Lecture 1, Jan 10, 2022

- Materials science:
    1. Understanding the structure and how it relates the properties of the materials and how to process the materials to have these properties
    2. Based on this understanding, select the right materials and recognize design opportunities
- Example: Hip implants: with age or illnesses joints with large loads such as the hip deteriorate
    - What material should we make the implant out of?
    - A lot of load, lots of loading/unloading cycles, needs to be biocompatible (the body can't reject it), can't be too heavy
    - Modern hip implants are primarily metallic (e.g. titanium) and very complex
    - Coatings attach the implant to the bone and allow the bone to grow around it
    - A ball joint allows movement
- Materials can be engineered to have properties we want; e.g. rapid cooling steel results in increasing hardness
- Types of materials:
    - Metals:
        * Strong and ductile
        * Lots of free electrons make it thermally and electrically conductive, and also opaque and reflective since EM waves are cancelled out by electrons moving in the metal
    - Polymers:
        * Covalent chains
        * Soft, light and low strength
        * Insulators
        * Translucent/transparent
    - Ceramics:
        * Ionic bonding (compounds of metallic and non-metallic elements)
        * No free electrons, so good insulators
        * Brittle
- The material selection process: Application →Properties →Candidate Materials →Required Processing
- Adding impurities can change material properties; e.g. adding nickel to copper increases resistivity; deforming it also increases resistivity
    - Sometimes we add impurities to copper intentionally to make cables more flexible – we need to balance aspects

Lecture 2, Jan 13, 2022

Wave-Particle Duality and The Bohr Model

- Classically particles and waves are distinct, but in the 20th century we found matter can behave like waves and waves can behave like particles
    - The photoelectric effect shows that light (which was known to be electromagnetic waves) behaving like particles through the photoelectric effect, described by Planck and Einstein
    - Exciting hydrogen atoms and other gases only emits specific discrete spectral lines
    - Shooting electrons through a diffraction grating (Ni crystals) show diffraction behaviour which is wavelike
- De Broglie relation: $p = \dfrac{h}{\lambda} = \hbar k$ proposes that particles can exhibit wavelike behaviour, relating classical momentum, which is a property of particles, to a wavelength (from $E^2 = p^2c^2 + m^2c^4$ and $E = h\nu = \dfrac{hc}{\lambda}$)
- Rutherford-Bohr model: negatively charged electron orbiting a positively charged electron
    - If we equate the centripetal force on the electron $\dfrac{mv^2}{r}$ to the Coulomb force $\dfrac{e^2}{4\pi\varepsilon_0 r^2}$ we get

    $v^2 = \dfrac{e^2}{4\pi\varepsilon_0 mr}$
  - Adding energy, i.e. adding velocity, will decrease the radius; however we get a continuous relation between r and v while in reality this is not true
  - Bohr added interference through $n\lambda = I_{orbit} = 2\pi r$ with n as a quantisation constant, because the radius has to be an integer multiple of the wavelength for the waves to constructively interfere
  - Invoking de Broglie's relation $mv = \dfrac{\hbar}{\lambda}$ and equating λ we get $v = \dfrac{hn}{2\pi mr}$ and angular velocity $L = mvr = n\hbar$, i.e. angular momentum is quantized in units of $\hbar$
  - Equating the expressions for v and solving for r, the allowed radii are $r_n = \dfrac{\hbar^2\varepsilon_0 n^2}{\pi me^2} = a_{Bohr}n^2$ where n is a positive integer, and the *Bohr radius* is the smallest radius, about 5.3×10^{-11} m
  - Solving for the total energy (sum of kinetic and Coulomb energy) gives energy inversely proportional to n^2 (and negative because the larger the n the less energy it has)
  - Using this we can write an expression for the energy emitted as the electron jumps between states, and we get the Rydberg equation back!
- Even though the Bohr model explains the hydrogen spectrum, it fails:
  - Assumes circular electron orbits, which is fundamentally incorrect, so it only works for hydrogen and fails miserably for helium
  - It treats electrons as things with definite radius and momentum, which is in violation of the uncertainty principle
  - Does explain where the emission lines are, but not why some are brighter than the others

Lecture 3, Jan 14, 2022

Quantum Waves

- Classical travelling waves $\Psi = Ae^{i(kx-\omega t)})$ with amplitude A, wavelength $\lambda = \dfrac{2\pi}{k}$, $\omega = 2\pi\nu$; velocity of the wave is $c = \dfrac{\omega}{k}$
- Such a wave conveys no position information since it has constant amplitude and wavelength everywhere
- The Born interpretation: the square of the wavefunction at any point is proportional to the probability of finding the particle in space at that point (i.e. Ψ^2 is the probability density)
- This interpretation leads to some restrictions on Ψ:
  - It must be continuous
  - It must not be multi-valued
  - It must be normalizable (implies finite, can't be zero or constant)
- Time evolution of wavefunctions is governed by the Schrödinger equation: $\hat{E}\Psi = i\hbar\dfrac{\partial}{\partial t}\Psi$
- Wave packets are fuzzy in both temporal and spacial extent

Lecture 4, Jan 17, 2022

Time-Independent Schrödinger's Equation

- Assume $\Psi(x,t) = \phi(t)\psi(x)$, giving $i\hbar\dfrac{1}{\phi}\dfrac{\mathrm{d}\phi}{\mathrm{d}t} = -\dfrac{\hbar^2}{2m\psi}\dfrac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V$
  - Since the two sides depend on different variables we argue that both need to be equal to a constant A
  - Therefore $i\dfrac{A}{\hbar}\phi = \dfrac{\mathrm{d}\phi}{\mathrm{d}t}$ and $A = -\dfrac{\hbar^2}{2m\psi}\dfrac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V$
- The first equation has a general solution of $\phi = Ce^{-i\frac{A}{\hbar}t}$ where C is a constant
  - We conclude that A must have units of energy, so we let $A = E$
  - The oscillation frequency is going to depend on the energy; more energy means the wavefunction

oscillates faster in time

- Substituting $A = E$ into the second equation and multiplying by ψ we get $-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V\psi = E\psi$, which is known as the time-independent Schrödinger equation

Lecture 5, Jan 20, 2022

Particle in a Box (Infinite Square Well)

- Particle of mass m in a 1-dimensional box box length L
- In side the box potential is 0, outside the box potential is infinite
- Inside the box the TISE reduces to $-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = E\psi$ since there is zero potential
- Solution of the form $\psi = A\sin(kx) + B\cos(kx) \implies \frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -k^2\psi$, and $E = \frac{\hbar^2 k^2}{2m}$ (the energy of a state depends on k)
- However since the potential is infinite outside the well we impose boundary conditions $|\psi|^2 = 0 \implies \psi = 0$ for $x \leq 0$ or $x \geq L$, and the normalization condition
    - At $x = 0$, the sine term is zero, so we conclude the cosine term should always be zero (i.e. $\psi = A\sin(kx)$ for all x)
    - At $x = L$, $\psi = 0$ means $A\sin(kL) = 0 \implies \sin(kL) = 0$ so $kL = n\pi$ (note $n \neq 0$ because that would make the wavefunction always zero), so now energies are quantized!
        - i.e. $k = \frac{n\pi}{L}$ where $n = 1, 2, 3, \cdots$
- $E_n = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 n^2 \pi^2}{2mL^2} = \frac{h^2}{8mL^2}n^2$ (note we switched from $\hbar$ to h)
- We also need to normalize, so $\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$
    - $1 = \int_0^L A^2 \sin^2\left(\frac{n\pi x}{L}\right)\,\mathrm{d}x \implies A = \sqrt{\frac{2}{L}}$
- These wavefunctions are standing waves; n is the quantum number; ψ_n has $n-1$ nodes
- Note the ground state doesn't have zero energy (zero point energy ZPE)
- Kinetic energy is proportional to the curvature of the wavefunction; more kinetic energy leads to higher curvature and faster oscillating wavefunctions
- A smaller box increases E and makes the wavefunction oscillate faster

Lecture 6, Jan 24, 2022

Hydrogen Atom

- In our infinite well there is only 1 degree of freedom so we only have E_n; in higher dimensions, more degrees of freedom create more quantum numbers, so we have $E_{n,m}$, etc
- In 3D the TISE becomes $-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi(x,y,z) + V(x,y,z)\psi(x,y,z) = -\frac{\hbar^2}{2m}\nabla^2\psi + V = E\psi$
    - ∇^2 is the Laplacian
    - $-\frac{\hbar^2}{2m}\nabla^2 + V$ is the total energy operator or *Hamiltonian* $\hat{H}$
- In a hydrogen atom electrons have Coulomb potential $V(r) = -\frac{e^2}{4\pi\varepsilon_0 r}$
- Use spherical coordinates (r, θ, ϕ) (θ is angle from z axis, ϕ is rotation in the x-y plane)
    - We also need to transform the Laplacian $\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\left(\frac{\partial^2}{\partial \theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \csc^2\theta\frac{\partial^2}{\partial\phi^2}\right)$
- Again use separation of variables; assume wavefunction is a product of $\phi(\boldsymbol{r}) = \phi(r,\theta,\phi) = R(r)Y(\theta,\phi)$

    - This allows us to take advantage of radial symmetry for the hydrogen atom since Coulomb potential only depends on r
    - This gives us two equations; do this a second time, $Y(\theta, \phi) = \Theta(\theta)\Phi(\phi)$
    - Azimuthal equation: $\frac{1}{\Phi}\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2} + B = 0$
        - This is easy to solve with trial solution $Ke^{im\phi}$ where $B = -m^2$
    - Solving for the energy eigenvalues gives the Bohr model
- Takeaway: the wavefunction is defined by 3 quantum numbers n, l, m for the 3 spacial degrees of freedom, and one m_s quantum number for the spin of the electron
    - n – Principal quantum number: Gives the Bohr model solution, for a spherical model it is the solution
        - $n = 1, 2, 3, \cdots$
        - Designation: K, L, M, N shells corresponding to $n = 1, 2, 3, \cdots$
        - Distance from the nucleus
    - l – (Subsidiary) Orbital angular momentum quantum number
        - $l = 0, 1, 2, \cdots, n-1$
        - $s \to 0, p \to 1, d \to 2, f \to 3$
        - Distribution/shape of electron density
    - m_l – Magnetic quantum number
        - $m_l = -l, -l+1, \cdots, 0, \cdots, l-1, l$
        - This and l describe orientation
    - m_s – Spin quantum number (quantized either up or down)
        - $m_s = \pm\frac{1}{2}$ for each m_t

Lecture 7, Jan 27, 2022

Electron Configurations

- Recall the restrictions on the atomic quantum numbers: $n > 0, 0 \leq l \leq n-1, |m_t| \leq l$
    - n designated $K, L, M, N, \cdots$, determines the "shell", i.e. average distance from the nucleus; within the principal energy state there are energy sub-states
    - l designated s, p, d, f, orbitals within the shell (angle from the z axis)
    - m_l, designated $1, 3, 5, 7, \cdots$ (number of states), (motion around the z axis)
    - m_s, $\pm\frac{1}{2}$, spin up or down
- As we go out we have more capacity for electrons ($n = 1$ has 2 spots, $n = 2$ has 8 spots, $n = 3$ has 18, etc), which matches the periodic table
- Each energy sub-level relates to a different orbital shape
    - s orbitals ($l = 0$) are all spherical, regardless of n
    - p orbitals are dumbbell shaped and oriented along the 3 spacial axes (p_x, p_y, p_z)
    - d orbitals have 5 orbitals, 4 with the same clover shape in different planes, and the 5th has its own shape
- Electrons have discrete energy states and tend to occupy the lowest energy state available
    - Energy increases as n increases
    - Within the principal quantum numbers the higher numbers of l have more energy
    - However the $3d$ shell has a higher energy than the $4s$ shell
- When a shell is completely filled (with its sub-shells) it is stable; most elements don't have a stable outer shell, the stable ones are the noble gases with the outer shells completely filled
- Electron configurations in the form e.g. $1s^2$ where the 1 indicates principal quantum number, s indicates shell (l) and the 2 is the number of electrons in that shell (spin up + spin down)

Lecture 8, Jan 28, 2022

Atomic Bonding

- Atoms try to achieve the most stable (lowest energy) configuration by achieving closed shells
- Two types of bonds: primary (ionic, covalent and metallic) and secondary (dipole interactions); we will focus on the former
  - Primary bonds have a high separation energy
  - Ionic: electron exchange, covalent: electron sharing, metallic: delocalized sharing
    - Delocalized electrons are not bound; they have enough energy that they're not stuck in a potential well
- Most elements have unstable electron configurations; e.g. Lithium $1s^2 2s^1$, while elements such as Neon $1s^2 2s^2 2p^6$ have fully filled outer shells and are stable
  - Recall: s orbital has 2 electrons, p orbital has 6, d has 10, f has 14, which comes from the constraints on the quantum numbers and spin up/down electrons
  - *Electropositive* elements readily give up electrons to become positive ions; *electronegative* elements readily acquire electrons to become negative ions
- Electronegativity is quantified using the Pauling scale, ranging from 0.7 (francium) to 4.0 (fluorine)
- Ionic bond: local and discrete (an absolute amount of charge is moved), between metal (gives electron to become +) and nonmetal (takes electron to become -)
  - Happens when two elements differ greatly in electronegativity
  - Electrons are transferred from one atom to another, creating a positively charged and negatively charged atom, and a Coulomb attraction force
  - Example: $\mathrm{NaCl}, \mathrm{MgO}$

Lecture 9, Jan 31, 2022

Atomic Bonding Continued

- Bonding depends on a balance of attractive and repulsive terms: $E_N = E_A + E_R = -\dfrac{A}{r} + \dfrac{B}{r^n}$
  - First term is the Coulomb force, second is the core shell repulsion
  - e.g. In ionic bonding $A = q_1 q_2$ (Coulomb potential)
  - At infinity there is zero potential; as we move closer the energy goes more negative as there is lower energy due to the attractive force
  - When we get too close the potential energy shoots up again as the two atoms begin to repel, due to the electrons getting too close and the electron densities start overlapping
    - The atoms are virtually incompressible so as we start to push them into each other the energy shoots up
  - The combined Coulomb potential and the core shell repulsion leads to a minimum in the energy curve where the atoms will settle
- For elements with similar electronegativity, electrons are shared to make covalent bonds
  - e.g. $\mathrm{CH_4}$ – C has 4 valence electrons, needs 4 more for the outer shell; H has 1 valence electron and needs 1 more; electronegativities of the two elements are comparable
- If electrons can be readily removed from the atoms, they become delocalized in an electron cloud and we get metallic bonding
- Ionic and covalent bonds can be mixed; in this case the *percentage ionic character* can be calculated as $1 - e^{-\frac{\Delta X_{AB}^2}{4}}$ where ΔX_{AB} is the difference in electronegativity between the two elements
  - e.g. MgO: $1 - e^{-\frac{(3.5-1.2)^2}{4}} = 73.4\%$ ionic
- Characters of bonds:
  - Ionic bonds: Large bond energy, nondirectional
  - Covalent bonds: Variable bond energy, directional
    - The other bonds are nondirectional because the s subshell is symmetric; if we have covalent bonding we're likely to have p subshells involved which can be directional

    - Also in ionic bonding the outer shell is completely filled
  - Metallic: Variable bond energy, nondirectional
- The shape of the potential curve for bonding gives the quantum harmonic oscillator when we're looking at a small section near the equilibrium, so we get energy levels that are evenly spaced (as opposed to proportional to n^2 for the infinite well)
- Bond properties:
  - Bond length r between two atoms
  - Bond energy E_0 (depth of the equilibrium energy from zero)
    - Energy is $-E_0$ at unstretched bond length r_0
  - Melting temperature T_m
    - Larger E_0 (deeper potential curve) means more work is required to rip the bonds apart, therefore higher melting temperature
  - Coefficient of thermal expansion α: $\dfrac{\Delta L}{L_0} = \alpha(T_2 - T_1)$
    - Deeper potential curve gives a smaller α since more energy is required to stretch or compress the atoms together
    - For small energy the energy curve is symmetric so heating it does not have much effect, but as we introduce more energy the curve goes to the right more than it does to the left, so there is a net elongation
- The local parabolic approximation also enables Hooke's law

Lecture 10, Feb 3, 2022

Crystalline Structures

- Often structures have regular patterns and ordered packing, since this allows the atoms to get closer on average and have lower energy
- Crystalline structures are typical of metals, many ceramics, and some polymers
- Non-crystalline (amorphous) materials have no regular periodic pattern; this occurs when the material has complex structures or undergo rapid cooling so it doesn't have time to settle into patterns
- Metals tend to be densely packed since only one element is present so all radii are identical, bonding is nondirectional, so simple crystalline structures are formed
- Atomic packing factor (APF) is defined as the ratio of the volume of the atoms in a unit cell to the volume of the unit cell (assuming atoms are hard spheres)
- Types of crystalline structures for metals:
  - Simple cubic: close-packed directions are cube edges

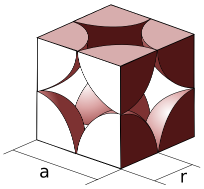

Figure 1: Simple cubic

    -
    - Coordination number is 6; 1 atom per cell (8 corners of eighth atoms)
    - APF is $\dfrac{\frac{4}{3}\pi(0.5a)^3}{a^3} = 0.52$
    - Packing density is rather low, so this structure is rare (found in Po)
  - Body centered cubic (BCC): Atoms touch along the cube diagonals (we still have a cube, but there's one big atom in the middle)

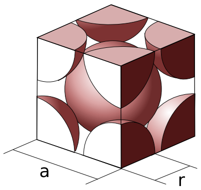

Figure 2: Body centered cubic

    -
    - Coordination number is 8 (8 other atoms touch each one); 2 atoms per unit cell
    - APF is $\frac{2 \cdot \frac{4}{3}\pi \left(\frac{\sqrt{3}}{4}a\right)^3}{a^3} = 0.68$
    - Packing density is higher and is more commonly found, e.g. $\mathrm{Cr}, \mathrm{W}, \mathrm{Fe}(\alpha)$
- Face centered cubic (FCC): Atoms touch along the atomic diagonals

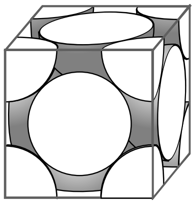

Figure 3: Face centered cubic

    -
    - Coordination number is 12, 4 atoms per unit cell (6 faces of half atoms, 8 corners of eighth atoms)
    - APF is $\frac{4 \cdot \frac{4}{3}\pi \left(\frac{\sqrt{2}}{4}a\right)^3}{a^3} = 0.74$
    - This is the theoretically maximum achievable APF
    - We can visualize the face-centered packing as hexagonal packing in layers

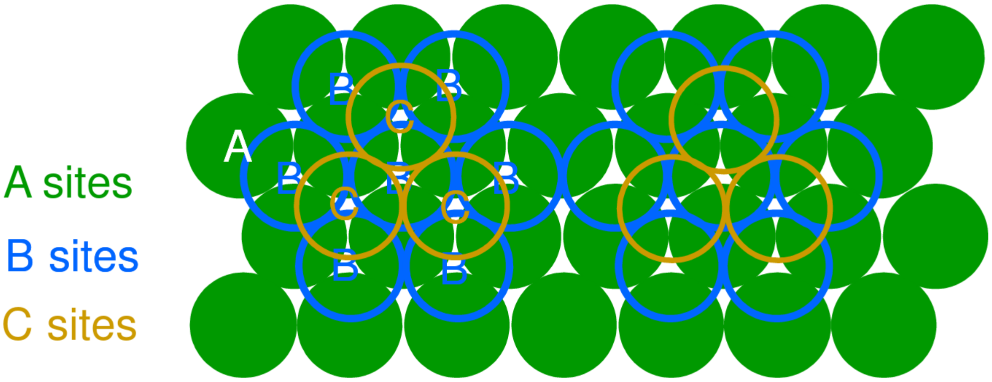

Figure 4: Hexagonal layers

    -
    - The diagonal of the unit cube is a plane of atoms
    -

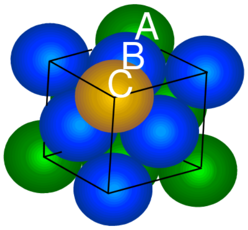

Figure 5: FCC hex unit cell

    - * (ABC) packing sequence
  - Hexagonal close packing (HCP): (AB) packing sequence

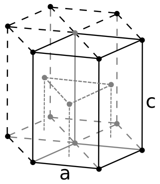

Figure 6: Hexagonal close packing

    - *
    - * Unlike FCC there are only 2 types of layers; the third later is directly aligned with the first
    - * Same coordination number of 12, 6 atoms per unit cell, and same APF
    - * Found in materials such as Cd, Mg

Lecture 11, Feb 4, 2022

Density of Crystalline Structures

- We can estimate theoretical density from the type of crystalline structure
- $\rho = \dfrac{nA}{V_c N_A}$ where n is the number of atoms per unit cell, A is the atomic weight, V_c is the unit cell volume, and N_A is Avogadro's number (atoms per mole)
- Example: Chromium
  - Structure is BCC so $\rho = 7.18\mathrm{g/cm^3}$ theoretically
  - Actual density is $7.19\mathrm{g/cm^3}$
- In general metals are denser than ceramics which are denser than polymers
  - In metals atoms typically have higher mass and are packed closer together

Single and Polycrystal Materials

- Single crystal materials are used in some applications such as diamond for abrasives
- A perfect single crystal has the same structure and translational symmetry everywhere
- Most engineering materials however are polycrystals – made of "grains" of single crystals
- Polycrystals can be isotropic in some parts and anisotropic in other parts
  - Difference in cooling rate, e.g. removing heat along one axis, will cause the material to solidify differently in different directions and create anisotropic grains
- Single crystals are anisotropic (properties vary with direction); e.g. Young's modulus for BCC iron is 125GPa on the edges but 273GPa diagonally
- Polycrystals may or may not be isotropic depending on how the grains are oriented – if grains are oriented randomly we get an isotropic material, but if the grains are textured (i.e. elongated in a certain direction) we have an anisotropic material

  - We can also introduce texture during processing by pulling on the material to give the grains a preferential orientation

Polymorphism/Allotropy

- The same material can take on several crystalline structures, e.g. carbon can form diamond or graphite, titanium has α and β
- Iron crystallizes into different structures depending on the temperature

Crystallographic Directions

- Coordinates are multiples of a, b, c the dimensions of the unit cell
- Crystallographic directions are denoted by $[uvw]$ where these are all smallest integer values and an overbar is used to indicate a negative index
- We don't really know which axis is the x, y or z with respect to the real world, so we have families of directions
  - Example: $\langle 100\rangle$ is a family with 6 elements: $[100], [010], [001]$ and their negative versions; $\langle 111\rangle$ is a family with 8 elements
- In HCP, we use $[uvtw]$ instead, where uvt are in the same plane and 120° apart (since unit cells are hexagonal)
  - uvt is in the *basal plane*

Lecture 12, Feb 7, 2022

Linear Density

- Linear density is how many atoms we have per unit length of a direction vector
- Example: Al's linear density in the [110] direction is $\frac{2}{\sqrt{2}a} = 3.5\text{nm}^{-1}$

Crystallographic Planes

- To identify the plane we use the normal vector
- Miller indices: reciprocals of the 3 axial intercepts cleared of fractions and common multiples (use (hkl)):
  1. Read off intercepts of the plane with axes in terms of a, b, c
  2. Take reciprocals
  3. Reduce to smallest integer values
- Curly brackets $\{hkl\}$ denote a family of planes
  - e.g. $\{100\} = (100), (010), (001), (\bar{1}00), (0\bar{1}0), (00\bar{1})$
  - As with directions we can orient the axes however we like
- For hexagonal unit cells (HCP) the same process applies

Planar Packing

- Crystallographic planes let us calculate planar densities (atoms per planar unit cell)
- To measure the spacing between planes we can shoot x-rays at it and measure the diffraction
  - Use x-rays for their short wavelength since we can't resolve distances that are less than the wavelength
  - $2d\sin\theta_C = n\lambda \implies d = \frac{n\lambda}{2\sin\theta_C}$ to get constructive interference
  - We can adjust the incident angle θ_C until we get a peak of constructive interference, then use the formula to calculate d for the spacing between planes
  - With the planar spacing we can relate this to the atomic radius a and use the relationship to identify the specific type of packing

Solidification

- Liquid settles into a solid in 2 steps: nucleation (nuclei of solids form in the liquid randomly or around imperfections), and growth (the nuclei grow to form crystals, and the crystal grows until all the liquid's been consumed, forming grains)
- At the boundaries where the crystals join we have grain boundaries (polycrystalline material)
  - Often misoriented – small-angle grain boundaries are larger boundaries
  - Grain boundaries have lower density, which leads to high diffusivity (motion of atoms) and high chemical reactivity
- Grains can be equilaxed (same size in all directions) or columnar (elongated)
  - When heat is removed in a preferential direction columnar grains form

Lecture 13, Feb 10, 2022

Imperfections

- There is no such thing as a perfect crystal – imperfections always exist
  - Certain types of defects are at equilibrium
  - Vacancies (missing atoms) create imperfections
  - The concentration of such defects affect how the material behaves
- Types of imperfections:
  - Point defects: Vacancies (missing atoms); interstitial/substitutional atoms (atoms that are on the wrong site)
    - Interstitial atoms are extra atoms between atomic sites, distorting planes by pushing the atoms apart
    - Self-interstitial is an interstitial atom that's the same atom as the crystal
    - Vacancies also distort the plane structure as the atomic forces pull the surrounding atoms in
      - This is called a *strain* and has stored elastic energy
  - Line defects: Dislocations
  - Areal defects: Grain boundaries

Point Defects

- $\dfrac{N_v}{N} = e^{\frac{-Q_v}{kT}}$
  - N_v is the number of defects and N the number of defect sites
  - Q_v is the activation energy, k is the Boltzmann constant and T the temperature
  - Higher temperature allows atoms to overcome activation energy
  - Each lattice site is a potential vacancy site
- Activation energy can be measured through experiments using the defect concentration
- Vacancies cause "islands" to form on the surface
- When an impurity is added to a host there are 2 outcomes (this happens when the two substances don't naturally bond but are compatible):
  - Solid solution (random distribution fof point defects)
    - Substitutional solid (impurity in places where the host atoms were) or interstitial solid (impurity in between host atoms)
  - Solid solution plus particles of a second phase (usually for a larger amount of impurities when we go past the solubility)
    - The impurity atoms and host atoms form a second phase with often different structure and composition
- Conditions for substitutional solid solution: Hume-Rothery rules
  1. $\Delta r < 15\%$ (atomic radii similar) (empirical)
  2. Proximity in the periodic table (similar electronegativity)
  3. Same crystal structure for pure metals

4. Valency: Metal will have a greater tendency to dissolve a metal of higher valency than one of lower valency

- Quantifying composition: Weight percent $C_1 = \dfrac{m_1}{m_1 + m_2}$ or atomic percent $C_1 = \dfrac{n_{m1}}{n_{m1} + n_{m2}}$

Line Defects

- Dislocations are line defects
- Crystal planes slip when the material is placed under stress, e.g. zinc (HCP) under tensile elongation causes the diagonal planes to slip so the material can elongate (slip steps)
- Dislocations produce permanent (plastic) deformations
- Linear defects: 1D defects around which atoms are misaligned; 2 types:
  - Edge dislocation: Extra half-plane of atoms inserted into the structure
    - *Burgers vector b* perpendicular to the dislocation line
    - The extra plane of atoms squeezed in deforms the crystal and pushes planes apart to make room
  - Screw dislocation: Half-planes shear due to twisting
    - Burgers vector is in the direction of the shear
  - The two types of dislocations can be mixed
- Dislocations can be seen with an electron microscope as scattering changes due to the imperfections
- Edge dislocations can move along the Burgers vector by only breaking one bond at a time

Lecture 14, Feb 11, 2022

Dislocations Continued

- Close-packed planes and directions are preferred when dislocations propagate since the least work is required
- In FCC there are many close-packed planes/directions; in HCP there's only one close-packed plane (the basal plane); BCC is not close packed
- Stacking faults (planar defect): for FCC an error in the packing can happen, e.g. ABCABABC

Diffusion

- Diffusion: Mass transport by atomic motion
- Diffusion occurs in fluids this happens through Brownian motion and occurs in solids through atomic movement via vacancies or interstitials
- Inter-diffusion: In an alloy atoms migrate from regions of high concentration to regions of low concentration
  - This smoothes out the concentration profile
- Self-diffusion: Atoms also migrate in an elemental solid (solid of one material!)
- Diffusion mechanisms:
  - Vacancy diffusion:
    - There's always a finite concentration of vacancies
    - Atoms around a vacancy jump into the vacancy so the atoms or the vacancy moves around
    - The rate depends on the concentration of vacancies (cost to form vacancies) and the activation energy for the exchange (cost to do the exchange)
  - Interstitial diffusion:
    - Smaller atoms of the impurity diffuse between host atoms
    - Interstitial atoms jump between spaces
    - Spaces are typically not close-packed so there is ample space
    - The interstitial atoms are typically not bound to the actual crystal structure so the cost of moving is a lot lower, and interstitial diffusion happens a lot faster

Processing Using Diffusion

- Case hardening: Diffusing carbon atoms into the host iron atoms at the surface (e.g. a case hardened gear)
  - The carbon in the structure makes the iron (steel) harder
  - Carbon strains the bonds (stretches the lattice) to make the crystal harder as the surface is under tension
- Doping: Diffusing phosphorus and other impurities into silicon crystals to make semiconductors
  - Phosphorus is deposited on the surface using a mask pattern
  - The silicon is heated and the phosphorus diffuses into the silicon

Quantifying Diffusion

- To measure the rate of diffusion we use flux J, the mass (or moles of atoms) diffusing per unit area per unit time, in units of $\frac{\text{mol}}{\text{cm}^2\text{s}}$ or $\frac{\text{kg}}{\text{m}^2\text{s}}$
- Flux is measured empirically
  - Membrane of known surface area is made and a concentration gradient is imposed on the two sides
  - The speed of diffusion through this membrane is measured
  - $J = \frac{M}{At} = \frac{I}{A}\frac{\mathrm{d}M}{\mathrm{d}t}$ where M is the mass diffused, t is the time passed
- Steady state diffusion: When the rate of diffusion independent of time
  - Fick's first law of diffusion: $J = -D\frac{\mathrm{d}C}{\mathrm{d}x}$
    - The minus sign is because things diffuse from high concentration to low
  - The flux is proportional to the concentration gradient
  - If linear this is approximately $\frac{\Delta C}{\Delta x}$
- Example: Chemical protective clothing
  - e.g. Gloves are used to protect against methylene chloride; if Butyl rubber gloves (0.04cm) thick are used, what is the diffusive flux of methylene chloride through the gloves?
    - Surface concentrations $C_1 = 0.44\text{g/cm}^3, C_2 = 0.02\text{g/cm}^3$
    - Diffusion coefficient given
- Diffusion coefficient increases with increasing temperature as atoms have more energy
  - $D = D_0 e^{-\frac{Q_d}{RT}}$ where Q_d is the activation energy, R is the ideal gas constant (note temperature is in Kelvin)

Lecture 15, Feb 14, 2022

Non Steady State Diffusion

- Fick's Second law: $\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$
  - Boundary conditions: at $t = 0$, $C = C_0$ for $x \leq x \leq \infty$ (assume bar has preexisting concentration of copper)
  - At $t > 0$, $C = C_s$ for $x = 0$ (constant surface concentration), and $C = C_0$ for $x = \infty$
- Solution is $\frac{C(x,t) - C_0}{C_s - C_0} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$ where the error function $\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}}\int_0^z e^{-y^2}\,\mathrm{d}y$
  - With increasing time, the concentration profile flattens and the material moves deeper into the bar
  - The $\sqrt{Dt}$ is the characteristic length that the diffusing atom has moved in time t
- Example: An FCC Iron-Carbon alloy initially containing 0.20% carbon by weight is carburized at an elevated temperature and in an atmosphere that gives a constant surface carbon concentration of 1.0% by weight. After 49.5h the concentration of carbon is 0.35% by weight at a position 4.0mm below the surface. Determine the temperature at which the treatment was carried out.
  - Using the solution equation we can get $\operatorname{erf}(z) = 0.8125$
  - Go to the table to find the value of z using an interpolation, and then solve for $D = 2.6 \times 10^{-11}\ \text{m}^2/\text{s}$

  - Now we have D, we need D_0 and Q to find the temperature
- Diffusion is faster for:
  - Open crystal structures
  - Smaller diffusing atoms
  - Lower density materials

Phase Diagrams

- Given the composition of a material and the temperature, we can determine how many phases it forms, what the composition each phase is and what the amount of each phase is
- Solubility limit: Maximum concentration for which only a single phase solution exists (i.e. a homogeneous solution e.g. syrup)
- Phase diagrams have 2 axes: composition (x) and temperature (y)
  - The composition axis goes between no substance 1, all substance 2, to all substance 1, no substance 2 (wt%)
  - The diagram is divided into two big regions; on the left we have a homogeneous solution (below the solubility limit); on the right we have the dual phase region where both solid and solution exist
- Components: Elements or compounds which are present in the alloy (e.g. Al or Cu)
- Phases: Physically and chemically distinct material regions that form (e.g. α, β)
  - e.g. aluminum-copper alloy under a microscope has β phases (lighter) and α phases (darker)
- State variables: temperature and composition
  - Higher temperature leads to greater solubility and moves us from a dual phase region to a single phase region
  - Changing the composition also changes between phase regions (isothermal changes)
  - Pressure is also a state variable but not in this course
- Solubility is affected by Hume-Rothery rules
  - Not meeting the criteria gives typically limited solubility
- e.g. nickel and copper are soluble in one another for all proportions
  - In the phase diagram there's a thin transition area where both liquid and solid solution exist, as the crystals have to from from the solid first
- A binary isomorphous system (e.g. copper and nickel) has only 2 components, and complete solubility of one component in another
  - i.e. it is possible to have the same phase for 0 to 100% composition
  - The *liquidus* divides the single phase liquid region and the mixed region; the *solidus* divides the single phase solid region and the mixed region

Lecture 16, Feb 17, 2022

Determining Phase Composition

- Given T and C_0 we can determine the composition of the phases present
- When there are multiple phases present, draw a horizontal tie line (isotherm), and the compositions are the compositions at the liquidus and solidus
- The tie line can be thought of as a lever: $M_\alpha S = M_L R$
- Compare the relative lengths of the isoterms

Cored and Equilibrium Structures

- In a equilibrium phase diagram we give infinite time to allow the material to reach equilibrium
- In practice there is often not enough time for equilibrium to form when cooling is fast
- With enough time diffusion smoothes out the grains; if cooling is too fast (quenching) the structure will be *cored*: the innermost layers have higher concentration and then lower concentrations in the outer layers

Mechanical Properties

- Combining metals in solid solution strengthens the materials
  - e.g. in nickel-copper alloy this increases tensile strength but decreases ductility

Binary Eutectic Systems

- "Low melting point" materials with limited solubility with each other
- 2 solid phases, each with limited solubility
  - The lines bounding the left and right regions are the solubility limits
- At the eutectic concentration:
  - Above the melting point we get a homogeneous liquid
  - Just below the eutectic line we get both phases
- For an alloy of composition $C_0 = C_E$, a lamella structure is formed
  - α and β phases alternate in micropatterns
  - Rapid diffusion over very small distances as the α and β phases form
- Going from above the eutectic temperature to below the eutectic temperature locks in the grains formed initially and the rest of the liquid forms lamellae
- Hypoeutectic: lower than the eutectic concentration; hypereutectic: above the eutectic concentration

Lecture 17, Feb 18, 2022

Intermetallic Compounds

- Intermetallic compounds have no solid solubility
- They exist as lines on a phase diagram, not an area due to stoichiometry (composition of the compound is fixed)
  - Lines can have thickness due to departures from the stoichiometry from e.g. vacancies

Invariant Reactions

- Eutectic: Liquid transforms into two slid phases
  - -ic suffix involves a liquid
  - $L \rightleftharpoons \alpha + \beta$
- Eutectoid: One solid phase transforms to two other solid phases
  - -oid suffix means solid phases
  - $S_1 \rightleftharpoons S_2 + S_3$
- Peritectic: A solid and a liquid transform into a second solid
  - $\gamma + L \rightleftharpoons \varepsilon$

Lecture 18, Feb 28, 2022

Material Properties

- Force must be normalized per unit area: stress $\sigma = \dfrac{F}{A}$ in pascals Pa
- Deformation must be normalized per unit length: strain $\epsilon = \dfrac{\Delta L}{L}$
- To quantify strength and material properties we plot these on a stress-strain curve
- When a material is in its linear region, stress is related to strain by $\sigma = E\epsilon$ where E in pascals is the Young's modulus

Lecture 19, Mar 3, 2022

Elastic Behaviour

- $F = -\frac{\mathrm{d}U}{\mathrm{d}r}$ where $U(r)$ is the potential between atoms with respect to interatomic distance
- $\left.\frac{\mathrm{d}U}{\mathrm{d}r}\right|_{r=r_0} \propto E$
- Young's modulus E is *independent of structure* in the linear region, i.e. it only depends on the atoms of the solid
  - Note this is only applicable to metals
  - e.g. E for carbon steel ranges from 190 to 210GPa; all steels have about the same stiffness, but some steels are stronger than others
- When a material is stretched beyond its elastic range, it will recover elastically with the same Young's modulus but won't return to the original length

Lecture 20, Mar 7, 2022

Lecture 21, Mar 10, 2022

Tensile Testing

- Recall that a stress strain curve has a linear region, then flattens out and then curves down before breaking
  - The peak of this curve is the *ultimate tensile stress*
- The curving down happens because of *necking*
  - One part of the sample is slightly weaker, so when it stretches the cross section reduces more, creating a positive feedback loop and the entire material breaks at that point
- A conventional tensile specimen (a dogbone specimen) has 2 large grip regions at the ends, a reduced section in the middle that actually deforms, and sometimes a strain gauge measuring the gauge length to measure strain
- Metals deform plastically by movement of edge dislocations, instead of moving an entire plane, because this way only one line of bonds need to be broken at once instead of an entire plane
- When a material is stretched beyond its yield point and then allowed to recover, the elastic recovery has the exact same slope, i.e. the Young's modulus is unchanged
  - When the material is put under stress again the yield point is now slightly higher
- Often in real life testing the yield point isn't exactly clear; the convention for yield point in this case is to draw a line from 0.2% strain with the same slope, and the yield point is when this line intersects the curve
- Different materials have different stress-strain curves:
  - Ceramics are brittle so they have a stiff linear section and then abruptly breaks
  - Polymers are considerably less stiff and can have considerably larger strain before breaking

Lecture 22, Mar 14, 2022

Tempered Glass

- Glass is made of SiO_2 or fused silica
  - A pure single crystal of SiO_2 is called quartz
- Typical glass is soda lime glass (70-74% SiO_2, 13% NaO and 10% CaO), added to lower the melting point and make it easier to work with
- Tempered glass is made by rapidly cooling the outside of glass and leaving the inside to cool slowly
  - The outside is frozen but the inside still contracts from cooling, so the outside zone is under compression since it's being pulled by the centre

  - Glass can also be chemically tempered, where the sodium ions are replaced with bigger ions to create the same compression
  - A Prince Rupert's drop is an extreme example of this

3-Point Test

- Since ceramics are brittle and have very low failure strain, it's hard to do a conventional tensile test
- A 3-point test is used instead, where the specimen is supported on 2 sides and a force is applied on the midpoint until the material breaks
- The maximum tensile stress can be found by $\sigma = \dfrac{3FL}{2wh^2}$

More About Stress-Strain Curves

- Since it is difficult to quantify where the linear relationship ends, the convention is to use a line at 0.2% strain with the same slope as the Young's Modulus
- Past the yield strength we have uniform plastic deformation, where the entire specimen stretches uniformly
  - Increased dislocation formation as the material strengthens under stress
- The peak of this curve is the ultimate tensile strength
- Past the ultimate tensile strength nonuniform plastic deformation happens as the material begins to neck
  - The strengthening of the necked area is not enough to keep up with the reduction of the cross-sectional area
  - Real stress goes up, but since engineering stress doesn't account for the reduced cross section, the engineering stress actually goes down

Lecture 23, Mar 17, 2022

Strengthening Metals

- Plastic deformation occurs by the movement of linear dislocations
- The presence of other imperfections, e.g. vacancies, interstitial atoms, etc can affect the dislocation movement
- A linear dislocation itself puts the atoms under tension, which can be slowed down by other imperfections as they also put compression or tension on the atoms
  - This is why alloying can make the metal stronger by affecting dislocation movement
- Annealing: Heating up a metal
  - This relieves residual stress introduced by processing and also promotes grain growth (reduces density grain boundaries)
  - Annealing makes the metal more ductile
- Plastically deforming the metal intrudes more defects, making it harder for dislocations to move and strengthening the metal
  - Repeatedly deforming introduces more and more defects, making it more brittle and eventually breaking
- Grain size has a huge effect on metal strength
  - When grain size is very small (nanocrystalline), the metal is effectively amorphous
  - Smaller grain size and amorphous metals make it much harder for dislocations to move and so makes the metal stronger
  - However it's very difficult to make amorphous metals
- Second phases are 3D defects
  - e.g. aluminum alloy precipitation hardening
- Summary: Strengthening mechanisms in alloys:
  - Work hardening: Plastically deforming the material to induce more dislocations (e.g. bending a bar to make it stronger)

  - Solid solution hardening: Introducing interstitial defects through a solid solution (e.g. putting carbon in iron to make steel)
  - Precipitation hardening: Forcing particles of a second phase to precipitate out (3D defect)
  - Grain refinement: Influencing the grain structure in various different ways (e.g. rolling, forging)

Lecture 24, Mar 21, 2022

Structure of Polymers

- Toughness: How much energy a material can absorb before it breaks
  - The area under a stress strain curve has a unit of $\mathrm{N/m^2}$ or $\mathrm{N\,m/m^3}$, or energy per volume
- Polymers are long chains of molecules
- Simplest polymer: polyethylene (PE)
  - Note polymers are named from the starting molecule
- The long molecule chains get tangled in a polymer and are loosely connected together; both intramolecular forces and intermolecular forces are at play
  - A polymer's strength is dependent on how easily the molecule chains slide past each other
- For a polymer, the yield strength is defined as the first peak of the curve; the tensile strength is the stress at which it breaks
- Some common polymers:
  - Polyethylene (PE): 2 carbons, every carbon has only 2 hydrogen
    - Has many varieties, e.g. high-density polyethylene (HDPE), low-density polyethylene (LDPE), ultra-high molecular weight polyethylene (UHMWPE, Dyneema)
  - Polypropylene (PP): 2 carbons, one carbon has 2 hydrogens, the other has 1 hydrogen and a methyl (CH_3) group
    - Used in plastic bags
  - Polyvinyl chloride (PVC): 2 carbons, one with 2 hydrogens, one with 1 hydrogen and 1 chlorine
    - Used in pipes
    - Typically stiff, but plasticizers can be added to make it flexible
  - Polytetrafluoroethlene (PTFE): Like PE but with fluorine instead of hydrogen
    - Also known as Teflon
    - Carbon-fluorine bond is strong so this material is very inert
  - Polymethylmethacrylate (PMMA): 2 carbons, one with 2 hydrogens, the other with a methyl group and (carbon with double bonded oxygen, and single bonded oxygen with methyl group)
    - Also known as acrylic
    - Glasses are made of this
    - The big side chain prevents the chains from stacking next to each other
- Putting a polymer under tension lines up the molecules in a single direction
  - This increases the tensile strength since more of the load is now carried by stronger intramolecular bonds rather than intermolecular bonds
  - Pulling it in the other direction afterwards is much easier to do, since the chains are now aligned in the wrong direction
  - Also changes optical properties (e.g. makes the plastic white)

Lecture 25, Mar 24, 2022

Molecular Weight in Polymers

- The main part of strengthening polymers involves making it harder for polymer chains to slide past each other
- Molecular weight: the size of each macromolecule
  - The longer the molecules (higher molecular weight), the more they will get tangled and so the polymer will become stronger

        - e.g. UHMWPE
- Not all molecules are the same weight, so several methods are used to describe the distribution:
    - Number average: $\bar{M}_n = \sum_i x_i M_i$
        - Broken into "bins" of mass/length ranges
        - x_i is the *number fraction*, the fraction of molecules that are in that bin
        - M_i is the mass of each molecule in that bin
        - Exactly like a normal weighted average
    - Weight average: $\bar{M}_w = \sum_i w_i M_i$
        - w_i is the *weight fraction*, $w_i = \frac{N_i M_i}{\sum_j N_j M_j}$
            - i.e. w_i is the total weight molecules in that bin divided by the total weight of all molecules
        - Bins with higher molecular weight are weighted more in the average
    - The weight average is always greater than the number average (except the hypothetical case where all chains are the same length)
    - $Đ = \frac{\bar{M}_w}{\bar{M}_n}$ ("D stroke") is the *dispersivity* or *polydispersivity index* and measures spread (width of distribution)
        - This number is greater than 1; the greater the dispersivity, the more wide the spread of molecular weights
        - Đ for isotatic commodity grade (i.e. cheap) polypropylene is about 3.5 (i.e. a very wide distribution)

Crystallinity of Polymers

- Sometimes polymers can fold into regular patterns and crystallize
    - It's impossible for the entire polymer to crystallize
    - There are crystallized regions with amorphous regions in between
- More crystallization implies higher density
- Since the chains are folded tightly, the intermolecular bonds are stronger so the polymer has higher strength, wear resistance, and higher resistance to chemicals

Lecture 26, Mar 28, 2022

Tacticity

- Polyethylene crystallizes readily, giving it higher density
- *Isotactic*: The functional group in the mer unit is always on the same side
- *Syndiotactic*: The functional groups alternate on both sides
- *Atatic*: Random placement of the functional groups
- In general isotactic is the easiest to crystallize, followed by syndiotactic and then atactic
- e.g. atactic polypropylene is amorphous (linear low density PP, clear and flexible, used in soda bottles), vs isotactic PP which is more crystalline, stronger and more rigid, used in detergent bottles

Side Chains

- PE chains are never perfect single chains; they always have side chains coming out
- HDPE has shorter side chains, making it easier for chains to line up and crystallize; LDPE has longer side chains, making it harder to crystallize, more flexible and less strong
    - The actual densities are not very different, but the crystallinity creates large differences in material properties

Changing Mer Units (Composition)

- Different mer units have different intermolecular bonding
- Example: PVC (changing one of the hydrogens on PE to chlorine)
    - Chlorine is much more electronegative and forms a dipole, creating a polar molecule
    - Since intermolecular forces are dipole-dipole interactions, the stronger polarization creates a stronger intermolecular bond

Cross Linking

- Creating covalent bonds between polymer chains (primary bonding between chains)
- Since primary bonds are much stronger than secondary bonds this makes the polymer stronger
- Cross linking also prevents plastic flow, i.e. plastic deformation
- Example: Vulcanization of rubber
    - Sulfur compounds build cross links between raw rubber chains
    - Raw rubber from the tree is a fluid, but after vulcanization the new bonds hold the rubber together
- Elastomer: A polymer with large elasticity (i.e. it can be stretched a lot without plastic deformation)
    - Elastomers can be created with cross linking, since the primary bonds pull the chains back to their original position
    - However too much cross linking makes the polymer brittle
- Hysteresis: The return curve upon unloading is not the same as the original loading curve
    - When some materials are loaded and then unloaded, the return path on unloading is different, even though there is full elastic recovery
    - Since the area under the stress-strain curve represents energy, loading and then unloading takes energy (converts to heat)
    - This can be used for shock absorption as the elastomer absorbs energy

Temperature Dependence

- Intermolecular bonds have much lower energy than covalent or ionic bonds
- Energy in intermolecular bonds is comparable to thermal energy, meaning relatively small variations in temperature near room temperature can have large impacts on a polymer
- At colder temperatures polymers are brittle and behave almost like ceramics; at warmer temperatures they are much more flexible and can be deformed a lot

Lecture 27, Mar 31, 2022

Time-Dependent Elastic Behaviour

- For metals and ceramics the stress-strain behaviour is independent of time (when below the yield strength), i.e. elastic response is instantaneous
- Some polymers have *viscous behaviour*: Under the same stress, strain keeps increasing with time, and this process is irreversible
    - This is referred to as *viscous flow*
    - The increase in strain is not necessarily a straight line, could be e.g. exponential decay
- Example: Silly putty (silicone) deforms when strained slowly, but fractures when strained quickly
    - Silly putty bounces without denting, which indicates elastic behaviour
- If we fix the strain and look at the stress (e.g. guitar string), it will slowly decrease
    - This is referred to as *stress relaxation* since length stays fixed but tension decreases
    - The shape resembles a decaying exponential
- Define the *relaxation modulus* $E_R(t) = \dfrac{\sigma(t)}{\varepsilon_0}$
- Stress relaxation behaviour depends on temperature; the warmer the temperature, the faster the stress relaxation
- Consider taking a fixed time t_0 and looking at the temperature dependence of E_R

    - For many polymers, it starts flat, then rapidly decreases, flatten outs again, and then decreases to 0
    - The final decrease is the melting temperature T_m
    - The first decrease happens at T_g, the *glass transition temperature*
        - Below T_g the polymer is brittle
        - Between T_g and T_m, the polymer is in the rubbery region (flexible and maintains shape)
        - Past the melting temperature the polymer exhibits viscous flow
    - The glass transition temperature exists due to crystalline and amorphous regions
        - When temperature above T_g the amorphous regions start breaking up
- Typical T_g values:
    - Polyethylene: 153K
        - PE has low T_g, which means it's flexible at room temperature
    - Polystyrene: 373K
    - PMMA: 378K
        - Acrylic has high T_g which is why it's rigid
    - Nylon: 323K
- Two classes of polymers:
    - Thermoplastics: Can be melted and molded without damaging the polymer
        - Polymer can enter viscous flow region with all the chains flowing past each other
        - Temperature reduces intermolecular forces
        - Cooling restores intermolecular forces again
        - Example: PE, nylon, polystyrene
    - Thermoset polymers: Cannot be melted without damaging the polymer (can't be remolded)
        - These are hardened via cross-linking (aka *curing*, an irreversible process)
        - Example: Epoxy
        - Network polymers don't melt since the strength comes from primary bonds

Lecture 28, Apr 4, 2022

Optical Properties of Polymers

- Crystalline and amorphous regions in polymers have different optical properties
- In a crystalline polymer the mix of amorphous and crystalline regions scatter light, making the polymer translucent or opaque
- Polymers that don't crystallize (e.g. PMMA) are 100% amorphous, no light scattering results in transparency

Optical Properties

- The visible light range is approximately $\lambda = 400\text{nm}$ to $\lambda = 700\text{nm}$
- The photon energy is $E = \dfrac{hc}{\lambda} = 1.77\text{eV}$ for 700nm, and 3.1eV for 400nm

Bonding

- Ionic bonding (ionic solids): exchange of electrons
    - Example: NaCl with the rock salt structure
        - Using $E = \dfrac{q_1 q_2}{4\pi\varepsilon_0 r}$ we can calculate the energy by calculating the sum of an infinite series
        - 6 attractive neighbours at a distance of a away; 12 repulsive neighbours at a distance of $\sqrt{2}a$ away, etc
        - This series converges to $M\dfrac{e^2}{4\pi\varepsilon_0}\dfrac{1}{a}$ where M is the Madeluing constant
- Covalent bonding: sharing of electrons
    - When two atoms are brought together for covalent bonding, their electron wavefunctions overlap

  - In the anti symmetric combination, this is the *anti-bonding state*
    - There's a node exactly in the middle of the two wavefunctions
    - The node results in the two electron clouds being separated
  - In the symmetric configuration, it is called the *bonding state*
    - There is now a nonzero probability for electrons to be between the two atoms to facilitate bonding
  - The bonding state is at a lower energy than the two individual atoms, and the antibonding state is higher
  - Electrons go into this bonding state since it has lower energy, and this makes a bond
- Metallic bonding: cloud of free electrons holding together nuclei

Lecture 29, Apr 7, 2022

Time Independent Schrodinger Equation and Hydrogen Orbits

- $-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} = (E - V)\psi$
- If $E > V$ then this means $\frac{\partial^2\psi}{\partial x^2}$ and ψ have different signs; this means the wavefunction curves towards zero (if $\psi > 0$ then it curves down, if $\psi < 0$ then it curves up)
  - This means we have oscillatory solutions
  - For the simple case where $V = 0$ (free electron), $\psi = \sin(kx)$ or $\cos(kx)$ where $E = \frac{\hbar^2 k^2}{2m}$
- If $E < V$, $\frac{\partial^2\psi}{\partial x^2}$ and ψ have the same sign; the wavefunction curves away from zero
  - This means we have exponential solutions
  - There can be 2 cases, either the solution blows up to infinity, or it decays towards zero
- In the infinite square well, in the well the solution oscillates, and outside the well the solution is always zero
- For the finite square well, in the well the solution still oscillates ($E > V$), but outside the well the solution decays towards zero ($E < V$)
  - There are a finite number of bound states (quantized states), because at some point $E > V$ everywhere
- For the quantum harmonic oscillator ($V = bx^2$):
  - For the $n = 1$ solution it resembles the finite square well
  - Since the potential gets wider as energy increase, increasing n makes the wavefunction wider
  - The place where $E = V$ is the *classical turning point*
  - In this case energy levels are evenly spaced (proportional to n instead of n^2)
- For the hydrogen atom energy is proportional to $\frac{1}{n^2}$; these 3 cases above are the only cases where there is a simple expression for E based on n
- The $2s$ state has a larger radius than the $1s$ state because the classical turning point is further away

Band Theory

- When two finite potential wells are brought near each other (like when two atoms approach each other during bonding), their wavefunctions overlap
  - The $n = 2$ state for hydrogen is bigger so there is more overlap
- Overlapping wavefunctions create bands; with n atoms there will be n bands
- The spacing between bands doesn't arbitrarily increase, so with a very large number of atoms, there is effectively a continuous range of energy levels
- Only valence electron wavefunctions overlap and form bands

Band Structure

- Metals have a partially filled band
    - States above a certain level are unfilled, below that level are filled
    - E_F is the Fermi level, below which all energy states are filled
    - Note there's a potential barrier at the edge of a metal so the electrons don't leak out (the work function Φ)
    - Since there are states immediately above the Fermi level, electrons can easily move in an electric field, so they can conduct electricity easily
- A semiconductor has 2 bands: the valence and conduction bands
    - The valence band is fully occupied at $T = 0$; the conduction band is unoccupied at $T = 0$
    - The band gap sits between the valence and conduction bands
        - The colour of light emitted by LEDs is the photon energy of its band gap
    - Electrons can only move if they have enough energy to cross the band gap and go into the conduction band
    - With enough energy, electrons leave the valence band and move into the conduction band, leaving behind a hole
        - The hole acts like a positive charge and can be a charge carrier
    - E_F for a semiconductor is usually somewhere in the band gap
- An insulator is similar to a semiconductor but the band gap is very large, making it very hard to cross
- A material appears as optically transparent if it does not absorb photons in the visible light range
    - If the band gap is large enough that photons in the visible range cannot excite electrons across the gap, then photons will not be absorbed and the material is transparent
    - For metals and other materials where the band gap is small, photons will be absorbed by electrons which jump to the conduction band, so the material is opaque

Lecture 30, Apr 11, 2022

Resistance and Resistivity

- Resistance is a property of a certain object, resistivity is a material property (resistance depends on length, area, etc)
- Resistivity is defined as $\rho = R\frac{A}{l}$ in units of Ωm
    - Resistance is proportional to length and inversely proportional to cross sectional area
- Conductivity is defined as $\sigma = \frac{1}{\rho}$ in units of Ω^{-1}/m
- For a metal, $\sigma = ne\mu_e$, where n is the density of free electrons (or holes in some rare cases) in m^{-3}, e is the electron charge, μ_e is the electron mobility (units of $\text{m}^2/\text{V s}$)

Semiconductors

- For an intrinsic semiconductor (i.e. no additives), charge is carried by both holes and free electrons in the valence band; $\sigma = n_i e(\mu_e + \mu_h)$ where μ_e and μ_h are the electron and hole mobilities
    - Increasing the temperature increases the charge density; $n_i \propto e^{-\frac{E_g}{2kT}}$ where E_g is the band gap, k the Boltzmann constant, and T the temperature in Kelvins
    - Optical absorption can also create charge carriers
    - Since charge carrier density changes with temperature, intrinsic semiconductor conductivity varies with temperature, so they're not often used
- Silicon semiconductors are tetrahedrally coordinated; if we put in a group 5 element, we get an extra electron; if we put in a group 3 element we get an extra hole
- In an extrinsic semiconductor, usually there are much more charge carriers introduced by doping, so we can approximate $\sigma = N_d e\mu_e$ for N-type (negative charge carrier) semiconductors, or $\sigma = Pe\mu_h$ for P-type (positive charge carrier) semiconductors

- Example: Doping silicon with 1 part per billion arsenic
  - As is a group 5 element, so this is a N-type semiconductor
  - 1 part per billion means the electron density is one one-billionth of the atomic density for silicon
  - For silicon $N = \frac{8}{a^3} = 4.997 \times 10^{22}\,\mathrm{cm}^{-3}$ where $a = 0.543\mathrm{nm}$ (8 because the diamond cubic structure has 8 atoms per unit cell)
  - So $N_d = 4.997 \times 10^{13}\,\mathrm{cm}^{-3}$
  - Using $\mu_e = 1350\mathrm{cm}^2/\mathrm{V\,s}$ and $\mu_h = 450\mathrm{cm}^2 V.s$, $\sigma = 1.08 \times 10^{-2}\,\Omega^{-1}\mathrm{cm}^{-1}$

Lecture 31, Apr 14, 2022

Review

- Chapter 2, 3, 6: Mechanical properties (metals)
  - Stress strain curves
  - Young's Modulus
  - Elastic vs. inelastic behaviour
  - 3-point bends
  - Tensile, yield strength, 0.2% offset for metals
- Chapter 7: Strengthening mechanisms
  - Defects: 0D (substitutional, interstitial, vacancies), 1D (edge, screw dislocations), 2D (grain boundaries), 3D (secondary phases)
  - Strengthening mechanisms for metals:
    1. Work hardening (introducing 1D defects, deforming the metal)
    2. Solid solution hardening (introducing of 0D defects, e.g. steel)
    3. Precipitation hardening (introducing second phase 3D defects)
    4. Grain refinement (introducing 2D grain boundaries, e.g. making amorphous metals)
- Chapter 8: Polymers
  - Calculating molecular weights
  - 5 mer units:
    1. Polyethylene
    2. Polypropylene
    3. Polyvinyl chloride
    4. Polytetrafluoroethlene (PTFE)
    5. Polymethylmethacrylate (PMMA)
  - Structure:
    - Mer unit
    - Crystallinity
    - Molecular weight
    - Dispersivity (i.e. width of the weight distribution)
    - Branching (e.g. HDPE vs LDPE)
    - Cross-linking and elastomers
    - Tacticity
  - Physical properties:
    - Mechanical properties
    - Density
    - Melting point
    - Glass transition temperature
    - Viscoelasticity
    - Optical transparency
- Chapter 9: Electronic properties
  - EM spectrum: $\nu = \frac{c}{\lambda}, E = h\nu$
    - Visible light: 400nm to 700nm
  - Types of bonding:

    - Ionic bonding (e.g. NaCl)
        - Hard sphere model
        - Coulomb model
        - Madelung constant
    - Covalent bonding
    - Metallic
    - Van der Waals
    - Mixed ionic/covalent, e.g. GaAs is mostly covalent but has an ionic part
- Electronic structure
- Metals vs nonmetals: partially vs completely filled bands
- Semiconductors, conductance calculations, band gap
    - Resistivity $R = \rho \frac{L}{A}$
    - Conductance $\sigma = ne\mu_e + pe\mu_h$
    - Group 3 vs group 5 elements
    - N vs P type doping
- Optical absorption
- Crystal structure: BCC, FCC for metals, NaCl and CsCl structures for ionic compounds, diamond cubic (silicon, germanium) or zincblende for semiconductors