

Engineering Chemistry & Materials Science (APS110)

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- **Chapter 1: Introduction**

- ❖ 3 MATERIAL CLASSES:

- METALS
- CERAMICS
- POLYMERS

- 1. Metals:

- Solids made by metallic elements
- Metallic Bonds
- Ductile- can be deformed permanently
- Electrically and thermally conductive
- Shiny
- Highly Organized at the Atomic level- Crystalline
- Examples: sodium, titanium, chromium, iron, nickel, copper, silver, gold, lead, and roentgenium

- 2. Ceramics:

- Often metal oxides
- Compounds held together by ionic bonds
- Hard and Brittle- Crack instead of deforming if an increasing load is applied
- Non-Conductive thermally and electrically
- Optically transparent, translucent or opaque
- Highly Organized at the Atomic level- Crystalline, or Disorganized or *Amorphous*(Not Organized)
- Examples- sapphire (alumina or Al₂O₃), quartz (crystalline silica or SiO₂), concrete, window glass (soda lime glass)
- Less common examples or allotropes of pure carbon- diamond, graphite, buckyball, and carbon nanotubes

- 3. Polymers:

- Collection of Atoms held together by covalent bonds
- Ductile (Not as strong as Metals)
- Non-Conductive thermally and electrically
- Optically transparent, translucent or opaque
- Examples- polyethylene, polypropylene, polyvinyl chloride, epoxy, Teflon®, GoreTex®, and Styrofoam®.

- Chapter 2: Elastic Behaviour

- ❖ Hooke's Law: The extension of a spring is proportional to the applied force

$$F = k \cdot x$$

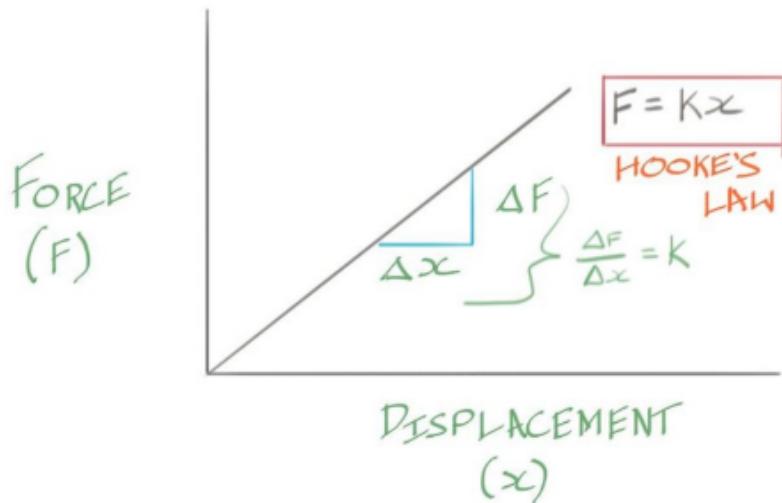
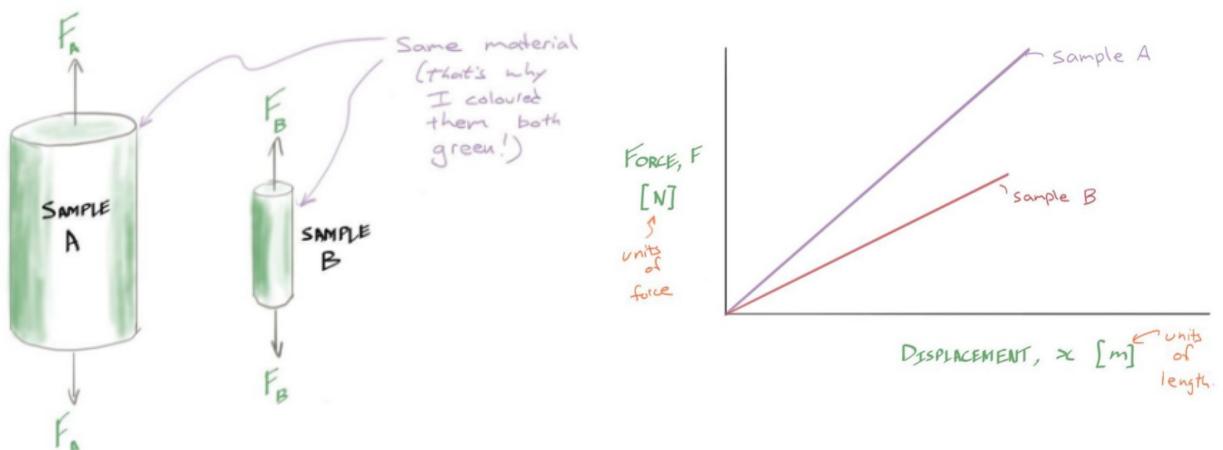


Figure 2: A general linear force versus displacement plot.

- ❖ Experiment:

- Consider two cylindrical samples of the **same** material
- Strength is **same**
- Sample A is longer and has greater cross sectional area
- Sample B is shorter and has smaller cross sectional area
- Sample A requires more Force for Elongation- thicker sample supports more load
- Sample A has higher spring constant-steeper



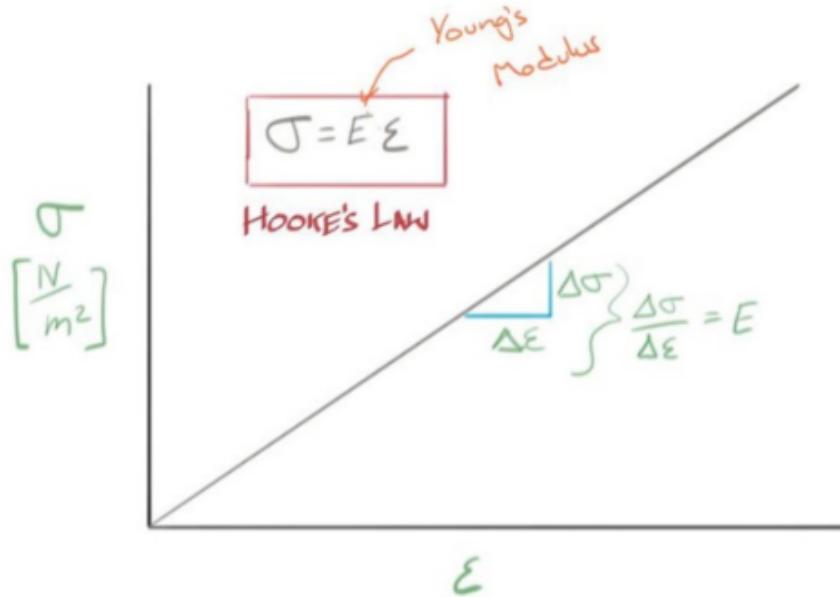
- ❖ Engineering Stress: force exerted per unit initial cross-sectional area of a material
 - Unit: N/m² or Pa

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

- ❖ Engineering Strain: extension per unit length
 - No unit- Dimensionless

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

- ❖ STRESS-STRAIN CURVE
 - Stress y-axis
 - Strain x-axis
 - Slope is Young's Modulus (E)
 - Young's Modulus = Stress/Strain
 - Unit- Pa

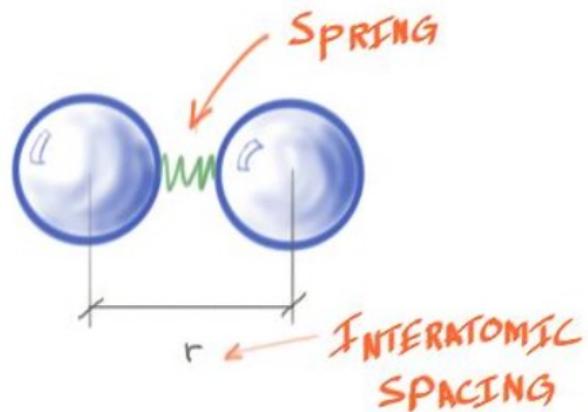


❖ ELASTIC DEFORMATION:

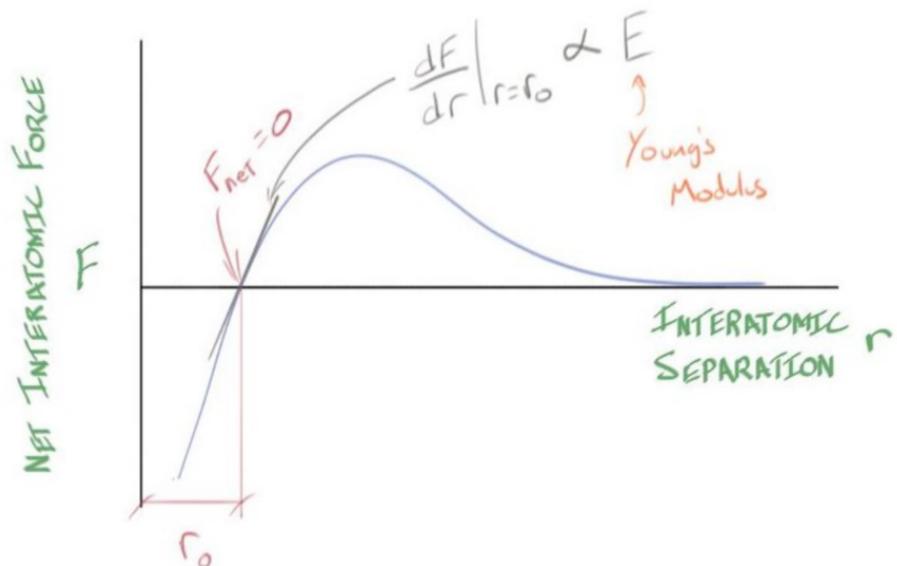
- During elastic deformation the sample dimensions return to their **original** dimensions upon unloading.
- During elastic deformation atoms return to their **original** positions upon unloading.
- Tensile Strain is recoverable

❖ Model for Net force between atoms in a solid:

- What if we modeled atoms in a solid as spheres connected to one another by little springs



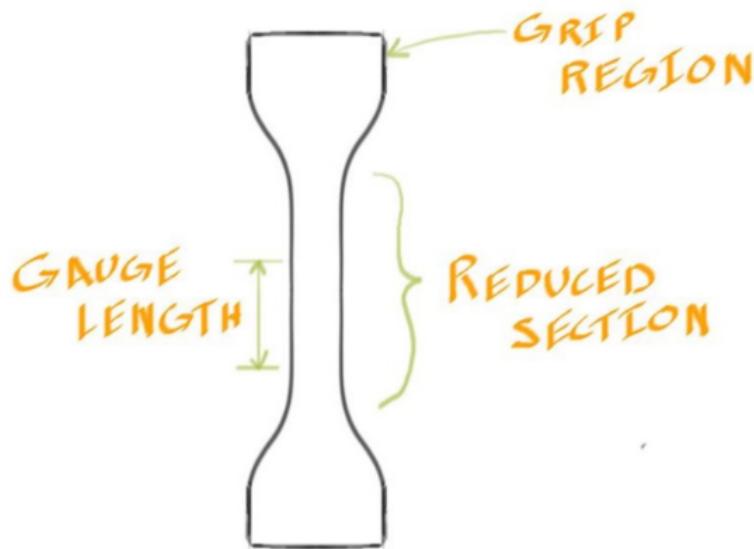
- There is an attractive force that pulls the atoms together, but then as the atoms get closer to each other there is a repulsive force that becomes significant.



- the letter “r” is used for interatomic spacing
- The point where the net force is equal to zero corresponds to the atoms at rest and so the value of the interatomic spacing at that point defines the so-called, equilibrium interatomic spacing.
- Young’s modulus is directly proportional to the spring constant of the tiny little interatomic spring

❖ **How is the stress-strain curve formed:**

- Use a tensile specimen
- These tensile specimens may be either cylindrical or rectangular in cross-section.



- Grip region: Where we grip the sample
 - Stress in grip region is lower due to large cross-sectional area
 - So we can squeeze it really hard without worrying about impacting the experiment
- Reduced Section: Section in the middle with parallel sides
 - Smaller cross sectional area
- Gauge Length: The initial length of the strain gauge is where we define the initial length l_0
 - Always shorter than reduced section

❖ **UNIAXIAL TENSILE TEST:**

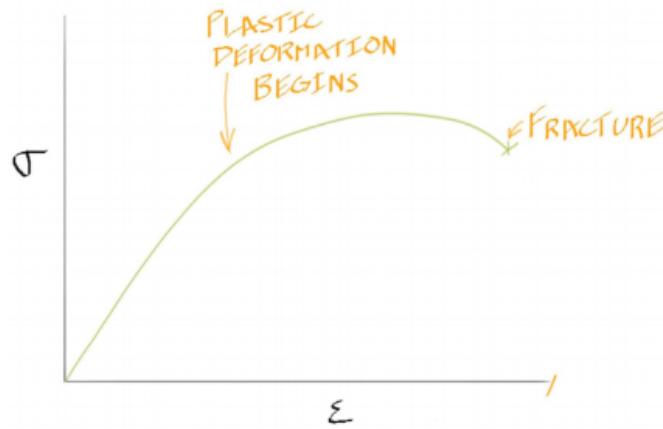
- Powerful grips to hold sample
- A load cell
- Accurate means to determine strain

- **Chapter 3: Plastic Behaviour**

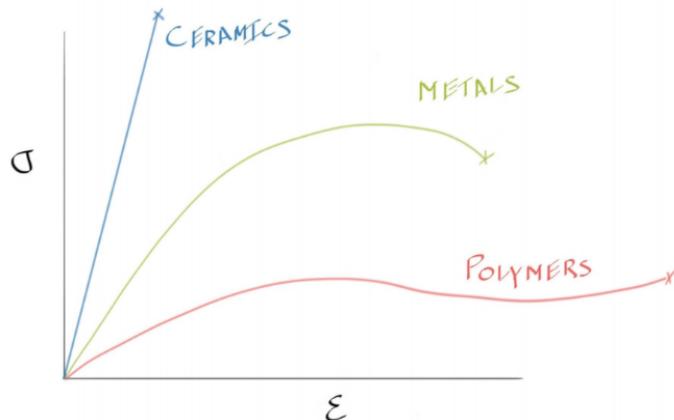
- ❖ PLASTIC DEFORMATION:

- when we apply enough load to move beyond the elastic region
- the sample dimensions will have changed
- the atoms must move to new positions, even when the load is released
- Tensile strain does not return to 0

- ❖ Plastic deformation begins close to the end of the linear elastic region.



- Stress-strain curves describe the properties of materials such as whether they are brittle, ductile and up to what stress and strain they obey Hooke's Law and have elastic and / or plastic behavior
- Each material will have a unique stress-strain curve



❖ Young's Modulus(highest to lowest):

- Ceramics
- Metals
- Polymers

- Strength follows the same trend

CERAMICS:

★ NOTE: This is only when ceramics are loaded in **compression**

- In **tension**- ceramics are really weak
- Ceramics are brittle so the curve is linearly elastic until fracture
- Do not undergo plastic deformation at room temperature

POLYMER:

The curve dips down and then comes back up a little.

❖ MECHANICAL TESTING OF CERAMICS:

- since ceramics are so strong and brittle it is very difficult to machine them into the nice tensile specimens
- It is very challenging to align a ceramic sample exactly along the loading axis as it is likely to shatter during the machining operation.
- Metals and polymers are relatively ductile, that is, they have high plastic strain to fracture so can use uniaxial tensile test

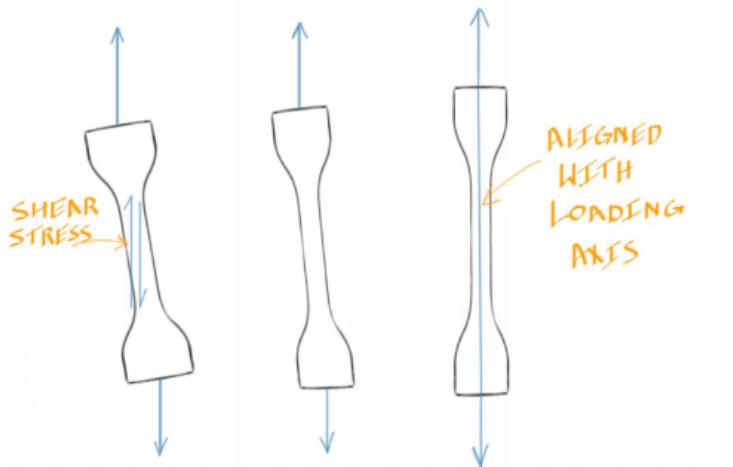


Figure 6: The challenge of aligning a sample with the tensile loading axis. Metals and polymers, even when loaded slightly off axis (exaggerated here) will deform and self-align with the loading axis. Ceramics fracture at a very low strain values while the sample is still subjected to significant shear stress.

BEND TEST(CERAMICS):

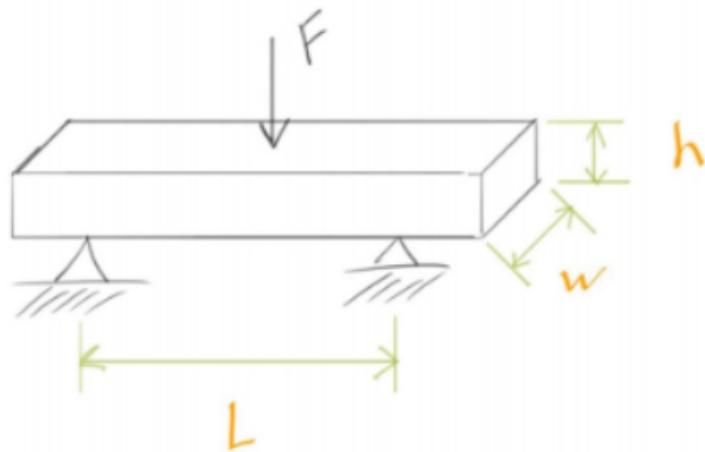


Figure 7: A cartoon sketch of a three point bend test on a rectangular cross-section beam.

- The lower surface of a beam loaded as shown will be in tension, while the top surface will be in compression.
- The stress state on the top and bottom surfaces actually have opposite signs.
- Since ceramics perform poorly in tension, the beam will fracture first on the lower surface, specifically near the middle, underneath where the load is applied.

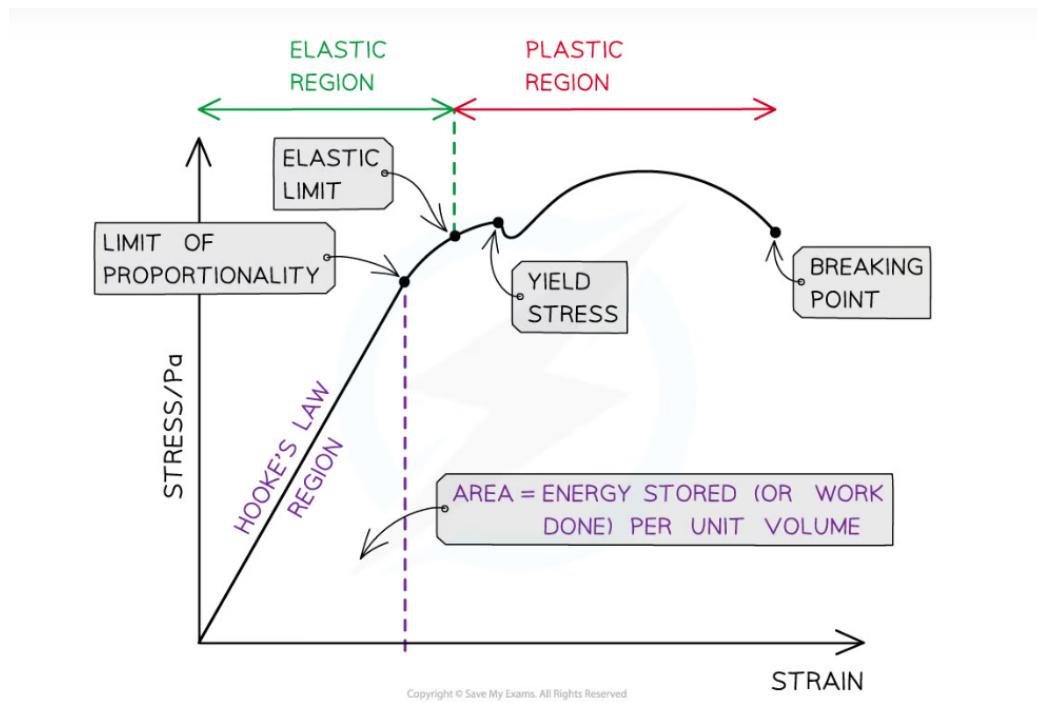
$$\sigma = \frac{3FL}{2wh^2}$$

❖ BALANCING ON A THIN SHEET OF GLASS:

Why is tempered glass stronger than conventional glass?

- When the glass is at a high temperature the surfaces are rapidly cooled.
 - There are 3-dimensional networks of bonds within the glass.
 - At elevated temperatures the molecules are further apart
 - When the surfaces are rapidly cooled some of this excess volume from the higher temperature is locked into the glass.
 - The central portion of the glass however continues to cool more slowly
 - The molecules are better able to organize and achieve a smaller final volume.
 - The final piece of tempered glass, once it has cooled, contains residual stresses.
 - The surfaces are being pushed together as the center tries to contract.
 - The surfaces are therefore in residual compression, while the center is in residual tension.
 - Since ceramics are strong in compression, the glass does not break
- Why does tempered glass break into small pieces if it does fracture?
This is because the residual strain energy in the glass attempts to convert to surface energy in the form of new surfaces during fracture.

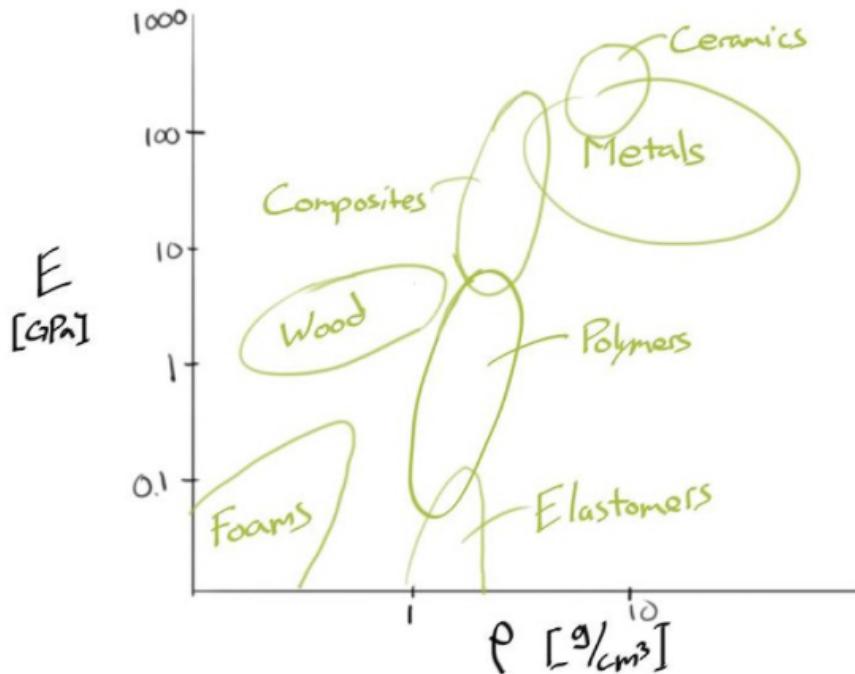
BOTTOM LINE:



- Yield Stress: The force per unit area at which the material extends plastically for no / a small increase in stress
- The elastic strain energy stored per unit volume is the area under the Hooke's Law (straight line) region of the graph
- Breaking point: The stress at this point is the breaking stress. This is the maximum stress a material can stand before it fractures
- Elastic region: The region of the graph up till the elastic limit. In this region, the material will return to its original shape when the applied force is removed
- Plastic region: The region of the graph after the elastic limit. In this region, the material has deformed permanently and will not return to its original shape when the applied force is removed

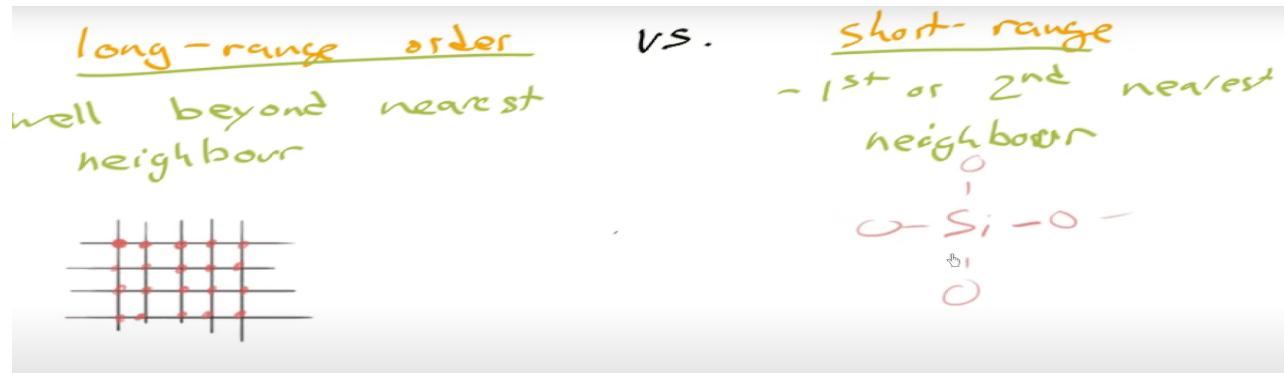
- **Chapter 4: Structure-Property Relationship**

- ❖ There is generally an increase in density as we move to higher Young's modulus.



- ❖ ORDERED SOLIDS:

- Metals are made of crystals (Polycrystalline)
- Each of these crystals is made of a massive number of atoms all positioned in regular repeating position
- Spaced roughly at the *atomic scale* = 10^{-10} m
- These crystals that make up polycrystalline materials are called **grains**.
- Example- galvanized steel lamp posts, street signs, railings
- **Grain Boundaries**- etching away atoms that exist at the boundaries between grains
- *Long range order*- **highly ordered** repeating structure that extends well beyond nearest neighbor atoms
- *Short Range order*- nearest neighbor atoms



❖ SIMPLE CUBIC STRUCTURE:

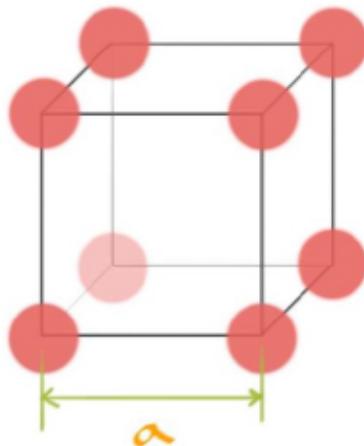


Figure 4: The simple cubic unit cell, showing an atom centred at each of the eight corners of a cube. The lighter red dots are the atoms located on the hidden parts of the cube. The cube edge length is known as the lattice parameter and is denoted with the letter a .

- The cube edge length is known as the *lattice parameter* a . *Coordination number*=8

❖ **FACE-CENTERED CUBIC (FCC):**

- Highly Organized Material
- The atoms are centered on each of the six faces of the cube

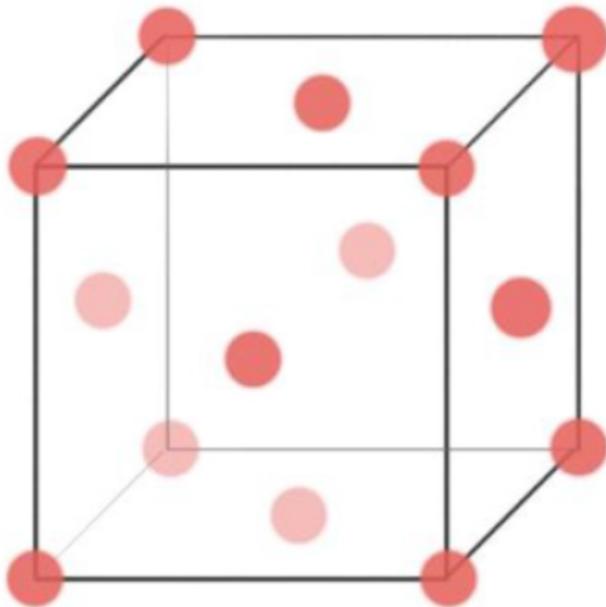
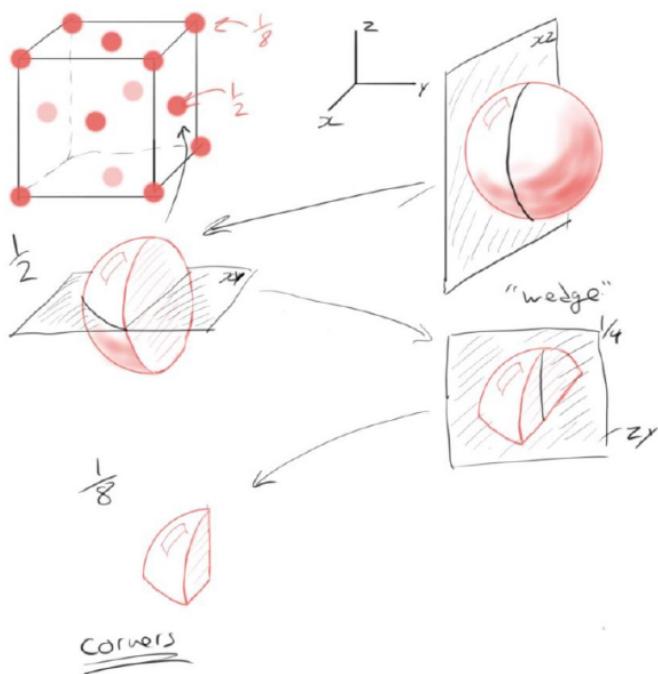


Figure 5: The FCC unit cell, showing an atom centred at each of the eight corners of a cube as well as one atom centred at the very centre of each of the six cube faces. The lighter red dots are the atoms located on the hidden parts of the cube.

FRACTIONAL ATOMS IN FCC:



- The **eight atoms** that result from a sphere being sliced in three orthogonal planes are found in the **eight corners**, while the **half atoms** are located at the face centered positions.

- **Coordination Number= 12**
- So, $8 \times \frac{1}{8} = 1$ atom from the corners
+ $6 \times \frac{1}{2} = 3$ atoms from the faces

- **4 atoms in the FCC unit cell**

$$n_{FCC} = 4$$

- **$a = 2\sqrt{2} R$**
- **Volume = a^3**

PROOF:

$$\begin{aligned} a^2 + a^2 &= (4R)^2 \\ 2a^2 &= 16R^2 \end{aligned}$$

$$\begin{aligned} a_{FCC} &= \\ 2\sqrt{2}R & \end{aligned}$$

❖ DENSITY OF CRYSTALLINE SOLID:

- Density = Mass/ Volume
- MASS:

$$\text{Mass}_{\text{Atoms in Unit Cell}} = \text{Number}_{\text{Atoms in Unit Cell}} \cdot \frac{\text{Molar Mass of Atom}}{\text{Avagadro's Number}}$$

or

$$m = n \cdot \frac{A}{N_A}$$

- So, Density (Divide by volume of unit cell):

$$\rho = \frac{nA}{V_C N_A}$$

- $N_A = 6.02 \times 10^{23}$
- V_c for FCC is calculated as $(2\sqrt{2} R)^3$

❖ ATOMIC PACKING FACTOR FCC:

This is a measure of the fraction of a volume that is occupied by atoms arranged in a particular crystal structure

$$\text{APF} = \frac{\text{Volume}_{\text{Spheres}}}{\text{Volume}_{\text{Unit Cell}}} \quad (5)$$

or, since the unit cell is a cube whose volume is a^3

$$\text{APF} = \frac{n \frac{4}{3} \pi R^3}{a^3} \quad (6)$$

and, specifically for FCC

$$\text{APF} = \frac{4 \frac{4}{3} \pi R^3}{a^3} \quad (7)$$

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

$$\text{APF}_{\text{FCC}} = 0.74$$

- **Chapter 5: More Structures**

- ❖ **ROCK SALT:**

- Position our negative ions or anions at the cube corners
- Position our positive ions or cations between the anions
 - This is because the anions are typically larger and it is easier for our human brains to visualize placing the large things first and then squeezing the small things in between the large ones.

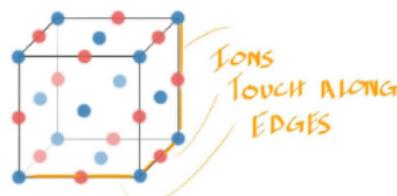
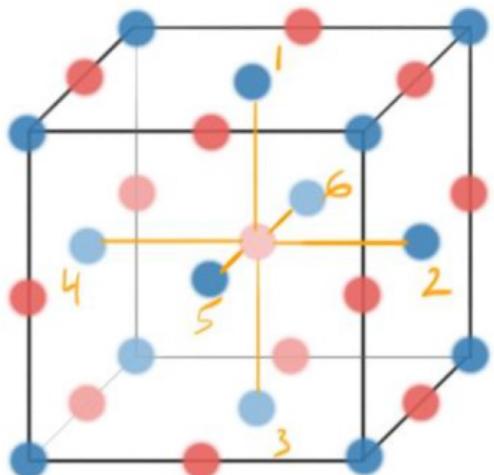


Figure 1: Anions represented as blue dots in the traditional FCC-type positions, with cations in the edge centre positions. Cations touch their nearest neighbour anions along the cube edges. Note: this is not yet Rock Salt - there is something missing.

- There must be a 1:1 ratio of anions to cations
- There are 4 anions within the unit cell, so there must also be 4 cations.
- The central cation touches each of the face centered anions, for a coordination number of 6.
- $a = 2(R_a + R_c)$, $n=4$



Cation Coordination Number_{RockSalt} = 6

Figure 3: The rock salt ceramic crystal structure.

- DENSITY FOR ROCK SALT:

$$\rho = \frac{n_C A_C + n_A A_A}{V_C N_A}$$

❖ BODY CENTERED CUBIC CRYSTAL(BCC):

- We start with atoms in each of the corner positions, again, each corner position only containing $\frac{1}{8}$ of an atom within a unit cell
- Then we position a final atom exactly in the center of the unit cell
- This gives us a total of 2 atoms within the BCC unit cell
- **nBCC = 2**
- **a = $4/\sqrt{3} R$**
- **Coordination number = 8**
- The direction of contact between atoms is across the cube diagonals.

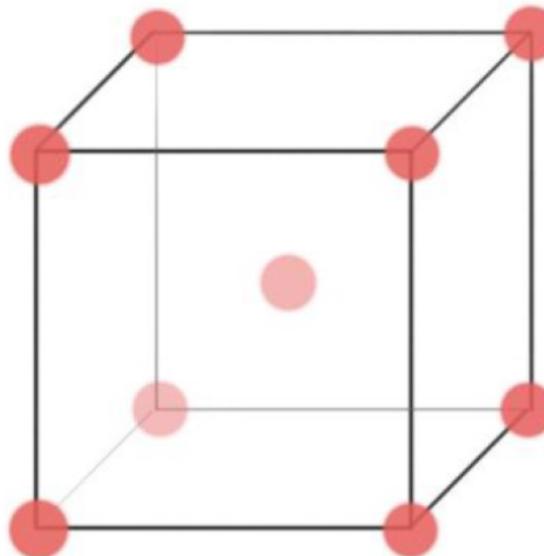


Figure 4: The body centred cubic crystal structure.

❖ APF BCC:

$$\begin{aligned} a^2 + a^2 + a^2 &= (4R)^2 \\ 3a^2 &= 16R^2 \end{aligned}$$

$$a_{\text{BCC}} = \frac{4}{\sqrt{3}}R$$

Which we can substitute back into our APF equation to give

$$\text{APF}_{\text{BCC}} = \frac{\frac{4}{3}\pi R^3}{\left(\frac{4}{\sqrt{3}}R\right)^3}$$

$$\text{APF}_{\text{BCC}} = 0.68$$

$$\text{APF}_{\text{BCC}} = \frac{\text{Volume}_{\text{Spheres}}}{\text{Volume}_{\text{Unit Cell}}}$$

or,

$$\text{APF}_{\text{BCC}} = \frac{\frac{4}{3}\pi R^3}{a^3}$$

and, specifically for BCC

$$\text{APF}_{\text{BCC}} = \frac{\frac{4}{3}\pi R^3}{a^3}$$

❖ INTERSTITIAL SITES:

Space between atoms

- Coordination number simple cubic: 8
- SIZE OF INTERSTITIAL SITES

$$(2R_A + 2R_C) \sin 45^\circ = 2R_A$$

$$2R_A \sin 45^\circ + 2R_C \sin 45^\circ = 2R_A$$

$$R_A \sin 45^\circ + R_C \sin 45^\circ = R_A$$

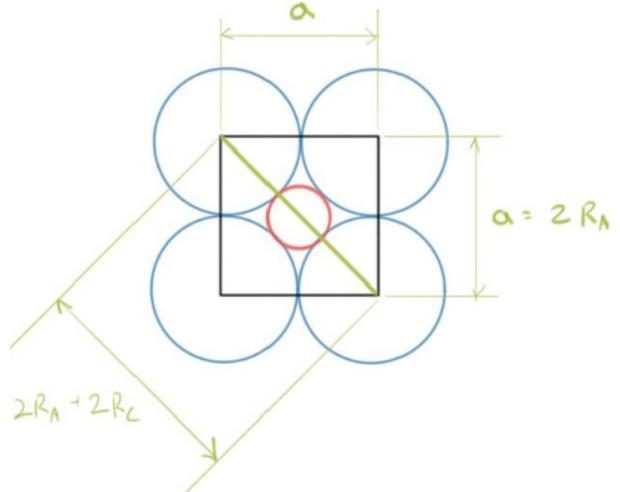
$$\frac{R_A}{R_A} \sin 45^\circ + \frac{R_C}{R_A} \sin 45^\circ = \frac{R_A}{R_A}$$

$$\sin 45^\circ + \frac{R_C}{R_A} \sin 45^\circ = 1$$

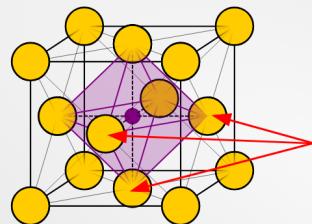
$$\frac{R_C}{R_A} \sin 45^\circ = 1 - \sin 45^\circ$$

$$\frac{R_C}{R_A} = \frac{1 - \sin 45^\circ}{\sin 45^\circ}$$

$$\left(\frac{R_C}{R_A}\right)_{CN=6} = 0.414$$

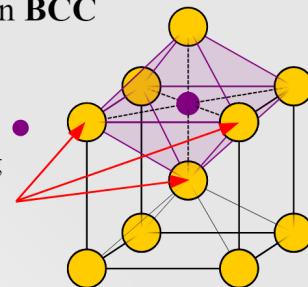


Octahedral Site in FCC



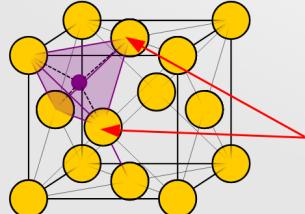
An interstitial site ● among neighboring
6 host atoms ●

Octahedral Site in BCC



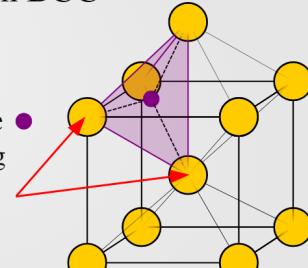
An interstitial site ● among neighboring
8 host atoms ●

Tetrahedral Site in FCC



An interstitial site ● among neighboring
4 host atoms ●

Tetrahedral Site in BCC



An interstitial site ● among neighboring
4 host atoms ●

❖ HEXAGONAL CLOSE PACKED (HCP)

- Metallic crystal structure with the same packing fraction as FCC - hexagonal close packed or HCP.
- APF for HCP must also be **0.74**
- A **close-packed plane** is a layer of atoms that is placed together as closely as possible, in two-dimensions.
- You will notice that the top and bottom planes are exactly in line with each other vertically.
- Since these planes are close-packed this gives us the **ABABAB** stacking sequence for **HCP**.
- The stacking sequence of FCC and HCP as **ABCABCABC** and **ABABABA** respectively (close-packed planes)
- c/a ratio for HCP, as formed here is 1.633.
- **Coordination number = 12**

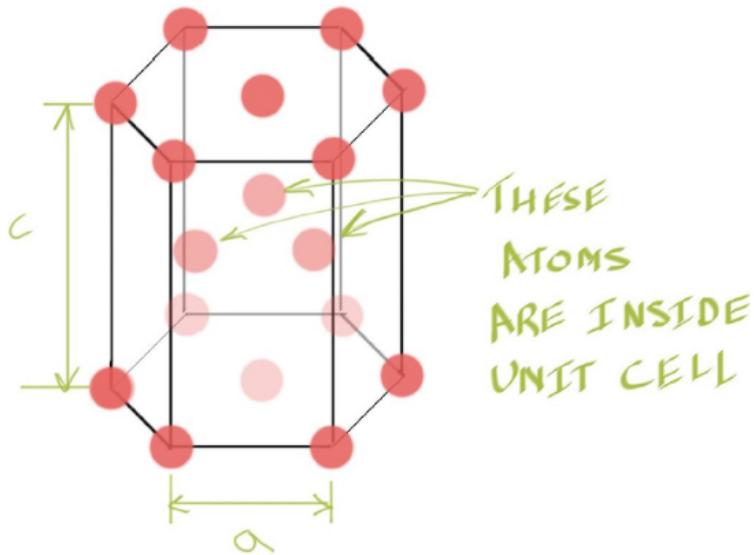
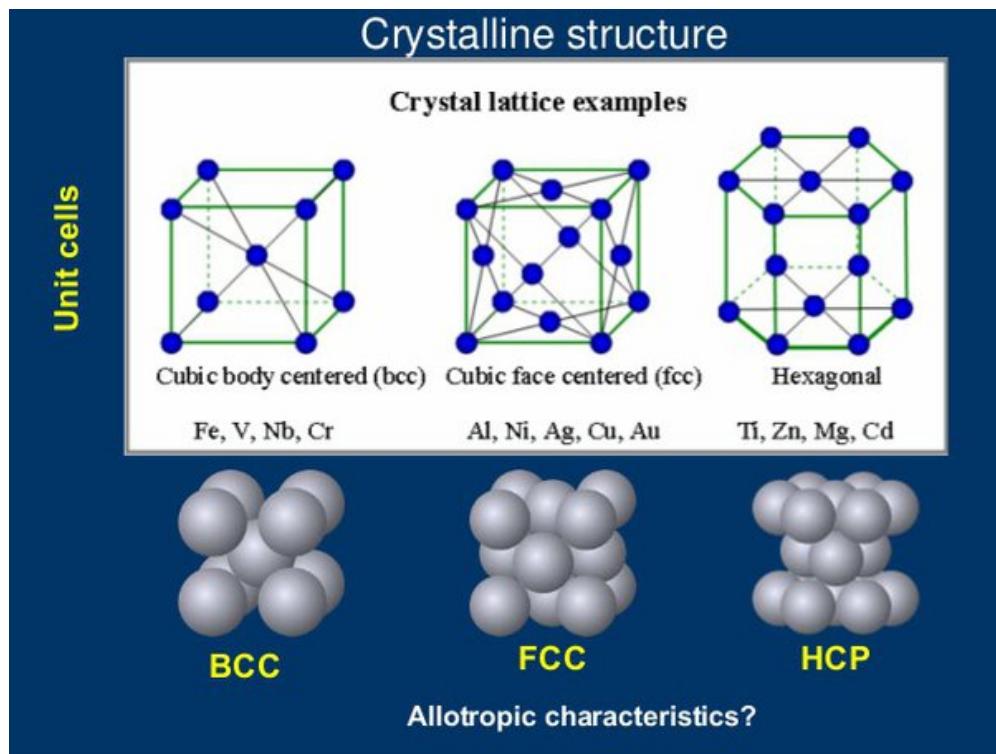


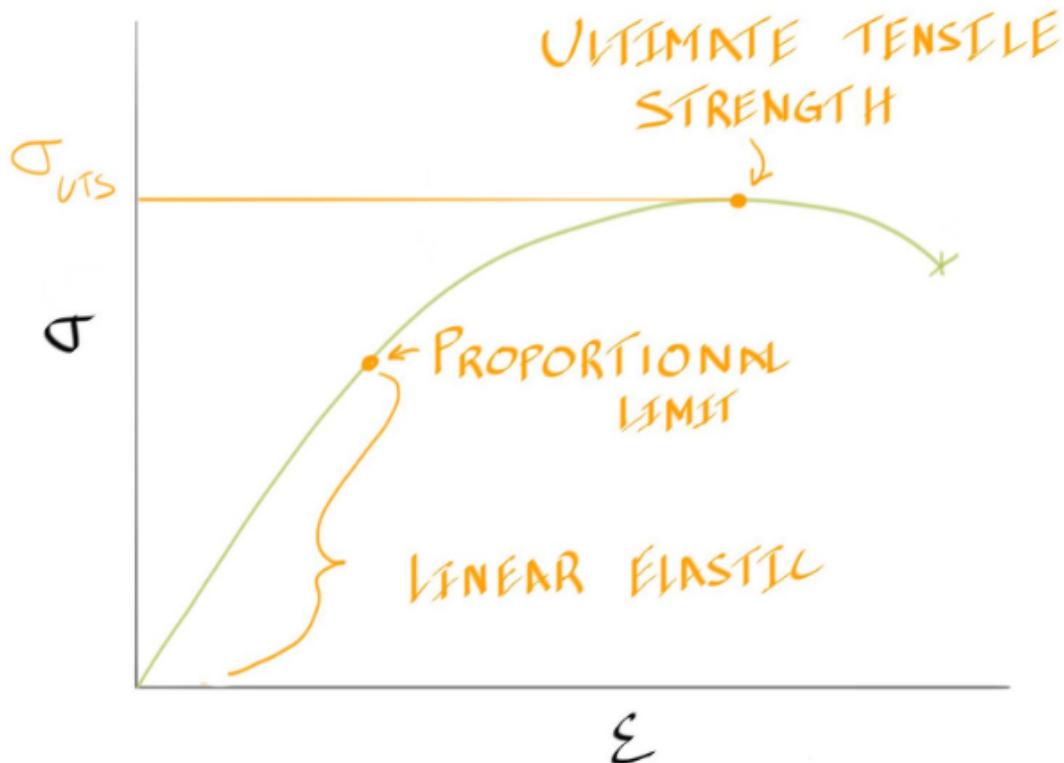
Figure 11: A hexagonal close packed unit cell. Note that the three atoms in the middle are inside the unit cell and are part of a close packed plane that is identical to the top and bottom planes.

COMPARISON FCC, HCP, BCC & ROCK SALT:

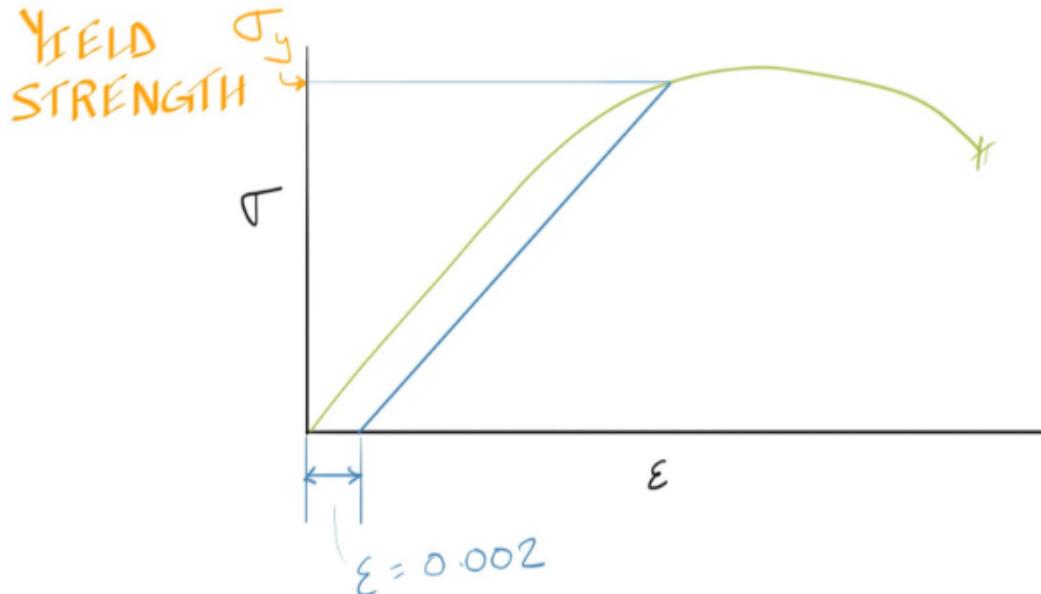
	FCC	HCP	BCC	Rock Salt	Simple cubic
Coordination Number	12	12	8	6	
Number of atoms in unit cell	4	4 OR 6	2	4	1
a	$2\sqrt{2} R$	$2\sqrt{2} R$ OR 2R and $h=1.633a$	$4/\sqrt{3} R$	$2(R_a + R_c)$	$2R$
Volume(a^3)	$(2\sqrt{2} R)^3$	$(2\sqrt{2} R)^3$ OR $(3 * \sqrt{3})/2 * h * a^2$	$(4/\sqrt{3} R)^3$	$(2(R_a + R_c))^3$	
APF	0.74	0.74	0.68	Calculate: $n * \text{Volume of sphere} / \text{volume unit cell}$	



- Chapter 6: More Technical with mechanical behavior



- ULTIMATE TENSILE STRENGTH: the maximum stress that a material can withstand while being stretched or pulled before breaking.
- PROPORTIONAL LIMIT: approximately where plastic deformation begins



- YIELD STRENGTH: the point where, we assume plastic deformation begins and also is where on a metallic stress-strain curve the stress-strain behavior stops being linearly proportional.
 - To determine the 0.2% offset yield strength we begin from a strain of 0.002 (note: $(0.002)(100\%) = 0.2\%$) and draw a line parallel to the original curve, or with the same slope as the Young's modulus of the metal being tested. Where this line intersects the curve is where we define the yield strength

- UNIFORM AND NON-UNIFORM DEFORMATION:

- Deformation is uniform until the ultimate tensile strength
- deformation is elastic until the yield strength and then plastic deformation begins.

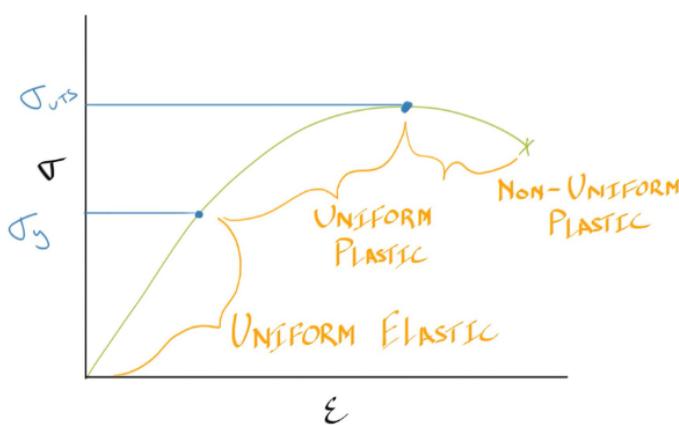


Figure 3: The generalized stress-strain behaviour for a metallic sample loaded in tension showing the regions of uniform elastic, uniform plastic, and non-uniform plastic deformation.

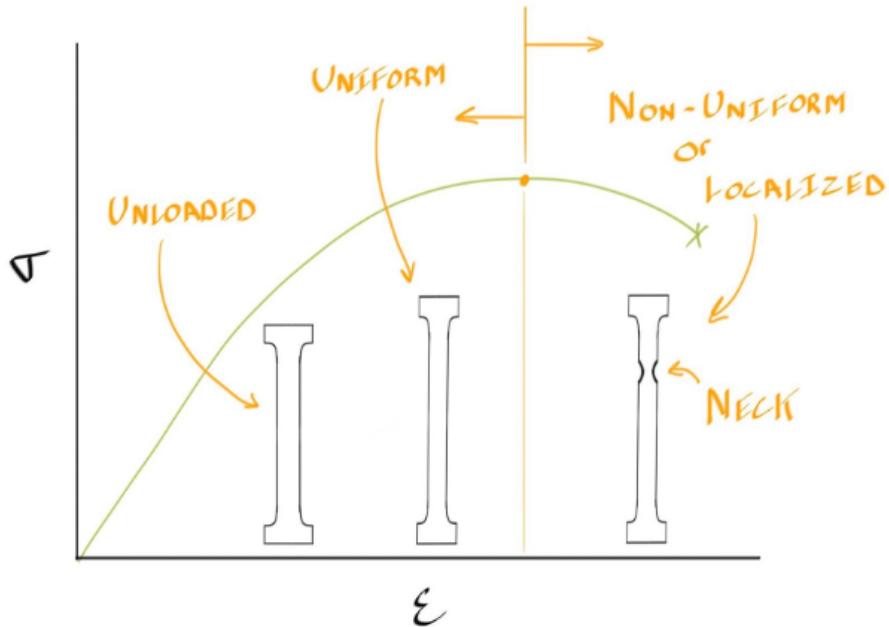


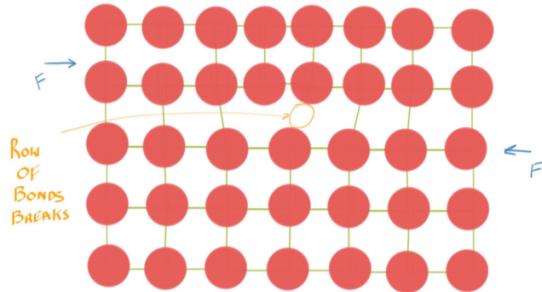
Figure 4: The generalized stress-strain behaviour for a metallic sample loaded in tension showing the sample geometry in the regions of uniform elastic, uniform plastic, and non-uniform plastic deformation.

- As a metal sample is loaded to progressively higher values of stress, eventually it will begin to fail.
- In tension, this begins when a few bonds break between metal atoms.
- this would occur randomly anywhere within the reduced section.
- Several regions of these few broken bonds will eventually come together and form a larger crack that eventually progresses to a larger crack leading to the final fracture event when the sample breaks into two pieces.
- Microscopically we observe that somewhere within the reduced section we see a sudden **narrowing of the cross-sectional area**. (NECKING)
- The cross-sectional area in the neck is reduced and although the metal itself does continue to get stronger within the neck, it does not strengthen as rapidly as the cross-sectional area is decreasing.
- The initial cross-sectional area is a constant and as the actual cross- sectional area decreases rapidly the force required to continue elongating the sample decreases and so we observe the engineering stress decreasing after the onset of necking, at the UTS.

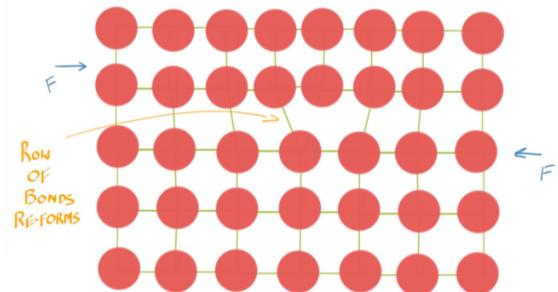
- **Chapter 7: Meddling with matter**

❖ MECHANISM FOR PLASTIC DEFORMATION:

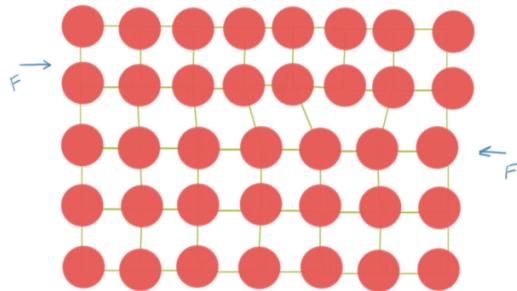
- Dislocation: crystalline imperfection that is responsible for the stepwise breaking and reforming of bonds during plastic deformation
- We can change the amount, or the dislocation density
 - by heating a metal (annealing), which lowers the dislocation density
 - by plastically deforming, which increases the dislocation density.
- **Plastic deformation** involves rows of bonds breaking and reforming in a step-by-step fashion (step-by-step movement of linear imperfections)



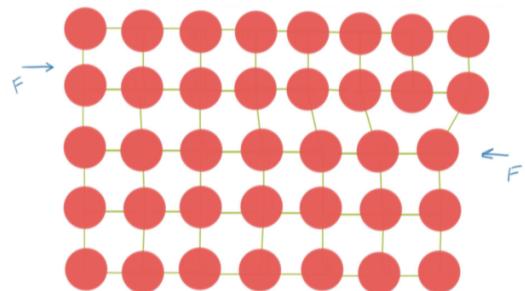
(a) As the force is applied the bonds to the right of the dislocation stretch and eventually break.



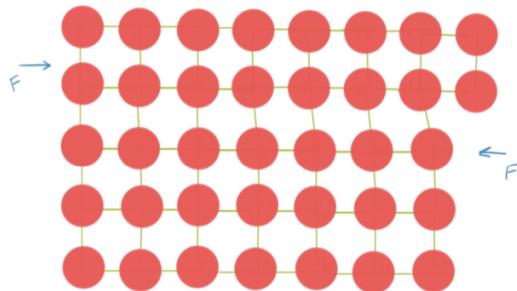
(b) A new set of bonds re-forms.



(c) This breaking and re-forming happens again.



(d) And again.



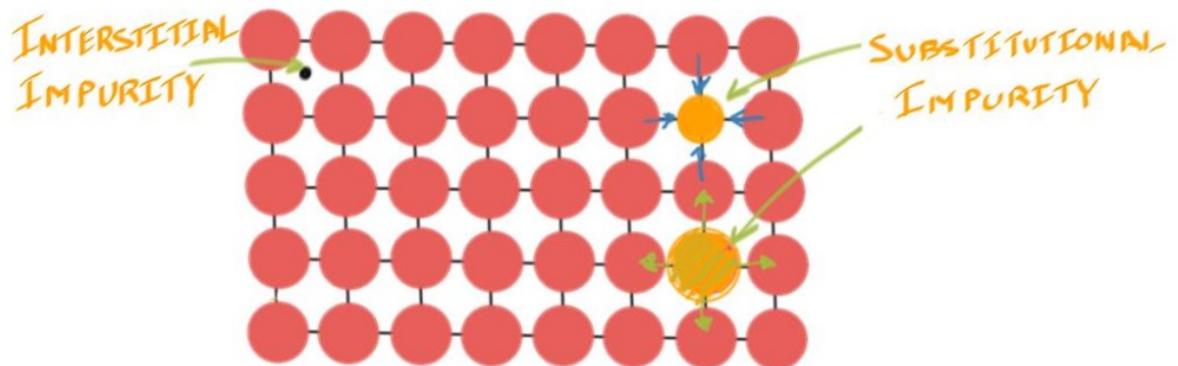
(e) And again.

❖ INTERFERING WITH DISLOCATION MOVEMENT:

- This makes dislocation movement more difficult, and will increase the strength of a metal
- Known as crystalline imperfections
- There are four general ways that we can strengthen a metal (organized according to dimensionality):
 1. Zero-dimensional imperfections (Point Defects)
 2. One-dimensional imperfections (Linear Imperfections or Dislocations)
 3. Two-dimensional imperfections (Interfacial Imperfections)
 4. Three-dimensional imperfections (Volume Defects)

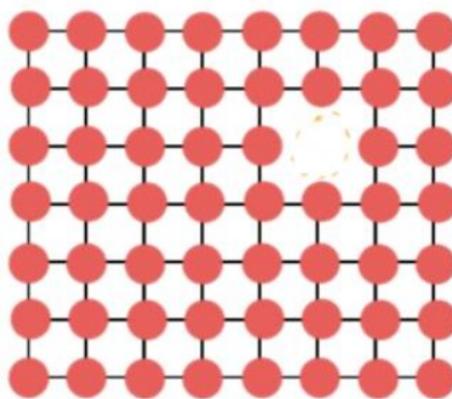
1. ZERO DIMENSIONAL IMPERFECTIONS // POINT DEFECTS:

- They occupy only one space in the lattice
- Types of point defects:
 - INTERSTITIAL IMPURITY: impurity atoms or molecules that occupy the spaces between the regularly arranged atoms or ions in this lattice.
 - SUBSTITUTIONAL IMPURITIES: are foreign atoms or ions that replace or substitute for the host atoms or ions in the crystal lattice of a material.
 - In contrast to interstitial impurities, which occupy spaces between the host atoms, substitutional impurities take the place of the original atoms in the lattice structure.



- The small arrows that are meant to show the strain imposed on the lattice as a result of the impurity atom.
- This strain field that results from the impurity atom interacts with the strain field surrounding a dislocation
- The net result is that it is more difficult for a dislocation to move through the lattice close to an impurity than it is to move through the undisturbed lattice.
- So, plastic deformation is more difficult.
- This is the reason that we add very small amounts of carbon to iron to make steel.
- Even very small concentrations, typically less than 1 weight percentage carbon, result in a significantly higher strength for steel versus iron.

- VACANCIES: an atom that has jumped out of its regular lattice position, leaving behind an empty site that would otherwise be occupied by an atom.
- They are the one crystalline imperfection that we don't use to increase the strength of a metal.



- A vacancy is formed when atoms are desperately vibrating in their lattice sites, trying to jump out of their sites.

- Most of the time they are unsuccessful because the binding energy is stronger than the thermal energy.
- But every so often an atom makes a successful jump from its lattice site and can move somewhere else in the lattice.
- This leaves behind a missing atom, or vacancy.

? If we raise the temperature so that the thermal energy wins out over the binding energy, then why doesn't the entire crystal just melt? How is it possible to have only a few atoms make successful jumps out of their lattice sites while the majority remain?

- Not all of the atoms have the same energy. There is a distribution of energies.
- So, it makes sense that a single atom may have enough energy to jump out of its lattice site, while the majority of the remaining atoms do not
- As we increase the temperature we find a larger number of atoms populate the higher energy states,
- As we approach lower temperatures we find fewer of the high energy states populated,
- At absolute zero, only the lowest energy state would be populated.

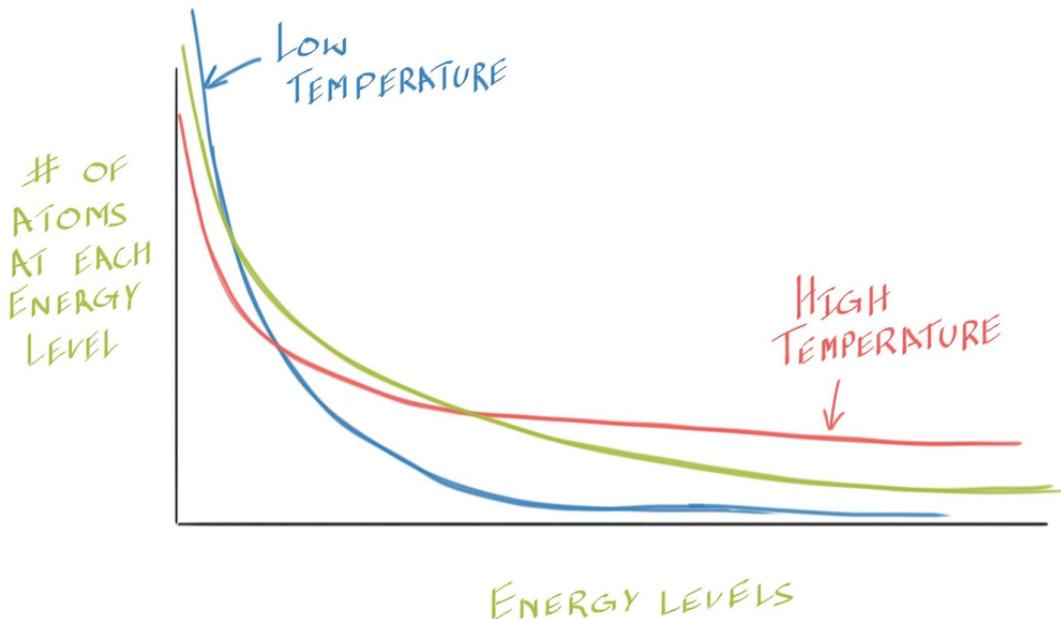


Figure 10: A cartoon depiction of the distribution of particles over permissible energy levels at high, medium and low

2. ONE DIMENSIONAL IMPERFECTIONS // DISLOCATIONS:

- When we plastically deform a metal we create new dislocations
- This increases the dislocation density and dislocations have difficulty moving past one another.
- The strain fields that surround dislocations interact with one another and can repel each other, or in certain cases, cancel one another out, leaving a small region of perfect crystal.

- Strengthening metal:
 - Cold work/ cold forging: referring to the fact that we obtain more strengthening when the metal is at a lower temperature.
 - Warm work/hot forging: the part warms up during deformation or we actually heat the part to make deformation easier and to prevent the part from becoming brittle and so we also call this strengthening
 - Strain hardening: Because the metal accumulates plastic strain during the strengthening process

3. TWO DIMENSIONAL IMPERFECTIONS // INTERFACIAL IMPERFECTION:

- FREE SURFACES:
 - Example: the surface of the sapphire lens cover on an iPhone.
 - Within the sapphire there are aluminum and oxygen atoms arranged in a regular crystalline lattice until you hit the surface and then suddenly there are missing nearest neighbor atoms - unsatisfied bonds with the atoms along the surface.
 - It is a crystalline imperfection, however, **we don't** really use this type of defect to increase the strength of a metal.

- INTERNAL INTERFACES OR GRAIN BOUNDARIES:
 - These occur anywhere one crystal contacts another.
 - the metal cooled from a liquid state, the crystals will often be randomly oriented and the atoms certainly don't line up with one another
 - if we consider a dislocation moving through one of these grains, to continue moving, it must cross the grain boundary
 - The dislocation must change direction, because the atomic plane that it is moving along in one crystal is at an angle relative to the corresponding plane in the next crystal.

- The atomic spacing at the grain boundary is not the same as it is in the rest of the crystal and the dislocation requires more energy to navigate past this disruption in the regular spacing of atoms.
 - Finally, the plane that the dislocation is moving along in one crystal does not line up with the plane in the next crystal
 - All of these challenges with crossing a grain boundary mean that grain boundaries can be used to inhibit dislocation movement, thereby increasing the strength of a metal.
 - How do we increase the number of grain boundaries in a metal?
 - use a powdered catalyst in aqueous chemistry to increase the surface area to volume ratio,
 - If we decrease the grain size of a metal we will create more grain boundaries and more obstacles to dislocation movement and can expect to **increase the strength** of a metal. [GRAIN SIZE REDUCTION]
4. THREE DIMENSIONAL IMPERFECTIONS // SECOND PHASE PARTICLES:
- if we have a region of a solid that has a different crystal structure we have a second phase, or three-dimensional imperfection.
 - These second phase particles are often hard and brittle compounds that are already very hard to deform.
 - This is a commonly used aluminum alloy that can be carefully heat treated to produce a fine distribution of second phase precipitates that greatly increases the strength of this alloy.
 - A pore
 - A region of FCC metal within an otherwise BCC metal
 - A ceramic particle within a metallic sample

ZERO DIMENSIONAL IMPERFECTIONS	ONE DIMENSIONAL IMPERFECTIONS	TWO DIMENSIONAL IMPERFECTIONS	THREE DIMENSIONAL IMPERFECTIONS
INTERSTITIAL IMPURITY	DISLOCATION	FREE SURFACES	A PORE
SUBSTITUTIONAL IMPURITIES		GRAIN BOUNDARIES	A REGION OF FCC METAL WITHIN AN OTHERWISE BCC METAL
VACANCIES		INTERFACE BETWEEN TWO PHASES	A CERAMIC PARTICLE WITHIN A METALLIC SAMPLE

- **Chapter 8: POLYMERS**

- Polymers are large molecules built by linking 50 or more smaller molecules called monomers
- It is a collection of very long molecules intertwined with one another
- Each of these great long strings of atoms is actually a very large molecule.
- The bonds that hold these atoms together within the molecule or string would be called **intramolecular bonds** (intra means within)
 - intramolecular bonds are so much stronger than any of the other bonds present we often call them **strong intramolecular bonds**
 - **Intramolecular forces** are the forces that hold atoms together within a molecule.(strong)
- **Intermolecular forces** are forces that exist between molecules.(weak)
 - When a polymer is plastically deformed, one of the things that occurs within the microstructure is that molecules slide past one another.
 - There are forces that occur between molecules, so we could call them intermolecular forces (inter means between)
- Plastic deformation occurs largely by the movement of long molecules past one another, overcoming weak forces between molecules as plastic deformation occurs
 - So, as we plastically deform a polymer and the molecules become aligned along the loading axis we get an **increase** in the amount of the load that is supported by primary bonds and less of the load supported by secondary bonds.

❖ The Stress-Strain Behaviour of a Typical Polymer:

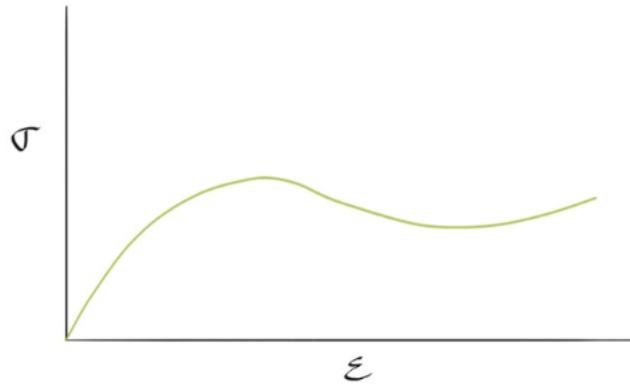


Figure 3. The generalized stress-strain curve for a plastic polymer.

- there is an initial portion of the curve that is approximately linear.
- This region is followed by a curved region and a peak stress.
- After that, the stress decreases, but the unique feature of the polymer curve is that the polymer is somehow able to continue load bearing after the peak
- Recall that metals will always break after the peak, or ultimate tensile strength, because this is where necking occurs and the metal can't strengthen fast enough to overcome the rapidly decreasing cross-sectional area in the neck.
 - This means that some polymers must have a microstructural mechanism that allows them to strengthen in the neck very significantly.
 - Something significant like, say, a change in the proportion of primary bonds to secondary bonds supporting the load.
 - The alignment of polymer molecules with the loading axis in this manner is frequently called **chain orientation**.
- Polymers are sometimes able to continue supporting load well beyond the ultimate tensile strength (onset of necking) as the molecules within a polymer can become elongated and oriented with the loading axis allowing the stronger intramolecular bonds to support the load

❖ DEFINING YIELD STRENGTH AND TENSILE STRENGTH

- Since the polymer continues to support load after necking, we can safely use the peak of the curve itself as an unambiguous point to define the yield strength.
- By convention, the point where the polymer fractures is called the tensile strength.

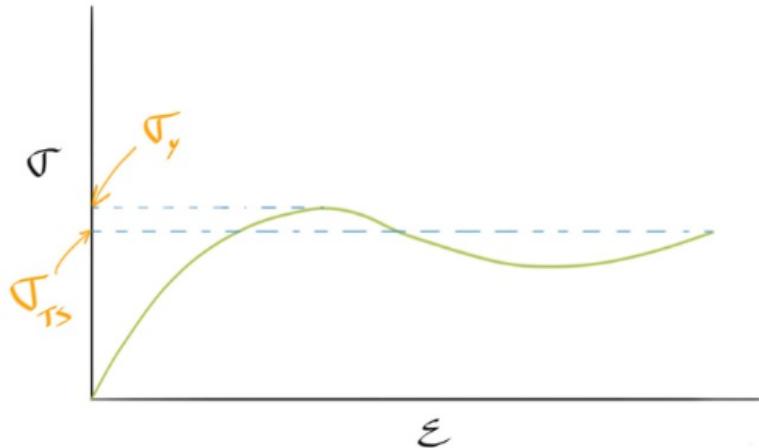


Figure 4. The generalized stress-strain curve for a plastic polymer, showing the yield strength and the tensile strength.

❖ POLYPROPYLENE (PP):

- The recycling code for PP is 5.
- Generally, PP is a little stronger and has a higher elastic modulus than polyethylene.
- This increase in mechanical properties comes from the extra CH₃ (methyl) group on the mer unit

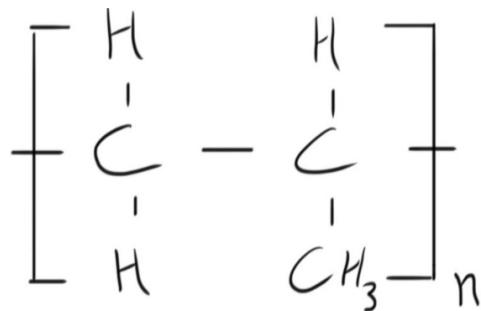
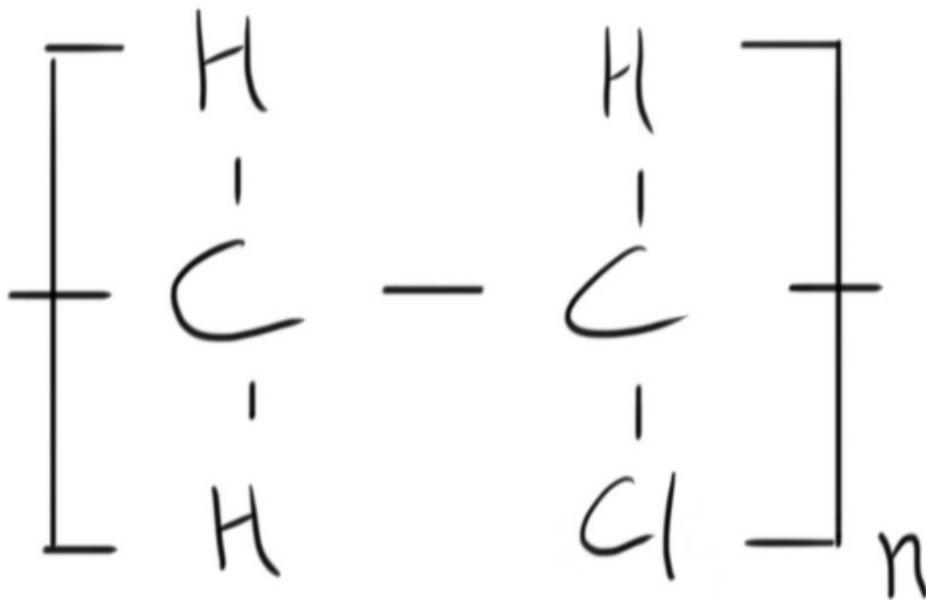


Figure 5. The mer unit for polypropylene. The methyl (CH_3) group makes it slightly harder for chains to slide past one another, increasing the strength.

❖ POLYVINYL CHLORIDE(PVC):

- PVC's name tells us that there must be a chlorine atom in the mer unit.
- The vinyl group is just two carbons bonded with a double bond and one hydrogen missing
- PVC is a very versatile polymer and can have a wide range of properties.
- In its simplest form, it is quite strong, with a relatively high elastic modulus.



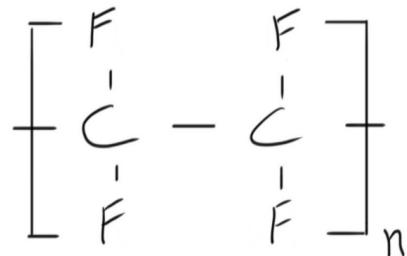
❖ The periodic table and electronegativity:

- As we move across the periodic table from left to right the elements get closer to a very low energy arrangement of their electrons.
- The rightmost column is called the inert gasses and these elements generally don't react with other elements, because they are so stable.
- This trend from left to right causes the elements towards the right to have a stronger attraction to electrons and the elements towards the left to be more likely to get rid of an electron.
- From the top to the bottom of the periodic table the atoms get larger
- Larger atoms mean that the electrons are further from the nucleus and that the nucleus attracts electrons less strongly.
- moving from the bottom left to the top right of the periodic table there is an increasing attraction to electrons.
- This trend is captured in the so-called electronegativity.
- Elements with higher electronegativity reside towards the top right of the periodic table.

- Coming back to PVC now, you'll notice that chlorine (Cl) sits in the second row from the top, just to the left of argon (Ar) and therefore has a high electronegativity.
- When we put a highly electronegative element into a molecule, as we do in PVC, that electronegative element actually pulls on the orbiting electrons and creates a bit of an imbalance across the molecule.
- Because the electron carries a negative charge, this imbalance in the electron cloud can create charged regions of the molecule.
- When a molecule has a negative and positively charged ends, or poles we say that it is a dipole

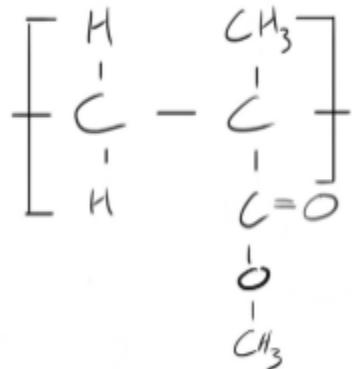
❖ POLYTETRAFLUOROETHYLENE:

- PTFE is used in non-stick surfaces.
- The key to PTFE's success as an nonreactive polymer lies in the large fluorine atoms bonded to each carbon.
- These fluorine atoms are quite large and protect the intramolecular bonds within PTFE from being broken easily.
- Note, that although fluorine is highly electronegative, the PTFE molecule is nonpolar since the fluorine atoms are geometrically symmetrical about the molecule and so the center of positive charge lies at the same point as the center of negative charge.
- Gore-Tex® is a form of PTFE that has been formed into thin films and stretched. The stretching introduces fine holes, or pores, in the film.
- PTFE, is a polymer that repels water (it is hydrophobic) so this means that water tends to form beads on the surface of PTFE.
- This prevents liquid water from passing through the pores in GoreTex®, however, individual molecules of water, as in the vapor phase, can freely diffuse through these pores.
- This is how GoreTex® used in outdoor clothing is able to keep the user dry in the rain while also allowing sweat to evaporate and diffuse out of the clothing.



❖ Polymethylmethacrylate (PMMA):

- The term acrylate tells us that this is an acrylic.
- You may know that some acrylics are used for windows because they can be made beautifully optically transparent.
- The reason that we are able to make PMMA optically transparent is very interesting and starts from the mer unit



- The large side group that is present on each mer unit prevents the molecules from organizing close to one another.
- This ensures the polymer is completely disorganized, or amorphous.
- You see, polymer molecules can become aligned with one another and highly organized, which we call crystalline.
- When a polymer crystallizes, the index of refraction is different from when it is amorphous.
- If the polymer contains parts that are amorphous as well as parts that are crystalline (so-called semicrystalline)
- then light passing through the polymer will not follow a direct path and the polymer will be translucent or opaque.
- So, part of the reason that PMMA is transparent is because the mer unit ensures that it stays 100% transparent.

❖ HOW LONG ARE THESE MOLECULES:

- When polymers are synthesized, it is somewhat difficult to control the length of the molecules
- So, we end up with a few molecules that are really short, a few that are very long and a bunch in between.
- WE ARE LEFT WITH A DISTRIBUTION OF MOLECULAR LENGTHS
- We could use an average.
- Simply sum up all of the molecule lengths and then divide by the total number of molecules.

- The average length of molecules in a polymer are typically described by The average mass of the molecules in the sample
- ❖ MOLECULAR WEIGHT:
 - 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.
 - Ultra high molecular weight polyethylene (UHMWPE) is commonly used as a bearing surface in artificial hip replacements because of the high strength and high wear resistance from the extremely long molecules.
- ❖ HOW DO THESE MOLECULES STACK UP:
 - We already know that polymer molecules, although often linear, are not straight.
 - But that doesn't mean that they are always totally disordered.
 - We also saw that some order can develop when a polymer is plastically deformed, so-called chain orientation.
 - Well, there are other ways that polymers can order themselves and in some cases they can do it on their own, without any external loading.
 - The molecules in a simple polymer like polyethylene will often fold back and forth on themselves, forming a so-called semi-crystalline polymer.



- Now, since the molecules are so long a polymer will never be able to crystallize 100%, which is why you see the amorphous tie molecules
- high density polyethylene (HDPE) has a higher percentage crystallinity than low density polyethylene (LDPE).
- Since the crystalline regions are held together more strongly by secondary bonds than the amorphous regions, these regions are stronger and, in fact, increasing the crystallinity of a polymer is another way to increase its strength.
- It will also typically increase the resistance to chemical dissolution and allow the polymer to be used at a higher temperature.

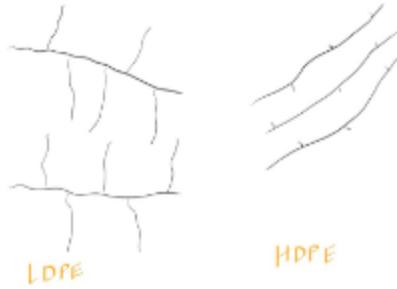


Figure 18. A cartoon sketch of LDPE and HDPE showing the increased and longer branches in LDPE, preventing extensive crystallization.

❖ CHANGING THE INTRAMOLECULAR BONDS:

- All Hydrogen needs is a somewhat electronegative element and hydrogen gets positive.
- Hydrogen is so special in this ability to create a strong dipole that we have named a special type of intermolecular bond after it: the Hydrogen Bond.
- The hydrogen bond may occur when hydrogen is bonded in a molecule to oxygen (O), nitrogen (N), or fluorine (F). Kevlar®, for example, contains a hydrogen bonded to nitrogen and this allows strong Hydrogen bonding between molecules, contributing to a very strong polymer.

❖ CROSS-LINKING OF POLYMERS:

- Cross-linking can also be used to increase the strength of polymers.
- Cross-linking involves strong bonds(**intramolecular** bonds(covalent))
- Example: Vulcanizing rubber
 - When the latex is harvested from latex trees it is a creamy white somewhat viscous liquid.
 - Once left to dry out the latex becomes a solid, but is not very strong and has a relatively low elastic modulus.
 - To make this a much more useful material sulfur compounds are added and the latex is heated.
 - In the process the sulfur compounds create new strong, primary, bonds between the original molecules.
 - This limits their ability to move past one another, thereby increasing the strength
 - These cross-links also ensure that the molecules are pulled back to their original positions after a load is applied and released

- Important in elastomers
- Too much cross-linking causes the polymer to become hard and brittle
- Example: polyethylene
 - used in some pressurized water distribution systems is cross-linked to ensure that it can withstand the pressure in the system
 - also withstand the higher temperatures of hot water in residential water systems.
- ❖ IMPORTANT FACTS:
 - increasing chain length increases the strength of a polymer
 - High molecular weight=high yield strength
 - HDPE mostly contains linear polymer chains
 - Van Der Waal forces are INTERmolecular(weak)
- ❖ TEMP CHANGES:
 - Polymers are sensitive to temperature changes
 - Much of the behavior of polymers is due to the weak, intermolecular, bonds.
 - These bonds, or interactions, can be disrupted much more easily by the thermal energy, even when the temperature is relatively low: close to room temperature.
 - In a metal or a ceramic, most of the properties are determined by the nature of the strong, primary, bonds holding them together
 - and these bonds have bond energies significantly higher than the thermal energy close to room temperature.

➤ the stress-strain behavior for a typical plastic polymer in different temperatures

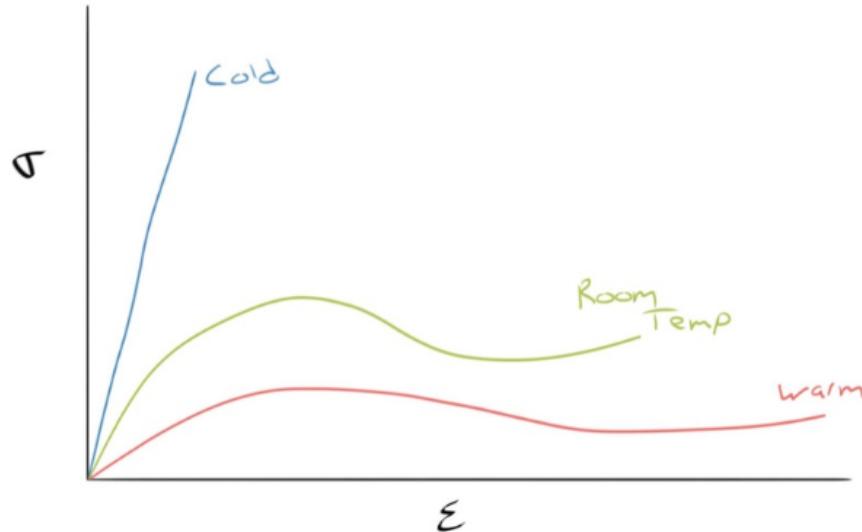


Figure 19. A stress-strain curve for a hypothetical plastic polymer at three temperatures. It is not uncommon for polymers to experience significant changes in mechanical properties with relatively small changes in temperature.

★ INCREASING HEAT ON POLYMERS:

- Polymers are viscoelastic
- PVC can be used at a higher service temperature.

- There are at least two important temperatures that you should be aware of when it comes to heating a polymer up:
 - glass transition temperature
 - and the melting temperature
 - Above the melting temperature the polymer will flow like a thick liquid because there is enough thermal energy to disrupt the weak intermolecular bonds and allow the molecules to flow freely past one another.
 - Upon heating, you may be able to imagine that the thermal energy will start to beat the intermolecular bond energy in the amorphous regions first, where the molecules are further apart. (glass transition temp)
 - With continued heating the thermal energy will eventually be enough to disrupt the intermolecular bonds in the crystalline regions and all of the molecules will be free to flow past one

another and the polymer will begin to flow like a thick liquid: melting.

- Therefore, the lower temperature, when the amorphous regions were disrupted is known as the glass transition temperature.

→ GLASS TRANSITION TEMPERATURE:

- ◆ The temperature upon heating, when molecules possess enough thermal energy to overcome the secondary, intermolecular interactions within the amorphous regions of the polymer

❖ TIME:

- polymers can have very different mechanical properties depending on how quickly we apply a load.
- polymers tend to behave in a more brittle fashion when loaded really quickly.
- When loaded quickly there is not enough time for them to move and instead the polymer fractures.
- However, Over the long time period, the molecules will slowly move past one another leading to a slow, but permanent, deformation process.
 - Example: A heavy desk is placed on a carpeted floor. If the desk is removed immediately there is only a small amount of deformation in the carpet and this deformation typically disappears within a matter of seconds or minutes. However, if the desk is left for several months, the deformation is significant and it will take a very long time, with a lot of vacuuming to reverse the load, for the deformation to disappear, if it ever does completely.

❖ Optical transparency of Plexiglas®:

- polymer being completely amorphous
- Photons of visible light interact with the electrons within a polymer, rather than by moving molecules relative to one another
- Crystalline and amorphous region have different index of refraction
- There will be scattering events which results in the semi-crystalline polymer to appear translucent
- HOW DO WE MAKE IT TRANSPARENT:
- Polymers are never 100% crystalline
 - 100% Amorphous (Plexiglas)

- This ensured that there were no boundaries between crystalline regions and amorphous regions that would scatter the light.
- Large side group prevents crystallization
 - Example: Sapphire(Al₂O₃)
 - Window glass-amorphous-clear
- When light passes through without scattering the polymer is transparent
- glassy metals that are fully amorphous but opaque.
- Even a single crystal metal, such as a silicon semiconductor, or a nickel-based single crystal jet turbine blade are both opaque, so neither being fully amorphous, nor fully crystalline ensures optical transparency.
- it all has to do with how the material absorbs light energy

❖ LOOK AT CHAPTER 9

- **Chapter 9: Atomic Model+more**

❖ LIGHT:

- Visible light is only a very tiny portion of a massive spectrum of radiation
- It includes radio waves, microwaves, infrared radiation, ultraviolet radiation, x-rays, and even gamma rays.
- This is called the electromagnetic spectrum

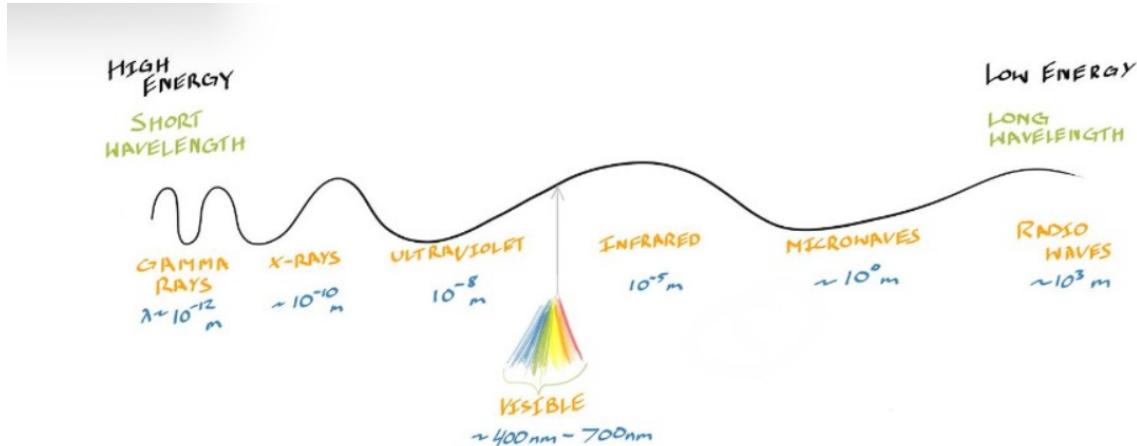


Figure 1. The electromagnetic spectrum. Visible light is only a tiny little bit of the spectrum.

- Another feature of electromagnetic radiation is that the energy within the electromagnetic spectrum exists as chunks of energy, or photons.
- When things exist only as individual, non-divisible units we say that they are quantized.
- So, energy in the electromagnetic spectrum is quantized, and it turns out that the amount of **energy** in each so-called quanta or photon is **inversely proportional** to the **wavelength** of the radiation.
- Frequency is inversely proportional to wavelength
- radio waves are less energetic and ultraviolet waves, x-rays and gamma rays are more energetic.
- As humans we worry more about exposure to higher energy radiation than low energy radiation.

➤ The value of energy in quanta can be calculated as:

$$E = \frac{hc}{\lambda}$$

- h is the Planck constant = 6.626×10^{-34} Js
- c is the speed of light = 3×10^8 m/s
- λ is the wavelength in m/s

OR

$$E = h\nu$$

- ν is frequency of light
- As speed = frequency \times wavelength

❖ $1\text{eV} = 1.6 \times 10^{-19} \text{C} = 1.6 \times 10^{-19} \text{J}$

❖ THE ATOM:

- A central nucleus contains positively charged particles called protons.
- The nucleus also contains particles having no charge, neutrons
- Mass proton=mass neutron= 1.67×10^{-27} kg
- Orbiting around the nucleus are negatively charged particles called electrons.
- Mass electron = 9.1×10^{-31} kg
- making each of protons and neutrons roughly 1800 times more massive than electrons.
- Most mass is in nucleus
- Protons = atomic number
- Differing numbers of neutrons in an atom give us so-called isotopes of an element.

❖ The Bohr Model of an Atom:

- The essential features of the Bohr model are a central nucleus with orbiting electrons
- electrons orbit at fixed distances from the nucleus
- electrons may jump to higher orbits if they absorb a quanta of energy exactly equal to the difference in energy between the two orbits
- similarly release a quanta of energy if the electron drops back down to a lower orbit

❖ PROBLEMS:

- It only allows calculations of atoms with one electron.
- That is, hydrogen H, a helium ion, or a doubly ionized lithium ion
- not being able to predict line splitting experiments, where closely spaced energy levels were revealed within the orbits further away from the nucleus than the first orbit.

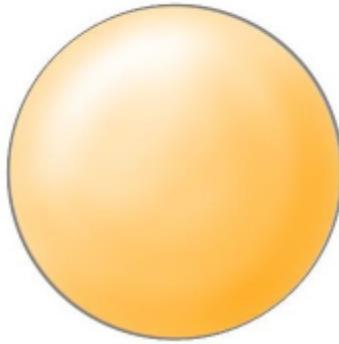
❖ QUANTUM-MECHANICAL MODEL OF AN ATOM:

- In this model, to fully describe the energy state of an electron, we must use four quantum numbers
- PRINCIPLE QUANTUM NUMBER:
 - The principal quantum number describes the **size** of the electron orbit.
 - Sometimes you'll see the principal quantum number described with letters instead of numbers.
 - The letters are always upper case and start at K and move along the alphabet from there so the
 - *K shell* is $n=1$,
 - the *L shell* is $n=2$,
 - the *M shell* is $n=3$, and so on.
- ANGULAR MOMENTUM NUMBER:
 - describes the **shape** of the electron orbital
 - the angular momentum quantum number can have any value ranging from zero to one less than the principal quantum number, that is
 - $\ell=0,1,2,\dots,n-1$..
 - $\ell=0$ is the *s subshell*,
 - $\ell=1$ is the *p subshell*,
 - $\ell=2$ is the *d sub-shell*, and

- $\ell=3$ is the *f subshell*.

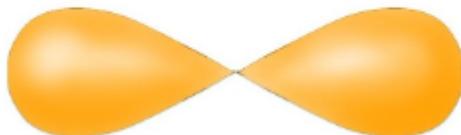
➤ S-subshell:

A SPHERE!



➤ P-subshell:

"DUMBBELL"



❖ MAGNETIC QUANTUM NUMBER:

- The magnetic quantum number describes how many different ways each subshell can be **orientated**.
- Each of the unique orientations is called an *orbital*.
- These are twice the angular momentum quantum number plus one and are written as integers ranging from the negative to the positive value of ℓ
- For example, for the *p* subshell, or $\ell = 1$, there are three orbitals and the magnetic quantum number could be -1, 0, or 1.
- Within each of these orbitals, or any orbital for that fact, there may be a maximum of two electrons.

- These electrons are distinguished from one another by the spin quantum number.

- ❖ The Spin Quantum Number:
 - The spin quantum number reflects the slightly different energy level for two electrons within a specific orbital.
 - The values of the spin quantum number are either positive or negative one half

- ❖ MAGNITUDES OF ELECTRON ENERGY LEVEL:
 - at this point that the electron shell closest to the nucleus, having the **highest** value of energy ($n=1$) s subshell



Figure 5. A common sketch used to describe and memorize the general rule for the relative energy levels of subshells. The shells and subshells are first drawn out using numbers for the principal quantum number and letters (s, p, d, f) for the angular momentum quantum number. Leftwards and downwards arrows are then drawn through these subshell labels, showing the order of filling of electrons into isolated atoms.

- ❖ ELECTRON CONFIGURATION:
 - Carbon: 1s₂ 2s₂ sp₂
 - Ca: 1s₂ 2s₂ 2p₆ 3s₂ 3p₆ 4s₂
 - Titanium: 1s₂ 2s₂ 2p₆ 3s₂ 3p₆ 4s₂ 3d₂
 - Titanium 2+: 1s₂ 2s₂ 2p₆ 3s₂ 3p₆ 3d₂

➤ EXCEPTIONS;

- Chromium: 1s₂ 2s₂ 2p₆ 3s₂ 3p₆ 4s₁ 3d₅
- Copper: 1s₂ 2s₂ 2p₆ 3s₂ 3p₆ 4s₁ 3d₁₀

❖ OCTET STABILITY:

Inert gasses, in fact what makes them inert or unreactive, is that their electron configurations are very stable. This stable configuration involves eight electrons in their outermost shell.

Sometimes the so-called octet rule is written as

$$ns^2 np^6$$

❖ ATOMIC BONDING:

➤ IONIC BONDING:

- involves a transfer of electrons followed by a subsequent charge attraction between oppositely charged ions.
- charge attraction is general, between all oppositely charged ions. Furthermore, the charge on an ion is not depleted by its participation in an ionic bond. For this reason, ionic bonding is said to be non-directional.
- We can explain the fact that ionic solids do not conduct electricity by noting the stability of these ions, with all their electrons strongly bound to their respective nuclei.

➤ COVALENT BONDING:

- involves the sharing of electrons.

➤ METALLIC BONDING:

- the sea-of-electrons model, and the band theory of solids.
 - In the sea-of-electrons model the valence electrons are not bound to a specific nucleus, but are instead thought to be free to move around while the nuclei are bound into their lattice positions
 - METALLIC BOND: collection of delocalised electrons holding together the ion cores

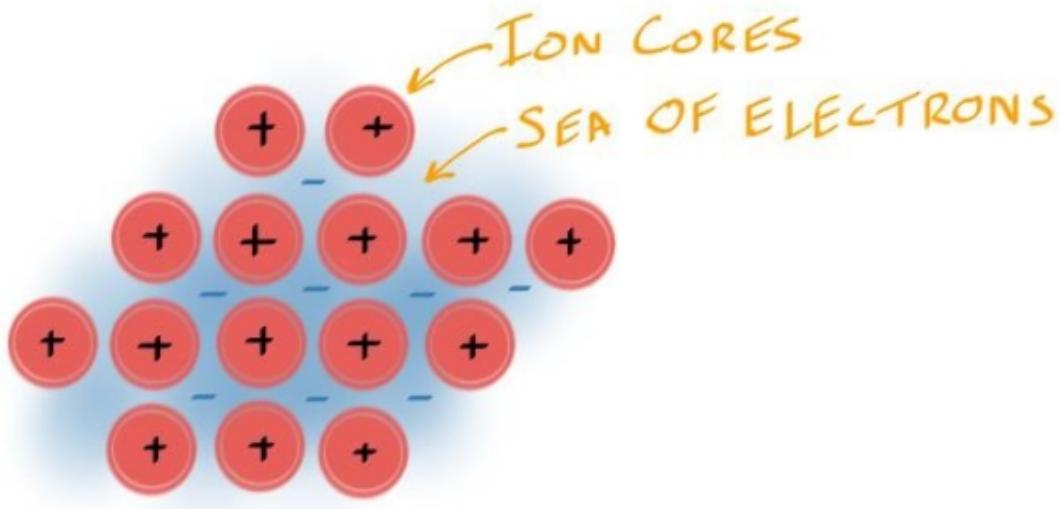


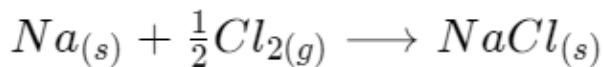
Figure 9. A cartoon depiction of a slice through a metal showing the sea-of-electrons bonding together the ion cores in a lattice.

- The sea-of-electrons model can also help to explain the ductility of most metals.
- If a sufficiently high stress is applied to a metallic crystal, eventually one plane of atoms will move past another
- There is an energy requirement to move the planes, however, it is generally possible for the planes to move past one another since they are always held together by the sea of negatively charged electrons.
- In a ceramic, for one plane to move past another we would need to have similarly charged ions pass through an intermediate position in which they come closer to one another.
- This significantly raises the stress required to move a plane of atoms in a ceramic and typically leads to fracture before deformation.

- When we consider the electrical properties of polymers we can quite easily explain their electrically insulating properties due to the lack of any free electrons; all of the valence electrons are tightly bound in the strong covalent bonds.

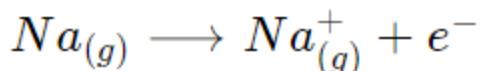
❖ Why does salt form a crystal?

➢ let's consider the formation of solid crystalline salt from gas phase chlorine and solid sodium:

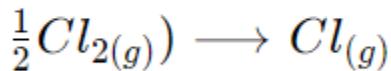


1.

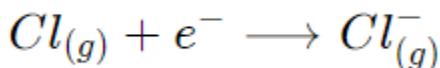
- look at the energy changes here to confirm that this was energetically favorable.
- solid going directly to a gas, without melting first is called sublimation and the so-called *sublimation enthalpy}*
- Positive values mean that we need to put energy into our system for the reaction to proceed from left to right.



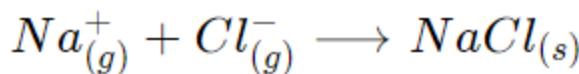
2.



3.



4.



5. crystallization
 6. It is energetically favorable for salt to form a crystal at room temperature.

❖ THE BAND THEORY:

- When atoms begin to get atomically close to one another, the electrons in each atom run the risk of having the same energy levels.
- This is called degeneracy
- Instead, as the atoms approach one another, the energy levels begin to spread out slightly so that, for a given electron energy level in an isolated atom, there are two corresponding energy levels when two atoms are close to one another, three for three atoms, four for four atoms, and so on.

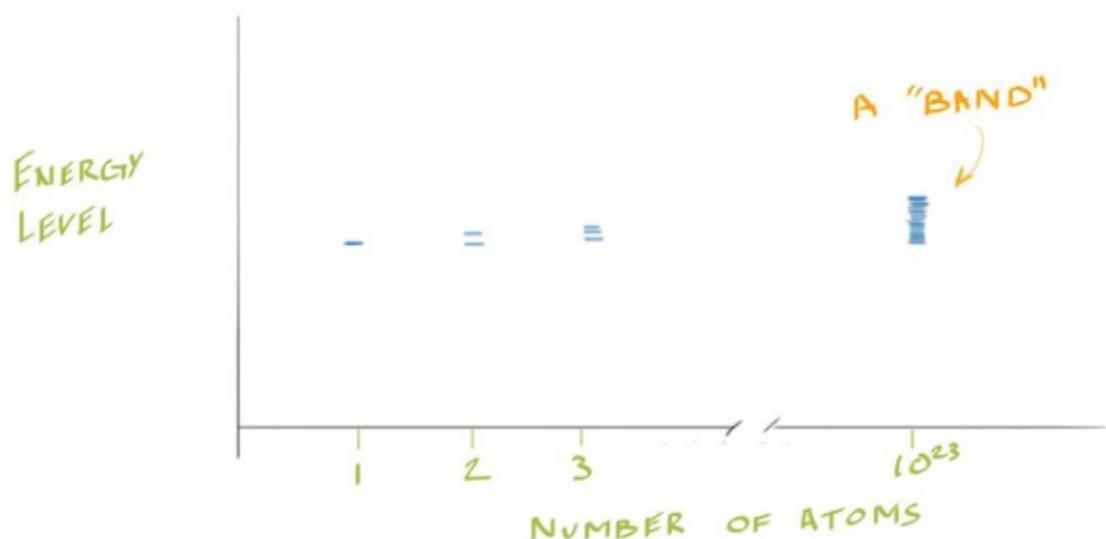


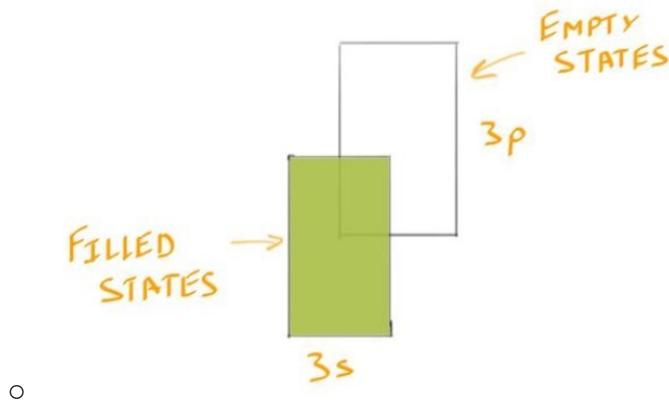
Figure 11. A schematic depiction of a particular energy level in an isolated atom, two atoms, three atoms, and so on up to a massive collection of atoms, as in a solid. The number of energy levels in a solid, for a corresponding single energy level in an isolated atom, is equal to the number of atoms, so that when we have a solid there are so many closely spaced energy levels as to be essentially continuous. We call this a band.

- Bonding in metals like copper:
 - Cu electronic configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$
 - When a massive collection of copper atoms come together in a solid,
 - The 4s energy levels spread out into a band, but notice that only half of these states will be filled.
 - 4s can accept two electrons, one spin up and one spin down.
 - Each of these states has a corresponding level in the band structure, even though only half are filled.



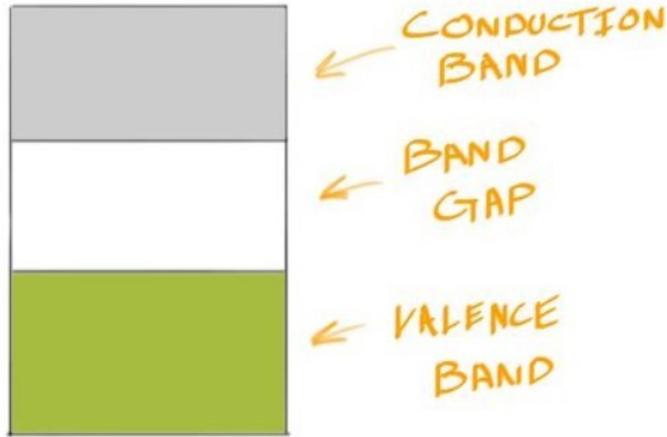
- This means that it is very easy to promote an electron up within the band structure into one of the empty states.

- Bonding in metals like Magnesium:
 - Mg electronic configuration: $1s^2 2s^2 2p^6 3s^2$
 - Even though the 3s band is filled, the energy levels for the 3p states actually spread out enough that they overlap with the 3s levels.
 - Just because the 3p levels are empty doesn't mean that they are not available.



- We can see that the unfilled states from the 3p levels provide available energy levels for electrons to be easily promoted into, from the 3s levels.
- Because of the overlap between the 3s and the 3p states, Mg still behaves like a metal

- Bonding in Ceramics and Polymers:
 - ceramics and polymers are electrically insulating
 - Ceramics tend to be held together by ionic bonds and ionic bonds involve electrons being transferred from one atom to another.
 - Remember also that this electron transfer happened so that each atom could achieve a filled valence shell.
 - Since the valence shell is filled there are no electron energy states immediately adjacent to filled states.
 - Also, these electrons are tightly bound to the nucleus, so there are no free electrons.
 - The same is true for polymers, except that the bonding is covalent.
 - Of course, in covalent bonds the valence electrons are shared between two atoms and are bound tightly to them.
 - Both of these types of materials are insulators.
 - Band structure for insulator:



- In order for electrical conduction to occur in an insulator, an electron would have to be given enough energy to cross the band gap.
- In such a case we say that it is promoted into the conduction band, where it is free to move.
- The valence band states arise from the valence electrons on the outermost parts of the atoms in the solid, which is why we call it the valence band.

- Bonding in Semiconductors:
 - semiconductors have a band gap that isn't as large as in an insulator.
 - This is important because it means that we can control the flow of electrons in these materials.
 - If a material has a band gap that is larger than 4 eV, we can consider it to be an insulator,
 - and if the band gap is less than 4 eV (but isn't zero) we can consider the material to be a semiconductor.
 - This means that, in many cases, thermal energy or photons of visible light can promote electrons across the band gap in semiconductors.
- DEFINING CONDUCTORS, SEMICONDUCTORS AND INSULATORS

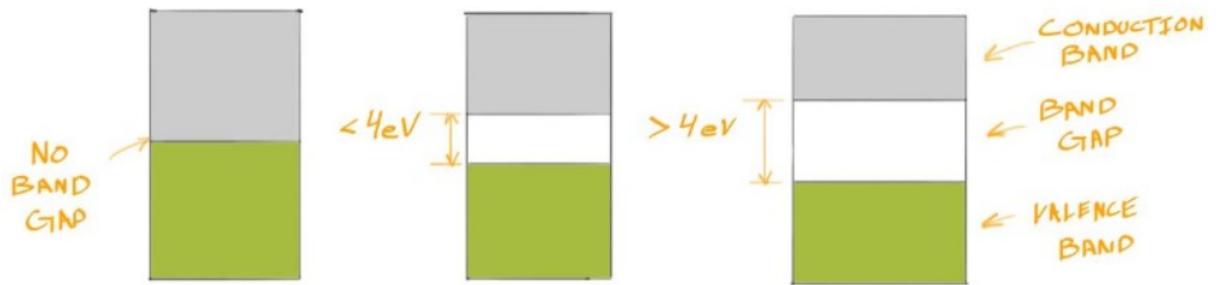


Figure 16. The band structures of conductors, insulators and semiconductors. For our purposes, we'll consider the dividing line between semiconductors and insulators to be 4 eV.

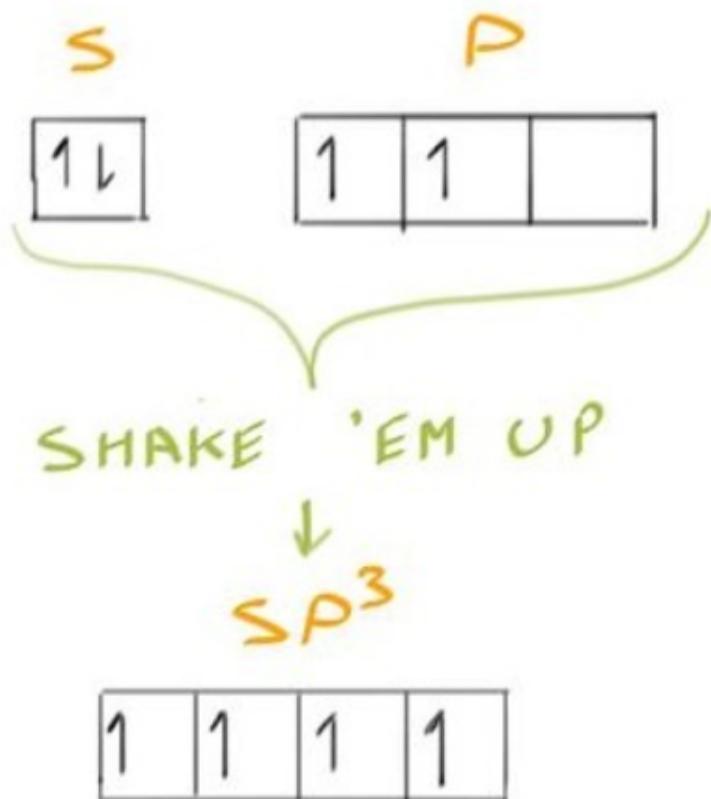
- if the material has a high band gap (greater than 3 eV) the photons will pass through and the material, barring any internal diffraction events, will be optically transparent.
- The visible photons will have no trouble promoting electrons, since there is no band gap in a metal.
- As a result, metals are opaque.
- The electron promotions are temporary and when the electrons drop back down to their lower energy states they re-emit the photons.
- As a result, metals are shiny.

❖ SILICON STRUCTURE:

- 1s² 2s² 2p⁶ 3s² 3p²
- 4 valence electrons in 3s and 3p
- The problem is that we have four electrons at two different energy levels that need to form four identical bonds

● Sp₃ hybridization

- let's just take the one s orbital and the 3 p orbitals and blend them together to form four equivalent energy levels,
- We call these new orbitals hybrid orbitals, and since we blended one s with 3 p orbitals we call the resulting orbitals sp₃ hybridized orbitals.



❖ DIAMOND CUBIC

➤ TETRAHEDRAL:

- Coordination number = 4

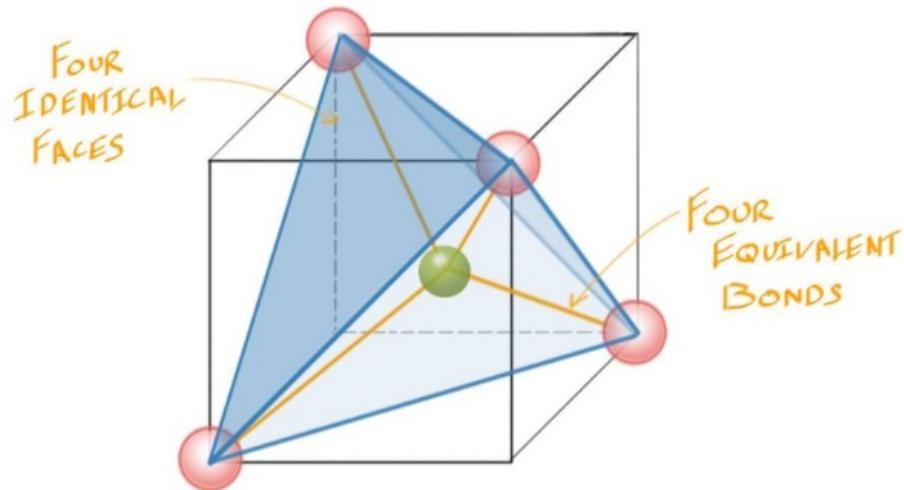


Figure 18. The tetrahedral interstitial site at the centre of a cube. Note that the coordination number is also 4, in addition to the number of faces on the solid formed by this site, however the name comes from the solid geometry, not the coordination number.

- with diamond cubic we will place atoms into the tetrahedral interstitial sites
- we can't fill each of the **eight** available tetrahedral interstitial sites.
- If we did this, we'd have too many bonds on each atom.
- Instead, we fill only half of the sites, and we place them as far apart from each other as possible,
- giving us the alternating arrangement shown with the shaded cubes:

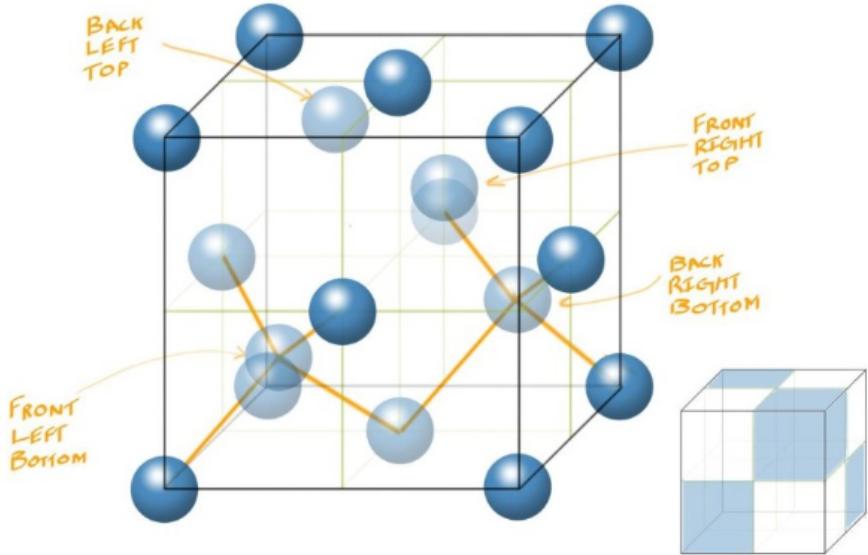


Figure 19. The structure of diamond cubic. This structure can be thought of as an FCC lattice of atoms with the same atoms occupying half of the available tetrahedral interstitial sites, in alternating positions. The alternating positions are illustrated with the shaded "sub-cube" faces in the second cube.

❖ SEMICONDUCTORS:

➤ INTRINSIC SEMICONDUCTORS:

- Everything that is available to conduct electricity comes from the semiconductor itself, not from anything that we add to it.
- when the temperature is raised, or a voltage is applied and we get some promoted electrons.
- When an electron is promoted into the conduction band, it leaves behind a broken bond.
- This broken bond is really a neutral charge, amongst an array of negative charges.
- When everything else is negative, something neutral looks positive and so we often refer to this missing electron as being a positive "thing"
- Since it is a missing electron, it looks a little bit like a hole in the structure, so we call this a **hole**
- if a hole is created for every promoted electron, these features are created in pairs.

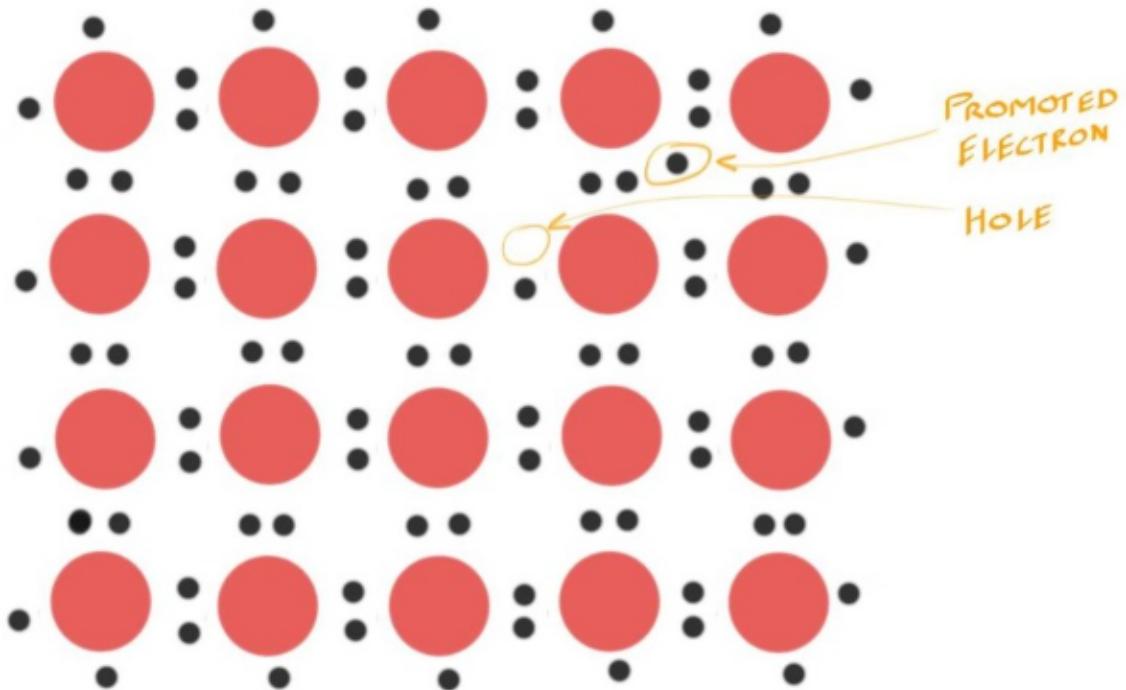


Figure 21. A cartoon depiction of the bonding in crystalline silicon with an electron promoted into the conduction band, leaving behind a broken bond, or a so-called **hole**.

- Since both the electron and the hole can be thought of as charged particles, it is possible for both of them to conduct electricity, just in opposite directions.
- CALCULATING CONDUCTIVITY OF INTRINSIC SEMICONDUCTOR:

$$\sigma = nq\mu_n + pq\mu_p$$

- n (-ve)=concentration of electrons (m^{-3})
- p (+ve)=concentration of hole (m^{-3})
- μ_n electron mobility (m^2/Vs)

- μ_p hole mobility (m^2/Vs)
- q =charge on electrons and holes= $1.6 \times 10^{-19}C$
- Conductivity unit: ohms/m or S/m

- Since one hole is created for every promoted electron $n=p$

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

➤ EXTRINSIC SEMICONDUCTORS:

- When impurities(DOPANTS) are added to semiconductors to control their conductivity
- When we add even a very small amount of dopant to a semiconductor, the conductivity introduced by the dopant overpowers any of the intrinsic semiconductor
- Two ways to dope a semiconductor
 - Extra electrons (n-type semiconductor)
 - Extra holes (p-type semiconductor)

1. Extrinsic n-type semiconductor:

- We need to add impurity atoms (point defects) that bring along with them some extra electrons.
- Example: Silicon semiconductor
 - Knowing that silicon has 4 valence electrons we need only look at atoms to the **right of silicon** in the periodic table to find atoms that will carry along **extra electrons**.
- DOPING SILICON WITH PHOSPHORUS:
 - Phosphorus: $1s^2 2s^2 2p^6 3s^2 3p^3$
 - P has 5 valence electrons and so when added as a point defect in a silicon lattice there will be one extra electron kicking around when four covalent bonds have been formed with the neighboring silicon atoms

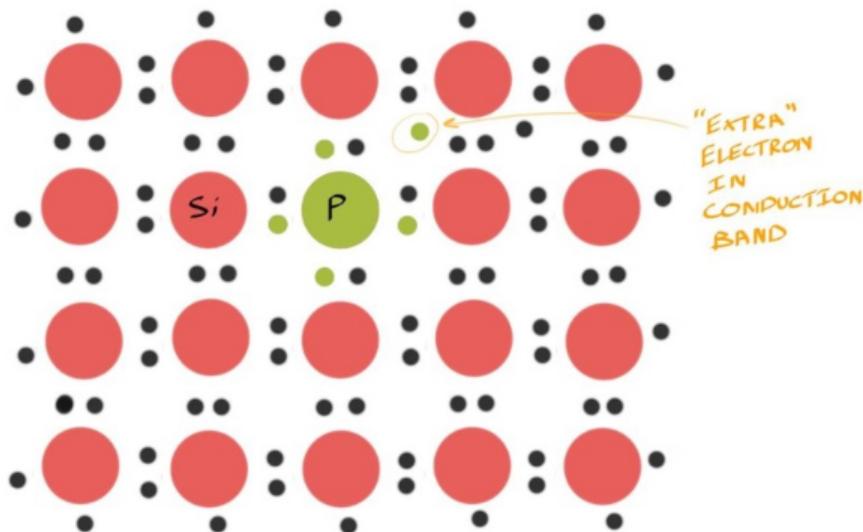


Figure 22. A cartoon depiction of the bonding in crystalline silicon with a phosphorous dopant atom. I've color coded the electrons for conceptual clarity, but remember that all of the electrons are actually equivalent. That is, a silicon electron is the same as a phosphorous electron.

- The extra electron from phosphorus is only weakly bound and can be easily promoted, and made available for conduction.
- That is, only a small amount of energy is required to get this extra electron, donated by the dopant, into the conduction band.
- For this reason, a n-type semiconductor is said to have a **donor energy level** within the band gap, close to the bottom of the conduction band

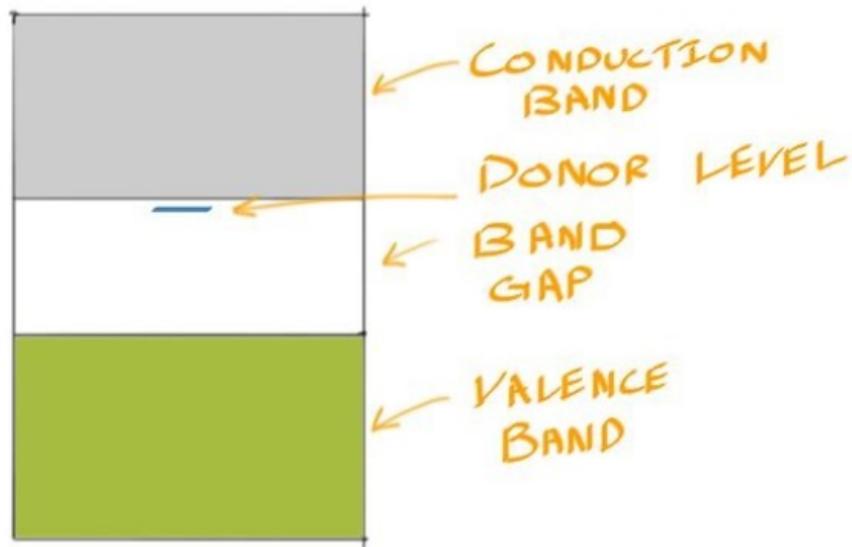


Figure 23. The band diagram for a n-type semiconductor, showing the donor level within the band gap, close to the bottom of the conduction band. Only a small amount of energy is required to free up that electron and get it conducting.

- Since the dopant atoms contribute so many more charge carriers to the semiconductor than are created through intrinsic promotion we can neglect the intrinsic semiconductor and calculate the conductivity of a n-type semiconductor with only the **electron concentration and mobility**:

$$\sigma_{n-type} = nq\mu_n$$

2. Extrinsic p-type semiconductor:

- If we dope with elements to the left of silicon there will be less than 4 valence electrons and there will be broken bonds, or holes introduced.
- For example, if we dope **silicon with boron**, the boron will only bring along 3 valence electrons, $2s^2\ 2p^1$
- This means that there will be **one broken bond**, or hole for every dopant atom

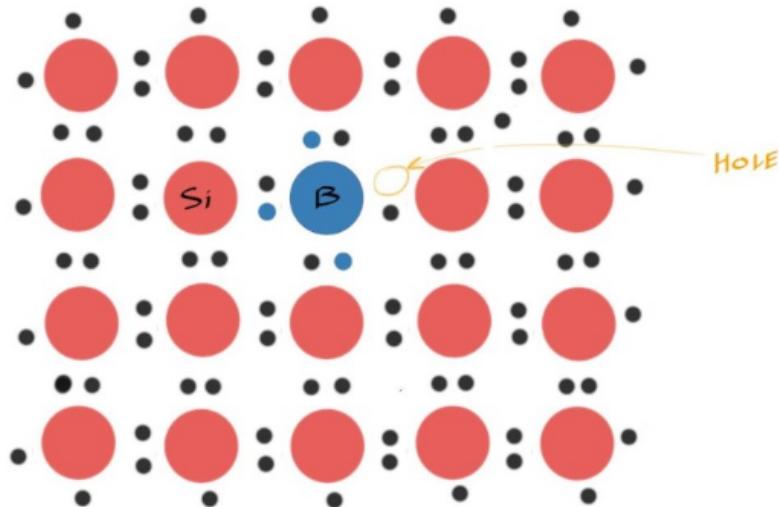


Figure 24. A cartoon depiction of the bonding in crystalline silicon with a boron dopant atom, creating a hole.

- Since the hole is now a place that an electron can be promoted into, we describe the energy level from the hole as an **acceptor level**
- this acceptor level is located within the band gap, close to the top of the valence band

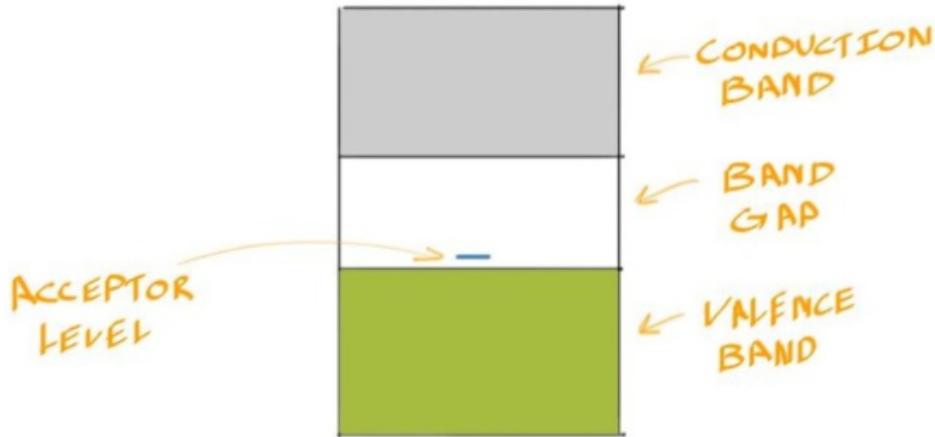


Figure 25. The band diagram for a p-type semiconductor, showing the acceptor level within the band gap, close to the top of the valence band. Only a small amount of energy is required to promote an electron up into that level.

- the conductivity of a p-type semiconductor can be calculated assuming that only **the holes are charge carriers**, neglecting any intrinsic semiconductor.

$$\sigma_{p\text{-}type} = pq\mu_p$$

- **Chapter 10: Energy**

- ❖ SECOND LAW OF THERMODYNAMICS:

- The entropy of the Universe increases during any **spontaneous** process.
 - Spontaneous: the process proceeds on its own, without the need for an input of energy.

- ❖ THE ENTROPY:

- it is a measure of how disordered a system is
- When a system becomes more disordered, its entropy will increase
- An increase in entropy means that the system becomes energetically more stable
- For example, during the thermal decomposition of calcium carbonate (CaCO_3) the entropy of the system increases:

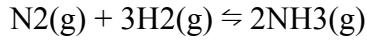


- In this decomposition reaction, a gas molecule (CO_2) is formed
- The CO_2 gas molecule is more disordered than the solid reactant (CaCO_3), as it is constantly moving around
- As a result, the system has become more disordered and there is an increase in entropy
- if the number of gaseous molecules in a reaction changes, there will also be a change in entropy
- The greater the number of gas molecules, the greater the number of ways of arranging them, and thus the greater the entropy
- For example the decomposition of calcium carbonate (CaCO_3)



- The CO_2 gas molecule is more disordered than the solid reactant (CaCO_3) as it can freely move around whereas the particles in CaCO_3 are in fixed positions in which they can only slightly vibrate
- The system has therefore become more disordered and there is an increase in entropy

- Similarly, a decrease in the number of gas molecules results in a decrease in entropy causing the system to become less energetically stable
- For example, the formation of ammonia in the Haber process



- In this case, all of the reactants and products are gasses
- Before the reaction occurs, there are four gas molecules (1 nitrogen and 3 hydrogen molecules) in the reactants
- After the reaction has taken place, there are now only two gas molecules (2 ammonia molecules) in the products
- Since there are fewer molecules of gas in the products, there are fewer ways of arranging the energy of the system over the products
- The system has become more ordered causing a decrease in entropy
- The reactants (N_2 and H_2) are energetically more stable than the product (NH_3)

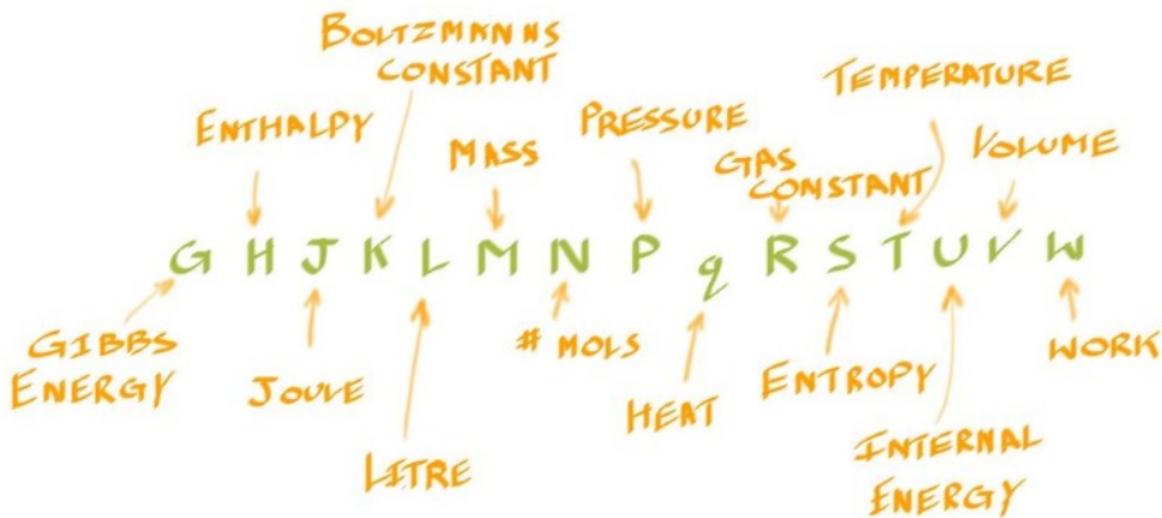
❖ ENTROPY FORMULA:

$$\Delta S = \frac{q_{rev}}{T} \quad (1)$$

where S is the entropy, q_{rev} is the heat transferred, and T is the *thermodynamic* temperature,

- Rev means that the heat is transferred reversibly.
- the system was at all times in equilibrium.

❖ COMMON ALPHABETS:



❖ SECOND LAW THERMODYNAMICS MATHEMATICAL:

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} > 0$$

❖ FIRST LAW THERMODYNAMICS:

- The first law of thermodynamics states that the energy of the universe is constant.
- The change in the internal energy of a system is the sum of the heat transferred and the work done.
- The heat flow is equal to the change in the internal energy of the system plus the PV work done.

$$\underbrace{\Delta U_{sys} = q + w}_{\text{First Law of Thermodynamics}}$$

❖ STANDARD STATE:

The most stable form of a pure element at 25°C and 105 Pa.

- STATE FUNCTIONS: a property whose value does not depend on the path taken to reach that specific value. Example: temperature, pressure, density, volume, Gibb's energy, potential energy, enthalpy, **internal energy**, and entropy.
- PATH FUNCTIONS: properties or quantities whose values depend on the transition of a system from the initial state to the final state. The two most common path functions are **heat and work**.

❖ CLOSED VS ISOLATED SYSTEM:

- In an isolated system no heat is exchanged with the surroundings
- In a closed system heat may pass the boundaries.

$$\Delta U = 0 \text{ Isolated System}$$

$$\Delta U = q + w \text{ Closed System}$$

- q is heat transferred into the system
- w is work done on the system
- U is change in internal energy
- IT IS IMPOSSIBLE TO DETERMINE THE ABSOLUTE VALUE OF INTERNAL ENERGY

❖ ENTHALPY

➤ The enthalpy change is just the heat supplied (or absorbed) by a reaction, when we account for the work done in pushing back the atmosphere.

$$\Delta H = \Delta U + P\Delta V$$

❖ GIBBS ENERGY:

- The Gibbs free energy (G) is the energy change that takes into account both the entropy change of a reaction and the enthalpy change
- The Gibbs equation is:

$$\Delta G^\circ = \Delta H^\circ_{\text{reaction}} - T\Delta S^\circ_{\text{system}}$$

- The units of ΔG° are in kJ mol⁻¹
- The units of $\Delta H^\circ_{\text{reaction}}$ are in kJ mol⁻¹
- The units of T are in K
- The units of $\Delta S^\circ_{\text{system}}$ are in J K⁻¹ mol⁻¹ (and must therefore be converted to kJ K⁻¹ mol⁻¹ by dividing by 1000)

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$

$$\Delta S_{\text{surroundings}} = \frac{q_{\text{surroundings}}}{T}$$

$$q_{\text{surroundings}} = -q_{\text{system}}$$

$$\Delta S_{\text{surroundings}} = \frac{-q_{\text{system}}}{T}$$

$$\Delta S_{\text{system}} + \frac{-q_{\text{system}}}{T} > 0$$

$$T\Delta S_{\text{system}} - q_{\text{system}} > 0$$

$$T\Delta S_{system} - \Delta H_{system} > 0$$

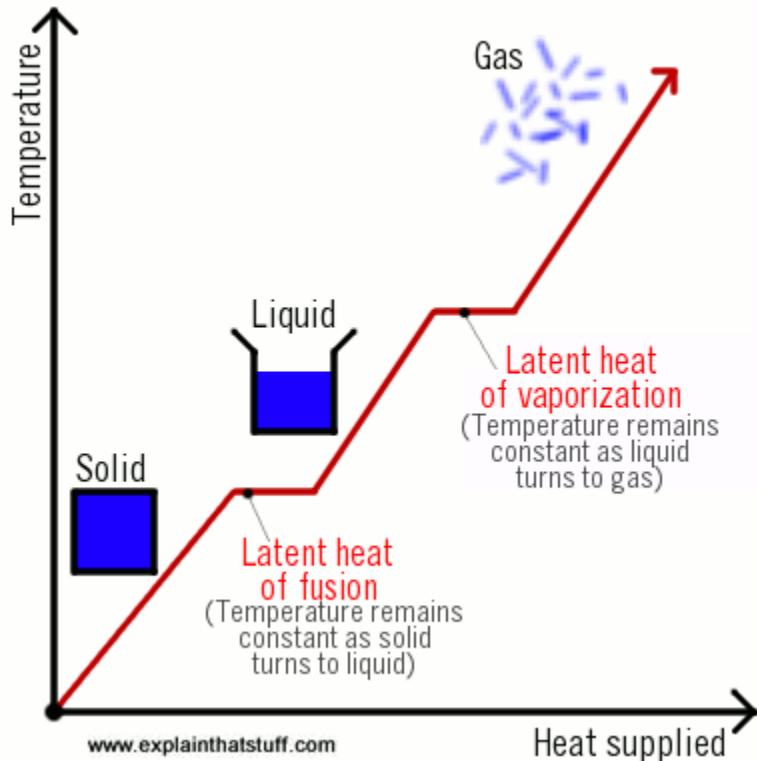
$$\Delta H_{system} - T\Delta S_{system} < 0$$

This means that when Gibbs energy decreases, it is just another way of saying that the entropy

increased, specifically

- **-ve G and +ve S means spontaneous**
- A reaction with a **positive** enthalpy change and a **positive** entropy change will be spontaneous under **high** temp
- A reaction with a **positive** enthalpy change and a **negative** entropy change will **NEVER** be spontaneous
- A reaction with a **negative** enthalpy change and a **negative** entropy change will be spontaneous under **low** temp

- **ENTHALPY OF FUSION:** the amount of energy that must be supplied to a **solid** substance (typically in the form of heat) in order to trigger a change in its physical state and convert it **into a liquid** (when the pressure of the environment is kept constant).
- **ENTHALPY OF VAPORIZATION:** the amount of energy (enthalpy) that must be added to a **liquid** substance, to transform a quantity of that substance into a **gas**.



$$q = mc\Delta T$$

- **Chapter 11: Phase Diagrams**

A phase diagram is nothing more than a graphical depiction of the equilibrium phases for all the possible combinations of temperature and composition.

1. THE TEMPERATURE AXIS:

- y-axis
- One dimensional phase diagram for pure water:



- As you can see, this simple phase diagram tells us that water below 0 C will exist as ice, between 0 C and 100 C it will form liquid water, and above 100 C it will exist as water vapor.
- These phases at these specific temperature ranges are the phases that result in the system being at the lowest energy level (the most thermodynamically stable).

2. THE COMPOSITION AXIS:

- We could add an "x-axis" that would represent the amount of sugar that we are adding to water

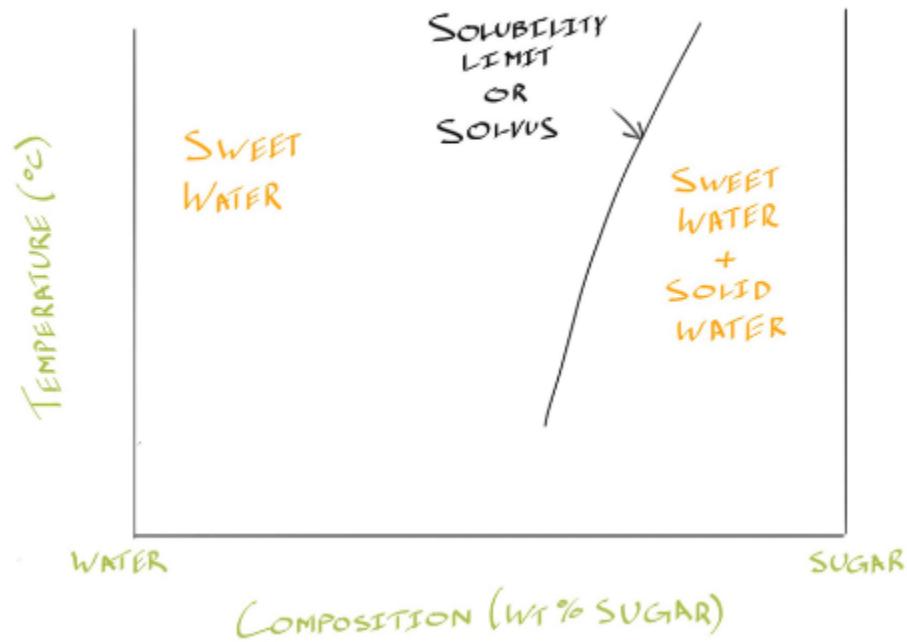


Figure 2: A schematic two-component (binary) water-sugar phase diagram. At sufficiently high sugar concentrations (compositions) we know from experience that solid sugar will persist, in equilibrium with the sweet water.

- Binary phase diagram
- This axis would be called the composition axis since it would indicate the amount of the second component, sugar, that we are adding to our first component, water.

3. SATURATION: THE SOLUBILITY LIMIT

- The maximum amount (limit) of solute that can be dissolved in a solvent is known as the solubility limit, or the solvus.
- add this line to our phase diagram, remembering that we know it must increase (towards higher compositions) as the temperature is raised.



★ TERMINOLOGY:

- PHASE: part of the system we are looking at that looks and behaves the same way. There are no separate parts in a single phase region. It all looks and behaves the same.
 - For example, if you add sugar to your coffee and stir it it forms a single phase, namely sweet water. All of the sweet water looks and behaves the same as any other bit of the sweetwater, because it is all the same phase. On the other hand, if we added sand to our coffee we would find that there were two phases, namely water and solid sand. The water looks and behaves differently from the sand.
- COORDINATES: The possible combinations of temperature and composition on a phase diagram

❖ BINARY PHASE DIAGRAM:

- binary phase diagram is one that has two components
- unary system would have only one component
- ternary system would have three components

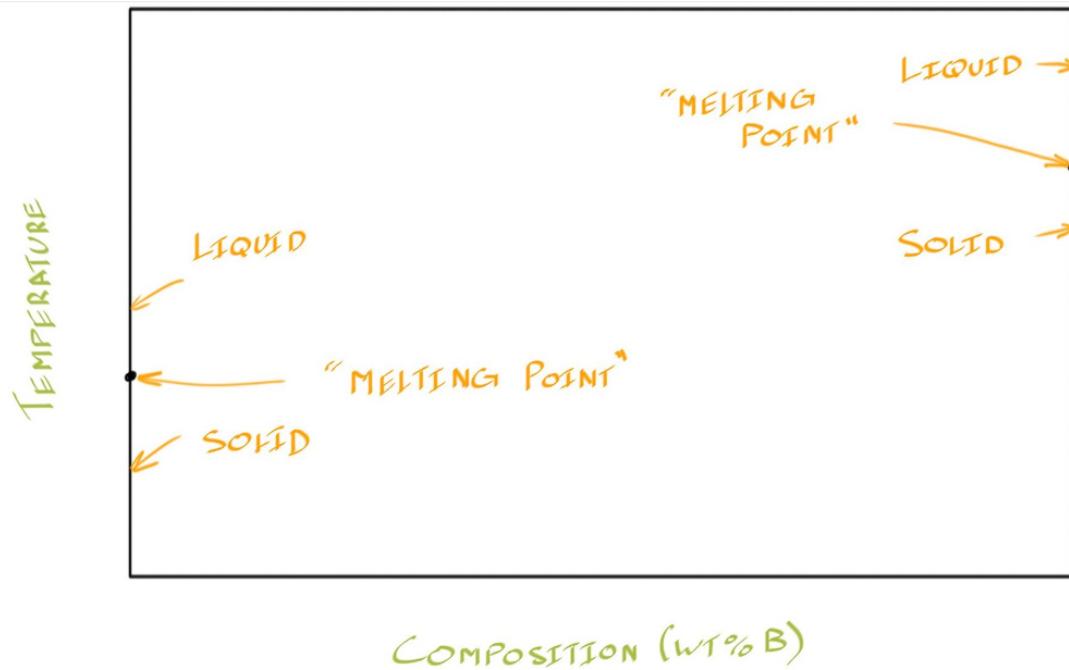


Figure 4: A schematic binary isomorphous phase diagram for the hypothetical two-component A-B system, showing only the melting points of the pure components.

- ISOMORPHOUS PHASE DIAGRAM:
 - ISOMORPHOUS SYSTEM: is one where both components are completely soluble in each other

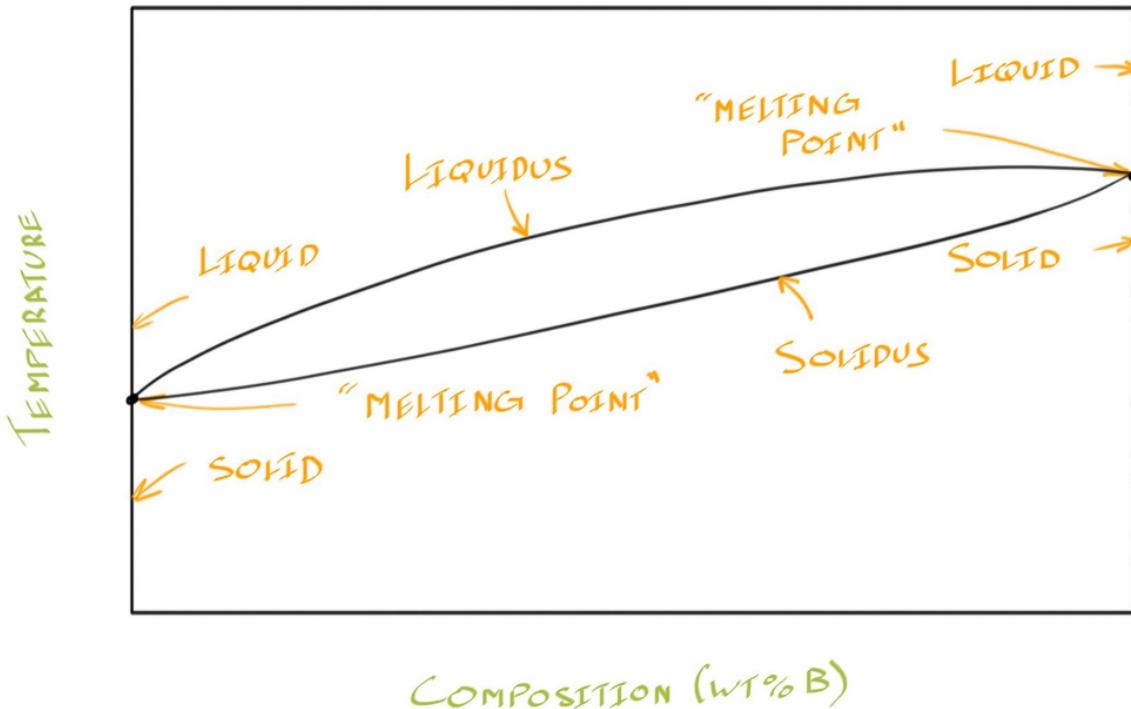
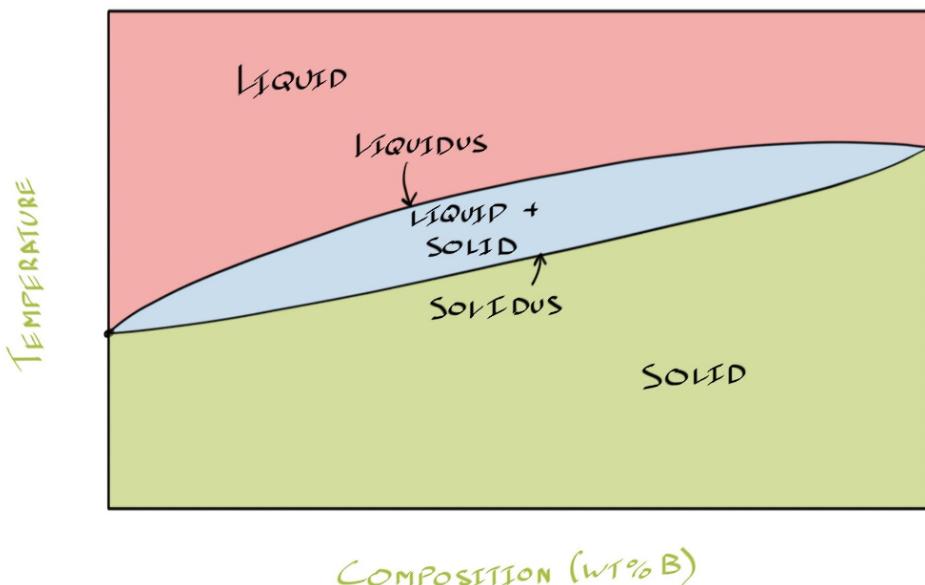


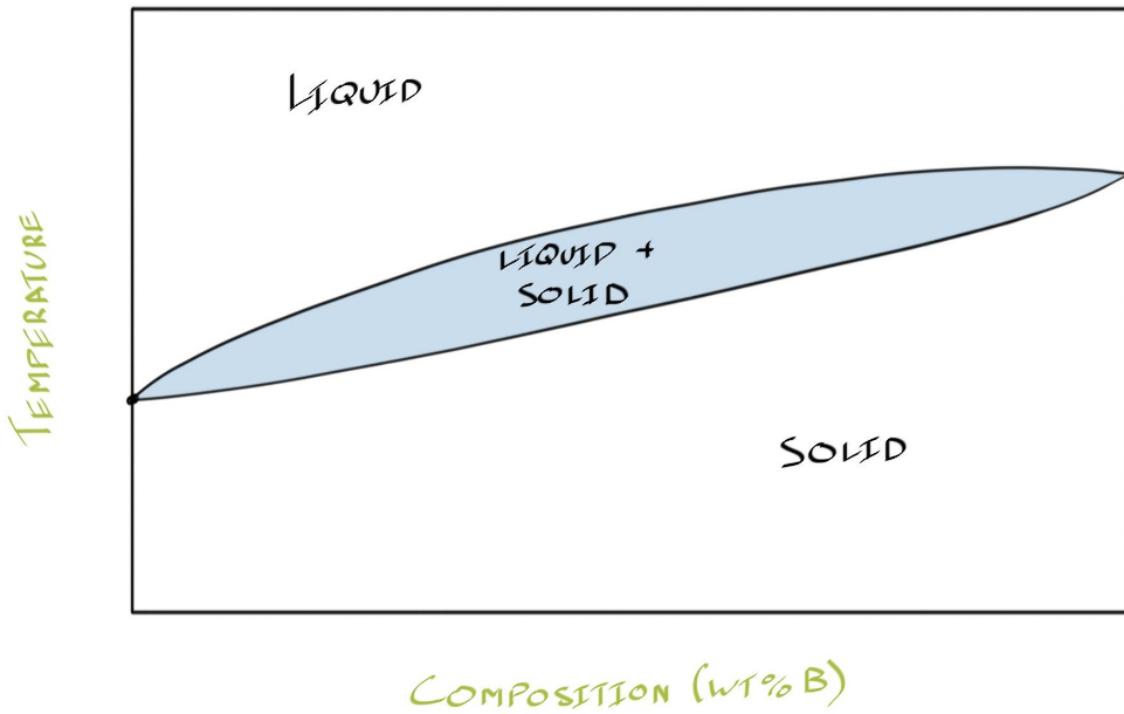
Figure 5: A schematic binary isomorphous phase diagram for the hypothetical two-component A-B system, showing the liquidus and solidus.

- The term isomorphous roughly means that there is only one structure in the solid phase.



- There is one area for the solid phase, with no phase boundaries breaking it up.
- we can dissolve as much component B in component A as we want without forming a second phase.
- Note that this is different from what we saw with water and sugar. Remember in the sugar-water system that when we added enough sugar to water we reached a solubility limit and the excess sugar formed a second phase.
- If you took a close look (with a microscope, for example) at the solid phase at a number of different compositions you would find that it looked generally the same in terms of its structure.

→ TWO PHASE REGION:



- For any combination of temperature and composition points that reside inside the little blue area our system will contain two phases in equilibrium, namely the liquid and the solid.
- You could say that the system was partly melted, or partly solidified in that region. And it would stay that way forever if you didn't change the temperature or composition.

→ COMPOSITION OF EACH PHASE:

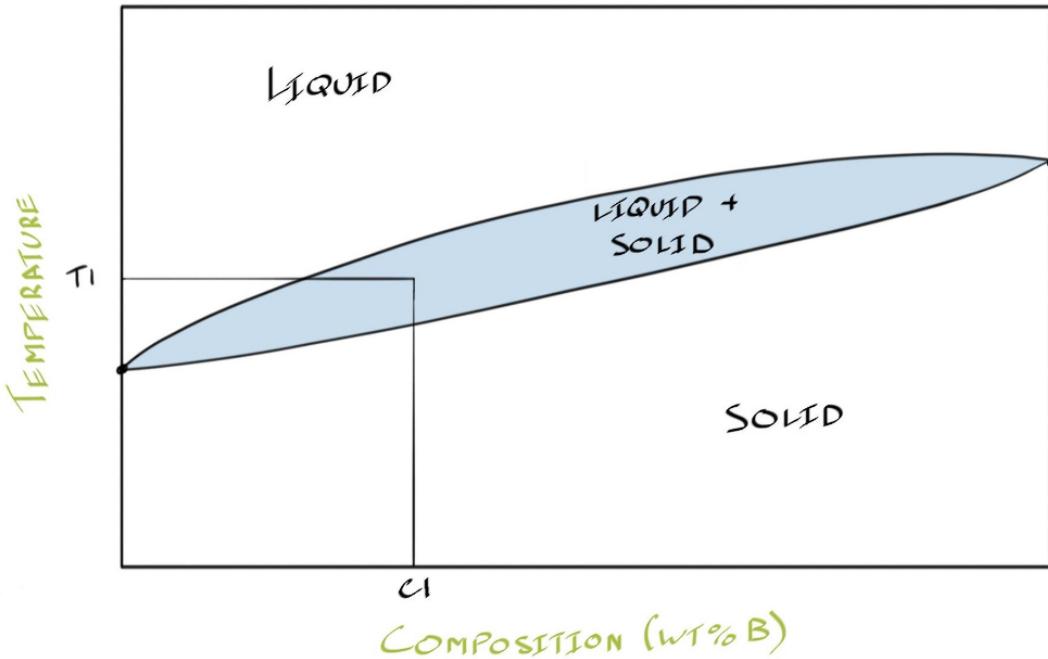


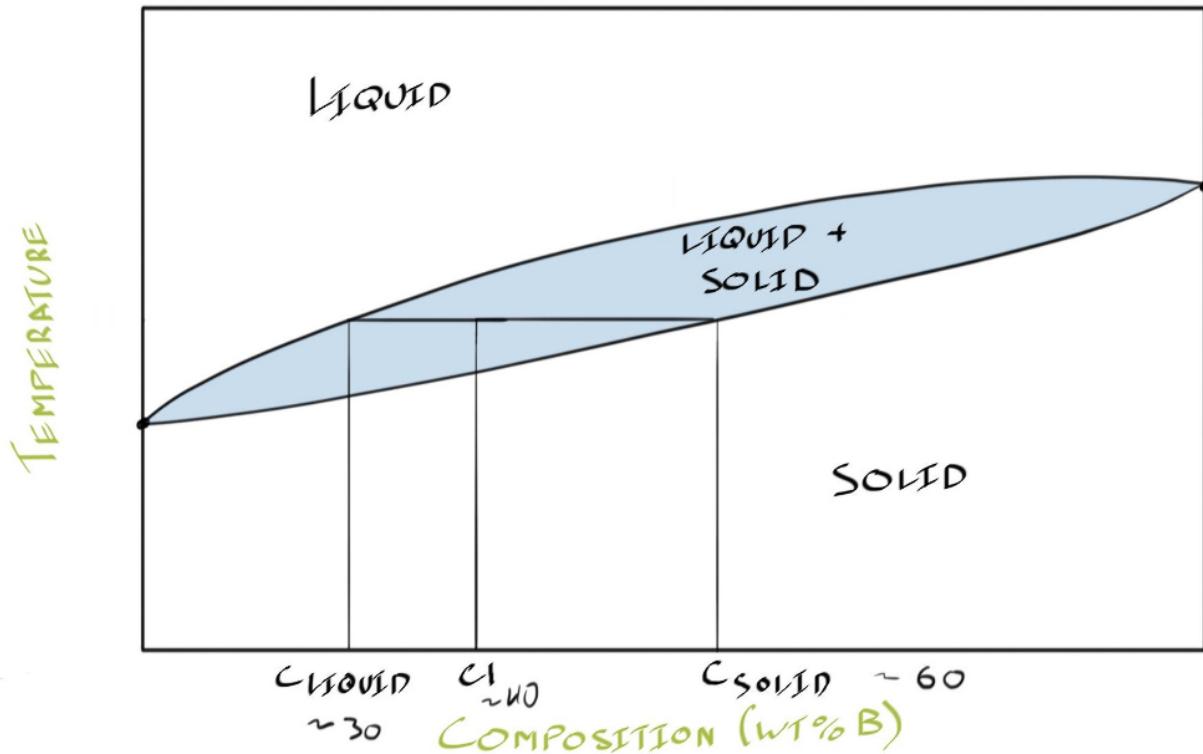
Figure 8: A hypothetical alloy of composition C1, heated to a temperature T1 is shown to exist as two-phases on this schematic binary isomorphous phase diagram for the two-component A-B system.

- That is, how much component A and component B are in each of the liquid and the solid.
- First, we would need to identify the temperature and composition on the phase diagram to confirm we were in the two phase region, as shown by the point at composition C1 and temperature T1

→ THE TIE LINE:

On a binary phase diagram, a tie line is simply a fancy term for a horizontal line spanning a two-phase region from a phase boundary (line) on one side to the phase boundary on the other side. Drawing a tie line from a given temperature and composition point does several things:

1. Tells us what phases are in the two-phase region
2. Tells us how much of each component is in each of the two phases (that is, the composition)
3. Forms the basis for our lever rule calculation, derived and explained in the next section.



★ THE LEVER RULE:

- To find out the concentration of different phases present

$$M_{B, Total} = M_{B, in\ Liquid} + M_{B, in\ Solid}$$

$$M_{B, Total} = M_L C_L + M_S C_S$$

$$\frac{M_{B, Total}}{M_{Total}} = \frac{M_L}{M_{Total}} C_L + \frac{M_S}{M_{Total}} C_S$$

$$C_0 = \frac{M_L}{M_{Total}} C_L + \frac{M_S}{M_{Total}} C_S$$

$$\frac{M_L}{M_{Total}} = W_L$$

$$\frac{M_S}{M_{Total}} = W_S$$

$$C_0 = W_L C_L + W_S C_S$$

$$W_L + W_S = 1$$

$$W_S = 1 - W_L$$

$$C_0 = W_L C_L + (1 - W_L) C_S$$

$$C_0 = W_L C_L + C_S - W_L C_S$$

$$C_0 = W_L(C_L - C_S) + C_S$$

$$W_L = \frac{C_0 - C_S}{C_L - C_S}$$

So the Lever rule is,

$$\text{Weight fraction of a phase} = \frac{\text{Opposite side of lever}}{\text{Total length of lever}}$$

★ EUTECTIC:

- A binary eutectic phase diagram is a phase diagram for a system that has one specific melting point that is below the melting point for each of the components.

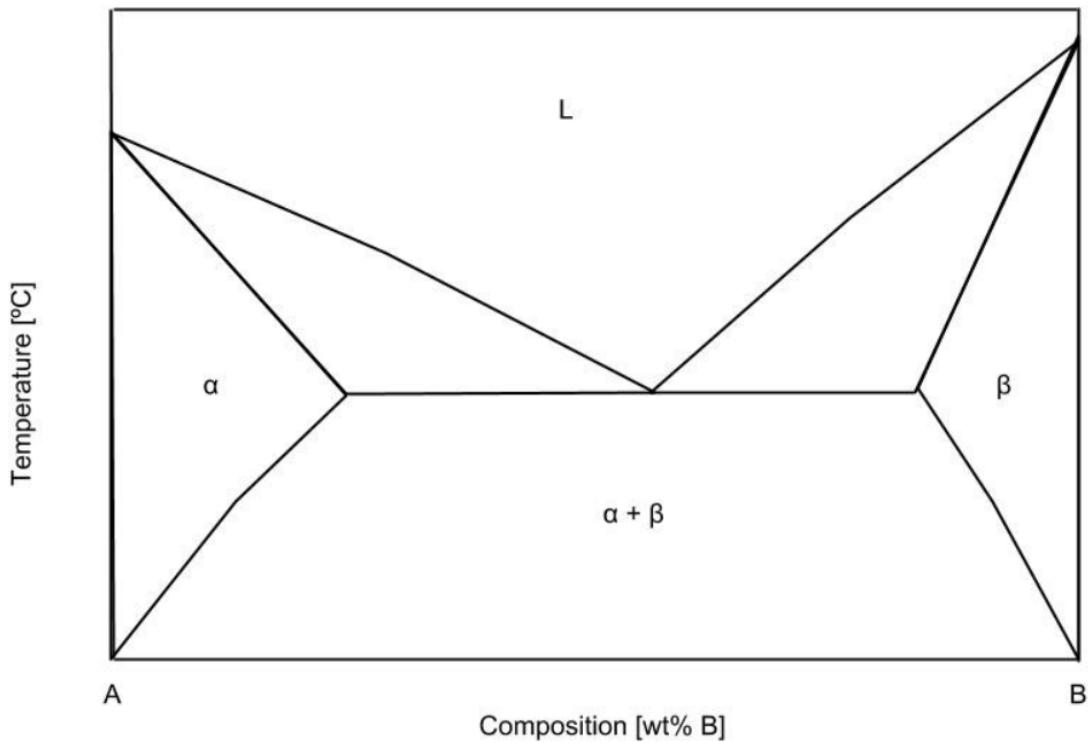


Figure 22: A schematic diagram of a generalized binary eutectic phase diagram. Note that the solid phases are named using lower case Greek letters and the liquid is just indicated with a capital L

★ IRON-CARBON SYSTEM

- Eutectic Point

Eutectic point is a point where multiple phases meet. For the iron-carbon alloy diagram, the eutectic point is where the lines A1, A3 and ACM meet. The formation of these points is coincidental.

At these points, eutectic reactions take place where a liquid phase freezes into a mixture of two solid phases. This happens when cooling a liquid alloy of eutectic composition all the way to its eutectic temperature.

The alloys formed at this point are known as eutectic alloys. On the left and right side of this point, alloys are known as hypoeutectic and hypereutectic alloys respectively ('hypo' in Greek means less than, 'hyper' means greater than).

- Phase Fields

The boundaries, intersecting each other, mark certain regions on the Fe3C diagram.

Within each region, a different phase or two phases may exist together. At the boundary, the phase change occurs. These regions are the phase fields.

They indicate the phases present for a certain composition and temperature of the alloy. Let's learn a little about the different phases of the iron-carbon alloy.

- ❖ Different Phases
 - α -ferrite

Existing at low temperatures and low carbon content, α -ferrite is a solid solution of carbon in BCC Fe. This phase is stable at room temperature. In the graph, it can be seen as a sliver on the left edge with Y-axis on the left side and A2 on the right. This phase is magnetic below 768°C.

It has a maximum carbon content of 0.022 % and it will transform to γ -austenite at 912°C as shown in the graph.

- γ -austenite

This phase is a solid solution of carbon in FCC Fe with a maximum solubility of 2.14% C. On further heating, it converts into BCC δ -ferrite at 1395°C. γ -austenite is unstable at temperatures below eutectic temperature (727°C) unless cooled rapidly. This phase is non-magnetic.

- δ -ferrite

This phase has a similar structure as that of α -ferrite but exists only at high temperatures. The phase can be spotted at the top left corner in the graph. It has a melting point of 1538°C.

- Fe₃C or cementite

Cementite is a metastable phase of this alloy with a fixed composition of Fe₃C. It decomposes extremely slowly at room temperature into iron and carbon (graphite).

This decomposition time is long and it will take much longer than the service life of the application at room temperature. Some other factors (high temperatures and the addition of certain alloying elements for instance) can affect this decomposition as they promote graphite formation.

Cementite is hard and brittle which makes it suitable for strengthening steels. Its mechanical properties are a function of its microstructure, which depends upon how it is mixed with ferrite.

- Fe-C liquid solution

Marked on the diagram as 'L', it can be seen in the upper region in the diagram. As the name suggests, it is a liquid solution of carbon in iron. As we know that δ -ferrite melts at 1538°C, it is evident that the melting temperature of iron decreases with increasing carbon content.