

# MSE160 Notes

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# 1 Introduction

## 1.1 Types of Material

- There are three classes of material (though not all materials fall under these categories):
  - Metals
  - Ceramics
  - Polymers
- **Metals** (e.g. Fe, Cr, Cu, Zn, Al) are held together with *metalic* bonds and is described by **bond theory**.
- **Ceramics** (e.g. porcelain, concrete) are held together with *ionic* bonds and are *brittle*. A lot of them are metal oxides.
- **Polymer** (Teflon®, Gore-tex®, polyethylene) *tend* to be from *covalent bonds*

**Warning:** The word plastic actually describes a material property, and not a material type. There are plastics that are not polymers.

- Examples of materials that do not fall under this classification scheme include wood, skin, superconductors, and more.

## 1.2 Elastic Behaviour

- Hooke's law tells us that  $F = -k\Delta x$ , where  $\Delta x$  is the displacement from equilibrium.
- **Engineering stress** is defined as  $\sigma = \frac{F}{A_0}$  where  $A_0$  is the *initial* (unloaded) cross-sectional area.

**Warning:** Due to material properties, the cross sectional area of a spring can change as it elongates or compresses, so the engineering stress only refers to the initial cross sectional area. The *true stress* refers to the force divided by the real area.

- **Engineering strain** is defined as  $\varepsilon = \frac{\Delta \ell}{\ell_0}$  and the two are related via the **Young's Modulus**:

$$\sigma = E\varepsilon \quad (1)$$

- There are two possible definitions for elastic deformation. When viewing it from a macroscopic perspective:

**Definition:** During elastic deformation, the sample dimensions return to their original dimensions upon unloading.

but it is also possible to view it from a microscopic perspective:

**Definition:** During elastic deformation, atoms return to their original positions upon unloading.

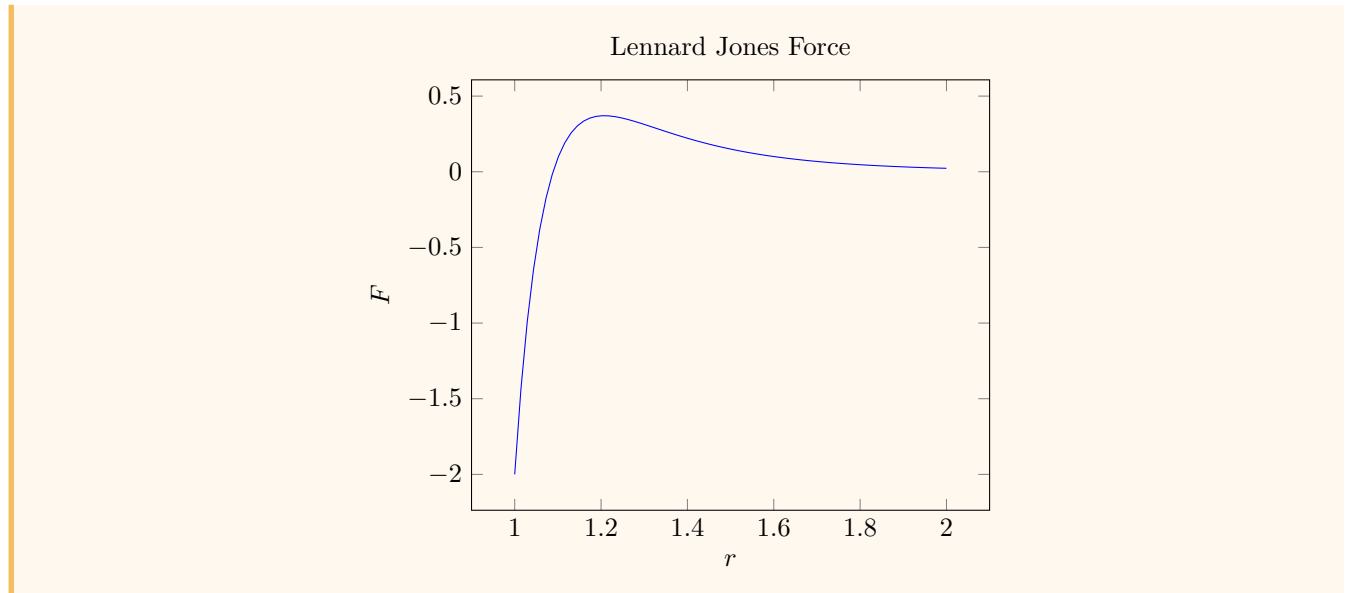
## 1.3 Simple Model for Bonding in solids

- A crude (but quite accurate) model is to assume nearby atoms in a solid are connected by springs. (This is actually Einstein's model of solid, except he modeled the interactions as quantum harmonic oscillators)

**Idea:** A more realistic model would be using the Lennard-Jones potential, which gives the force between two atoms as:

$$V = -\frac{a_1}{r^{13}} + \frac{a_2}{r^7} \quad (2)$$

and is graphically represented below (here,  $a_1 = 5$  and  $a_2 = 3$  for illustration purposes only)



When the two atoms are close to each other, the force scales roughly linearly with displacement, which is exactly the description of Hooke's Law.

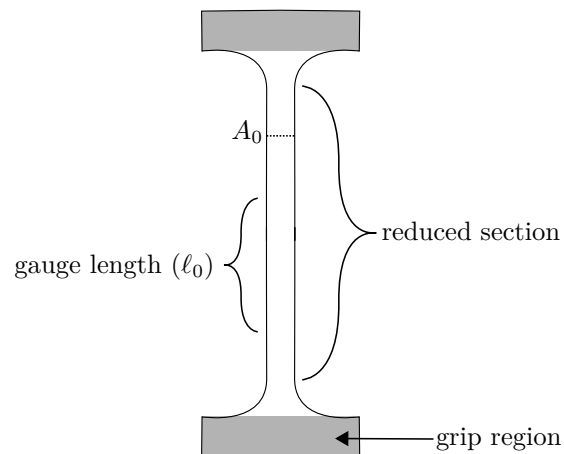
- Specifically, the Young's Modulus can be recovered by defining it as:

$$E \propto \left. \frac{dF}{dr} \right|_{r=r_0} \quad (3)$$

where  $r_0$  is the equilibrium distance and is only dependent on the material. Permanently deforming a metal will not change its Young's Modulus.

## 1.4 Getting a stress-strain curve

- The tensile specimen is in a **dogbone** shape as illustrated below: and the test is performed by gripping the grip



regions and performing a uni-axial tension test.

## 1.5 Poisson's Ratio and Shear

- When a material deforms, it does not deform in only one direction. The **poisson's ratio**  $\nu$  relates the strain in all three directions:

$$\nu = -\frac{\varepsilon_R}{\varepsilon_Z} = -\frac{\varepsilon_x}{\varepsilon_z} = -\frac{\varepsilon_y}{\varepsilon_z} \quad (4)$$

for a cylindrically symmetrical material.

- Shear stress is defined as

$$\tau = \frac{F}{A_0} \quad (5)$$

and shear strain is defined as:

$$\gamma = \frac{\Delta \ell}{\ell_0} \quad (6)$$

- Similarly, shear stress and strain is related via the shear modulus  $G$ :

$$\tau = G\gamma \quad (7)$$

- The Young's modulus and the shear modulus is related via the poisson ratio:

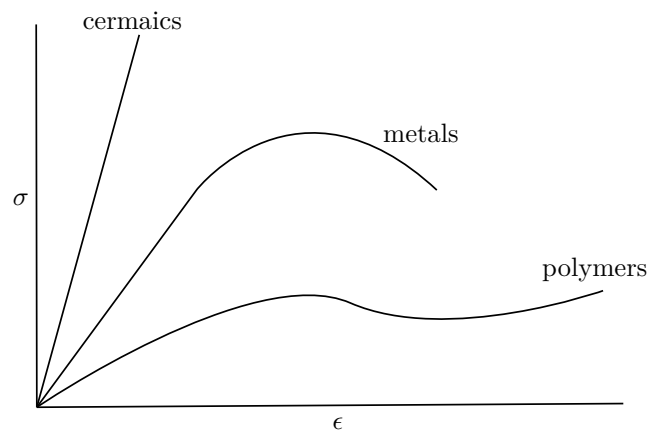
$$E = 2G(1 + \nu) \quad (8)$$

## 2 Inelastic Behaviour

- Permanent deformation can be defined in three ways:
  1. Upon unloading, sample does not return to original dimensions
  2. Strain does not return to zero
  3. Atoms move to new positions
  4. Occurs near the end of linear behaviour
- Plastic comes from the greek word *plastikos*, which means to shape or to sculpt. In this course, plastic does not refer to the material type but instead the permanent deformation.
- The **strength** of a material describes when the permanent deformation occurs.

**Warning:** Strength depends on context and is not always defined as above.

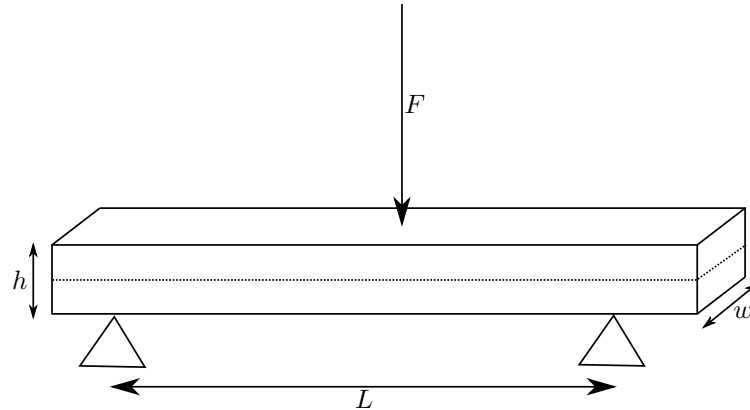
- The stress strain curve for different materials resemble different shapes.
  - Polymers have a distinct yielding region
  - Metals start a concave down behaviour as soon as elastic deformation ends
  - Ceramics have linear behaviour all the way until they fracture



- For polymers, the use of *Young's Modulus* is misleading since the elastic behaviour depends on several different types of bonds, while Young's Modulus is related to the behaviour of a single bond. As a result, the term **elastic modulus** is used to describe polymers and composite materials.

## 2.1 Ceramics

- Ceramics are not typically tested in tension because:
  1. It is difficult to grip because it crumbles easily
  2. It is difficult to shape it into a dogbone shape
  3. Machine alignment is difficult to achieve.
- Instead, we test them by **3-point bending**:



- The dotted line is the neutral axis and since it is weak in tension, the plate will break in the lower half at a stress value of:

$$\sigma = \frac{3FL}{2wh^2} \quad (9)$$

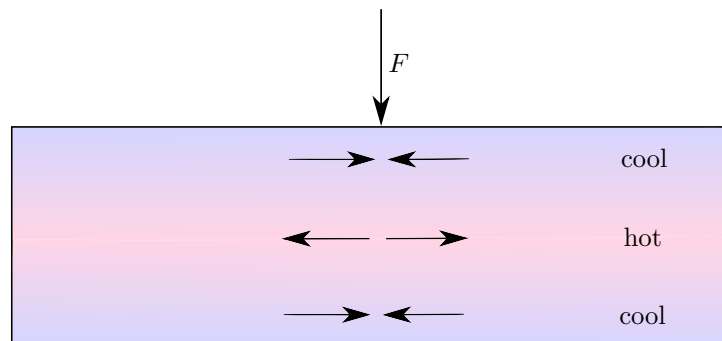
## 2.2 Tempered Glass

- **Tempered glass** has a very high strength and is relatively “safe” when it fractures (small pieces instead of large ones)

**Idea:** Initially, tempered glass is very hot in a large volume. However, as it rapidly cools, the surfaces cool faster than the center. Since glass is made of silica bonded to four oxygen, it forms a very complex network structure. Therefore, during this rapid cooling, it “fixes” in excess volume.

The regions in the middle that are cooling more slowly is trying to contract but is constrained by the outer surface that it goes into tension. The fast cooling regions on the other hand will be in tension.

- When the glass bends, the opposite side of the window can still be in considerable compression even though for a regular ceramic it should be in tension. This increases the strength.



- The stress distribution creates **residual stress** which results in stored strain energy. When the glass gets fractured, the stored strain energy gets transformed into **surface energy**.

- Since surface energy is proportional to surface area, this means that the fractured pieces are smaller.
- **Chemical processes** can also be used to create tempered glass, such as gorilla glass. Ions with a larger size diffuse into the surface and take up a larger space in the network resulting in an increase in volume at the surface.

### 3 Structure Property Relationship

- If we plot the relationship between the Young's Modulus and the density, we find that there are no materials with a high Young's Modulus and a low density and that most materials fall on a single line.
- The **materials performance index**  $MPI$  for a beam is defined as:

$$MPI = \frac{E^{1/2}}{\rho} \quad (10)$$

*Proof.* The deflection of a beam takes the form of:

$$\delta = \frac{FL^3}{CEA^2} \implies A = \left( \frac{FL^3}{CE\delta} \right)^{1/2} \quad (11)$$

and using the equation:

$$m = AL\rho \quad (12)$$

we are able to retrieve the equation above.  $\square$

- If we were to plot the Young's Modulus against the density on a log-log scale and draw out the curve:

$$\log E = 2 \log \rho + \log MPI \quad (13)$$

then materials on the same line would have the same materials performance index. If we shift this line to the left, the performance index of the material improves.

- For a beam, performing this analysis will give us composites such as carbon fibre. Ceramics also belong in this category but because they are susceptible to catastrophic brittle fracture, we can ignore them.
- For a loaded plate, the MPI is:

$$MPI = \frac{E^{1/3}}{\rho} \quad (14)$$

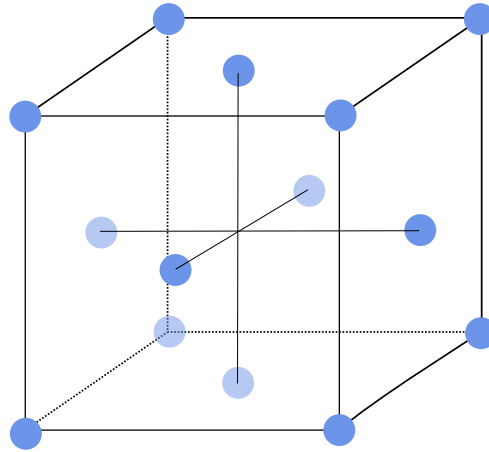
and the best in this category is wood.

- **Polycrystalline** refers to materials made of crystals, typically around the micron scale.
- Most metals and some ceramics are crystalline (e.g. sapphire), but not everything is. **Amorphous** materials are not organized, an example being window glass.
  - Long-range order refers to a organization at a distance well beyond the nearest neighbour
  - Short-range order refers to organization at only the first or second nearest neighbour.
- One such highly organized material has a **face-centered cubic** (FCC) structure. Many metals have this organization:
- Each of the eight corners have  $\frac{1}{8}$  of an atom and each of the six faces have  $\frac{1}{2}$  of an atom, which gives:  $n_{\text{FCC}} = 4$  atoms in a unit cell.
- Given  $n$ , we can calculate the density of an FCC material such as aluminium, via:

$$\rho = \frac{nA}{a^3 N_A} \quad (15)$$

where  $a$  is the length of the unit cube known as the **lattice parameter**,  $A$  is the molar mass, and  $N_A$  is Avocado's number.

- Based off of the hard sphere model, we treat atoms in ordered solids as hard spheres that make contact with their nearest neighbours. However, this is very hard to draw so we will go by the *reduced sphere* model by drawing atoms smaller.



**Example 1:** Suppose we wish to find the theoretical density of Aluminum, which is a FCC structure. We are given:

$$A = 26.892 \text{ g mol}^{-1}$$

$$R = 143 \text{ pm}$$

The lattice parameter is given by:

$$a = 2\sqrt{2}R \quad (16)$$

which gives us:

$$\rho = \frac{nA}{(2\sqrt{2}R)^3 N_A} = 2.71 \text{ g cm}^{-3} \quad (17)$$

- The **atomic packing factor** is given by:

$$\text{APF} = \frac{V_{\text{spheres}}}{V_{\text{unit cell}}} \quad (18)$$

Since the unit cell is a cube with volume  $a^3$ , we have:

$$\text{APF} = \frac{4\pi R^3 n}{3a^3} \quad (19)$$

and for FCC:

$$\text{APF} = \frac{16\pi R^3}{3a^3} \quad (20)$$

We can also relate the  $R$  and  $a$  together via:

$$a = 2\sqrt{2}R \quad (21)$$

for FCC packing, which yields:

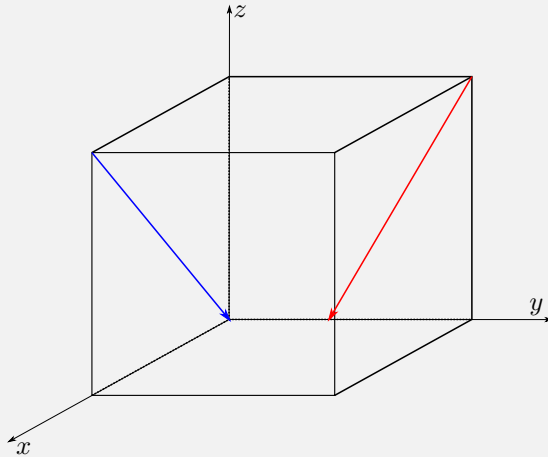
$$\text{APF}_{\text{FCC}} = \frac{\pi}{3\sqrt{2}} \approx 0.74 \quad (22)$$

which is the highest possible value. The maximum fraction that a volume can be filled up is 74%.

## 4 Crystallographic Planes and Directions

- We develop a set of notation to describe directions. It comes with a set of rules:
  - Translate vector, if it simplifies things.
  - Determine projection onto  $x$ ,  $y$ ,  $z$ .
  - Reduce to lowest integers.
  - Enclose in square brackets (negative signs are moved above, no commas)

**Example 2:** We can find the crystallographic directions of both the blue and the red vectors in the figure below.



For the blue vector, we first let the tail be by the origin. The vector travels 1 in the negative  $x$  direction, 0 in the  $y$  direction, and  $-1$  in the negative  $z$  direction, which gives  $[\bar{1}0\bar{1}]$ .

For the red vector, it travels in the negative  $y$  direction for 0.5 and in the negative  $z$  direction for 1 so we get, after getting rid of fractions:  $[0\bar{1}2]$ .

- To denote a family of directions, we can use bracket notation. All face diagonals can be written as:

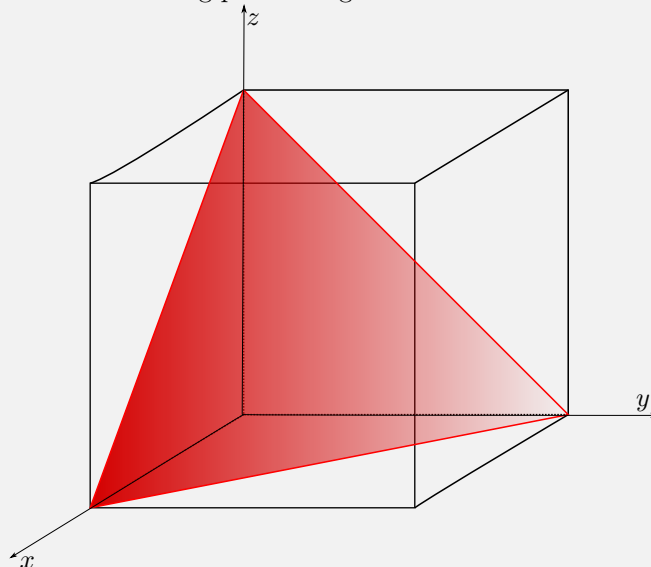
$$\langle 011 \rangle \quad (23)$$

which includes:

$$[011], [0\bar{1}1], [01\bar{1}], [101], \dots \quad (24)$$

- To determine crystallographic planes, we use **crystallographic planes**. It uses the following set of rules:
  - Translate plane so origin is not on the plane (defining new origin).
  - Determine distance to intercept plane by travelling along each axis, from the origin.
  - Take the reciprocal of the distance.
  - Enclose in parentheses (use  $h, k, \ell$ ). Negatives go above, no commas.

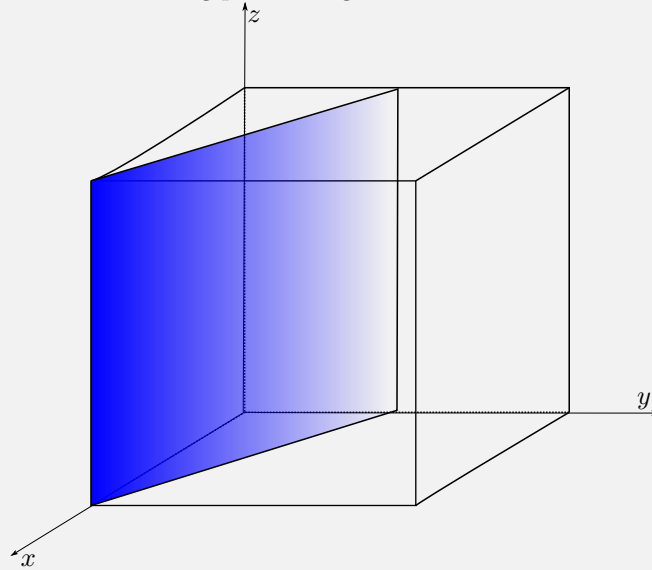
**Example 3:** We can represent the following plane using Miller indices:



We can start from the origin and travel a length of 1 in both the positive  $x$ ,  $y$ , and  $z$  direction. Taking the reciprocal, we still have 1, 1, 1, so the final miller index is  $(111)$ .



**Example 4:** We can represent the following plane using Miller indices:



We can start from the origin and travel a length of 1 in the  $x$  direction,  $1/2$  in the  $y$  direction, and  $\infty$  in the  $z$  direction. Taking the reciprocal we get  $(1\ 2\ 0)$ .

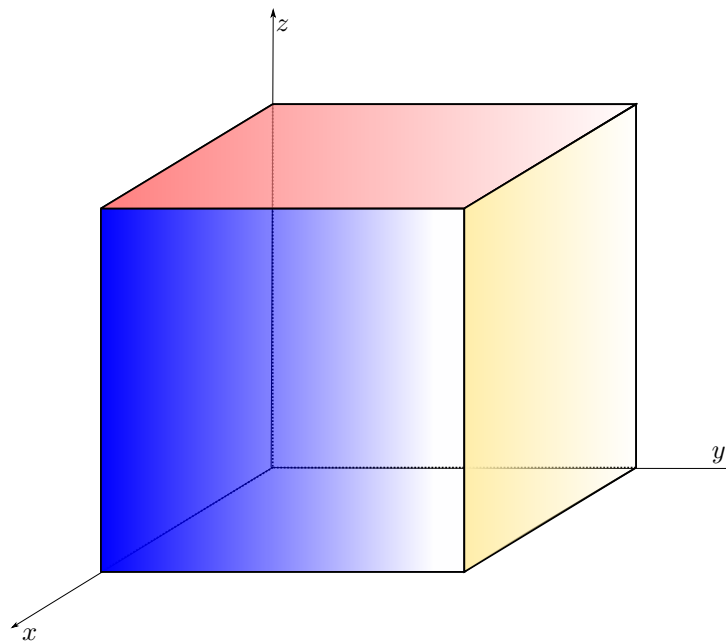
- We can represent **families of planes** using curly braces. For example, faces of a cube can be represented by:

$$\{001\} \quad (25)$$

which represent the following planes:

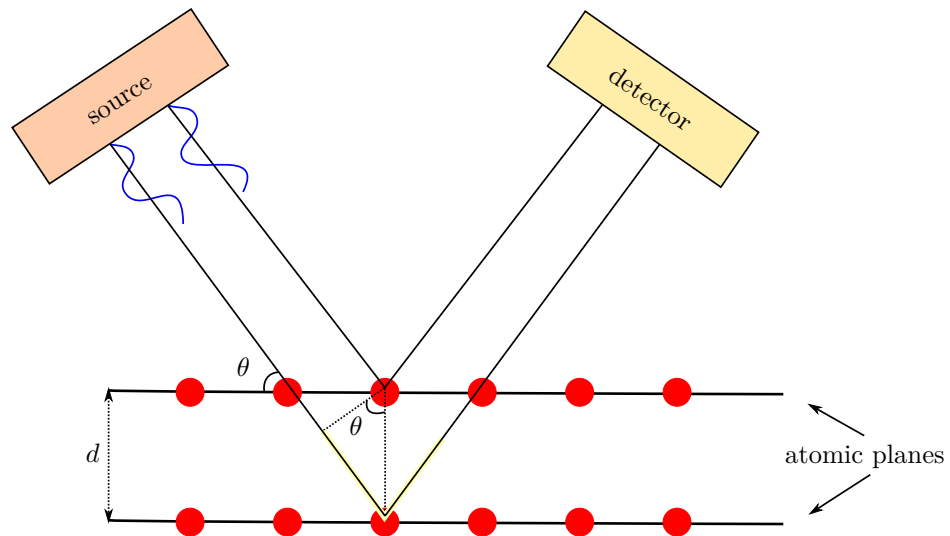
$$(100), (010), (001) \quad (26)$$

corresponding to the below blue, yellow, and red plane respectively:



## 5 X Ray Diffraction

- Suppose there is an x-ray source that reflects off a sample and hits a detector at a certain angle  $\theta$ . If we plot the intensity as a function of  $\theta$ , we see that it peaks at very specific values.



- This is a result of constructive interference where the peaks of both wavelengths add up at the detector.
- This will only occur if the extra distance (shown in yellow) is an integer multiple of the wavelength  $\lambda$ . Mathematically:

$$2d \sin \theta = n\lambda \quad (27)$$

known as **Bragg's Law**, where  $n$  is an integer.

- The interplanar spacing is related to the  $hkl$  miller indices via:

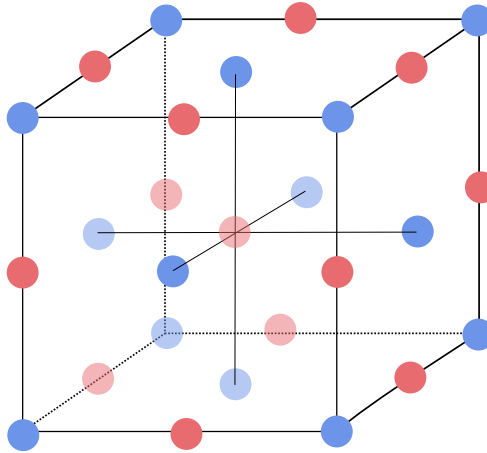
$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (28)$$

## 6 More Structures

- We begin our discussion of various more complicated crystal structures.

### 6.1 Rock Salts

- A common crystal structure are **rock salts**, such as NaCl, MgO, FeO, ...
- The rock salt structure is visualized below, with blue representing anions (negative) and red representing cations.



Notice that the number of cations and anions are equal in a unit cube. It consists of three layers, with cations and anions alternating across each layer such that all adjacent neighbours have a parity charge. As a result, we have  $n = 4$ .

- We can define the **coordination number** as the number of atoms directly adjacent to a particular atom. For rock salts, the coordination number is 6.
- The theoretical density can be calculated as:

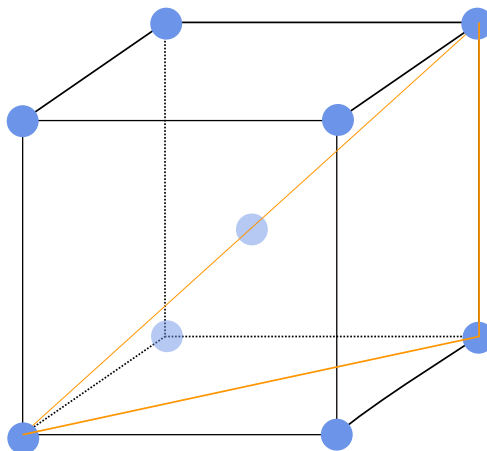
$$\rho = \frac{n_c A_c + n_A A_A}{V_c N_A} \quad (29)$$

where for a rock salt,  $a = 2R_A + 2R_c$ .

**Warning:** Anions do *not* touch along face diagonals for a rock salt. Instead, they touch their adjacent neighbours only.

### 6.2 Body Centered Cubic

- Another common structure are **body centered cubic (BCC)** crystals.

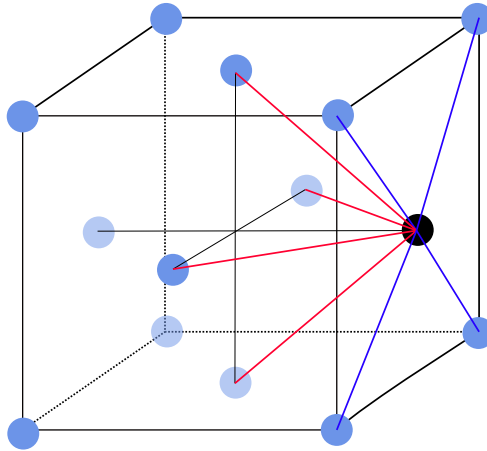


They consist of atoms at the corners of the cube with another atom at the very beginning. As a result, we have  $n = 2$ .

- To calculate the lattice parameter, we can apply Pythagorean's theorem:

$$a^2 + a^2 + a^2 = (4R)^2 \implies a = \frac{4}{\sqrt{3}}R \quad (30)$$

- The coordinate number of a BCC structure is 8 since each atom is directly adjacent to eight other atoms.
- The coordinate number of a FCC structure is 12. This is harder to see but can be illustrated below:



Suppose we look at the black atom located on the rightmost plane. It is  $a/\sqrt{2}$  away from the other four atoms on its face, but it's also  $a/\sqrt{2}$  away from four other atoms (shown in red). Since the unit cell pattern repeats forever, by symmetry, there must be four more atoms it touches on the other side (if pattern continues).

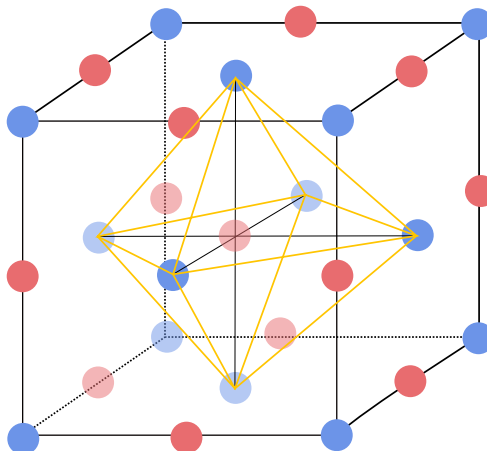
- The atomic packing factor for BCC is given by:

$$APF_{\text{BCC}} = \frac{n \frac{4}{3}\pi R^3}{a^3} \approx 0.68 \quad (31)$$

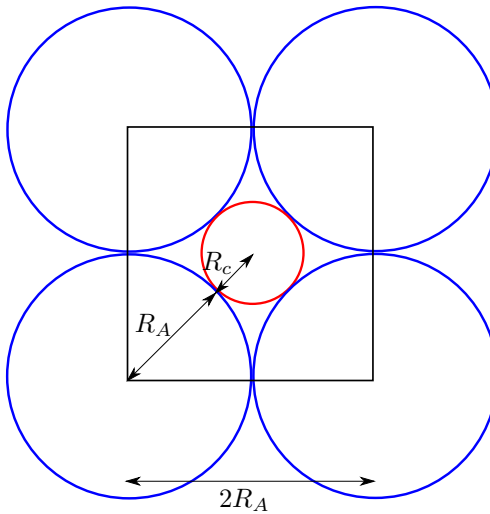
which is below the 0.74 atomic packing factor for FCC.

### 6.3 Interstitial Sites

- An interstitial site is a position between the atoms that can be occupied by other atoms.
- An octahedral interstitial site exists within rock salt crystals, illustrated below:



The yellow outline forms an octahedron with eight faces, and the red ion is placed in the octahedral site. We can calculate exactly the maximum size of  $R_c$  with respect to  $R_A$  by consider a two dimensional plane:



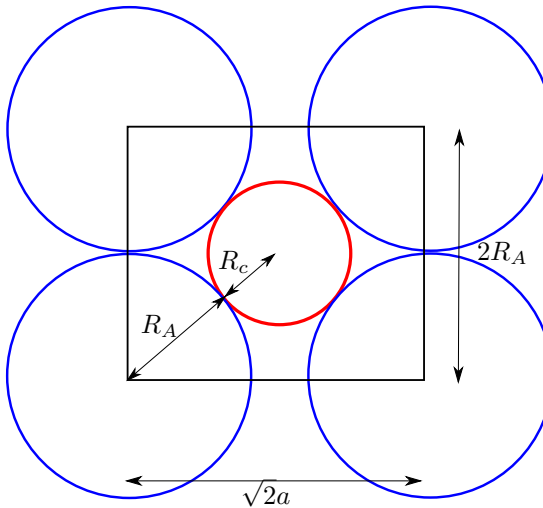
We see that:

$$R_A = (R_A + R_c) \sin(45^\circ) \quad (32)$$

and we get the ratio to be:

$$\frac{R_c}{R_A} = \frac{1 - \sin(45^\circ)}{\sin(45^\circ)} \approx 0.414 \quad (33)$$

- We can perform a similar calculation for a body centered cubic by slicing a plane across the diagonal:



and we get a similar result:

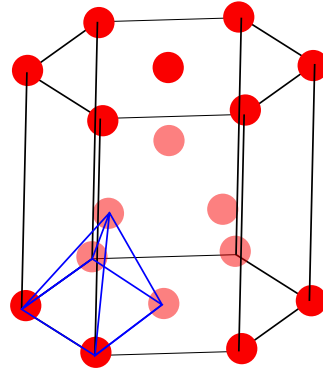
$$\frac{R_c}{R_A} = \frac{1 - \sin \theta}{\sin \theta} \quad (34)$$

Here,  $\theta = \tan^{-1}\left(\frac{1}{\sqrt{2}}\right) = 35.3^\circ$  which gives:

$$\frac{R_c}{R_A} \approx 0.732 \quad (35)$$

## 6.4 Hexagonal Close Packed

- Another common packing structure is **hexagonal closed packed** (HCP). It has the same atomic packing factor as FCC:



It consists of atoms stacked in an *ABA* pattern in hexagons. If we continue the pattern for several unit cells and connect the centers of the atoms in each layer, it will form a hexagonal honeycomb shape.

- The height of this unit cell is  $c = 1.633a$  where  $a = 2R$  is the side length. The volume of the prism is given by:

$$V = \frac{3\sqrt{3}}{2}a^2c \quad (36)$$

- Similar to an FCC structure, each atom in HCP has a coordinate number of 12.
- These similarities between FCC and HCP are not a coincidence. It's possible to stack face centered cubic unit cells such that it forms a HCP structure.

## 6.5 Examples

- Aluminum is a fascinating example of a FCC structure. It starts off as a thin flat piece of aluminum and through a series of plastic deformations, it's able to elongate.

This shows that FCC and HCP lead to materials that can experience greater plastic deformations. This is because the layers can shift and “snap” into place.

- Recall that iron has a BCC structure. The spacing of atoms along the diagonal and the edges are not the same. As a result, we can expect the Young's Modulus in these two directions to also differ and this is verifiable.
- We can also look at the differences between the behaviour of a metal versus the behaviour of a ceramic.
  - In metals, planes are able to slide past each other. The result is plastic deformation.
  - In ceramics, we cannot have a lot of plastic deformation using the rock salt crystal structure. If planes do attempt to slide, like charges would overlap and would create fracture.

## 7 Technical Mechanical Behaviour

- The ultimate tensile strength, denoted as *UTS* or  $\sigma_{UTS}$  is the highest stress that a material can occur in a material.
- The *proportional limit* describes the point on the tensile stress-strain curve where elastic deformations no longer occur.
- Along with the yield strength, it is difficult to define this objectively. Instead, we use the following convention:

**Definition:** The yield strength is the stress value at which if the material is unloaded at that point, the strain will be  $\epsilon = 0.002 = 0.2\%$ .

- Uniform deformation occurs when the thickness of the material is uniform. Non-uniform deformation occurs when an increase in strain results in a decrease in stress. This is known as **necking**.
- Crystalline imperfections are called **dislocations**. The dislocation density can be reduced by heating (annealing), and plastic deformation can increase the density.
- Dislocations are known as **linear imperfection** as they can form a “tunnel” like bonding environment where there is a dislocation line.

- Plastic deformation is the result of the step by step movement of linear imperfections:
  1. As a force is applied, the bonds to the right of the dislocation stretch and eventually break
  2. A new set of bonds re-forms
  3. This breaking and re-forming happens again
  4. And again, and so forth.

**Warning:** Remember that this mechanism is *not* the breaking of all bonds at the same time on a plane of atoms.

- It is possible to classify imperfections:
  - 0-dimensional: point defect
  - 1-dimensional: linear imperfections (dislocations)
  - 2-dimensional: interfacial imperfections (grain boundaries, free surfaces)
  - 3-dimensional: volume defects (pores, 2nd phases)

## 7.1 Point Defects

- An example of a 0-dimensional imperfection is an **interstitial impurity**, for example putting in the much smaller carbon atoms in a lattice with iron atoms.
- A substitutional impurity is when an atom gets replaced by another atom, and satisfies the following conditions:
  - Same crystal structure
  - Similar size (usually 10%)
  - Similar electronegativity (prevent unwanted reactions)
- These impurities can disrupt the intermolecular interactions, causing other atoms to move slightly from their original equilibrium location. This is known as **lattice strain**.
- A **vacancy** is when an atom is missing altogether. The number of vacancies is given as:

$$N_v = N \exp\left(-\frac{Q_v}{kT}\right) \quad (37)$$

where  $Q_v$  is the energy to form vacancies,  $k$  is the Boltzmann constant,  $T$  is the temperature, and  $N_v$  is the number of vacancies.

- We can obtain interesting behaviour if we introduce two impurities (i.e. a dislocation and a interstitial impurity). We can often find that impurities diffuse towards dislocations (state with less energy). This is known as a **pin dislocation**
- Impurities can also inhibit dislocation movements.
- Adding impurities creates defects, but defects aren't bad. Most of the time, they are able to inhibit dislocation movements, which actually increases the strength of the material!

## 7.2 One-dimensional Dislocations

- There exists strain fields that surround dislocations (areas of tension and compression). They can repel or under special circumstances, cancel out, leaving a small region of a perfect crystal structure.
- Since plastic deformation is able to increase the dislocation density, it makes it harder for lattices to slide past each other. As an industry practice, this is known as **cold work** and plastic deformation is known as **forging**
- **cold forging** and **hot forging** is used to classify the different types of forging, as it can involve very high temperatures sometimes.
- Because the metal accumulates plastic strain during the strengthening process we also use the term strain hardening.

### 7.3 Two-dimensional Dislocations

- Atoms at a free surface have fewer nearer neighbours cause be a smaller amount of unsatisfied bonds. This causes atoms at the surface to be at a higher energy state. For water, this behaviour at the surface is known as the **surface tension**.
- However, we are interested in what happens at an internal surface. Suppose we have two separate crystals (or grains) initially growing independently. However, when these two grains come into contact, it creates a *two-dimensional dislocation*.
- The dislocation at the grain boundary will have to:
  - Change direction
  - Planar Mismatch
  - Lattice Strain

As a result, grain boundaries inhibits dislocation movement and strengthens metals by decreasing grain size.

### 7.4 Three-Dimensional Dislocations

- Pores can be thought of “bubbles” in a material. They can be visible to the naked eye or may be finer.
- A second phase is when we insert a different material with a different crystal structure to strengthen materials (i.e.  $Fe_3C$ )
- Similarly to before, it is difficult to navigate across these phases.

## 8 Polymers

- A useful analogy for polymers is to imagine a *molecular hand*. A polymer is consisted of several twisted and tangled chains of molecules. This is known as *entanglement*. This is due to the non-linear nature of the polymers and the fact that bonds can rotate.
- To plastically deform a polymer, we can imagine a microscopic hand pulling a polymer. If you are able to do so, then it is seen as plastic deformation
- The molecular chains are connected via weak intermolecular forces. Increasing the temperature increases the vibration, allowing the molecular hand to more easily separate them.

**Idea:** When a polymer undergoes a physical transformation (i.e. melting, dissolving, deforming), it is due to the intermolecular interactions, not the intramolecular interactions.

**Case Study:** Plastic exhibits very interesting behaviour when it is stretched. During plastic deformation, the molecules can line up, which can cause the following physical changes:

- Color change (lighter)
- Strong in the direction of stretching
- Weaker in the direction perpendicular to stretching

The polymers become *oriented* (also known as *conditioned*) with the loading axis. This is a great demonstration that shows how polymers can be thought of as an interconnected mix of long polymer chains.

- We define the yield strength as the point in which necking occurs (first local maximum in the stress-strain curve)

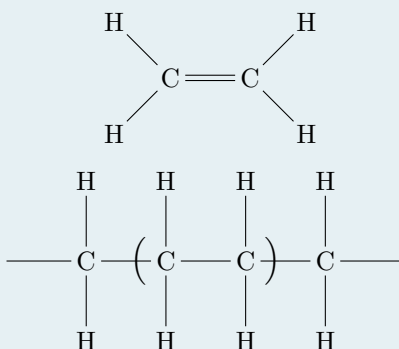
### 8.1 Chemical Basics

- To describe the polymers on a molecular level, we look at it from an organic chemistry perspective. Instead of unit cells, we look at *mer* units (the suffix of *polymer*), which is the starting molecule when building the polymer.

**Case Study:** Polyethylene (PE) is a polymer that is consisted of ethene (or more commonly known as ethylene), shown below:



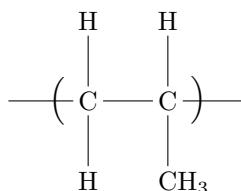
and polyethylene looks like:



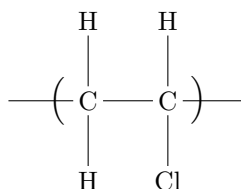
Notice the absence of the double bond. This is due to the chemical reaction that is required to take the mer unit and add it to the polymer.

• Here are some other examples:

- Polypropylene (PP) is a very common polymer used in many areas (e.g. Starbucks reusable cups). It is a material that is generally stronger and has a higher elastic modulus than polyethylene. This is because it has an extra  $\text{CH}_3$  methyl group, as shown below:

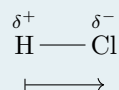


- Polyvinylchloride (PVC), along with PE and PP are the three most produced polymers in the world. The structure is similar, except with a chloride atom in the monomer unit:



The term *vinyl* describes two carbon atoms connected via double bond.

**Case Study:** PVC is very strong and has a high elastic modulus. We can explain this by looking at the chemical properties of the chloride atom. Chlorine is an extremely electronegative atom, meaning it tends to attract electrons. This allows it to attract electrons from the hydrogen of neighbouring polymers, forming a hydrogen bond<sup>a</sup>. This forms a dipole moment, which can be illustrated below via the following notation:

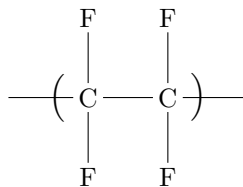


The  $\delta^+$  and  $\delta^-$  signify the *partial charges* and the arrow is the shorthand notation for the direction of the dipole (which will always point in the direction a proton would move in)

Since this bond is so strong, it is harder for nearby polymers to move against each other due to stronger intermolecular forces. Similarly, PP is strong for similar chemical properties. However instead of hydrogen bonds, it is the extra methyl group increasing London dispersion forces between neighbouring groups.

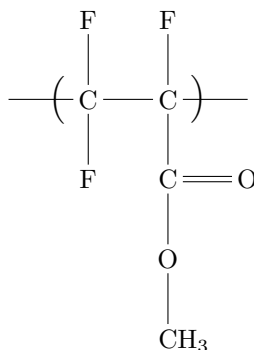
<sup>a</sup>Hydrogen bonds are actually much more complicated than this, but this isn't a chemistry course.

- Polytetrafluoroethylene (PTFE) is used for non-stick surfaces. As a result, it is very non-reactive, and it is able to do so due to the large fluorine atoms bonded to each carbon:



Their large size helps protect intramolecular bonds within PTFE from being broken and although they are highly electronegative, they are actually nonpolar due to its symmetry.

- Polymethylmethacrylate (PMMA) are often used for windows because they can be made optically transparent. The reason they are transparent is because of a bulky side group in their monomer unit that prevents close packing of polymer chains, creating an *amorphous* structure.

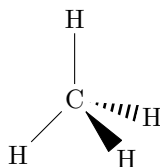


**Case Study:** We investigate what makes a material transparent, translucent, and opaque from a materials science perspective. Polymers can easily align with one another and become organized, which is known as crystallization. When it crystallizes, the index of refraction is different from when it is amorphous. Therefore, if it contains parts that are both amorphous and crystalline (known as *semicrystalline*), the light will not follow a direct path and the polymer will become translucent or opaque.

So how do we make a polymer transparent? If it is completely crystalline, then it would be transparent but polymers can never be 100% crystalline. Instead, we want them to be 100% amorphous.

Moving away from the domain of polymers, sapphire has a crystalline structure, made of  $Al_2O_3$ , and is clear and transparent. Window glass made from silica is amorphous and also clear and transparent. While polycrystalline metals are opaque, we can also have glassy metals, but they are also opaque. To get the full picture, we need a better understanding of how light works.

- To draw bonds going out and in of the page, we use a shaded triangle and dashed triangle, respectively. For example, we would draw methane as:



- We often use the symbol  $R$  to denote an arbitrary functional group.

## 8.2 Length

- We can characterize the length of a polymer with its linear mass density and the total mass.

**Case Study:** Ultrahigh Molecular Weight Polyethylene is often used in hip replacements. It often replaces part of the hip to prevent parts of it from wearing it away. It has high strength, high tolerance, and biocompatible.

As we increase molecular weight in a polymer, we increase the strength and typically increase the strain to fracture due to the increased entanglement of the long molecules.

- The **number average molecular weight** can be defined as:

$$\overline{M}_{\text{number}} = \sum_{n=1}^i M_n x_n \quad (38)$$

for a polymer containing  $i$  groups where  $M_n$  is the molecular weight of the  $n^{\text{th}}$  group and  $x_n$  is the number fraction of the  $n^{\text{th}}$  group.

- Similarly, the **weight average molecular weight** can be defined as:

$$\overline{M}_{\text{weight}} = \sum_{n=1}^i M_n w_n \quad (39)$$

where  $w_n$  is the weight fraction of the  $n^{\text{th}}$  group. The weight average will always be larger (and maintains equality) than the number average.

*Proof.* Suppose we have  $i$  groups with molecular weights of  $\{M_1, M_2, \dots, M_n\}$  and number fractions of  $\{x_1, x_2, \dots\}$ . We can calculate the weight fraction to be:

$$w_n = \frac{M_n x_n}{M_1 x_1 + M_2 x_2 + \dots + M_i x_i} = \frac{M_n x_n}{\overline{M}_{\text{number}}} \quad (40)$$

so we have:

$$\overline{M}_{\text{weight}} = \frac{1}{\overline{M}_{\text{number}}} \sum_{n=1}^i M_n^2 x_n \quad (41)$$

We propose that  $\overline{M}_{\text{number}} \leq \overline{M}_{\text{weight}}$  such that:

$$\overline{M}_{\text{number}} \leq \frac{1}{\overline{M}_{\text{number}}} \sum_{n=1}^i M_n^2 x_n \quad (42)$$

$$\overline{M}_{\text{number}}^2 \leq \sum_{n=1}^i M_n^2 x_n \quad (43)$$

$$\sum_{n=1}^i M_n x_n \leq \sqrt{\sum_{n=1}^i M_n^2 x_n} \quad (44)$$

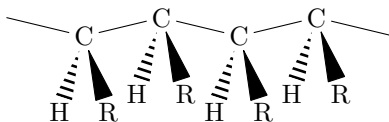
The right hand side gives the RMS average and the left hand side gives the arithmetic average. According to the RMS-AM inequality, the RMS mean is always greater or equal to the arithmetic mean.  $\square$

This **disparity** is actually quite important, and is also known as the **polydispersity index** and is defined as:

$$D = \frac{\overline{M}_{\text{weight}}}{\overline{M}_{\text{number}}} \quad (45)$$

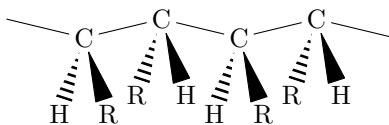
### 8.3 Close Packing and Crystallization

- As polymer chains line up, the density can increase. Since the chains get closer together, the strength of the intermolecular interactions may also increase, increasing the elastic modulus.
- When polymers line up, they form a crystalline structure (i.e. zigzag pattern). However, there will always still be some amorphous sections. As a result, there is an incentive to increase crystallinity and this can be accomplished by having simple mer units and regular repeating structures.
- When functional groups are on the same side, such as shown below, it is easier for the polymer to have a close packing behaviour:



The **tacticity** describes how the functional groups line up. If they are all on the same side, it is known as **isotactic**.

- If functional groups alternate, it is known as **syndiotactic**



- If it is random, then it is known as **atactic**.

**Idea:** One model of crystallization is known as the **chain folded model**. Plate-like structures form in polymers and the molecules fold on itself in an organized pattern on a thin plate (i.e. with thickness 10nm).

**Case Study:** Let us examine high density polyethylene (HDPE) and low density polyethylene (LDPE). There are branched in polyethylene. HDPE is processed such that the branches are very short, allowing it to crystallize more easily. In LDPE, the branches are much longer, resulting in a lower percent crystallinity and a lower strength.

## 8.4 Cross Linking and Network Polymers

- To prevent molecules from sliding past each other, we can cause them to “lock up” with each other. This is accomplished by creating strong covalent, intramolecular bonds between chains.

**Case Study:** Rubber is cross-linked, allowing it to have elastic behaviour without plastic deformation.

- Cross-linking is important in elastomers.
- If it is cross-linked too much, the material can become rigid and have very high strength, although they may be brittle. These are known as **networks** and occurs when mer units have multiple functional groups that form a three dimensional interconnected network (i.e. epoxy).

## 8.5 Effects of Temperature and Viscoelasticity

**Idea:** Polymers are very sensitive to temperature changes close to room temperature. This is due to the weaker secondary interactions between polymers.

- At higher temperature, the stress-strain curve flattens out and both the elastic modulus and yield strength will decrease.
- Temperature creates a large effect on a polymer’s viscoelasticity. Polymers are **viscoelastic**, which means that exhibit both viscous and elastic characteristics when undergoing deformation.
- To do so, we apply a fixed strain  $\varepsilon_0$  and we observe the stress relaxing with time  $\sigma(t)$ .

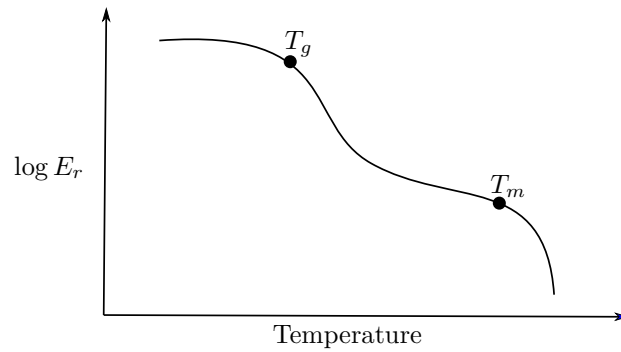
**Warning:** Note that we are not applying a fixed stress and look at the strain response (which is the more familiar everyday experience)

- We can define the **relaxation modulus** as

$$E_r = \frac{\sigma(t)}{\varepsilon_0} \quad (46)$$

We expect the stress (and therefore  $E_r$ ) to decrease with time, and at higher temperatures, the stress decreases faster. We can examine how  $E_r$  at a certain fixed point in time depends on the temperature. Before  $T_g$ , the material is mainly made up of an amorphous structure. However, increasing the temperature past this point, known as the glass transition temperature, the molecules have enough energy to overcome secondary bonds<sup>1</sup> and form a crystalline shape.

<sup>1</sup>Secondary bonds have smaller energies than primary bonds and are caused by permanent or temporary dipoles between different molecules



**Idea:** At low temperature, polymers usually become glassy and brittle.

$T_m$  refers to the melting point. At high temperatures, polymers will start to melt and start to undergo viscous flow (again overcoming secondary bonds). At cooler areas, there are both crystalline and amorphous regions.

## 8.6 Time Dependence

**Case Study:** Silly Putty is an interesting material as it is extremely ductile if stretched slowly. However, when stretched extremely quickly it snaps and fractures without undergoing plastic deformation. This leads to the idea that time scales play an important part in polymer interactions.

This is because there isn't enough time for polymers to slide past each other.

- Polymers are sensitive to strain rate.
- If a load is applied for a very long time (i.e. heavy desk on carpet), the polymer will undergo plastic deformation. However, if the load is applied for a short time, the polymer will more likely go back to its original orientation.
- This is known as **viscous deformation**, which is time dependent.

## 9 Model of the Atom

- Light can have a wavelength that ranges from  $10^{-11}$  m to  $10^3$  m. We can list some common ranges below, listed from shortest wavelength to highest wavelength:
  - Gamma Rays
  - X-Ray
  - Ultraviolet
  - Visible (400-700 nm)
  - Infrared
  - Microwave
  - Radio wave
- The energy is related to the wavelength via:

$$E = \frac{hc}{\lambda} \quad (47)$$

where  $h$  is Planck's constant and  $c$  is the speed of light. Oftentimes, we use the electron-volt (eV) unit to characterize energy where:

$$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J} \quad (48)$$

- In the Bohr-ing model of the atom, it is consisted of a nucleus (with protons + neutrons) and electrons. This model states the following:

- The orbitals are well defined and correspond to a specific energy. Therefore, energy is quantized.
- Electrons are able to absorb a specific amount of energy to move into a higher energy state.
- In the quantum-mechanical model of the atom, which describes electron orbitals using quantum numbers.
  - The principal quantum number  $n = 1, 2, 3, 4, \dots$  describe the orbital shell. This corresponds to the Bohr model.
  - The angular momentum quantum number  $\ell = 0, 1, 2, \dots, (n - 1)$  or  $s, p, d, f$  and they describe the shape of the electron orbital.
  - The magnetic quantum number, which ranges from  $-\ell \leq m_\ell \leq \ell$ . They describe the orientation of the orbitals.
  - Spin quantum number:  $m_s = \pm \frac{1}{2}$ .
- Subshells are described by the principal and angular momentum quantum numbers and have a very specific energy. Electrons fill these subshells from lowest to highest energy. It is ordered by:

$$1s \rightarrow 2s \rightarrow 2p \rightarrow 3s \rightarrow 3p \rightarrow 4s \rightarrow 3d \rightarrow 4p \rightarrow 5s \rightarrow \dots \quad (49)$$

For example, carbon has  $Z = 6$  protons and its electronic configuration is  $1s^2 2s^2 2p^2$ .

- For iron with  $Z = 26$ , we may be tempted to write the electronic configuration as:

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6 \quad (50)$$

However, the electronic configuration (due to quantum reasons) that has a lower energy is actually:

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2 \quad (51)$$

Since the last two electrons in the 4s orbital is what will be taken away during ionization.

**Idea:** In this course, we will write electron configurations in increasing principal numbers.

- Noble (inert) gases don't react easily. A general rule is that octets are stable, and this rule is sometimes written as:

$$ns^2 np^6 \quad (52)$$

as many atoms want to achieve this configuration.

- Covalent, ionic, and metallic bonds exist (sorry if this isn't high school review, i would write more but I still have 8 questions left and it's almost the deadline)
- Ionization and crystallization energy exist. Salt forms a crystal. Electron affinity also exists. Planning on revisiting this part later so if you're that lone visitor google analytics told me about, please remind me.
- In the **Band Theory**, it attempts to model electrons in a bond. One may naively say that the two electrons share the same state (i.e. same energy, orientation, etc.), but the Pauli exclusion principle forbids that. As a result, they separate out a tiny bit. If we have a large sample, they seem to form a band with a range of possible energies.
- Alternatively, if we plot the energy against the intermolecular spacing, we notice that the range of energies separate out if we move from  $r = \infty$  to the equilibrium radius  $r = r_0$ . If we plot it out for the energy of multiple subshells, we'll notice that sometimes there are certain energies in between the bands that no electron can have. This is known as a **band gap**.

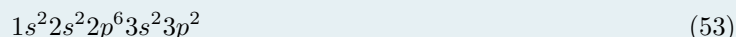
**Idea:** Bonding creates three bands: The valence band, the band gap, and the conduction band, listed from lowest to highest energy. If the band gap is higher than 4 eV, then it is an insulator and if it is less, than it is called a semi-conductor.

- The important distinction is that for a single atom, the energy of each electron is quantized but if bonding occurs, the energy no longer needs to be quantized.

**Idea:** We can explain conduction using this model by promoting electrons from the valence band to the conduction band. This reminds us of the "continuous sea of electron" analogy for metallic bonding. If there is a band gap, then it becomes a "Bohr-model" analogy with electrons jumping up and down between discrete

states.

**Case Study:** The electron configuration of silicon is:



The problem arises is that we know from experiments that silicon has four identical bonds. However, we have 4 electrons at two different energy levels. This shows a limitation in our model and introduces  $sp^3$  hybridization.

- $sp^3$  hybridization is caused by merging the  $s$  and  $p$  orbitals during bonding, such that the one  $s$  orbital and the three  $p$  orbitals form into four identical  $sp^3$  orbitals. These are known as hybridized orbitals.
- It is important to control the electrical conductivity of semiconductors. This is possible by introducing impurities into semiconductors to change their electrical conductivity. The general idea is to delocalize electrons such that they can conduct electricity. In the band theory, it results in a “hole.” Although the hole is neutral, since it is surrounded by negative electrons, it can be seen as positive.
- This hole is unstable, and as a result electrons will fill it in, creating a new hole from where that electron came from. How quickly electrons can fill this hole characterizes the material’s conductivity.
- The conductivity  $\sigma$  is given by:

$$\sigma = nq\mu + n \quad (54)$$

where  $n$  is the number of electrons,  $q$  is the fundamental charge,  $\mu_n$  is the electron mobility,  $p$  is the number of holes, and  $\mu_p$  is the hole mobility. For  $n = p$ , we have:

$$\sigma = nq(\mu_n + \mu_p) \quad (55)$$

- The conductivity follows the Boltzmann distribution (the textbook said it was the Arrhenius dependence, but that’s just chemists trying to steal something physicists came up with):

$$\sigma = e^{-E_g/(2kT)} \quad (56)$$

where  $E_g$  is the band gap.

- So far, this discussion has revolved around *intrinsic* semi-conductors, which are un-doped. They are not very practical as they are very temperature dependant. If we dope them, the electric properties of the dopant has a large effect on the overall behaviour, and the semi-conductor becomes *extrinsic*.
- Extrinsic  $n$  type semiconductors are created by adding in free electrons in it. For example, we can add in a *pentavalent* atom (i.e. point defect), which has four electrons that bond with neighbouring carbon electrons, but it has an *extra* free electron. The conductivity is given by:

$$\sigma = nq\mu_n \quad (57)$$

Note that in the background, there is still effects from the instrinsic effects, though they are typically much smaller.

- Instead of adding electrons, we can add extra holes in  $p$ -type extrinsic semiconductors. This is done in a similar way, by adding trivalent impurities such as Boron. The conductivity is then:

$$\sigma = pq\mu_p \quad (58)$$

## 10 Thermodynamics

- The laws of physics are time symmetric, meaning on *microscopic* scales, it is impossible to tell the difference between an event happening forwards and happening in reverse. However, on a *macroscopic* scale, an “arrow of time” exists.

**Definition:** A reaction that proceeds without continued input of energy is spontaneous.

- This definition may create the misconception that exothermic reactions are spontaneous. This is not true, since there is an initial activation energy that is needed to kickstart the reaction, even though it gives off *net* heat. *One reason* is because reactions have multiple steps. Suppose we take the reaction:



which consists of the following steps:



And the total energy released is  $-414\text{kJ mol}^{-1}$ . However, note that endothermic reactions can also be spontaneous. We need to take a look at the second law of thermodynamics.

- During a quasistatic (not sudden) process, the change in entropy is given by:

$$\Delta S = \frac{Q_{\text{rev}}}{T} \quad (65)$$

where  $Q$  is the transferred energy, and  $T$  is the temperature.

- The rev subscript denotes that the heat transferred is reversible.
- The Second Law of Thermodynamics says that a reaction is spontaneous if and only if:

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0 \quad (66)$$

- The First Law of Thermodynamics states that in an isolated system, the change in energy of the system is zero (i.e. conserved)

$$\Delta U_{\text{sys}} = 0 \quad (67)$$

- For a closed system (where no matter travels in and out), we have:

$$\Delta U_{\text{sys}} = Q + W = 0 \quad (68)$$

where  $W$  is the work done *on* the system.

**Warning:** For some reason, some papers define  $W$  to be the work done by the system, making the equation  $U_{\text{sys}} = Q - W$ .

- We will also examine the difference between the change in enthalpy  $\Delta H$  against the change in energy  $\Delta U$ .
- We can define the standard state to be the most stable form of an atom at  $25^\circ \text{C}$  and 1 atm.
- Enthalpy only depends on the current conditions; it is a **state function** (depends only on the current state, not how we get there)
  - Other state functions are entropy, the Gibbs energy, and the potential energy.
- We can quantify the enthalpy as:

$$H = U + PV \quad (69)$$

, which gives the total energy needed to create a system out of nothing (i.e. the energy of the thing and the energy to make room for the thing)

- Alternatively, an equivalent definition of enthalpy is the energy transferred at constant temperature.
- At constant pressure, we have:

$$\Delta H = \Delta U + P\Delta V \quad (70)$$



- The first law of thermodynamics can be re-written as:

$$\Delta H = Q + W_{\text{other}} \quad (71)$$

- The Gibbs energy is given by:

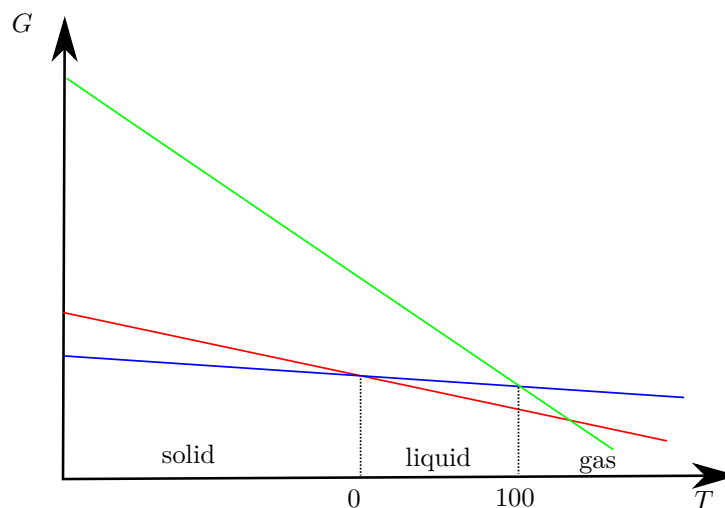
$$G = H - TS \quad (72)$$

and at a constant temperature, we have:

$$\Delta G = \Delta H_{\text{system}} - T\Delta S_{\text{system}} = -T\Delta S_{\text{universe}} \quad (73)$$

A nice thing about this is that when the Gibbs energy decreases, the entropy of the universe increases. As a result, reactions are spontaneous when  $\Delta G < 0$ .

- We can plot out  $G = -ST + H$  for water at *standard conditions*:



Here,  $S_s < S_p < S_g$  (from smallest slope to largest slope in magnitude, we have solid, liquid, gas). We can interpret the intersection as the shift from one phase being more thermodynamically favourable than another.

- If the pressure was higher, then the gas line could intersect the solid line before the liquid. This is represented by a larger  $S_g$  and appears physically in **sublimation**.

**Case Study:** There's two interesting demonstrations we can do with freezing water:

- If we put water in a smooth plastic bottle overnight (see link) at a temperature of around  $-7^\circ$ , it can remain liquid since there are no nucleation sites, known as a metastable state. In other words, it lacks activation energy to crystallize.
- Sometimes, water which we would expect to freeze is actually slushy at  $0^\circ$  C. The reason for this is because freezing is an exothermic reaction, so while the water freezes, it produces some heat that remelts part of it.

- The change in temperature is related to the heat provided through:

$$q = nC_p\Delta T \quad (74)$$

or<sup>2</sup>:

$$q = mc\Delta T \quad (75)$$

<sup>2</sup>The heat capacity is almost always measured at constant pressure. In literature, values of  $C_V$  may also be reported which is the heat capacity at constant volume. However, it turns out we need to provide tremendous amounts of pressure to ensure the object stays at constant volume for most things.