

Thermal Physics & The Properties of Matter

Outline

Ideal Gas

Liquids / Solids

Crystal Structures (6)

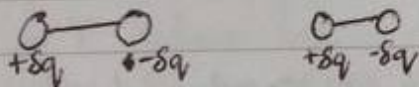
Real Gas (Van der Waals (1) Bonding (2))

Phase Transition (Phase diagrams) Properties (2)

1. Real Gases and Liquids

- When we derived: $pV = nRT \Rightarrow p'V' = nRT$, we assumed that:
 - 1) Point particles (i.e. they occupy zero volume)
 - 2) Non-interacting (the forces between the molecules are zero).

- Atoms and molecules experience Coulomb attraction between nuclei and electrons. We classify molecules and atoms into two types, zero dipole moment and finite dipole moment:



- Molecules will tend to align in a way to minimise total energy, causing an electrostatic attractive force between molecules.
- Some molecules will have no permanent dipole moment, but all molecules will experience temporary dipole moments due to electron density fluctuation, inducing temporary dipoles. This is the Van der Waals interaction.

$$U_{int} \propto -\frac{1}{r^6}$$

U_{int} = intermolecular energy



Demonstration of induced dipoles.

- Addressing the first assumption of the equation of state; molecules have a finite size so the volume accessible to the molecules is smaller than the volume of the container.

By noting that molecules cannot come closer than $2r$ to each other (where the radius of the molecules is r);

$$V' = V - V_{\text{inaccessible}} \quad (V = \text{Volume of container})$$

$$V_{\text{inaccessible}} = n \frac{4}{3} \pi (2r)^3 \quad (n = \text{Number of molecules})$$

$$V' = V - n \frac{4}{3} \pi (2r)^3$$

$$V' = V - nb \quad (\text{where } b = \frac{4}{3} \pi (2r)^3)$$

Note: This approximation tends to underestimate b , but gives the order of magnitude.

- The Second correction to the equation of State arises from the interaction between molecules. Molecules exert an attractive force on each other (van der Waals). So molecules in the centre of a container will experience no net force while molecules close to the walls will experience a force away from the wall. This acts to reduce pressure.

$$P = P' - A \quad \text{Where } A \text{ is correction due to interaction}$$

Since: $A \propto \text{density and number of molecules interacting with wall.}$

$$\Rightarrow A = a \left(\frac{n}{V} \right)^2 \quad \text{where } a \text{ is a material dependent constant.}$$

$$P' = P + a \left(\frac{n}{V} \right)^2$$

$$P' V' = nRT$$

$$\left(P + a \left(\frac{n}{V} \right)^2 \right) (V - nb) = nRT$$

a, b are constant

• b is large for large molecules

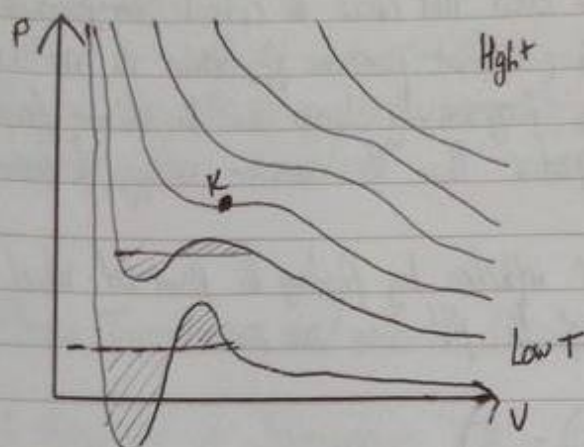
• a is large for high dipole moment.

By substituting for molar Volume: $V_m = \frac{V}{n}$

$$\Rightarrow \left(P + \left(\frac{a}{V_m^2} \right) \right) (V_m - b) = RT$$

- When volume is large ($V_m \gg b$) or the temperature is high, we can neglect the corrections and recover ideal gas behaviour.

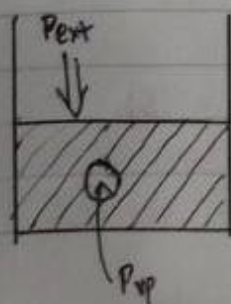
- If we multiply the equation by V^2 , we get an equation with cubic V . Under certain conditions, the equation has three roots.



- High T Large T - 1st term dominates
 - Similar to ideal gas
 Low T - 2nd term significant
 - Cubic in V_m
 - 3 roots

- We note:
- At one particular T , known as the critical temperature T_c , the isotherm has a point of inflection (K).
 - At low T , isotherms have one minimum and one maximum.
 - Low T isotherms are very steep at low volume - compression is difficult in this regime.
 - Low T isotherms have a region where pressure increases with volume. This is ~~unphysical~~ unphysical. We plot a straight line using Maxwell equal area construction to represent observed behaviour.
- At the region of the horizontal line, this is two-phase region where both liquid and gas are in equilibrium.
- The Saturated Vapour pressure is the pressure of a gas that is in equilibrium with its liquid and it is a function of temperature.

Boiling



- Boiling temperature is reached when $P_{vp} = P_{ext}$
- Temperature increases, pressure remains constant
- As pressure P_{vp} increases above P_{ext} , gas bubbles form.
- $P_{vp} < P_{atm}$ bubbles collapse
- $P_{vp} > P_{atm}$ bubbles grow.

- We note: $P_{vp}(T_{boiling}) = P_{atm}$ \therefore Lower $P_{atm} \rightarrow$ Lower $T_{boiling}$
- From the PV plot, it is seen that above the critical temperature, (T_c) , where the point of inflection is at pressure P_c , there is no liquid-gas transition. The gas becomes progressively denser as the volume decreases. In this case, thermal energy is greater than the interaction energy between molecules.
- We can find the point of inflection by finding the point at which the first and second derivatives of the PV curve are zero.

$$\left(P + a\left(\frac{1}{V_m}\right)^2\right)(V_m - b) = RT \quad (1)$$

$$\Rightarrow P = \frac{RT}{(V_m - b)} - \frac{a}{V_m^2}$$

$$\text{At critical point} \Rightarrow \left(\frac{\partial P}{\partial V}\right)_T = 0 \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$$

Differentiating P wrt V, holding T constant:

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT_c}{(V_c - b)^2} + \frac{2a}{V_c^3} = 0$$

$$\Rightarrow \frac{RT_c}{(V_c - b)^2} = \frac{2a}{V_c^3} \quad (1)$$

Differentiating again:

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = +\frac{2RT_c}{(V_c - b)^3} - \frac{6a}{V_c^4} = 0$$

$$\Rightarrow \frac{2RT_c}{(V_c - b)^3} = \frac{6a}{V_c^4} \quad (2)$$

Dividing (1) by (2):

$$\Rightarrow \frac{(V_c - b)}{2} = \frac{V_c}{3} \Rightarrow V_c = 3b$$

$$\text{Sub } V_c \text{ into (2)} \Rightarrow T_c = \frac{8a}{27bR}$$

- We see that with weak interaction (low a), T_c is low.

* Liquid Structure.

- From the isotherms, we see that liquids are difficult to compress as volume changes very slowly with increasing pressure. Therefore atoms are close together, but disordered.

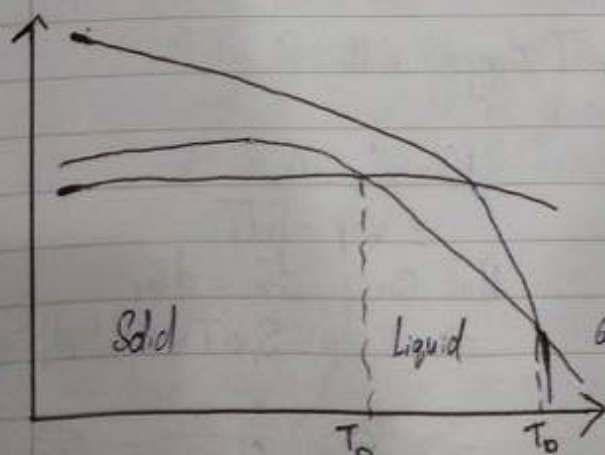
2. Phase Transitions and Phase Diagrams.

- A phase is a homogeneous portion of matter with uniform physical properties and composition. The equilibrium phase is the lowest Gibbs free energy (G).

Gibbs Free Energy: $G = H - TS = U + pV - TS$

	U	$-TS$	$+pV$
Solid	U large + Negative	Low T as highly ordered	Close to minimum
Liquid	U large + Negative	Higher than Solid	Similar to Solid
Gas	U is small Positive	Very high as highly disordered	Very High

G/T Plot for Solid/Liquid/Gas



$$dG = dU + pdV + Vdp - Tds - SdT$$

$$= Vdp - SdT$$

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

Gradient of G vs T is always negative

G is continuous / $\left(\frac{\partial G}{\partial T}\right)$ is discontinuous

$$\left(\frac{\partial G}{\partial T}\right)_L - \left(\frac{\partial G}{\partial T}\right)_G = -S_L + S_g$$

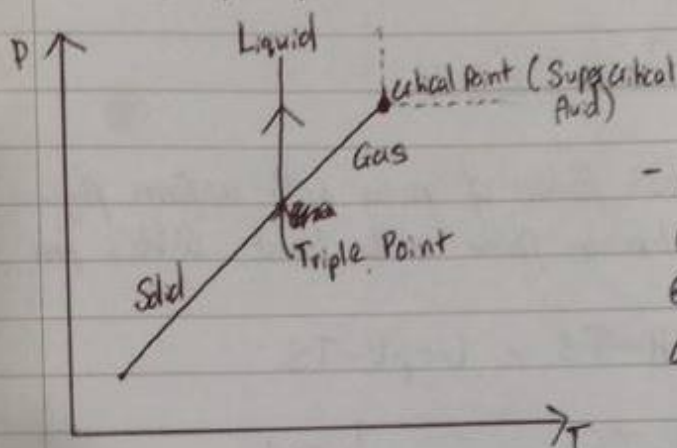
- L is the heat added at the phase transition the latent heat going from low T phase to high T phase.

- L is released changing from high T phase to low T phase.

- We see: $\left(\frac{\partial G}{\partial T}\right)_2 - \left(\frac{\partial G}{\partial T}\right)_1 = -\Delta S \Rightarrow L = T \Delta S$
 \uparrow
 Latent Heat

Phase Diagrams

- A map of equilibrium phase as a function of 2 or more variables.



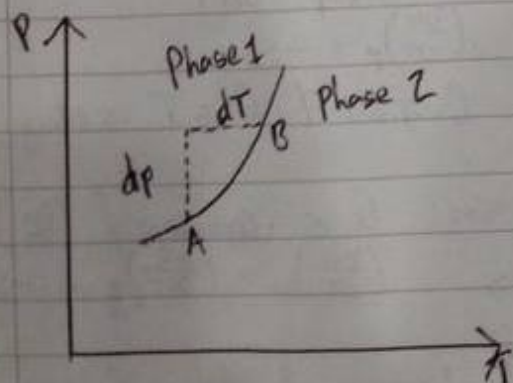
- At the critical point densities of the liquid and gas phases become equal. Therefore there is no density change at the transition (see PV plots).

- The lines on a 2D phase diagram are coexistence lines or phase lines. At certain points on these lines 2 phases can exist in equilibrium.

- At the triple point, where all three lines meet, the three phases exist in equilibrium.

The Clapeyron Equation

- Description of how transition T changes with P .



$$dG = G_B - G_A = V dp - S dT$$

But since $dG_1 = dG_2$

$$\Rightarrow V_1 dp - S_1 dT = V_2 dp - S_2 dT$$

$$\Rightarrow \frac{dp}{dT} = \frac{S_1 - S_2}{V_1 - V_2} = \frac{\Delta S}{\Delta V} = \frac{L}{T \Delta V}$$

Note: $\Delta S = \frac{L}{T}$ & $\Delta V = \frac{1}{P_1} - \frac{1}{P_2}$

If ΔT is small:

$$\Delta P = \frac{L}{T \Delta V} \Delta T \quad (\text{Generally true for Solid} \rightarrow \text{Liquid})$$

$$\text{Becomes } \Rightarrow \int_{P_A}^{P_B} dP = \frac{L}{\Delta V} \int_{T_A}^{T_B} \frac{dT}{T} \quad (L, \Delta V \text{ are constants})$$

$$\left[P_B - P_A = \frac{L}{\Delta V} \quad \frac{T_B}{T_A} \rightarrow T_B - T_A e^{\frac{\Delta V}{L} (P_B - P_A)} \right]$$

Clausius - Clapeyron Equation

$$\text{We have } dp = \frac{L}{\Delta V} \frac{dT}{T}$$

For a liquid (or solid) ^{to} gas transition, the volume of the gas is much greater than the volume of the liquid (or solid):

$$\Delta V = V_{\text{gas}} - V_{\text{liquid}} \approx V_{\text{gas}} \quad \text{and for an ideal gas: } V_{\text{gas}} = \frac{RT}{P}$$

$$dP = \frac{L}{\Delta V T} dT = \frac{L}{V_{\text{gas}} T} dT = \frac{P L}{R T^2} dT$$

$$\Rightarrow \int_{P_A}^{P_B} \frac{dP}{P} = \frac{L}{R} \int_{T_A}^{T_B} \frac{dT}{T^2} \Rightarrow \boxed{\ln\left(\frac{P_B}{P_A}\right) = -\frac{L}{R} \left(\frac{1}{T_B} - \frac{1}{T_A}\right)}$$

We have assumed:

- 1) The latent heat is independent of temperature.
- 2) The specific volume of the gas is much larger than the specific volume of the liquid at the phase transition.
- 3) The gas follows the ideal gas law.

Bonding

- We have seen that for gases, molecules are far apart and the main intermolecular forces of attraction are Van der Waals forces or permanent dipole-dipole attractions.

- In Solids, the type of bonding experienced is governed by ~~electronegativity~~ ^{electronegativity}, the ability of an atom to attract electrons.
- Elements with low electronegativity (left side of the periodic table) tend to lose electrons in bonding while elements with high electronegativity (right side of the periodic table) tend to gain electrons.
- In an isolated atom, we have a spherically symmetric distribution. With atoms close together, electrons rearrange to lower energy configurations.
- Ionic bonds form in solids between atoms with largely different electronegativities. There is a transfer of electrons from the low electronegative atom to the high electronegative atom. This results in the formation of positive ions (cations) and negative ions (anions). Ionic substances are governed by the Coulomb interaction, and are strong with high melting points.
- Covalent bonds form between atoms with similar electronegativities, electrons occupy orbitals of nearby atoms when atoms are close together, instead of their own orbitals as in an isolated atom case. Atoms share electrons, and electrons are concentrated along bonds between atoms. Covalent substances are very strong and have very high melting points.
- Metallic bonds form between atoms with similar but low electronegativities, electrons are free to move and form a sea of delocalised electrons. The substances are fairly strong and have moderately high melting points.
- Molecular or Van der Waals bonds arise from the interaction between dipole moments of atoms or molecules in the solid. These bonds are weak, and favour the minimal rearrangement of electrons. Solids with this type of bonding have low melting points.
- Many ionic solids have some degree of covalency in their bonding, this can vary greatly.

Interatomic Potentials

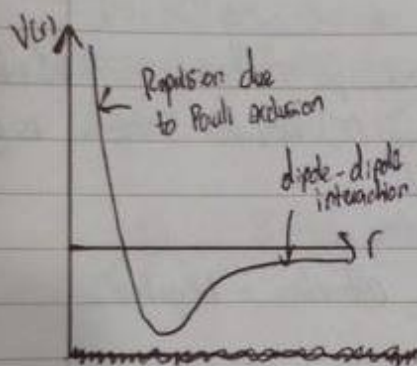
- These are equations that describe the interaction energy between atoms as a function of separation. They are approximate and widely used in materials modelling.

Lennard Jones Potential:
$$V(r) = -4\epsilon \left[\left(\frac{\sigma}{r} \right)^6 - \left(\frac{\sigma}{r} \right)^{12} \right]$$

- This equation is the sum of an attractive r^{-6} term and a repulsive r^{-12} term.

Attractive force: Dipole-dipole interaction $\propto \frac{1}{r^6}$

Repulsive force: At close separation, electron orbitals overlap and due to the Pauli exclusion principle, electrons move to higher energy orbitals causing a strong repulsive force.



The depth of the well (ϵ) is a measure of the bond strength. Since ϵ is lower than when atoms are infinitely far apart.

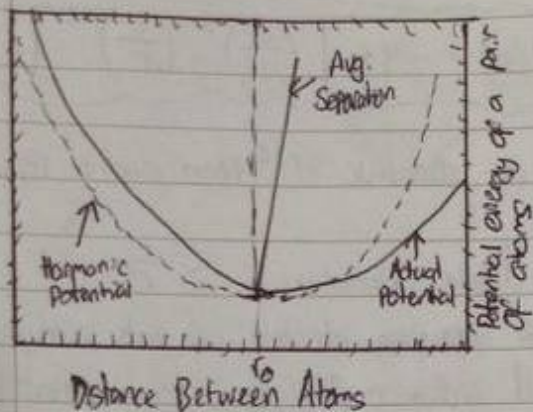
Minimum in interatomic potential: $\left[\frac{dV}{dr} \right]_{r_0} = 0$

For the Lennard Jones potential, this is $\Rightarrow r_0 = 2^{1/6} \sigma$ $V(r_0) = -\epsilon$

Several material properties are related to the interatomic potential curve:

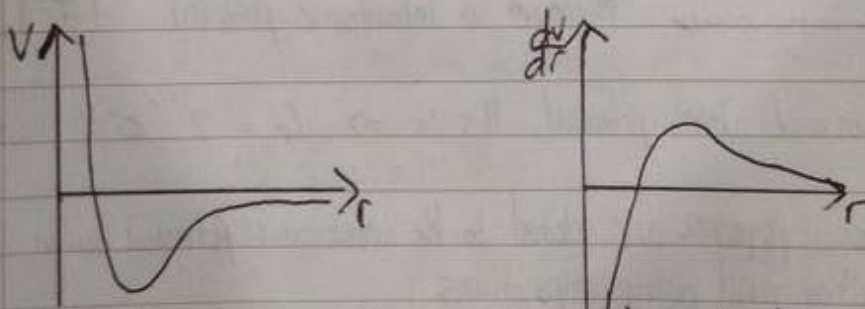
- 1) Melting and boiling temperatures
 \rightarrow Substances with deep wells have high cohesive energies and therefore high melting and boiling temperatures.
- 2) Stiffness (Young's Modulus)
 \rightarrow Young's modulus is related to the curvature of the interatomic potential at the minimum.
- 3) Thermal expansion coefficient α
 $\rightarrow \alpha$ is defined as the fractional change in length $\left(\frac{\Delta L}{L} \right)$ of a solid divided by the temperature change (ΔT) i.e. $\frac{\Delta L}{L} = \alpha \Delta T$. Atoms vibrate about the minimum energy position when heated, as T increases, the amplitude

of oscillation increases, therefore average separation increases
The thermal expansion coefficient depends on the anharmonicity of the interatomic potential.



- Lennard Jones form of potential is appropriate for materials in which van der Waals interactions are dominant. The force (F) between 2 atoms is given by the spatial derivative of the interatomic potential:

$$F(r) = -\frac{dV(r)}{dr} \Rightarrow \text{Positive} = \text{Repulsive, attractive} = \text{Negative.}$$



- Therefore we see a strong repulsion at short distances, an attraction at large separation and zero force at the equilibrium separation.

Ionic Bonds

- Ionic bonds are governed by the Coulomb interactions, the potential between 2 ions with charges q_1 and q_2 separated by distance r is given by:

$$V(r) = -\left(\frac{q_1 q_2}{4\pi\epsilon_0 r}\right)$$

(Including repulsive term due to Pauli exclusion Principle)

$$\Rightarrow V(r) = -\frac{q_1 q_2}{4\pi\epsilon_0 r} + \frac{A}{r^n}$$

Covalent Bonds

- Covalent interactions are described by the Morse potential:

$$V(r) = D \left(e^{-2a(r-r_0)} - 2e^{-a(r-r_0)} \right)$$

D = Bond dissociation energy
 r_0 = Equilibrium bond length

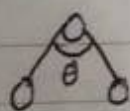
repulsive at very short range Attractive at short range

$$\left. \frac{dV}{dr} \right|_{r_e} = 0 \Rightarrow e^{-2a(r_e-r_0)} = 2e^{-a(r_e-r_0)}$$

$$e^{-a(r_e-r_0)} = 1 \Rightarrow r_e = r_0 \text{ (Bond length is } r_0)$$

$$V(r_e) = -D$$

- We will only consider 2-body interactions, but in covalently bonded molecules, energy will also depend on the angle (θ) between two neighbouring bonds, and therefore the position of three atoms.



3-body potentials have the form: $V(\theta) = \frac{1}{2k(\theta-\theta_0)^2}$

Cohesive Energy

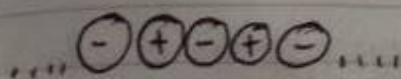
- Cohesive energy is defined as the energy required to separate all the atoms to infinity.

$$\Rightarrow E_{\text{coh}} = -V_{\text{pot}}$$

Internal Energy Per Atom: $u = \frac{U}{N} = \frac{1}{2N} \sum_{i,j=1}^N V(r_{ij})$ [N = total no. of atoms]
 (i, j atoms labels)

$$r_{ij} = |\vec{r}_j - \vec{r}_i| \quad V(r_{ij}) = \text{interatomic potential at } r_{ij}$$

Consider Coulomb interaction for a linear array of ions spaced r_0 apart and of charge $\pm q$.



Coulomb energy: $V(r_{ij}) = \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}$

$$U = \frac{1}{4\pi\epsilon_0} \left[-\frac{q^2}{r_0} - \frac{q^2}{r_0} + \frac{2q^2}{2r_0} - \frac{2q^2}{3r_0} + \dots \right]$$

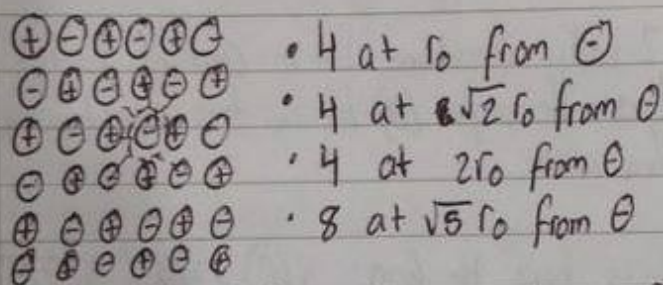
$$U = \frac{1}{4\pi\epsilon_0} \frac{q^2}{r_0} \left[-1 + \frac{1}{2} - \frac{1}{3} + \frac{1}{4} - \dots \right] = \left(\frac{1}{2} \right) \left(\frac{ze^2}{4\pi\epsilon_0 r_0} \right) \left(-\frac{1}{1} + \frac{1}{2} - \frac{1}{3} + \frac{1}{4} - \dots \right) \quad [\text{Note: Each interaction counted twice}]$$

$$\text{Now, } \ln(1+x) = \left(x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \dots \right) = \sum_{n=1}^{\infty} (-1)^{n+1} \frac{x^n}{n}$$

$$\therefore \ln(2) = 1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \dots$$

$$\therefore U = -\left(\frac{1}{2} \right) \left(\frac{ze^2}{4\pi\epsilon_0 r_0} \right) \ln 2$$

- Now Consider a Square array:



Coulomb potential of an ionic crystal in 2D

$$U = \frac{q^2}{4\pi\epsilon_0} \left[-\frac{4}{r_0} + \frac{4}{\sqrt{2}r_0} + \frac{4}{2r_0} - \frac{8}{\sqrt{5}r_0} \dots \right]$$

\downarrow opposite sign \downarrow same sign

- For a 3D array, with the NaCl structure, we find that the Coulomb energy per ion of a NaCl crystal is:

$$U = \left(\frac{-1.748e^2}{8\pi\epsilon_0 r_0} \right) + \frac{6C}{r_0^{12}}$$

With the positive term being the repulsive force at very close ranges. (Pauli exclusion principle).

$$\text{Now, } E_{\text{coh}} = -U$$

$$= -3V(r_0) - 6V(\sqrt{2}r_0) \quad [6 \text{ neighbours at } r_0 \text{ separation, and } 12 \text{ neighbours at } \sqrt{2}r_0 \text{ separation. Each bond is shared between 2 atoms}]$$

The Value of r_0 can be found by setting:

$$\left. \frac{dE_{\text{coh}}}{dr_0} \right|_{r_0} = 0 \quad \text{Minimum potential energy (Maximum cohesive energy).}$$

Lennard Joule: $\frac{U}{N} = \frac{1}{2} [n_1 V(r_1) + n_2 V(r_2) + n_3 V(r_3) \dots]$
 \hookrightarrow Negative

$\rightarrow n_1 = \text{no. of 1}^{\text{st}}$ nearest neighbours (etc)

$\rightarrow r_1, r_2 = 1^{\text{st}}, 2^{\text{nd}}$ nearest neighbour distance

Covalent: Very short range, therefore only need to consider first nearest neighbours

$V(r_0) = -D$ $\frac{U}{N} = u = -\frac{1}{2} n_1 D$ $n_1 = \text{no. of nearest neighbours.}$

Mechanical Properties of Solids

- Stress is defined as the force over unit area: $\sigma = \frac{F}{A}$
- Strain is defined as the change in length over length: $\epsilon = \frac{\Delta L}{L}$
- Different geometrical arrangements of forces produce different types of deformation and have different elastic moduli. We define 3 different types:

① Tensile Stress (σ) and deformation (ϵ): Equal and opposite ^{forces} acting parallel to the faces on opposite faces.

② Shear Stress (τ) and deformation (γ): Equal and opposite forces acting parallel to the faces on opposite faces.

③ Equal forces acting on all faces (Pressure): Causes a change in volume.

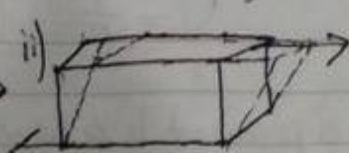
- $\sigma = E \epsilon$ ($E = \text{Young's modulus (tensile modulus)}$).

- $\tau = G \gamma$ ($G = \text{Shear modulus}$)

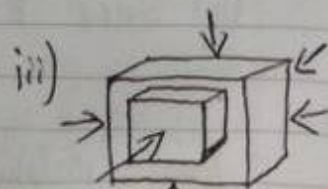
- $P = -K \left(\frac{\Delta V}{V} \right)$ ($K = \text{Bulk modulus}$)



Tensile



Shear



Pressure

- Let's consider this from an atomic point of view. When a force is applied to the surface of a material, the atoms will move from their equilibrium positions. Since the restoring force acting to pull the atom back to the equilibrium position increases with displacement, the atom will continue to move until the forces balance.

We tend to consider a small cube inside the material, where there are forces acting on the cube from bonds outside the cube, and a ^{tensile} restoring force acting ~~on the~~ from the bonds inside the cube. Three components of stress ($\sigma_x, \sigma_y, \sigma_z$) and three components of shear stress ($\tau_{xy}, \tau_{xz}, \tau_{yz}$). The forces are equal and opposite as the cube does not move.

- We can find Young's modulus from the interatomic ($V(r)$) potentials by considering a cube of atoms with bond length a .

We apply a force F , balanced by a restoring force:

$$\Rightarrow F = F'(a + \delta r)$$

Use Taylor expansion in δr :

$$\Rightarrow F(a + \delta r) = F'(a) + \delta r \left. \frac{dF'}{dr} \right|_a$$

But at equilibrium, $F'(a) = 0$

$$\Rightarrow F(a + \delta r) = \delta r \left. \frac{dF'}{dr} \right|_a$$

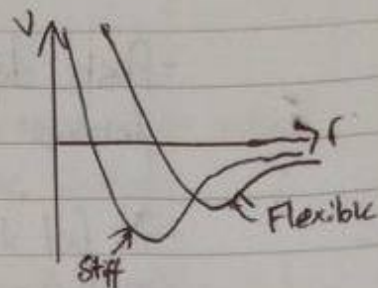
Now, Stress $\sigma = \frac{F}{A} = \frac{F}{a^2}$ and Strain $\epsilon = \frac{\delta r}{a}$

$$\sigma = \frac{-F'(a + \delta r)}{a^2} = -\frac{1}{a^2} \delta r \left. \frac{dF'}{dr} \right|_a = -\frac{1}{a} \frac{\delta r}{a} \left. \frac{dF'}{dr} \right|_a = -\frac{1}{a} \epsilon \left. \frac{dF'}{dr} \right|_a$$

But since $E = \frac{\sigma}{\epsilon} \Rightarrow E = \left. \frac{-\frac{1}{a} dF'}{d\epsilon} \right|_a = \left. \frac{-\frac{1}{a} dF'}{d\left(\frac{\delta r}{a}\right)} \right|_a = \left. \frac{-1}{d\delta r} \right|_a$

- Young's modulus is proportional to the second derivative of the interatomic potential curve at the equilibrium separation.

- A Strongly Curved well in the interaction potential will result in a stiff material and a potential with a flat well will result in a flexible material.

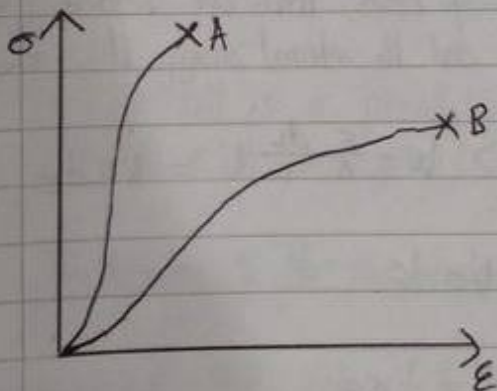


- We have assumed:

- Only nearest neighbour interactions were considered.
- Crystals do not (generally) have cubic structures.

Bond Type	E_{car} (GPa)
Covalent	200 - 1000
Ionic	30 - 100
Metallic	60 - 300
Van der Waals	2 - 4

Stress/Strain Curves



- Stress/Strain Curves allow us to explore the mechanical properties of a solid.
- In the low stress regime, the curve is linear, and the gradient of the line is equal to Young's modulus.

- Curve A denotes a material stiff and difficult to deform, typically these are solid covalent or ionic substances. These materials are brittle (will shatter when hit).
- Curve B denotes a more ductile material, one with weaker bonds than ionic or covalent, typically these are solid metallic substances.
- Elastic deformation is where a solid recovers its original shape when stress is removed. Removing stress after the curve part of the plot (elastic limit), the solid remains deformed.

- Plastic deformation is where a solid becomes permanently deformed. This phenomenon can be explained using dislocation lines.
- At first it was thought that entire planes of atoms would slide to a new equilibrium position, but this predicted a far greater stress than was observed.
- We introduce dislocations into structures. Dislocations are line defects, for example a partial plane of atoms which ends inside the material. Whilst planes of atoms have the tendency to slide over each other, it is relatively easy to move the dislocation line through the crystal.
- For ductile materials (metals), it is easy to create and move these dislocations.
- For brittle materials (covalent), it is difficult to create and move dislocations.

Elastic Energy

- When a force is applied to the surface of atoms, bonds are stretched (interatomic separation increases), so work is done and the internal energy U is changed.

$$W = FdL \quad (\text{but since } V = AL) \Rightarrow W = \frac{F}{A} \frac{dL}{L} V = V \sigma d\epsilon$$

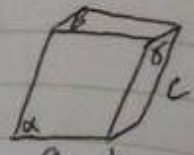
$$\text{If all work goes into } U \Rightarrow dU = V \sigma d\epsilon$$

$$\frac{U}{V} = \int \sigma d\epsilon = E \int \epsilon d\epsilon = \frac{1}{2} E \epsilon^2 = \frac{1}{2} \sigma \epsilon$$

- The units of this are in energy per unit volume, the area of a stress strain curve gives the work done in bringing the material from ϵ_1 to ϵ_2 .
- Yield Stress: Stress at which σ/ϵ curve deviates from linear behaviour.
- Toughness: Area under σ/ϵ curve up to fracture.

Crystal Structures and Defects

- In the lowest energy state of a solid, atoms are arranged in an ordered configuration and this arrangement is known as the crystal structure.
- An ideal crystal is a repetition of identical structural units (parallelepipeds) in space, these structural units are described in terms of a lattice and a basis.
- A ~~lat~~ (Bravais) lattice is a regular arrangement of points in space such that the environment of every point of the lattice is identical.
- Every point on a lattice can be defined by a set of linearly independent vectors. In 3D (a_1, a_2, a_3) and in 2D (a_1, a_2) .
- Each lattice point can be defined by a set of positive or negative integers (l, m, n) and defining one lattice point as the origin, we have:
$$r = la_1 + ma_2 + na_3$$
- A unit cell is a parallelepiped (3D) whose vertices are lattice points (in 2D this is a parallelogram).
- The volume of the parallelepiped made from lattice vectors a, b and c is $a \cdot b \times c$.
- A primitive unit cell is the smallest possible unit cell for a given lattice and it must only contain one lattice point. ($a=b, \alpha=60^\circ$)
- The type of lattice can be classified by the relative lengths of the unit cell vectors and the angles between them. There are 14 lattices grouped into 7 types.
- Need to know:
 - Cubic: $a=b=c$; $\alpha=\beta=\gamma=90^\circ$
 - Hexagonal: $a=b \neq c$; $\alpha=\beta=90^\circ$; $\gamma=120^\circ$
- Lattice + basis = Crystal structure



- The atoms in the unit cell are known as the basis. The positions of atoms in the basis are generally described by fractional coordinates.

- A lattice vector is a vector joining any two lattice points. It can be written as a linear combination of unit cell vectors.

$$t = Ua + Vb + Wc \quad \text{or} \quad [U.V.W] \quad \text{where } U, V, W \text{ are integers}$$

- The positions of atoms in a unit cell as 3 numbers representing fractions of the lattice vectors.

Miller Indices (h, k, l)

- Miller Indices are used to describe planes and directions in crystals.

→ Lattice is described by a set of 3 linearly independent vectors (a_1, a_2, a_3) , known as unit cell vectors

→ Length of these vectors are the lattice parameters (a, b, c) of the crystal.

- To determine Miller indices:

→ Draw the plane in the unit cell and determine where it intercepts the unit cell vectors.

→ Write intercepts as fraction of the unit cell vectors $\left(\frac{1}{h}, \frac{1}{k}, \frac{1}{l}\right)$, and take reciprocals to get (h, k, l) .

→ Miller indices must be integers, so multiplication may be necessary.

→ If plane is parallel to any axis (no intercept), then the intercept is taken to be infinity, and the reciprocal is 0.

→ If the intercept is negative, the number is written with a bar.

- Round brackets denote a particular plane and curly brackets denote a set of equivalent planes that are related by symmetry.

Metallic Crystal Structures

- Metallic Bonding is non-directional and most metals can lower their energy by maximising the number of neighbours around each atom, therefore closely packed structures are favoured.
- Two types of structure:
 - Face centred cubic (fcc)
 - Hexagonal close packed.

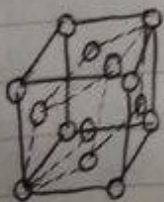
Face centred cubic

- Cubic unit cell - 4 atoms in the unit cell (1 at the corner, 3 in the face centres).
 - An atom at the corner of the unit cell only counts as 1 atom in that cell, even though there are 8 corners. This is because each corner is shared between 8 neighbouring unit cells.
 - Atoms on the edges of unit cells are shared between 4 unit cells, and atoms on faces are shared between 2 unit cells.
 - Atoms in the centre of the faces count for $6 \div 2 = 3$ atoms in the unit cell.

Unit cell vectors are: $(a, 0, 0)$; $(0, a, 0)$; $(0, 0, a)$

Basis atoms: $0, 0, 0$; $0, \frac{1}{2}, \frac{1}{2}$; $\frac{1}{2}, \frac{1}{2}, 0$

Each atom has 12 nearest neighbours at $\frac{a}{\sqrt{2}}$



Primitive unit cell
(rhombohedron)

- Primitive unit cell vectors: $\frac{a}{2}(\hat{i} + \hat{j})$, $\frac{a}{2}(\hat{j} + \hat{k})$, $\frac{a}{2}(\hat{i} + \hat{k})$

- Packing fraction: Maximum fraction of space occupied by hard spheres sitting on the lattice sites.

- For an fcc crystal, we have a stack of closely packed planes with an ABCABC... stacking sequence.

- Spheres form a triangle shape, and are placed to cover half the triangle of the plane below.

Hexagonal Closed Packed Crystal Structure

- Similar to fcc structure, but different symmetry means that hcp metals have different properties.
- Unit Cell Vectors are: $(a, 0, 0)$; $(-a/2, (\sqrt{3}/2)a, 0)$; $(0, 0, \sqrt{2/3}a)$
- 2 atoms in the basis: $(0, 0, 0)$ and $(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$
- The spheres are arranged in the same triangular structure, but the spheres in the next plane are aligned with the spheres in the bottom plane. The sequence is therefore ABABAB...

* Body Centred Cubic

- Bonds have some directional character (like covalent bonds).
- Has cubic lattice vectors, but only 2 atoms in cubic unit cell: $(0, 0, 0)$ & $(0.5, 0.5, 0.5)$
- Each atom has 8 nearest neighbours at $\sqrt{3} \frac{a}{2}$

	FCC	bcc	hcp
Examples of Metals	Al, Cu, γ Fe	Cr, Mo, α Fe	Co, Zn, Ti
Coordination Number	12	8	12
Packing Fraction	0.74	0.68	0.74


Covalent Crystal Structures

- Covalent crystal structures are dominated by the directionality of the covalent bonds, imposed by the directionality of the atomic orbitals of the interacting atoms.
- The positions of the atoms surrounding a particular atom are determined by the lengths and direction of the bonds.

Ionic Crystal Structures

- Dominated by the necessity of surrounding positive ions (cations) by negative ions (anions) and vice versa.
- Electrostatic energy is minimised by maximising the number of ions of opposite

Charge in contact with the ion.

- To predict structure, we impose the rule that all surrounding neighbours must touch the ion. This limits the number of neighbours, and the number decreases as the size of neighbours ~~decreases~~ increases.
- Geometric calculations about the size of the holes when a number of spheres arranged so that they touch tell us how many neighbours to expect for a particular ratio of ion size. The lower limit of these ratios can be estimated by calculating the size of the largest sphere that can fit inside a set of spheres (radii 1 unit) arranged in the shape. 
- Cations tend to be smaller than anions because there is less screening of the nuclear charge by the inner electrons.

X-Ray Diffraction

- We can observe diffraction phenomena by x-rays incident on planes of atoms in a crystal.
- Reflected waves will be in phase if the path difference is an integer number of wavelengths:

Bragg's Law: $n\lambda = 2d\sin\theta$

θ = angle between wave & crystal plane

n = order of reflection

λ = Wavelength of x-rays

d = Spacing between plane.

- x-rays tend to have $\lambda \rightarrow 0.1\text{nm}$ to 10nm
- λ of 0.154nm comparable to interatomic distances.

- The Spacing, d , is given by: $d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$ (Spacing between plane)

Note: Since $\sin\theta \leq 1$, the smallest interplanar spacing that can be measured is $\frac{\lambda}{2}$

- In these diffraction processes, the probability of satisfying the Bragg condition is very small, we either use a broad range of λ or a broad range of θ .

- For a rotating crystal, we fix λ and then rotate the crystal, the intensity of the signal is measured at various values of θ .
- Low angle Diffraction utilises a broad spectrum of λ , and we fix the crystal in place. A pattern of spots is obtained. The spots become smeared or deformed if the crystal is strained or defective in some way. We can use this to determine how perfect a crystal is.

Defects

- Defects in a crystal structure are imperfections in the lattice, they can affect:
 - Mechanical properties: Defects can increase yield strength.
 - Electrical properties: Semiconductors are doped with impurities.
 - Optical properties.
- Three types of defect:
 - Point defects (classified by dimensionality)
 - Line defects
 - Planar defects

Point defects

- Several types:
 - Vacancy: An atom missing from a lattice site.
 - Interstitial: An atom in a position that is not a lattice site.
 - Substitutional impurity: A crystal atom is replaced by a different type of atom.
 - Interstitial impurity: Impurity atom sitting between lattice sites.
- Point defects (vacancies and interstitials) cost energy to create in a crystal. We can estimate the vacancy energy by counting the number of broken bonds and multiplying by the bond energy.
- Defects also increase the entropy of a crystal, therefore at a finite temperature there is a finite concentration of vacancies in equilibrium. Gibbs free energy can be lowered by creating vacancies.

- It can be shown that the equilibrium concentration of Vacancies is given by:

$$\frac{N_v}{N} = e^{-\left(\frac{E_v}{k_B T}\right)}$$

Where N_v = number of Vacancies E_v = Vacancy Energy
 (Don't need to remember) N = Number of lattice sites T = Temperature

- As temperature increases, the number of Vacancies increases.
- Frenkel Pairs: When atoms have enough thermal energy to move from a lattice site into a nearby interstitial site. This can also occur by radiation.

Line Defects

- Dislocations are line defects, where the crystal structure is disrupted along a continuous line. The structure is well-defined, but the bonds are stretched and atoms are moved from ideal positions.
- Dislocations have a strong influence on the mechanical properties of solids. They make it possible for planes of atoms to slip over each other.
- The simplest type of dislocation can be visualised as an extra partial plane of atoms in a crystal. The crystal structure is not defined along the edge of the plane - this is the line defect.

Properties:

- 1) Dislocation lines are continuous, they either form loops or they end at the surface.
- 2) Dislocations are sources of long range stress fields in crystals.
- 3) Cost a lot of energy - never an equilibrium property
- 4) Motion is inhibited by other defects.

- Dislocations move under an applied shear stress, planes of atoms slip past each other, resulting in permanent deformation known as plastic deformation.

- Adding defects will increase the value of σ at which a solid breaks

Planar Defects

- Grain boundaries - Most solids are polycrystalline, they are made from grains with different crystallographic orientations. The grain boundary is the plane between grains of different orientation.