugging and chugging we get

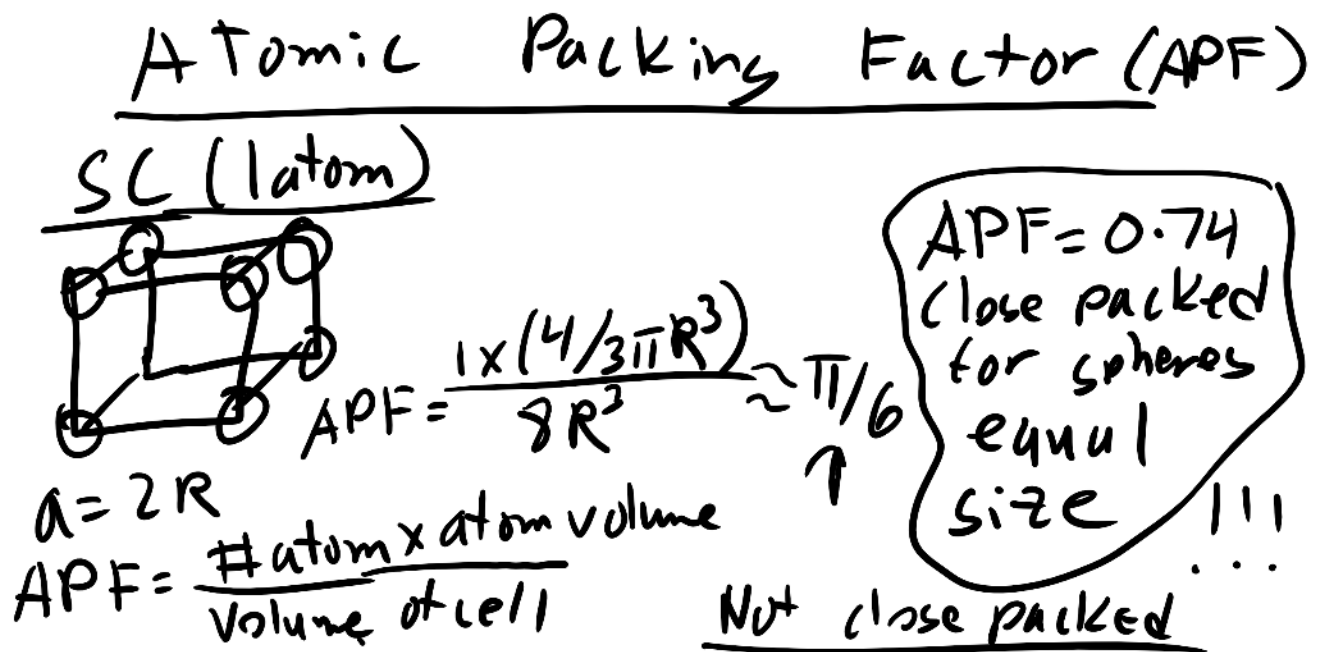


Figure Chapter2.8: Simple Cubic Unit Cell Atomic Packing Factor Calculation

2.5 Body Center Cubic (BCC)

Let's look at a little more complicated cubic structure, **body centered cubic (BCC)**. BCC is the structure for Li, Fe, V, Mo.

BCC is described by the primitive $a_1 = \frac{a}{2}[1\bar{1}1]$, $a_2 = \frac{a}{2}[11\bar{1}]$, and $a_3 = \frac{a}{2}[\bar{1}11]$ and $\alpha = \beta = \gamma = 90^\circ$.

What is a now? Is it still 2R? No it is not!!

Now $a = \frac{4R}{\sqrt{3}}$ where again R is the atomic radius which can be solved using a little bit of geometry.

How many atoms in a BCC conventional unit cell?

It is 2 atoms this time one in the interior and then 8 shared atoms so 2 total.

How many NN?

8.

How many NNN?

6.

What is the NN distance?

2R.

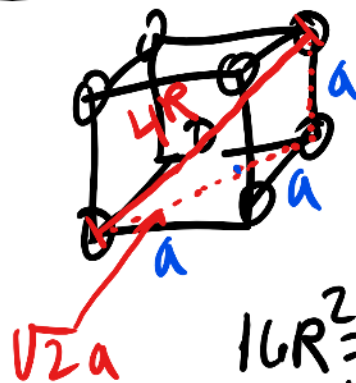
What about the second nearest neighbor distance?

It is simply $\frac{4R}{\sqrt{3}}$.

What about the atomic packing factor?

Atomic Packing Factor (APF)

BCC



$$APF = \frac{2 \times \left(\frac{4}{3} \pi R^3 \right) (3)^{3/2}}{64 R^3} \approx 0.68$$

Not CP!!!

$$4R^2 = a^2 + 2a^2$$

$$a = \frac{4R}{\sqrt{3}}$$

Figure Chapter2.9: Body Centered Cubic (BCC) Atomic Packing Factor

It is 0.68.

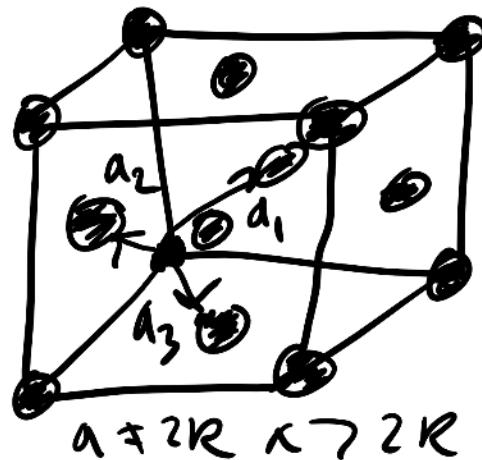
How did we get that? Well again how many atoms in a conventional BCC unit cell? 2 atoms.

We also know the volume of our unit cell know since we found a. Double check!

2.6 Face Centered Cubic (FCC)

Next is face centered cubic (FCC). FCC is the structure for Ni, Cu, Ca and it is described by the primitive lattice vectors $a_1 = \frac{a}{2}[011]$, $a_2 = \frac{a}{2}[101]$, and $a_3 = \frac{a}{2}[110]$ and $\alpha = \beta = \gamma = 90^\circ$. Here $a = 2\sqrt{2}R$ where again R is the atomic radius. Remember that the primitive unit cell will have only a single atom but a conventional cell may not.

Face-Centered Cubic (FCC)



$$a = 2\sqrt{2}R$$

Figure Chapter2.10: Face Centered Cubic (FCC).

Remember that the primitive unit cell will have only a single atom but a conventional cell may not.

How many atoms in a FCC unit cell?

It is 4 atoms this time 8 share on the edges and 6 shared on the faces.

How many NN?

12.

How many NNN?

6.

What is the NN distance?

$2R$

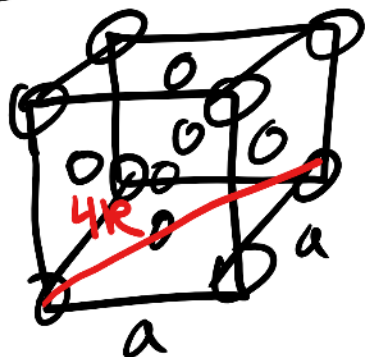
What about the second nearest neighbor distance?

$2R\sqrt{2}$

What about the atomic packing factor?

Atomic Packing Factor (APF)

FCC 4 atoms



$$2a^2 = 16R^2 \quad a = 2\sqrt{2}R$$

$$APF = \frac{4 \times \left(\frac{4}{3}\pi R^3\right)}{\left(\frac{2\sqrt{2}}{2}\right)^3 R^3} \approx$$

$$\boxed{0.74 \text{ (P!!!)}}$$

Figure Chapter2.11: Atomic packing factor of FCC.

What about the atomic packing factor?

It is 0.74.

This is the maximum possible packing factor for spheres having all the same diameter.

A **close-packed plane** is defined as a plane with an **packing density** of approximately 0.9069.

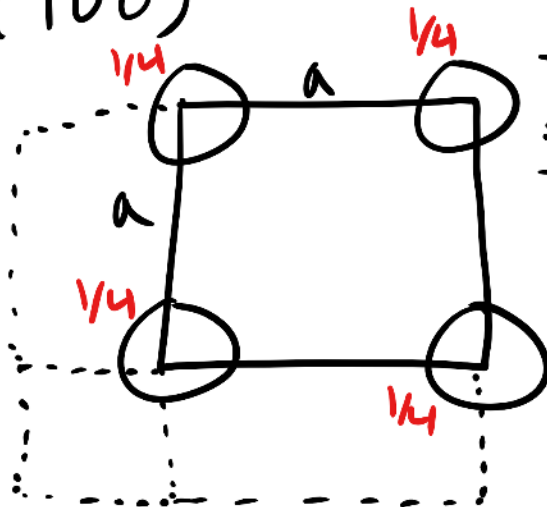
What is the packing density for the (100) plane in SC?

Close Packed Planes (CCP)

SC (100)

$$a = 2R$$

$$a^2 = 4R^2$$



Packing density =

$$\frac{\# \text{circles} \times \text{area}}{\text{plane area}}$$

$$= \frac{1 \times \pi R^2}{4R^2}$$

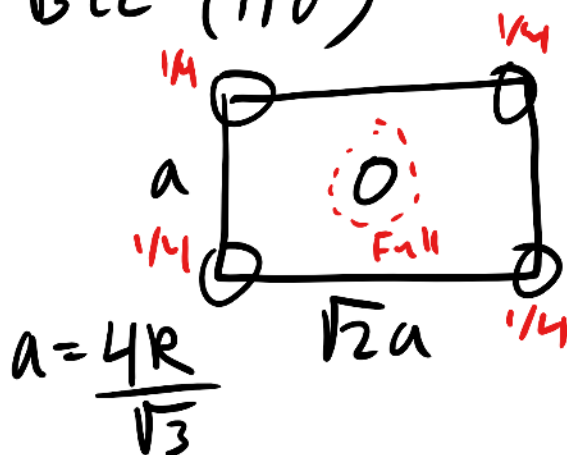
$$= \frac{\pi}{4} \text{ Not CCP}$$

Figure Chapter2.12: Planar Density of (100) in SC.

What about the (110) plane in BCC?

Close Packed Planes (CCP)

BCC (110)



Packing density:

$$\frac{2 \times \pi R^2}{a^2 \cdot 2}$$

$$\frac{2 \times \pi R^2 \cdot 3}{32 \cdot R^2} \approx 0.589$$

Not CCP!!

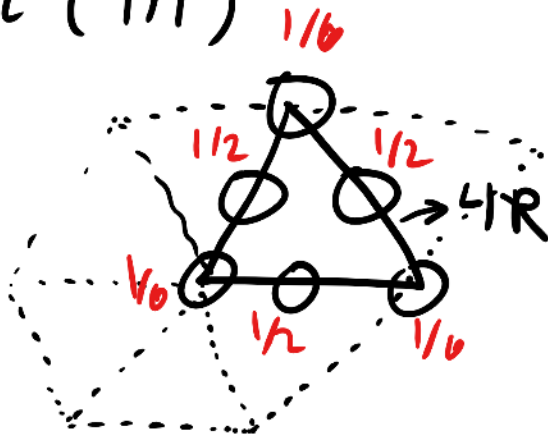
Figure Chapter2.13: Planar Density of (110) in BCC.

What about the (111) plane in FCC?



Close Packed Planes (CCP)

FCC (111)



Packing

$$\frac{2 \times \pi R^2}{\sqrt{3}/4 a^2} =$$

$$\frac{2 \pi R^2 \cdot 4}{\sqrt{3} 16 R^2} = 0.9069 \text{ CCP!!}$$

Figure Chapter2.14: Planar Density of (111) in FCC. Note here a is 4R in this notation not lattice parameter.

Note that only close packed structures can have close packed planes but often we will be concerned (especially when we talk about diffusion, defects, and mechanics) about the **closest** packed plane in a crystal and that doesn't have to have a density of **0.9069**.

What are the close packed planes and directions for BCC, FCC, and HCP?

Now when materials have more than one crystals structure they are polymorphic. In elemental solids this phenomenon is called **allotropy**. You have encountered a number of polymorphic materials, some of you may be holding one in your hand. At least in the old days before tablets. It's carbon! Carbon can adopt a number of different structures i.e. diamond, graphite, fullerenes, graphene.) Iron (BCC and FCC) and Titanium (HCP and BCC) are also polymorphs. We will also investigate lead titanate, a polymorph, in our XRD lab.

2.7 Structure of Non-Crystalline Materials:

2.7.1 Polymers, Liquids, Glasses, Gas, and Liquid Crystals:

Now so far we have focused only on crystalline materials primarily because they are the simplest materials to characterize in terms of structure. However there are many more materials that do not adopt a simple crystalline structure with short range, long range translational, and long range orientational order. Specifically, polymers, liquids, gases, liquid crystals, glasses, and many others.

With crystalline materials we were able to translate a unit cell to essentially infinity. **That is because we had both short range order, long range translational order, and long range orientational order.** In polymers, glasses, and liquid crystals typically we will only have **short range order (SRO)** and perhaps **some degree of long range order either translational or orientational but typically not both** and not to the periodic nature of crystalline materials. So how are we going to talk about structure in these non-crystalline materials which are often incorrectly called disordered materials. Well we are going to use a **dimensionless pair distribution function (PDF) or the radial distribution function (RDF)**, this is also called the **pair correlation function** as well I know very confusing, which is our key **descriptor** for quantifying the SRO present in a material.

The PDF or RDF, $g(r)$, is:

$$g(r) = \frac{1}{\langle \rho \rangle} \frac{dn(r, r+dr)}{dv(r, r+dr)} \quad (\text{Chapter 2.1})$$

where ρ is the average particle number density, dn is the number of particles counted in a small spherical shell sampling volume element of size dv at each distance r from a particle chosen as the origin. The number of particles in each shell is counted at each subsequent dr shell. This is shown schematically below

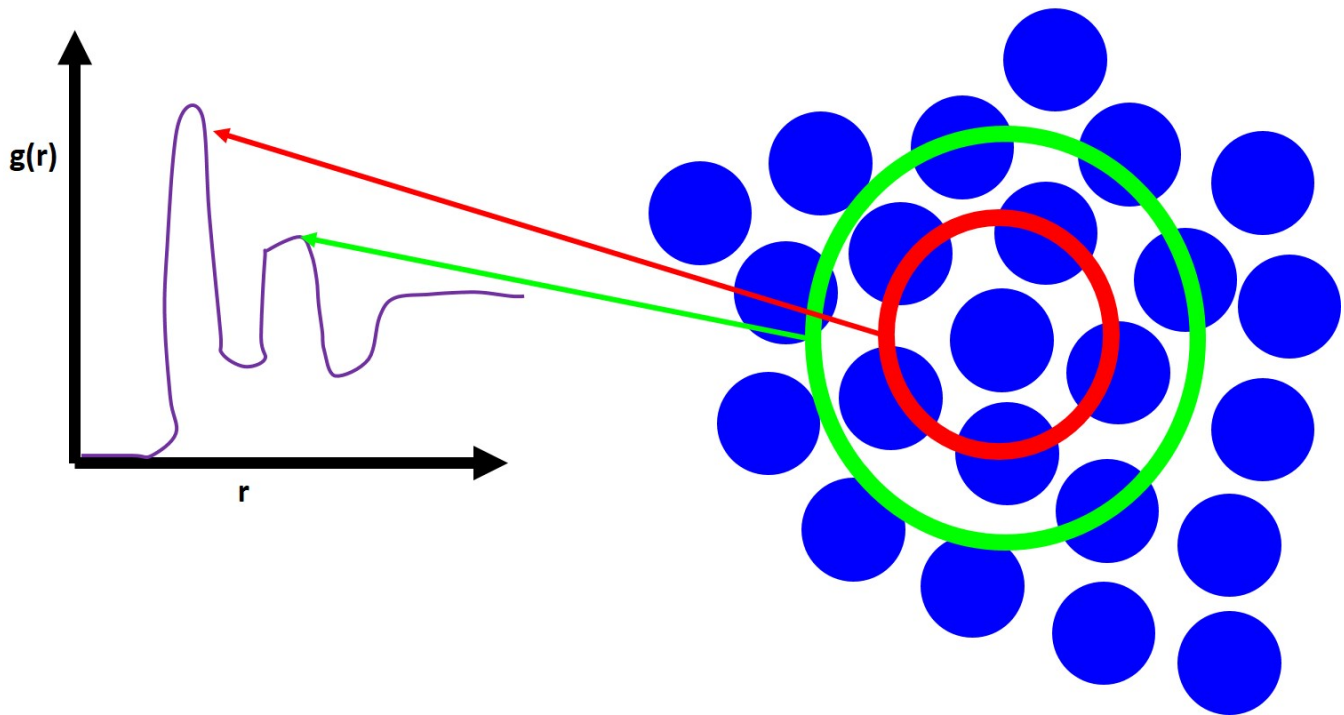


Figure Chapter2.15: PDF/RDF

To get a smooth curve you want to pick a very small dr so that is **much smaller than the radius of the particle** and we must average this over multiple particles chosen as the origin. **For perfect crystals we will see the PDF exhibit a series of sharp and discrete peaks at precise values of interatomic spacings which will correspond to the particular crystal structure.** Now for **liquids you will see a large peak and then some much smaller peaks.** This first peak corresponds to your number of nearest neighbors which can be derived by the following equation:

$$\langle NN \rangle = \rho \int_{peak} g(r) 4\pi r^2 dr \quad (\text{Chapter 2.2})$$

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Chapter 3: Defects in Crystalline Materials

“Crystals are like people, it is the defects in them which tend to make them interesting! - Professor Sir Colin Humphreys”

A crystal is at a state of thermodynamic equilibrium when its free energy $G = H - TS$ is minimized. When are we (humans) at equilibrium?

We have two **knobs** that we can tune to lower the free energy of the system above and that is **entropy** and **enthalpy**. At low temperatures our entropy knob becomes negligible and energy is minimized by minimizing H . This is done via binding and forming the ordered structures that we discussed previously. At the limit of $T = 0$ that perfect crystal is the equilibrium configuration. When temperature increases the free energy is minimized by adopting a less well ordered atomic/molecular arrangement because that increases the entropy. Entropy increases when imperfections exist so when the temperature is not zero the **equilibrium state will most likely contain imperfections**. We can calculate the equilibrium concentration by looking at the change in free energy ΔG and the ΔS by adding imperfections and the enthalpic ΔH_f cost of forming those defects.

3.1 Crystalline Point Defects (0D)

I have recorded a series of videos to supplement this text which can be found in the playlist below:

<https://www.youtube.com/playlist?list=...0gUPDmo3Kg69Tr>

3.1.1 Vacancies

A **vacancy** exists when a site that is normally occupied in the perfect crystal is **unoccupied**. This can occur in many ways for example, forcing an atom onto an interstitial site, into a dislocation core, or to a grain boundary or free surface. You can see a couple of examples of a vacancy below

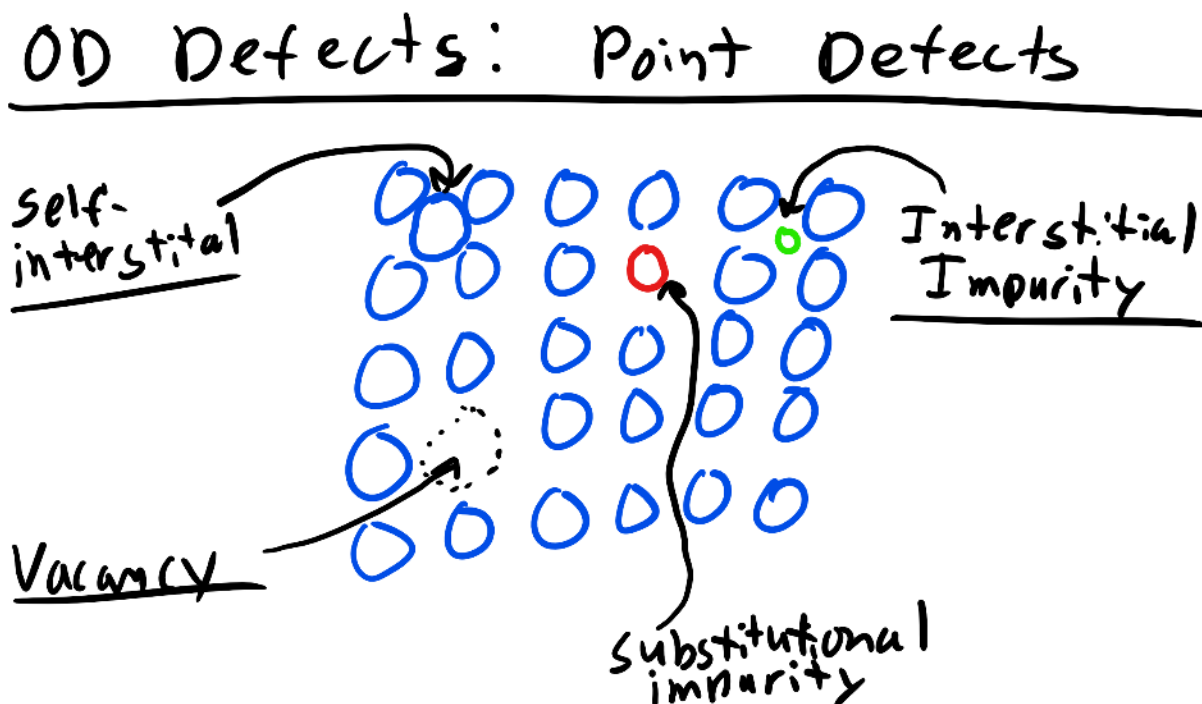


Figure Chapter3.1: 0D Point Defects

We can actually calculate the equilibrium concentration of vacancies, n ! Consider a reference state of a **perfect crystal of N atoms** and a **continuous set of vacancies, n** . The new state is a crystal containing a mixture of N atoms and vacancies. The total enthalpy change is then

$$\Delta H_f = n\Delta h_f \quad (\text{Chapter 3.1})$$

where Δh_f is the enthalpy of formation of a single vacancy. We can also get an idea about the change in configurational entropy from creating vacancies if we remember Boltmann's entropy equation (he had it carved on his tombstone...show off)

$$S = k \ln \Omega_m \quad (\text{Chapter 3.2})$$

where k is the Boltmann constant and Ω_m is the number of distinguishable ways you can arrange the system. The configurational entropy ΔS_c is then given by

$$\Delta S_c = S_{mix} - S_{ref} = k \ln \left(\frac{\Omega_m}{\Omega_{ref}} \right) = k \ln \Omega_m = k \ln \frac{(N+n)!}{N!n!} \quad (\text{Chapter 3.3})$$

where Ω_m is the number of distinguishable ways of arranging N atoms and n vacancies on $N+n$ sites and Ω_{ref} is the number of configurations in the ideal reference state, which is 1 since there are no defects. So the total Gibbs energy change is

$$\begin{aligned} \Delta G &= \Delta H - T\Delta S \\ &= n(\Delta h_f - T\Delta S_v) - kT[(N+n) \ln(N+n) - N \ln N - n \ln n] \end{aligned} \quad (\text{Chapter 3.4})$$

where ΔS_v is the vibrational entropy of the atoms surrounding the vacancy and we used Sterling's approximation $\ln X! \approx X \ln X - X$ to get to the equation above. Now how do we minimize Gibbs? Well we take the derivative and set it equal to zero:

$$\frac{\partial \Delta G}{\partial n} = \Delta h_f - T\Delta S_v + kT \ln \frac{n}{n+N} = 0 \quad (\text{Chapter 3.5})$$

We can now solve for the equilibrium fraction of vacant sites x_v

$$x_v = \frac{n}{n+N} = \exp \left(\frac{\Delta S_v}{k} \right) \exp \left(- \frac{\Delta h_f}{kT} \right) \quad (\text{Chapter 3.6})$$

You should notice in this equation that there is an **exponential temperature dependence, known as Arrhenius dependence or Arrhenius's law**. This is critical because there are many behaviors in Materials Science which are Arrhenius. Let's take a look at how strongly the concentration of vacancies varies with temperature by looking an example Arrhenius plot below

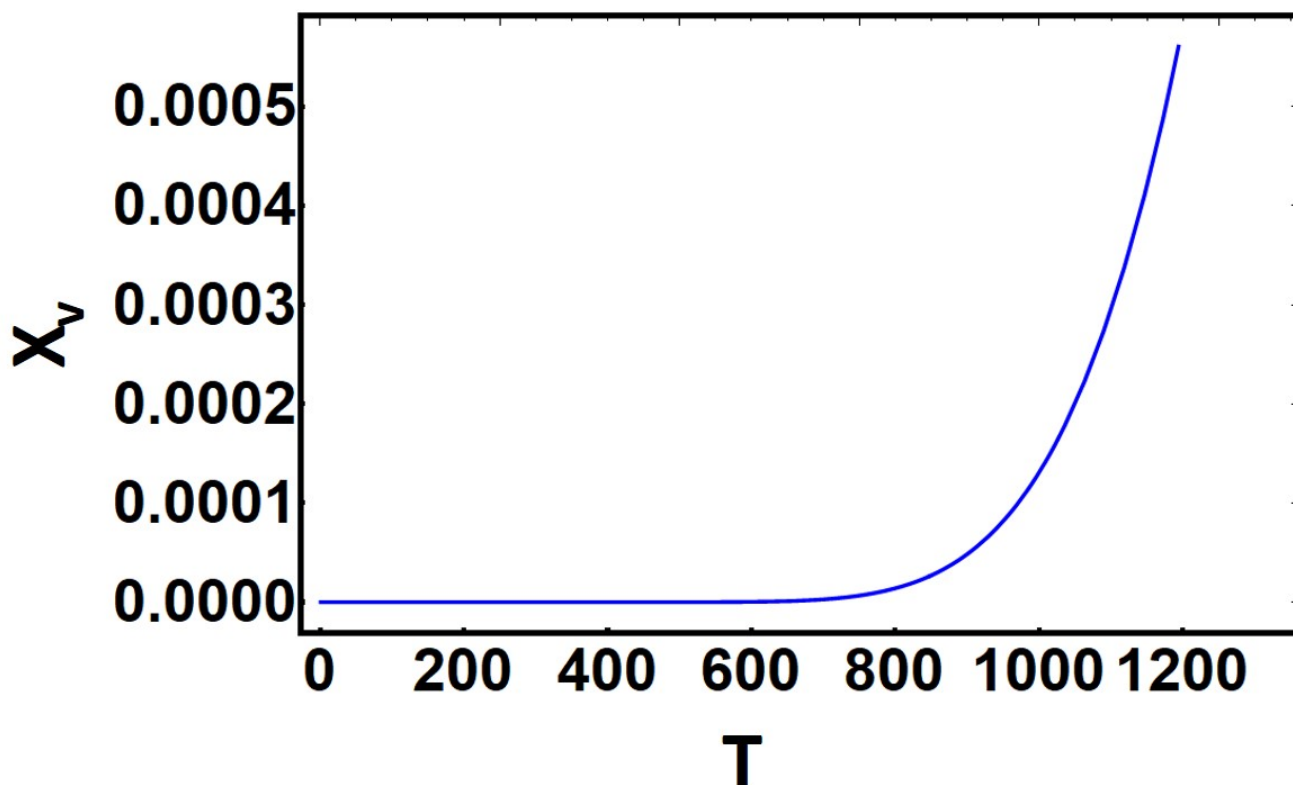


Figure Chapter3.2: Arrhenius Behavior of equilibrium concentration of vacancies.

Now typically we can assume that the $\exp\left(\frac{\Delta S_v}{k}\right) \approx 1$. The **enthalpy of formation of vacancies for metals is typically on the order of 15-150 kJ (kJ = 0.026 eV)** So we can clearly see that at room temperature the probability of forming vacancies will be pretty low already. Is this supported by the graph?

This method is not the typical way Arrhenius graphs are presented. It is actually better to plot the Log of the equilibrium concentration of vacancies as a function of the reciprocal temperature $\frac{1}{T}$. That way we can extract the activation energy or energy of formation of the vacancy.

3.1.2 Interstitials

An **interstitial defect** occurs when an atom occupies an interior site which is not normally occupied. If the interstitial is of the same species in a single component crystal it is a **self-interstitial** and we have the following equation for the equilibrium number of self-interstitials

$$x_i = \frac{n}{n + N} = \exp\left(\frac{\Delta S_v}{k}\right) \exp\left(-\frac{\Delta h_f}{kT}\right) \quad (\text{Chapter 3.7})$$

however now the ΔS_v and Δh_f represent the enthalpy of formation and vibrational entropy for interstitial formation. As you might imagine the **energy of formation for interstitial is lower for more open and less densely packed structures**. Obviously there are also **higher numbers of these 0D defects for nonequilibrium processes like quenching, irradiation, ion implantation, or cold working**.

3.1.3 Alloys

An **alloy** is formed when one or more species is mixed to form a solid or liquid solution (brass, Ti-64, stainless steel, etc.) **The major component is the solvent and the minor component is the solute.**[1] When the solute occupies sites normally unoccupied by the solvent in the crystal then it is an **interstitial solid solution**. If the solute occupies a site normally occupied by the solvent then the crystal is a **substitutional solid solution**. Typically alloys should have

1. **Atomic radii differences of $\pm 15\%$**
2. **Same crystal structure**
3. **Maximum allowable concentration of interstitial impurities less than 10%.**

Just for definition's sake to calculate weight percent (wt%) it is simply

$$WT\% = \frac{m_A}{m_A + m_B} \times 100 \quad (\text{Chapter 3.8})$$

where m_a is the mass of component A and m_b is the mass of component B. And atomic percent (at%) is simply the number of moles of one element over the total number of moles in the alloy.

3.2 Point Defects, Kroger-Vink Notation, and Schottky and Frenkel Defects

Point defects in ionically bonded crystals typically have an associated **charge**. Now the **net charge of a perfect crystal is zero**. **Cations** have lost one or more electrons and thus have a net positive charge. **Anions** have gained one or more electrons and thus have a net negative charge. A **cation vacancy** is created by removing a cation from a site in the crystal to a site on the surface. This vacant site then has a **net negative charge**. An **anion vacancy** is created by removing an anion site in the crystal to a site on the surface and the **vacant site then has a net positive charge**.

Now the way we describe these point defects is by using **Kroger-Vink** notation and schematically it is represented by:

$$X_Y^Z \quad (\text{Chapter 3.9})$$

where **X represents what is on the site**: either V for a vacancy or if occupied by an element, the element symbol. **Y represents what type of site is occupied by X**, either i for interstitial or if normally occupied by an element the symbol for that element. **Z represents the charge relative to the normal ion charge on the site Y** using **dots** to represent **positive** relative charges, **primes** to indicate **negative** relative charges, and **x** to indicate zero relative charge.

There are two idealized forms of charge-compensating point defects which are the **Schottky and Frenkel Defects**.

A **Schottky defect** consists of **charge-compensating anion and cation vacancies**[2]. Let's consider KCl for example. What is a Schottky defect? Well it would be



What about TiO₂?



A **Frenkel defect** is formed when an **ion moves from its normal site in the crystal into a nearby interstitial site, forming a Frenkel pair**. Let's examine the **cation Frenkel pair** in Li₂O which is



and the **anion Frenkel pair** would be



}

What about the cation and anion Frenkel pair in UO₂ respectively?



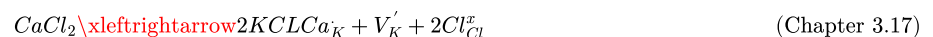
You need to have **charge and mass balance** in the above equations. **Charge balance** is attained when the sum of the charges on the right hand side equals the sum of charges on left hand side. **Mass balance** requires that the total number of ions or atoms of a given species is the same on both sides of the reaction. **The equilibrium concentrations of charged Schottky defects and Frenkel defects is:**

$$x_{pairs} = \exp\left(-\frac{\Delta h_f}{2kT}\right) \quad (\text{Chapter 3.16})$$

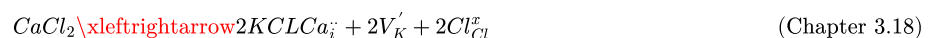
where the formation enthalpy is for a pair of ions either Schottky or Frenkel pair. Among the myriad of defects there will be a **dominant defect**, known as an **intrinsic defect** and typically it will be the one with the **lowest enthalpy of formation**.

3.3 Impurities in Kroger-Vink

We can also describe how impurities can induce formation of a variety of point defects using Kroger-Vink notation. Let's think about CaCl₂ impurities in KCl, specifically via incorporation of Ca onto K sites. We assume that the Cl sites can easily be integrated into the structure provided enough vacancies. So one type of impurity incorporation reaction could be:

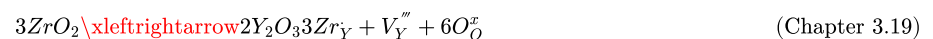


Note that we write 2KCl for mass balance. Another defect could be

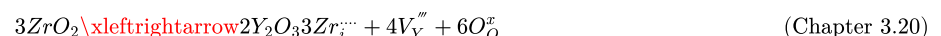


where we have Ca inserting into an interstitial site.

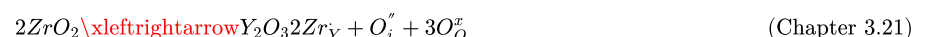
Let's practice with ZrO₂ (zirconia) impurities in Y₂O₃ (yttria), two very important ceramic materials, i.e. yttrium stabilized zirconium bio-engineering mechanical applications[2]. Let's look again at some possible impurity incorporation reactions



or another reaction



or yet another reaction



Yes you can expect many questions on this topic!

3.4 Dislocation Defects (1D)

Imperfections that are localized along a space curve passing through an ordered medium are **line imperfections**. A **dislocation** is one such defect. A **dislocation** is a linear or one dimensional line defect which involves translation of one part of a crystal with respect to another part. A **disclination** involves rotation of one part with respect to another. We will deal with two types of dislocation in this class: **edge and screw dislocations**.

An **edge dislocation** is essentially an extra half plane of atoms that is inserted into the perfect crystal and it terminates within the crystal. You can see this below

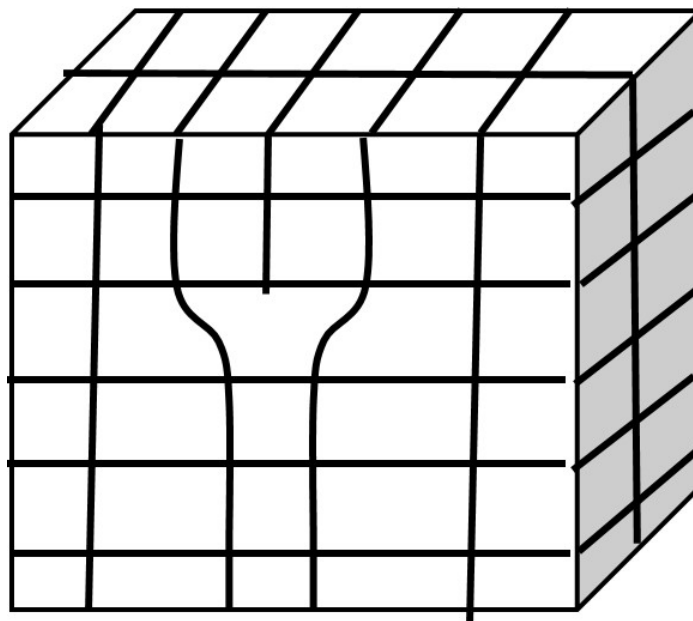


Figure Chapter3.3: Edge Dislocation

A **screw dislocation** is a bit harder to visualize but you can imagine that a screw dislocation can be formed by an applied shear stress, seen below:

You can see that in this example some of the differences between edge and screw dislocations one begin that the **screw dislocation motion** will be **perpendicular** to the **applied force** but more on that in a little bit. There are also **wedge and twist disclinations** as well.

Associated with each dislocation is a **dislocation core** which is where the largest displacements of atoms from the ideal sites occur and they are concentrated along a **dislocation line**. We describe dislocations via a **unit tangent vector**, t , and the **Burgers vector**, b . The tangent vector is a unit vector that is **tangential to the dislocation line at any given point**. The **Burgers vector**, b , is defined in reference to the Burgers circuit. Now in this class we will use the **SF/RH** (start to finish, right-hand) **convention** to define the Burgers vector. **To define the Burgers vector:**

- Choose the **positive sense** of the **unit tangent vector** of the dislocation line
- By traveling along rows of lattice points make a **right hand circuit** in the crystal **containing the dislocation**. Define a Start Point, S, and Finish Point F.
- This circuit would be a **closed circuit in the perfect crystal** but in this instance the circuit is **only closed by the Burgers vector which connects your Start and Finish points**.

A couple of other quick notes about some of the properties of dislocations. It should be noted that the Burgers vector will be conserved and that for a given dislocation there is one constant Burgers vector, even as the tangent vector changes.

- A dislocation cannot end inside a crystal.

- A pure edge dislocation has b perpendicular to t everywhere along the dislocation curve and $t \times b$ points toward the extra half plane of atoms
- A pure screw dislocation is either parallel or antiparallel to t everywhere along the dislocation curve. A right-hand screw is parallel and a left-hand screw is anti-parallel.
- A dislocation that is neither pure edge or pure screw is a mixed dislocation and the vector component that is parallel to t is the screw component and the component that is perpendicular to t is called the edge component.
- Reversing the sense of t also reverses the sense of b .

Let's do an edge dislocation

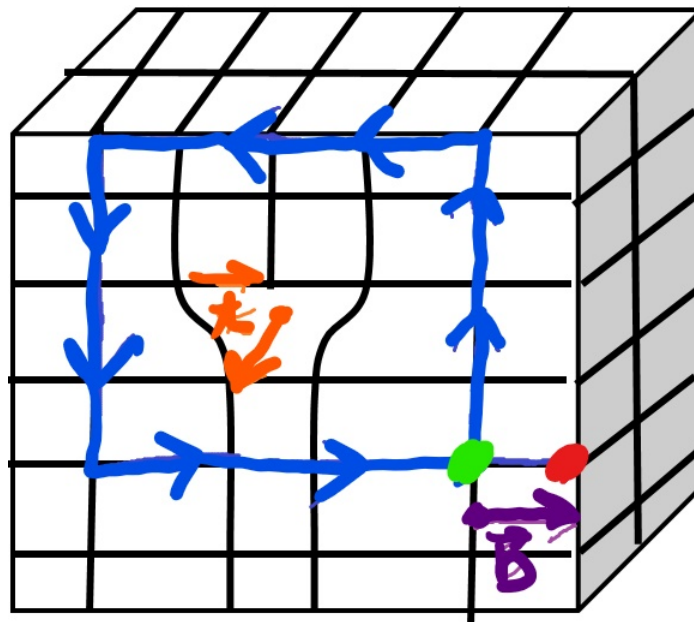


Figure Chapter3.4: Edge Dislocation Burgers Circuit

How about another screw dislocation?

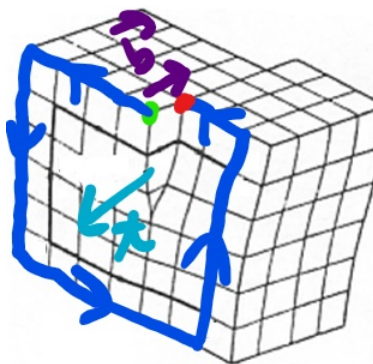


Figure Chapter3.5: Screw Dislocation Burgers Circuit

While we are speaking of dislocations one of the key material properties that you will come across is the dislocation density, ρ , which has units of m^{-2} . A **highly cold worked** material may have a **dislocation density** of $10^{14}m^{-2}$ whereas a **highly annealed material** can be as low as 10^7m^{-2} . Dislocations are additional **motile** and they can move via **slip and climb**.

3.5 Grain Boundaries, External Surfaces, Phase Boundaries, Twin Boundaries, and Stacking Faults (2D)

Perhaps the most obvious 2D defect is just an **external surface** where the **bonds at the surface are not satisfied** which gives rise to an increase surface energy or surface tension.

Grain Boundaries are interfaces at which crystals of different orientations abut. There are special types of grain boundaries like low angle tilt and twist boundaries when the angle of misorientation of grains is not too large. In fact they are considered simple periodic arrays of dislocations.

2D Defects: Grain Boundaries (GB)

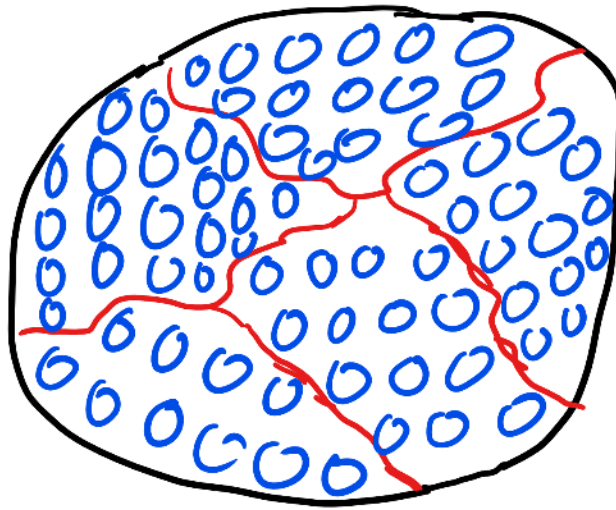


Figure Chapter3.6: Grain Boundary 2D Defect

Phase boundaries exist in multiphase materials where a different phase exists on each side of the boundary.

A **twin boundary** is a special type of grain boundary across which there is a specific mirror lattice symmetry. The region of material between these boundaries is a twin. Twins typically appear due to shear stresses or during annealing heat treatments after deformation. Annealing twins are more common in FCC crystals while mechanical twins are more common in BCC and HCP crystals.

Stacking faults are interfaces in crystals across which one part of the crystal is displaced relative to the other part by a displacement vector that is not a translational symmetry operation for that crystal. Remember that for FCC we had this ABCABC stacking and HCP we had ABABAB.

A stacking fault in FCC would be ABCBCABCABC. If the fault is missing a layer that is an **intrinsic stacking fault** but if there is an **extra layer that is an extrinsic stacking fault**. Stacking fault energy has severe implications on the strain hardening behavior of materials.

There are also **antiphase/interphase boundaries** which are separate regions of the crystal by a relative translation that is not a symmetry operation of the crystal. It is a special type of stacking fault, one that connects the crystallographically nonequivalent occupied sites in a perfect crystal. They can be **coherent, semi-coherent, incoherent**.

3.6 Bulk or Volume Defects (3D)

Finally there are also bulk or volume defects which include pores, cracks, foreign inclusions, and other phases.

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Chapter 4: Phase Diagrams

4.1 Lowest Energy Wins!

I have recorded a series of lectures to supplement the text which can be found in the playlist below:

<https://www.youtube.com/playlist?list=PL1CCqf55NMUHEA>

Materials can exist as **different phases**, i.e. **solid, liquid, gas, vapor, plasma** and each of those phases are described by their own unique free energy curve. **The thermodynamically stable phase is the one with the lowest free energy at any given temperature, pressure, composition, etc.** And **crossing points** in the free energy curves will **define the locations of phase transitions**. We can see this schematically when considering a pure single component material going through melting and we can plot the free energy as function of temperature and see the phase transition.

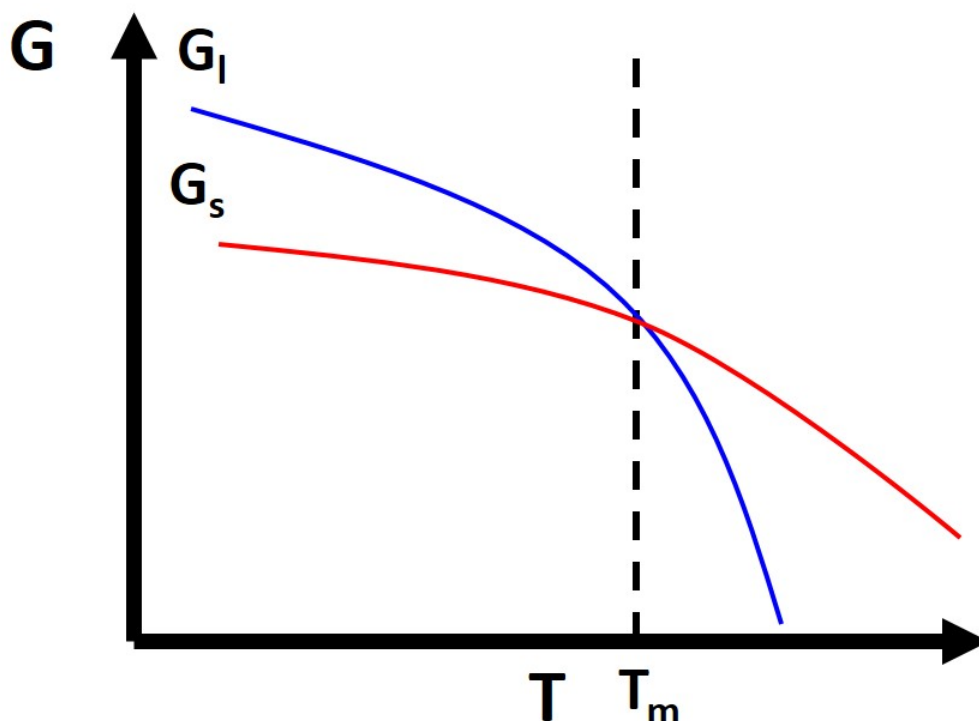


Figure Chapter4.1: Free energy curves for Solid to Liquid Phase Transition

where G_l is the molar Gibbs free energy of the liquid phase and G_s is the molar Gibbs free energy of the solid phase. I will try to be as consistent as possible to keep liquid as blue color, like water.

We can also draw this out for the complete phase transition spectrum for a given material as the solid **melts**, the liquid **boils**, and the solid can **sublimate** directly to vapor.

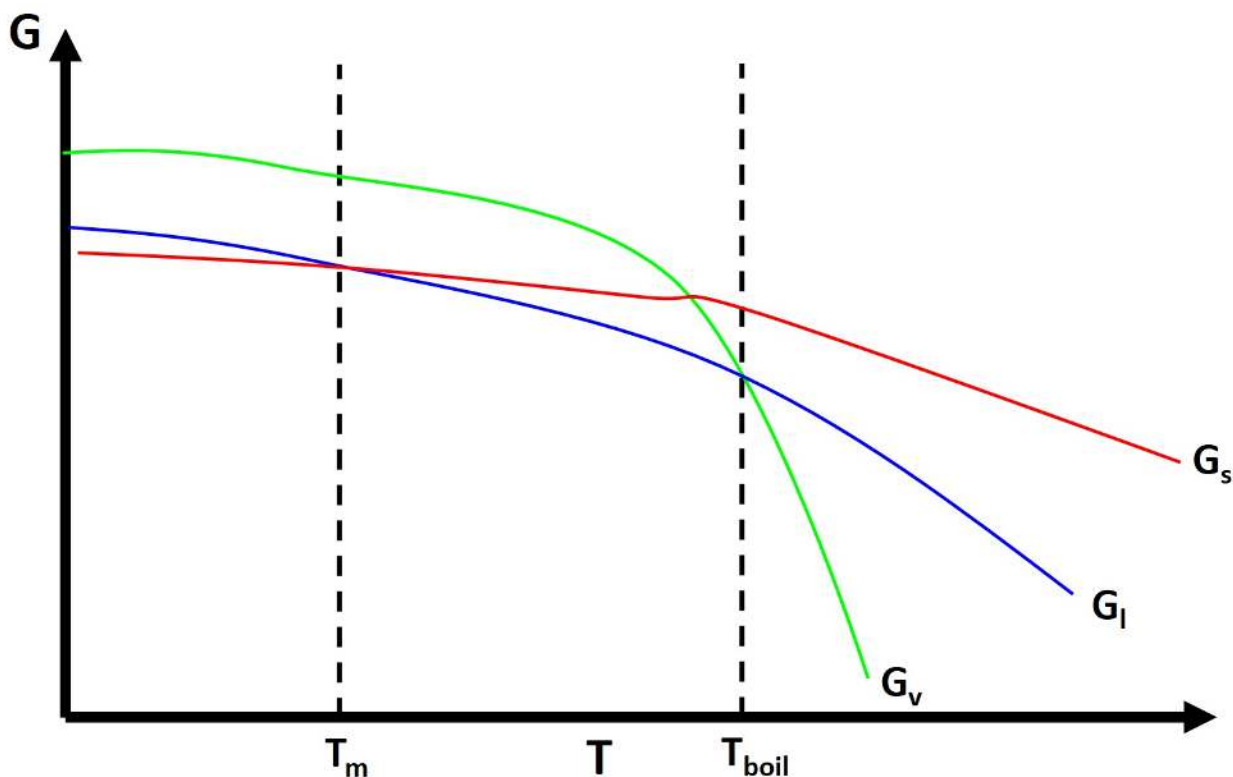


Figure Chapter 4.2: Free Energy Curves for Solid, Liquid, and Vapor Transition

However as we touched upon in structure materials can exhibit different crystalline forms in the solid state depending on the conditions of temperature and pressure.

What was the special name for these materials?

Polymorphs/allotropes.

Wouldn't it be useful to have some type of diagram that would allow us to visualize these different phases....hmmm....!

4.2 Phase Diagrams of Single-Component Materials

Phase diagrams illustrate the phases of a system at equilibrium as a function of 2 or more thermodynamic variables.

Phase diagrams are also particularly useful because they **obey the laws of thermodynamics** and there are constraints on the structure of phase diagrams, particularly the **Gibbs Phase Rule**.

4.3 Gibbs Phase Rule

The **Gibbs Phase Rule** determines how many phases can be in equilibrium simultaneously and when those phases are stable along a field, line, or point in the phase diagram. There are **two criteria for phase equilibrium at a constant temperature and pressure** are that the **chemical potential of each component must be equal in each phase**:

$$\mu_1^\alpha = \mu_1^\beta = \mu_1^\gamma = \mu_1^P \dots \quad (\text{Chapter 4.1})$$

$$\mu_2^\alpha = \mu_2^\beta = \mu_2^\gamma = \mu_2^P \dots \quad (\text{Chapter 4.2})$$

$$\mu_C^\alpha = \mu_C^\beta = \mu_C^\gamma = \mu_C^P \dots \quad (\text{Chapter 4.3})$$

So we end up with C(P-1) equations. And we also have the **second condition which is given by the Gibbs-Duhem equation**

$$V^{\alpha}dP - S^{\alpha}dT - \sum_{i=1}^c n_i^{\alpha}d\mu_i^{\alpha} = 0 \quad (\text{Chapter 4.4})$$

$$V^{\beta}dP - S^{\beta}dT - \sum_{i=1}^c n_i^{\beta}d\mu_i^{\beta} = 0 \quad (\text{Chapter 4.5})$$

$$V^{\gamma}dP - S^{\gamma}dT - \sum_{i=1}^c n_i^{\gamma}d\mu_i^{\gamma} = 0 \quad (\text{Chapter 4.6})$$

So here we end up with **P equations**. So the **degrees of freedom (DOF)** is total number of variables - the total number of equations.

$$D = (CP + 2) - (C(P - 1) + P) \quad (\text{Chapter 4.7})$$

$$D = C - P + 2 \quad (\text{Chapter 4.8})$$

where D is the degrees of freedom, C is the number of components, P is the number of phases. The 2 comes from T and P as independent variables.

So let's do a couple of examples where we apply the Gibbs phase rule! Let's look at the single-component phase diagram below:

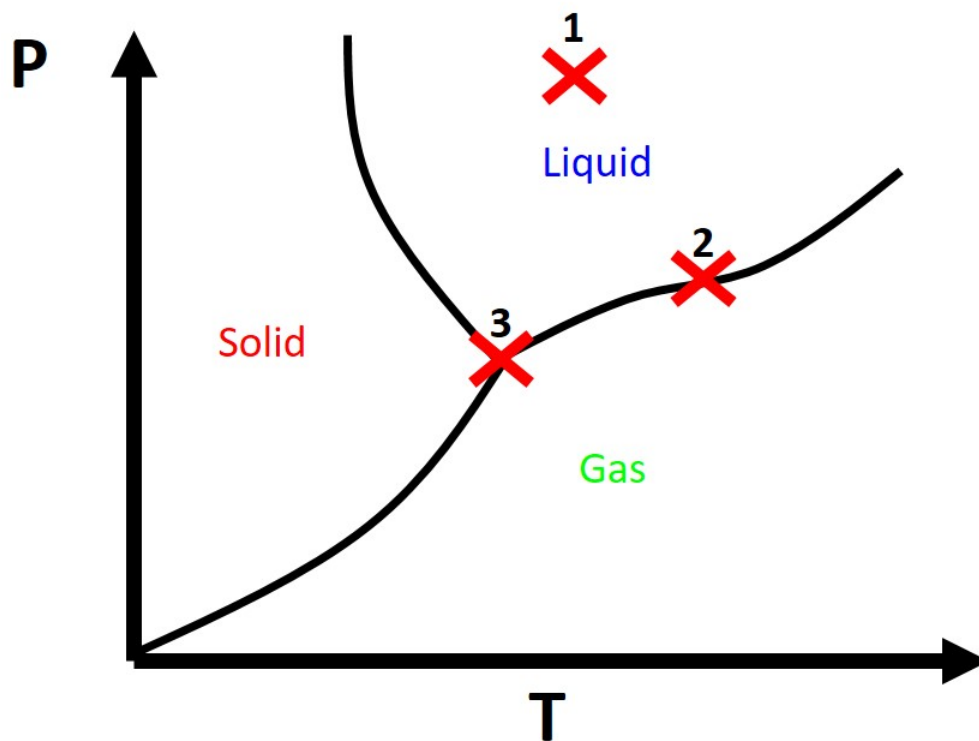


Figure Chapter4.3: Single Component Phase Diagram

What is the DOF for the 1st X location?

The DOF is 2.

$$D + P = C + 2$$

$$D + 1 = 1 + 2$$

(Chapter 4.9)

(Chapter 4.10)

That means we can vary both T and P and still be in the liquid phase.

What is the DOF for the 2nd X location?

The DOF is 1. We can now only vary T or P freely the other is fixed.

What is the DOF for the 3rd X location?

The DOF is 0. We can not move anywhere. This is an **invariant or triple point**.

Now there is one unique point, an **invariant point**, called the **triple point** that can allow the 3 phases to co-exist, i.e. any change in the variables will cause the equilibrium to shift to either 1 or 2 phases in equilibrium. The slope of the 2-phase line on the P vs. T diagram is determined by the **Clausius-Clapeyron equation** evaluated at the coexistence curve:

$$\frac{dP}{dT} = \frac{\Delta \bar{S}^{S \rightarrow L}}{\Delta \bar{V}^{S \rightarrow L}} = \frac{\Delta \bar{S}_m}{\Delta \bar{V}_m} = \frac{\Delta \bar{H}_m}{T_m \Delta \bar{V}_m} \quad (\text{Chapter 4.11})$$

We know that typically the enthalpy of melting is positive so the slope of the P-T diagram for the solid-liquid coexistence curve should be positive. Let's look at iron on the lecture slides.

4.4 Multi-Component Phase Diagrams

So far we have only dealt with phase diagrams of pure components but typically you will deal with either **binary, ternary, quaternary, etc. phase diagrams**.

Let's take a look at a relatively simple phase diagram, a **Binary Lens phase diagram** which holds for ideal solution scenarios.

(Side Note: When I say something is simple please do not interpret this as the concept being easy. These concepts are very difficult but what I mean by the problem is simple I want to encourage and show you that all these problems can be solved. When we say that this or that problem is really difficulty that problem is a given a special mystique and students might be wary about going about solving the problem or learning that concepts. By saying something is simple I want to remove that mystique.)

Note here that we are not varying pressure now because typically we are working in a **constant pressure environment**, although that is not necessarily always the case. **Now this will change our Gibbs phase rule condition to:**

$$\mu = \left(\frac{\partial G}{\partial n} \right)_{T,P} \quad (\text{Chapter 4.12})$$

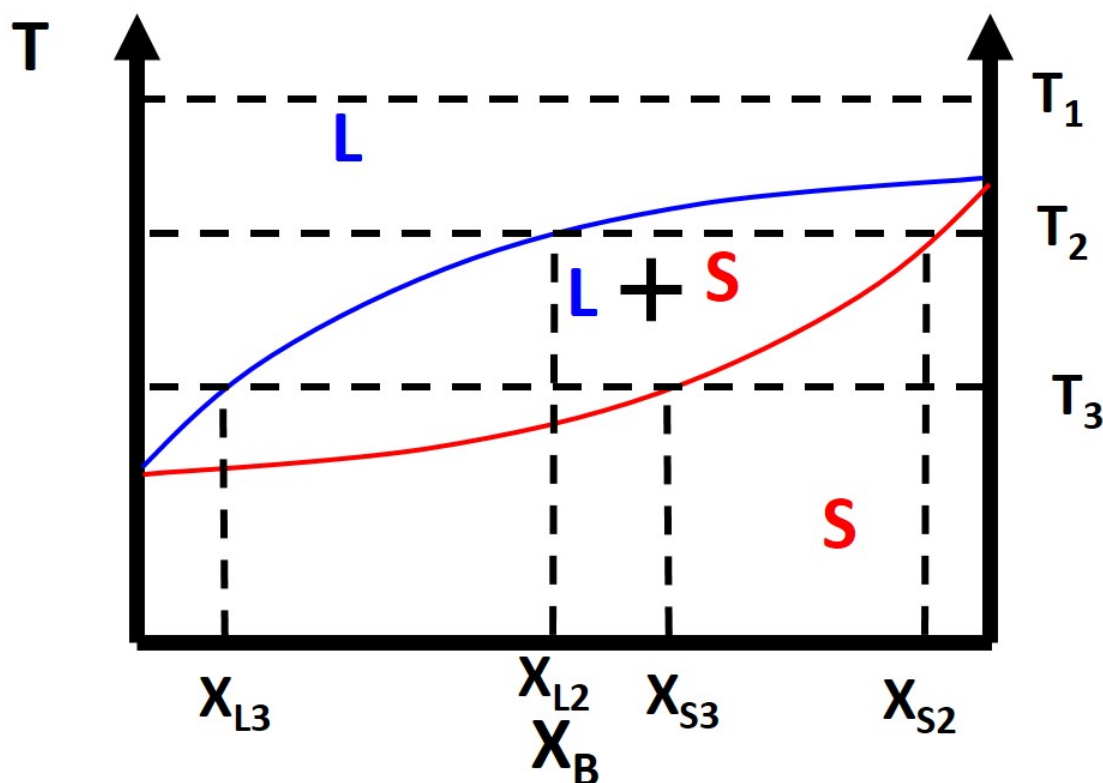


Figure Chapter4.4: Binary Lens Phase Diagram

We can also take a look at the free energy diagrams as well to conceptualize the phase diagrams. At T_1 everything is as usual in terms of our free energy diagram with liquid phase being lower energy than the solid phase. Things start to get a little funky at where we have the two phase region of a solid and liquid. What happens here? Why does this occur? Well at compositions less than X_{L2} and greater than X_{S2} everything is normal. What happens is in between these compositions. You see that we can draw a common tangent line (purple). When you have a **common tangent** line the system can phase separate from a 1-component system (liquid) to a weighted mixture of two components (solid and liquid) which has a lower free energy than the starting 1-component phase. This is because the requirement for equilibrium as we previously mentioned is that the chemical potential of each component must be equal in all phases and we have the expression that the chemical potential μ is

$$\left(\frac{\partial G}{\partial X}\right)_{X=X^\alpha} = \left(\frac{\partial G}{\partial X}\right)_{X=X^\beta} \quad (\text{Chapter 4.13})$$

So **common tangent rule** will allow us to find your equilibrium volume fraction of species in each phase via the **common tangents in free energy curves** and the slope is essentially the chemical potential so when the slope is equal. So between the common tangent points equilibrium will have the components in both phases, i.e. mixed as given below

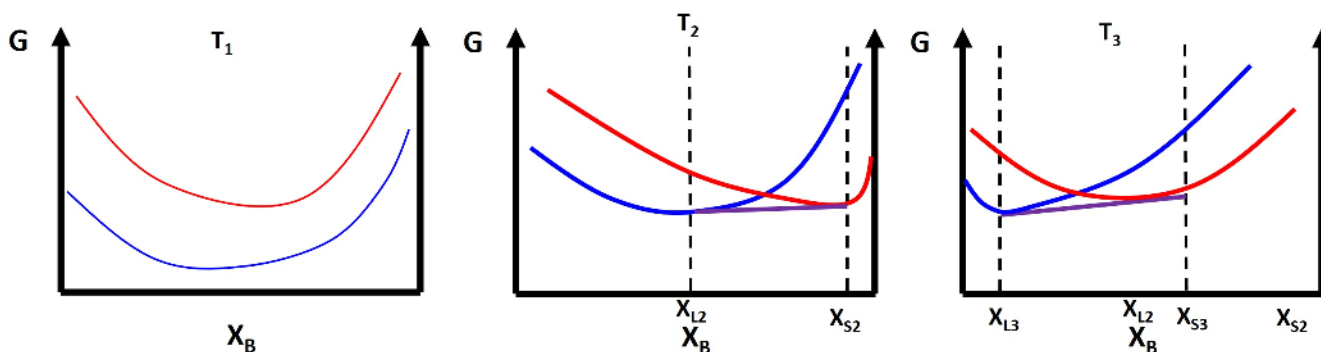


Figure Chapter4.5: Binary Lens Phase Diagram

4.5 The Lever Rule:

Typically we are also interested in finding at a particular composition and temperature what will be the relative **fractions** of the **different phases of the material**, or in the case of a simple lens diagram, what fractions will be solid and liquid. To calculate these **phase fractions** we will use the **lever rule**. Once you pick a temperature of interest, T_1 , and a composition, X_B^o then you draw a **horizontal isotherm** which connects or ties together the boundaries of a two phase regions. These horizontal isotherms are also called **tie lines**.

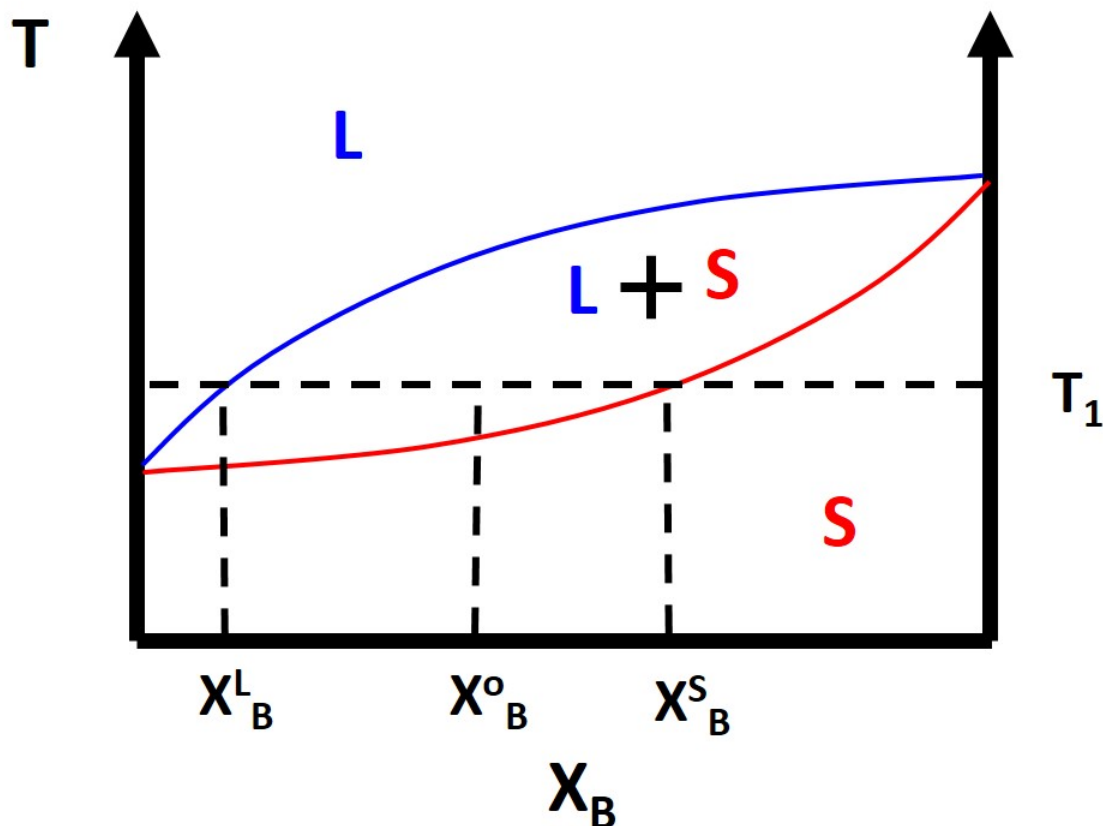


Figure Chapter4.6: Lever Rule

The composition of the liquid and solid phases, X_B^L and X_B^S , respectively are simply where the tie line intersects the **liquidus or solidus lines**, again respectively. The **liquidus** line defines the two phase coexistence between a liquid and a solid phase. The **solidus** line represent the two phase coexistence between a solid and another solid phase, for binary phase diagrams. We can also calculate the fraction of phases that are present by using the lever rule. What you do is simply take the length of the tie line from the composition, X_B^o , to the phase boundary for the other phase and divide by the total tie line length. For example:

$$f^S = \frac{X_B^o - X_B^L}{X_B^S - X_B^L} \quad (\text{Chapter 4.14})$$

$$f^L = \frac{X_B^S - X_B^o}{X_B^S - X_B^L} \quad (\text{Chapter 4.15})$$

where f^S and f^L are the phase fractions of solid and liquid respectively. This is typically the simplest type of phase diagram that you will find and it is actually the phase diagram for Cu-Ni. This also hold for ideal solution scenarios but typically most binary solutions or alloys will not be miscible at all compositions and temperatures. We know from structure that different materials have different crystal structures so those crystal structures might not always be compatible.

4.6 Phase Transitions Congruent vs Incongruent

A phase transition can occur **congruently** or **incongruently**. A **congruent** phase transition occurs when there is a complete transformation from one phase to another with no change in composition as seen in the examples below. An **incongruent** phase transition is a partial transformation from one phase to another and there will be a change in composition like we just saw with the lens diagram.

4.7 Eutectic Phase Diagram

So far we have only discussed the **simple binary lens phase diagram** which only applied to several real experimental systems. There is another relatively simple phase diagram that corresponds to many more experimental systems and that is the **binary eutectic phase diagram**.

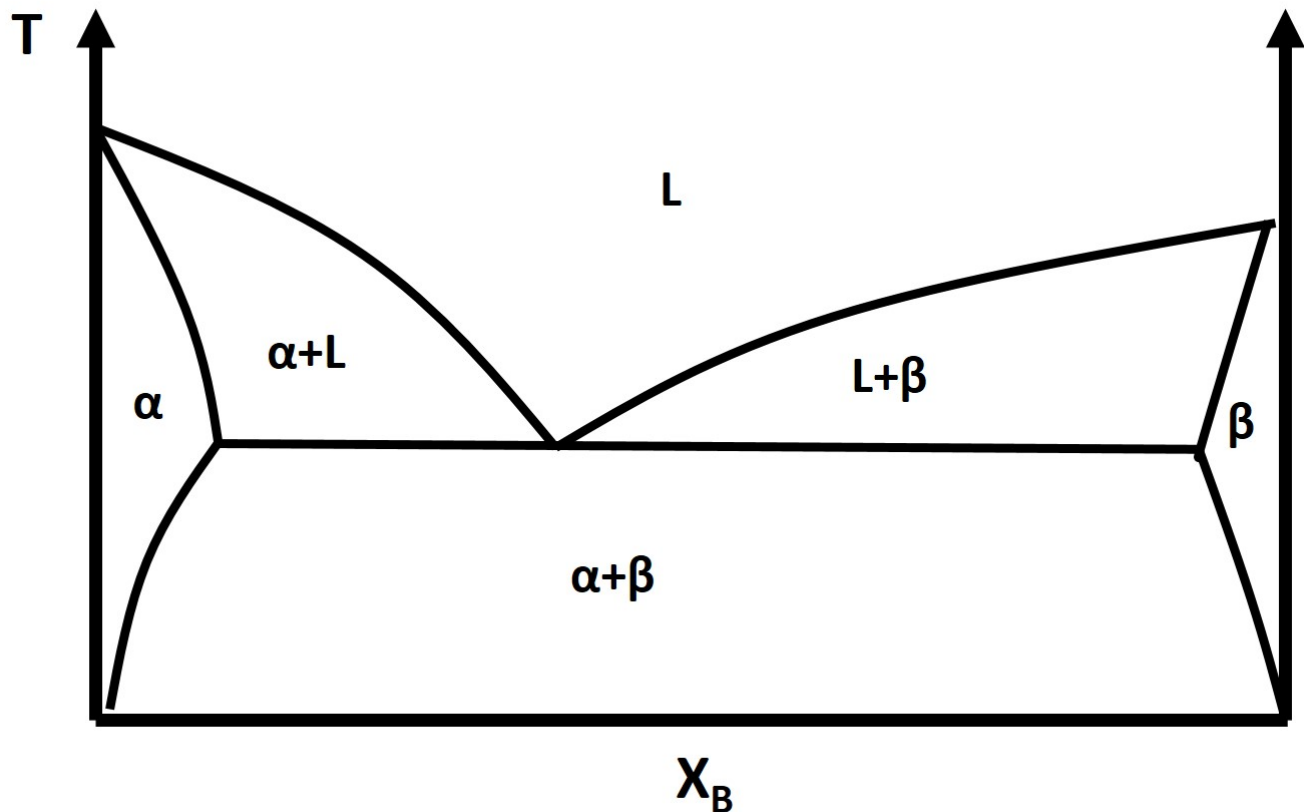


Figure Chapter4.7: Eutectic Phase Diagram

The binary eutectic phase diagram has several distinctive features one being a **solid-solid phase mixture, limit of solubility at different temperatures, and an invariant point in the phase diagram, the eutectic point**.

The **solubility limit** is the maximum amount of solute that you can integrate into the structure (or phase) or the solvent to form a solid solution. The solubility limit is a function of temperature and must be defined at a given temperature.

What is the solubility limit of B into A at T_1 ?

What about A into B?

Identify the Solidus Line

The **eutectic point** is an **invariant point**, $D = 0$, and it describes the constant composition transformation from a pure liquid phase to a two phase solid solution/mixture or alternatively



There are also a number of different invariant points beyond the simple eutectic.

4.8 Eutectic, Eutectoid, Peritectic, Peritectoid, and Monotectic

We have already discussed one invariant point, the eutectic. There is also another invariant point called the **eutectoid**. The **eutectoid** describes the constant composition transformation from a **pure solid phase to two phase solid solution/mixture** as described below

$$\gamma \rightleftharpoons \alpha + \beta \quad (\text{Chapter 4.17})$$

There is also a **peritectic** invariant point. The peritectic describes where a solid and liquid phase mixture will transform into a pure solid phase which is described by the equation below

$$L + \alpha \rightleftharpoons \beta \quad (\text{Chapter 4.18})$$

Finally the last invariant point is described by the **peritectoid** which is a transformation of two solid phases in a mixture to a single solid phase again described by the equation below

$$\gamma + \alpha \rightleftharpoons \beta \quad (\text{Chapter 4.19})$$

There is also a **monotectic** invariant point that does not appear in to many phase diagrams but this invariant point describes the transformation from a pure liquid to another liquid and solid phase which is described by the equation below:

$$L_1 \rightleftharpoons L_2 + \alpha \quad (\text{Chapter 4.20})$$

Let's do a couple of examples where we identify the invariant points in a couple of phase diagrams and calculate the fraction of phases at a given composition and temperature.

4.8.2 Ternary and Quaternary Phase Diagrams

So far we have dealt with relatively simple binary phase diagrams however there are also much more complicated ternary and quaternary phase diagrams. These types of phase diagrams are crucial, particularly in the field of ceramics. We can perform the same type of analysis on these diagrams but of course it becomes more complex.

4.9 Stable vs. Metastable Phase Boundaries: Cahn-Hilliard Spinodal Decomposition

We just touched upon the concept of stability and metastable with martensite. So let us define the **conditions for stability**. For a closed system at constant temperature and pressure the **Gibbs free energy is minimized with respect to fluctuations in other extensive variables, particularly fluctuations in composition**. To be stable against these fluctuations we have an additional condition on the second derivative of the free energy which is given by **Le Chatelier's principle**: A system perturbed by a **small fluctuation** will elicit a **thermodynamic driving force** to return to the **stable equilibrium state**. Or in terms of fluctuations in composition the condition for stability is

$$\frac{\partial^2 G}{\partial X_B^2} > 0 \quad (\text{Chapter 4.21})$$

Let's take a look at this condition in the graph below

Binodal Vs Spinodals

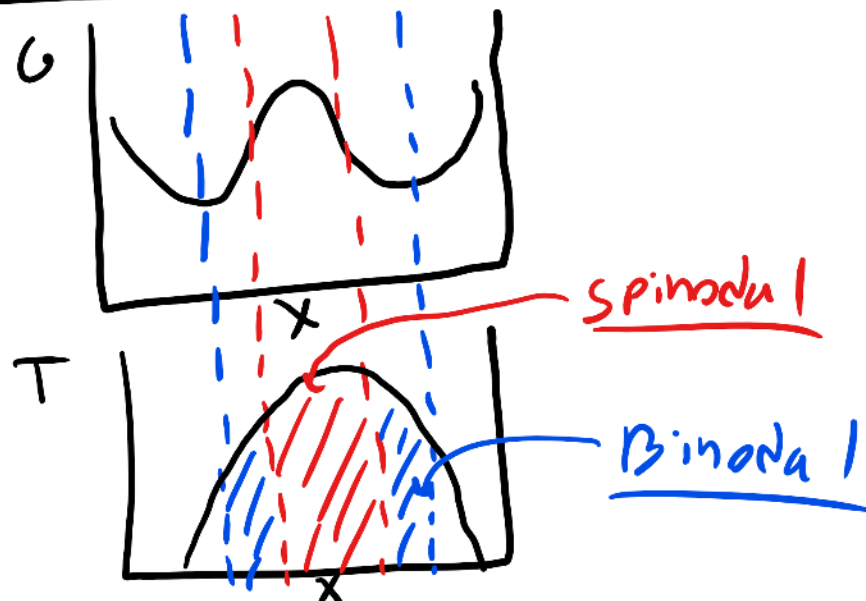


Figure Chapter 4.8: Binodal and Spinodal Decomposition

We can clearly see here that we have several special points **binodals** and **spinodals**.

Binodals are defined by the following mathematical relations

$$\frac{\partial G}{\partial X_B} = 0 \quad (\text{Chapter 4.22})$$

$$\frac{\partial^2 G}{\partial X_B^2} > 0 \quad (\text{Chapter 4.23})$$

while **spinodals** are defined by

$$\frac{\partial^2 G}{\partial X_B^2} = 0 \quad (\text{Chapter 4.24})$$

We can also see a point in this diagram that is unstable where

$$\frac{\partial G}{\partial X_B} = 0 \quad (\text{Chapter 4.25})$$

$$\frac{\partial^2 G}{\partial X_B^2} < 0 \quad (\text{Chapter 4.26})$$

The **spinodal** points will define the **spinodal boundary** and the **binodal** points will define the **boundaries of the 2-phase regions**. Systems that are initially unstable will undergo spinodal decomposition while systems that are initially stable or metastable will evolve via nucleation and mechanisms. Spinodal decomposition is a homogeneous transformation while nucleation and growth is typically dominated by a heterogeneous process.

4.10 First Order vs Second Order Phase Transitions

This discussion brings us nicely to a discussion on the **order of phase transformations**. So far we have really been focused on **first order phase transformations** like a crystal melting, water boiling, allotropes, etc, these are all first order phase transformations.

Why is that?

Well when we discuss order we are talking about whether the **transformation** is accompanied by a **discontinuity** in a **first, second, or higher order derivative of Gibbs free energy**.

The **second order transitions** are also called **continuous phase transitions** because the first derivative of Gibbs is continuous and it is not until there is a second order derivative that a discontinuity is observed. Some examples of second order transitions are **ODT (Order Disorder Transitions), glass transitions, superconducting transitions, ferromagnetic to paramagnetic transitions**.

We can see how these transitions look like by looking at Gibbs free energy.

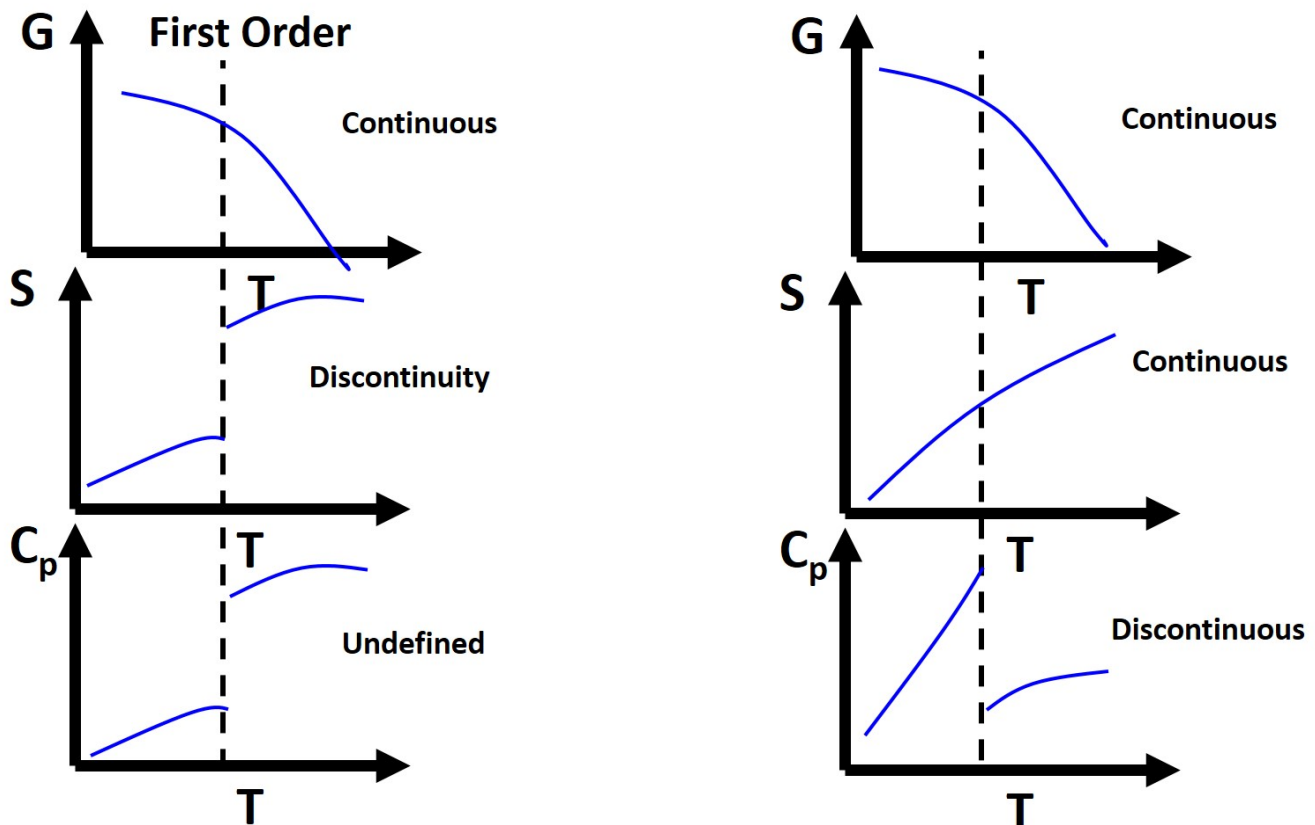


Figure Chapter4.9: First and Second Order Phase Transition

Remember from thermo that:

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,n} \quad (\text{Chapter 4.27})$$

$$C_p = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_{P,n} \quad (\text{Chapter 4.28})$$

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Chapter 5: Mechanical Behavior of Materials Part I

5.1 Sign Conventions

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**. Additionally we will consider moments that are **counter clockwise as positive** and **clockwise as negative**.

There are a series of recorded lecture videos to supplement this text which can be seen in the playlist here:

<https://www.youtube.com/playlist?list=PL9kJM2yOTyBCApd>

5.2 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.

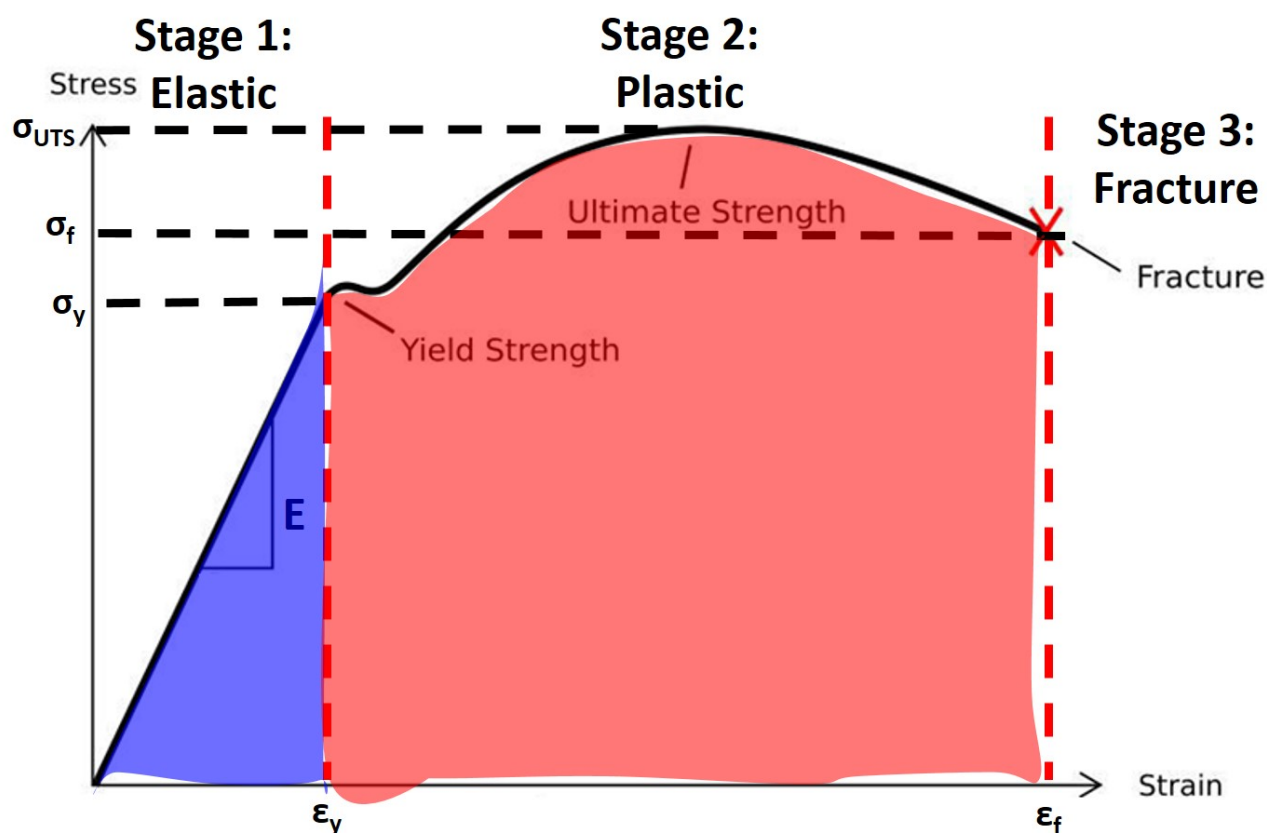


Figure Chapter5.1: Stress Strain Curve

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):

$$\sigma = E\epsilon \quad (\text{Chapter 5.1})$$

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**[9]. 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 σ_y which is the **yield stress** and ϵ_y the **yield strain**. The σ_{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 σ_f which is the **fracture stress** and the ϵ_f 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 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 **elastic strain energy (ESE)** which is defined as:

$$U_{ESE} = V \int_0^{\epsilon_y} \sigma_{11} d\epsilon_{11} \quad (\text{Chapter 5.2})$$

where V is the volume which gives us units of energy. This is the blue shaded portion. **Toughness** is defined as

$$U_T = V \int_0^{\epsilon_f} \sigma_{11} d\epsilon_{11} \quad (\text{Chapter 5.3})$$

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**.

Let's look at a couple of stress strain curves...

5.3 Elastic Regime:

Stress, σ , is a force normalized by the area over which it acts and the force is perpendicular to the area:

$$\sigma = \frac{F}{A} = \frac{N}{m^2} = Pa \quad (\text{Chapter 5.4})$$

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**. In this class we will use the engineering stress primarily in this class. **Shear stress**, τ , is a force normalized by the area over which it acts and the force is parallel to the area.

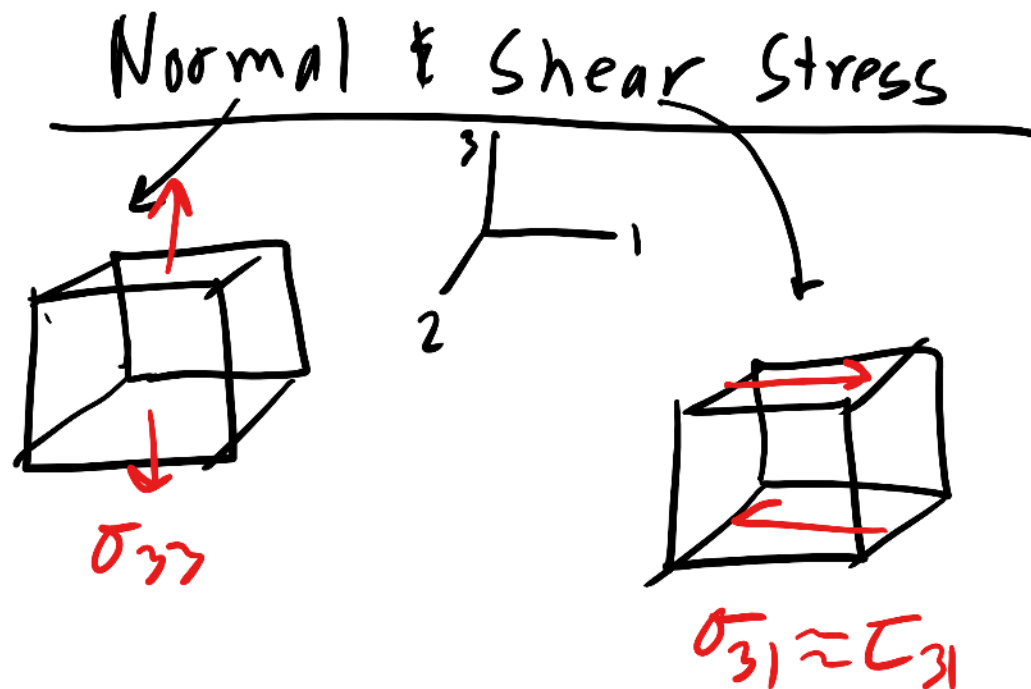


Figure Chapter5.2: Normal and Shear Stress

The shear stress is similarly defined as:

$$\tau = \frac{F}{A} \quad (\text{Chapter 5.5})$$

Now it should be noted here that stress is a second rank tensor, σ_{ij} , and so is strain, ϵ_{ij} . For stress i denotes the **normal to the plane, on which the force is acting** and j is the **direction of the force**:

$$\sigma_{ij} = \frac{F_j}{A_i} \quad (\text{Chapter 5.6})$$

So our full stress tensor or our most generic stress state would be:

$$\sigma = \begin{bmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{bmatrix} \quad (\text{Chapter 5.7})$$

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

$$\sigma_{12} = \sigma_{21} \quad (\text{Chapter 5.8})$$

$$\sigma_{23} = \sigma_{32} \quad (\text{Chapter 5.9})$$

$$\sigma_{31} = \sigma_{13} \quad (\text{Chapter 5.10})$$

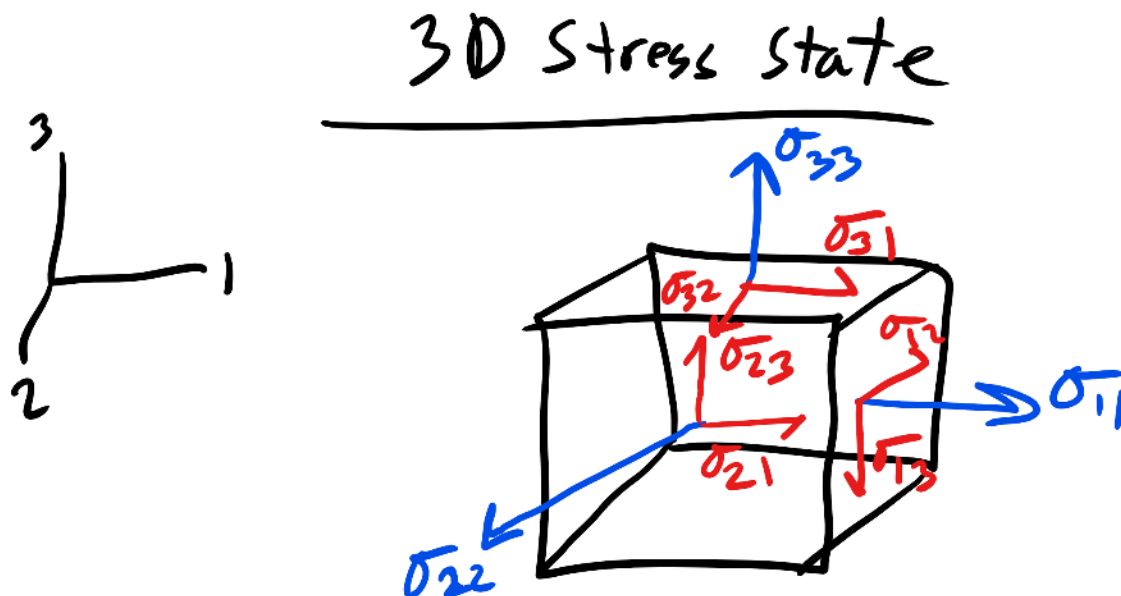


Figure Chapter 5.3: 3D Stress State

so our matrix reduces to 6 independent components for our RVE

$$\sigma = \begin{bmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{12} & \sigma_{22} & \sigma_{23} \\ \sigma_{13} & \sigma_{23} & \sigma_{33} \end{bmatrix} \quad (\text{Chapter 5.11})$$

Additionally we will encounter several special stress states like Uniaxial stress which gives the following stress state

$$\sigma = \begin{bmatrix} \sigma_{11} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (\text{Chapter 5.12})$$

and Biaxial stress which gives us

$$\sigma = \begin{bmatrix} \sigma_{11} & \sigma_{12} & 0 \\ \sigma_{12} & \sigma_{22} & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (\text{Chapter 5.13})$$

but more on those a bit later. Additionally we define the **hydrostatic stress** as

$$P = \frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33}) \quad (\text{Chapter 5.14})$$

5.4 Strain:

All machines, structural members, and materials will deform to some extent when externally loaded by a force or stress. That deformation results in a displacement or **strain**, ϵ

$$\epsilon = \frac{dL}{L} \quad (\text{Chapter 5.15})$$

$$\epsilon_t = \int_{L_1}^{L_2} \frac{dL}{L} = \ln \frac{L_2}{L_1} \quad (\text{Chapter 5.16})$$

where L_1 is the original length. This is the definition of **true strain**, ϵ , but typically we work with a simpler form called the **engineering strain**, ϵ_e

$$\epsilon_e = \frac{L_2 - L_1}{L_1} = \frac{\Delta L}{L_1} \quad (\text{Chapter 5.17})$$

Typically engineers work with *microstrain* or parts per million. And the shear strain is:

$$\begin{aligned} \gamma &= \frac{dx}{y} = \tan \theta \end{aligned}$$

as seen in the figure below

Engineering Shear Strain

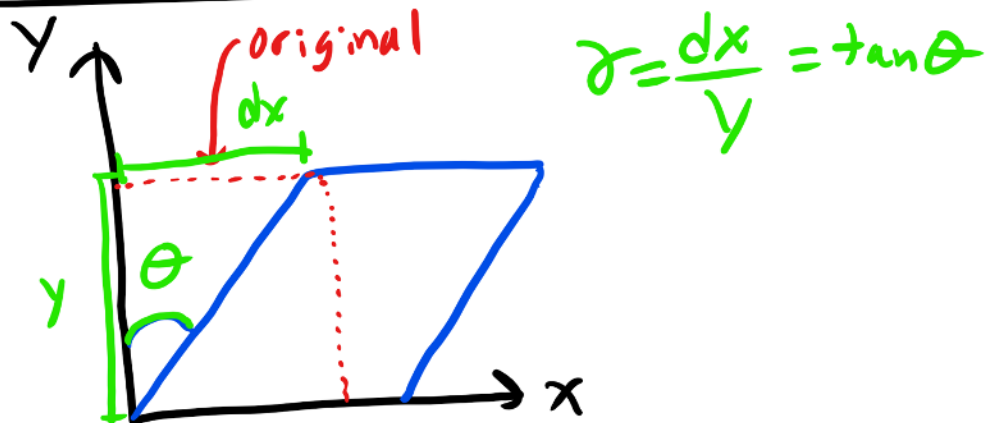


Figure Chapter5.4: Engineering Shear Strain

Also for a material subjected to shear stresses we **observe a proportional relationship between shear stress and strain in the elastic regime** which is defined as:

$$\tau = G\gamma \quad (\text{Chapter 5.18})$$

where G is the shear modulus.

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**. This **lateral strain** is described by the **Poisson's Ratio**:

$$\nu = -\frac{\epsilon_L}{\epsilon_A} \quad (\text{Chapter 5.19})$$

where ϵ_L is the lateral strain and ϵ_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**.

5.5 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 θ** ? 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.

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.

Consider the element which is initially stressed in the 1 direction by applying σ_{11} . There will be a resultant strain:

$$\epsilon_{11} = \frac{\sigma_{11}}{E} \quad (\text{Chapter 5.20})$$

$$\epsilon_{22} = \frac{-\nu\sigma_{11}}{E} \quad (\text{Chapter 5.21})$$

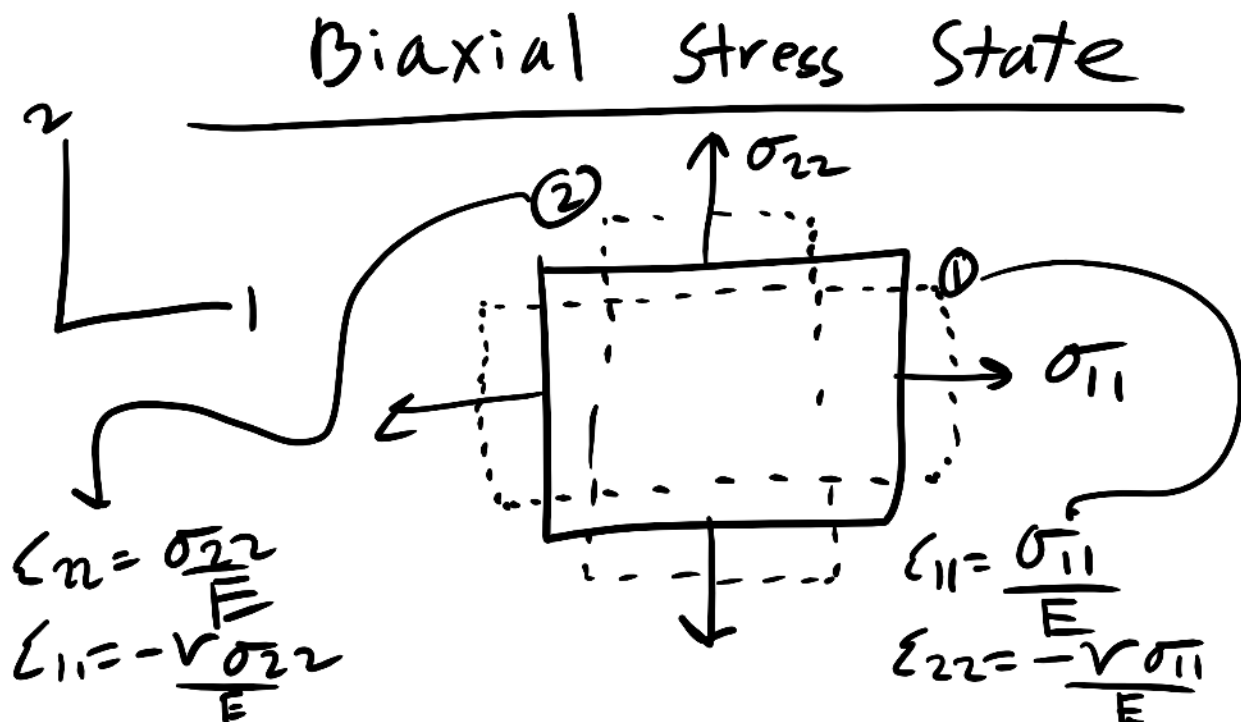


Figure Chapter5.5: Biaxial Stress State

The element is **then stressed in the 2 direction** by applying σ_{22} . The resultant strain will be:

$$\epsilon_{22} = \frac{\sigma_{22}}{E} \quad (\text{Chapter 5.22})$$

$$\epsilon_{11} = \frac{-\nu\sigma_{22}}{E} \quad (\text{Chapter 5.23})$$

therefore the **total strain** in 1 and 2 directions will be:

$$\epsilon_{11} = \frac{\sigma_{11} - \nu\sigma_{22}}{E} \quad (\text{Chapter 5.24})$$

$$\epsilon_{22} = \frac{\sigma_{22} - \nu\sigma_{11}}{E} \quad (\text{Chapter 5.25})$$

$$\epsilon_{11} = \frac{1}{E}[\sigma_{11} - \nu(\sigma_{22} + \sigma_{33})] \quad (\text{Chapter 5.26})$$

$$\epsilon_{22} = \frac{1}{E}[\sigma_{22} - \nu(\sigma_{33} + \sigma_{11})] \quad (\text{Chapter 5.27})$$

$$\epsilon_{33} = \frac{1}{E}[\sigma_{33} - \nu(\sigma_{11} + \sigma_{22})] \quad (\text{Chapter 5.28})$$

5.6 Thermal Expansion Coefficient

Let's go back once again to our gold old friend the LJ potential when temperature increases we know that the thermal energy increases, causing the atoms to vibrate and oscillate around their equilibrium distance r_o . Now if the potential was symmetric or harmonic (like at the minimum of a quadratic function) then the atoms would equally be distributed at distances less than or greater than the equilibrium distance. However, as you can see the LJ and **most atomic potentials are asymmetric or anharmonic** and thus when the atoms fluctuate they will tend to occupy positions with the lowest energy and one can see that as temperature increase and as the molecules deviate further and further from their equilibrium position they will tend to adopt positions with lower energies. Thus, as you can see on average the molecules will tend to expand because the larger interatomic distances have lower energies and thus the materials will tend to expand.

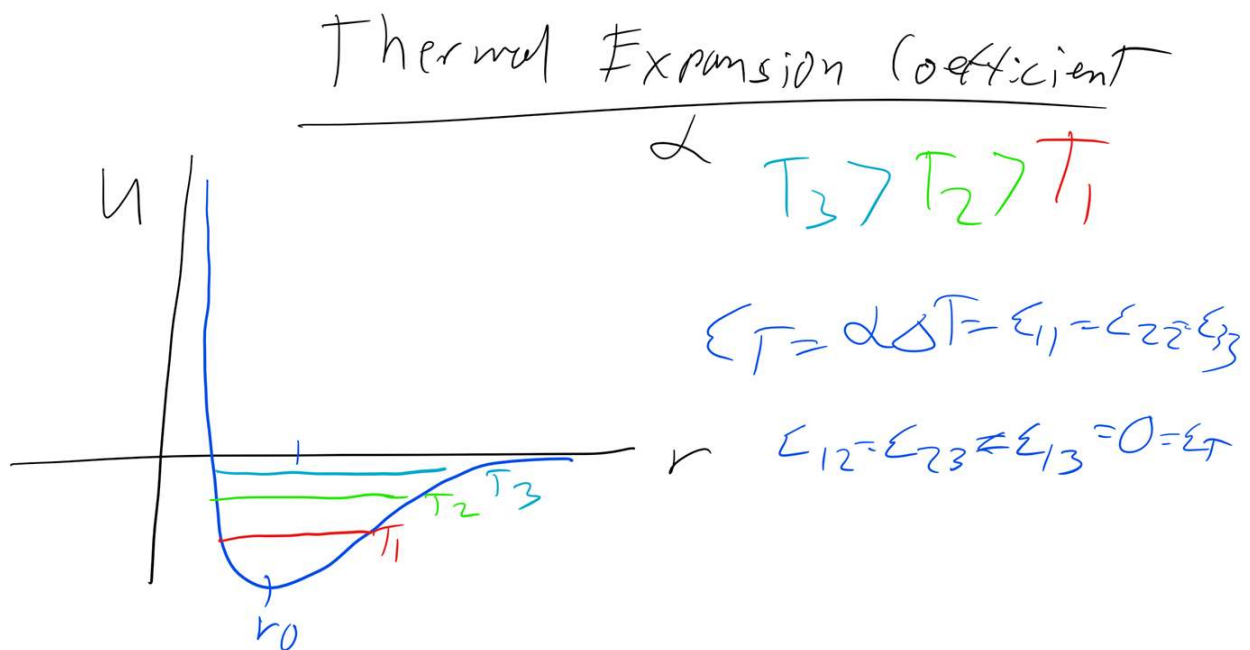


Figure Chapter5.6: Thermal Expansion Coefficient

So to put it simply at $T = 0K$ the atoms will be at their equilibrium distance r_o and then as temperature increase the atoms will essentially move up the anharmonic potential to lower their energy. The **equilibrium distance thus shifts to the right** depending on the **thermal expansion coefficient** α and thus we can write this thermally induced strain as

$$\epsilon_T = \alpha \Delta T \quad (\text{Chapter 5.29})$$

Now for **linear elastic isotropic materials the material will expand uniformly in all directions** and there will be no shear strain from thermal expansion. Some typical thermal expansion coefficients for some materials can be seen below, all $\times 10^{-6} K^{-1}$

- Polymers 50-500
- Metals 5-50
- Ceramics 1-10

- Glasses 1-2

Taking into account thermal strain is incredibly important in and in many materials processes when you heat a material that is a composite and cool it can **induce residual stresses due to the incompatible thermal strains**.

It should be noted that thermal strain will only occur along normal directions and you must add it on to the expression for strain if there is a change in temperature during your operation.

5.7 General Linear Elastic Isotropic Cubic Material Stress and Strain Expression

To write the most general expression of stress and strain for linear elastic isotropic cubic materials and thermal expansion

$$\epsilon_{ij} = \frac{1}{E} \left[(1 + \nu) \sigma_{ij} - \nu \sigma_{kk} \delta_{ij} \right] + \alpha \Delta T \delta_{ij} \quad (\text{Chapter 5.30})$$

where δ_{ij} is the **Kronecker Delta** which will be 1 when $i = j$ and 0 when $i \neq j$

5.7.1 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.

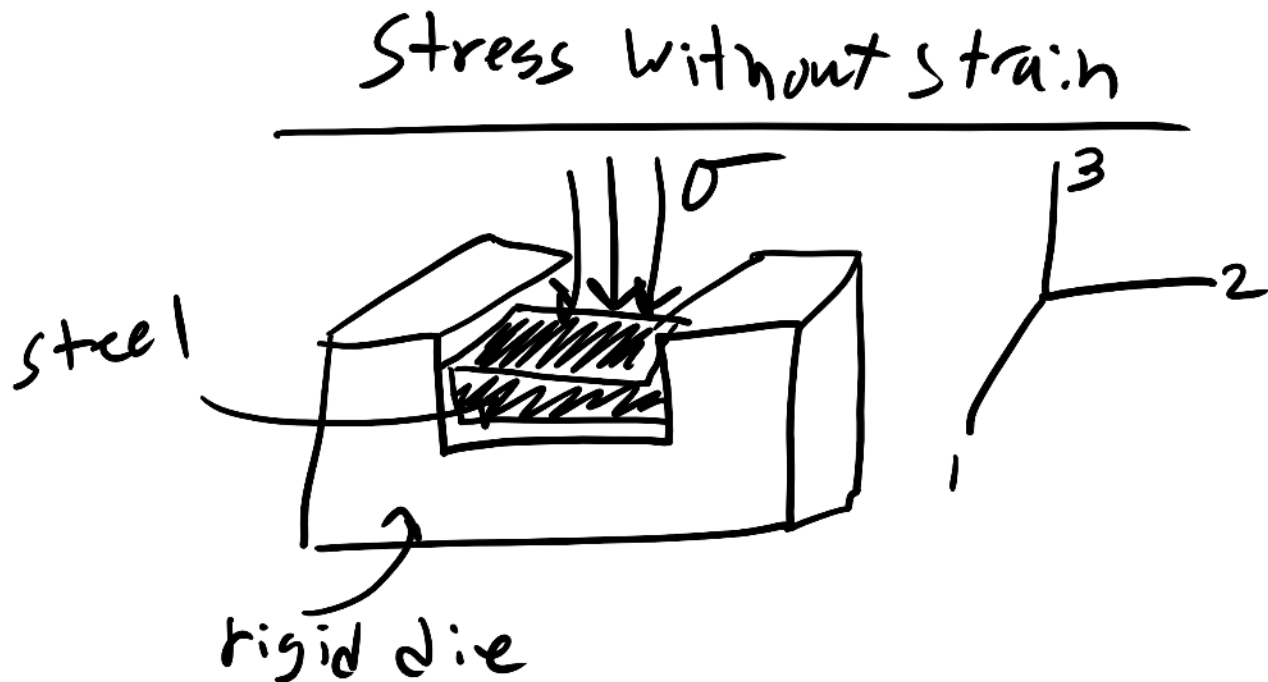


Figure Chapter5.7: Complex Stress State Problem

- State all the components of the stress tensor under the applied stress.
- Which normal strain components are zero and why?
- Use your answers in part a) and b) to express the relationship between the non-zero stresses in this system.

The solution to this problem can be seen in the video here:

<https://youtu.be/lxK4eL9n-ZM>

5.8 Resolving Stress on Plane of Interest:

Now I know that all of you are statics experts so one way that we can resolve the stresses in a new coordinate system is by first applying our static equilibrium conditions for the forces in our new coordinate system. So 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').

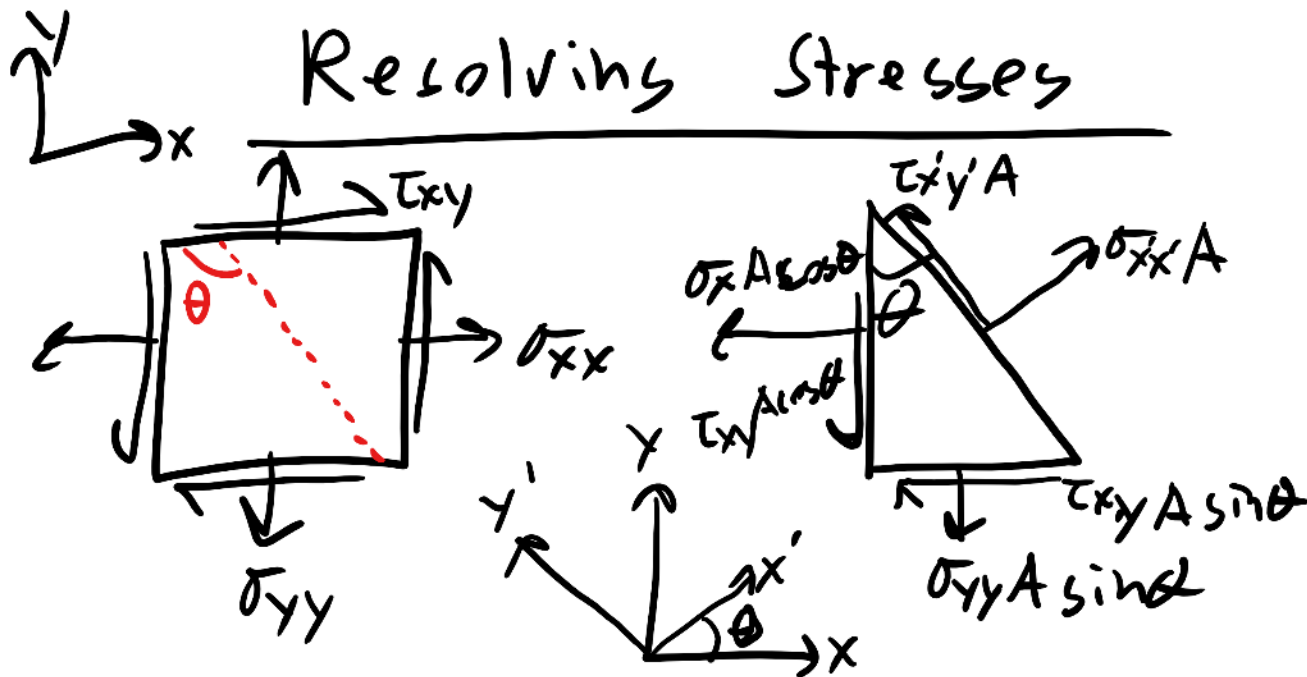


Figure Chapter5.8: Stress-State Rotation

Then we balance out the forces assuming **static equilibrium**:

$$\sum F_{x'} = 0 = \sigma_{x'x'}A' - (\tau_{xy}A' \sin \theta) \cos \theta - (\sigma_{yy}A' \sin \theta) \sin \theta - (\tau_{xy}A' \cos \theta) \sin \theta - (\sigma_{xx}A' \cos \theta) \cos \theta \quad (\text{Chapter 5.31})$$

After some rearranging and trig transformations:

$$\sigma_{x'x'}(\theta) = \frac{\sigma_{xx} + \sigma_{yy}}{2} + \frac{\sigma_{xx} - \sigma_{yy}}{2} \cos 2\theta + \tau_{xy} \sin 2\theta \quad (\text{Chapter 5.32})$$

$$\sigma_{y'y'}(\theta) = \frac{\sigma_{xx} + \sigma_{yy}}{2} - \frac{\sigma_{xx} - \sigma_{yy}}{2} \cos 2\theta - \tau_{xy} \sin 2\theta \quad (\text{Chapter 5.33})$$

$$\tau_{x'y'}(\theta) = -\left(\frac{\sigma_{xx} - \sigma_{yy}}{2}\right) \sin 2\theta + \tau_{xy} \cos 2\theta \quad (\text{Chapter 5.34})$$

We have successfully transformed the stress state to our new coordinate system!

Now in addition to finding the stress state in a new coordinate system it is also helpful to find the principal stress state which is the stress state where there only exists normal stresses all shear stresses are equal to zero. To do this we can simply solve for when the normal stresses are maximized or when the shear stress values are zero and we will find that the principal stress angle will be simply

$$\tan 2\theta = \frac{\tau_{xy}}{\frac{\sigma_{xx} - \sigma_{yy}}{2}} \quad (\text{Chapter 5.35})$$

We can then substitute this back into the above equations and get:

$$\sigma_1 = \frac{\sigma_{xx} + \sigma_{yy}}{2} + \sqrt{\left(\frac{\sigma_{xx} - \sigma_{yy}}{2}\right)^2 + \tau_{xy}^2} \quad (\text{Chapter 5.36})$$

$$\sigma_2 = \frac{\sigma_{xx} + \sigma_{yy}}{2} - \sqrt{\left(\frac{\sigma_{xx} - \sigma_{yy}}{2}\right)^2 + \tau_{xy}^2} \quad (\text{Chapter 5.37})$$

σ_1 and σ_2 are the **principal normal stresses** and you can see by definition that $\sigma_1 > \sigma_2$. We can do the same for the **maximum shear stress** and find that

$$\tau_{xy,max} = \sqrt{\left(\frac{\sigma_{xx} - \sigma_{yy}}{2}\right)^2 + \tau_{xy}^2} \quad (\text{Chapter 5.38})$$

Now how many of you can do this upon request at a job interview or memorize these equations for 30+ years? My guess is probably not many of you can do so. Additionally, I like to refer this as the plug and chug method as it does not leave much intuition or thoughts students tend to just plug and chug into the equations. Plus I will tend to not ask questions that you can solve easily using these expressions so I would not utilize this method. Additionally, it is not general for the 3D stress state but let's hold off on that for a while. But if we have the following stress-tensor below can we answer the questions below:

$$\sigma = \begin{bmatrix} 15 & 4 & 0 \\ 4 & 5 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (\text{Chapter 5.39})$$

Now what is the principal stress state and the values of principal stress? What about the stress state 15° CW rotation around the 3 axis?

Now we can find this by plugging and chugging it into the equations we defined above.

However, this is not physical and we don't really gain any intuition and most importantly it is a pain to do and when I ask harder questions this will be very difficult to do. But let's see how it is possible

<https://youtu.be/Pu0ktuwGtqg>

5.8.1 Mohr's Circle: A Graphical Approach

Another approach that is often the bane of many mechanics students is Mohr's Circle. But today we will de-mystify Mohr's circle and more importantly learn when it is useful to utilize this technique and when it is better and perhaps more appropriate to use our linear algebra approach.

Otto Mohr, a German engineer in the 1800's, recognized that we can **represent the principal stress state graphically**. We can re-write the equations and

$$\left[\sigma_1 - \left(\frac{\sigma_{xx} + \sigma_{yy}}{2}\right)\right]^2 + \tau_{xy,max}^2 = \left(\frac{\sigma_{xx} - \sigma_{yy}}{2}\right)^2 + \tau_{xy}^2 \quad (\text{Chapter 5.40})$$

You should notice that this form has a similar form to the equation of a circle, i.e.

$$(x - c)^2 + y^2 = r^2 \quad (\text{Chapter 5.41})$$

where the center of the circle is $\frac{\sigma_{xx} + \sigma_{yy}}{2}$ and the radius of the circle is $\sqrt{\left(\frac{\sigma_{xx} - \sigma_{yy}}{2}\right)^2 + \tau_{xy}^2}$. We can **plot Mohr's circle for an arbitrary initial stress state**.

The way that we will practically utilize Mohr's circle is as follows, note that this works when considering plane stress states only

1. Draw a plot with normal stress on the x-axis and shear stress τ on the y-axis
2. Treat the stress tensor as a coordinate system with x-axis values for normal stress and y-axis values for shear stress. Plot the coordinates on the graph
3. The 4 coordinates that you may possible have (or 2 coordinates) are points that will lie on your Mohr's circle. Draw a line connecting two of the points

4. When drawing the line pick the line such that the smaller normal stress has a positive shear stress value and the larger stress has the negative value, i.e. draw the top part of the line on the left and bottom on right.
5. Determine the length of this line as this will determine the diameter of your circle and thus the radius as well
6. Determine where the line crosses the x-axis this is the center of your Mohr's circle.
7. Determine the angle between your line and the x-axis, this angle is 2θ . IT IS 2θ DUE TO THE EQUATIONS AND TRANSFORMATIONS DESCRIBED ABOVE
8. Once you have the center, radius, and 2θ values you can find the principal stress state, principal stress state angle, maximum shear stress value and angle, and then you can do geometry to get other stress states.

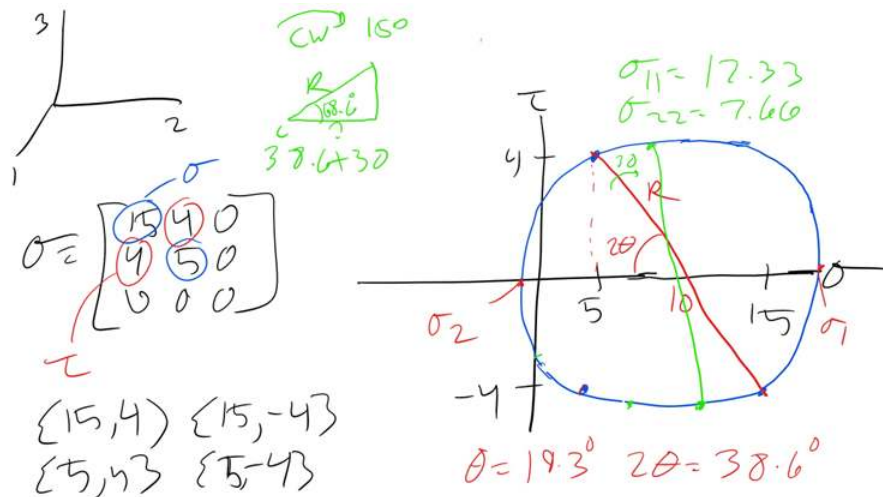


Figure Chapter5.9: Mohr's Circle

We can see this solved in the video here:

<https://youtu.be/paMHd574zWI>

5.8.2 Plane Stress Linear Algebra Transformations

Now as we see above Mohr's circle can be very useful for the geometrically gifted or inclined but I am not one of those people. Also, I find that when trying to determine the stress-state at an arbitrary rotation Mohr's circle can become a bit cumbersome and I always fear that I may possibly forget the 2θ caveat.

So I would suggest instead or better yet to supplement Mohr's circle we can use a linear algebra approach and a rotation matrix to convert stresses in one coordinate system to another coordinate system. Again, remember that we are still only working with plane stress states here, not 3D stress state transformations. So let's get started.

Let's start by first defining our transformation matrix T where

$$[T] = \begin{bmatrix} c^2 & s^2 & 2sc \\ s^2 & c^2 & -2sc \\ -sc & sc & c^2 - s^2 \end{bmatrix} \quad (\text{Chapter 5.42})$$

where $c = \cos \theta$ and $s = \sin \theta$.

So we now write that

$$\sigma' = T\sigma \quad (\text{Chapter 5.43})$$

or similarly

$$\begin{bmatrix} \sigma_{11}' \\ \sigma_{22}' \\ \sigma_{12}' \end{bmatrix} = \begin{bmatrix} c^2 & s^2 & 2sc \\ s^2 & c^2 & -2sc \\ -sc & sc & c^2 - s^2 \end{bmatrix} \begin{bmatrix} \sigma_{11} \\ \sigma_{22} \\ \sigma_{12} \end{bmatrix} \quad (\text{Chapter 5.44})$$

So we can utilize this linear algebra approach and solve the same question but as you can see it is a very elegant way to solve these problems and requires minimal coding but you still have a clear intuition for how to solve these problems. However, often I will still draw the circle to keep the rotations clear. Here is the linear algebra approach solved here

<https://youtu.be/Cu77Q2QcYxU>

5.8.4 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** ΔP between the internal pressure and the environment. The **wall thickness is sufficiently small** where we can say $t \ll r$ or that $\frac{r}{t}$ **What is the stress state?** It is **plane stress state** due to symmetry considerations. Therefore we need to find σ_1 and σ_2 which we will accomplish by **drawing free body diagrams**.

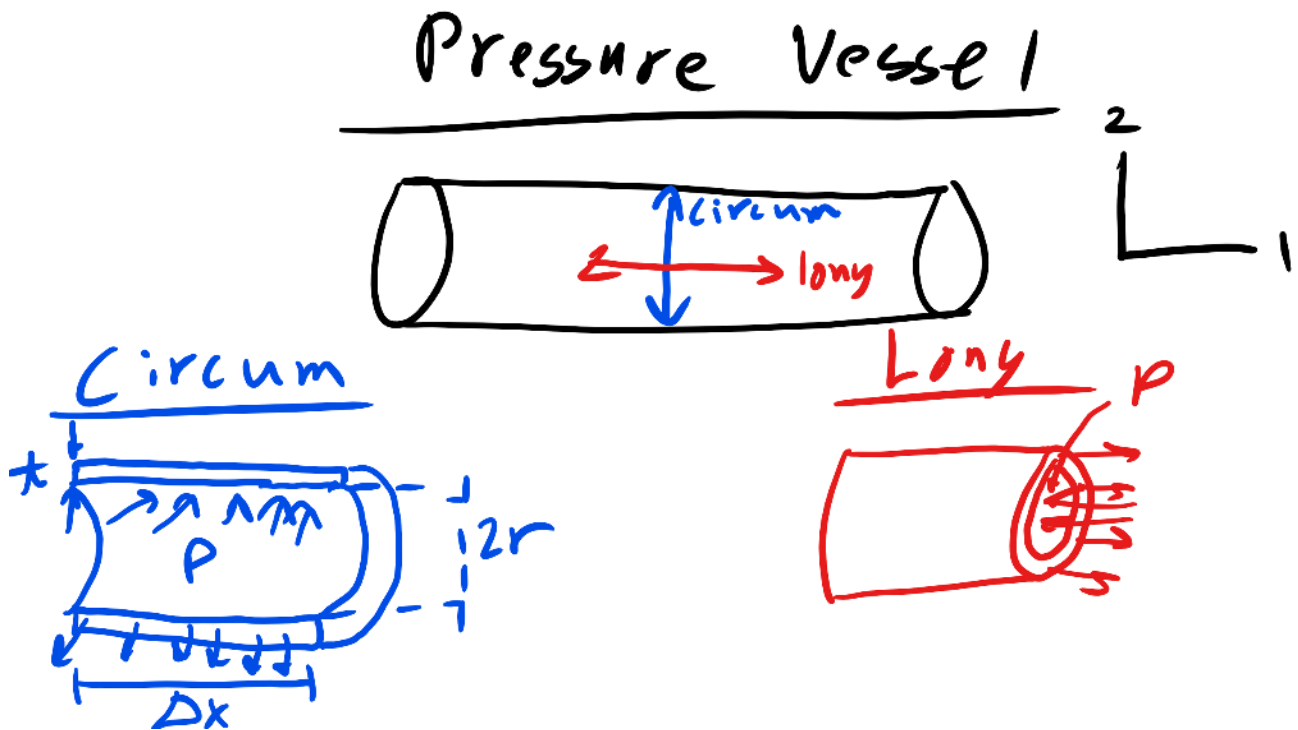


Figure Chapter5.10: Thin-Walled Pressure Vessels

Let us first **consider the longitudinal direction**. Remember that the **forces must sum to zero**.

$$\sum F_1 = 0 = \Delta P \pi r^2 - \sigma_{11} 2\pi r t \quad (\text{Chapter 5.45})$$

$$\sigma_{11} = \sigma_{Longitudinal} = \frac{\Delta P r}{2t} \quad (\text{Chapter 5.46})$$

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:

$$\sum F_2 = 0 = -\Delta P \Delta x 2R + \sigma_{22} \Delta x t 2 \quad (\text{Chapter 5.47})$$

$$\sigma_{22} = \sigma_{Hoop} = \frac{\Delta P R}{t} \quad (\text{Chapter 5.48})$$

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.**

5.9 Beam Bending

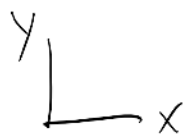
Before we move into linear viscoelasticity, plasticity, fracture, and fatigue we have three elastic loading topics to discuss and these still very important and relevant loading states and phenomenon those being **bending, buckling, and torsion** respectively.

You have probably already encountered beam bending in other course and perhaps buckling but we again are going to take a slightly different approach specifically approaching this from the materials perspective.

Specifically we can define a **beam** as anything that can carry transverse loads and this can range from your typical civil engineering structural applications (bridges, trusses, pool diving boards, etc.) but also to some more exotic applications like Atomic Force Microscopy (AFM) which utilizes a cantilever beam, creating thin filmed substrate which have thermal mismatch which results in bending, cellular solids like foams, honeycomb structures, tissues, etc, sporting equipment like ski poles, and much much more!!

When dealing with beam bending problems we must consider several things before we start to approach the problem specifically we must consider

- Support Reactions
 - Internal Forces
 - Internal Moments
 - Internal Stresses
 - Deflections
 - Support Type: roller, pin, or fixed end
- Additionally, different supports will have different reaction forces and moments for example
- Roller: Reaction force in the y-direction
 - Pin: Reaction force in the x and y direction
 - Simple Friction-less Surface: Reaction force in the y-direction
 - Fixed Support: Reaction force in x, y, and reaction moment



Beam Bending Basics



→ Cantilever

Roller



→ simple support

Pin



Simple Frictionless Surface

Fixed support

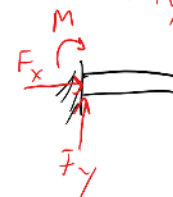


Figure Chapter5.11: Beam Bending Basics

Soon we will be working with **free body diagrams** as well as **shear force and moment distributions** within structures, now why do we want to do this? We need to find the locations of maximum shear forces and bending moments because material failure will often occur at regions of **maximum shear forces** which we will denote as V and **bending moments** M . These shear forces and bending moments can vary along the length of the beam. Moreover we will see that shear stress depends on the shear forces whereas normal stresses will depend on the bending moment. Finally the amount of deflection will also depend on the bending moment. Let's start off with some background on how we will work with beams and support reaction diagrams, this should have been covered in other courses but let's give us a nice little reminder.\

5.9.1 Sign Convention and Coordinate System Reminder Once Again

But again before we get started that let's do one more reminder of our coordinate system and what we will determine as positive and negative forces, shears, moments, etc.

In terms of stresses tension will be defined as positive, compression as negative, shear is positive if the force is acting on a face with a normal in the positive direction and also has a force pointed in the positive direction.

For forces, forces which point in the positive direction relative to our coordinate system will be defined as positive. Also CCW moments are positive and CW moments are negative.

For beams a positive internal shear force V will be positive if it acts downward on the right hand face of a beam or upward on a left hand face of a beam. A positive internal bending moment M acts CCW on the right hand face of beam and CW on the left hand face of a beam. You can also consider a bending moment as positive if tension is on the bottom of the beam and negative if tension is at the top.

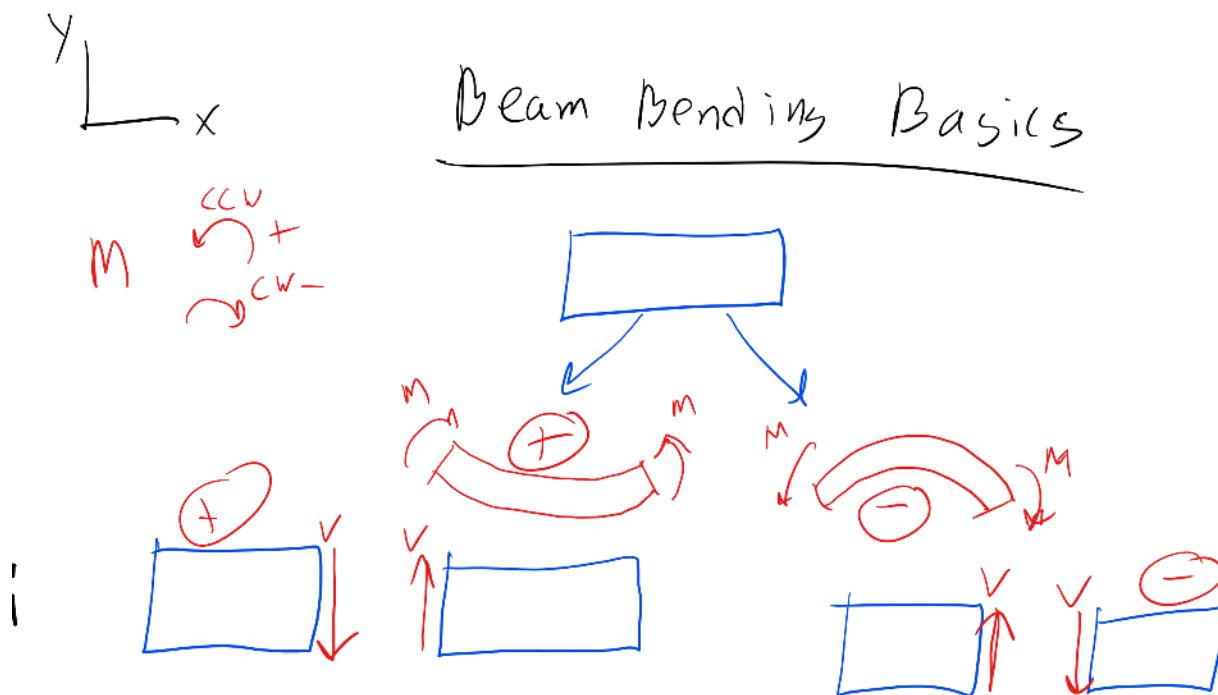


Figure Chapter5.12: Sign Conventions Beam Bending

The key point to this entire discussion is before you approach any any any mechanics problem if there is not a coordinate system defined you must define one before you start anything. Keep this in mind it will be very important that you double check this as you approach problems.

5.9.2 Support Reactions in Beams

Let's first consider a fixed end supported cantilever beam of length of length l with a load P applied at the end. At the fixed end we will have one reaction force F_y at the end.

For virtually all of our beam bending problems we will start as follows to develop our problem solving framework:

1. Coordinate System
2. Free Body Diagram
3. Equilibrium Expressions
4. Solve for Unknowns

As you can see below we have defined our coordinate system and we have drawn our free body diagram now we can apply our equilibrium conditions

$$\begin{aligned}\Sigma F &= 0 & (\text{Chapter 5.49}) \\ \Sigma M &= 0 & (\text{Chapter 5.50})\end{aligned}$$

and solve for the reaction moment

$$\begin{aligned}\Sigma F_y &= 0 = -P + F_y & (\text{Chapter 5.51}) \\ \Sigma M_0 &= 0 = M_0 - Pl & (\text{Chapter 5.52})\end{aligned}$$

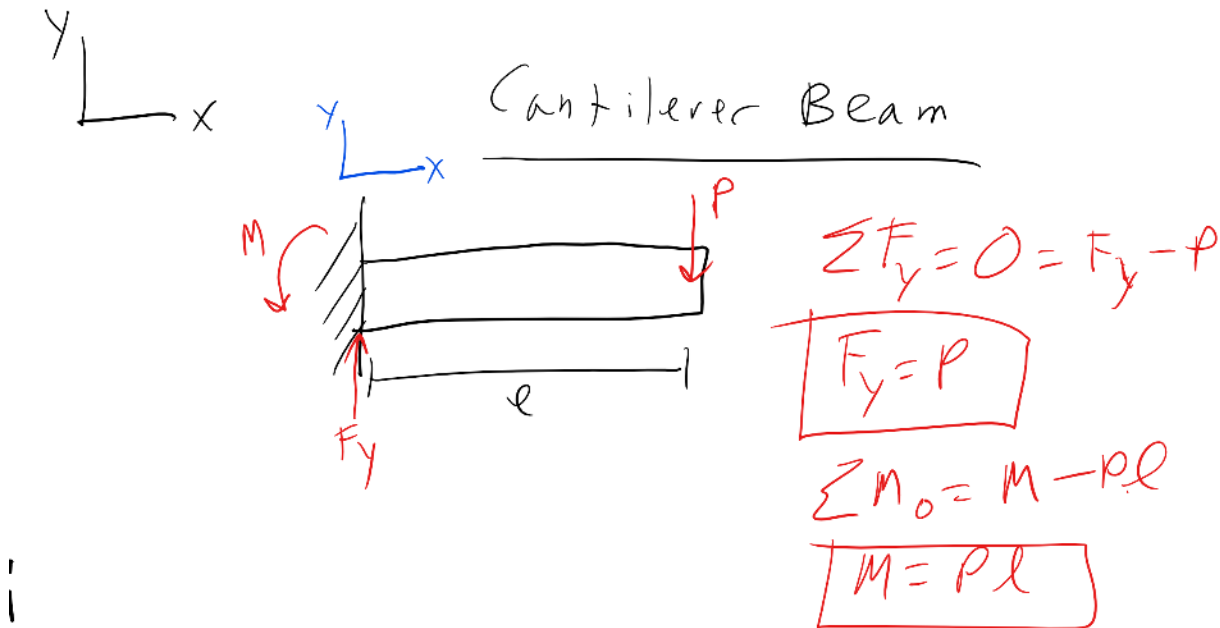


Figure Chapter5.13: Cantilever Beam Reaction Moment Calculation

5.10 Stresses in Beams

Beam Bending Assumptions

So far we have demonstrated that when we apply a load on a beam internal shear and bending moments are created. This gives rise to both shear and normal stresses and typically as we will show the normal stress are much much greater than shear stresses, in particular when the length to height ratio of the beam is large, i.e. $\frac{l}{h} > 10$. Again our entire purpose of learning about this topic is to avoid material failure so we will make sure to focus on regions of maximum stress. Now in doing so we will make several critical assumptions

- Beam is straight
- Material is linear elastic, isotropic, and cubic
- X-section is symmetric
- Beam is stable, i.e. no lateral buckling

Thus as the schematic below indicates typically we will be dealing with scenarios as we have done previously where one face is in tension and the other is in compression. There is also a plane along the longitudinal axis called the **neutral axis** that experiences no stress.

We must also distinguish between **pure bending** which exhibits a constant bending moment and **non-uniform bending** where the bending moment is not constant.

So typically when we bend a beam such that it experiences positive bending near the top the beam will be in compression and as we make our way to the bottom of the beam (height-wise) we will transition from compression to no stress at the neutral axis and then tension at the bottom of the beam. If the material is brittle failure will occur via crack propagation in the tensile regime whereas if a material is weak under compression failure will occur via buckling at the top surface. We have a good idea conceptually of what is going on but now we need to develop an expression that will tell us how this stress will be distributed in a beam. So let's begin and we will derive this relationship in the following steps

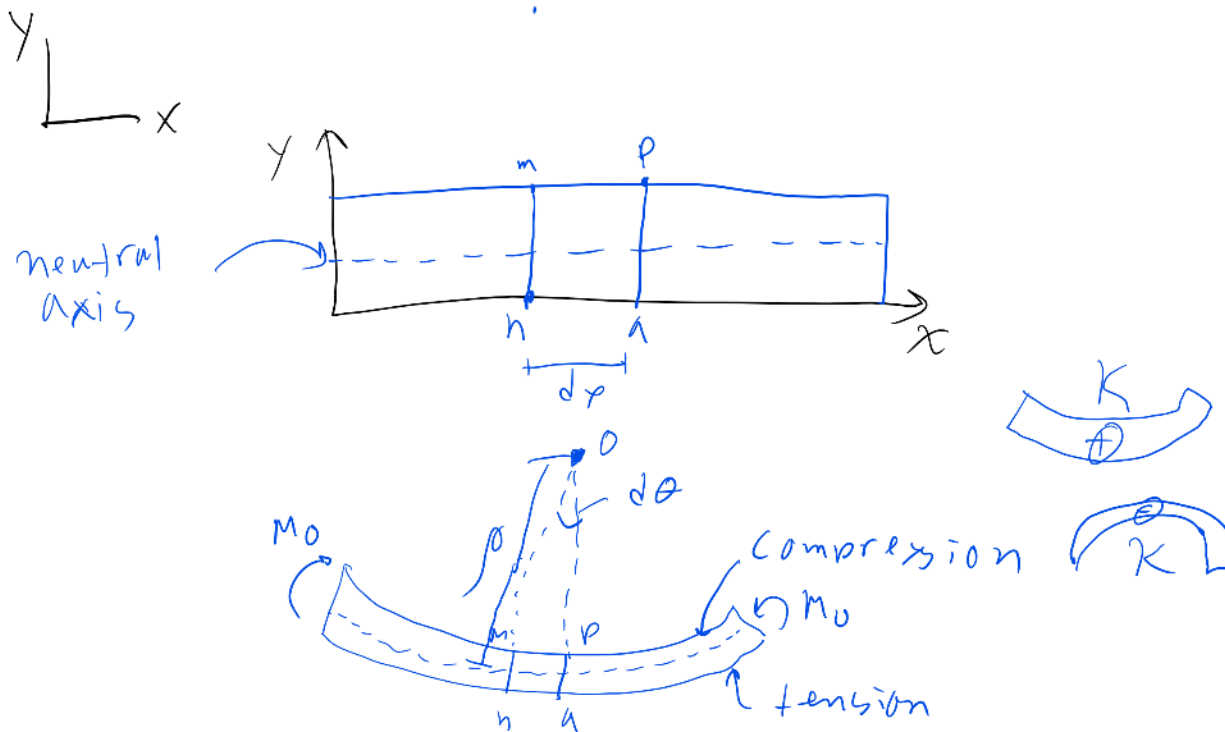


Figure Chapter 5.14: Bending Schematic

1. Geometric Statement
2. Constitutive Equation
3. Equilibrium Conditions

So let's start with our **Geometric Statement**

Geometric Statement

Let's look at our schematic of our beam here and we can clearly see that sections $\overline{mn}$ and $\overline{pq}$ will rotate with respect to one another and if we extrapolate these lines that will intersect a particular point O which also the center of curvature. Additionally we can see that the distance from O to the neutral axis is given by the radius of curvature r . We will also assume that the distances between $\overline{mn}$ and $\overline{pq}$ at the neutral axis is constant dx so we can develop the following relationship such that our curvature κ is given by

$$\kappa = \frac{1}{\rho} = \frac{d\theta}{dx} \quad (\text{Chapter 5.53})$$

and remember that if we have pure bending that ρ is constant and it will not be if we are in non-uniform bending. Additionally for curvature we have the same sense of positive and negative as the bending moment and as we have previously defined in other courses.

Constitutive Equation

We can now obtain that the normal strain in the x direction because we know that along all longitudinal planes other than the neutral axis will change length and produce strain in this direction. Let's do a quick thought experiment and think about a segment $\overline{ef}$ that is some distance y away from the neutral axis.

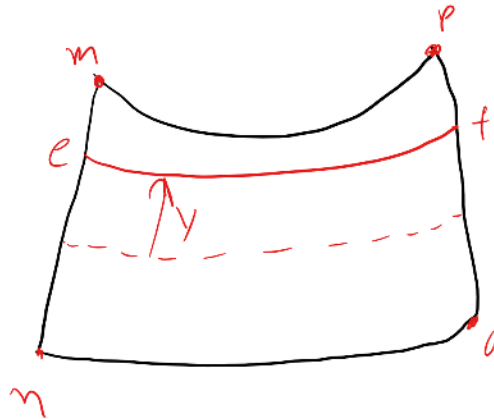
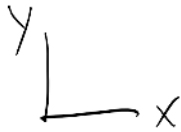


Figure Chapter5.15: Bending Schematic for Beam Strains and Stress

Here we find that

$$\begin{aligned} l_o &= dx = \rho d\theta & (\text{Chapter 5.54}) \\ l_f &= (\rho - y) d\theta & (\text{Chapter 5.55}) \\ \epsilon_{xx} &= \frac{l_f - l_o}{l_o} = -\frac{y}{\rho} = -y\kappa & (\text{Chapter 5.56}) \end{aligned}$$

Let's look at this expression and that we see when the distance y approaches zero the strain also goes to 0 when we approach the neutral axis. Also when y is positive we have negative or compressive strain at the top of the beam and vice versa for the bottom all of which matches our intuition.

Now again we have been assuming that we are working in pure bending and that at the moment we are linear elastic isotropic and that we can neglect shear stresses because our beam is long so we can use Hooke's law here but again be careful

$$\sigma_{xx} = E\epsilon_{xx} = -Ey\kappa \quad (\text{Chapter 5.57})$$

so we see the stress varies linearly from the neutral axis. Additionally because we are dealing with simple uniaxial bending stress in the x direction we will also have the following strains ϵ_{xx} , ϵ_{yy} , and ϵ_{zz} which can be expressed as

$$\begin{aligned} \epsilon_{xx} &= -y\kappa & (\text{Chapter 5.58}) \\ \epsilon_{yy} &= \nu y\kappa & (\text{Chapter 5.59}) \\ \epsilon_{zz} &= \nu y\kappa & (\text{Chapter 5.60}) \end{aligned}$$

Equilibrium Conditions

We are almost done but now we have to apply our equilibrium conditions in order to relate our new fancy stress condition to the bending moment so let us first start with a differential element dA and we must find that the sum of all the forces in the x direction to be zero so we obtain

$$\Sigma F_x = 0 = \int_A \sigma_{xx} dA = \int_A -yE\kappa dA \quad (\text{Chapter 5.61})$$

and since we know that both the curvature and Young's modulus cannot be zero we will find that for our forces to sum to zero we must have that

$$\int_A y dA = 0 \quad (\text{Chapter 5.62})$$

and remember from our previous discussion way back about the centroid and you will see that this is equivalent to saying that the centroid y must be equal to 0. So our z axis must pass through the centroid of the cross section and our neutral axis is in fact our z axis and thus our neutral axis must also pass through the centroid. Now all that is left is to take care of the moments and we find that if we consider the moment at our centroid or origin even though our force values sum to zero over the length of the beam there is a CW moment from our bending and that moment must be equivalent to the value of $M(x)$ so we get the following relationship

$$\Sigma M_o = 0 = -M - \int_A \sigma_{xx} y dA \quad (\text{Chapter 5.63})$$

and rearranging we get

$$M = - \int_A \sigma_{xx} y dA = E\kappa \int_A y^2 dA \quad (\text{Chapter 5.64})$$

where we see that

$$I = \int_A y^2 dA \quad (\text{Chapter 5.65})$$

where I is the moment of inertia and has units of m^4 . If we have a rectangular beam cross section as seen below we can calculate the moment of inertia.....

and we can obtain that

$$I_z = \int_A y^2 dA = \frac{bh^3}{12} \quad (\text{Chapter 5.66})$$

We can do the same for for a circular cross section as well where J is the polar moment of inertia defined as

$$J = \int_A r^2 dA = \int_A (z^2 + y^2) dA = 2I_z = \frac{\pi r^4}{4} \quad (\text{Chapter 5.67})$$

Now with our definitions of moment of inertia clear we can now obtain our expression for the bending moment. Note that there are several cross-sections that are very good to resist bending based on the moment of inertia those being I-beams and honeycomb or cellular sandwich beams.

$$M = \kappa EI \quad (\text{Chapter 5.68})$$

So we can now re-write our stress expression as a function of the bending moment as follows

$$\sigma_{xx} = -E\kappa y = -\frac{My}{I} \quad (\text{Chapter 5.69})$$

Again we see that when the bending moment is positive and y is positive we have compression on the top and vice versa for the bottom.

5.11 Beam Deflection

Thus far we have been focused almost exclusively on the forces, bending, and the stresses that develop in a beam when a load is applied. However, often it is extremely important to know how far a beam will deflect from the neutral axis. This is critical because certain materials or applications will have limitations on the amount of deflection which can occur. Additionally, we can also quite easily measure the amount of deflection and then back out the load or material properties as well.

Let's take a look at a beam bending scenario below where we have some given amount of deflection v and there will also be some Δ that describes the angle between the x axis and the tangent to the deflection curve. Now the question becomes what is the deflection at m_2 in this scenario well we know that

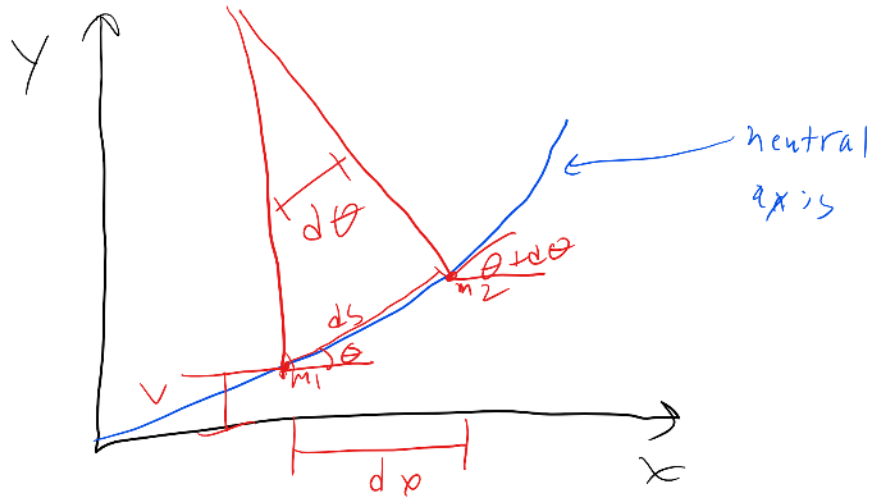


Figure *Chapter5.16*: Cantilever Beam Deflection Schematic

$$\rho d\theta = ds \quad (\text{Chapter 5.70})$$

$$\kappa = \frac{1}{\rho} = \frac{d\theta}{ds} \quad (\text{Chapter 5.71})$$

We can also use the small angle approximation here such that for example

$$\cos \theta = \frac{dx}{ds} = 1 \quad (\text{Chapter 5.72})$$

therefore $ds \approx dx$ so we can use this to obtain another expression for curvature such that

$$\kappa = \frac{d\theta}{ds} = \frac{d\theta}{dx} = \frac{d^2v}{dx^2} \quad (\text{Chapter 5.73})$$

and we can also write the following very useful relationships

$$\frac{d\theta}{dx} = \frac{d^2v}{dx^2} = \frac{M}{EI} \quad (\text{Chapter 5.74})$$

This is a very useful relationship because we can integrate our $M(x)$ twice to get the deflection and we can obtain the constants of integration by establishing boundary conditions. Additionally, this term EI is also referred to as the **flexural rigidity** which is very important for deflection

But we can develop an even more general equation for beam bending using the **Euler-Bernouli equation** which simply rearranges the equation we had above in terms of a general distributed load q as seen here

$$\frac{d^2}{dx^2} \left(\frac{EI dv^2}{dx^2} \right) = q \quad (\text{Chapter 5.75})$$

and if we assume that the flexural rigidity is a constant we can simplify this equation as follows

$$EI \frac{d^4 v}{dx^4} = q(x) \quad (\text{Chapter 5.76})$$

We can relate this equation now to bending moments and shear moments respectively as follows

$$M = EI \frac{d^2 v}{dx^2} \quad (\text{Chapter 5.77})$$

$$V = \frac{d}{dx} \left(EI \frac{d^2 v}{dx^2} \right) \quad (\text{Chapter 5.78})$$

So we have a 4th order ODE that we will have to solve in order to find the equation for beam deflection so we need 4 total boundary conditions for these problems....time to use Mathematica!!

Here it is critical to observe that the bending moment is related the second derivative of the deflection, and the shear moment is related to the third derivative of the displacement, this will be critical as we determine our boundary conditions, speaking of which....

5.11.1 Boundary Conditions for Beam Bending

Here we can see some common boundary conditions for common beam bending scenarios

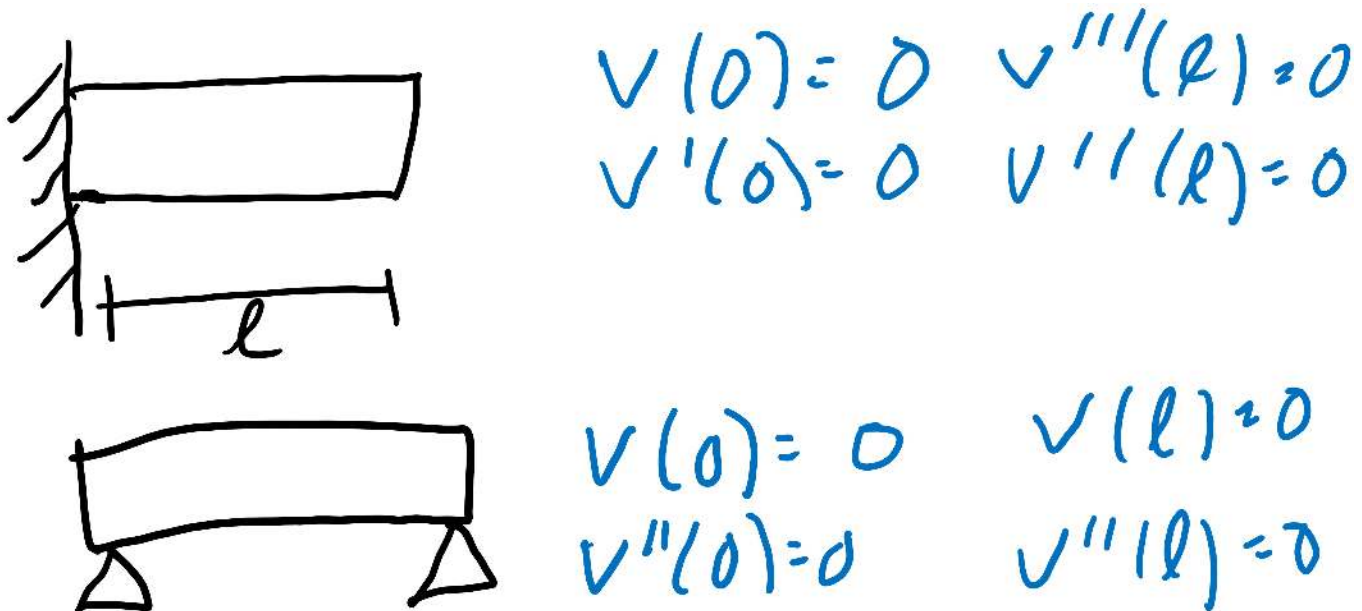


Figure Chapter5.17: Beam Bending Boundary Conditions

Here we can see some common boundary conditions. For a cantilever beam bending scenario at a fixed support there can be no deflection and thus there will be no slope at the fixed boundary. There will however be a shear moment and bending moment here however.

At the free end of the beam with no force added there will be no bending or shear moment.

When we have simple supported beam we now see at the supports we will have no deflection however if there is a load applied there will be a change in slope at these locations. However, as there is no clamp here there will be no restoring moment so the moment will be zero at these supports.

5.11.2 Deflection for Simple End Loaded Cantilever Beam Fixed Support

So let's look at the problem below here we can identify several boundary conditions.

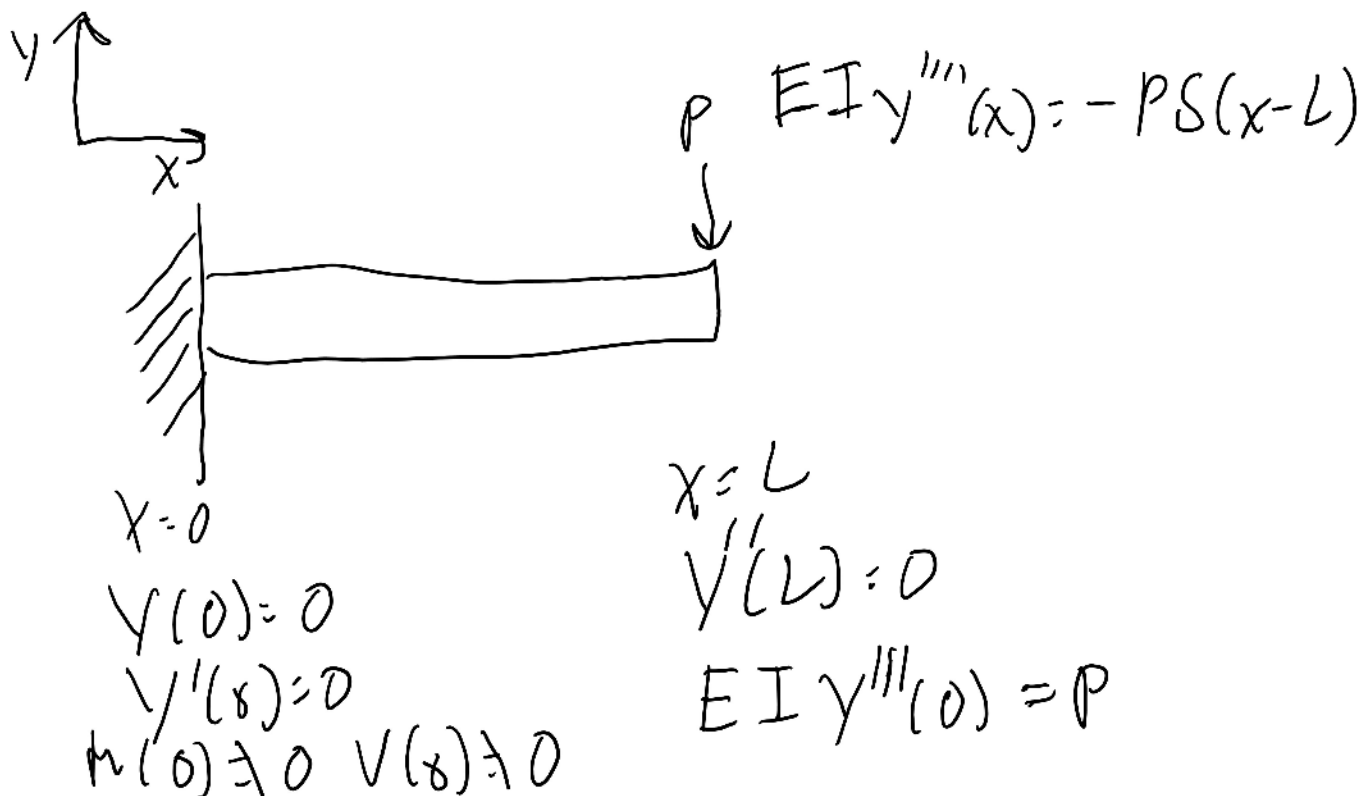


Figure Chapter5.18: Cantilever Beam Bending Scenario

So for a cantilever beam we know that at the wall the beam will not deflect and that the slope of deflection should also be zero so the boundary conditions here will be

$$v(0) = 0 \quad (\text{Chapter 5.79})$$

$$v'(0) = 0 \quad (\text{Chapter 5.80})$$

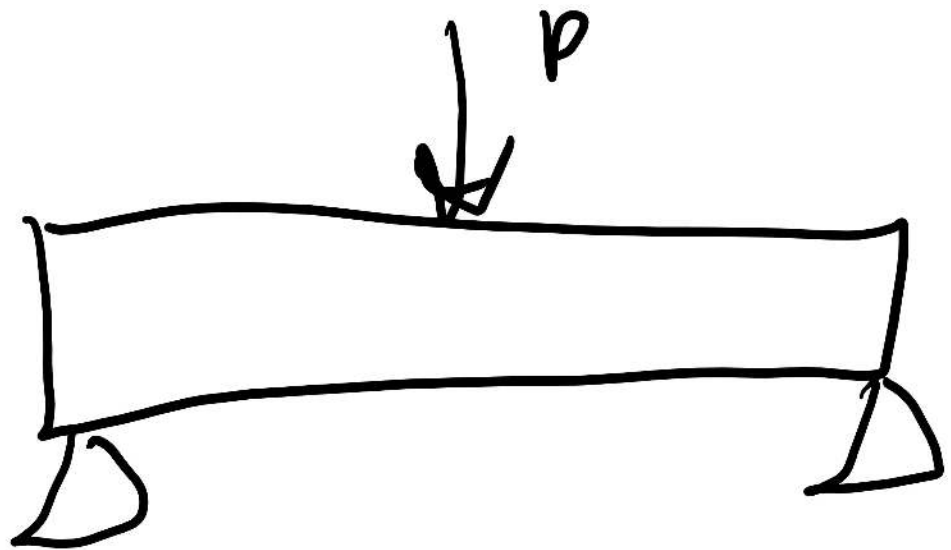
We also know that at the we have a free end so we know that the bending moment must be zero here and that the shearing moment must also be zero so

$$v''(l) = 0 \quad (\text{Chapter 5.81})$$

$$EI v'''(0) = P \quad (\text{Chapter 5.82})$$

So finally we will also have to input our expression for the load applied as a function of x and we can do that in mathematica.

3 Point Bending Test



$$v(0) = 0$$

$$v''(0) = 0$$

$$v(l) = 0$$

$$v''(l) = 0$$

Figure Chapter5.19: Three Point Bending Scenario

What about a very common bending test a 3 point bending which can be seen below

We can see our boundary condition and our fundamental equation here.

Distributed Load

We can even do distributed loads as seen below

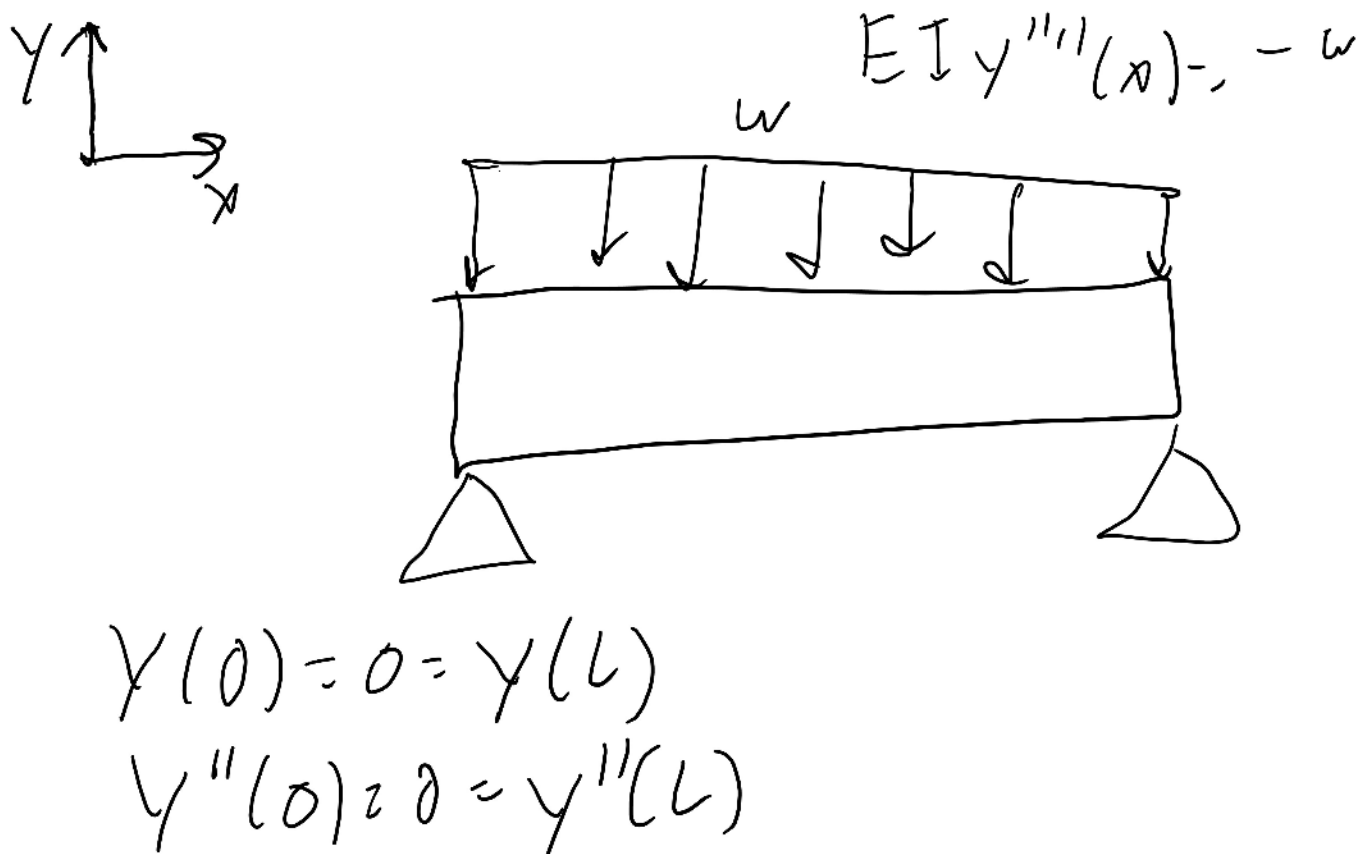


Figure Chapter5.20: Distributed Load on Beam

We can see our boundary condition and our fundamental equation here and plugging into Mathematica we can find our solution below here

Now all of this beam bending leads us to a very important phenomenon and material failure mode, that being **buckling**.

5.12 Buckling

When a materials is placed under compression the material will not typically fail via crack propagation as compressive stress does not assist in crack propagation, typically. Instead many materials under pure compressive stress will fail via buckling.

We will examine a particularly ubiquitous but important problem that being **column buckling**. A **column** is defined as a long slender member that is being loaded in compression and **buckling** is an instability phenomenon. Now when we mention **stability** we are referring to whether the system will return to it's initial state when perturbed from this initial state. **Stable** systems will return to the initial state whereas **unstable** systems will not. You have most likely seen this illustrated in a physics course where a ball rolling down a hill is unstable but one at the bottom of the well is stable. There are also **neutral** and **metastable** systems as well but more on that in other courses.

Now you may imagine that if I have a column a longer column will buckle at lower applied loads and if I increase the cross sectional area it will increase applied load required for buckling. Also associated with this phenomenon of buckling will cause a change in shape, i.e. bending will occur.

Let's develop a framework to describe buckling.

First, lets start off with an **ideal column with pinned ends**.

Ideal Column with Pinned Ends

No for an ideal column with pinned ends we have several assumptions that must be met which include

- Straight Beam
- Linear elastic material

- Load aligned with Column axis

As the column is the process of buckling will proceed in several states first elastic shortening. The column is stable at this stage and will compress linearly and elastically. As the applied load increases there will be some critical load where the become will become unstable and it will start to curve/bend and become unstable. What is this critically applied load? how does it relate to flexural modulus, beam length, and beam geometry? Well let's figure this out!!!

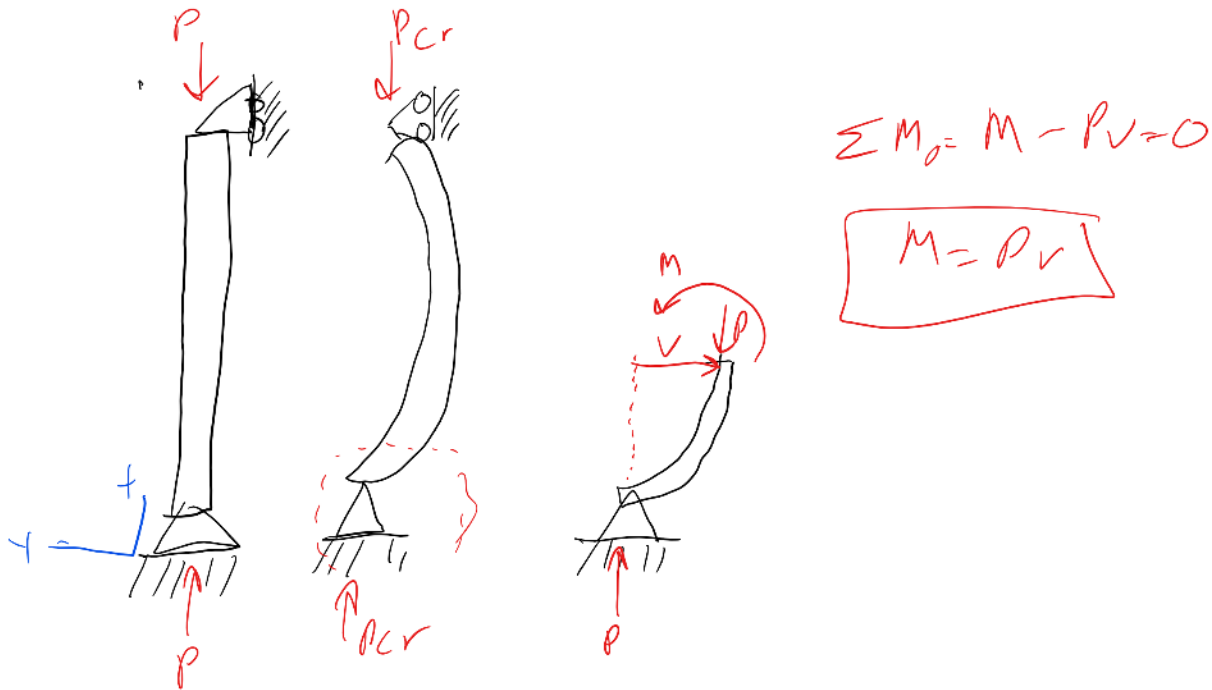


Figure Chapter5.21: Buckling Instability

Let's first start as usual by defining our coordinate system and drawing a free body diagram at the top of our beam and there will be some deflection v here

From the FBD we see that the material will experience a bending moment $M = Pv$ and we can relate this to our old friend

$$\frac{d^2v}{dx^2} = \frac{M}{EI} = \frac{Pv}{EI} \quad (\text{Chapter 5.83})$$

with this differential equation we also have the following boundary conditions that

$$v(0) = 0 \quad (\text{Chapter 5.84})$$

$$v(l) = 0 \quad (\text{Chapter 5.85})$$

We will get an expression in the form

$$v = c_1 \sin \sqrt{\frac{P}{EI}}x + c_2 \cos \sqrt{\frac{P}{EI}}x \quad (\text{Chapter 5.86})$$

And thus we find that $c_2 = 0$ but we also have a requirement that the sine term must go to zero so we have the following relationship that

$$\sqrt{\frac{P}{EI}}l = n\pi \quad (\text{Chapter 5.87})$$

So the lowest value of loading that will lead to a deformed shape or buckling and thus the critical load for buckling is

$$P_{cr} = \frac{\pi^2 EI}{l^2} \quad (\text{Chapter 5.88})$$

Now in terms of what n refers to physically it is the number of half-wavelengths along a column of length l . We see several interesting but expected phenomenon in this equation the first is that the critical load for buckling is linearly dependent on the flexural modulus but also scales as l^{-2} so the longer the beam the lower the critical load which makes sense intuitively. So if we ideally we would also want a constant I about all cross sectional axes and to have the same buckling load about all axes.

5.13 Torsion

Torsion is a critical loading state and is extremely ubiquitous when it comes to the automotive industry. A twisting moment or **torque** are forces that act through a distance or a **lever arm**

$$T = r \times F \quad (\text{Chapter 5.89})$$

where r is the vector representation of the lever arm and F is the force vector. Now when a material is under torsion the material experiences torsional stresses and displacements.

We can determine the torsional stresses and displacement using a very similar methodology as we did for the normal stresses and deflection in bending so we will follow our similar steps

1. Geometric Statement
2. Constitutive Equation
3. Equilibrium Conditions

Geometric Statement

Looking at our figure below we can defined some differential element dz which rotates some amount $d\theta$ and so we can then relate the displacement δ as follows

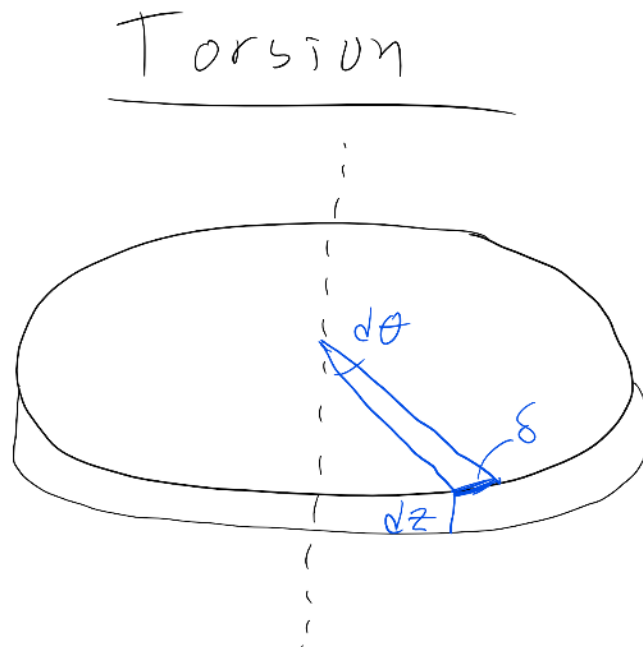


Figure Chapter5.22: Torsion Geometric Statement

$$\delta = r d\theta \quad (\text{Chapter 5.90})$$

Constitutive Equations

We know that this is very similar to our expression for shear strain so we can write that

$$\gamma_{z\theta} = \frac{\delta}{dz} = r \frac{d\theta}{dz} \quad (\text{Chapter 5.91})$$

Additionally, assuming that we are in the linear elastic regime the shear stress is then given by

$$\sigma_{z\theta} = G\gamma_{z\theta} = Gr \frac{d\theta}{dz} \quad (\text{Chapter 5.92})$$

Equilibrium Equations

Now we can apply our equilibrium conditions and here we will be concerned with summing the moments on a differential area dA and we can find that

$$T = \int_A \sigma_{z\theta} r dA = G \frac{d\theta}{dz} \int_A r^2 dA \quad (\text{Chapter 5.93})$$

Also we have already found the expression for the moment of inertia for a hollow circular cross section as

$$I = \int_{r_i}^{r_o} r^2 2\pi r dr = \frac{\pi(r_o^4 - r_i^4)}{2} \quad (\text{Chapter 5.94})$$

We can also deal with part of the the expression below

$$\frac{d\theta}{dz} = \frac{T}{GJ} \quad (\text{Chapter 5.95})$$

$$\theta = \int_z \frac{T}{JG} dz \quad (\text{Chapter 5.96})$$

where T , J , and G are constant in terms of z so we find that

$$\theta = \frac{Tl}{GJ} \quad (\text{Chapter 5.97})$$

where the l is the length in the z direction.

Now we can finally plug back in to find that

$$\sigma_{z\theta} = G\gamma_{z\theta} = Gr \frac{d\theta}{dz} = \frac{Tr}{J} \quad (\text{Chapter 5.98})$$

This is a very interesting expression because we see that these torsional stresses are independent of the choice of material because G has been removed from our expression.

This has a very nice analogy to our thin-walled pressure vessel expressions, there too we did not have any dependence on material selection but instead just on geometry.

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Chapter 6: Mechanical Behavior of Materials Part II

6.1 Linear Viscoelasticity (LVE):

I have recorded a series of lectures videos to supplement this text which can be found in the playlist below:

<https://www.youtube.com/playlist?list=PLb5i6HX2SGPPNyA>

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, today we will 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**. The elastic solid will again behave Hookean with the relationship

$$\sigma = E\epsilon \quad (\text{Chapter 6.1})$$

and the viscous fluid will be governed by this new equation

$$\sigma = \eta \dot{\epsilon} \quad (\text{Chapter 6.2})$$

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

$$\tau = \eta \dot{\gamma} \quad (\text{Chapter 6.3})$$

where η 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 σ and ϵ for some time or temperature.

We can make a couple of linear viscoelastic (LVE) models which describe some LVE behavior phenomenologically 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.

Maxwell & Voigt Models

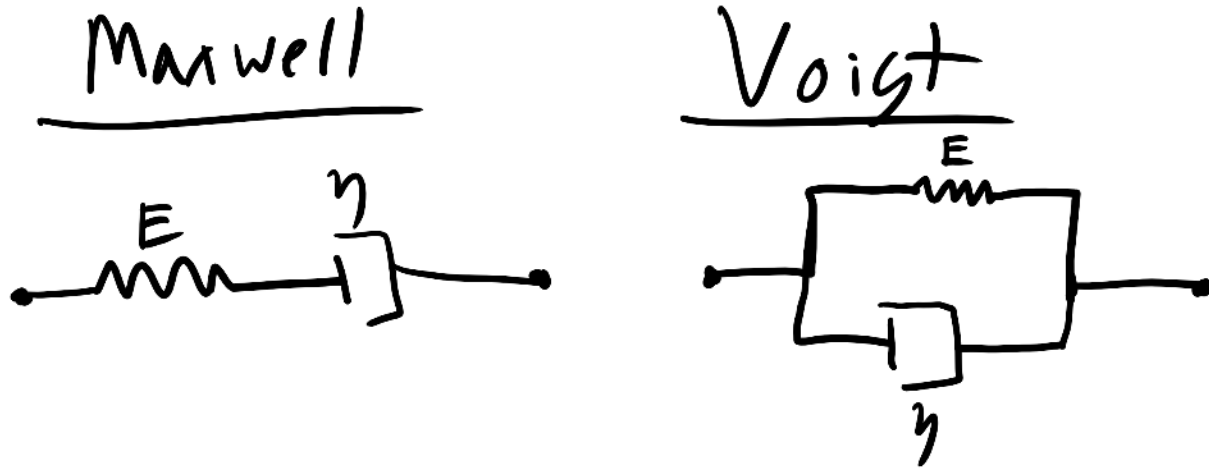


Figure Chapter6.1: Maxwell and Kelvin-Voigt Models

The spring is described by the following equation:

$$\sigma_s = E_s \epsilon_s \quad (\text{Chapter 6.4})$$

where σ_s is the stress in the spring, E_s is the stiffness of the spring, and ϵ_s is the strain in the spring

The dashpot is described by:

$$\sigma_d = \eta_d \dot{\epsilon}_d \quad (\text{Chapter 6.5})$$

where σ_d is the stress in the dashpot, η_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 (this should be reminiscent of the composites pulled transverse to the fiber direction when we get to this) the **stresses should be the same for the spring and the dashpot** however the **strains in the dashpot and the spring will be different** which gives us the following equation:

$$\sigma_M = \sigma_s = \sigma_d \quad (\text{Chapter 6.6})$$

$$\epsilon_M = \epsilon_s + \epsilon_d \quad (\text{Chapter 6.7})$$

$$\dot{\epsilon}_M = \dot{\epsilon}_s + \dot{\epsilon}_d \quad (\text{Chapter 6.8})$$

$$\dot{\epsilon}_M = \frac{\dot{\sigma}_M}{E} + \frac{\sigma_M}{\eta} \quad (\text{Chapter 6.9})$$

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:

$$0 = \frac{1}{E} \frac{d\sigma}{dt} + \frac{\sigma}{\eta} \quad (\text{Chapter 6.10})$$

$$\int_{\sigma_0}^{\sigma} \frac{d\sigma}{\sigma} = \int_0^t \frac{-E}{\eta} dt \quad (\text{Chapter 6.11})$$

$$\sigma(t) = \sigma_0 \exp\left(\frac{-Et}{\eta}\right) \quad (\text{Chapter 6.12})$$

$$\sigma(t) = \sigma_0 \exp\left(\frac{-t}{\tau}\right) \quad (\text{Chapter 6.13})$$

where $\tau = \frac{E}{\eta}$ is the relaxation time. Similarly for **creep**:

$$\frac{d\epsilon}{dt} = 0 + \frac{\sigma_0}{\eta} \quad (\text{Chapter 6.14})$$

$$\int_{\epsilon_0}^{\epsilon} d\epsilon = \int_0^t \frac{\sigma_0}{\eta} dt \quad (\text{Chapter 6.15})$$

$$\epsilon(t) = \epsilon_0 + \frac{\sigma_0 t}{\eta} \quad (\text{Chapter 6.16})$$

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** but now the **stresses are different** so we get:

$$\epsilon_{KV} = \epsilon_s = \epsilon_d \quad (\text{Chapter 6.17})$$

$$\sigma_{KV} = \sigma_s + \sigma_d \quad (\text{Chapter 6.18})$$

$$\sigma_{KV} = E_s \epsilon_s + \eta_d \dot{\epsilon}_d \quad (\text{Chapter 6.19})$$

$$\dot{\epsilon}_{KV} = \frac{\sigma_{KV}}{\eta_d} - \frac{E_s}{\eta_d} \epsilon_{KV} \quad (\text{Chapter 6.20})$$

Now for **stress relaxation** we get the final equation for stress vs time as:

$$\sigma(t) = E\epsilon_0 \quad (\text{Chapter 6.21})$$

and for **creep** we get:

$$\epsilon(t) = \frac{\sigma_0}{E} \left(1 - \exp\left[-\frac{t}{\tau}\right] \right) \quad (\text{Chapter 6.22})$$

You can now build even more complex combinations to model viscoelastic properties like the Standard Linear Viscoelastic Solid Model. Perhaps a more useful experimental measurement for viscoelastic behavior is accomplished by **Dynamic Mechanical Testing**.

6.2 Dynamic Mechanical Testing:

The more utilized characterization technique is typically some type of **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

$$\sigma_{applied} = \sigma_o \sin \omega t \quad (\text{Chapter 6.23})$$

This is the applied stress but remember we are dealing with a viscoelastic material so there will be a phase lag, δ , in the strain behavior which will also be sinusoidal

$$\epsilon = \epsilon_o \sin \omega t \quad (\text{Chapter 6.24})$$

So what we will end up with is that the material will actually experience a stress that contains the phase lag as shown below

$$\sigma = \sigma_o \sin(\omega t + \delta) \quad (\text{Chapter 6.25})$$

$$\sigma = \sigma_o \sin \omega t \cos \delta + \sigma_o \cos \omega t \sin \delta \quad (\text{Chapter 6.26})$$

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

$$E' = \frac{\sigma_o \cos \delta}{\epsilon_o} \quad (\text{Chapter 6.27})$$

and the **loss** modulus is the out of phase component is

$$E'' = \frac{\sigma_o \sin \delta}{\epsilon_o} \quad (\text{Chapter 6.28})$$

We can now re-write our expression for the stress in the material as

$$\sigma = E' \sin \omega t + E'' \cos \omega t \quad (\text{Chapter 6.29})$$

then by definition we have that

$$\tan \delta = \frac{E''}{E'} \quad (\text{Chapter 6.30})$$

This is sometimes called the **loss tangent** and essentially represents the amount of energy lost over the energy stored[9]. You might also see these expressions written using complex variables like so

$$\epsilon = \epsilon_o \exp i\omega t \quad (\text{Chapter 6.31})$$

$$\sigma = \sigma_o \exp i\omega t + \delta \quad (\text{Chapter 6.32})$$

$$E = \frac{\sigma_o}{\epsilon_o} \exp i\delta = \frac{\sigma_o}{\epsilon_o} (\cos \delta + i \sin \delta) = E' + E'' \quad (\text{Chapter 6.33})$$

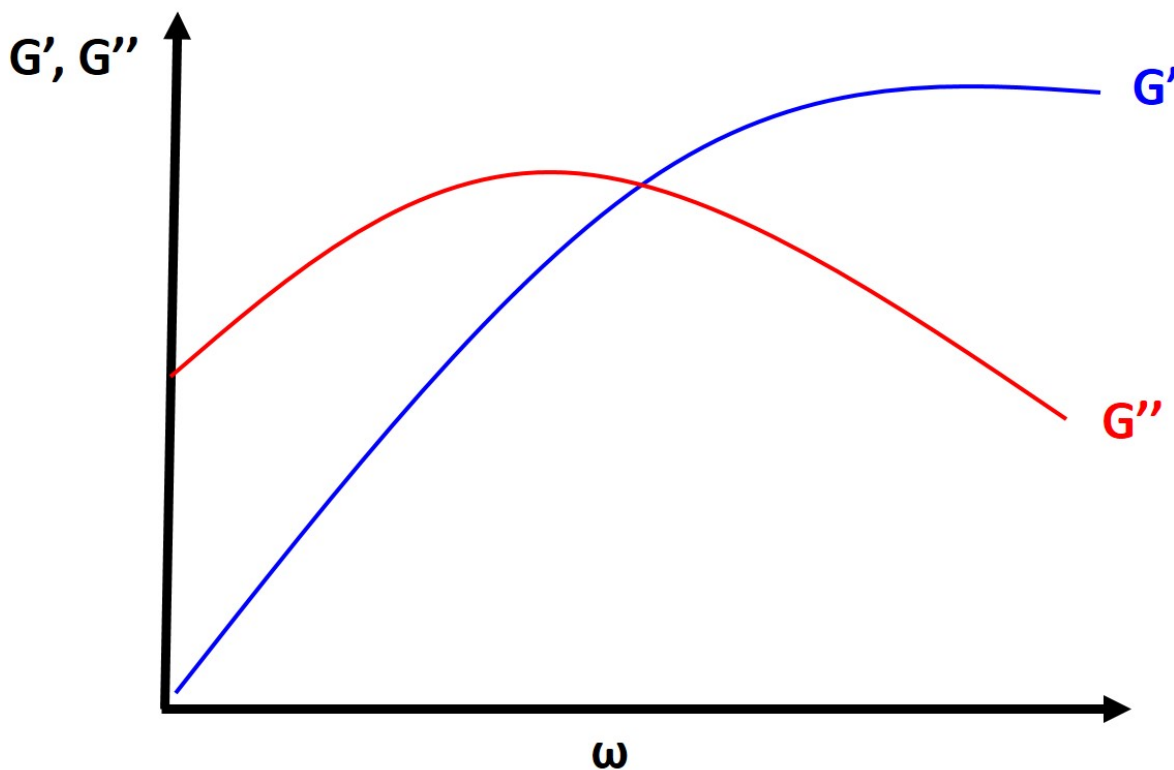


Figure Chapter6.2: Storage and loss modulus as a function of frequency.

Analysis of DMA 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 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 viscous fluid.

More importantly from this analysis we can determine experimentally the **characteristic relaxation time** from the point where **Missing open brace for superscript** and **Missing open brace for superscript** intersect. More often we will find that typical DMA experiments where **Missing open brace for superscript**, **Missing open brace for superscript**, and $\tan \delta$ are plotted as a function of temperature. Here you will typically see larger peaks and changes in these parameters. 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.

6.3 Composite Mechanics:

So far we have been talking about the mechanics of primarily metals 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

$$E_{composite} = E_m f_m + E_p f_p \quad (\text{Chapter 6.34})$$

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.

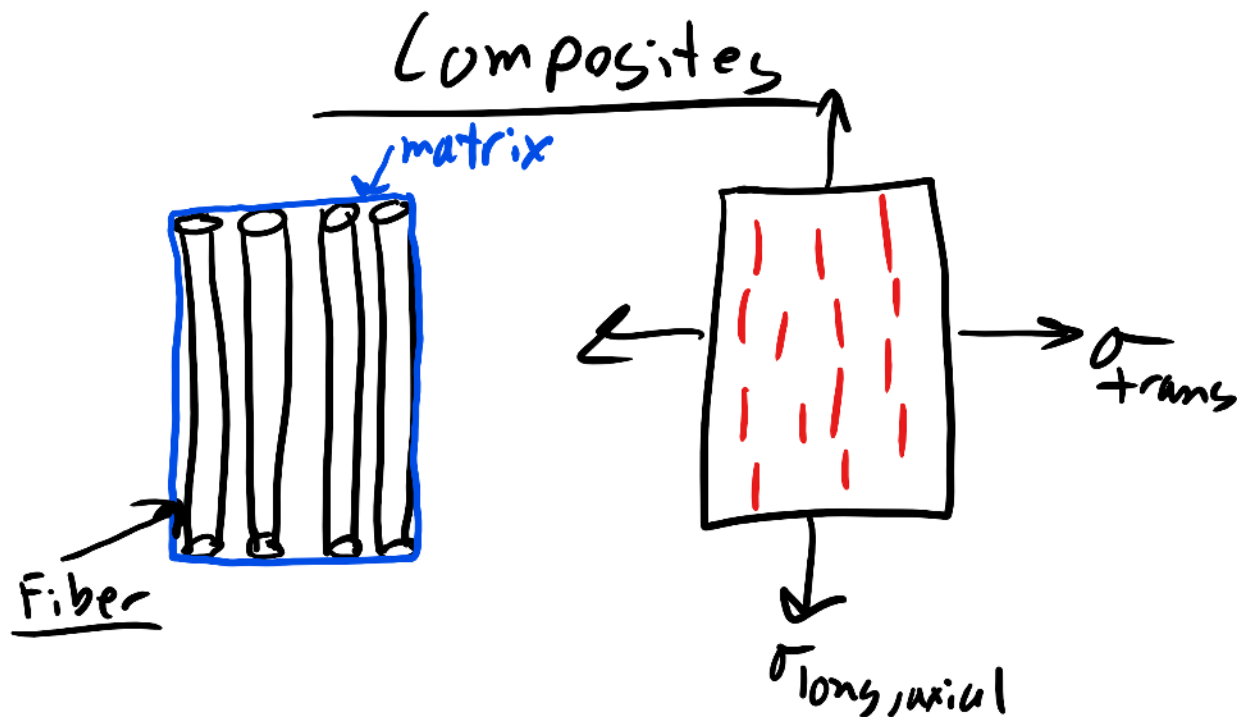


Figure Chapter6.3: Composites pulled in the transverse or longitudinal/axial direction.

Let's now look at a **fiber reinforced composite** that is pulled or stressed in the **transverse direction** with respect to 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:

$$\sigma_m = \sigma_f = \sigma \quad (\text{Chapter 6.35})$$

$$\epsilon_c = \epsilon_m f_m + \epsilon_f f_f \quad (\text{Chapter 6.36})$$

$$\epsilon_c = \sigma \left(\frac{f_m}{E_m} + \frac{f_f}{E_f} \right) \quad (\text{Chapter 6.37})$$

$$\frac{1}{E_c} = \frac{f_f}{E_f} + \frac{f_m}{E_m} \quad (\text{Chapter 6.38})$$

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

$$\sigma_c = \sigma_f f_f + \sigma_m f_m \quad (\text{Chapter 6.39})$$

$$\epsilon_c = \epsilon_m = \epsilon_f \quad (\text{Chapter 6.40})$$

$$\sigma_c = E_f \epsilon_f + E_m \epsilon_m \quad (\text{Chapter 6.41})$$

$$E_c = E_f f_f + E_m f_m \quad (\text{Chapter 6.42})$$

We can see the difference in the Young's modulus in both of these directions as function of volume fraction in the plot below

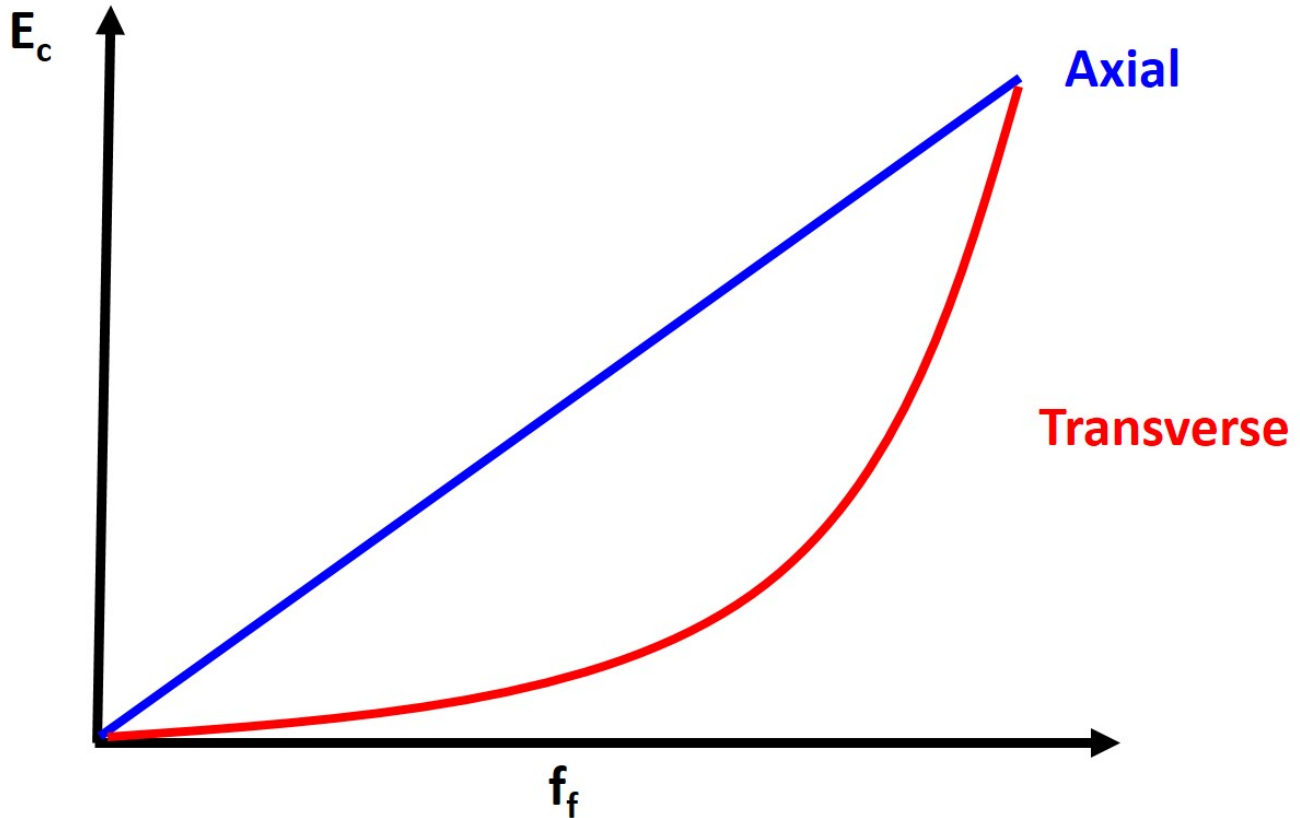


Figure Chapter6.4: Composite modulus as a function of fiber fraction

Composites are also useful tools to help blunt crack propagation.

6.4 Plastic Regime

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**.

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 (σ_1) reaches the value where the material yields in uniaxial tension or compression so the material will yield when:

$$\sigma_1 \geq \sigma_y \quad (\text{Chapter 6.43})$$

Rankine doesn't accurately describe material yielding, it is **missing shear stress**.

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:

$$\sigma_1 - \sigma_3 \geq \sigma_y \quad (\text{Chapter 6.44})$$

This is better, but in 1913 for WWI/WWII subs because they found that the Tresca criterion was a poor predictor for yielding.

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:

$$\sigma_{eff} = \sqrt{\frac{1}{2}[(\sigma_{11} - \sigma_{22})^2 + (\sigma_{22} - \sigma_{33})^2 + (\sigma_{33} - \sigma_{11})^2 + 6(\sigma_{23}^2 + \sigma_{31}^2 + \sigma_{12}^2)]} \geq \sigma_y \quad (\text{Chapter 6.45})$$

or in terms of the principal stresses:

$$\sigma_{eff} = \sqrt{\frac{1}{2}[(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2]} \geq \sigma_y \quad (\text{Chapter 6.46})$$

You can see by drawing the yield loci of these different criterion that Rankine is the most conservative yield criterion.

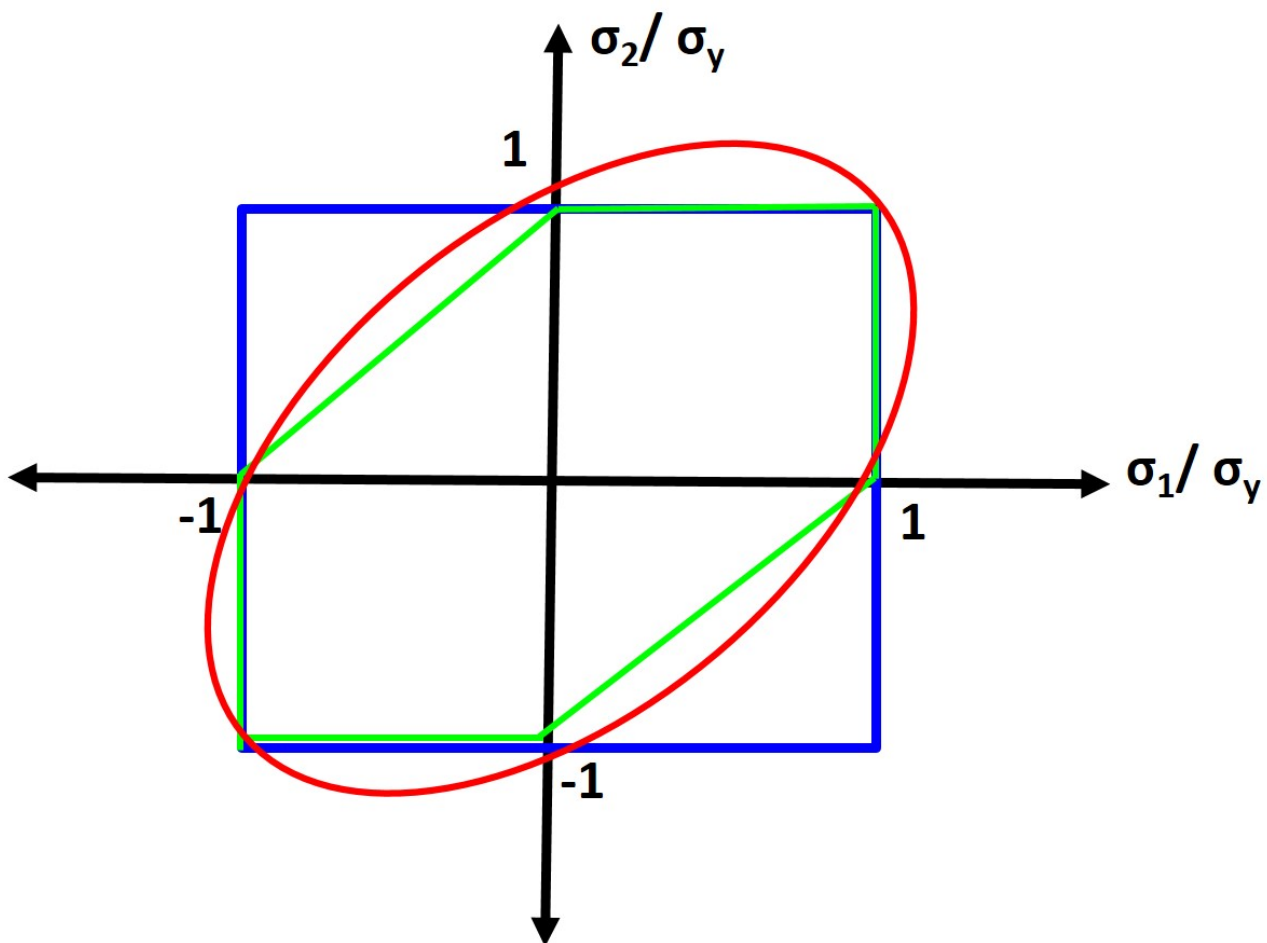


Figure Chapter6.5: Yield Criterion. Rankine (blue), Tresca (green), Von Mises (red).

6.5 Yielding Mechanisms:

In a **perfect copper crystal** I can prove that the **yield stress should be approximately 20GPa** however the actual yield stress of copper is approximately **40MPa**. **What can explain the 3 order of magnitude difference?** A nice approximation is that the theoretical yield stress is typically $\frac{\sigma}{30}$ and the theoretical fracture strength is $\frac{E}{10}$.

Well remembering back to structure real materials have **defects** that allow atomic motion and in **particular dislocation motion and slip a shear stress much lower than the theoretical prediction!** We have talked quite a bit about the structure of dislocations but as of yet not too much about the **motion of dislocations**. **What direction of motion will contribute most to yielding and dislocation motion?**

The direction that require the least amount of energy to move! And remembering back to structure this corresponds to the shortest distance in your cell, i.e. the **close paced planes and directions**[9]. So for **FCC the primary slip systems are the $\langle 110 \rangle$ directions and the 111 planes**. For **BCC it is the $\langle 111 \rangle$ directions and the 110 planes** even though these aren't close packed[9]. Remember as well that dislocations are also characterized by **dislocation density** which is again

$$\rho = \frac{N}{A} \quad (\text{Chapter 6.47})$$

where N is the number of dislocations in a given area A. A material that is **highly cold worked** with a high dislocation density would be 10^{14} dislocations per m^2 . A **highly annealed material** would exhibit a dislocation density closer to 10^7 dislocations per m^2 . You can also get a quick estimate of the distance between dislocations by the following relationship

$$\rho = \frac{1}{l^2} \quad (\text{Chapter 6.48})$$

where l is the distance between dislocations!

6.6 Strengthening Mechanisms:

Now we have talked quite a bit about material constants and how they are often not really a constant. They **vary depending on the material processing history!** Perhaps no other material constant varies more depending on the processing history than **yield stress**. But as material scientists this gives us a fantastic knob to tune our materials for different applications. And the basic relationship to remember is that the **yield stress increases when it becomes harder for dislocations to move or propagate**. So when there are **obstacles** to dislocation motion the **yield stress increases** and we can do this via 4 primary mechanisms:

1. **Work Hardening (more dislocations)**
2. **Solute Strengthening (more solute atoms)**
3. **Grain Size Strengthening (decrease grain size)**
4. **Precipitate/Particle Strengthening (add precipitates or particles)**

6.7 Work Hardening: Increase ρ via Plastic Deformation

$$\Delta\sigma_y = \alpha G b \sqrt{\rho} \quad (\text{Chapter 6.49})$$

where G is the shear modulus, b is Burgers vector, and α is the materials constant (close to 1). During the work hardening process you plastically deform the material and initiate or create dislocations in the material. This is often done in rolling sheet metal via cold-rolling. You create more dislocations which serve as obstacles for dislocation motion which then increases the yield strength as seen below

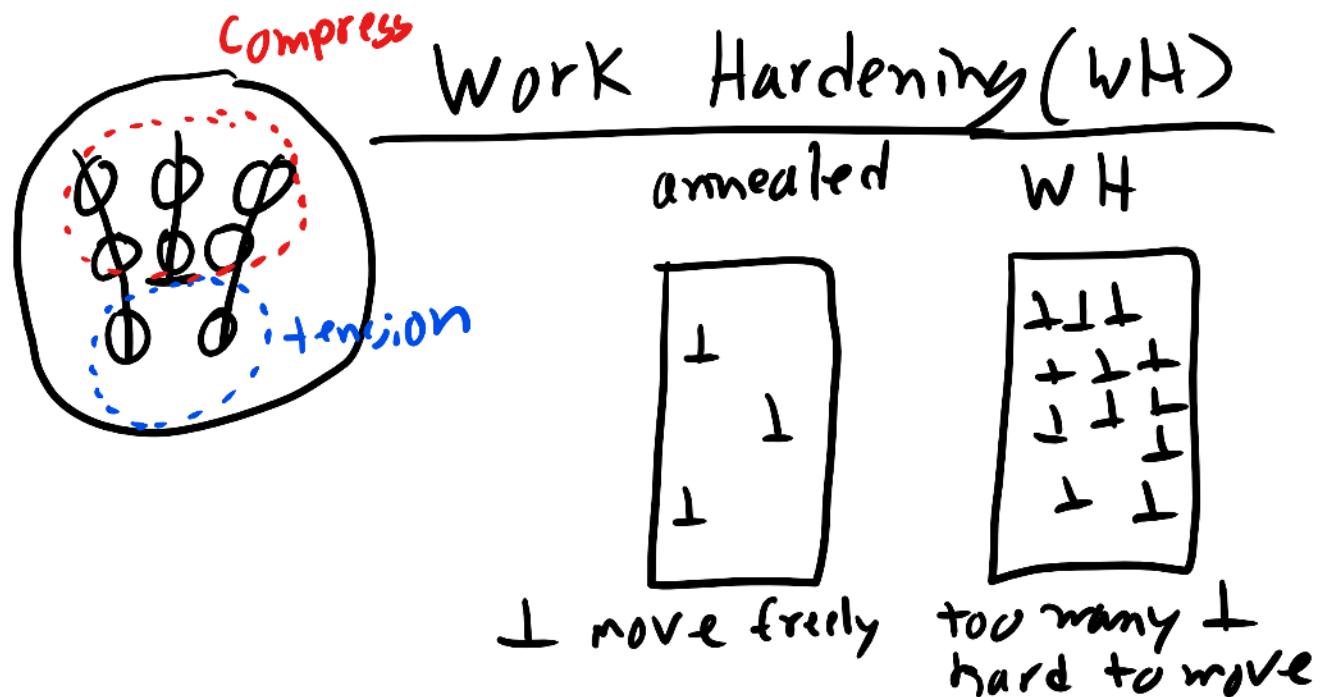


Figure Chapter6.6: Work Hardening

6.8 Solute Strengthening

$$\Delta\sigma_y = Gb\sqrt{c_{sol}\epsilon_{sol}^{\frac{3}{2}}}$$

(Chapter 6.50)

where c_{sol} is the concentration of the solute and ϵ_{sol} is the lattice strain due to any size mismatch. We talked about this phenomenon a bit during structure. When you replace the a solvent atom with a larger solute atom you create a region with a localizes stress field that will interact with dislocation and again impede dislocation motion, causing yield stress to increase.

Solute Strengthening



Figure Chapter6.7: Solute Strengthening

6.9 Grain Size Strengthening

$$\Delta\sigma_y = \frac{\kappa}{d_g} \quad (\text{Chapter 6.51})$$

where κ is a materials constant and d_g is the diameter of the grain. As you decrease the grain size there is less area for dislocation pile-up which is one method of reducing stress in your material. Smaller grain sizes can only accommodate so many dislocations before the dislocations can no longer pile up and they must be removed from the grain. It should be noted here the the yield stress does not blow up to infinity as the grain size shrinks to zero. Instead at about **less than 10nm** we see the yield stress begins to fall once again because now the grain is so small that only a single dislocation can fit inside a grain so you do not get enough dislocation pile-up.

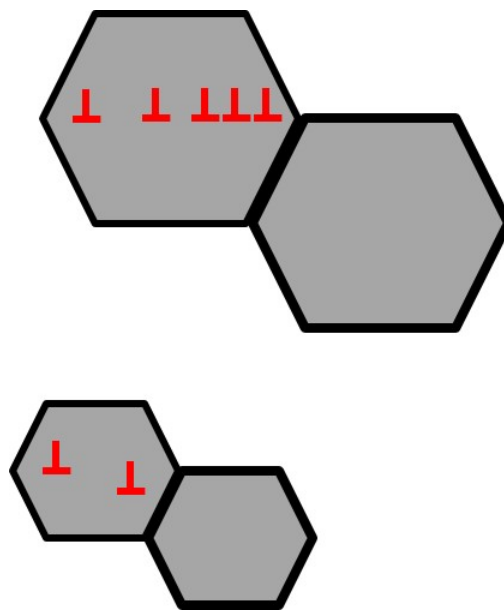


Figure Chapter6.8: Grain Size Strengthening

6.10 Precipitate/Particle Strengthening

In this case the obstacle to dislocation motion is not a point defect, a dislocation, or a grain boundary, but instead we have a **new phase with a defined particle radius, spacing, and mechanical/structural properties**. So when the dislocation encounters a defect the dislocation can do one of two things: **1.) Cut the precipitate/particle or 2.) Bow around the precipitates/particle**. To cut through the particles we find the increase in yield stress to be:

$$\Delta\sigma_y = \frac{\gamma_{p-m}\pi r_p}{bl} = \kappa^3 \sqrt{r_p f_p} \quad (\text{Chapter 6.52})$$

where γ_{p-m} is the additional surface energy added when the particle is cut and thus is the surface energy of the particle/precipitate matrix, r_p is the radius of the particle, b is the burgers vector, l is the average particle spacing, κ is a materials constant, and f_p is the concentration or volume fraction of the particles.

To **bow around the precipitates/particle** the increase in yield stress is

$$\Delta\sigma_y = \frac{Gb}{l - 2r_p} \quad (\text{Chapter 6.53})$$

where G is the shear modulus, b is the burgers vector, l is the average distance between particles and r_p is the radius of the particle. You can see energetically that at **very small particle diameters it is more energetically favorable to cut the particles** because the **energy penalty of creating an increased surface is less for smaller particles**. As the particles become **larger bowing is more energetically favorable**, for the same volume fraction of particles. **As the volume fraction of particles or precipitates increases the critical radius for cutting vs. bowing decreases as you are now cutting even more particles which creates more surface area and an even larger energy penalty.**

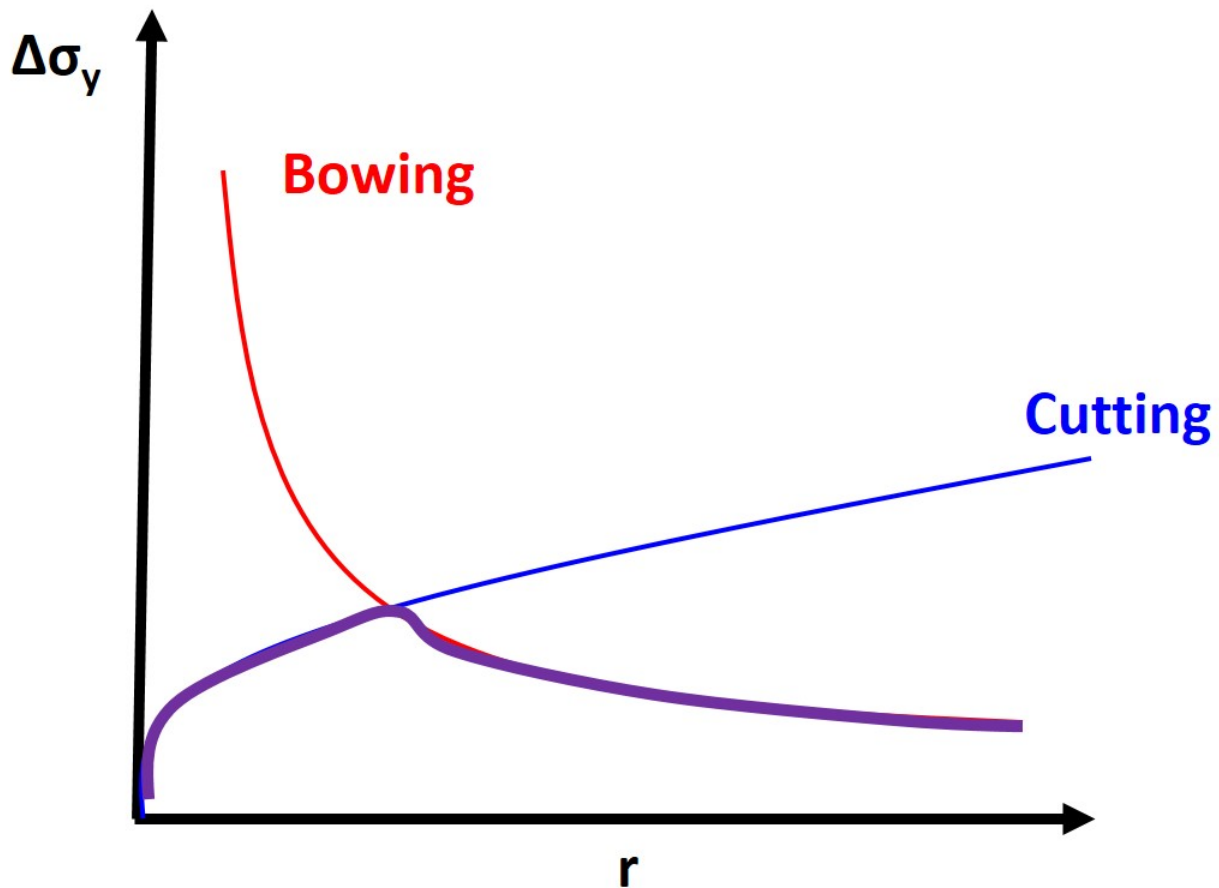


Figure Chapter6.9: Bowling vs. Cutting

6.11 Polymer Yielding: Shear Banding and Crazing

Shear Banding:

Are zones of material alignment that are **1000s of nm wide** and **nucleate at stresses** that are approximately 1000s of nms wide 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° relative to the applied stress**(at locations of maximum shear stress).

Here is a good opportunity to talk about some asymmetry in yield criterion. Typically we find that the **yield stress for uniaxial compression is larger than the yield stress for uniaxial tension**. In polymers this is particularly true as tensile stress will tend to open up more free volume which makes it easier for chains to align.

Craze formation:

Also 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**[9]. You can **modify the von Mises criterion when considering shear banding** and Tresca when considering crazing.

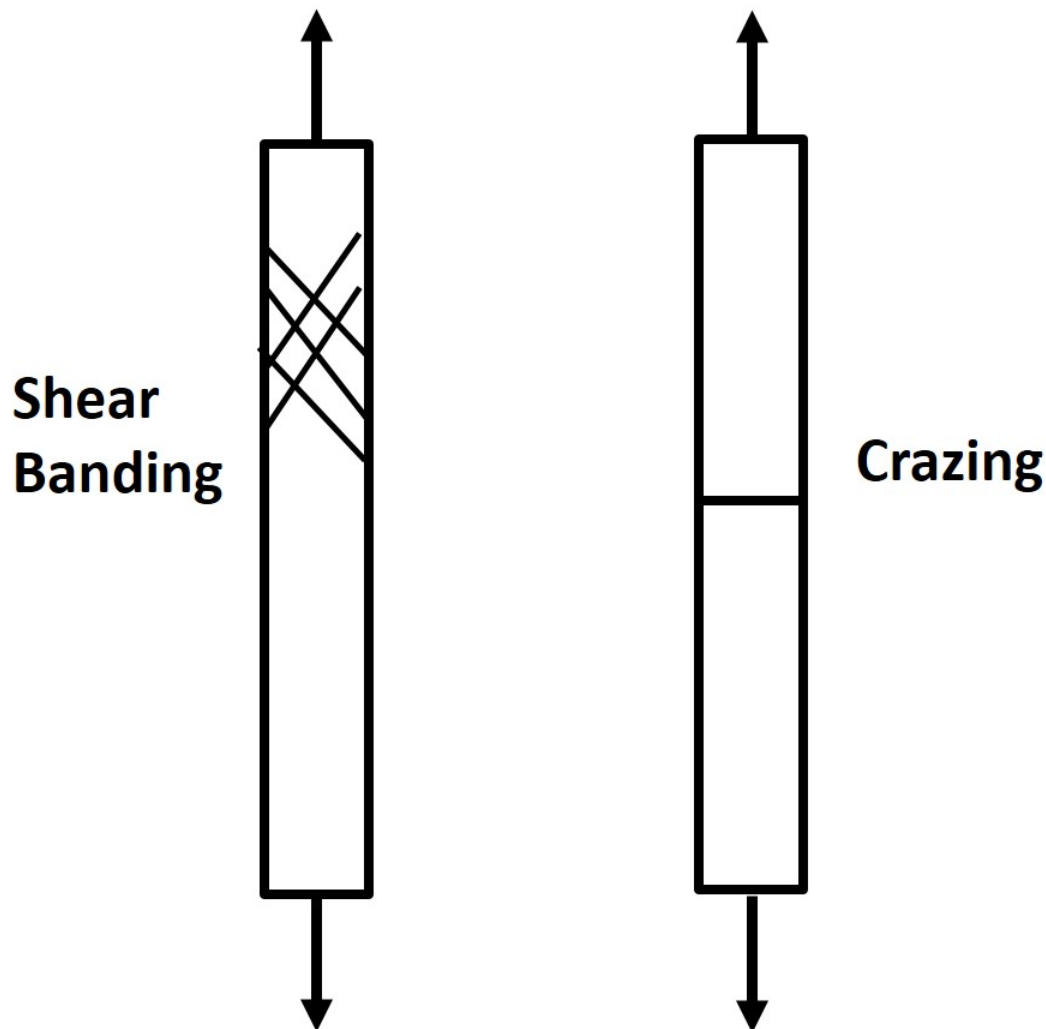


Figure Chapter6.10: Shear Banding vs. Crazeing

6.12 Time-Temperature Dependent Plasticity:

We have previously discussed creep in relation to polymer LVE. **Creep is time or temperature dependent plastic deformation in crystalline materials.** Creep is particularly insidious because like fatigue the **stress where creep or fatigue ensues is much much less than the reported or measured yield stress of a material.** This is because there are new plastic deformation mechanisms accessed at high T, high stress, and long times.

There are three typical creep regimes:

- **Primary or Transient Creep**
- **Secondary or Steady State Creep**
- **Tertiary or Runaway Creep**

Again as materials scientists we want to focus on predicting the creep strain rate, $\dot{\epsilon}_c$

$$\dot{\epsilon}_c = K_c \sigma^x d_g^y D_c = K_c \sigma^x d_g^y D_o \exp\left(\frac{-Q_c}{kT}\right) \quad (\text{Chapter 6.54})$$

where K_c is an empirical material specific creep constant, σ is the applied stress, d_g is the grain diameter, and Q_c is the activation energy for that creep mechanism. Now those diffusion mechanisms are diffusion of vacancies through the lattice or bulk diffusivity, diffusion of vacancies along grain boundaries, and diffusion of vacancies to dislocations.

6.12.1 Lattice/Volume/Bulk Diffusion: Nabarro-Herring Creep

We have our equation for Nabarro-Herring Creep below:

$$\epsilon_{\dot{N}H} = \frac{K_{NH} \sigma D_o \exp\left(\frac{-Q_L}{kT}\right)}{d_g^2} \quad (\text{Chapter 6.55})$$

the key things to see in this equation is the activation energy for lattice diffusion and the scaling behavior with the grain size.

6.12.2 Grain Boundary Diffusion: Coble Creep

Here the number of diffusive pathways increases as the grain size decreases and remember that the **activation energy for grain boundary diffusion is lower than for bulk**.

$$\epsilon_{\dot{C}C} = \frac{K_{CC} \sigma D_o \exp\left(\frac{-Q_{GB}}{kT}\right)}{d_g^3} \quad (\text{Chapter 6.56})$$

6.12.3 Dislocation Creep or Power Law Creep

Here the **net motion of dislocation cores moves in direction of applied stress**, i.e. macroscopic creep. The dependence on applied stress is critical as you can see the scaling behavior in the equation below. Additionally dislocation climb is the rate-limiting process.

$$\epsilon_{\dot{D}LC} = K_{NH} \sigma^{4-6} D_o \exp\left(\frac{-Q_L}{kT}\right) \quad (\text{Chapter 6.57})$$

We can now take a look at some key aspects of creep and in particular the scaling behavior of creep. We can see that DLC will dominate at high temperatures and high stress and Coble creep will dominate at lower temperatures compared to NH.

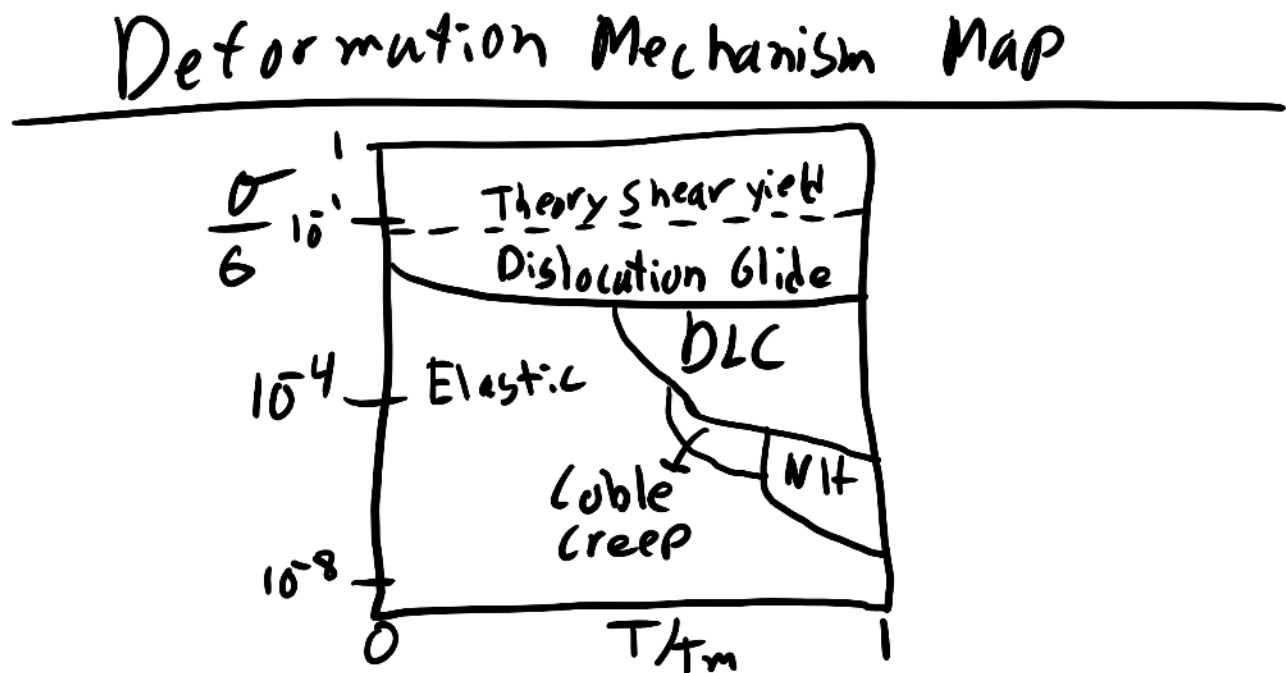


Figure Chapter6.11: Deformation Mechanism Maps.

6.13 Fracture Regime

Finally Fracture!!

Fracture is the last resort for material deformation mechanisms when all **other elastic/plastic mechanisms are exhausted**. Energy is **dissipated by bond breaking**. In uniaxial loading, the stress required to break the material in two pieces, at the stress fracture. Again as in the case of yielding the theoretical stress required to fracture materials (Steel 4340 65GPa, Al 20GPa, Si 7GPa) is order of magnitudes lower than the actual stress required to fracture materials (Steel 4340-3GPa, Al .7GPa, Si .3GPa). This is because **real materials typically contains cracks** (inside, at surface, or at interfaces) and these **micro-cracks act as stress concentrators**. And for an elliptical hole we can define the stress as a function of the distance from the stress concentrator

$$\sigma = \sigma_o \left(1 + 2\sqrt{\frac{a}{R}} \right) \quad (\text{Chapter 6.58})$$

and R at the tip of the crack is $\frac{b^2}{a}$. Brittle fracture occurs when the stress concentrates at a pre-existing crack tip is so high that the material will break catastrophically.

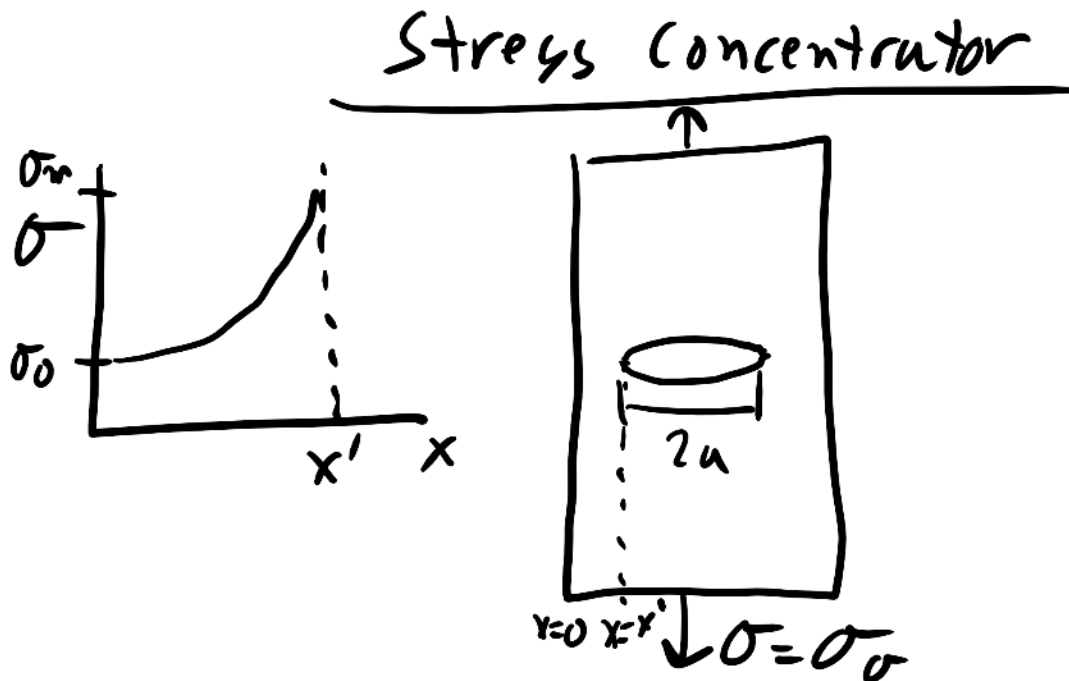


Figure Chapter6.12: Stress Concentrator

Griffith's Theory of Brittle Fracture:

We can develop an equation for brittle fracture from Griffith by considering the **surface area created** as the crack grows and **relieving stored elastic energy**.

Creating Surface Area as Crack Grows

To create the surface area of the crack as it grows we will have a change in the internal energy of the system

$$\Delta U_{surf} = 4at\gamma \quad (\text{Chapter 6.59})$$

Relieving Stored Elastic Energy

A similar change in internal energy will occur for the the relieved stored elastic energy

$$\Delta U_{el} = -\frac{\pi a^2 t \sigma^2}{2E} \quad (\text{Chapter 6.60})$$

The crack will reach critical length when we **minimize the total energy**

$$\Delta U_{tot} = \Delta U_{surf} + \Delta U_{el} = 0 \quad (\text{Chapter 6.61})$$

Giving us the critical crack length

$$\sigma_f = \sqrt{\frac{2\gamma E}{\pi a_{crit}}} \quad (\text{Chapter 6.62})$$

6.13.1 Orowan Theory of Ductile Fracture:

There are a number of materials, metals and polymers, which **won't fracture in a completely brittle manner** but instead from a **small plastic zone prior to each crack elongation**. For these materials **Orowan** has a theory for ductile fracture which is:

$$\sigma_f = \sqrt{\frac{EG_c}{\pi a}} \quad (\text{Chapter 6.63})$$

where G_c the strain energy release rate.

6.13.2 Fracture Toughness:

The final theory for **fracture toughness** considers when a material breaks when the **stress intensity factor** reaches a **critical factor**. The **critical stress intensity factor** depends on the mode of fracture: I, II, and III.

$$K_c = f\sigma\sqrt{\pi a} \quad (\text{Chapter 6.64})$$

where f is a geometric constant factor and K_c is the fracture toughness and $K_{I,II,III}$ is the critical stress intensity factor under Mode I, II, or II loading.

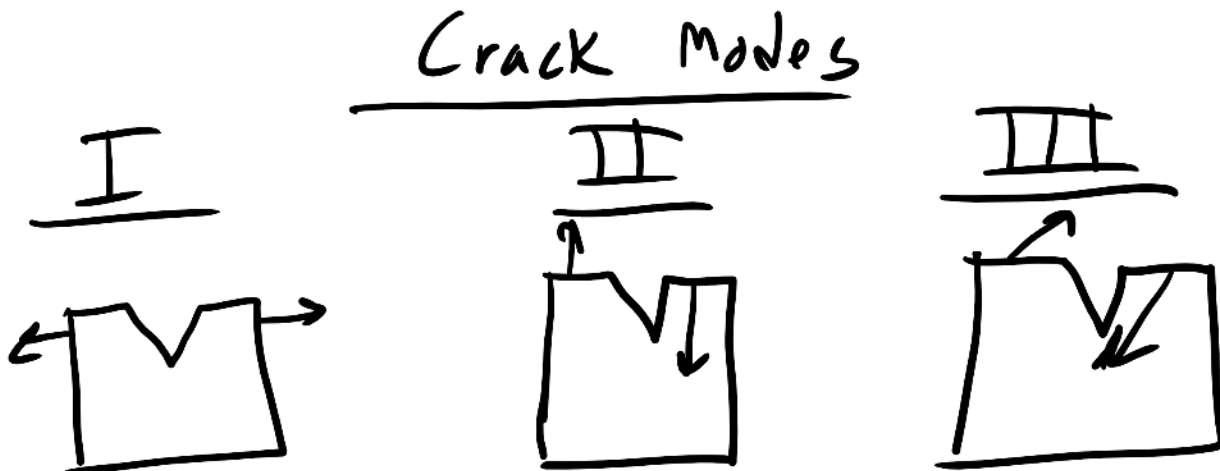


Figure Chapter6.13: Crack Modes

When one looks at the impact energy or fracture toughness as a function of temperature for brittle materials (like BCC which doesn't have close packed slip planes) you will see a ductile to brittle fracture transition where the fracture toughness decreases dramatically as temperature decreases. For ductile materials like FCC which has a number of slip planes you will not see this sharp transition.

6.14 Fatigue

Fatigue (cyclic) loading occurs at applied stresses that are much much less than the stress at fracture but again like creep can lead to **catastrophic failure** at these low applied stresses.

Fatigue failure: fracture due to crack growth every cycle of loading or the crack growth increment per loading cycle which is defined below

$$\frac{da}{dn} \quad (\text{Chapter 6.65})$$

where a is the crack length and n is the number of loading cycles.

We will deal with **Static Fatigue** and **Cyclic or Classical Fatigue**. **Static fatigue** occurs when a material is placed under a **static or constant load** and the crack faces of a material interacts with the environment, the **crack tip becomes embrittled** due to interaction with environment (stress corrosion cracking), the crack tip sharpens, the crack propagates, and the process repeats.

The more common fatigue scenario is **cyclic or classical fatigue** where a material is under a **cyclic load/stress**. We need to define the cyclic applied stress specifically the frequency of the applied load, f , which is $f = 1/\tau$ where τ is the period of the applied stress. We also want to quantify the **stress ratio, R**

$$R = \frac{\sigma_{min}}{\sigma_{max}} \quad (\text{Chapter 6.66})$$

As materials scientists we want to avoid catastrophic failure and for fatigue that involves trying to **estimate the number of cycles to failure, N_f** , which is the number of cycles to grow a crack from initial length, a_o , to the **critical or catastrophic crack length, a_c** .

There three distinct regimes of fatigue crack growth: **I) The Slow-Growth Rate or NearThreshold Regime, II) Mid-Growth Rate or the Paris Regime, and III) High-Growth**

Rate Regime

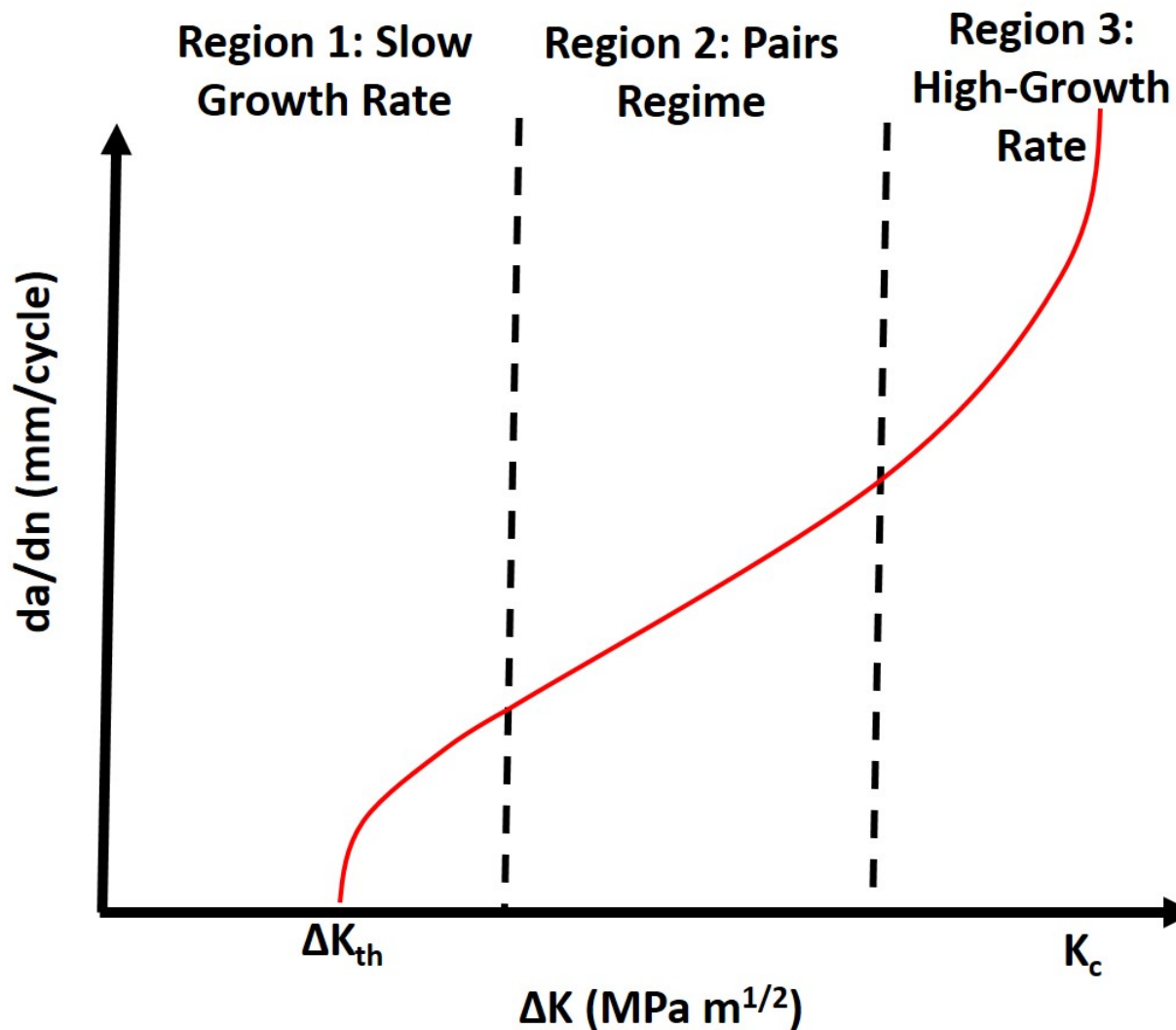


Figure Chapter6.14: Fatigue Regimes

I) Slow-Growth Rate or Near-Threshold Regime

In the slow-growth rate regime the crack won't grow initially until the threshold stress intensity factor, ΔK , is reached where

$$\Delta K = f \Delta \sigma \sqrt{\pi a} \quad (\text{Chapter 6.67})$$

Typically we say that **when the rate of crack growth is 10^{-8} mm/cycle or less the crack is dormant or growing at a near undetectable rate**. Once the threshold stress intensity factor is reached the crack growth rate will increase but still the **growth rate is extremely slow**, still below one lattice spacing per cycle until we reach the Mid-Growth Rate or the Paris Regime.

II) Mid-Growth Rate or Paris Regime

In the **Mid-Growth Rate or Paris Regime** we actually have an equation or law to describe fatigue crack growth, aptly named the **Paris Law**:

$$\frac{da}{dN} = C \Delta K^m \quad (\text{Chapter 6.68})$$

where C and m are empirical constants which depend on the material, the applied stress, frequency, and R . We can use Paris law to predict the number of cycles to failure, N_f

$$\int_0^{N_F} dN = \int_{a_o}^{a_c} \frac{da}{C(f\Delta\sigma\sqrt{\pi a})^m} \quad (\text{Chapter 6.69})$$

which leads to

$$N_f = \frac{1}{C(f\Delta\sigma\sqrt{\pi})^m} \left[\frac{a_c^{1-\frac{m}{2}} - a_o^{1-\frac{m}{2}}}{1-\frac{m}{2}} \right] \quad (\text{Chapter 6.70})$$

where a_o is the initial crack length and remember that a_c

$$a_c = \frac{1}{\pi} \left(\frac{K_{IC}}{\sigma_{max}} \right)^2 \quad (\text{Chapter 6.71})$$

Fatigue cracks are marked via striations on the fracture surface.

III) High-Growth Rate Regime

The last stage is the high-growth rate regime is characterized by **an orders of magnitude increase in the crack growth rate and additional cleavage in the material or microvoid coalescence**. This is the end region where catastrophic crack failure will occur throughout the material. We need to take the material out of service before we reach this regime.

One way that we can try to predict the lifetime of materials is by looking at empirically determined S-N curves. S is the stress amplitude so the difference between the maximum and minimum applied stress. N is again the number of cycles. We can look at the curve and determine when the material will fail.

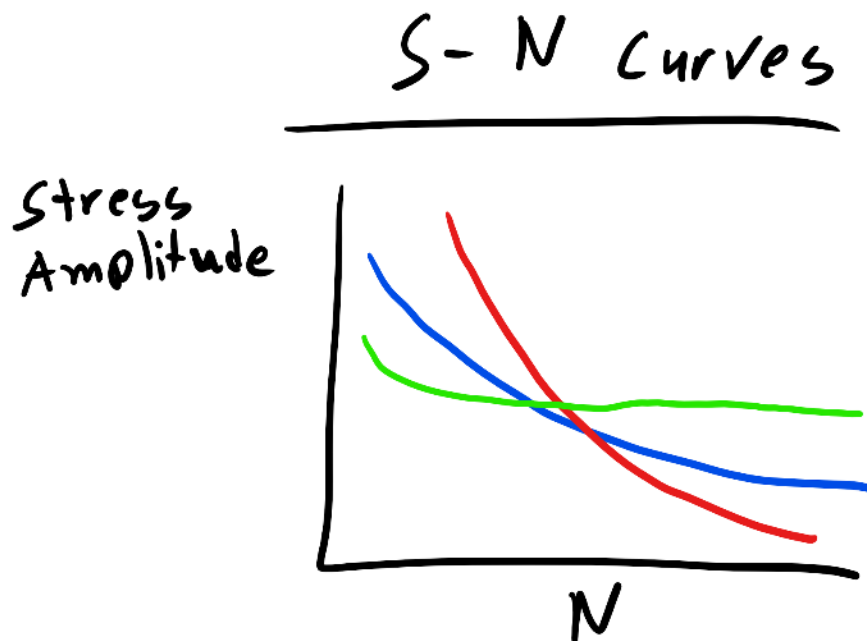


Figure Chapter6.15: Fatigue S-N Curves.

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Chapter 7: Electrochemistry and Corrosion

Over time eventually all materials will degrade. Polymers can be dissolved in organic solvents or crosslinks can be destroyed by UV radiation. Ceramics typically deteriorate in applications where they are utilized at very high temperatures or other extreme environments. And metals will typically undergo **corrosion**. Corrosion is often the unintentional attack typically at the surface. It is a very significant problem which we typically spend **5% of the GDP each year to prevent corrosion, perform maintenance, or deal with the catastrophic failures due to corrosion**. So this is a very stable career choice for Materials Scientists and Mechanical Engineers and one that is very in-demand as the old guard of corrosion engineers are retiring.

What are some examples of corrosion that you have encountered?

There are multiple types of corrosion including:

7.1 Types of Corrosion:

I have recorded a series of lecture videos to supplement this text which can be found in the playlist below:

<https://www.youtube.com/playlist?list=...NFEkLqZgWxQhGw>

- **Uniform Attack**

- Occurs uniformly over the entire exposed surface

- **Galvanic Corrosion**

- Occurs when two different metals are electrically connected and exposed to conducting medium

- **Crevice Corrosion**

- Concentration difference of ions builds up in the crevices between materials. Very localized corrosion

- **Pitting**

- Localized corrosion occurring in small pits or holes

- **Intergranular Corrosion**

- Occurs preferentially along grain boundaries

- **Erosion-Corrosion**

- Combined chemical attack and mechanical wear

- **Stress Corrosion**

- Insidious form of corrosion associated with stress corrosion cracking (SCC). Corrosion of a material under applied or residual stress.

- **Hydrogen Embrittlement**

- Hydrogen induced cracking, H attack

We will cover most of these forms but all of these forms of corrosion are similar in the fact that they involve an **electrochemical** reaction whereby **electrons are lost and gained**. These reactions are also called **redox** reactions which is an abbreviation of **reduction** and **oxidation** reactions.

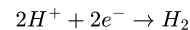
7.2 Electrochemical Nature of Corrosion: Redox Reactions

Corrosion is an electrochemical process where by an element will either gain or lose electrons. During **oxidation** the element will **lose** its valence **electrons**. During **reduction** electrons are **gained**.

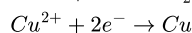
Let's look at a couple of examples for **oxidation**:



Now how about **reduction**



(Chapter 7.3)



(Chapter 7.4)

7.3 Electrochemical Cell

These type of reactions which involve only half of the entire redox reaction process are called **half cell reactions**. They are also called half-cell reactions because they are only describing one half of our typical electrochemical cell which can be seen below:

A couple of key things to note about this diagram. The **cathode** is defined as **positive** because it is the electrode where **electrons flow in**. The **anode** is defined as **negative** as it **gives up electrons**. Additionally, you can see that **cathode** is where the **reduction** reaction occurs and that at the **anode** the **oxidation** reaction occurs. In an electrochemical cell or in a redox reaction reduction cannot occur without corresponding oxidation from mass and charge balance consideration. We should also think about the sign of the potential that we measure. If the electrons actually do flow from the anode to the cathode as shown in the figure above the potential should be positive. If the electrons flow in the opposite direction from cathode to anode then we will measure a negative potential and we have mistakenly set up our cell and misidentified the cathode and anode materials.

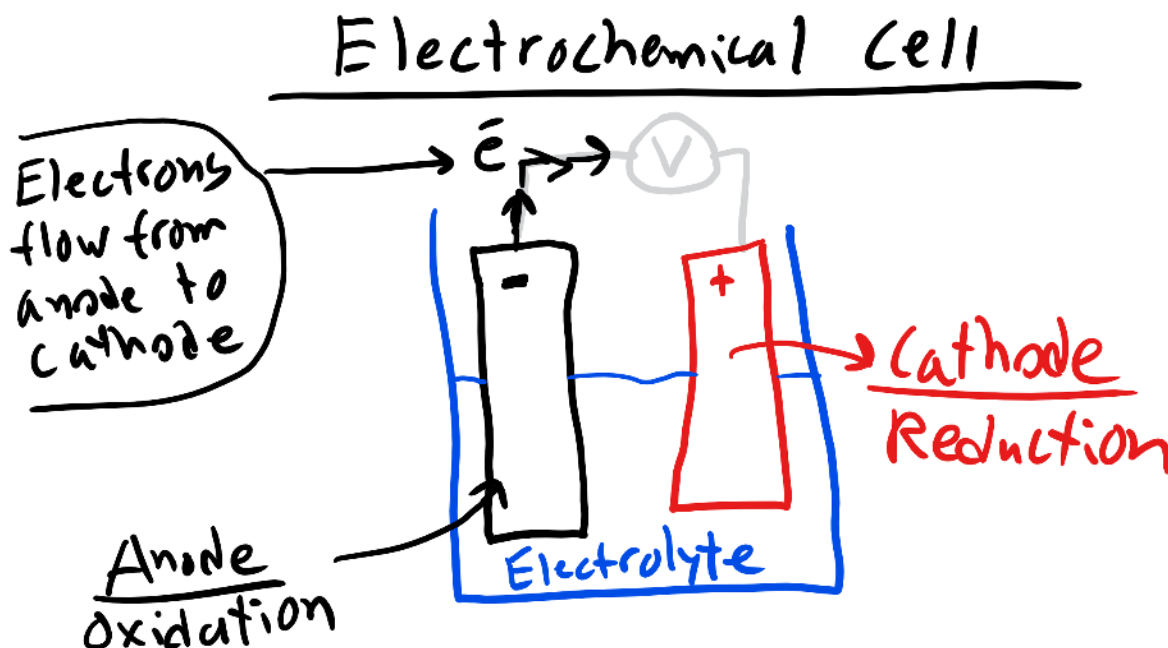


Figure Chapter7.1: Electrochemical Cell.

Let's take a look at on typical electrochemical cell composed of iron as one of the electrodes and copper for the other. The iron is immersed in a 1M solution containing Fe^{2+} ions and the copper is immersed in a 1M solution containing Cu^{2+} ions and it is separated by a membrane as seen below:

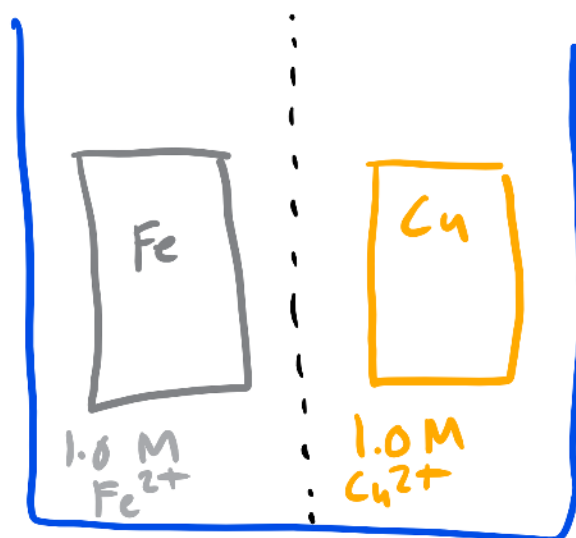


Figure Chapter7.2: Cu-Fe Electrochemical Cell.

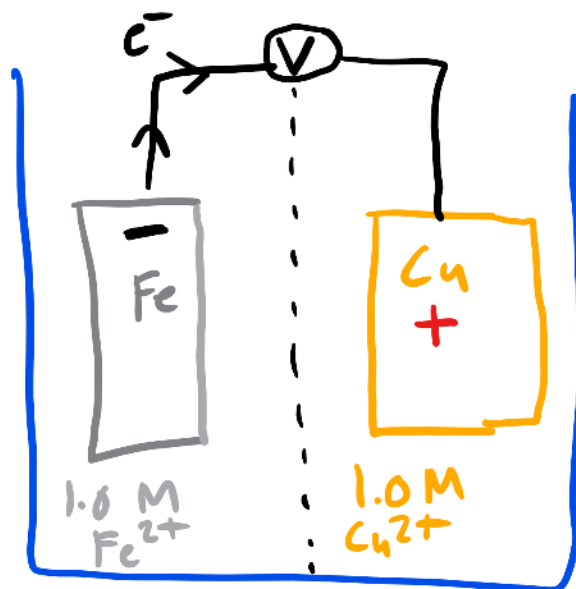


Figure Chapter7.3: Cu-Fe Electrochemical Cell.

Let's start simple where will the electrons flow in this cell?

Well the only way that we can find that out is by actually measuring the potential but we can get some idea by looking at the **electronegativity** of each material. The electronegativity of **Cu** is **1.9** and the electronegativity of **Fe** is **1.83**. Thus we should expect that Cu should pull electrons from Fe.

7.4 Standard emf Series:

We can also get an idea about the willingness of a material's affinity to either give up or gain electrons by looking at a **Standard emf Series** or a **Standard Electrode Potential Series**.

You can see that the potential that are at the top of the list are positive and they are materials that are increasingly inert or noble. In other words these materials have a large electronegativity and want to grab electrons. Thus they are typically cathode materials where reduction will take place. As you move down the list you see that the materials become less noble, more active, and these materials have a very low electronegativity. They want to give away electrons. Note above these are all reduction reactions so the values are assessing in a standard cell how well these materials would fair as cathode materials (positive good, negative bad cathodes should be anodes).

7.5 Half Cell and Full Cell Reactions:

So let's look back at our old friend the Cu-Fe cell. Let's assume that from our investigation into electronegativity and looking at the the Standard emf chart that we think that Cu is going to be the cathode where electrons will be gained and reduction will occur and the anode material will be iron where electrons are lost and oxidation occurs[1]. Let's write these two half cell reaction first at the cathode:

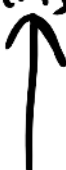
<u>Emf Series</u>		
	<u>Electrode Reaction</u>	<u>Standard Potential (V)</u>
cathodic (inert)   anodic (reactive)	$\text{Au}^{3+} + 3e^- \rightarrow \text{Au}$	1.42
	$\text{Pt}^{2+} + 2e^- \rightarrow \text{Pt}$	1.2
	$\text{Ag}^+ + e^- \rightarrow \text{Ag}$	0.8
	$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$	0.34
	$\text{Pb}^{2+} + 2e^- \rightarrow \text{Pb}$	-0.126
	$\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}$	-0.250
	$\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe}$	-0.440
	$\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}$	-0.763

Figure Chapter 7.4: Standard Electrode Potential Series measured with reference to a standard hydrogen electrode which consists of an inert platinum electrode in a 1M solution of H^+ ions saturated with hydrogen gas.



This half cell reaction will be referred to as the $E_{\text{cathode}}^{\circ}$.

Now for the anode:



This half cell reaction will be referred to as the E_{anode}° . So the full cell reaction will be simple the cathode plus the anode reaction which gives us:



The overall potential of the cell will then be given as:

$$E_{cell}^{\circ} = E_{cathode}^{\circ} - E_{anode}^{\circ} \quad (\text{Chapter 7.8})$$

where in this case the values of $E_{cathode}^{\circ} = 0.340$ according to our table and the value of $E_{anode}^{\circ} = -0.440$. **Notice the negative sign here because at the anode we don't have reduction we have an oxidation reaction.** So the **overall potential is 0.780V**. This value is positive and thus the reaction will proceed spontaneously. If you get a value that is negative then the reaction cannot proceed and you

7.6 What Material Corrodes in Galvanic Corrosion?

You have just done an experiment with a Galvanic electrochemical cell, two metals immersed in a conducting medium and electrically connected. But now you might be asking which material will corrode. Well let's look at what is happening at the cathode first. Electrons are being pulled to copper and they are going to combine with the Cu^{2+} ions in the solution and electrodeposit Cu on the surface of the cathode. So the copper electrode will grow essentially. Now on the other side at the anode the Fe is losing electrons and must dissociate and form Fe^{2+} ions in solution so the Fe anode will start to corrode! We can also tell which material in a standard cell configuration will corrode by simply looking at the Standard emf chart and seeing which is more anodic or active, that is the material that will corrode!

Let's do another example with Fe-Zn

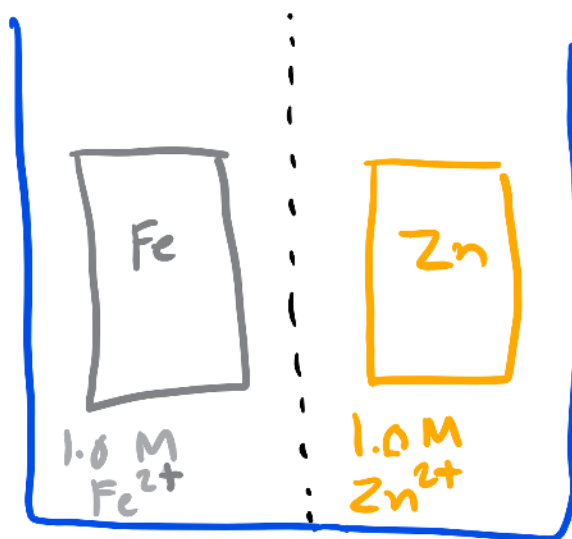


Figure Chapter7.5: Fe-Zn Electrochemical Cell.

What is the electronegativity of each material?

Fe is 1.8 and Zn is 1.65.

Which is more noble and which is more active according to the Standard emf?

Fe is more noble and Zn is more active.

Write the half cell reactions



Write the full cell reactions



Calculate the overall potential

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = -0.440 + 0.763 = 0.323\text{V} \quad (\text{Chapter 7.12})$$

Which material will corrode? Which will electrodeposit?

Zn will corrode and Fe will electrodeposit.

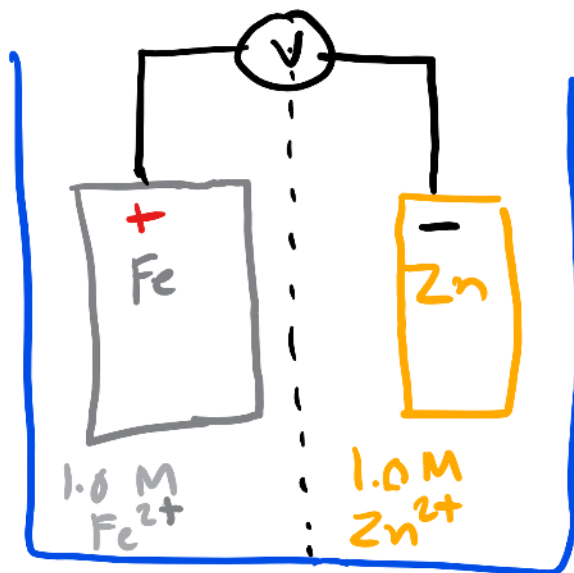


Figure Chapter7.6: Fe-Zn Electrochemical Cell.

7.7 Nernst Equation:

So far we have been dealing with a very idealized situation, we have always been at room temperature and at 1M solutions. But this is often not the case as temperature and concentrations will typically deviate from this idealized scenario. Luckily we can derive from thermodynamics an equation which describes this change in potential as a function of temperature and activity/concentration. The electrochemical work is defined as:

$$W = \Delta G = QE = -nFE \quad (\text{Chapter 7.13})$$

where Q is charge (Coulomb), n is the number of moles of electrons exchanged in a chemical reaction, F is the Faraday Constant ($F = N_{\text{av}}e$) and is $96485 \frac{\text{C}}{\text{mol}}$, and E is the cell voltage. At standard conditions, the conditions we have been working with up to this point, the change in Gibbs free energy is

$$\Delta G^{\circ} = -nFE^{\circ} \quad (\text{Chapter 7.14})$$

Now in general we have the relation that the change in free energy for a chemical reaction is

$$\Delta G - \Delta G^{\circ} = RT \ln \frac{\Pi a_{\text{products}}}{\Pi a_{\text{reactants}}} \quad (\text{Chapter 7.15})$$

where Πa_{products} are the arithmetic products and reactants. Or similarly

$$E - E^o = -\frac{RT}{nF} \ln \frac{\Pi a_{products}}{\Pi a_{reactants}} \quad (\text{Chapter 7.16})$$

or for our Cu-Fe example

$$E - E^o = -\frac{RT}{nF} \ln \frac{a_{Fe^{2+}}}{a_{Cu^{2+}}} \quad (\text{Chapter 7.17})$$

This is the Nernst equation which is a function of temperature and the activity/concentration.

7.8 Methods to Protect Against Galvanic Corrosion:

There are some relatively simple and straightforward methods to protect against corrosion which can include adding an insulating layer or a coating layer between two metals to break the metal or conducting contact. Polymers are great materials for this. You should also avoid leaving any pockets or crevices uncoated as these are insidious sites for corrosion, specifically crevice corrosion to occur. One of the more creative ways to avoid this issue of corrosion is to provide **cathodic protection** using a **sacrificial anode**.

7.8.1 Cathodic Protection:

This mode of protection will be effective for every type of corrosion we previously discussed. Remember that corrosion will occur when the material gives up electrons so to avoid having our material of interest corrode we have to find another source to give up electrons. This can be done using a **sacrificial anode** or using an **imposed current** to force electrons to flow in the desired direction. Let's talk about the sacrificial anode method first.

7.8.2 Sacrificial Anode

Let's consider an example of an electrochemical cell where we have Cu as the cathode, Fe as the anode which is also connected to Zn. What will happen in this cell? Well look at the electronegativities of Cu, Fe, and Zn. Cu is the most electronegative, then Fe, then Zn. So Cu will pull electrons from Zn and Fe. Fe is going to give electrons to Cu but also pull electrons from Zn. And Zn will give electrons to both Cu and Fe. So the Cu will not corrode and will electrodeposit. While Fe will give up electrons to Cu it will also gain electrons from Zn so it will not electrodeposit. Additionally remember reactions proceed in the direction where the energy barrier is the lowest so pulling electrons from Zn is easier than Fe.

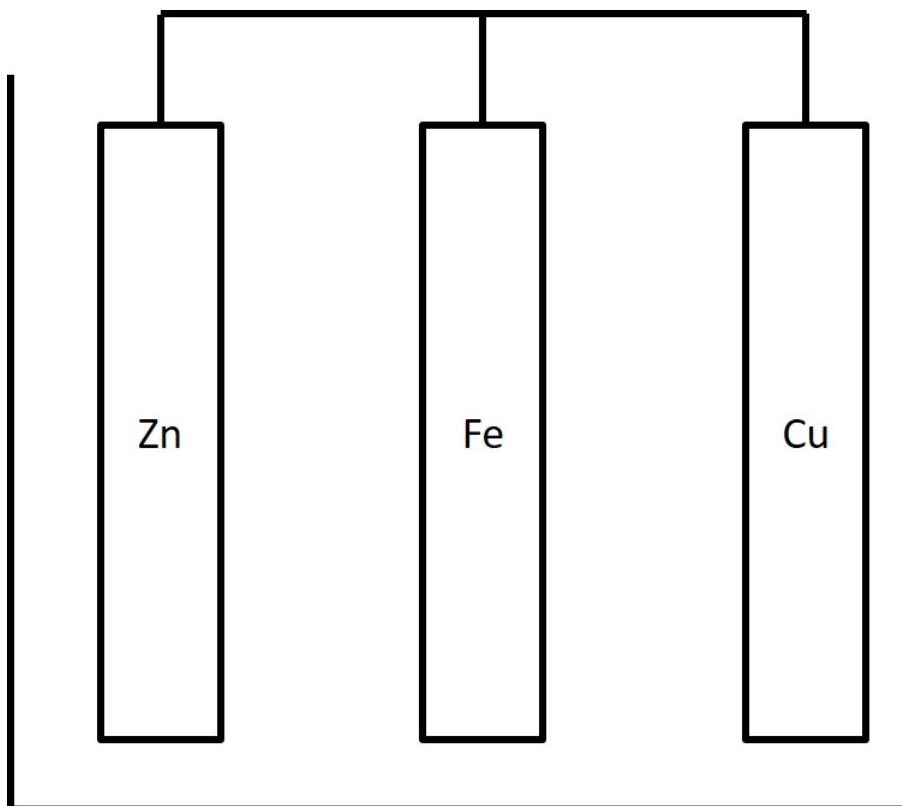


Figure Chapter7.7: Sacrificial Anode.

Finally Zn will corrode as electrons are being pulled away by Fe and Cu. This is the sacrificial anode method of protecting against corrosion because we are adding an anode material that is more active than the material we are trying to protect against corroding and we are sacrificing this new material to die a corrosion death, but for a very good cause.

This technique is commonly done for ships and first discovered by Davy and Faraday in 1824 when they placed iron sacrificial anodes to the copper sheath of the hull below the waterline.

This technique is also used in pipelines as well.

7.8.3 Imposed Current

Another and often more costly methods is to apply a biased or imposed current on your system to prevent a material from corroding. What you do is insert a power supply into your circuit as seen below.

You can increase the applied voltage and bias the flow of electrons towards the material that you are trying to protect from corrosion.

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Chapter 8: Polymers and Soft Matter

8.1 Soft Matter

I have recorded a series of videos to supplement this text which can be found in the playlist below:

<https://www.youtube.com/playlist?list=PL4HrNeEDCchR8V1>

Soft materials is a class of materials that includes **polymers, colloids, liquid crystals, nanoparticles, and hybrid organic-inorganic materials systems**. We are primarily going to focus on polymers but the governing physics and foundation that we will develop will apply more broadly to soft materials and be particularly relevant to biological systems as well as most biological systems are composed primarily of soft materials.

The key to the interesting properties of soft matter is that most intermolecular interactions in soft matter systems have **energies (enthalpies) on the scale of approximately 1 kT**. By comparison, most hard materials such as metals or ceramics are held together by much stronger covalent bonds, which have energetic interactions on the order of 10-100 kT. In other words, **soft matter is held together by very weak intermolecular interactions**, which leads to large fluctuations in thermodynamic quantities that determine the interesting physical behavior of polymer systems. In particular, this means that intermolecular bonds can be easily broken by applied stimuli, such as a pulling force. One consequence of the prevalence of weak intermolecular bonds is that soft matter is highly **adaptive**, meaning that systems can undergo significant changes in response to stimuli. Adaptive behavior is particularly prominent in biological systems. For example, many proteins, such as transporters or receptors, rely on large conformational changes that are only possible in soft matter systems because bonding interactions are relatively weak. That said, soft matter systems can still be strong and robust with respect to physical stimuli, since very strong properties can be built up from a very large number of weak interactions. For example, Kevlar, a prominent synthetic polymer, is used in bulletproof vests due to its ability to withstand impact, a property derived from a large number of weak interactions that are enhanced by the structure of the Kevlar backbone. The physical consequences of these weak enthalpic interactions will become more apparent when we start discussing the thermodynamics of polymeric systems in future lectures. As we continue in the class we will also clarify the origin of different types of bonds, the impact of molecular geometry and structure, the role of fluctuations in position and conformation, and the interplay of enthalpy and entropy over several important length scales.

Throughout the study of soft matter, we will be interested in understanding polymeric behavior on different length scales, or equivalently, we will be interested in **hierarchical** behavior. This is due to the multitude to length scales associated with soft matter systems. Typically, we can think of bonding behavior as relevant on the Angstrom or nanometer length scale, while selfassembled biological structures such as DNA, viruses, and cellular components have properties associated with the 10s to 100s of nanometers, or even up to the micrometer length scale.

What we will find, though, is that the properties of soft matter relies on the bridging of length scales - polymers that have widths on the order of nanometers, but lengths of up to meters. It is a challenge to study systems across these length scales, and is unusual in the study of hard materials!

8.2 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 adopt 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.

8.2.1 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

$$\langle r^2 \rangle^{\frac{1}{2}} \quad (\text{Chapter 8.1})$$

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

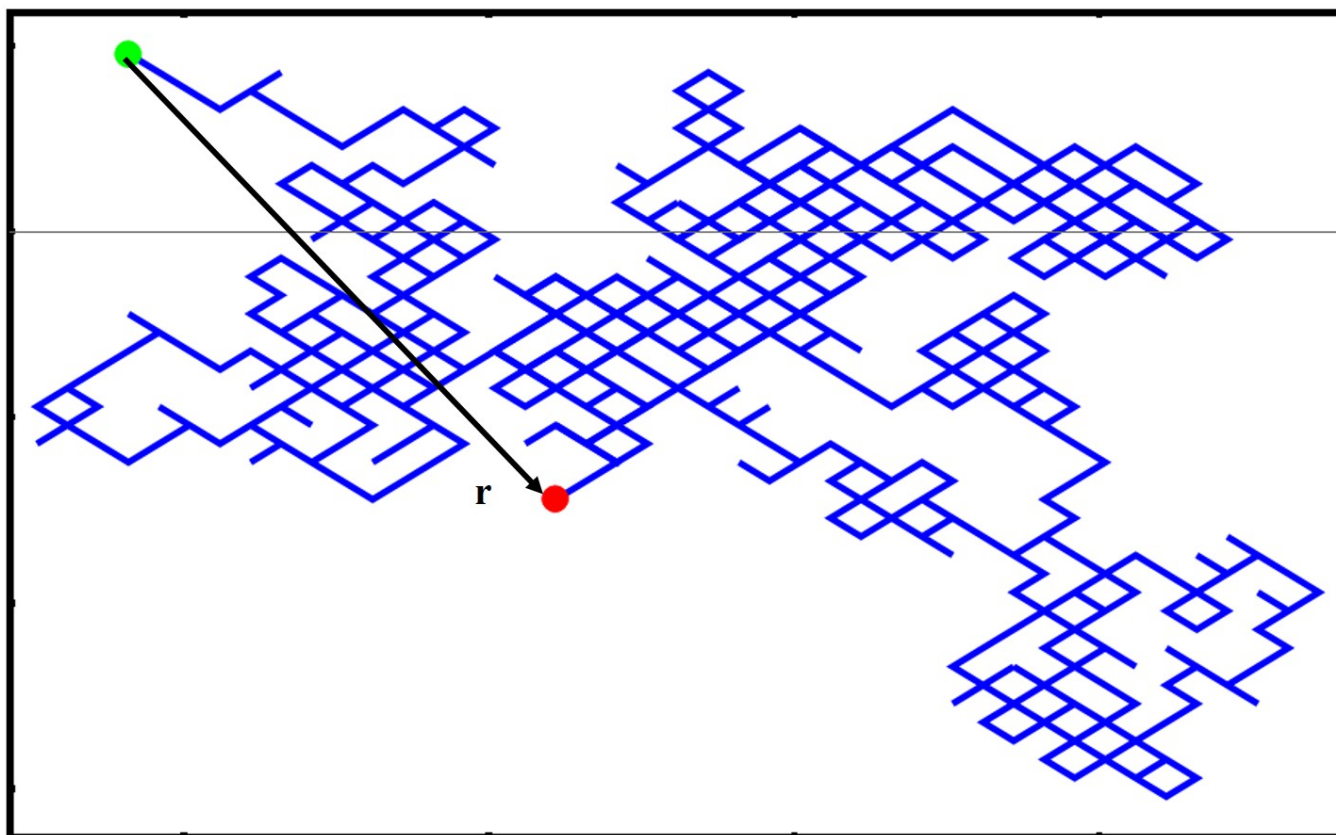
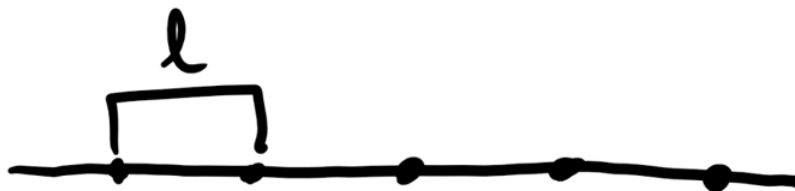


Figure Chapter8.1: End-to-End Distance

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?

Rigid Chain



Coiled Chain



Figure Chapter8.2:Rigid vs Coiled Polymer

Well let's start with the r vector?

It is nl ! So

$$\langle r^2 \rangle^{\frac{1}{2}} = nl = L \quad (\text{Chapter 8.2})$$

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

8.2.2 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**.

Ideal / FJC Chain Model



Figure Chapter8.3: 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**.

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

We can derive the MSD 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

$$\vec{r} = \vec{l}_1 + \vec{l}_2 + \dots + \vec{l}_n = \sum_{i=1}^n \vec{l}_i \quad (\text{Chapter 8.3})$$

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

$$\langle \vec{r}_i \cdot \vec{r}_j \rangle = \left\langle \sum_{i=1}^n \vec{l}_i \cdot \sum_{j=1}^n \vec{l}_j \right\rangle \quad (\text{Chapter 8.4})$$

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

$$\vec{l}_i \cdot \vec{l}_j = |\vec{l}_i| |\vec{l}_j| \cos \theta_{ij} \quad (\text{Chapter 8.5})$$

We can show the MSD in matrix notation as well

$$\langle \vec{r}_i \cdot \vec{r}_j \rangle = \begin{bmatrix} \vec{l}_1 \cdot \vec{l}_1 & \vec{l}_1 \cdot \vec{l}_2 & \vec{l}_1 \cdot \vec{l}_3 & \dots & \vec{l}_1 \cdot \vec{l}_n \\ \vec{l}_2 \cdot \vec{l}_1 & \vec{l}_2 \cdot \vec{l}_2 & \dots & & \\ \vdots & & & \ddots & \\ \vec{l}_n \cdot \vec{l}_1 & \dots & & & \vec{l}_n \cdot \vec{l}_n \end{bmatrix} \quad (\text{Chapter 8.6})$$

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° and then $\cos 0^\circ = 1$.

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

$$\langle \vec{r}_i \cdot \vec{r}_j \rangle = \begin{bmatrix} l^2 & 0 & 0 & \dots & 0 \\ 0 & l^2 & \dots & & \\ \vdots & & & \ddots & \\ 0 & \dots & & & l^2 \end{bmatrix} \quad (\text{Chapter 8.7})$$

The sum of this matrix becomes

$$\langle r^2 \rangle = nl^2 \quad (\text{Chapter 8.8})$$

just as we obtained previously with our other probabilistic method!

8.3 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 steric hindrance along the backbone chain as 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_∞ and α , 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_∞ is used to take into account restrictions due to bonding and steric hindrance from the polymer chain, while the parameter α takes into account effects from the solvent. This improved model 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

$$\langle r^2 \rangle = nl^2 C_\infty \alpha^2 \quad (\text{Chapter 8.9})$$

Let's figure out 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 θ , makes sense thinking of polyethylene. Now the dot product of monomer i and $i + 1$ will be

$$\vec{l}_i \cdot \vec{l}_{i+1} = l^2 (-\cos \theta) \quad (\text{Chapter 8.10})$$

where m is an integer denoting the number of monomers away from monomer i , the θ 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

$$= \begin{bmatrix} l^2 & l^2(-\cos \theta) & l^2(\cos \theta)^2 & \dots & l^2(-\cos \theta)^{n-1} \\ l^2(-\cos \theta) & l^2 & \dots & & \\ \vdots & & & \ddots & \\ l^2(-\cos \theta)^{n-1} & \dots & & & l^2 \end{bmatrix} \quad (\text{Chapter 8.11})$$

And once you sum this matrix we find that

$$\langle r^2 \rangle = nl^2 \left(\frac{1 - \cos \theta}{1 + \cos \theta} \right) \quad (\text{Chapter 8.12})$$

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

$$C_\infty = \frac{1 - \cos \theta}{1 + \cos \theta} \quad (\text{Chapter 8.13})$$

so now we get that

$$\langle r^2 \rangle = nl^2 C_\infty \quad (\text{Chapter 8.14})$$

Chemists Chain Model

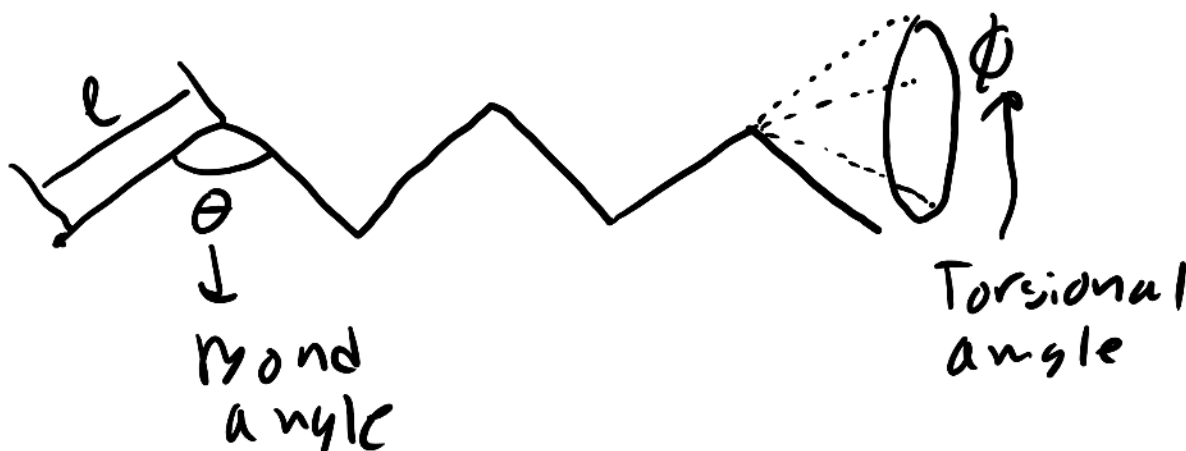


Figure Chapter 8.4: Chemist's Chain Model

where C_∞ 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 $\theta = 109.5^\circ$. Much more on Flory to come.

8.3.1 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 $V(\phi)$. There are 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** $\pm$ 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 we 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 RIS angles based on the number of microstates for each angle** so we will use

$$\langle \cos \phi \rangle = \frac{\int \cos \phi V(\phi) d\phi}{\int V(\phi) d\phi} \quad (\text{Chapter 8.15})$$

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

$$\langle r^2 \rangle = nl^2 \left[\left(\frac{1 - \cos \theta}{1 + \cos \theta} \right) \left(\frac{1 + \langle \cos \phi \rangle}{1 - \langle \cos \phi \rangle} \right) \right] \quad (\text{Chapter 8.16})$$

And now we have our new and improved Flory Characteristic Ratio C_∞ which is

$$C_\infty = \left(\frac{1 - \cos \theta}{1 + \cos \theta} \right) \left(\frac{1 + \langle \cos \phi \rangle}{1 - \langle \cos \phi \rangle} \right) \quad (\text{Chapter 8.17})$$

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 **bond angles and rotations** we get fairly accurate values of C_∞ compared to experimental measurements and usually this value **varies between 1-20**. It's important to note that C_∞ **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_∞ 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**.

8.3.2 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 its **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 decrease and vice versa**.

Remember that the solvent is the majority component and solute is the minority component.

8.4 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. **solvents where 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 **θ 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 θ solvent**.

The parameter that we use to quantify the effect of **solvent quality** is measured via a factor α . Luckily α 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 θ solvent

$$\alpha^2 = \frac{\langle r^2 \rangle}{\langle r^2 \rangle_\theta} \quad (\text{Chapter 8.18})$$

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

What will be the value of α^2 in a good solvent?

Well $\alpha^2 > 1$ for a good solvent.

What about a bad solvent? $\alpha^2 < 1$ for a bad solvent What about a θ solvent? $\alpha = 1$ for a θ solvent

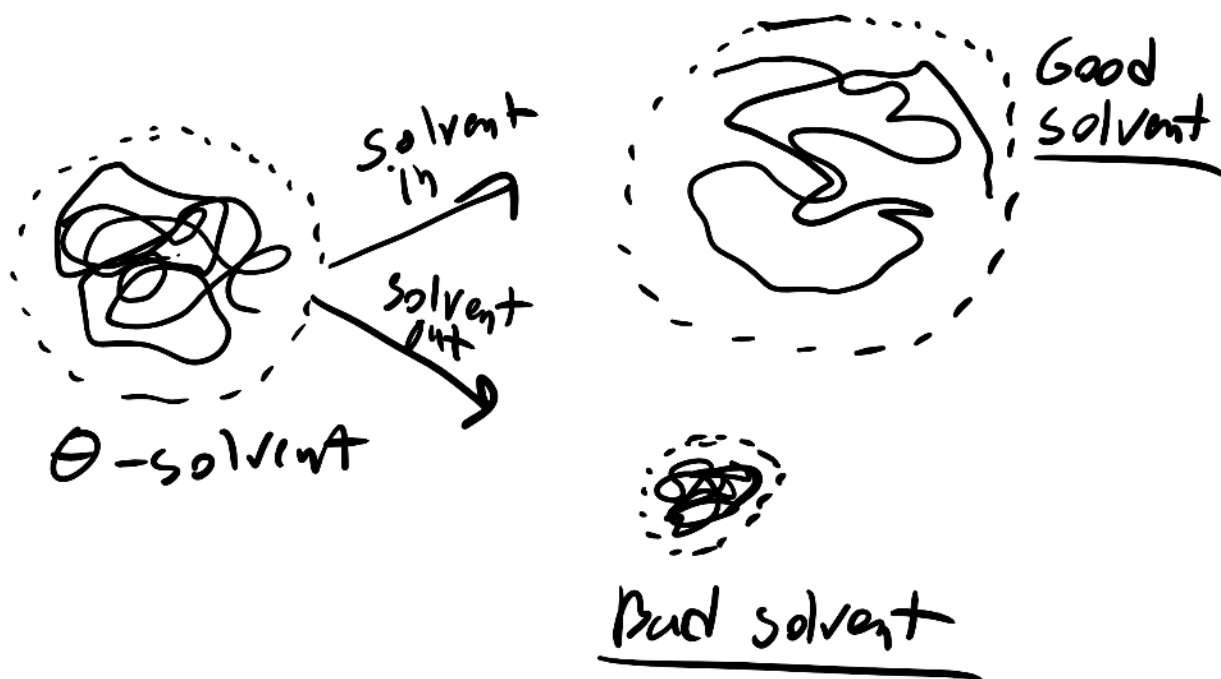


Figure Chapter8.5: Solvent Quality

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** (ϵ_{m-m}), **monomersolvent interactions** (ϵ_{m-s}), and **solvent-solvent** (ϵ_{s-s}) interactions. Remember from the thermodynamic lecture that we always want lower or negative energies so **for a good solvent ϵ_{m-s} should be the lowest energetic interaction** and for **bad solvent ϵ_{m-s} should be larger**. Much more on this when we get to Flory.

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 interactions, or solvent/excluded volume interactions. Captures behavior of θ solvent and melt state fairly well.

2. Chemist's Chain Model In Solution and Melt $\langle r^2 \rangle = nl^2 C_\infty \alpha^2$

- θ Solvent or Melt $\langle r^2 \rangle \approx nl^2$

- Good Solvent $\langle r^2 \rangle \approx n^{\frac{6}{5}}$

- Poor Solvent $\langle r^2 \rangle \approx n^{2/3}$

- Takes into account preferred bond angles, steric interactions, RIS states, solvent, and excluded volume interactions.

8.9 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.

8.9.1 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**.

8.9.2 Glass Transition Temperature:

We have just discussed how non-crystalline amorphous polymers can be distinguished from semicrystalline 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 θ 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, 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 ϵ_{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 fluidlike 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.

8.9.3 Relaxation Time τ^*

The physical properties of amorphous polymers (and materials in general) are influenced by τ^* , 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 $\tau^* \ll t$ and $De \ll 1$. Because the relaxation 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 $\tau^* \gg t$ and $De \gg 1$. 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.

8.9.4 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 scale 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.

8.9.5 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_∞ to the rigidity of a backbone, and hence expect T_g to increase with C_∞ .

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 . 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.

8.10 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. 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.

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 (2θ). 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?

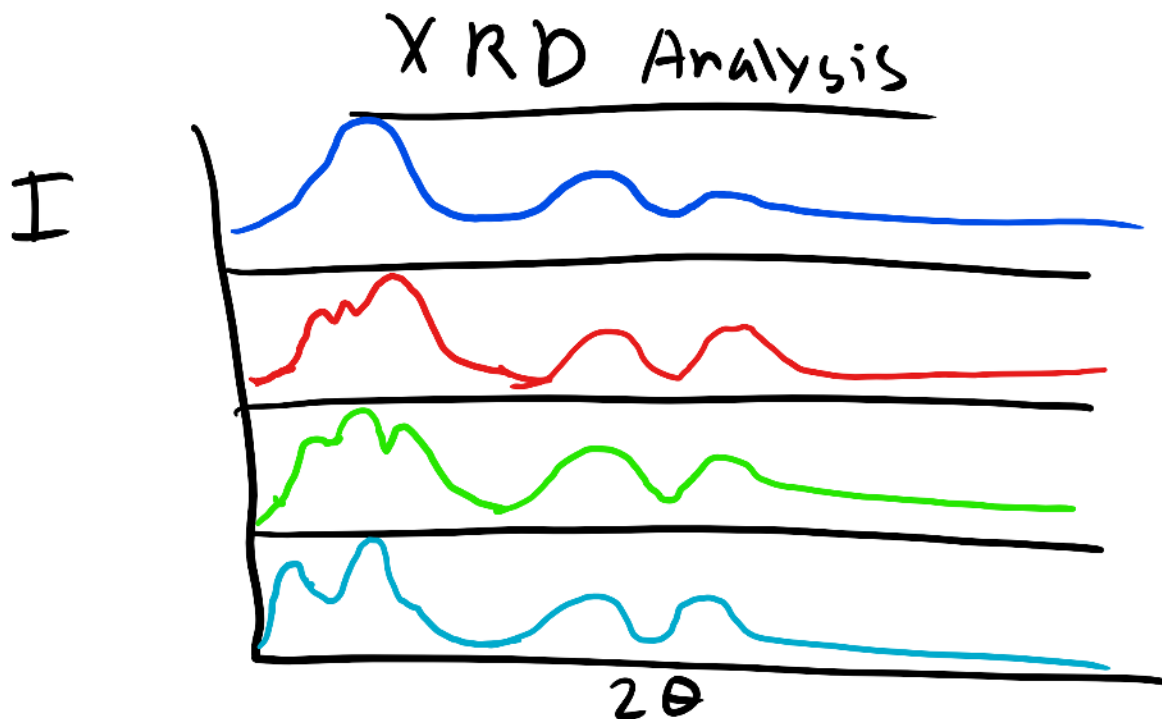


Figure Chapter8.6: XRD Curves of Methacrylate Family.

Well again remember that we observe peaks in the XRD curves when there is constructive interference which occurs when at that particular incident angle there is some local order perhaps even long-range order of some type.

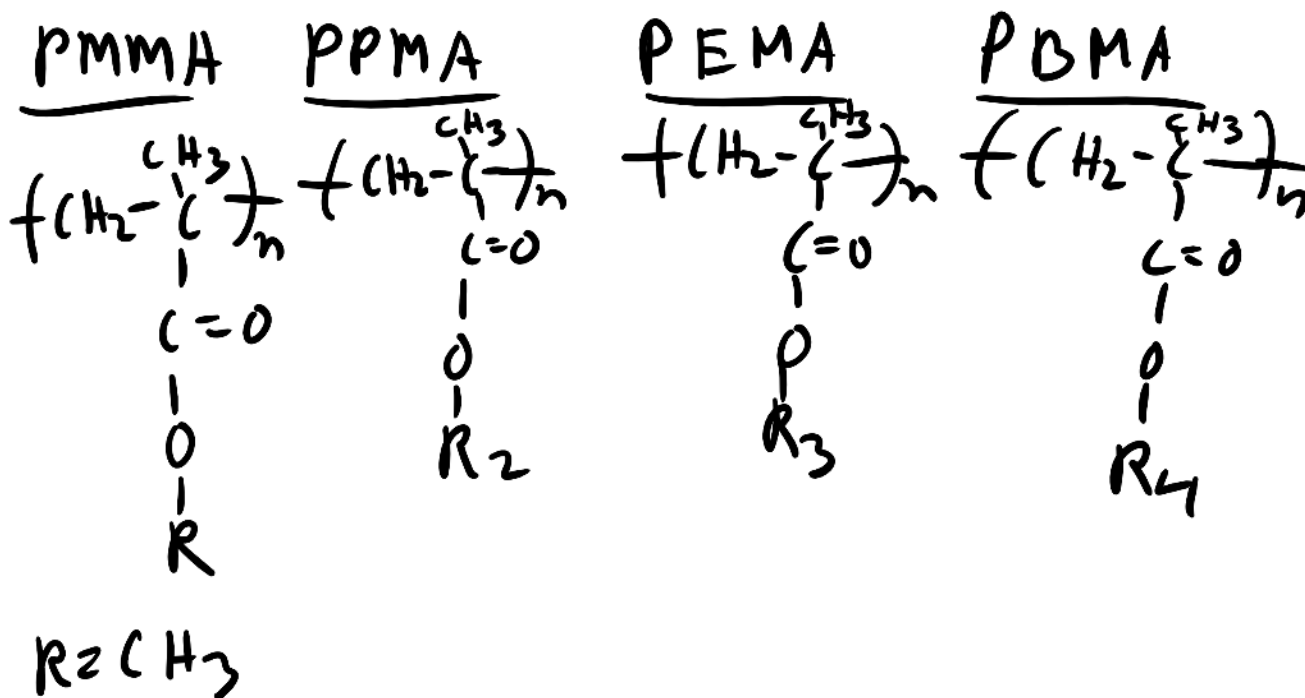


Figure Chapter8.7: Methacrylate Family of Polymers

We also know from Bragg's law that the Bragg Angle $\theta \propto \frac{1}{d}$. So the characteristic distance where this local order appears is inversely proportional to the incident angle. Let's think about the structure 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 depending on the polymer we are looking at in this family. These small distances correspond to large angles and so this explains why the peaks are conserved for the different polymers.

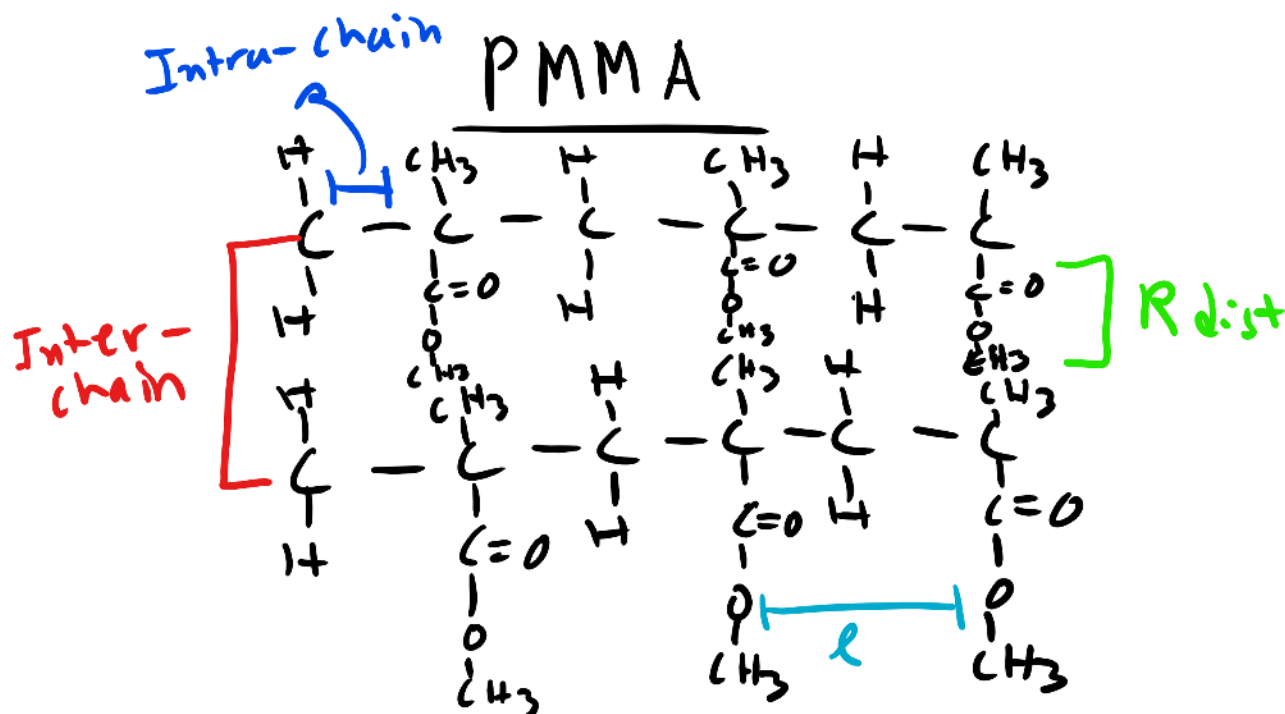


Figure Chapter8.8: PMMA Chain Schematic

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. 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.

8.11 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.

DSC Analysis of Amorphous vs. Crystalline

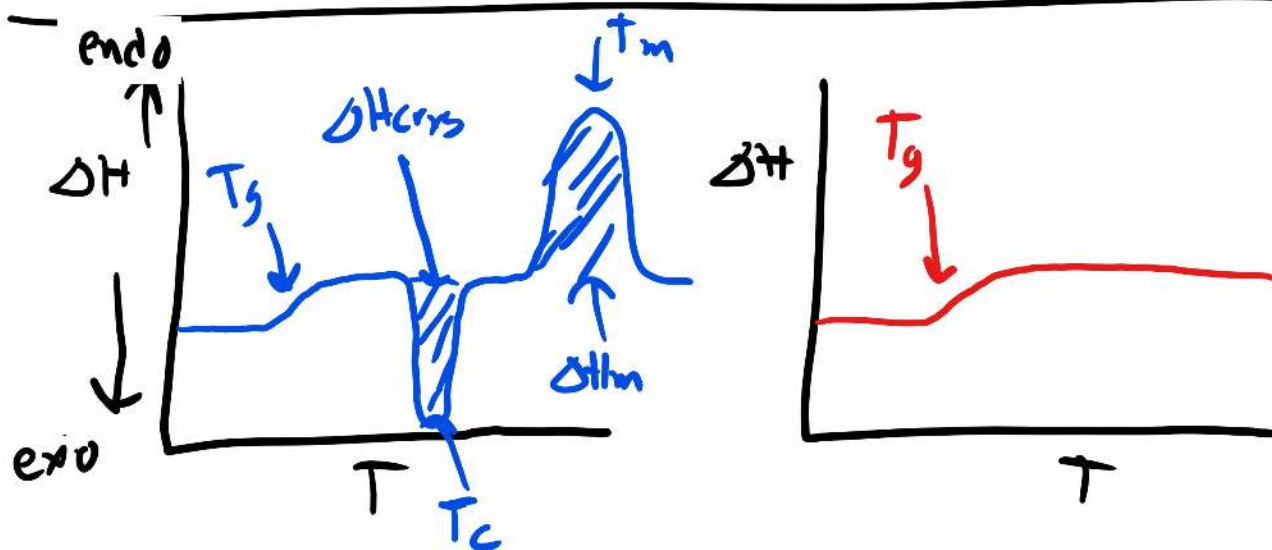


Figure Chapter 8.9: Amorphous Vs. Crystalline Thermoset Polymer DSC Curves

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 ΔH 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.

DSC Analysis of Thermoplastic vs Set

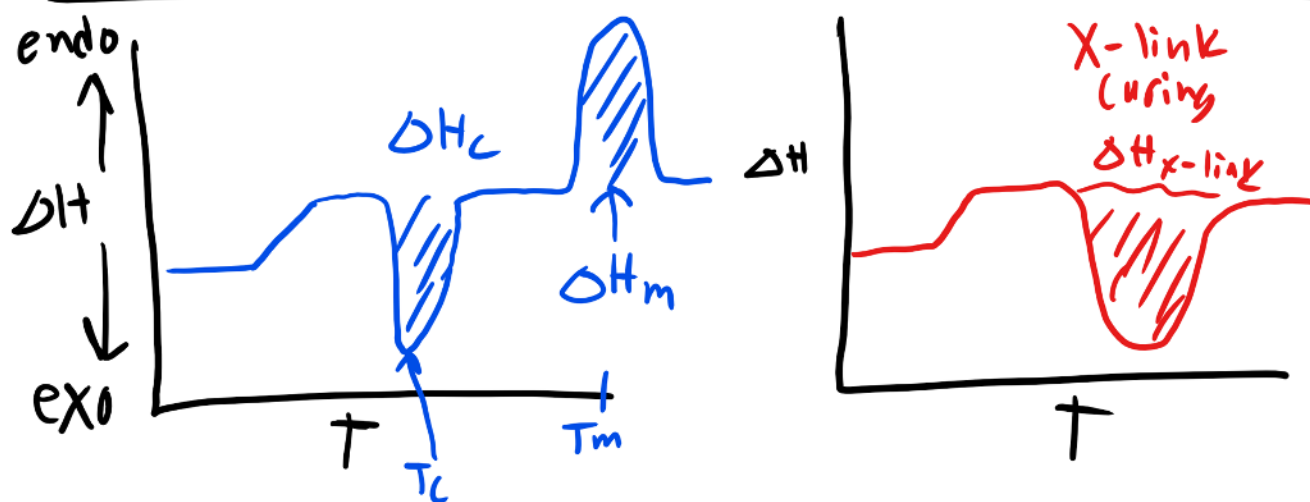


Figure Chapter8.10: Thermoplastic Vs. Thermoset DSC Curves

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 that 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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