# APS110: Engineering Chemistry and Materials Science

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# Contents

# Preface and Acknowledgements

APS110: Engineering Chemistry and Materials Science is a course at the University of Toronto's Faculty of Applied Science and Engineering. According to the Faculty's Academic Calendar, the course is built on the principle of the structure-property relationship. This is one of the five courses taken by ALL undergraduates in the Fall semester of their first year.

I took this course in Fall 2023 under Professor Scott Ramsay. While heavy in content, this course was also my favourite among those I took in my first semester of university. I doubt I will ever encounter content from this course again in my degree; regardless, I enjoyed this course and its thrice-weekly 9 AM lectures fueled by the Myhal Second Cup.

**This notes package is in no way a complete representation of the course.** That being said, these notes cover all the content in the textbook and lectures. I used the original Goodnotes version of these notes to study for both the midterm and final exam.

These notes were transcribed from my original notes for this course, found here [click me!]. This document was written in LaTeX using Overleaf; the source project can be viewed here [click me!]. If you find any errors (or just want to provide feedback) feel free to reach out to arnav.patil@mail.utoronto.ca!

# 1 Introductions

**"The World According to Scott"**

- There are three classes of materials: metals, ceramics, and polymers.

- Metals held together by metallic bonding - we'll cover this later in Band Theory.

- Ceramics largely held together by ionic bonds, and will shatter - classified as being brittle.

  - Ceramics are usually composed of metal oxides.

- Polymers are held together byy covalent bonds - chains of atoms.

- There's some exceptions, such as wood, skin, composites, and semiconductors. However, we don't cover them as much in this course.

**Metals**

- Typically metals + metalloids (elements that don't always act like metals).

- Characterized by being ductile, and are almost always crystalline.

**Ceramics**

- Tend to be hard and brittle, non-conductive.

- Usually compounds of more than 1 element, held by ionic bonds.

- At the atomic level, are either highly organized or disorganized (amorphous).

- Allotropes can also be argued to be ceramics.

**Polymers**

- Generally what people call plastics, but that term does not cover everything.

- Ductile, but not as strong as metals, and are generally non-conductive.

- Held together by covalent bonds.

# 2 Elastic Behaviour

**Hooke's Law**

$$F = -k\Delta x \tag{1}$$

What most people covered as the spring law in high-school physics. This equation will provide the basis for the content that we'll be covering ahead.

**Engineering Stress and Strain**

Engineering stress is defined as the applied force divided by the initial cross-sectional area of the object.

$$\sigma = \frac{F}{A_0} \tag{2}$$

Engineering strain is defined as the change in the object's length divided by its initial length.

$$\varepsilon = \frac{\Delta l}{l_0} \tag{3}$$

We can manipulate the equations above to substitute into Hooke's Law, and end with:

$$\sigma = E\varepsilon \tag{4}$$

which is still Hooke's Law!

**Defining Elastic Deformation**

- **Definition 1:** Sample dimensions return to their original dimensions upon unloading.

- **Definition 2:** Atoms return to their original positions upon unloading.

**Simple Model for Bonding in a Solid**

- If we apply load within the elastic region, atoms must move back to original position after unloading.

- Sample gets longer when load applied, but again, recovers once unloaded.

- When atoms pulled apart, there is an attractive force between them, but when pushed closer together, there is a strong repulsive force.
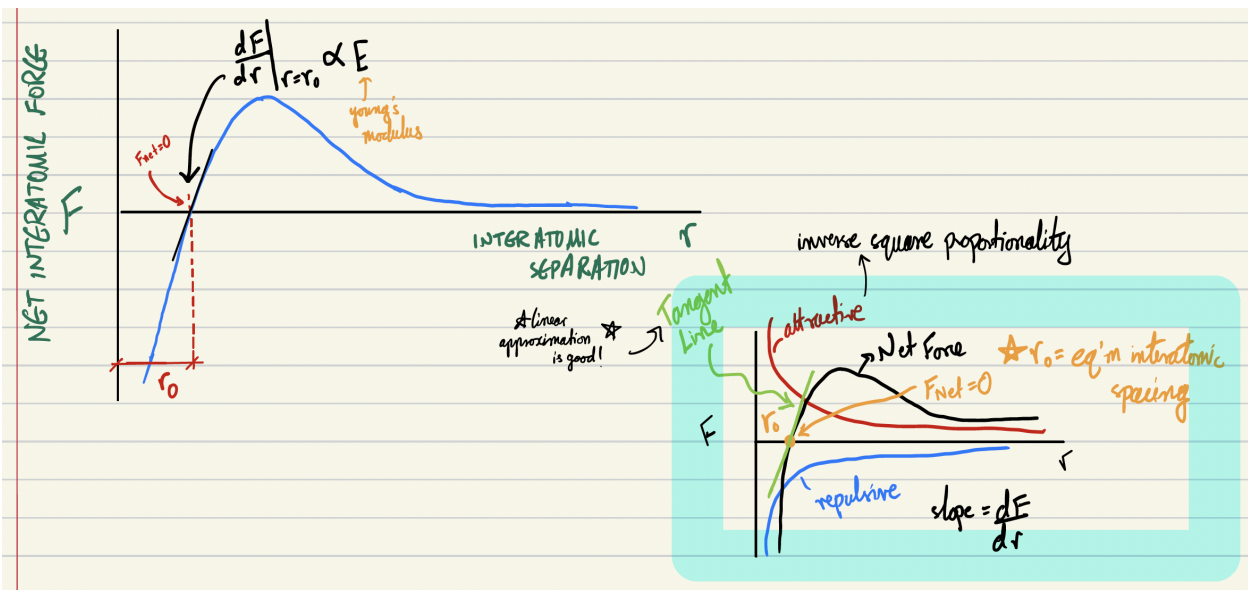


Figure 1: Interatomic Separation vs Interatomic Force Between Particles

**Structure Independence of Young's Modulus**

- What is elasticity?

  1. Sample returns to its original geometry.
  2. Strain is recoverable.
  3. Atoms return to their original positions.

- Young's Modulus is dependent only on the type of atom being spaced, therefore is structure independent.
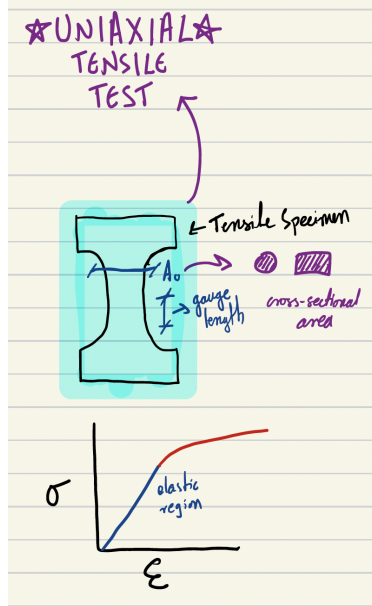
Figure 2: Uniaxial Tensile Test

# 3   Non-Elastic Behaviour

If we load beyond a sample beyond its elastic region, the material will be permanently deformed, even after the load is removed. When the load is removed the strain is reversed, the atoms will remain in their new positions. **Permanent deformation is also called plastic deformation.**

**Etymology of Plastic**

- When we say plastic, we really mean polymer.

- Plastic refers to permanence of the deformation and derives from the Greek word *plastikos*, meaning sculpt or shape.

**Plastic Deformation**

- What happens to stress-strain behaviour beyond the elastic region?

- PD begins close to the end of the linear region, although it's a little tricky to tell exactly where it begins.

**Plastic Deformation of Other Materials**

- Ceramics being the strongest is generally true, but only in compression. In tension, they tend to be very weak.

- Ceramics' curves appear to be very linear because they are brittle.

- Sometimes, you will see "elastic modulus" used instead of Young's Modulus when referring to polymers and composites.

**Mechanical Testing of Ceramics**

We test ceramics' strength a little differently because they perform so poorly under tension.
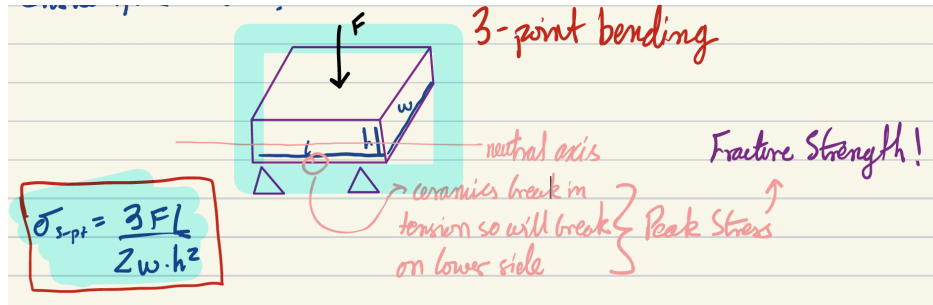
Figure 3: 3-Point Bending Test for Ceramic Materials

**Why Would I Balance on a Thin Sheet of Glass?**

- Tempered Glass $\rightarrow$ At elevated temperatures, the molecules are further apart, however, when the surface rapidly cools, some expanded volume is locked into the glass.

- But the central portion of the glass continues to cool more slowly and the molecules are better able to organize and achieve a smaller final volume.

- Final piece of glass, once cooled, contains residual stress.

**Models Have All the Fun**

- Models are like analogies that allow us to simplify really complication things and predict behaviour.

- As conflicting data is presented or flaws are discovered, models need to be updated too.

- A model does not need to be fully complete or accurate. It only needs to be valid for the purpose it is being used for.

# 4 Structure-Property Relationship
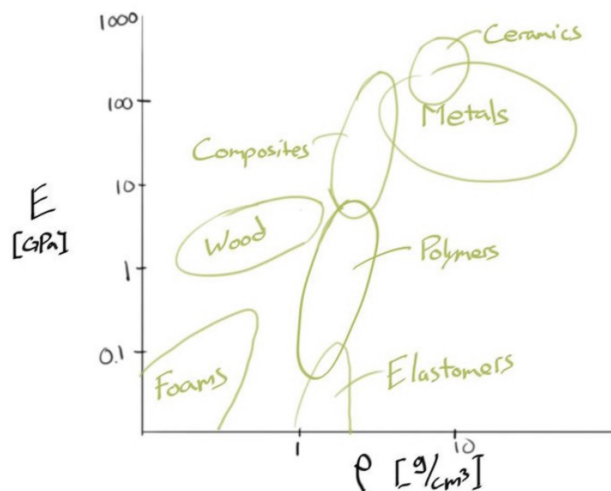
**Material Groups**



Figure 4: Material Groups

- Generally an increase in density as we look for materials with a higher Young's Modulus.

- Oval regions were introduced by Mike Ashby at Cambridge University.

- Upper left region is empty, but composites and carbon fibres are helping us get into the region.

**Objective Function**

- Mike Ashby's material selection process involves with the objective function, something to you want to maximize or minimize.

$$m = A \cdot L \cdot \rho \tag{5}$$

- Then we define a constraint: let's consider elastic bending, meaning we impose a maximum deflection constant.

  - Meaning, if it bends more than a certain amount even without bending, it fails the criteria.
  - The beam deflection formula:

$$\sigma = \frac{FL^3}{CEA^2} \tag{6}$$

- Length is prescribed by the design, therefore it cannot be changed, so we solve for area:

$$A = \left( \frac{FL^3}{CE\sigma} \right)^{1/2} \tag{7}$$

- Considering only material properties, to minimize the mass, we must minimize $\rho/E^{1/2}$, or maximize its reciprocal.

- This reciprocal is called the **Materials Performance Index**.

- We can plot our E vs $\rho$ chart by logging both sides and rearranging.

$$\log E = 2 \log \rho + 2 \log MPI \tag{8}$$

- Above equation gives a slope of 2, which we can move higher to yield higher values and find materials better to use as a light stiff beam.

  - Eliminate ceramics because they're vulnerable to catastrophic brittle fracture. This leaves composites as the strongest.
  - Particularly, carbon fibre reinforced polymer (CFRP) is the best.

- Similar analysis for the light stiff beam, in which thickness is the free variable, with the horizontal area of the fixed yields an MPI of $E^{1/2}/\rho$.

- Wood emerges as an unsurprising contender as a light stiff beam.

**Ordered Solids**

- Most metals around us are polycrystalline, meaning it is made of crystals.

  - Inventory control tags are glassy or amorphous metals, while modern jet turbines are made a single crystal.
  - Each of these crystals is made of a massive number of atoms all positioned in regular repeating positions, spaced roughly at the atomic scale, which is the Angstrom.
  - In materials science, or solid state chemistry, these crystals that make up polycrystalline materials, are called grains.

- The smallest convenient repeating unit that we can use to represent overall crystal unit cell.

&ndash; Type of highly ordered repeating structure that extends well beyond the scale of the atom is known as **long range order**.

- Some materials we only have knowledge of the positions of nearest neighbour atoms, but beyond that, there is no long range order.

  &ndash; These materials only have **short range order**.

**Face-Centred Cubic**

- We will position the centre of an atom at each of the corners of a cube.

- Also known as simple cubic but is not particularly useful since only one element forms this structure.

- Since it is a cube, there is only one dimension called the lattice parameter $a$.

- Other atoms in the FCC unit cell: the face centred atoms, which are centred on each of the six faces of the cube.

- Our crystal structures are based on a model known as the hard sphere model that treats atoms in ordered solids as spheres that make contact with the nearest neighbour atoms at distances defined by atomic radii.

- $n_{FCC} = 4$

**Back to Density Again**

- How could we calculate density using the basis of a single unit cell?

$$\rho = \frac{n \cdot A}{V_C \cdot N_A} \tag{9}$$

**The Atomic Packing Factor**

- Concept closely related to the mass density is the Atomic Packing Factor, or Volume Packing Fraction.

- Measure of the fraction of a volume that is occupied by atoms arranged in a particular crystal structure.

$$\textbf{APF} = \frac{\textbf{volume of sphere}}{\textbf{volume of unit cell}} \tag{10}$$

- Since the atoms in the FCC unit cell touch along the face diagonals. Since the length is $a$, we can use Pythagoras to calculate the lattice parameter in terms of the atomic radius.

  &ndash; $a_{FCC} = 2\sqrt{2}R$

  &ndash; $\textbf{APF}_{FCC} = 0.74$

- APF of 0.74 is actually the highest possible for packing with a single diameter of sphere. The interesting feature of this result is that it is structure independent.

# 5 More Structure

**Common Ceramic Crystal Structure or Rock Salt**

- In ceramic structures involving more than one type of atom, structures may be depicted in more than are way, but only viewed from a different perspective.

- Cations exist in between the anions and push them apart so that the anions no longer touch each other across the face diagonals of the unit cell.

**Coordination Numbers for Cations in Rock Salt**

- Coordination number is the number of atoms touching a specific atom.

- Central cation touches each of the face centred anions, for a coordination number of 6.

**Theoretical Density of Ceramics**

- First, there is more than one type of atom to present, and we must account for the molar mass of both types.

- Secondly, we must be careful to carefully calculate the unit cell volume $a^3$ by determining the lattice parameter $a$ using both anion and cation radii, keeping in mind that the cations will always be touching the anions.

$$\rho = \frac{n_C A_C + n_A C_A}{V_C N_A} \tag{11}$$

**Body-Centred Cubic Crystal (BCC) Structure**

- Each corner position containing only 1/8 of an atom.

- Final atom goes in the centre of the unit cell.

- $n_{BCC} = 2$

- $\mathbf{CN}_{BCC} = 8$

- $\mathbf{APF}_{BCC} = 0.68$

**Interstitial Sites**

- Interstitial sites are spaces between other atoms.

- By convention, we name sites according to the spaces that they create.

- The interstitial site with a coordination number of 6, which is the site that the cations exist in within rock salt is called the OCTAHEDRAL INTERSTITIAL SITE.

**Hexagonal Close Packed (HCP)**

- HCP is another metallic crystal structure with the same packing fraction as FCC, 0.74.

- Second later is placed in the low spots of the first layer, nor directly above the first.

- The low spots amongst atoms of a close-packed plane are actually too close to let an atom into each location.

- $\mathbf{CN} = 12$

**FCC Oranges and Apples**

- Stacking close-packed layers is not the only way to create a close-packed structure.

- Think of fruit being stacked at a supermarket, the bottom layer is a simple square layer.

  - This is the front face of an FCC unit cell, an 001 plane.
  - Second later is placed into the low spots between the bottom layer, forming another square lattice 001 plane.
  - Third layer is then stacked into low spots of the 2nd layer, which is directly above the 1st layer.

- The c/a ratio for HCP is 1.633

# 6   Mechanical Behaviour

**Revisiting Stress-Strain Behaviour of Metals**

- The peak of the curve is called the ultimate tensile strength.

- It is denoted as $\sigma_{UTS}$.

- Proportional limit is where elastic regions stops having a linear proportionality.

**Defining the Start of Plastic Deformation**

- Yield strength is where, in practice, we assume plastic deformation begins and where stress-strain curve stops being proportional.

- 0.2% offset yield strength is a convention that allows us to define a value close to the start of plastic deformation.

  - We begin from a strain of 0.002 and draw a line parallel to the original curve, or with the same slope (E) as metal being tested.
  - Yield strength, or $\sigma_y$ is where this line intercepts the curve.
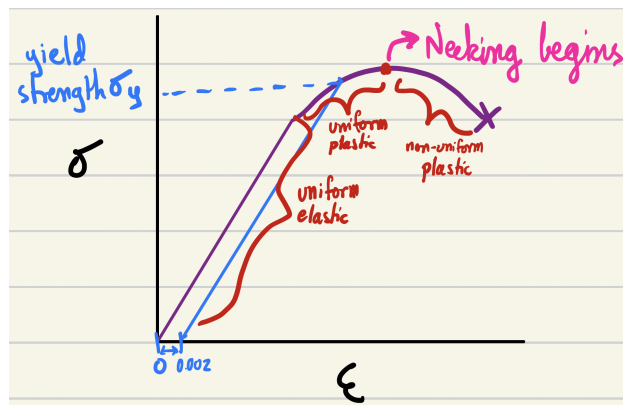


Figure 5: Labelled Stress-Strain Curve

**Uniform and Non-Uniform Deformation**

- Deformation is uniform until the ultimate tensile strength of unit yield strength.

- If deformation is distributed evenly and equally throughout the sample or if it is isolated to a region - physically manifests itself as necking.

- In tension, non-uniform deformation begins when a few metal bonds begin to break.

- In theory, bond breakage happens anywhere randomly on the sample. However, in practice, this happens on a spot of a small defect on the surface.

- During necking, the cross-sectional area in the neck gets smaller. Although the metal in the neck gets smaller, it does not get stronger as rapidly as the area decreases.

- The initial CSA is a constant whereas the actual CSA is rapidly decreasing.

- The force required to continue elongating the sample decreases and so we see the engineering stress decrease.

**Wrapping Up**

- Once we understand mechanism behind plastic deformation, we can look at how to design ways to make it more difficult.

- The mechanism involves rows of bonds breaking in a step-by-step fashion.

- Crystals are not all actually as perfect, they have imperfections that enable this.

# 7 Meddling With Matter

**The Dislocation**

- If we know the bond density, bond strength, and shear area, you could calculate the theoretical density of the crystal.

    - **WRONG!!!** This was tested and the theoretical value was found to be 5 times higher.

- The crystalline imperfection responsible for the step wise breaking down and reforming of bonds during plastic deformation is called the **dislocation**.

- Dislocations are always present in metals. We can lower the amount (called the dislocation density) by annealing (heating) a metal or increase it by plastically deforming.

- Dislocations are classified as linear imperfections.

    - When arrays of atoms are stacked on top of each other, one would see a dislocation line.
    - Step-by-step bond forming and breaking results in shearing.

- Interfering with dislocation movement, specifically making it more difficult, will make it stronger.

- There are four generally ways to strengthen a metal, they are organized according to the dimensionality of the defect population.

1. Zero-dimensional imperfections (point defects)

2. One-dimensional imperfections (linear imperfections/dislocations)

3. Two-dimensional imperfections (interfacial imperfections)

4. Three-dimensional imperfections (volume defects)

## Point Defects

**Interstitial Impurities**

Occurs when a single atom among many (remember atomic scale) exists where there is usually not a lattice point.

**Substitutional Impurities**

- When we find a carbon atom in a sample of steel - example of a solid solution impurity.

- Since carbon is much smaller than iron solvent, it's an interstitial impurity. Nickel, which fits in with iron, would have been a substitutional impurity.

**Vacancies**

- Vacancies are another type of point defect, whereby an atom has simply jumped out of its regular position.

- Atoms are trying really hard to jump out of their sites, because the binding energy is stronger than the thermal energy.

- We can consider vacancy formation as an ongoing battle between binding energy and the thermal energy trying to knock the atom out of its lattice site.

  - Arrhenius-type equation

  $$\frac{Nv}{N} = e^{-\frac{Q_v}{kT}} \tag{12}$$

  - $Nv/N$ is the ratio of the number of vacancies to the total number of possible atom sites, $Q_v$ is the energy required to form a vacancy, $k$ is the Boltzmann constant, and $T$ is the temperature in Kelvin.
  - Product of the Boltzmann constant and absolute temperature describes the thermal energy, which negative of the energy represents the energy holding the atom in the lattice (AKA binding energy).

- Question: if we raise the temperature to that thermal energy wins over binding energy, why doesn't the crystal just melt?

  - Short answer is that not all of the atoms have the same energy - it's a distribution.

- Vacancies have important implications in solid state chemistry, but we do not use them to improve the strength of metals.

# One-Dimensional Imperfections (or Dislocations)

- When we plastically deform metals, we create new dislocations.

- Dislocation density increases and dislocations have difficulty moving past one another.

- Strain fields surrounding dislocations interact, repelling each other or in some cases, cancelling each other and making small regions of perfect crystal.

- If unloaded and reloaded a sample, it would not physically deform until we reach stress we left it at in the earlier cycle.

- Industrially, we would typically perform the plastic deformation by rolling or pulling a metal part through or pressing a die.

- Most commonly we call this strengthening COLD WORK referring to fact that we get more strength with a cold metal.

  - However, we may warm up the metal to prevent it from becoming brittle - also called warm work.
  - There is also forging, warm and cold forging, STRAIN HARDENING.

# Two-Dimensional Imperfections

**Free Surfaces**

- When the material has a regular crystalline lattice until you hit the surface, where there are missing neighbour atoms.

- We don't usually use this type of defect to increase strength of a metal.

**Internal Interfaces or Grain Boundaries**

- A grain boundary is a type of internal surface.

- Crystals are formed individually as metal cools from liquid, they are randomly oriented and atoms certainly don't line up.

- For a dislocation to continue moving through these grains, it must cross grain boundary, which is a challenge.

  – The dislocation must change direction, because atomic plane that it is moving along is at an angle to other.

  – The atomic spacing along grain boundaries is higher, meaning dislocation needs more energy to navigate past the disruption.

  – Plane of dislocation does not line up with the plane in next crystal, meaning dislocation has to make a jump up or down.

- In general, increasing grain boundaries makes inhibits distribution movements.

## Three-Dimensional Imperfections

**Second Phase Particles**

- 3D imperfections happen when there is a second phase within a solid.

  – A region of a solid that has a different crystal structure, we have a second phase.

- A dislocation moving in a crystal has to then deal with everything discussed with grain boundaries.

  – Additionally, second phase particles are often hard & brittle compounds that are already hard to deform.

- Second-phase strengthening is a very important mechanism as many alloys contain solid phases.

# 8 Plastics and Polymers

**What is a Polymer Anyway?**

- Polymers are groups of largely repeating "mer" units.

  – In metals and ceramics we have unit cells that repeat many times, but in polymers it is this mer unit.

  – In polymers, the repeating unit usually repeats over one dimension (curvilinear).

- Each long string is really just a giant molecule.

  – The bonds that hold the atoms within the molecule is then the intramolecular force.

- Simple model of polymer a long string is a good way to explain and predict polymer behaviour.

  – Can also be used to explain softening and melting at elevated temperatures as well as chemical dissolution.

**Explaining Plastic Bag Stretch**

- Plastic bag handles stretch but at one point they stop.

- The string molecule in the bag are randomly oriented along the plane.

    - When stretched, the molecules begin to get parallel to each other in direction of applied stretch.
    - Bonds become aligned along the loading axis, actually makes bonds stronger.

- When a polymer is physically deformed, molecules slide past one another, overcoming a frictional force.

    - In a molecule, this friction force is between molecule, thus it's INTERMOLECULAR.
    - When atoms come together they first form primary then secondary bonds.

- Therefore, when we plastically deform a polymer and the molecule become aligned along the loading axis, we get an increase in load on primary bond.
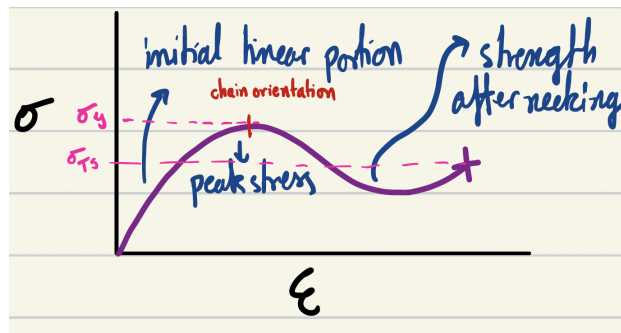
**Stress-Strain Behaviour of Polymers**



Figure 6: Stress-Strain Graph of a Polymer

- Polymers have some microstructural mechanism that allows us to strengthening in the neck very significantly.

- Change in proportion of primary to secondary bonds.

- Onset of necking is still at the peak of the curve.

- Alignment of polymer molecules with the loading axis is called CHAIN ORIENTATION.

**Defining Yield Strength and Tensile Strength**

- Difficulty to determine the point on the stress-strain curve for a metal where plastic deformation led to the establishment of the 0.2% offset yield strength.

- Since polymers can safely support a load after necking, we can use peak of curve to define peak strength.

- By convention, the point where the polymer fractures is called the tensile strength.

**How Long Are These Molecules, Really?**

- How do we quantify length of a specific batch of polymer?

  – When polymers are synthesized, it becomes somewhat difficult to control the length of the resulting molecules.

  – We are left with a distribution of molecule lengths.

- One way to consider molecule length is average of the distribution.

  – We generally use molar mass, but less commonly, molecular weight.

  – Number average molecular weight:

$$M_{number} = \sum_{n=1}^{j} M_n x_n \tag{13}$$

  for a sample containing $i$ groups, $M_n$ is the molecular weight of the nth group, and $x_n$ is the number fraction of the nth group.

- The number average calculated does not match the mass of any individual molecule.

  – The most descriptive way to convey the molecules is to convey the distribution itself.

- This molecular weight is another average. It's called th weight average molecular weight and is defined as:

$$M_{weight} = \sum_{n=1}^{j} M_n w_n \tag{14}$$

  for a sample containing $i$ groups, where $M_n$ is molecular weight of the nth group, and $w_n$ is the weight fraction of the nth group.

- By comparing averages we can get an indication of how broad the distribution is.

  – This is called dispensity but is sometimes called the the polydispensity index.

$$D = \frac{M_{weight}}{M_{number}} \tag{15}$$

- If all molecules were the same length, the dispensity would be one and distribution would be a vertical line.

- As the distribution spreads out, the dispensity increases from one.

**Why Do I Care About Molecular Weight Anyway?**

- It is difficult to separate one molecule because others are so long.

- Same is true for polymers and this is why molecular weight is so important.

- As we increase molecular weight, we increase polymer strength and increase strain to fracture because molecules get more entangled.

**How Do These Molecules Stack Up?**

- Polymer molecules, although linear, are not straight.

- Some order can develop when it is plastically deformed, called chain orientation.

- There are some ways that polymers can order themselves without any external loading.

  – Molecules like polyethylene can fold back on themselves, forming a semi-crystalline polymer.
  – Polymers are too long to crystallize 100%, which is why we see the amorphous regions.

- Crystalline domains are held together more strongly because they are on average more spread apart.

- HDPE has higher % crystallinity than LDPE. Since the crystalline regions are held together more by secondary bonds than amorphous regions, increasing crystallinity makes a polymer stronger.

  – It will also typically increase resistance to chemical dissolution and allow polymers to be used at a higher temperature.

**Changing the Intramolecular Bonds**

- If we wanted to make a strong polymer we can use elements with high electronegativity.

- We can bond it to something that is easy to make positive, like hydrogen.

- Hydrogen is special in its ability to create a strong dipole - we call it a special kind of bond called the **hydrogen bond**.

**Strong Primary Bonds**

- What if we created bonds like intramolecular bonds between a polymer?

  – That's what happens when we cross-link a polymer.

- Cross-links are ensure that molecules are pulled back to their original positions once a load is applied and released - an essential property of any elastomer.

- We want to avoid creating too many cross-links as that will make the polymer hard and brittle.

**Temperature Changes**

- Much of polymer behaviour is attributed to weak intramolecular bonds.

- These bonds, also called interactions, can be disrupted by the thermal energy.

**Increases in Temperature**

- There are two important temperatures when it comes to heating a polymer up.

  – Glass transition temperature, $T_g$, and
  – Melting temperature, $T_m$.

- Above melting temperature the polymer will flow like a thick liquid because enough thermal energy to disrupt intramolecular bonds and allow molecules to flow freely past each other.

- First thermal energy starts to beat bonds in amorphous region, before crystalline region, that temperature when amorphous regions are disrupted, is called glass temperature.

**Polymer Behaviour Over Time**

- Polymers can have very different behaviour depending on how quickly load is applied.

    - Tend to behave more brittle when loaded really quickly.

        * When loaded quickly, there is not enough time for them to move and polymer fractures.

- When load is applied over time, the polymer will become plastically deformed different amounts.

    - Will take a longer time for deformation to disappear as well.

        * Long-scale deformation is also called viscous deformation.

    - Molecules will move past one another more slowly, leading to a slow but permanent deformation process.

- Putting these two types of deformation together gives a good description of VISCOELASTIC DEFORMATION.

**Tell Me Again Why Plexiglass is Transparent?**

- What are the limitations to the noodle model?

- Optical transparency of Plexiglass comes from polymer being amorphous.

    - Doesn't explain why amorphous = transparent.

- The metal has a very complicated crystal structure so crystallization is slow - disorder does not get frozen in.

- So why is it that amorphous PMMA is optically transparent while amorphous metals always shiny and opaque.

# 9   We Need a Better Model

**What's Light Got to Do With It?**

- Optical transparency requires a lack of scattering events.

    - Neither full amorphous nor full crystallinity ensures 100% transparency.

    - Has to do with the way light is absorbed.

- Visible light makes up only a small portion of the electromagnetic spectrum.

- EMR is quantized, it exists as set units of energy called **quanta**, or **photons**.

$$E = \frac{hc}{\lambda} = hv \tag{16}$$

**Photoelectric Effect**

- Seen in experiments that measure electron emissions from a surface that results from energy deposited by incoming light.

    - By classical mechanics, light should accumulate energy gathers, but data showed that electron emission was a function of the frequency of light.

    - Einstein then explained in terms of quantization of light and won a Nobel Prize.

**Accelerating an Electron**

- We can find energy of a photon in joules but the unit is a little tedious.

    - Instead, we use a convenient unit of energy called the electron volt (eV).
    - Energy level is that you might find if we took an electron which is a charged particle and accelerated it through a volt.

- Electron charge is known as the fundamental charge, $1.602 \times 10^{-19} C$.

**The Bohr Model of the Atom**

- Niels Bohr developed the first model that explained quantitatively the experimental results of the time.

- Essential feature is a central nucleus with orbiting electrons at a fixed distance and may jump to a higher orbital.

- Issue is that it only allows for atoms with one electron - hydrogen.

**Quantum-Mechanical Model of the Atom**

- Current-best model takes a bit of quantum mechanics a but of classical mechanics to explain the atom.

- Also called the wave-mechanical model.

- We use four quantum numbers to fully explain the energy state of an electron.

**Principal Quantum Number**

- Describes the size of the electron orbit - which orbital level it lives in.

- Can have any integer value $\geq 1$.

**Angular Momentum/Azimuthal Quantum Number**

- Describes shape of the electron orbital.

- Can have any value from $l = 0, 1, 2, ..., n - 1$.

- Used for s, p, d, f subshells.

**Magnetic Quantum Number**

- Describes how many different ways each shell can be oriented.

- Each orientation is called an orbital.

- Has an integer value between $-l \leq m_l \leq l$.

- In any orbital there can be a maximum of two electrons.

**Spin Quantum Number**

- Does not describe anything intuitive.

- Describes the two slightly different energy levels any electron can have.

- $m_s = 1/2$.

**Magnitude of Electron Energy Levels**

- Energy level nearest to nucleus has the most energy.

- 4s subshell gets filled first, before 3d.

**When 4s is Closer Than 3d**

- Electron configuration before 4s gets filled is $3p^6$.

    – This is EC of argon, denoted as [Ar].

- At scandium and higher, with enough electrons to populate 3d shell, there is a shift in energy and 4s is filled after 3d.

    – When transition metals exist as ions, they lose 4s first.

# Atomic Bonding

**Ionic Bonding**

- Involves a transfer of electrons followed by a subsequent charge attraction between oppositely charged ions.

- Sodium has one more electron than stable octet, while chlorine has one less.

- Charge attraction is in general between all oppositely-charged ions.

    – The charge on an ion is not depleted by its participation in an ionic bond.
    – For this reason, ionic bonding is non-directional.

- Ionic solids do not conduct electricity since electrons are so strongly bound to their nuclei.

**Covalent Bonding**

- Covalent bonding involves the sharing or electrons.

- Because covalent bonds occur between specific atoms we call them directional bonds.

**Metallic Bonding**

- There are two main models used to describe metallic bonding: the sea of electrons model and the band theory of solids.

- Sea of electrons - Models the valence electron as not bound to a specific nucleus, but are instead thought to be free to move around while the nuclei are bound to their positions.

- Metal nuclei form what is known as the ionic curve.

**Explaining Some Properties**

- Understanding of covalent bonding, with electrons shared between atoms, helps explain electrical insulating property of polymers.

- Sea of electrons model can also be used as a model to explain durability of most models.

    – If sufficiently high stress is applied to a metallic crystal, eventually one plane of atoms will move past one another.
    – Generally possible for planes to move past each other since held by a sea of electrons.

- Ceramics would need to have similarly charged ions to allow planes to pass, but not possible since no sea of electrons.

- Polymers have much stronger covalent bonds, generally not broken.

- Electrical properties of polymers can be quite easily explained because all valence electrons are tightly bound in the strong covalent bonds.

**Bonding in Solids - Band Theory**

- Need to consider what happens to all these electron levels when a massive collection of atoms comes together.

- When atoms get close to each other, electrons risk having the same energy levels - called degeneracy.
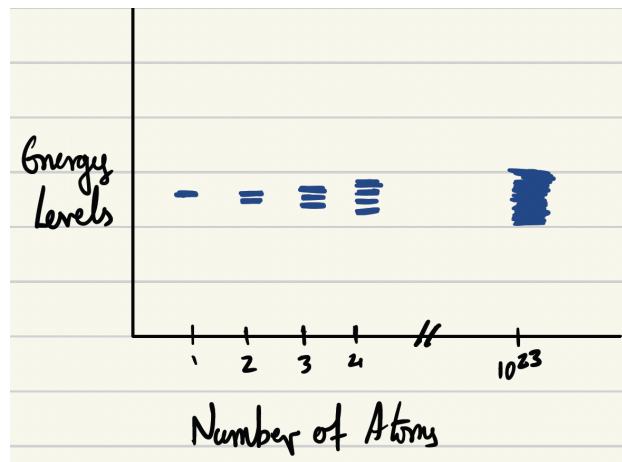


Figure 7: Energy Levels vs Number of Atoms

- As atoms approach one another, energy levels begin to spread out slightly so that for a given energy level in an isolated atom, there are two corresponding energy levels when two atoms close and so on.

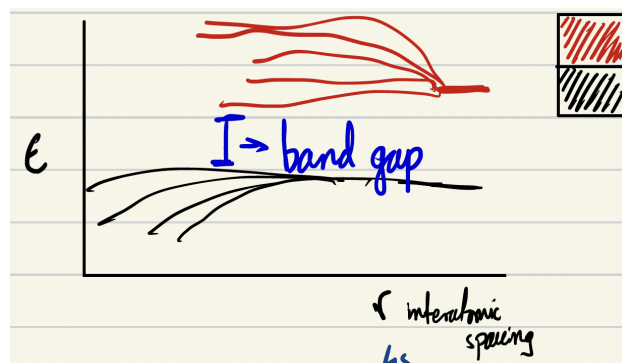- We have the possibility of electrons being promoted to energy levels that are essentially continuous.



Figure 8: Band Gap Between Two Electron Levels

20

**Bonding in Metals Like Copper**

- When a massive collection of copper comes together in a solid, the 4s energy levels spread out into a band, but only half of them will be filled.

- 4s can accept two electrons. Each of them has corresponding level in the band structure even though half are filled.

- Another metal that is a very good conductor is aluminum.

**Bonding in Metals Like Magnesium**

- Magnesium is a good conductor also.

- Even though 3s is filled, energy levels for 3p states spread out enough that they overlap with 3s levels.

**Bonding in Ceramics and Polymers**

- Ionic transfers happened so that each atom can achieve filled valence shell.

- Valence shell is filled so no electron energy states and also no free electrons.

- The above is also true for polymers.

**Bonding in Semiconductors**

- Semiconductors have a band gap that's not nearly as big as that of an insulator.

  - Means we can control the flow of electrons.
  - There is no formal band size of the gap that distinguishes semiconductors from insulators, but 4eV is good.
    * >4eV we can generally consider an insulator.

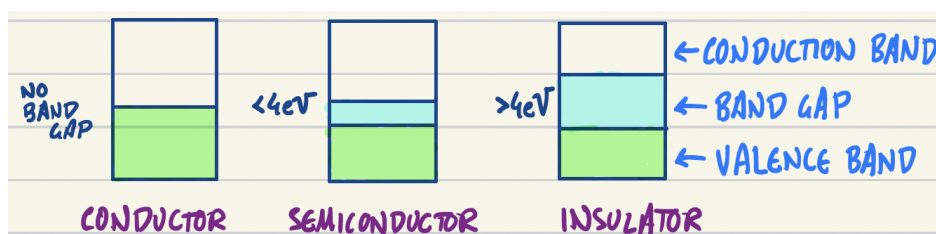- Thermal energy or photons can promote electrons across band gap in semiconductors.



Figure 9: Defining Conductors, Insulators, and Semiconductors

**Back to Light Again**

- Now we can consider what happens when a photon of 2-3 eV range interacts with the band structure of solid materials.

- If the material has a high band gap then photons will pass through and the materials will be transparent as all internal diffraction is barred.

- To minimize heat coming into a building, glass is coated with a thin layer of metal that absorbs photons in the UV spectrum.

  - Metals have no trouble promoting electrons and re-emitting them, thus are opaque and shiny.

## $sp^3$ Hybridization

- When a model fails, we propose a new one, or update the old one.

    - Proposed fix was to merge one s and three p orbitals to form 4 equivalent energy orbitals.
    - This helps solve the Si bond length problem we saw earlier.

## Semiconductors

We will introduce chemical imperfections into semiconductors to charge electrical conductivity.

### Intrinsic Semiconductors

- At very low temperatures, electrons become bound to the atoms sharing them.

- When temperature is raised or a voltage is applied, we get promoted electrons.

    - When an electron gets promoted into the conduction band, it leaves a broken bond.
        * This broken bond is a neutral charge among an array of negative charges (essentially positive).
    - However, when all else is negative, we see the broken bond/"missing thing" as a positive charge.
        * We call it a **hole**.

- We see that every electron promoted comes with a hole.

    - This type of semiconductor is called **intrinsic** because everything used to conduct electricity comes from the semiconductor itself.

- Not especially useful in practice since we always add impurities to control the flow.

- Since we think of electrons and holes as charged particles, it's possible for a current to exist.

    - Conductivity, $\sigma$, can be found if we know the concentration of electrons promoted to the conduction band.
    - We would also need the concentration of holes in the valence band, which we would call p.
    - We use $\mu$ to describe the electron and hole mobility.

- Finally, conductivity of an intrinsic semiconductor is:

$$\sigma = nq\mu_n + pq\mu_p \tag{17}$$

### Getting Excited

- Conductivity plotted versus 1/T follows Arrhenius dependence, and slope is a function of semiconductor band gap.

- In absorbing a photon of visible light, it excites an electron pair.

    - When electric field is put across silicon, electrons are detected as a current.

### Extrinsic Semiconductors

- To make intrinsic SCs practical, we typically add some impurities (called **dopants**) to control the conductivity.

    - Even when a small amount of dopant is added, its conductivity overpowers any intrinsic SC conductivity.

- We can dope a semiconductor in two ways:

- n–type doping, add electrons to the SC – electrons are Negative.
- p–type doping, add holes to the SC – holes are Positive.

- Since dopant atoms contribute so many more charge carriers to SC than are created through intrinsic promotion, we can neglect all intrinsic promotion and calculate conductivity of an n–type SC.

# 10 Free Energy?

**The Finger of Time**

- Two main laws that govern thermodynamics:
  - Internal energy is equal to difference of heat transfer in a system.
  - Entropy of the universe increases in any spontaneous reaction.

- Spontaneous reactions are those that proceed on their own without input of energy.
  - Spontaneity has nothing to do with a reaction being instantaneous.

- Basic understanding of entropy is disorder - measure of chaos and randomness in the universe.

**Reversibility**

- Subscript 'rev' stands for reversibility, meaning that heat is transferred reversibly.

- However, this is only a concept and not achievable in real life.

- It sets a theoretical limit that a process can occur in such tiny steps that it appears to always be in equilibrium.

**State Functions and Path Functions**

- To find the change in energy, we'd like to be able to calculate the energy change required to make the products and subtract energy required to make reactants.

- Potential energy and temperature are state functions.

- Other quantities, like work, are path functions as how we get from final to initial matters.

**The Gibbs' Energy**

- An extremely useful property that allows us to quickly determine spontaneity for a system without the need to calculate entropy changes for both the system and the surroundings.

- We'll first define a quantity called Gibbs' Free Energy, then determine why it's so useful.
  - $G = H - TS$
  - $\Delta G = \Delta H_{sys} - T\Delta S_{sys}$

- Return to second law of thermodynamics, written for spontaneity:
  - $\Delta S_{sys} + \Delta S_{surr} > 0$
  - Notice that Gibbs' energy is defined completely in terms of the system, so need to calculate anything for the surroundings.
  - At constant temperature, entropy change of the surrounding is heat entering divided by the temperature.

– With some manipulation, we end up with:

$$T\Delta S_{system} - \Delta H_{system} > 0 \qquad (18)$$

- We see that $\Delta S$ must have units in joules, meaning it is a type of energy. However, we're not comfortable with energy increasing in a spontaneous process, so we multiply it by $-1$.

$$\Delta H_{system} - T\Delta S_{system} < 0 \qquad (19)$$



Figure 10: Reaction Spontaneity Chart

# 11 Phase Equilibrium and Phase Diagrams

**The Temperature Axis**

- In material science the ordinate or y-axis usually depicts temperature.

- These phases result in the system being in the lowest energy level - or thermodynamically stable.

**The Composition Axis**

- We can add an abscissa or x-axis.

- Called the composition axis because it indicates the amount of the second component, sugar, that we are adding to our first component.

**Saturation: The Solubility Limit or Solvus**

- Maximum amount of solute that can be dissolved in a solvent is called the solubility limit, or solvus.

- Line must increase towards higher composition as the temperature is raised.

## Equilibrium Phase Diagram

- Phases indicated are the ones that would form if the reaction was allowed to run as long as needed to reach equilibrium.

- ANALOGY: Phase diagram for a spoon of sugar in coffee tells us it should dissolve, but now how long we need to stir it.
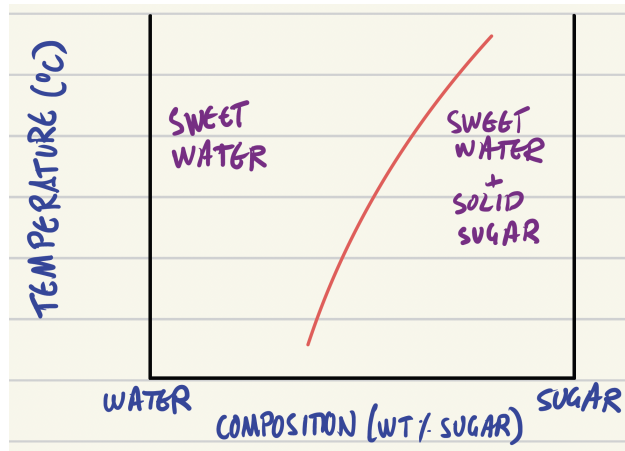
Figure 11: Temperature and Composition Chart

**Some Terminology**

- Phase - a part of the system we are looking at that behaves and looks the same way.

- No separate parts in a single phase region.

- An area on a phase diagram bounded by lines, or phase boundaries, is nothing more than temperatures and compositions that have the same phase as the stable phase.
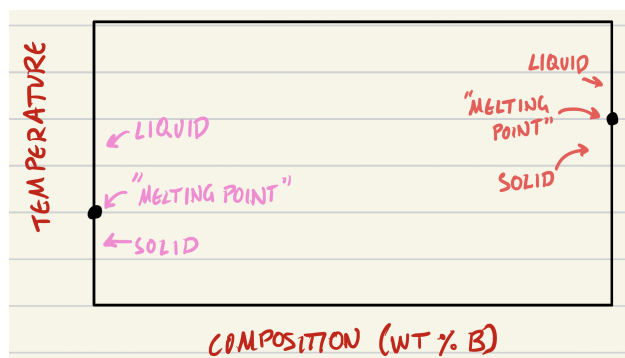


Figure 12: Binary Phase Diagram

**The Tie Line**

- On a binary phase diagram, the tie line is a fancy term for a horizontal line spanning two phase regions from a phase boundary on one side to a line on the other side.

- Drawing the tie line does several things.

  - Tells us what phases are in the two phase region.
  - Tells us how much of each component is in each of the two phases (the composition).
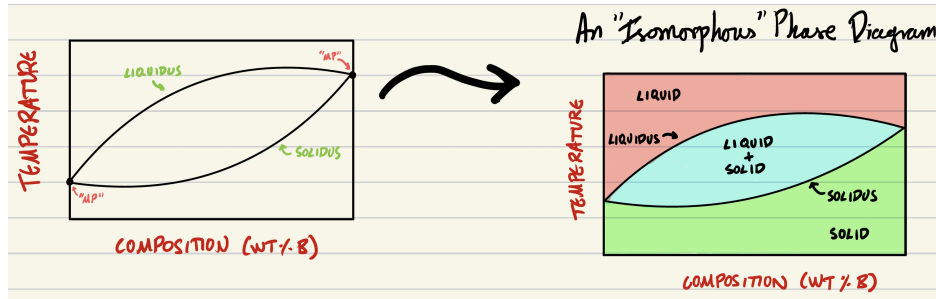  - Forms the basis of the lever rule calculation.

Figure 13: Isomorphic Phase Diagram

**The Lever Rule**

- To find the amount of component B, we can multiply the overall composition by 1 kg.

- But should it be more liquid or more solid?

- If system is close to solidus, then it should be mostly solid and vice versa.

- Same logic applies if the system was heated to a point where it's a liquid.

**Mass Balance Gives Us the Lever Rule**

- We commonly call this the Lever Rule.

$$W_L = \frac{C_S - C_O}{C_S - C_L} \tag{20}$$

- It defines the fraction of the tie line on one side of the overall composition divided by the total length of the line.

- Always take the opposite side of the lever than the one we're interested in.
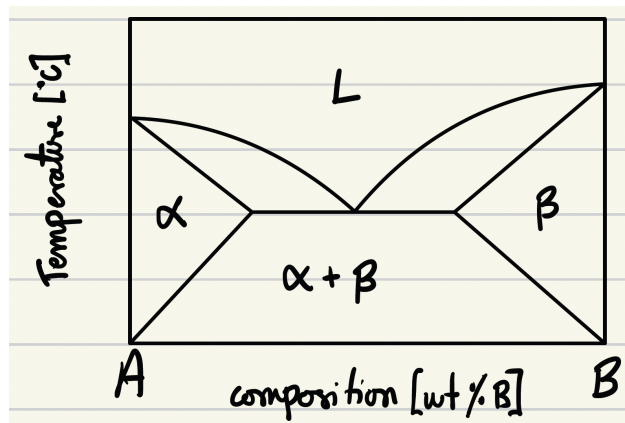
**So What is a Eutectic?**



Figure 14: Binary Eutectic System

- Binary eutectic phase diagrams for a system with one specific melting point that is below the melting point for each of the components.