MSE160 – Midterm Study Notes

1 CATERGORIZATION OF MATTER

-   3 material classes:

Metals	- Held together by <u>metallic bonds</u> - Ductile (can be deformed permanently), electrically + thermally conductive, shiny - Highly organized at atomic level – <u>CRYSTALLINE</u>
Ceramics	- <u>Ionic bonds</u> - Brittle, non-conductive - Can be <u>crystalline</u> or <u>amorphous</u> (disorganized) - E.g. porcelain, concrete, often metal oxides
Polymers ("plastics")	- <u>Covalent bonds</u> - Tend to be ductile, not as strong as metals - Non-conductive - E.g. Teflon, Gore-Tex, polypropylene, polyethylene, PMMA, etc.

-   Exceptions: wood, tissue (e.g. skin), composites, semiconductors, etc.

2 ELASTIC BEHAVIOUR

2.1 Engineering Stress and Strain

- Stress and strain calculated from using <u>original sample's cross-sectional area/length</u>
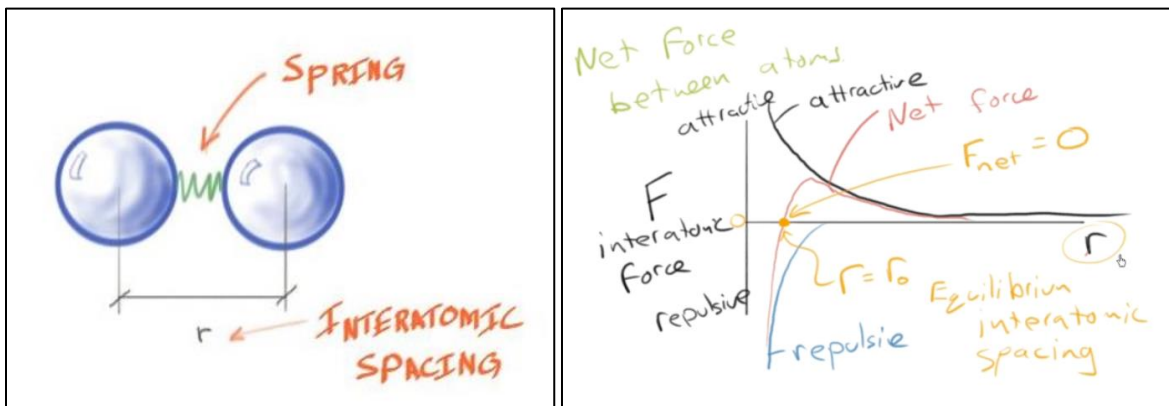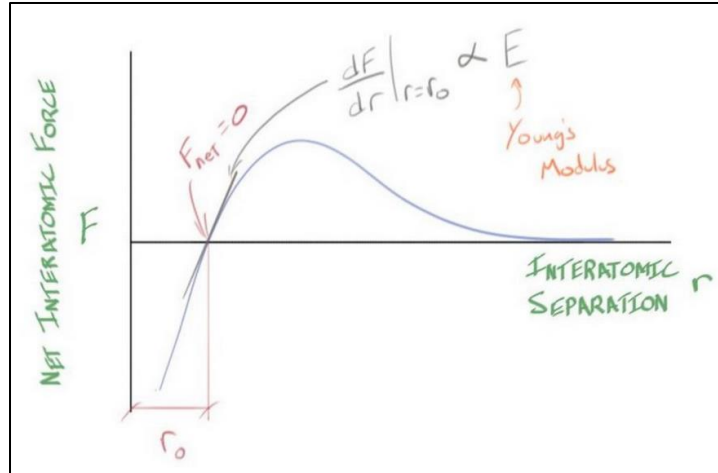   - o X-section area decreases in reality (true stress and strain)
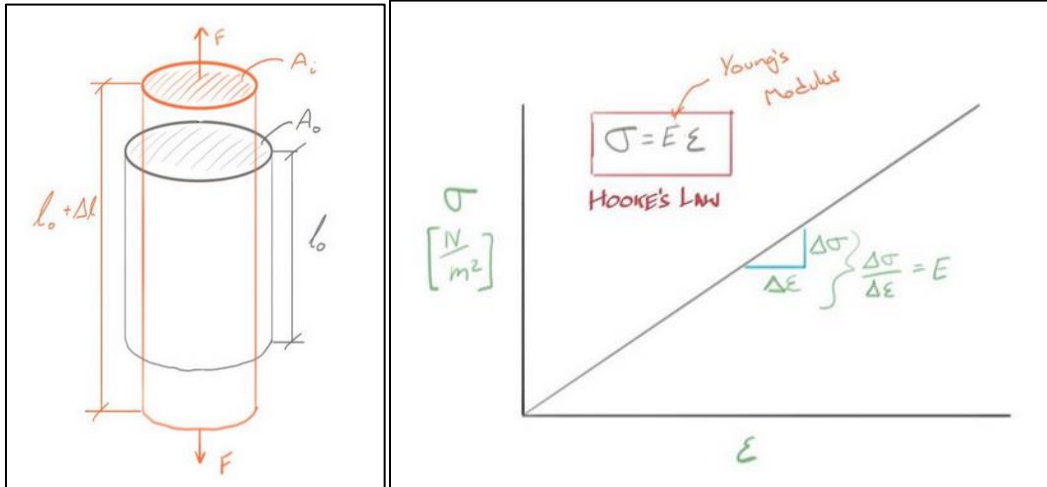
$$\sigma = \frac{F}{A_0} \qquad\qquad \epsilon = \frac{\Delta l}{l_0}$$

2.2 Atomic Definition of Young's Modulus

- "Elastic":
    - o Sample returns to original geometry upon unloading
    - o Strain is recoverable
    - o <u>Atoms return to original positions upon unloading</u>
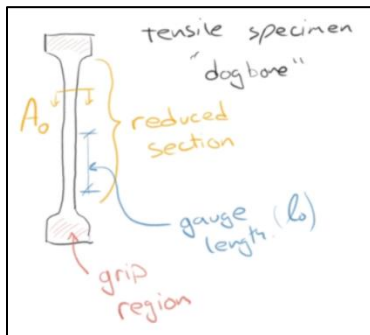- Model for bonding in a solid:

- E is exactly proportional to interatomic force curve when $r = r_0$:

$$E \propto \frac{dF}{dr}|_{r=r_0}$$

- E depends only on type of atoms: <u>STRUCTURE INDEPENDENT</u>
  - Small changes to microstructure (composition/concentration) or strengthening do not change E
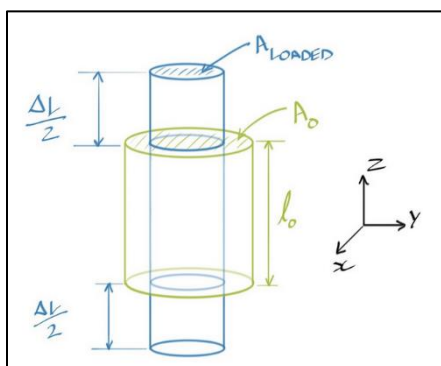
2.3 Tensile Tests

- Tensile specimen ("dogbone"):

  - Strain can be measured by strain gauge

2.4 Poisson's Ratio

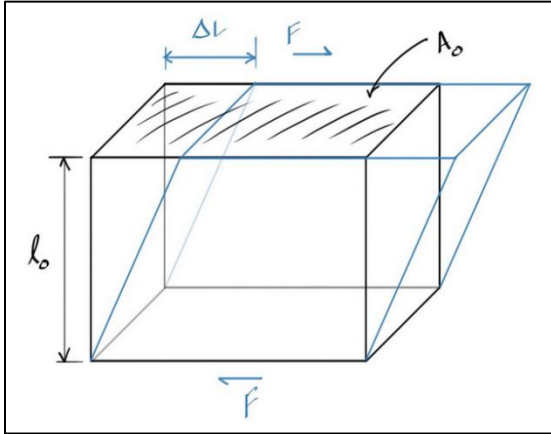- Extent to which a material shrinks/fattens (in x-sectional area) when elongated/compressed

- Negative ratio of radial (perpendicular) strain to axial strain:

$$v = -\frac{\epsilon_R}{\epsilon_z} = -\frac{\epsilon_x}{\epsilon_z} = -\frac{\epsilon_y}{\epsilon_z}$$

2.5 Shear Stress and Strain

- Shear loading: force applied parallel to an area
  - Causes sample to become <u>skewed</u>

<u>Shear Stress</u>: $\tau = \dfrac{F}{A_0}$

<u>Shear Strain</u>: $\gamma = \dfrac{\Delta l}{l_0}$

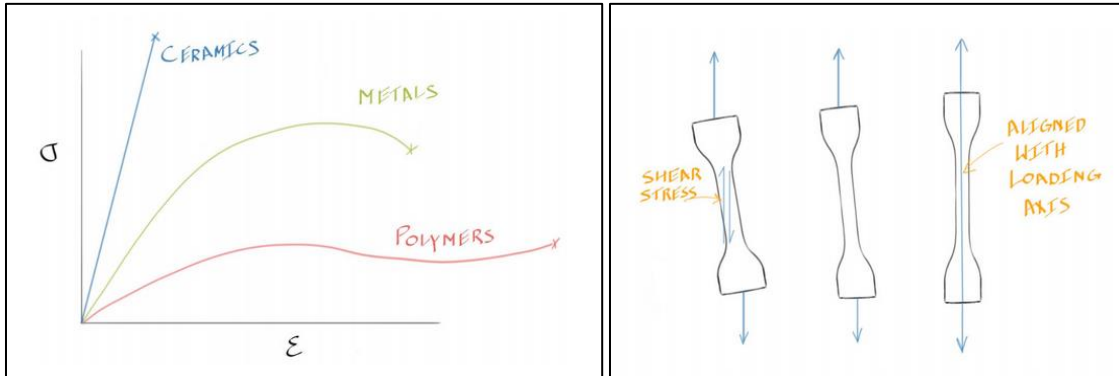<u>Hooke's Law for shear stress and strain</u>: $\tau = G\gamma$

- G = shear modulus
- G is related to Young's Modulus, E:

$$E = 2G(1 + v)$$

3 INELASTIC BEAHVIOUR

3.1 Permanent Deformation ("Plastic Deformation")

1. Upon unloading, sample doesn't return to original dimensions
2. Strain does not return to 0
3. Atoms move to new positions
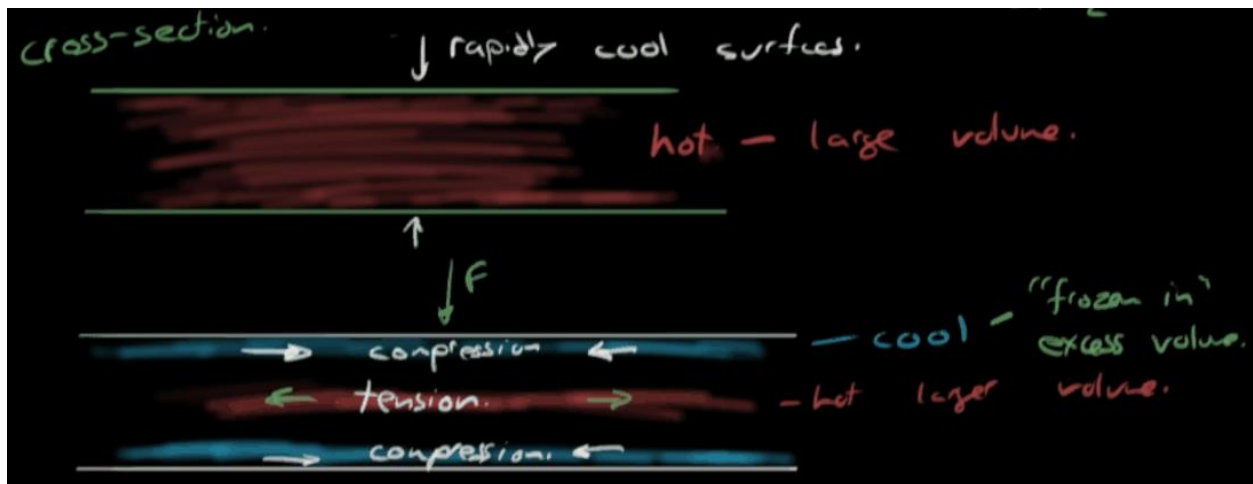4. Near end of linear region

- Ceramics:
  - o Usually don't test in tension:
    - ▪ Crumbles in grip
    - ▪ Difficult to form/machine
    - ▪ Machine alignment difficult
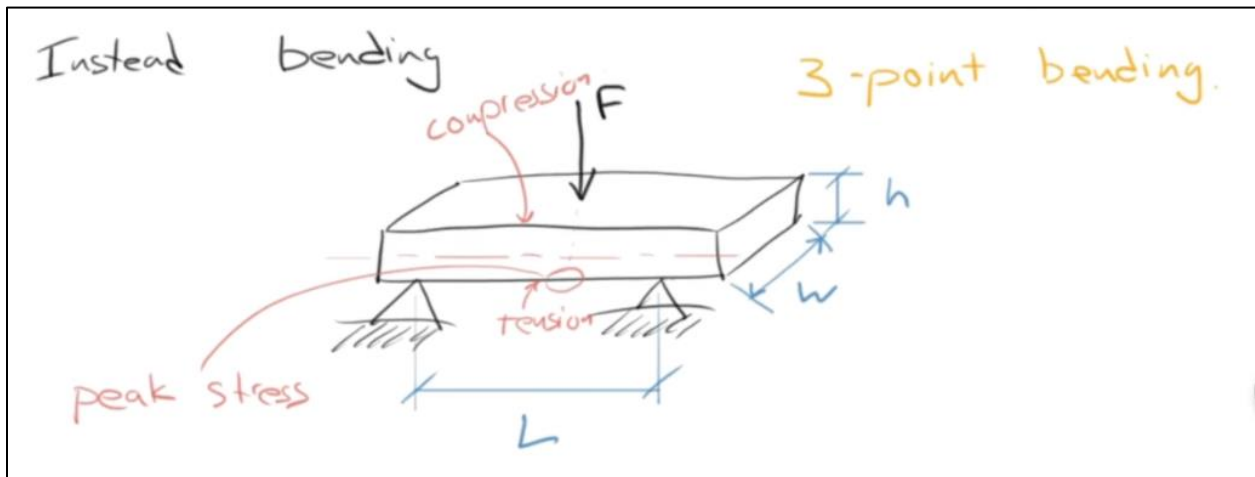
$$\sigma_{3pt} = \frac{3FL}{2wh^2}$$

3.2 Tempered Glass

- High strength
- "safe" when fractured – breaks into small pieces

cross-section.

↓ rapidly cool surfaces.

hot — large volume.

↑
↓ F

→ compression ←
← tension. →
→ compression. ←

— cool — "frozen in" excess volume.
— hot larger volume.

- Hot middle tries to shrink – pulls on cold outer part
- But ceramics are good under compression (won't break)
  - If you put it in bending, it takes more force to get other side to get to tensile state (since it's prestressed in compression)
- Residual stress in glass = stored strain energy
- When glass fractures: liberated as surface energy = surface area = small pieces = safer
- Tempered glass also can be made chemically (e.g. gorilla glass)
  - Diffusing ions into glass

4 STRUCTURE-PROPERTY RELATIONSHIP

4.1 Modulus vs Density Chart

$$Density = \frac{mass}{volume} [=] \frac{g}{cm^3} \; or \; \frac{kg}{m^3}$$
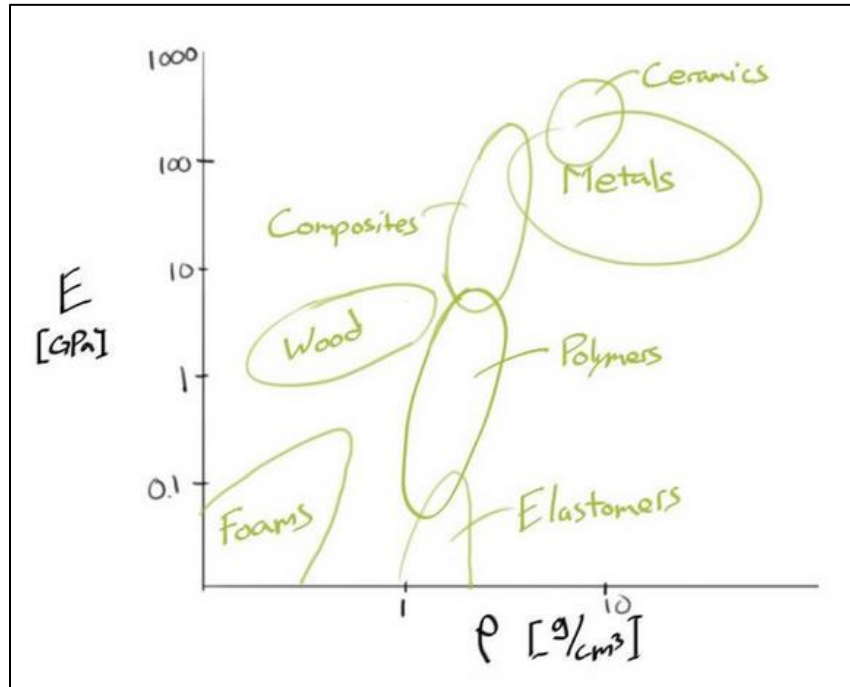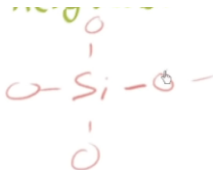
4.2 Intro to Ordered Solids

Atomic scale (10^{-10}m, the Angstrom)
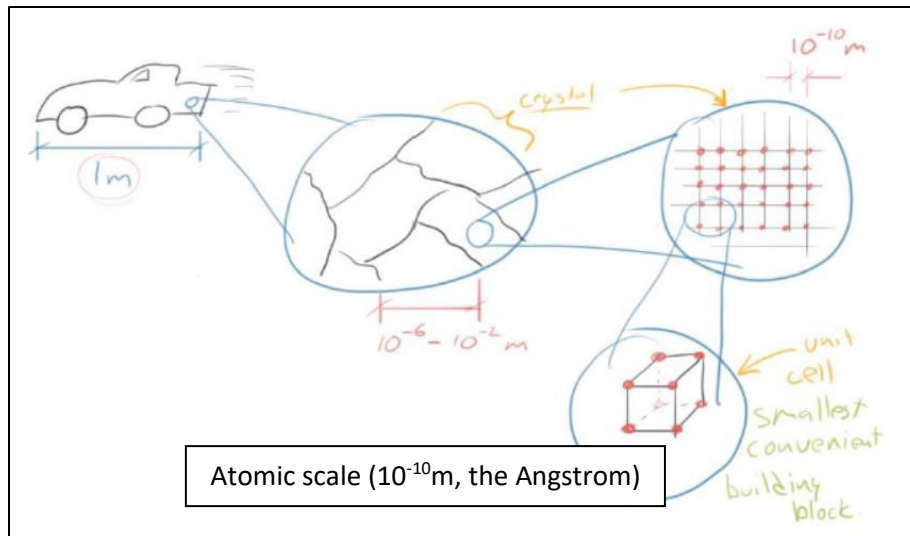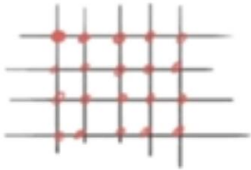
- Polycrystalline: made of crystals
  - o Around the micron scale
  - o Crystals that make up polycrystalline materials are called "grains"
- Many materials are crystalline

- o Most metals, some ceramics (e.g. sapphire)
- Not everything is crystalline
  - o Amorphous – not organized (e.g. window glass)

Long-range order	Short-range order
- Has order well beyond nearest neighbour atoms - Ex.	- Order at level of 1st or 2nd nearest neighbour $O-Si-O-$ - Ex. - Don't know the order beyond this^

5 STRUCTURES

5.1 Face-Centred Cubic (FCC)
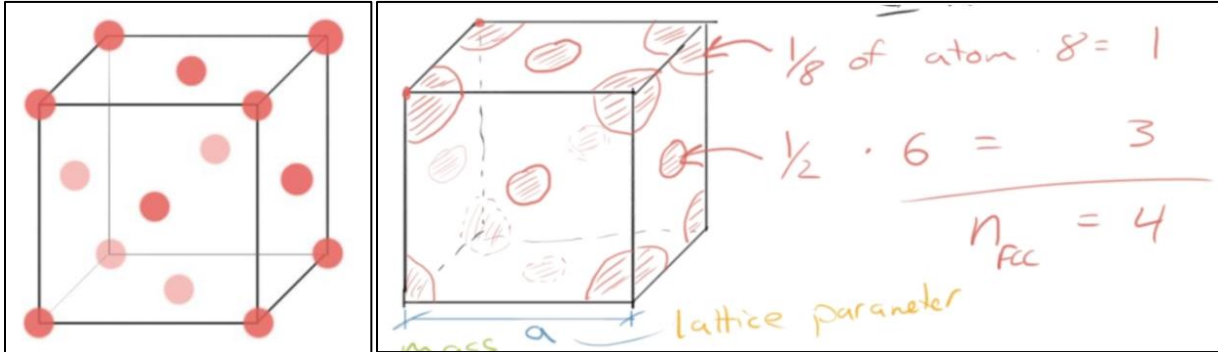
- Many metals

- Calculating Theoretical Density:

$$\rho = \frac{mass}{volume} = \frac{nA}{N_A} \cdot \frac{1}{V_c} = \frac{nA}{V_c N_A} \ [=] \ \frac{g}{m^3}$$

  - n = # atoms per unit cell
  - A = molar mass
  - V_c = volume of unit cell
  - N_A = Avogadro's Number
- Atomic Packing Factor (APF)

$$APF = \frac{V_{atoms}}{V_{unitcell}} = \frac{n \cdot \frac{4}{3}\pi R^3}{a^3}$$

$$APF_{FCC} = 0.74 = 74\%$$

5.2 Rock Salt Ceramic Crystal Structure
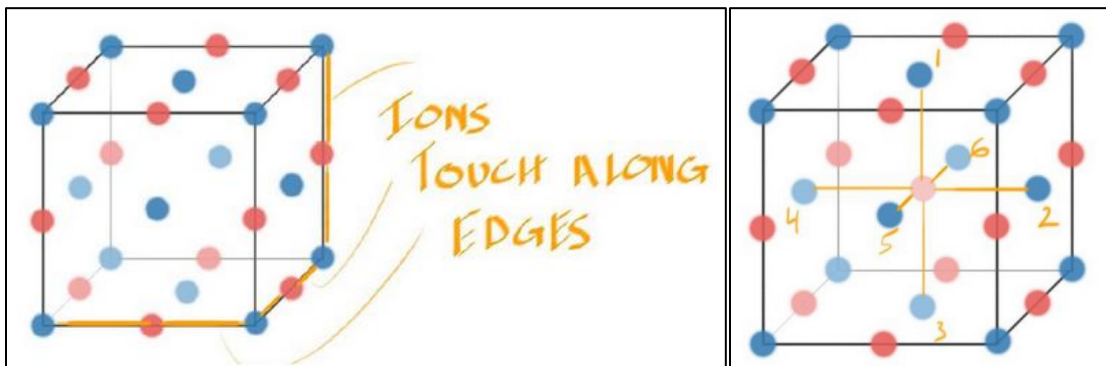
- Coordination number = # of atoms that are touching any give atom

$$coordination\ number_{rocksalt} = 6$$

- Lattice parameter: $a_{rocksalt} = 2(R_A + R_C)$

STRUCTURES SUMMARY

Structure	Picture	a	n	Coord #	
FCC		$2\sqrt{2}R$	4	12	
Rock Salt		$2(R_A + R_C)$	4 cat, 4 an	6	
BCC		$\dfrac{4}{\sqrt{3}}R$	2	8	
HCP		$2R$	6	12	
Simple Cubic		2R	1	6	

SECTION 4.1 CRYSTALLOGRAPHIC PLANES AND DIRECTIONS

4.1.1 Crystallographic Directions

1. Translate vector if it simplifies things
2. <u>Proj</u>ection onto x, y, z
3. <u>Red</u>uce to lowest integer values
4. <u>Encl</u>ose in square brackets
    a. Negatives go above (bar), no commas

Families of directions: vectors with same atoms in same positioning

- Same process as above, drop negative, move zeroes to front, triangular brackets

4.1.2 Crystallographic Planes (Miller Indices)

1. Translate plane so origin is not on plane or redefine origin
2. Determine distance to <u>int</u>ercept plane by travelling along each axis from origin
3. Take <u>reciprocal</u>
4. <u>Encl</u>ose in parentheses (h k l)
    a. Negatives go above (bar), no commas

Families of planes: same atoms in same positions – look the same in 2D, same planar packing fraction

- Move zeroes to left, square brackets
- Reduce negative signs (multiply by -1)

4.1.3 Bragg's Law for X-ray Diffraction

- Condition for constructive interference: $n\lambda = 2d_{hkl}\sin\theta$
    o n is a positive integer
    o lambda = wavelength
    o d_{hkl} = interplanar spacing
   o θ = incident angle

6 MECHANICAL BEHAVIOUR

6.1 Stress-Strain Behaviour

- Proportional Limit: when <u>linear elastic region ends</u>
    - o Hard to define without experiment
- Defining <u>start of plastic deformation</u>:
    - o Yield strength: when plastic deformation begins (in practice)
    - o 0.2% offset yield strength: at $\epsilon = 0.002$, draw parallel line to curve (slope = E), line intercepts original curve = 0.2% offset yield strength
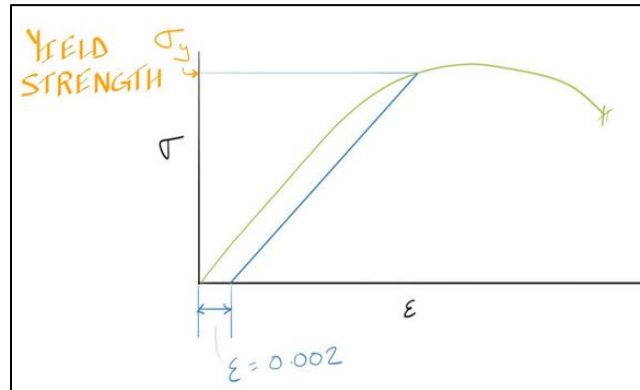
6.2 Uniform and Non-uniform Deformation

- Uniform: deformation is distributed evenly and equally throughout sample
- Non-uniform: deformation is localized/isolated to a particular region
- Why stress strain curve decreases after UTS:
    - o As metal is loaded to higher stress, bonds start to break between metal atoms
    - o In theory: bond breaking could occur anywhere in sample
    - o In practice: bond breaking occurs around defect/scratches/pores/oxide inclusions, etc.
    - o Regions of broken bonds come together, forms larger crack
   - o Larger crack leads to final fracture
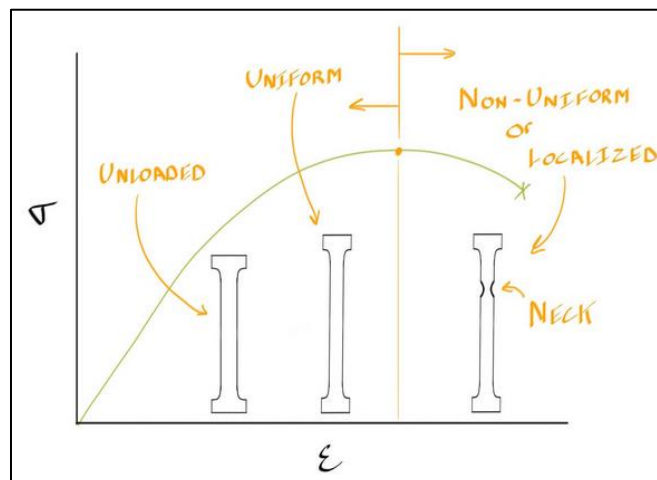
- In tensile specimen necking occurs – cross sectional area is reduced
- Cross sectional area reduced = less force needed to keep deforming metal
    - Note: true stress still increases, but not fast enough to counter decreasing cross sectional area
- We plot <u>engineering stress</u> = force/<u>original</u> area
- Original area is constant, force decreases, so engineering stress decreases
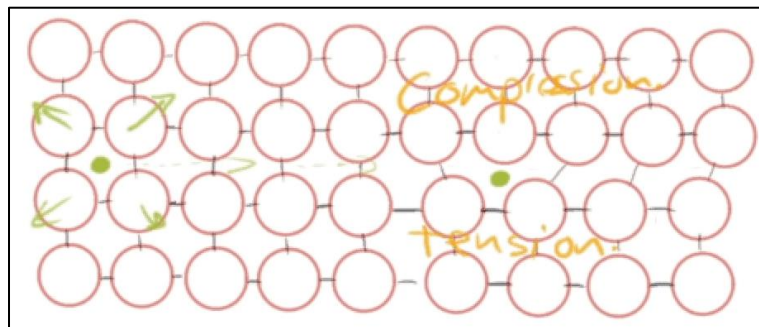
7 IMPERFECTIONS

7.3 0D Imperfections (Point Defects)

Interstitial (e.g. C in Fe)
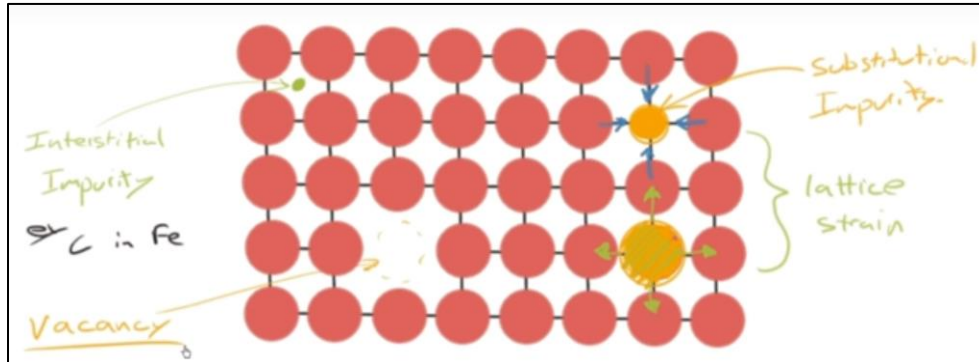
- Solute atoms are typically much smaller than solvent atoms
- Pushes atoms apart – creates lattice strain

- Impurities tend to diffuse towards dislocations (decreases energy of system)
- Impurity atoms "pin" dislocation
  o Makes it harder for dislocation to move – harder for plastic deformation

Substitutional (e.g. Cu in Ni)

- Tend to have similar size (within 10%), electronegativity, etc.
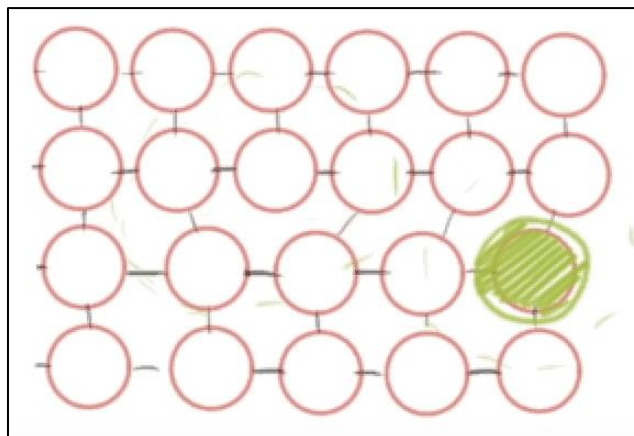
- Strain fields created by dislocation and impurity interact
- More difficult for dislocation to move through lattice when close to an impurity vs an undisturbed lattice
- **Impurities inhibit dislocation movement**
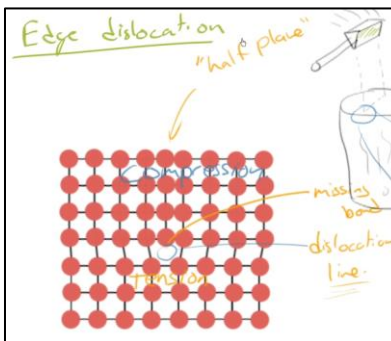- **Impurities strengthen materials**

Vacancies

- Vacancy formation = battle between temperature and binding energy of lattice
    o Greater temperature = more vacancies
- Population of vacancies:

$$\frac{N_v}{N} = \exp(-\frac{Q_v}{kT})$$

    o N = number of sites
    o k = Boltzmann constant
    o Q_v = energy to form vacancy
    o T = temperature (K)
- Vacancies are the only crystalline imperfection NOT used to strengthen materials

7.1, 7.4 1D Imperfections – the Dislocation

- A 1D imperfection (a line)

- Step by step motion of linear imperfections is mechanism for plastic deformation

(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.
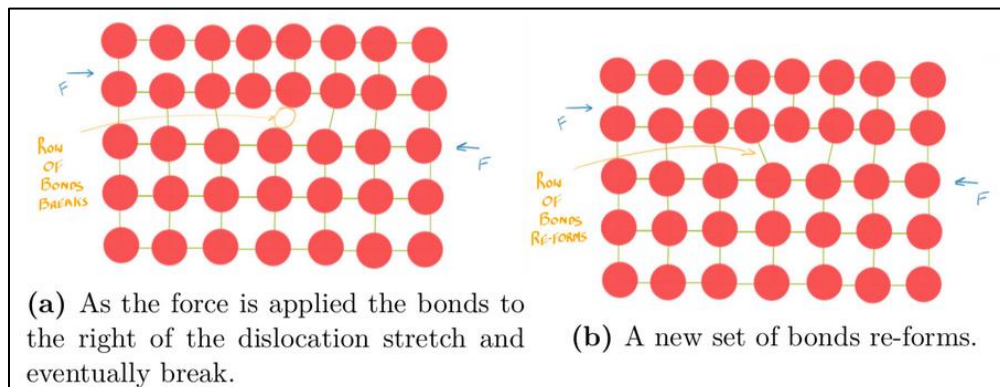
- Step by step breaking and reforming of bonds = mechanism for plastic deformation

- Dislocation density: typically 10^4/mm^2 (annealed/heated to relieve internal strain energy) to 10^{10}/mm^2 (heavily deformed – plastic deformation increases dislocation density)
- High dislocation density = high strength
    o Dislocations have difficulty moving past each other (strain fields interact)
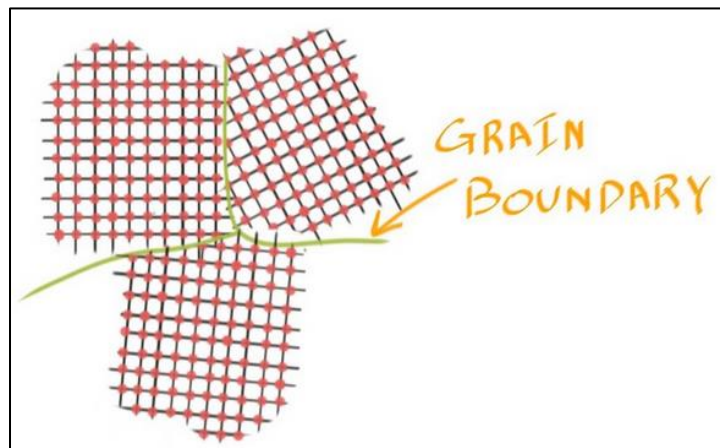

7.5 2D Imperfections (Interfacial)

Free Surface

- Free surfaces have fewer nearest neighbour atoms
- Unsatisfied bonds
- Elevated energy (surface energy)
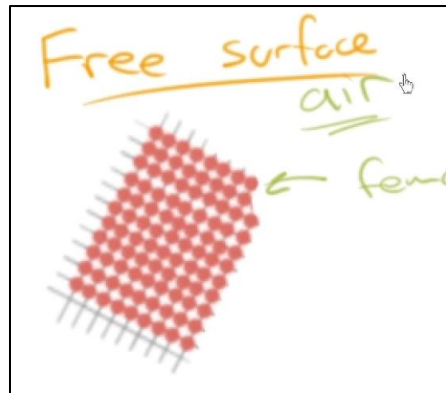
- Example: drops of water tend to come together
    o Individually they have greater surface energy
   o Together = lower surface energy, lower surface/volume

Internal Surface

- Elevated energy (unsatisfied bonds) at boundaries
- Behaviour of dislocations at grain boundaries:
    o Must change direction
    o Planar mismatch
    o Meets lattice strain (due to irregular spacing of atoms)
- Grain boundaries inhibit dislocation movement
- **Strengthen metal by decreasing grain size** (small grain size = more grain boundaries)

7.6 3D Imperfections

- Types: pores (bubbles), second phases

Second Phase (e.g. Fe_3C in steel)
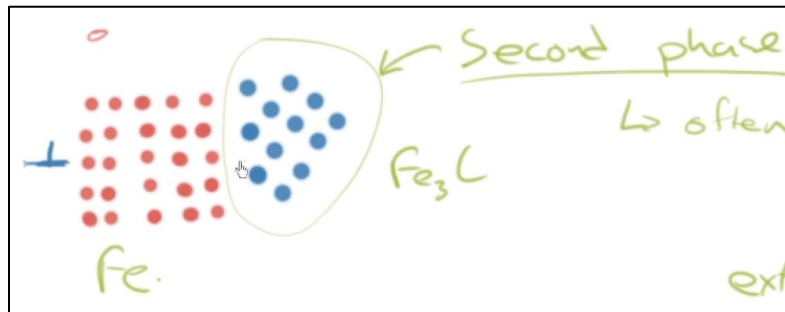
- Second phase is often hard (high strength) – difficult for dislocation movement in them
- Difficulties for dislocation movement at grain boundary between phases
- Many aluminum alloys strengthened by precipitation hardening
    o 2nd phase particles precipitate out of solution

8 POLYMERS

- Plastic deformation, dislocation, melting – all overcome INTERmolecular bonds, not intra

8.2 Mechanical Behaviour of Polymers

- General stress-strain curve:
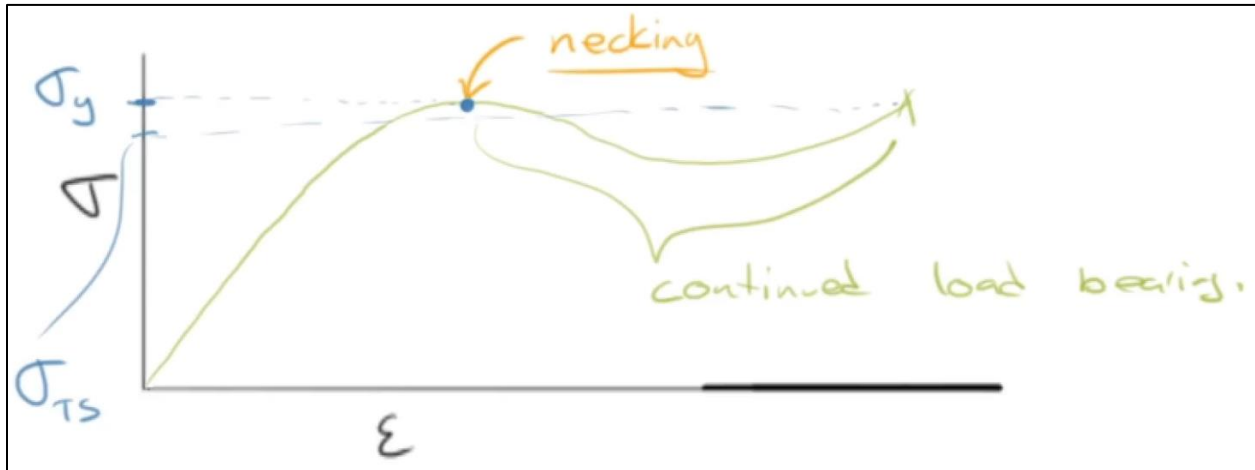
- Think of polymers as noodles, chains, strings, etc. tangled together
- Each chain has a "mer unit" – basic repeating unit
    o Naming based on this unit

- When you apply tension to polymer:
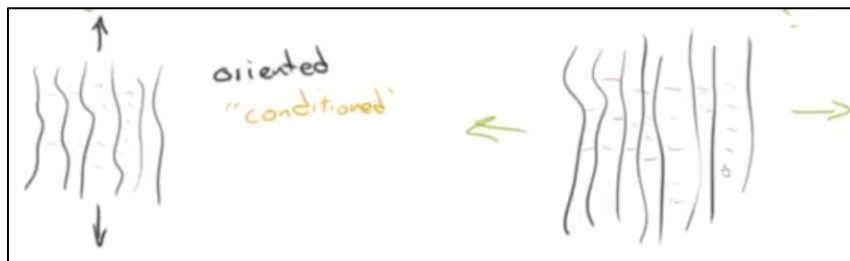
- Chains become oriented
    o Very difficult to break intramolecular bonds – why polymers can continue to bear load
    o Alignment of polymer molecule with loading axis = "chain orientation"
- Pulling in perpendicular direction – pulling on weak intermolecular bonds – easy to deform

8.3 Some Polymers

- Refer to notes

8.4 Molecular Weight

- Use mass to describe length of chains:
    - Number average: $\bar{M} = \sum \overline{M_i}\, x_i$
        - M_i = average molar weight of bin
        - x_i = number of molecules in bin i
    - Weight average (molecular weight): $\bar{M} = \sum \overline{M_i}\, w_i$
        - w_i = weight fraction of total weight of bin i
- Weight average is always greater than number average (counts heavier molecules more)
    - Dispersity: gives indication of breadth of distribution

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

8.5 Polymer Crystallinity and Tacticity

- Crystalline: ordered, more weak bonds
    - Greater strength, greater elastic modulus (kind of Young's modulus)
- Amorphous: not ordered, less weak bonds
- Semi-crystalline: both crystalline and amorphous sections

- How to increase crystallinity?
    - Simpler mer units (bulky ones do not pack as well)
    - TACTICITY: arrangement of repeating structures
        - Isotactic – same side
        - Syndiotactic – alternating side
        - Atactic – random arrangement
    - Longer branches are bad for crystallinity

8.6 Intramolecular Bonds

- How to increase strength of weak bonds?
    - Dipoles
    - Hydrogen bonds – strongest intermolecular bonds = strong polymers
        - Occur when H is bonded to O, N, or F

8.7 Cross-Linking and Network Polymers

Cross-Linking:

- Strong covalent bonds between chains (instead of weak secondary bonds)
- E.g. vulcanizing rubber, PEX tubing
- Important in elastomers

Network Polymers:

- 3D interconnected network
- High strength, brittle
- E.g. Epoxy, diamond

8.8 Effects of Temperature on Stress-Strain Behaviour

- In metals/ceramics: strong intramolecular bonds = not easily affected by temperature
- In polymers: weak intermolecular bonds = affected much more by temperature
 - Competition between binding energy and thermal energy
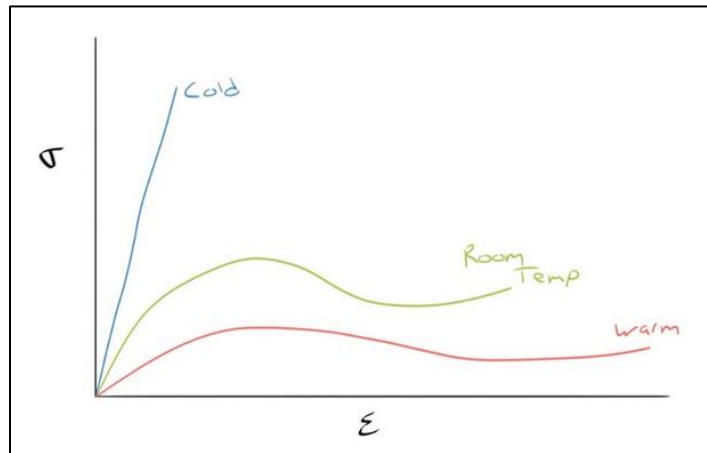
8.9 Relaxation Modulus

- When applying a fixed strain, stress relaxes overtime
  - E.g. Nylon strings on guitar, piano wires
- Relaxation Modulus: $E_R = \frac{\sigma(t)}{\epsilon_o}$
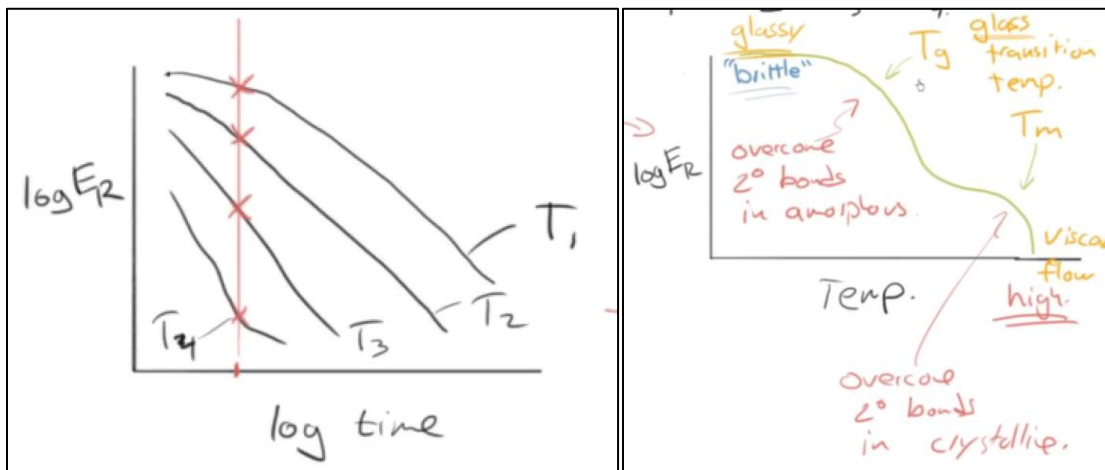
- Plotting relaxation modulus against time: decreases over time
- Plotting relaxation modulus at a specific time at different temperatures: decreases at higher temperatures
    o 2 sudden drops in modulus: glass transition temp, melting temp
    o Glass transition temp: overcoming secondary bonds in amorphous region
    o Melting temp: overcoming secondary bonds in crystalline region
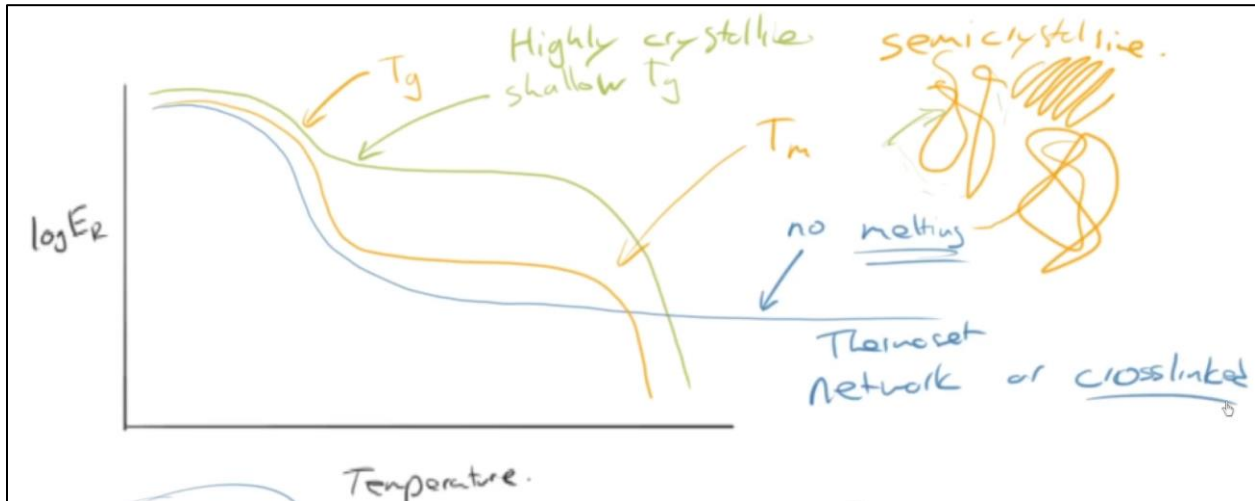
- Network polymers don't melt – can't break strong covalent bonds
    o Polymers that don't melt are called "Thermoset"
- Highly crystalline polymers will melt – called "Thermoplastic"


8.10 Viscoelasticity

- Polymers are sensitive to strain rate – how fast you deform them
- They are viscoelastic – both viscous and elastic
    o Viscous: resistant to fast changes
    o Elastic: instantaneous return to original structure
- Longer amount of time deformed = more viscous
- Less amount of time deformed = elastic

8.11 Optical Transparency

- Crystalline and amorphous regions have different index of refraction – scatters light
    o Scattering light (light doesn't go straight through) = translucency
- To be transparent:
    o Can't be semicrystalline
    o Polymers can never be 100% crystalline
    o Must be 100% amorphous
- E.g. PMMA has large side group – prevents crystallization, remains 100% amorphous – transparent

9 ATOMIC BONDING STRUCTURE AND SEMICONDUCTORS

9.1 The Electromagnetic Spectrum
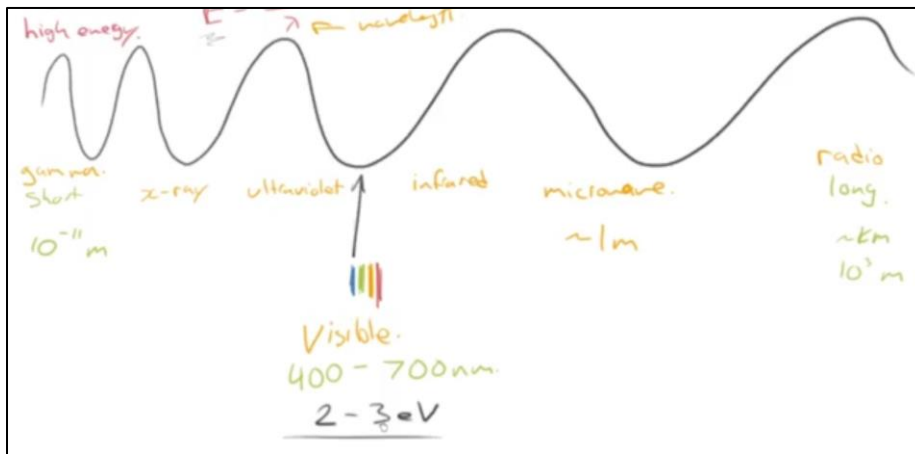
- Energy of photon:

$$E = \frac{hc}{\lambda} \quad \text{OR} \quad E = h\nu$$

  o h = Planck's constant = 6.626e-34 J s = 4.136e-15 eV s
    ▪ eV = "electron volt" = amount of energy an electron, has accelerated through 1V
    ▪ 1 eV = 1.602e-19 J
  o c = speed of light = 3e8 m/s
  o λ = wavelength
  o v = frequency of wave = c/λ [Hz]

9.2 The Atom

Wave Mechanical Model

4 quantum numbers (QN):

1. Principal – shells/size
    a. n = 1, 2, 3, 4… or n = K, L, M, N…
2. Angular/Azimuthal – subshell shape
    a. l = 0, 1, 2, …, (n-1) or l = s, p, d, f
3. Magnetic – orbital spatial orientation
    a. -l <= m_l <= l
    b. E.g. p subshell: p_x, p_y, p_z, m_l = -1, 0, 1
4. Spin – "spin"
    a. m_s = +/- ½

9.3 Electron Configuration

- Shorthand: [largest noble gas] + valence
- Always write in increasing shell number

- Always ionize higher shell number first
- Inert gases will always have octet stability (ns^2np^6)

9.4 Atomic Bonding

<u>Ionic</u>

- 2 logical steps
    - Achieving low energy (by electron transfer) (achieve stable octet)
    - Charge/coulombic attraction
- Non-directional attraction (not between specific nuclei)

<u>Covalent</u>

- Electron sharing to achieve octet stability
- Hybridization often occurs

<u>Metallic</u>

- Valence electrons contribute to a sea of electrons
- Sea of electrons conducts electricity

9.5 Band Theory of Solids

- Energy levels in different atoms split when they get close since electrons can't have same energy level (Pauli Exclusion principle)
- Forms continuous range of energy levels – a band
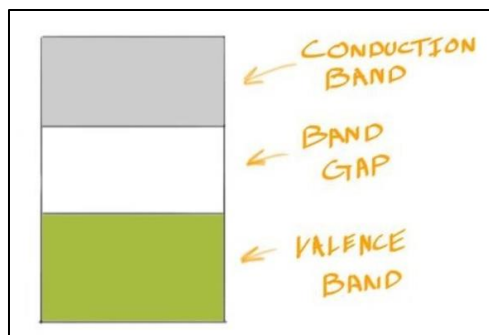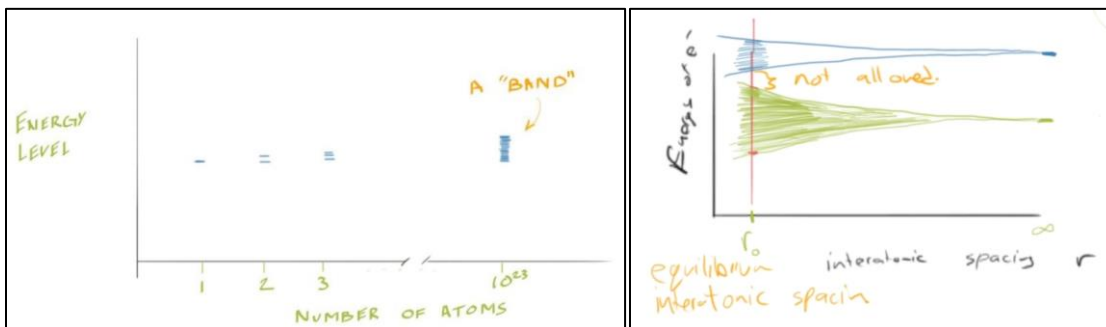
- Bandgap > 4 eV = insulator
- Bandgap < 4 eV = semiconductor
- Higher bandgap = transparent (visible light can't be absorbed – passes right through)
- Lower bandgap = more photon absorption and emission (less transparent)

9.6 Diamond Cubic Crystal Structure

- Same as zinc-blende but just all same atom
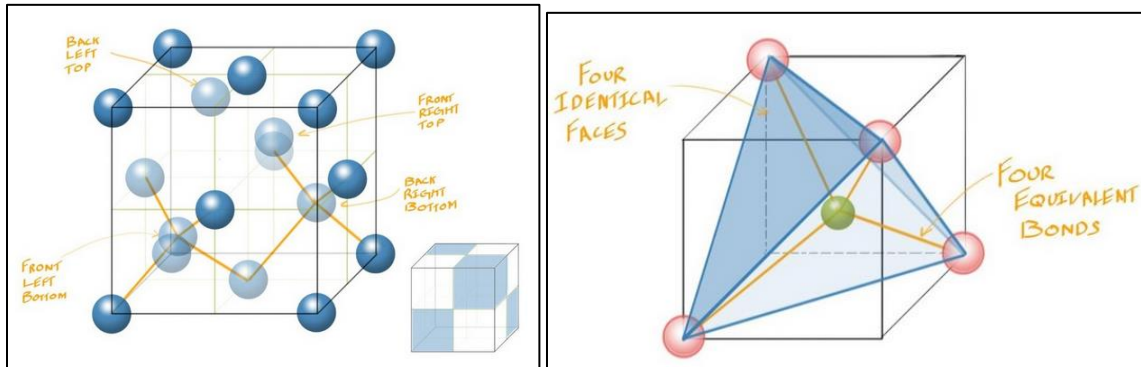
- Tetrahedral configuration/interstitial site in subcubes
- Coordination number = 4
- n = 4 (from FCC positions) + 4 (from tetrahedral sites) = 8 atoms

9.7 Semiconductors

Intrinsic

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

- n = concentration of charge carrier [#/m^3]
- q = fundamental charge [C]
- μ = charge carrier mobility [m^2/Vs]

Extrinsic n-type

- Add something pentavalent
- Majority charge carrier = weakly bonded 5th electron (negative)
- Donor energy level right under conduction band

Extrinsic p-type

- Add something trivalent
- Majority charge carrier = holes (positive)
- Acceptor level right above valence band

9.8 Compound Semiconductors and Mixed Bonding

- Compound semiconductors have mixed bonding (characteristics between ionic and covalent bonding)
- Compound semiconductors: emit and absorb light
    - Emitted light is equal to bandgap of semiconductor
- Ex: GaAs and AlAs have different bandgaps

$$Ga_xAl_{1-x}As$$
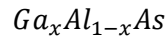
- As is 50%
- Other 50% is 100x% Ga and 100(1-x)% of Al
- Emits photon with chosen energy between bandgaps of GaAs and AlAs

9.9 Size of Tetrahedral Interstitial Site

$$\frac{R_C}{R_A} = 0.225$$

10 THERMODYNAMICS

- **Entropy:** uncertainty in knowing precisely the energy that an atom/molecule will have
    - How spread out energy is (the more spread out, the more possible microstates there are)

$$\Delta S = \frac{q_{rev}}{T}$$

- **Second Law:** entropy of universe must increase
- **First Law:** energy cannot be created/destroyed
    - For isolated system: $\Delta U_{sys} = 0$
    - For closed system: $\Delta U_{sys} = q + W$
        - q = heat (heat in is positive)
        - W = work done on system (work done on system is positive)

- **Enthalpy:**

11 PHASE EQUILIBRIUM