MSE 160 Lecture Notes

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The up-to-date version of this document can be found at `https://github.com/HaysonC/skulenotes`

"In this class we are mostly understanding solids"
- Prof. Scott Ramsay

1 Mechanical Behavior

Classes of Materials In this class, we look at three classes of materials (non-exhaustive):

- **Metal** held together with metallic bonds, typically **ductile** and **conductive**.
- **Ceramics** (often metal oxides [excp: diamond]) held together via covalent & ionic bonds, typically **brittle** and **insulating**.
- **Polymers** Molecules (often hydrocarbons) typically **ductile** and **insulating**

Engineering Stress For normal stress, we know that:

$$\sigma = \frac{F}{A_0} \tag{1}$$

Engineering Strein Also:

$$\epsilon = \frac{\Delta l}{l_0} \tag{2}$$

Young's Moduclus For elastic deformation, E, is given, by Hooke's Law, as follows:

$$\sigma = E\epsilon \tag{3}$$

Tensile Test We apply force as to the ends of a dogbone-sample, with l_0 being the gauge length and A_0 being the area of the cross-section at the middle.

Tensile Strein Maximum tensile strain on the engineeging stress-strain curve.

1.1 Understanding Elastic Properties in terms of Atomic Configuration

Atomic Configuration We can understand the elastic properties of a material by looking at the atomic configuration. Skemetically, we can represent the atomic configuration as a spring system:

1. **Intial - Before Loading** Atoms are in equilibrium, with the interatomic forces being balanced.
2. **Loading** We apply a force to the material, causing the atoms to move from their equilibrium positions. The bond stretches and the atoms move further apart.
3. **Unloading** We remove the force, causing the atoms to return to their equilibrium positions.

Atom Positions Elastic modulus is dependent on the atomic interatomic bonding force. Thus, The elastic modulus is prootionaly to the slope of the interatomic force-seperation curve.

Force-Seperation Curve The force-seperation curve is a plot of the force between two atoms as a function of the distance between them. The slope of the curve is proportional to the elastic modulus near the equilibrium position.

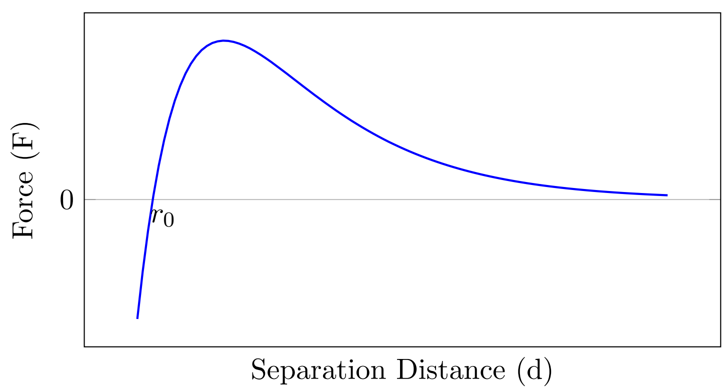

Figure 1: Force-Separation Curve (Lennard-Jones Force)

$$E \propto \left.\frac{dF}{dr}\right|_{r_0} \tag{4}$$

Definiton 1.1.1 (Equilibrium interatomic seperation distance)**.** The equilibrium interatomic seperation distance, r_0, is the distance between two atoms at which the interatomic force is zero. This is due to the interatomic forces being the sum of attractive and repulsive forces.

Elastic Modulus Thus, strongly bonded materials have a higher elastic modulus and the slope of the force-seperation curve is steeper at r_0.

1.2 Understanding Other Properties in terms of Atomic Configuration

Potential Energy-Separation Curve The potential energy-seperation curve is a plot of the potential energy between two atoms as a function of the distance between them. The potential energy is the area under the force-seperation curve.

Depth of the Minimum Energy Well The depth of the minimum energy well, E_0, is the energy required to break the bond between two atoms. This is the energy required to move the atoms from the equilibrium position to infinity. It is proportional to the melting temperature of the material.

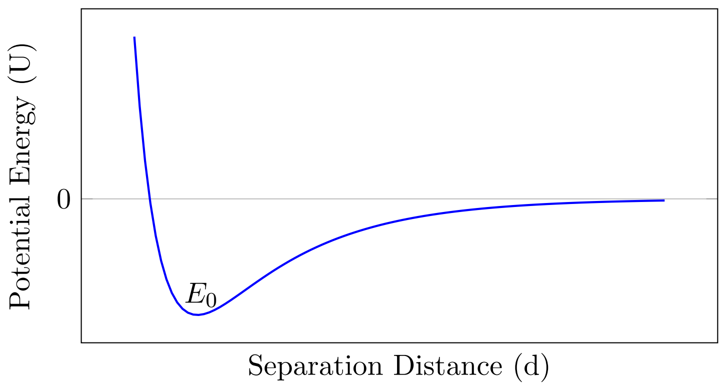

Figure 2: Potential Energy-Separation Curve

Coefficient of Thermal Expansion The coefficient of thermal expansion, α, is the fractional change in length per degree change in temperature.

Depth of Potential Energy Curve The deeper the potential energy curve, the higher the melting temperature and more symetric the curve near E_0. This would give the follwoing three properties:

1. **Higher Melting Temperature** The higher the melting temperature, the deeper the potential energy curve.
2. **Higher Elastic Modulus** The steeper the slope of the force-seperation curve at r_0, the higher the elastic modulus.
3. **Lower Coefficient of Thermal Expansion** The more symetric the potential energy curve near E_0, the lower the coefficient of thermal expansion.

1.3 Shear and Tensile Stress

1.3.1 Shear

Shear Stress Shear stress is the force per unit area acting parallel to the surface. It is given by:

$$\tau = \frac{F}{A_0} \tag{5}$$

Shear Strain Shear strain is the change in angle between two lines originally perpendicular to each other. It is given by:

$$\gamma = \frac{\Delta l}{l_0} \approx \tan\theta \approx \theta = \frac{\pi}{2} - \phi \tag{6}$$

Shear Modulus The shear modulus, G, is the ratio of shear stress to shear strain. It is given by:

$$\tau = G\gamma \tag{7}$$

Relationship between Shear and Tensile Modulus The shear modulus is related to the tensile modulus by the following equation:

$$G = \frac{E}{2(1+\nu)} \tag{8}$$

where ν is the Poisson's ratio.

Poisson's Ratio Poisson's ratio, ν, is the ratio of lateral strain to axial strain. It is given by:

$$\nu = -\frac{\epsilon_{\text{lat}}}{\epsilon_{\text{axial}}} \tag{9}$$

1.4 Testing

Definiton 1.4.1 (Gauge Length)**.** The gauge length, l_0, is the length of the sample over which the strain is measured.

Definiton 1.4.2 (Reduced Section)**.** The reduced section is the part of the sample where the cross-sectional area is reduced to a smaller value.

Gauge length is always no longer than the reduced section. The reduced section is where the sample will likely break.

Testing Ceremics In relation to tensile testing, ceramics have the following properties:

- **Brittle** Ceramics are brittle and will break suddenly.
- **High Strength** Ceramics have high strength and thus difficult to machine the sample.
- **Sample Alignment** The sample must be aligned properly to test for pure tension. Unlike metals and polymers, which are self-aligning.
- **Fracture** Ceramics will fracture while still off-axis. Hence, there would be a large shear component.

Thus, we often approxiate tensile behaviour with a point loading on a horizontal beam, with two point support (3 point bending test). Peak stress is given by:

$$\sigma_{\text{peak}} = \frac{3FL}{2bd^2} \tag{10}$$

, where:

- L (span) is the distance between the two supports.
- b is the width of the sample
- d is the thickness/depth of the sample

2 Seleection of Materials

2.1 Material Performance

Example 2.1.1 (Aircraft Wing Spar)**.** The aircraft wing spar is beam (loaded in bending) that supports the wing. The spar is made of a material with the objective of minimize mass under the following constraints:

- **Deflection** There is a maximum allowable deflection of the wing.
- There is more..., but for this example, we will only consider the deflection.

The material selection solve for a **light stiff beam**.

Mass The mass of the beam is given by:

$$m = \rho V = \rho AL$$

Deflection The deflection of the beam is given by:

$$\delta = \frac{FL^3}{48EI} \tag{11}$$

For a beam with a rectangular cross-section, we have:

$$\delta = \frac{FL^3}{48E} \cdot \frac{12}{bh^3} = \frac{FL^3}{4Ebh^3}$$

We can set b proportional to h:

$$\delta = \frac{FL^3}{cE} \cdot \frac{1}{A^2}, \quad \text{for some constant } c$$

We can then isolate for A, the free variable, and minimize the mass via the objective equation $m = \rho AL$:

$$A = \sqrt{\frac{FL^3}{cE\delta}}$$
$$m = \rho L\sqrt{\frac{FL^3}{cE\delta}} = \rho L\sqrt{\frac{FL^3}{cE\delta}}$$

Arrange into the form (functional)(geometric)(material):

$$m = \left(\frac{F}{c\delta}\right)^{\frac{1}{2}} \cdot \left(L^{\frac{5}{2}}\right) \cdot \left(\frac{\rho}{E^{\frac{1}{2}}}\right)$$

Material Peformance Index The material performance index is given by:

$$\text{Material Performance Index (MSI)} = \frac{E^{\frac{1}{2}}}{\rho} \tag{12}$$

MPI Graph We plot $\log E$ against $\log \rho$ to get the MPI graph.

Tempered Glass Temperglass are made to resist tension. It is done by applying a compressive stress to the surface of the glass. This is done by cooling the surface of the glass faster than the core or chemically treating the surface.

2.2 Density

Density The density of a material is given by:

$$\rho = \frac{m}{V} \tag{13}$$

Archimedes' Principle The buoyant force on an object is equal to the weight of the fluid displaced by the object. Derive from that, we have:

$$\rho = \frac{m}{V} = \frac{m_{\text{object}}}{m_{\text{object}} - m_{\text{object in fluid}}} \tag{14}$$

3 Atomic Structures

3.1 General Definitions

Ordered structures We have the following three orders:

1. **Long Range Order (LRO)** Atoms are arranged in a well-defined pattern over long distances in repeating units.
(Example) Diamonds, some polymers, most metals, many ceramics, graphite, quartz, etc.
2. **Short Range Order (SRO)** Periodic arrangement of atoms over a few atomic or molecular spacings.
(Example) Most polymers, glasses, amorphous materials, etc.
3. **No Order (NO)** Atoms are randomly arranged.
(Example) Ideal gases, etc.

Describing Crystal Structures We can describe crystal structures by the following:

- **Unit Cell** The smallest repeating unit of a crystal structure that could be used to represent the entire crystal.
- **Lattice** The repeating arrangement of points that repersent the positions of atoms in the unit cell.
(Example) Simple Cubic, Body-Centered Cubic, Face-Centered Cubic, etc.
- **Lattice Plus Basis** *Not required for this course*

Theortical Density of Metals The theoretical density of metals is given by:

$$\rho = \frac{nM}{V_c N_A} \tag{15}$$

, where:

- n is the number of atoms in the unit cell.
- M is the atomic mass of the element (amu = g/mol).
- V_c is the volume of the unit cell.
- N_A is Avogadro's number ($6.022 \times 10^{23}\text{mol}^{-1}$)

3.2 Describing Basic Unit Cells

Definiton 3.2.1 (Coordination Number (CN))**.** The coordination number is the number of nearest neighbors an atom has in a crystal structure.

Definiton 3.2.2 (Atomic Packing Factor (APF))**.** The atomic packing factor is the fraction of the volume of the unit cell that is occupied by hard spheres. It is given by:

$$\text{APF} = \frac{\text{Volume of atoms in unit cell}}{\text{Volume of unit cell}} \tag{16}$$

Simple Cubic (SC) The simple cubic structure has the following properties:

- **Centers of atoms** Located at the eight corners of a cube
- **Rare Packing Density** Due to low packing density (only known example: Polonium, Po)
- **Close-packed directions** As cube edges.
- **Coordination Number** Number of nearest neighbor: 6

Face-Centered Cubic (FCC) The face-centered cubic structure has an atom on the centre of each face of the cube. It has the following properties:

- **Ductile** and **Malleable** due to the close-packed planes. Common examples include: $\text{Al}, \text{Cu}, \text{Au}, \text{Ag}$.
- **Coordination Number** Number of nearest neighbor: 12
- **Close-packed directions** As cube diagonals.
- **Theortical Density** The theoretical density of FCC is derived from Equation (15):

  $$\rho = \frac{nM}{V_c N_A}$$

  With $n = 4$ (8 corners $\times\frac{1}{8}$ atom each + 6 faces $\times\frac{1}{2}$ atom each) and $V_c = a^3$ (where a is the **lattice parameter**):

  $$\rho_{\text{FCC}} = \frac{4M}{a^3 N_A}$$

  We can then obtain a via the relationship between the atomic radius, r, and the lattice parameter via the geometry on the close-packed direction (face diagonal):

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

  Substitute a back into the equation:

  $$\begin{aligned} \rho_{\text{FCC}} &= \frac{4M}{(2\sqrt{2}r)^3 N_A} = \frac{4M}{16\sqrt{2}r^3 N_A} \\ &= \frac{M}{4\sqrt{2}r^3 N_A} \end{aligned} \tag{17}$$

- **Atomic Packing Factor** The atomic packing factor of FCC is given by:

$$\mathrm{APF}_{\mathrm{FCC}} = \frac{\text{Volume of atoms in unit cell}}{\text{Volume of unit cell}} = \frac{4 \times \frac{4}{3}\pi r^3}{a^3} = \frac{4 \times \frac{4}{3}\pi r^3}{(2\sqrt{2}r)^3} = \frac{\pi}{6\sqrt{2}} = \mathbf{0.74} \tag{18}$$

  This is the highest possible packing factor for spheres. Thus, no other structure can have a higher packing factor.

- **Stacking** The FCC structure can be thought of as stacking close-packed planes. The stacking sequence is ABCABC... (where A, B, and C describe the orientation hexagonal close-packed planes).

Hexagonal Close-Packed (HCP) The hexagonal close-packed structure is **crytal structure** by stacking close-packed hexagonal planes. It has the following properties:

- **Coordination Number** Number of nearest neighbor: 12
- **Close-packed directions** As cube diagonals.
- **Theortical Density** The theoretical density of HCP is derived from Equation (15):

$$\rho = \frac{nM}{V_c N_A}$$

  With $n = 6$ (12 corners $\times \frac{1}{6}$ atom each) and $V_c = a^3$:

$$\rho_{\mathrm{HCP}} = \frac{6M}{a^3 N_A} \tag{19}$$

- **Atomic Packing Factor** The atomic packing factor of HCP is given by:

$$\mathrm{APF}_{\mathrm{HCP}} = \frac{\text{Volume of atoms in unit cell}}{\text{Volume of unit cell}} = \frac{6 \times \frac{4}{3}\pi r^3}{a^3} = \frac{6 \times \frac{4}{3}\pi r^3}{a^3} = \mathbf{0.74} \tag{20}$$

- **Stacking** The HCP structure can be thought of as stacking close-packed planes. The stacking sequence is ABAB...

Example 3.2.3 (Density of Aluminum)**.** Given that the atomic radius of aluminum is $r = 143$ pm and the atomic mass is $M = 26.98$ g/mol, we can calculate the density of aluminum with FCC structure. We have:

$$\begin{aligned}\rho_{\mathrm{Al}} &= \frac{M}{4\sqrt{2}r^3 N_A} = \frac{26.98}{4\sqrt{2} \times (143 \times 10^{-12})^3 \times 6.022 \times 10^{23}} \\ &= \frac{26.98}{4\sqrt{2} \times (143 \times 10^{-12})^3 \times 6.022 \times 10^{23}} = 2.7 \text{ g/cm}^3\end{aligned}$$

Body-Centered Cubic (BCC) The body-centered cubic structure has an atom at the centre of the cube. It has the following properties:

1. **Coordination Number** Number of nearest neighbor: 8
2. **Atomic Packing Factor** The atomic packing factor of BCC is given by:

$$\text{APF}_{\text{BCC}} = \frac{\text{Volume of atoms in unit cell}}{\text{Volume of unit cell}} = \frac{2 \times \frac{4}{3}\pi r^3}{a^3} = \frac{2 \times \frac{4}{3}\pi r^3}{(4r/\sqrt{3})^3} = \mathbf{0.68} \tag{21}$$

3. **Close Packed Directions** As cube diagonals.
4. **Theortical Density** The theoretical density of BCC is derived from Equation (15):

$$\rho = \frac{nM}{V_c N_A}$$

With $n = 2$ (8 corners $\times \frac{1}{8}$ atom each + 1 center atom) and $V_c = a^3$:

$$\rho_{\text{BCC}} = \frac{2M}{a^3 N_A} \tag{22}$$

5. **Stacking** The BCC structure can be thought of as stacking close-packed planes. The stacking sequence is ABAB...

4 Geometric Properties of Crystals

4.1 Crystallographic Directions and Planes

Point Coordinates A lattice positon in a unit cell is determined as fractional multiples of the unit cell edge lengths a, b, and c. (Defining the origin at one corner of the unit cell and $a = b = c = \mathbf{1}$)

Crystallographic Directions A crystallographic direction is a line between two points in a crystal. It is denoted by square brackets, $[uvw]$. The direction is determined from the "tail" to the "head" of the vector. Also:

1. It **shall not** include commas; and
2. It **shall be reduced**to the smallest integers; and
3. Negative signs are represented by a bar over the number.

Example 4.1.1. The crystallographic direction from $(0, 0, 0)$ to $(-1, 0, 1/2)$ is $[\bar{2}01]$.

Family of Directions A family of directions is a set of directions that are parallel to each other. It is denoted by $< uvw >$.

Example 4.1.2. The family of directions $< 100 >$ is the set of directions [100], [010], [001], $[\bar{1}00]$, $[0\bar{1}0]$, and $[00\bar{1}]$.

Angle between Directions The angle between two directions in a **cubic** crystal is given by:

$$\cos\theta = \frac{h_1h_2 + k_1k_2 + l_1l_2}{\sqrt{h_1^2 + k_1^2 + l_1^2}\sqrt{h_2^2 + k_2^2 + l_2^2}} \tag{23}$$

, which is simply the normalized dot product of the two vectors.

Crystallographic Planes A crystallographic plane is a set of parallel planes in a crystal. It is denoted by (hkl). The plane is determined by the intercepts on the x, y, and z axes.

Generally, we find the intercepts by finding the points where the plane intersects the axes. We then take the reciprocals of the intercepts and multiply by the smallest integer to get the Miller Indices.

Family of Planes A family of planes is a set of planes that are parallel to each other. It is denoted by $\{hkl\}$.

Distance between Planes The distance between two planes with miller indices $(h_1k_1l_1)$ and $(h_2k_2l_2)$ is given by:

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \tag{24}$$

, where a is the lattice parameter.

4.2 X-Ray Diffraction

The diffraction pattern is used to determine the crystal structure. By measuring the n$^{\text{th}}$ order peak angle θ_c and the wavelength of the X-ray, we can determine the distance between planes:

$$\begin{aligned} 2d\sin\theta &= n\lambda \\ d &= \frac{n\lambda}{2\sin\theta_c} \end{aligned} \tag{25}$$

Thus, we could determine the lattice parameter a by the following equation:

$$a = \frac{n\lambda}{2\sin\theta_c}\sqrt{h^2 + k^2 + l^2} \tag{26}$$

4.3 Geometrcally Ideal Crystal Structures

Coordination Number and Ratio The coordination number increases with $\frac{r_{\text{cation}}}{r_{\text{anion}}}$ (The ionic radii ratio). It relates to coordination number as follows:

Ionic Radii Ratio	Coord. Number	Name
< 0.155	2	Linear
0.155 - 0.225	3	Trigonal Planar
0.225 - 0.414	4	Tetrahedral
0.414 - 0.732	6	Octahedral
0.732 - 1.0	8	Cubic

Table 1: Coordination Number and Ionic Radii

Definiton 4.3.1 (AX Type)**.** The AX type is a crystal structure where the cation and anion are of the same ratio.

Example 4.3.2 (AX Type: NaCl rock salt)**.** The NaCl structure is an AX type structure. The cation and anion are of the same ratio. Soldium (Cation) has radius $r_{\text{Na}} = 0.102$ nm and Chlorine (Anion) has radius $r_{\text{Cl}} = 0.181$ nm. The ratio is:

$$\frac{r_{\text{cation}}}{r_{\text{anion}}} = \frac{0.102}{0.181} = 0.56$$

Thus, the coordination number is 6.
Additionally, we could calculate its theoretical density. It has 4 cation and 4 anion in the unit cell. The volume of the unit cell is a^3, and it follows a FCC structure. Thus, the density is:

$$\begin{aligned}\rho &= \frac{4M_{\text{Na}} + 4M_{\text{Cl}}}{a^3 N_A} = \frac{4(22.99) + 4(35.45)}{a^3 N_A} \\ &= \frac{4(22.99) + 4(35.45)}{(2\sqrt{2} r_{\text{Na}})^3 N_A} = \frac{4(22.99) + 4(35.45)}{(2\sqrt{2} \times 0.102)^3 N_A} \\ &= \frac{4(22.99) + 4(35.45)}{(2\sqrt{2} \times 0.102)^3 N_A} = 2.16 \text{ g/cm}^3\end{aligned}$$

Example 4.3.3 (AX Type: ZnS, Zinc Blende)**.** The ZnS structure is an AX type structure. It has a FCC structure with CN = 4. The radius of Zinc (Cation) is $r_{\text{Zn}} = 0.074$ nm and the radius of Sulfur (Anion) is $r_{\text{S}} = 0.184$ nm. The ratio is:

$$\frac{r_{\text{cation}}}{r_{\text{anion}}} = \frac{0.074}{0.184} = 0.40$$

Example 4.3.4 (AX_2 Type: CaF_2)**.** The CaF_2 structure is an AX_2 type structure. It has a FCC structure with CN = 8. The radius of Calcium (Cation) is $r_{\text{Ca}} = 0.099$ nm and the radius of Fluorine (Anion) is $r_{\text{F}} = 0.133$ nm. The ratio is:

$$\frac{r_{\text{cation}}}{r_{\text{anion}}} = \frac{0.099}{0.133} = 0.74$$

5 Stress-Strain Behavior

Uniformly Distributed Elongation The elongation of a material is uniformly distributed within the gauge length. The initial values, referred to as the "elastic region," are characterized as uniformly elastic.

Non-Linear Elastic There is also a non-linear region where the material remains elastic but is not uniformly distributed.

Localized Plastic Deformation The material then enters the plastic region where the deformation is localized. The material is permanently deformed. This is characterized by the ultimate tensile strength (this is bad when it happens).

Necking The material then necks, where the cross-sectional area decreases. The material is then strained until it breaks.

True Stress The true stress is given by:

$$\sigma_T = \frac{F}{A_i} \tag{27}$$

, where A_i is the instantaneous cross-sectional area.

Ultimate Tensile Strength The ultimate tensile strength is the maximum stress on the stress-strain curve.

Strengthening Plastic deformation is made more difficult by the following mechanisms:

1. **Strain Hardening** Preloading beyond the elastic region - upon plastic deformation, the material will have a higher yield strength.
2. **For Metals and Alloys** The following mechanisms are used:

Strain Hardening Equation The true stress-strain curve can be emprically described by the following equation:

$$\sigma_T = K\epsilon_T^n \tag{28}$$

, where K is the Strain Hardening coefficient and n is the strain hardening exponent. Both of these values are material properties.

True Strain Since $\epsilon_i = \frac{\Delta l_i}{l_0 + \Delta l_{i-1}}$ we can compute a Rieman sum to get the true strain:

$$\epsilon_T = \int_{l_0}^{l_f} \frac{dl}{l} = \ln\left(\frac{l_f}{l_0}\right) \tag{29}$$

Strain Rate The strain rate is the rate at which the material is deformed. It is given by:

But, before necking, we can assume $V_0 = V_i$ and $A_i = \frac{A_0 l_0}{l_i}$. Thus, we have:

$$\begin{aligned}\sigma_T &= \frac{F}{A_i} = \frac{F}{\frac{A_0 l_0}{l_i}} = \frac{F l_i}{A_0 l_0} = \frac{F}{A_0} \cdot \frac{l_i}{l_0} = \sigma \cdot \frac{l_i}{l_0} \\ &= \sigma \cdot (1 + \epsilon) \end{aligned} \tag{30}$$

and,

$$\epsilon_T = \ln(1 + \epsilon) \tag{31}$$

5.1 Imperfections

Dislocation Recal that plastic deformation occurs by step-wise breaking of atomic bonds. This is done by the movement of dislocations. **Strengthening mechanisms in Metals** rely on inhibiting the movement of dislocations.

Definiton 5.1.1 (Dislocation)**.** A dislocation is the breaking and reforming of bonds, one row at a time. It is a line defect in the crystal structure.

Crystalline Imperfections We use crystalline imperfections to inhibit the movement of dislocations. These imperfections include:

- **Point Imperfections (Defects)** Vacancies, interstitials, and substitutional atoms. (Example) Solid solution strengthening.
- **Line Imperfections** Dislocations.
- **Area Imperfections** Grain boundaries of the interface between two grains and free surfaces.
- **Volume Imperfections** Second phase particles.

Solid Solution Strengthening [Alloying] The addition of a solute to a solvent to inhibit the movement of dislocations. There is two types:

1. **Interstitial Impurities** The solute atoms are smaller than the solvent atoms. This the impurites to be in the interstitial sites.
2. **Substitutional Impurities** The solute atoms are larger than or as large as the solvent atoms ($< 10\% \Delta\varnothing$, similar electornegativity.). This causes the impurities substitute the lattice sites.

Vacancies Vacancies are missing atoms in the lattice. They are created by thermal vibrations. They are used to inhibit the movement of dislocations. It slightly nudges nearby atoms, creating **lattice strain** that make it harder for dislocations to move.

Machaism - Diffusion of Impurities In positve edge dislcation, it has compession above disvlation line, and tension below. The impurities will 'pin' the dislocation, making it harder to move.

Plastic Deformation We can also strengthen the material by increasing the number of dislocations. This is done by plastic deformation methods:

1. Cold Work
2. Forging/Strain Hardening

Mechanisms of Strengthening Plastic deformation increases number of dislocations, which inhibits one another due to the strain fields.

Definiton 5.1.2 (Grain Boundaries)**.** Grain boundaries are the interface between two grains. Grains are regions of the same crystal structure but with different orientations.

Grain Size Reduction Dislcations tend to move in the direction of the grain boundry (GB). Thus, reducing the grain size reduces the distance the dislocation can move. In addition, there are atomic strain due to the difference of bond lenght between grains, contributing to the strain field. It is given by:

$$\sigma = \sigma_0 + \frac{K_y}{d} \tag{32}$$

Second Phase Particles Second phase particles are particles of a different phase in the material. They can be used to inhibit the movement of dislocations. They are often hard, brittke phases.

Dislcations (Slips) Occurs on the plane with the highest planar density. The slip direction is the direction with the highest linear density. The slip system is the combination of the slip plane and slip direction.

FCC has 4 unique planes, each with 3 unique directions. Thus, there are 12 unique slip systems. Compare this to HCP, which has only base plane.

Resolved Stear Stress Consider single crystal with a certain plane. Let ϕ be the angle between the normal of the plane and the direction of the applied stress, and λ be the angle between the plane and the orthonal of the applied stress. The resolved shear stress is given by:

$$\tau = \sigma \cos\phi \cos\lambda \tag{33}$$

Critcal Resolved Shear Stress The critical resolved shear stress is the minimum shear stress required to move a dislocation. When the resolved shear stress equal the critical resolved shear stress, the dislocation will move, and:

$$\sigma = \sigma_y \tag{34}$$

So,

$$\tau_{\text{CRSS}} = \sigma_y \cos\phi \cos\lambda \tag{35}$$

Note Most crystals are polycrystalline, so dislocation must be able to move to the neibouring crystal.

Burgers Vector The Burgers vector is the vector that describes the dislocation. It is the vector that closes the loop of the dislocation. It is given by:

$$\vec{b} = \vec{b}_1 + \vec{b}_2 \tag{36}$$

6 Polymers

Polymer Polymers could be britte or elastic (elastomers). They are made of long chains of monomers. Interestingly, polymers have necking points lower than its ultimate tensile strength.

"Why does polymers continue to stretch after necking?"

Polymer Structure Polymers are made of long chains of monomers. The chains are held together by weak van der Waals forces. The chains are entangled.
(Example) Polyethylene are made of long chains of carbon atoms with two hydrogen atoms attached to each carbon atom.

Ans: (Chain-Oriented) The chains are originally entangled. When the polymer is stretched, the chains are straightened to align with the load. More of the load is taken by the covalent bonds, which are stronger than the van der Waals forces. This serves as an important strengthening mechanism.

Note In a polymer, the elastic response is from numerrous bond types.

Crylistallinity Polymers cannot be 100% crystalline. A polymer could be semi-crystalline, where the polymer has both crystalline and amorphous regions. Since the crystalline regions are stronger, increasing the crystallinity is a important strengthening mechanism.

1. **Tmerpeature** Increasing the crtystallinity permits the polymer have higher service temperature.
2. **Chemical Resistance** Crystalline regions are more resistant to chemcial dissolution.

Different Mer Units Different mer units have different properties. Listed below are some common mer units:

- **Polyethylene** (PE) - Made of long chains of carbon atoms with two hydrogen atoms attached to each carbon atom.
- **Polypropylene** (PP) - Similar to PE, but with a methyl group attached to the carbon atom.
- **Polyvinyl Chloride** (PVC) - Made of long chains of carbon atoms with a chlorine atom attached to each carbon atom. Chlorine are more electronegative than carbon, so the bond is polar and form stornger van der Waals forces.
- **Polystyrene** (PS) - Made of long chains of carbon atoms with a phenyl group attached to each carbon atom.
- **Polytetrafluoroethylene** (PTFE) - Made of long chains of carbon atoms with two fluorine atoms attached to each carbon atom. The florine is to protect the carbon backbone. Hoowever, it is mechanically weak as the dipole moment is low.
- **Polymethyl Methacrylate** (PMMA) - Made of long chains of carbon atoms with a methyl group and a methacrylate ($-OC(=O)$) group attached to each carbon atom. It is opticall tranparnet the methacrylate group prevent crtystallinity, hence amorphous and no crystal boundaries.

6.1 Viscoelasitcity and Thermal Properties

Viscoelasticity Polymers are viscoelastic. They have both viscous and elastic properties. The viscous properties are due to the entanglement of the chains. The elastic properties are due to the covalent bonds.

Time-Dependent Behavior For a given stress/strain, the strain/stress will decrease with time. This is due to the viscous properties of the polymer.

Relaxation Modulus The relaxation modulus is the modulus of the polymer as a function of time. It is given by:

$$E(t) = \frac{\sigma(t)}{\epsilon_0} \tag{37}$$

The relaxation modulus is also relate to the temperature of the polymer. The relaxation modulus decreases with temperature.

Glassy Transition The glassy transition is the temperature at which the polymer changes from a glassy state to a rubbery state. The glassy state is characterized by a high modulus and low strain. The rubbery state is characterized by a low modulus and high strain. The temperature is denoted as T_g. This is due to the temperature overcoming the intermolecular forces of the amorphous reigions, but the crystalline regions are still intact as the van der Waals foce is stronger.

Melting THe melting temperature is the temperature at which the polyme the intermolecular forces of the crystalline regions are overcome. The polymer then melts as chains slide past each other.

Thermosat Thermosat are polymers that do not melt. They are made of cross-linked chains or network polymers. The cross-links prevent the chains from sliding past each other. Elastomers are typically thermosets.

6.2 Optical Properties

PMMA PMMA is a transparent polymer. It is used in optical applications. The transparency is due to the lack of **scattering events**.

Definiton 6.2.1 (Scatter Event)**.** A scatter event is an event that causes light to be scattered. It is due to the difference in refractive index between the polymer and the air.

Constants and conversions

$1\,\text{atm} = 101.325\,\text{kPa} = 1.01325\,\text{bar} = 14.696\,\text{psi}$

N_A	$6.022 \times 10^{23}\,\text{mol}^{-1}$
e	$1.602 \times 10^{-19}\,\text{C}$
1 eV	$1.602 \times 10^{-19}\,\text{J}$
ϵ_0	$8.854 \times 10^{-12}\,\text{F m}^{-1}$
R	$8.314\,\text{J mol}^{-1}\,\text{K}^{-1}$
	$0.082067\,\text{L atm mol}^{-1}\,\text{K}^{-1}$
0 °C	$273.15\,\text{K}$
k	$8.62 \times 10^{-5}\,\text{eV atom}^{-1}\,\text{K}^{-1}$
	$1.38 \times 10^{-23}\,\text{J atom}^{-1}\,\text{K}^{-1}$
F	$96486\,\text{C mol}^{-1}$
h	$6.626 \times 10^{-34}\,\text{J s}$
	$4.136 \times 10^{-15}\,\text{eV s}$
c	$2.99 \times 10^{8}\,\text{m s}^{-1}$
g	$9.81\,\text{m s}^{-2}$

Microstructure

$LD = \frac{\#}{\text{Length}}$ $\quad LPF = \frac{\text{length of atoms}}{\text{length of vector}}$

$PD = \frac{\#}{\text{Area}}$ $\quad PPF = \frac{\text{area of atoms}}{\text{area of plane}}$

$V = \frac{4}{3}\pi r^3$ $\quad A = \pi r^2$

$A_{\text{triangle}} = \frac{1}{2}bh$ $\quad \rho = \frac{nA}{V_C N_A}$

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

$N = \frac{N_A \rho}{A}$ $\quad N_V = N\exp(-\frac{Q_V}{kT})$

$a = 2\sqrt{2}R$ $\quad a = \frac{4}{\sqrt{3}}R$

$d_{\text{hkl}} = \frac{a}{\sqrt{h^2+k^2+l^2}}$ $\quad n\lambda = 2d_{\text{hkl}}\sin\theta$

$n_n = \frac{\overline{M_n}}{\overline{m}}$ $\quad n_w = \frac{\overline{M_w}}{\overline{m}}$

Mechanical Behaviour

$\sigma = \frac{F}{A_0}$ $\quad \epsilon = \frac{\Delta l}{l_0}$

$\sigma = E\epsilon$ $\quad \sigma_{\text{3-point}} = \frac{3FL}{2wh^2}$

$\sigma_T = \sigma(1+\epsilon)$ $\quad \epsilon_T = \ln(1+\epsilon)$

$\sigma_T = \frac{F}{A_i}$ $\quad \sigma_T = K\epsilon_T^n$

$E = 2G(1+\nu)$ $\quad \nu = -\frac{\epsilon_x}{\epsilon_z} = -\frac{\epsilon_y}{\epsilon_z}$

Magnetic Behaviour

$H = \frac{NI}{L}$ $\quad B_0 = \mu_0 H$

$M = \chi_m H$ $\quad B = \mu_0 H + \mu_0 M$

$B = (1+\chi_m)\mu_0 H$ $\quad \mu_B = \frac{e\hbar}{2m_e} = \beta$

$\beta = 9.27 \times 10^{-24} Am^2$

Electrical Behaviour

$\sigma = n|e|\mu_e + p|e|\mu_h$ $\quad \sigma = n|e|\mu_e$

$\sigma = p|e|\mu_h$

Electrochemistry

$E = E^\circ - \frac{RT}{nF}\ln Q$ $\quad I = \frac{nC}{t}$

$E_{\text{at } 25\,°\text{C}} = E^\circ - \frac{0.0592}{n}\ln Q$

$w = nFE^\circ$

Thermodynamics

$PV = nRT$ $\quad \Delta U = q + w$

$\Delta U = q - P_{\text{ext}}\Delta V$ $\quad H \equiv U + PV$

$G \equiv H - TS$ $\quad \Delta S = \frac{q_{\text{rev}}}{T}$

constant T: $\Delta G = \Delta H - T\Delta S$

$q = mc\Delta T$ $\quad q = nC_P\Delta T$

For $aA + bB \rightarrow cC + dD$, $Q = \frac{a_C^c a_D^d}{a_A^a a_B^b}$

$\Delta_r G = \Delta G^\circ + RT\ln Q$

$\Delta_r H^\circ = (\Sigma v_i \Delta_{f,i} H^\circ)_{\text{prod.}} - (\Sigma v_i \Delta_{f,i} H^\circ)_{\text{react.}}$

$\Delta_r S^\circ = (\Sigma v_i \Delta_{f,i} S^\circ)_{\text{prod.}} - (\Sigma v_i \Delta_{f,i} S^\circ)_{\text{react.}}$

$W_{\text{phase}} = \frac{\text{length of opp. side of lever}}{\text{total length of lever}}$

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

Specific heats and heat capacities

Substance	c ($\frac{J}{g\cdot K}$)	C_P ($\frac{J}{mol\cdot K}$)
Air(g)	1.0	-
$CO_2(g)$	0.843	37.1
$H_2(g)$	14.304	28.836
$H_2O(g)$	2.03	36.4
$H_2O(l)$	4.184	75.3
$H_2O(s)$	2.09	37.7
$NaCl$	0.853	50.5
$O_2(g)$	0.918	29.378

Temperatures and enthalpies of phase changes

Substance	M.P. ($°C$)	$\Delta_{fus}H$ $\frac{kJ}{mol}$	B.P. ($°C$)	$\Delta_{vap}H$ $\frac{kJ}{mol}$
Al	658	10.6	2467	284
Ca	851	9.33	1487	162
CH_4	-182	0.92	-164	8.18
H_2O	0	6.01	100	40.7
Fe	1530	14.9	2735	354

Standard formation enthalpy, standard entropy and standard formation Gibbs energy at 298.15 K

Species	$\Delta_f H^\circ$ ($\frac{kJ}{mol}$)	S° ($\frac{J}{mol\cdot K}$)	$\Delta_f G^\circ$ ($\frac{kJ}{mol}$)
C	0	5.74	0
$CH_4(g)$	-74.81	186.2	-50.75
$C_2H_2(g)$	-83.9	200.93	-
$C_3H_8(g)$	-103.8	269.9	-23.49
$CaC_2(s)$	-59.8	70.3	-
$CaO(s)$	-635	38.1	-
$CaF_2(s)$	-1225	68.87	-1162
$CaF_2(l)$	-1186	92.6	-
$Ca(OH)_2(s)$	-987.0	83.0	-
$CO_2(g)$	-393.5	213.6	-394.4
$Cu_2O(s)$	-168.6	93.1	-
$Cu_2O(l)$	-154.79	-	-
$Cu(s)$	-	33.2	-
$Fe(s)$	0	27.3	0
$Fe_2O_3(s)$	-824.2	87.4	-
$H_2(g)$	-	130.68	-
$H_2O(g)$	-241.8	188.7	-228.6
$H_2O(l)$	-285.8	69	-
$O_2(g)$	0	205.0	0

Miscellaneous enthalpies

Substance	Reaction	$\Delta H(\frac{kJ}{mol})$
F_2	$F_2 \rightarrow F(g)$	157
F	$F(g) \rightarrow F^-(g)$	-328
Ca	$Ca(g) \rightarrow Ca^{2+}(g)$	1734
NaCl	$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$	3.9

Scott Ramsay, December 2024

IUPAC Periodic Table of the Elements

Key:

atomic number **Symbol** name abridged standard atomic weight

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 **H** hydrogen 1.0080 ± 0.0002																	2 **He** helium 4.0026 ± 0.0001
3 **Li** lithium 6.94 ± 0.06	4 **Be** beryllium 9.0122 ± 0.0001											5 **B** boron 10.81 ± 0.02	6 **C** carbon 12.011 ± 0.002	7 **N** nitrogen 14.007 ± 0.001	8 **O** oxygen 15.999 ± 0.001	9 **F** fluorine 18.998 ± 0.001	10 **Ne** neon 20.180 ± 0.001
11 **Na** sodium 22.990 ± 0.001	12 **Mg** magnesium 24.305 ± 0.002											13 **Al** aluminium 26.982 ± 0.001	14 **Si** silicon 28.085 ± 0.001	15 **P** phosphorus 30.974 ± 0.001	16 **S** sulfur 32.06 ± 0.02	17 **Cl** chlorine 35.45 ± 0.01	18 **Ar** argon 39.95 ± 0.16
19 **K** potassium 39.098 ± 0.001	20 **Ca** calcium 40.078 ± 0.004	21 **Sc** scandium 44.956 ± 0.001	22 **Ti** titanium 47.867 ± 0.001	23 **V** vanadium 50.942 ± 0.001	24 **Cr** chromium 51.996 ± 0.001	25 **Mn** manganese 54.938 ± 0.001	26 **Fe** iron 55.845 ± 0.002	27 **Co** cobalt 58.933 ± 0.001	28 **Ni** nickel 58.693 ± 0.001	29 **Cu** copper 63.546 ± 0.003	30 **Zn** zinc 65.38 ± 0.02	31 **Ga** gallium 69.723 ± 0.001	32 **Ge** germanium 72.630 ± 0.008	33 **As** arsenic 74.922 ± 0.001	34 **Se** selenium 78.971 ± 0.008	35 **Br** bromine 79.904 ± 0.003	36 **Kr** krypton 83.798 ± 0.002
37 **Rb** rubidium 85.468 ± 0.001	38 **Sr** strontium 87.62 ± 0.01	39 **Y** yttrium 88.906 ± 0.001	40 **Zr** zirconium 91.224 ± 0.002	41 **Nb** niobium 92.906 ± 0.001	42 **Mo** molybdenum 95.95 ± 0.01	43 **Tc** technetium [97]	44 **Ru** ruthenium 101.07 ± 0.02	45 **Rh** rhodium 102.91 ± 0.01	46 **Pd** palladium 106.42 ± 0.01	47 **Ag** silver 107.87 ± 0.01	48 **Cd** cadmium 112.41 ± 0.01	49 **In** indium 114.82 ± 0.01	50 **Sn** tin 118.71 ± 0.01	51 **Sb** antimony 121.76 ± 0.01	52 **Te** tellurium 127.60 ± 0.03	53 **I** iodine 126.90 ± 0.01	54 **Xe** xenon 131.29 ± 0.01
55 **Cs** caesium 132.91 ± 0.01	56 **Ba** barium 137.33 ± 0.01	57-71 lanthanoids	72 **Hf** hafnium 178.49 ± 0.01	73 **Ta** tantalum 180.95 ± 0.01	74 **W** tungsten 183.84 ± 0.01	75 **Re** rhenium 186.21 ± 0.01	76 **Os** osmium 190.23 ± 0.03	77 **Ir** iridium 192.22 ± 0.01	78 **Pt** platinum 195.08 ± 0.02	79 **Au** gold 196.97 ± 0.01	80 **Hg** mercury 200.59 ± 0.01	81 **Tl** thallium 204.38 ± 0.01	82 **Pb** lead 207.2 ± 1.1	83 **Bi** bismuth 208.98 ± 0.01	84 **Po** polonium [209]	85 **At** astatine [210]	86 **Rn** radon [222]
87 **Fr** francium [223]	88 **Ra** radium [226]	89-103 actinoids	104 **Rf** rutherfordium [267]	105 **Db** dubnium [268]	106 **Sg** seaborgium [269]	107 **Bh** bohrium [270]	108 **Hs** hassium [269]	109 **Mt** meitnerium [277]	110 **Ds** darmstadtium [281]	111 **Rg** roentgenium [282]	112 **Cn** copernicium [285]	113 **Nh** nihonium [286]	114 **Fl** flerovium [290]	115 **Mc** moscovium [290]	116 **Lv** livermorium [293]	117 **Ts** tennessine [294]	118 **Og** oganesson [294]

57 **La** lanthanum 138.91 ± 0.01	58 **Ce** cerium 140.12 ± 0.01	59 **Pr** praseodymium 140.91 ± 0.01	60 **Nd** neodymium 144.24 ± 0.01	61 **Pm** promethium [145]	62 **Sm** samarium 150.36 ± 0.02	63 **Eu** europium 151.96 ± 0.01	64 **Gd** gadolinium 157.25 ± 0.03	65 **Tb** terbium 158.93 ± 0.01	66 **Dy** dysprosium 162.50 ± 0.01	67 **Ho** holmium 164.93 ± 0.01	68 **Er** erbium 167.26 ± 0.01	69 **Tm** thulium 168.93 ± 0.01	70 **Yb** ytterbium 173.05 ± 0.02	71 **Lu** lutetium 174.97 ± 0.01
89 **Ac** actinium [227]	90 **Th** thorium 232.04 ± 0.01	91 **Pa** protactinium 231.04 ± 0.01	92 **U** uranium 238.03 ± 0.01	93 **Np** neptunium [237]	94 **Pu** plutonium [244]	95 **Am** americium [243]	96 **Cm** curium [247]	97 **Bk** berkelium [247]	98 **Cf** californium [251]	99 **Es** einsteinium [252]	100 **Fm** fermium [257]	101 **Md** mendelevium [258]	102 **No** nobelium [259]	103 **Lr** lawrencium [262]

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For notes and updates to this table, see www.iupac.org. This version is dated 4 May 2022.

6.3 Matter-Energy Interactions

Photo Wavelength-Frequency The wavelength of a photon is inversely proportional to its frequency. The relationship is given by:

$$c = f\lambda \tag{38}$$

Energy of a Photon The energy of a photon is given by:

$$E = hf = \frac{hc}{\lambda} \tag{39}$$

Visible Light Visible light is the range of wavelengths that the human eye can see. It is between 400 nm and 700 nm (3eV to 2eV).

Bohr's Model Bohr's model is a model of the atom that describes the electron as a particle in a circular orbit around the nucleus. It discribes electrons in well-defined qunatized orbits. Thus, electrion promotes and demotes between orbitals, creating discrete spectra.

Lmitation of Bohr's Model Bohrs model cannot captures the energy levels and orbitals of atoms with more than one electron. It also cannot explain the fine structure of the spectra.

Wave-Mechanical Model The wave-mechanical model describes the electron as a wave. It describes the electron as a wavefunction, ψ, that describes the probability of finding the electron at a certain position.

Quantum Numbers The wave-mechanical model uses quantum numbers to describe the electron. The quantum numbers are:

1. **Principal Quantum Number** $n = 1, 2, 3, \ldots$ - Describes the energy level of the electron (size of the orbital).
   (note) n is sometimes given by $n = K, L, M, \ldots$
2. **Angular Momentum Quantum Number** $l = 0, 1, 2, \ldots, n-1$ - Describes the shape of the orbital. (note) Those are the s, p, d, f orbitals.
   (a) $l = 0$ **or** s Spherical
   (b) $l = 1$ **or** p Dumbbell
   (c) $l = 2$ **or** d Four-leaf clover
   (d) $l = 3$ **or** f Complex
3. **Magnetic Quantum Number** $m_l = -l, -l+1, \ldots, 0, \ldots, l-1, l$ - Describes the orientation of the orbital.
4. **Spin Quantum Number** $m_s = \pm\frac{1}{2}$ - Describes the spin of the electron.

Relative Energy Levels The energy levels of the orbitals are given by:

$$E = -\frac{Z^2}{n^2}\mathrm{Ry} \tag{40}$$

Electron Configuration The electron configuration is the distribution of electrons in the orbitals. It is given by:

$$\text{Element} = [n]l^m \tag{41}$$

(Example) The electron configuration of Carbon is $1s^2 2s^2 2p^2$. That for iron is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$.

Stable Octet The $ns^2 np^6$ is a stable configuration that forms the basis for the primary bonds. Atoms tend to gain, lose or share electrons to achieve this configuration. As we know, if we share electrons, we form covalent bonds; if we lose or gain electrons, we form ionic bonds.

Half filled and Fully Filled Orbitals Half filled and fully filled orbitals are more stable than partially filled orbitals. Thus at d^5 and d^{10}, the d orbitals are more stable and it tends to lend electron from the s orbital.
(Example) Chromium is $[Ar]3d^5 4s^1$ and Copper is $[Ar]3d^{10} 4s^1$.

Pauli Exclusion Principle The Pauli Exclusion Principle states that no two electrons can have the same set of quantum numbers.

Tightly Packed Atoms When atoms are packed, due to the pauli exclusion principle, it creates a bend of energy levels of the same orbital. In ground state, the electrons will fill the lower energy levels first.

6.4 Band Theory

Conductivity At room temperature, the thermal promotion within the bend makse it possible for conduction in conductors.

Overlaping Energy Level In some atoms, the bend of energy level gets larger and overlap with the energy level of the next orbital.

Conductive Band and Valence Band The conductive band is the band of energy levels that are above the valence band. The valence band is the band of energy levels that are filled with electrons. There is a band gap between the two bands, the size of the band gap determines the conductivity of the material.

Conductors Conductors have a no band gap. The valence band and conductive band overlap. Thus, electrons can easily move between the two bands.

Insulators Insulators have a large band gap. The valence band and conductive band are far apart. Thus, electrons cannot easily move between the two bands.

Semiconductors Semiconductors have a small/moderate band gap. The valence band and conductive band are close together. Thus, electrons can move between the two bands with the addition of energy. **For This Coruse, we take the band gap for semiconductors to be ≤ 4 eV.**

Optically transparency A material would be optically transparent if the band gap is larger than the energy of the visible light (3 eV).

6.5 Silicon

Intrinsic Silicon Intrinsic silicon is pure silicon. When electron is promoted to the conduction band, it leaves a hole in the valence band. The hole can move through the lattice as a postive charge. The electron can move through the lattice as a negative charge. The electron-hole pair is called an exciton. For intrinsic silicon, the number of holes is equal to the number of electrons. Also, the charge carrier contcentration is given by:

$$\frac{n = p}{a^3} \tag{42}$$

For silicon, at room temperature, the charge carrier concentration is 10^{16} m^{-3}.

Doping Doping is the addition of impurities to a semiconductor. They are point defects in the lattice. Doping is used to increase the conductivity of the semiconductor. There are two types of doping:

1. **N-Type Doping** N-type doping is the addition of impurities that increase the number of electrons. The extra electron is in the higher end of the band gap. The impurities are called donor impurities. The donor impurities are typically group 15 elements. The donor impurities are negatively charged.
2. **P-Type Doping** P-type doping is the addition of impurities that increase the number of holes. The impurities are called acceptor impurities. The acceptor impurities are typically group 13 elements. The acceptor impurities are positively charge the the hole is on the higher end of the valence band and to be promoted to the lower end of the band gap.

7 Thermaldynamics

"Free Time, Free Money, Free Energy?"

Thermaldynamics Thermaldynamics is the study of heat and work. It is the study of the relationship between heat, work, and energy.

7.1 System, Surroundings, Universe and Boundary

System The system is the part of the universe that we are interested in. It is the part of the universe that we are studying.

Surroundings The surroundings are the part of the universe that is not the system. It is the part of the universe that interacts with the system.

Universe The universe is the system and the surroundings. It is the entire system that we are studying.

Boundary The boundary is the interface between the system and the surroundings. It is the interface that allows the system and the surroundings to interact.

Open System An open system is a system that can exchange both matter and energy with the surroundings.

Closed System A closed system is a system that can exchange energy but not matter with the surroundings.

Isolated System An isolated system is a system that cannot exchange matter or energy with the surroundings.

7.2 Thermaldynamics Variables

State Function A state function is a function that depends only on the state of the system. It does not depend on the path taken to reach the state.
(Example) Any energy is a state function: enthalpy, internal energy, Gibbs free energy, Helmholtz free energy, temperature, pressure, volume, entropy, etc.

Path Function (Process Variable) A path function is a function that depends on the path taken to reach the state. Examples of path functions include heat and work. (Example) Heat and work are path functions.

Heat Heat is the transfer of energy between a system and its surroundings due to a temperature difference. It is denoted by q.

Work Work is the transfer of energy between a system and its surroundings due to a force acting through a distance. It is denoted by w.

8 First Law of Thermaldynamics

Internal Energy The internal energy of a system is the sum of the kinetic and potential energies of the particles in the system. It is denoted by U.

First Law of Thermaldynamics The first law of thermaldynamics is the law of conservation of energy. It states that the change in internal energy of a system is equal to the heat added to the system plus the work done on the system. It is given by:

$$\Delta U = Q + W + W_{\text{other}} \tag{43}$$

, where Q is the heat added to the system, W is the work done on the system, and W_{other} are all other kinds of work done on the system. W is given by:

$$W = -P\Delta V \tag{44}$$

Thus, the energy in the universe is conserved, and the energy of a isolated system is constant.

Infinitesimal Change For an infinitesimal change in the system, the first law of thermaldynamics is given by:

$$dU = \delta Q + \delta W + \delta W_{\text{other}} \tag{45}$$

Sign Convention The sign convention for heat and work is as follows:

- **Heat** Heat added to the system is positive. Heat removed from the system is negative.
- **Work** Work done on the system is positive. Work done by the system is negative.

8.1 Second Law of Thermaldynamics

Second Law of Thermaldynamics The entropy of an isolated system always increases in the course of a spontaneous process. It is given by:

$$\Delta S \geq 0 \tag{46}$$