

# CHAPTER I: REAL GASES

## VAN DER WAALS EQUATION OF STATE

(non-ideal gas equation / real gas equation)

> real gas equation :  $pV = nRT$

> van der Waals - 2 modifications

gas molecules have a size  
gas molecules ATTRACT each other

• charge-density fluctuations lead to attraction of neutral atoms/molecules

atom 1 atom 2



dipole & fluctuating charge density



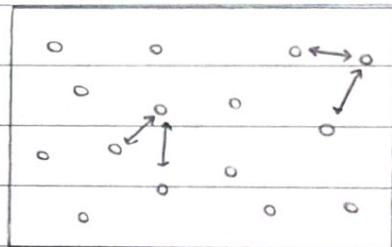
dipole induced by el. field atom atom 1

• MODIFICATION 1: There is an attraction between the molecules \*

→ REDUCTION IN PRESSURE :  $P_{\text{real}} < P_{\text{ideal}}$

$$P_{\text{r}} = P_i - a \left( \frac{n}{V} \right) \left( \frac{n}{V} \right)$$

related to strength of interaction  
(attraction between molecules)

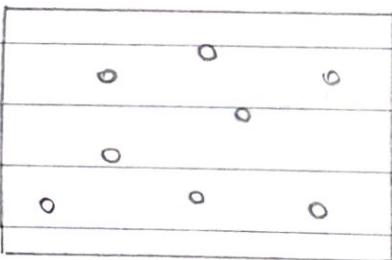


• MODIFICATION 2: molecules have a volume \*

$$V_{\text{real}} > V_{\text{ideal}}$$

$$V_{\text{real}} = V_{\text{ideal}} + b n$$

related to the size of the molecules



⇒ add in modifications,  $P_{\text{r}} = P_i + a \left( \frac{n}{V} \right)^2$

to ideal gas equation:  $V_i = V_r - bn$

$$P_i V_i = nRT$$

⇒

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

van der Waals equation of state

> we define:

$$V_m = \frac{V}{n}$$

→ volume per mole (specific volume)

→ intensive parameter (p,T)

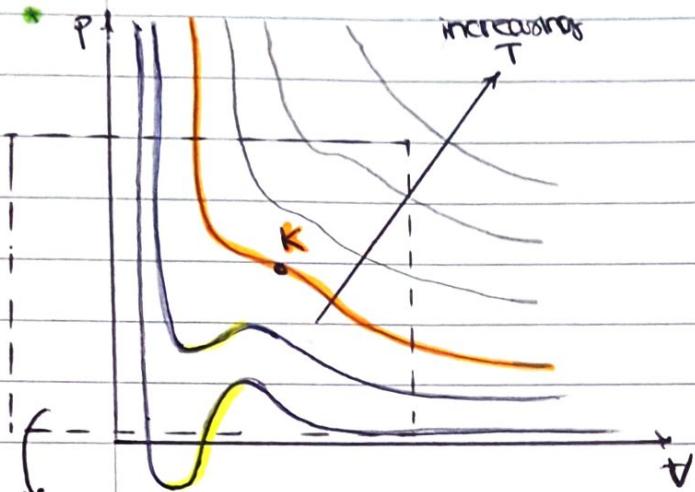
→ it is the same for any gas

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

$$\Rightarrow PV_m^3 - (pb + RT)V_m^2 + aV_m - ab = 0$$

↳ 3 solutions for volume for 1 pressure

## MAXWELL'S AREA CONSTRUCTION

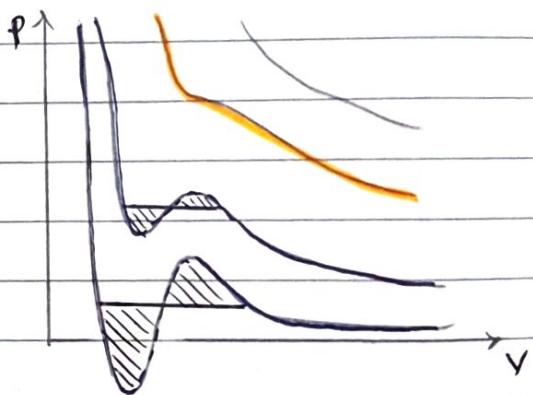


- > Van der Waals equation is expected to be valid near the critical point
- > for low T and V - difficult to compress atoms close together
- >  $K = \text{critical temperature}$

regions at lower temp: increase in pressure  $\Rightarrow$  decrease in volume

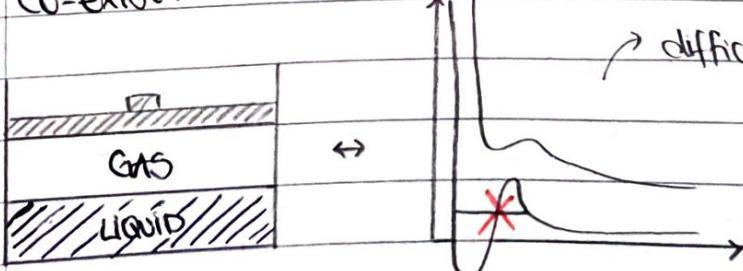
### MAXWELL'S AREA CONSTRUCTION

1. Draw straight lines so that equal area above and below line
2. This mimics the experiment
3. Occurs at one value p / Temp point
4. Liquids and gases can co-exist



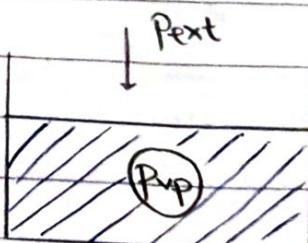
### Liquid phase co-existence

- \* Pressure of gas in equilibrium with its liquid phase (or with its solid phase) is called the 'saturated vapour pressure',  $p_{\text{vp}}(T)$ .
- > for each temperature there's a pressure where liquid and gas co-exist.

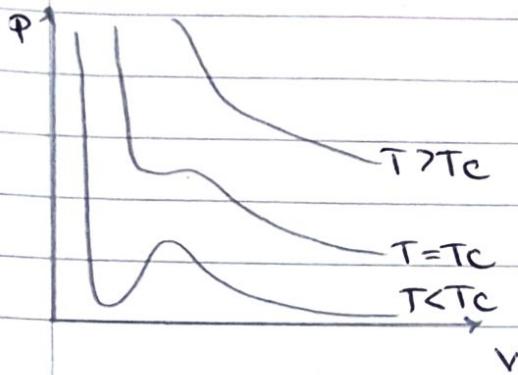


### Boiling

- > open container:  $T^* = p_{\text{vp}} > p_{\text{ext}}$
- $\rightarrow$  liquid will boil



## \* CRITICAL TEMPERATURE / PRESSURE / VOLUME



$$\left[ p + \frac{a}{V_m^2} \right] (V_m - b) = RT \quad (*)$$

Turning points:  $\left( \frac{dp}{dV} \right)_T = 0$

Point of inflection:  $\left( \frac{d^2p}{dV^2} \right)_T = 0$

$$(*) p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

① Find critical volume

$$\begin{aligned} \left( \frac{dp}{dV} \right)_T &= -\frac{RT}{(V_m - b)^2} + \frac{2a}{V^3} = 0 \Rightarrow RT = \frac{2a(V_m - b)^2}{V_m^3} \\ \left( \frac{d^2p}{dV^2} \right)_T &= \frac{2RT}{(V_m - b)^3} - \frac{6a}{V^4} = 0 \Rightarrow RT = \frac{6a(V_m - b)^3}{V_m^4} \end{aligned} \quad \left. \begin{aligned} \frac{2a(V_m - b)^2}{V_m^3} &= \frac{6a(V_m - b)^3}{V_m^4} \Rightarrow \frac{3(V_m - b)}{V_m} = 2 \Rightarrow V_m = 3b \\ V_c &= 3b \end{aligned} \right\} =$$

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

② Find critical temp

$$\text{Substitute: } RT_c = \frac{2a(3b - b)^2}{(3b)^3} = \frac{2a \cdot 4b^2}{27b^3}$$

$$\Rightarrow T_c = \frac{8a}{27bR}$$

③ Substitute  $V_c$  &  $T_c$  in vdW

Find critical pressure

$$p_c = \frac{RT_c}{V_c - b} - \frac{a}{V_c^2} = \frac{R \cdot 8a}{27bR} \cdot \frac{1}{3b - b} - \frac{a}{9b^2} = \frac{4a}{27b^2} - \frac{a}{9b^2} = \frac{a}{27b^2}$$

$$\Rightarrow p_c = \frac{a}{27b^2}$$

$\times V_c = 3b$

$\times T_c = \frac{8a}{27bR}$

$\times p_c = \frac{a}{27b^2}$

POINT OF INFLECTION = there is no liquid-gas transition

= CRITICAL POINT

→ above it ( $T$ ) gas & liquid are indistinguishable

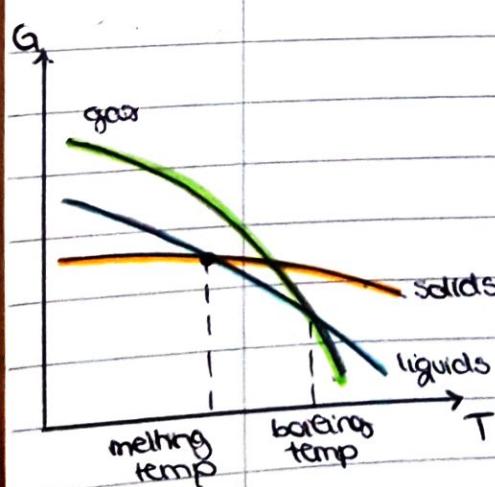
# CHAPTER 6: PHASE DIAGRAMS & PHASE TRANSITION

- \* Phase = homogeneous portion of matter with uniform properties and composition
  - \* e.g.: solid, liquid, gas  
colloids, liquid crystals, plasma, gel, solution
- \* Equilibrium phase = phase with the lowest Gibbs free energy
  - $G = H - TS$
  - $= U + PV - TS$

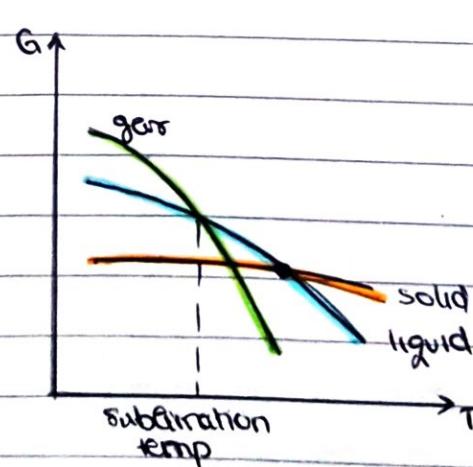
|         | U  | -TS   | PV                        |
|---------|--|---|---------------------------|
| SOLID:  | <ul style="list-style-type: none"> <li>- atoms close together</li> <li>- U large &amp; negative</li> </ul> | <ul style="list-style-type: none"> <li>- solids highly ordered</li> <li>- S is low</li> </ul> | - V close to minimum      |
| GAS:    | <ul style="list-style-type: none"> <li>- atoms far apart</li> <li>- U small &amp; negative</li> </ul>      | <ul style="list-style-type: none"> <li>- atoms are disordered</li> <li>- S is high</li> </ul> | - V is very high          |
| LIQUID: | <ul style="list-style-type: none"> <li>- similar</li> <li>- less negative than solid</li> </ul>            | <ul style="list-style-type: none"> <li>- S slightly higher than solid</li> </ul>              | - V very similar to solid |

- \* G vs T plots for solid, liquid and gas

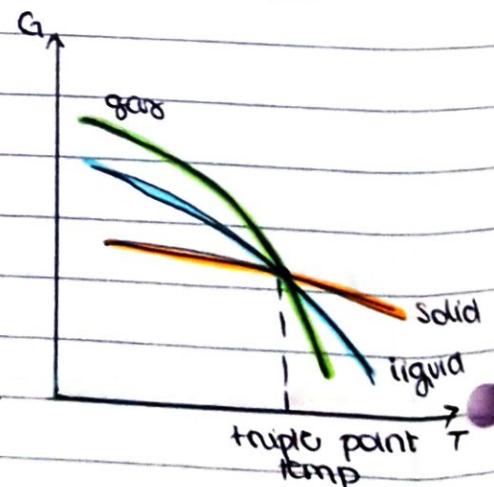
①  $P > P_{\text{triple}}$



②  $P < P_{\text{triple}}$

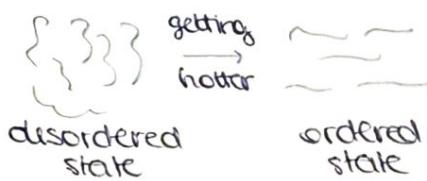


③  $P = P_{\text{triple}}$



Phase transition = discontinuous change in the properties of a substance as its environment is changed only infinitesimally

- we showed : heating the elastic band  $\Rightarrow$  heat up



- heating elastic bands with a device  $\Rightarrow$  they contract

$$Q_L = L \cdot m \quad Q_L = T \Delta S$$

$$\Delta S = Q_{rev} / T$$

### Co-existing phases

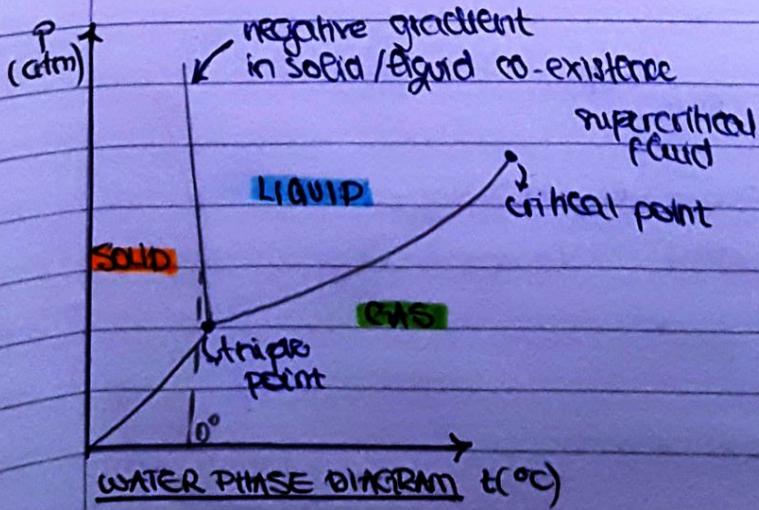
$\rightarrow$  the 'lines' on a 2D phase diagram are co-existence lines or phase lines.

- $\rightarrow$  at points on those lines 2 phases can co-exist in equilibrium
  - $\hookrightarrow$  they have the same Gibbs free energy
- $\rightarrow$  triple point = a point on a phase diagram where all 3 lines meet (G<sub>e</sub> = G<sub>s</sub> = G<sub>g</sub>)

### SUPERCRITICAL CO<sub>2</sub>:

Critical point = the point on the phase diagram above which the liquid and gas phases have the same density / are indistinguishable

$\rightarrow$  above critical temp  $\Rightarrow$  no phase transition



$\rightarrow$  solid water (ice) is less dense than liquid water!

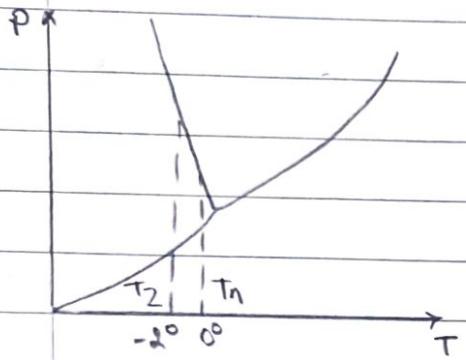
## THE CLAPEYRON EQUATION

- $\frac{dp}{dT} = \frac{L}{T\Delta V_s}$

$p$  = pressure  
 $T$  = temperature [K]  
 $L$  = latent heat [ $J/kg$ ]  
 $V_s$  = specific volume [ $m^3/kg$ ]

example: estimate the excess pressure required to decrease the melting point of ice by  $2^\circ C$ .  $f_{ice} = 916 \text{ kg/m}^3$ ;  $f_{water} = 10^3 \text{ kg/m}^3$

$$L = 334 \cdot 10^3 \text{ J/kg}$$



$$\frac{dp}{dT} = \frac{L}{T\Delta V_s} \leftrightarrow$$

$$\Rightarrow \Delta p = \frac{L}{\Delta V_s} \frac{1}{T} dT \quad (=)$$

$$(\text{F}) \int_{P_1}^{P_2} dp = \frac{L}{\Delta V_s} \int_{T_1}^{T_2} \frac{1}{T} dT \quad (=)$$

$$(\text{F}) P_2 - P_1 = \frac{L}{\Delta V_s} (\ln T_2 - \ln T_1) \quad (=)$$

$$(\text{F}) \Delta p = \frac{L}{\Delta V_s} \ln \frac{T_2}{T_1} \quad (=)$$

$$\Delta V_s = \frac{1}{f_{water}} - \frac{1}{f_{ice}} = \frac{1}{1000} - \frac{1}{916} = -9,17 \times 10^{-5} \text{ m}^3/\text{kg}$$

$$(\text{F}) \Rightarrow \Delta p = \frac{334 \times 10^3}{-9,17 \times 10^{-5}} \times \ln \left( \frac{273,15 - 2}{273,15} \right) = 26,6 \text{ MPa}$$

## THE CLAUSIUS-CLAPEYRON EQUATION

### DERIVATION:

$$\frac{dp}{dT} = \frac{L}{T\Delta V_s} \quad (\text{F}) \quad \Rightarrow \quad dp = \frac{L}{T\Delta V_s} dT$$

- Assumption 1:  $\Delta V_s = V_{gas} - V_{liquid} \approx V_{gas}$

- Assumption 2: gas is ideal  $\Rightarrow V_{sgas} = \frac{RT}{P}$ ;  $V_s = \frac{V}{n}$

$$\Rightarrow dp = \frac{LP}{RT^2} dT$$

- Assumption 3: L has no T dependence

$$\int_{P_1}^{P_2} \frac{1}{P} dP = \int_{T_1}^{T_2} \frac{L}{R} \frac{1}{T^2} dT \quad (\rightarrow)$$

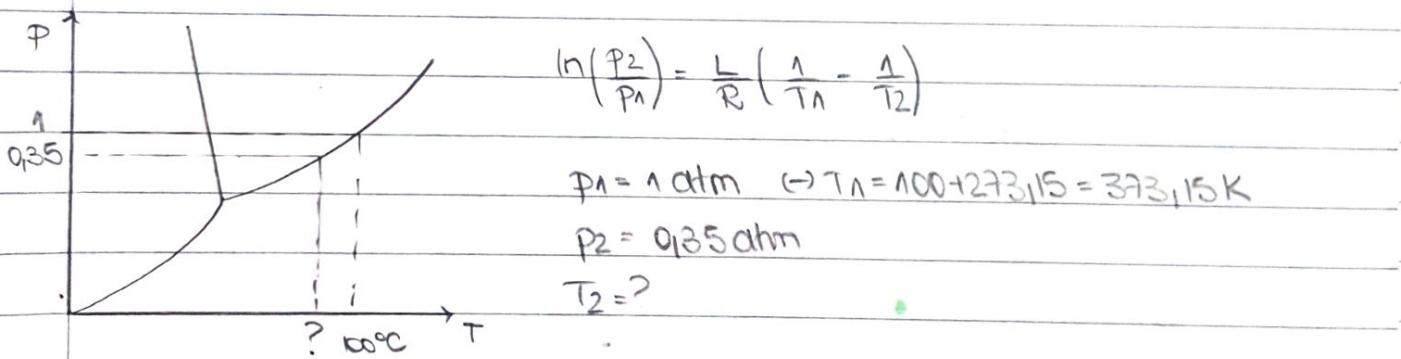
$$\Leftrightarrow \ln P_2 - \ln P_1 = \frac{L}{R} \cdot \left[ -\frac{1}{T} \right]_{T_1}^{T_2} \quad (\rightarrow)$$

$$\Leftrightarrow \ln \left( \frac{P_2}{P_1} \right) = \frac{L}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\bullet \ln \left( \frac{P_2}{P_1} \right) = \frac{L}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right] \rightarrow$$

Clausius-Clapeyron equation.

example: Calculate the boiling temperature of water at the top of a mountain where the atmospheric pressure is 0,35 atm. The latent heat of vaporization of water is 40,5 kJ/mole.



$$\ln \left( \frac{P_2}{P_1} \right) \frac{R}{L} = \frac{1}{T_1} - \frac{1}{T_2} \rightarrow \frac{1}{T_2} = \frac{1}{T_1} - \frac{R}{L} \cdot \ln \left( \frac{P_2}{P_1} \right) =$$

$$= \frac{1}{373,15} - \frac{8,3145}{40,5 \cdot 10^3} \cdot \ln \left( \frac{0,35}{1} \right) = 2,895 \times 10^{-3}$$

$$\Rightarrow T_2 = \frac{1}{2,895 \times 10^{-3}} = 345,423 \text{ K} \Rightarrow t_2 \approx 72,2^\circ \text{C}$$

# CHAPTER III. SOLIDS

SOLIDS = that which is dimensionally stable, i.e. has a volume of its own

## CLASSIFICATION:

### A. ORDERED

- regular arrangements of atoms
- long-range order
- crystalline
- CRYSTAL

### B. DISORDERED

- random arrangement of atoms
- short-range order
- amorphous
- GLASS

Electronegativity (PAULING) → a measure of an atom's tendency to attract electrons toward itself.

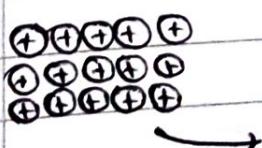
### ① ionic Bonding

- > compounds of elements with very different electronegativity
- > salts, rocks
- > hard, brittle, insulators, high melting temp.
- > electrostatic interactions described by COULOMBS POTENTIAL



### ② covalent bonding

- > solids with one or more element with similar electronegativities



> silicon, diamond

- > very hard, brittle, insulators or semiconductors
- > interactions described by MORSE POTENTIAL

### ⑤ METALLIC BONDING

- > between atoms with low electronegativity
- > delocalized electrons & metal ions
- > copper, aluminium
- > ductile, moderate melting temp., electrical / thermal conductors, opaque
- > prop. described by models in which  $e^-$  move in a COULOMBIC POTENTIAL of nucleus (next year)

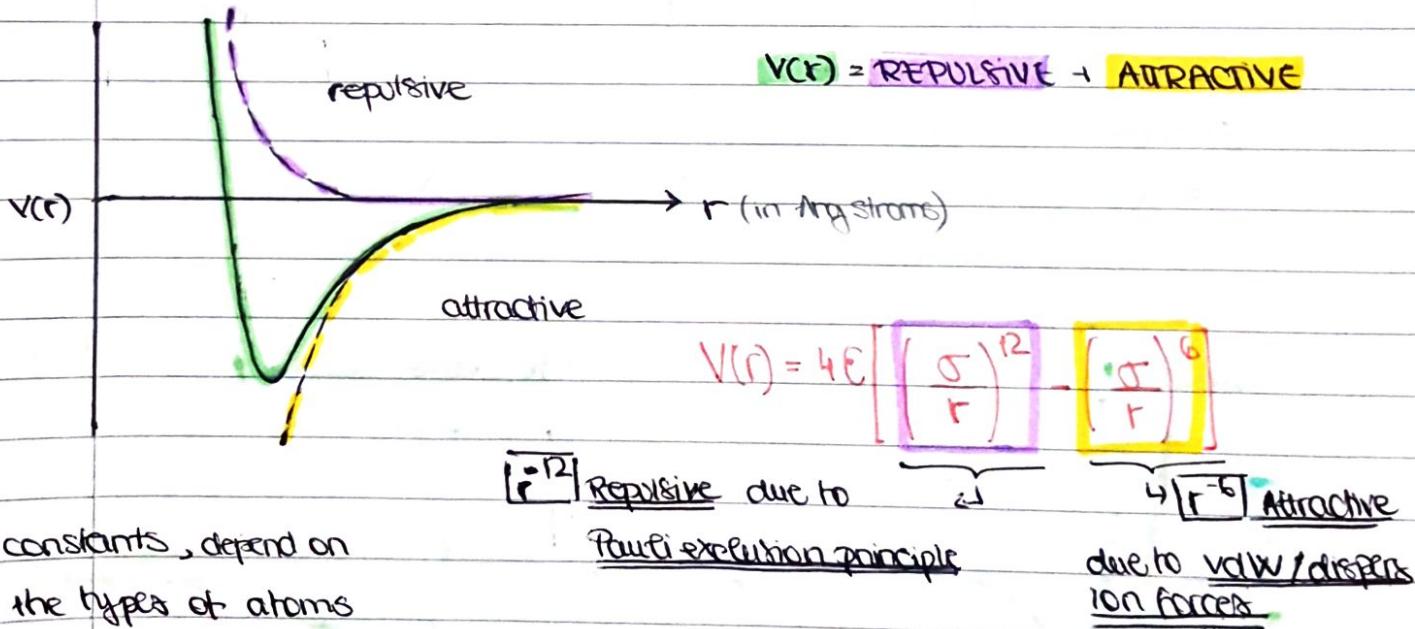
### ⑥ VAN DER WAALS / MOLECULAR BONDING

- > soft, weak, low melting temp., el. insulators
- > noble gases, wax, CO<sub>2</sub>
- > interactions described by VAN DER WAALS POTENTIAL

bond strength: VAN DER WAALS < METALLIC ~ COULOMB < COVALENT

INTERATOMIC POTENTIALS - a mathematical function for calculating the potential energy,  $V(r)$ , of one atom as a function of distance from another.

### VAN DER WAALS POTENTIAL / LENNARD JONES POTENTIAL

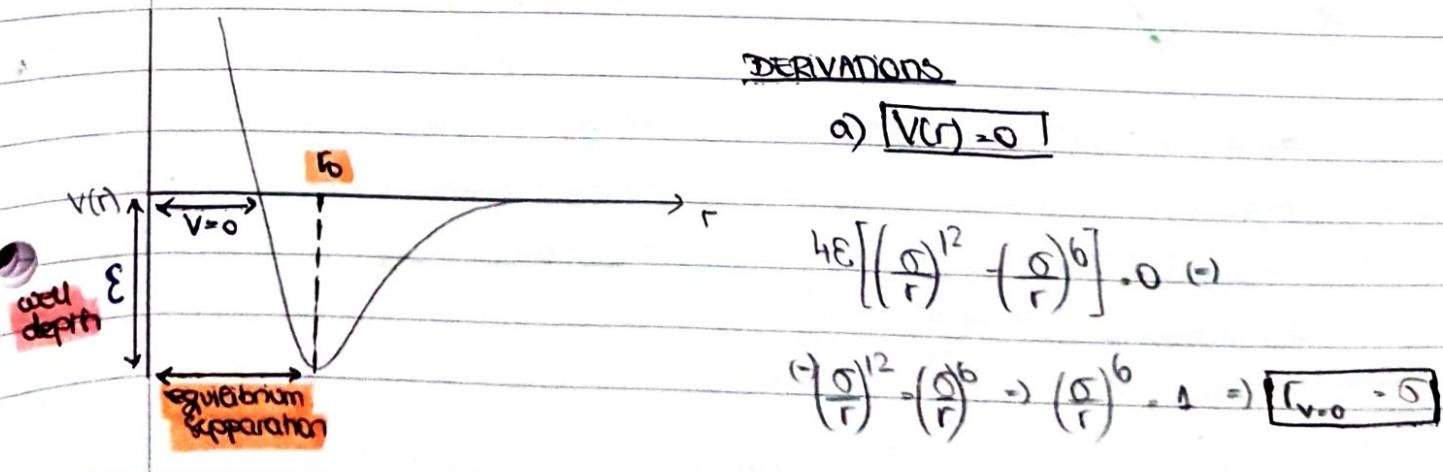


### DERIVATIONS

a)  $[V(r) = 0]$

$$4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] = 0 \quad (-)$$

$$\left( \frac{\sigma}{r} \right)^{12} = \left( \frac{\sigma}{r} \right)^6 \Rightarrow \left( \frac{\sigma}{r} \right)^6 = 1 \Rightarrow r_{v=0} = \sigma$$



## b) EQUILIBRIUM SEPARATION

For the minimum:  $\frac{dV(r)}{dr} = 0$  key!

$$\frac{dV}{dr} = 4\epsilon \left[ -\frac{12\sigma^{12}}{r^{13}} + \frac{6\sigma^6}{r^7} \right] = 0 \quad (\Rightarrow)$$

$$\Leftrightarrow \frac{12\sigma^{12}}{r^{13}} = \frac{6\sigma^6}{r^7} \quad (\Rightarrow) \quad \frac{2\sigma^6}{r^6} = 1 \Rightarrow 2\sigma^6 = r^6$$

$$\Rightarrow r_0 = 2^{1/6} \sigma$$

## c) WELL DEPTH

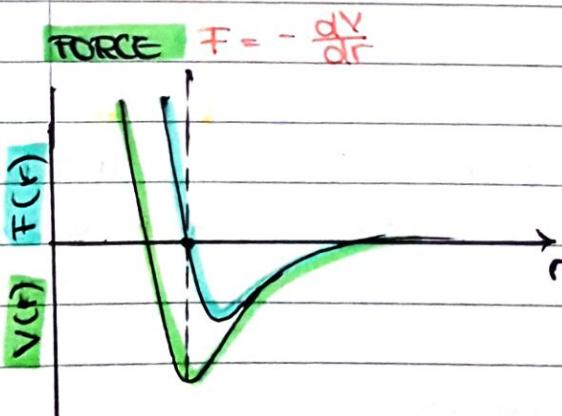
$$V(r_0) = 4\epsilon \left[ \left(\frac{\sigma}{r_0}\right)^{12} - \left(\frac{\sigma}{r_0}\right)^6 \right] ; \quad r_0 = 2^{1/6} \sigma \quad \text{key!}$$

$$V(r_0) = 4\epsilon \left[ \left(\frac{\sigma}{2^{1/6}\sigma}\right)^{12} - \left(\frac{\sigma}{2^{1/6}\sigma}\right)^6 \right] = 4\epsilon \left[ \frac{1}{4} - \frac{1}{2} \right] = -4\epsilon \frac{1}{4} = -\epsilon$$

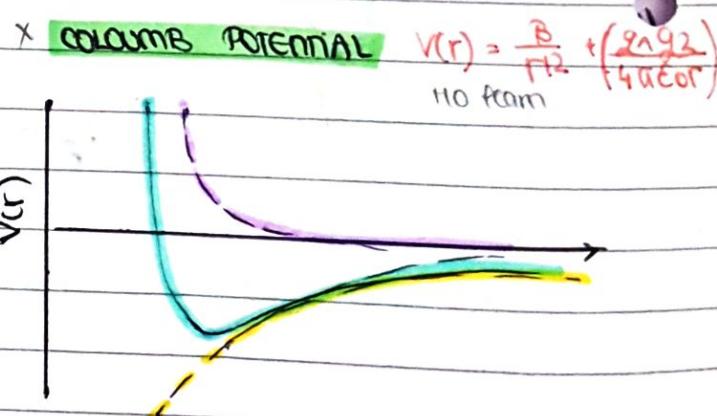
$$\Rightarrow \text{Well depth : } -\epsilon$$

Relationship between:

- > cohesive energy & well depth
- > equilibrium separation (minimum)



- strong repulsive force at short r
- attractive force at longer
- force is 0 at equil sep.

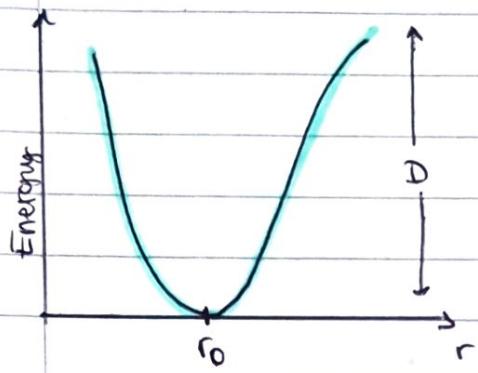


- $g_1, g_2$  charges of particles 1 & 2
- $\epsilon_0$  = permittivity of free space
- Ionic Bonding

### MORSE POTENTIAL

$$V(r) = D(e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)})$$

r₀ = min



$\alpha$  = constant related to width of potential

$D$  = well depth (different for diff atoms)

$r_0$  = equiv sep.

- COVALENT BONDING

$$E \propto \frac{d^2V}{dr^2} \text{ at } r_0$$

↳ young's modulus

### Thermal Expansion

Thermal expansion coefficient  $\alpha$  is defined as the fractional change in length ( $\Delta L/L$ ) of a solid divided by the temperature change ( $\Delta T$ )

$$\Delta L = \alpha L \Delta T$$

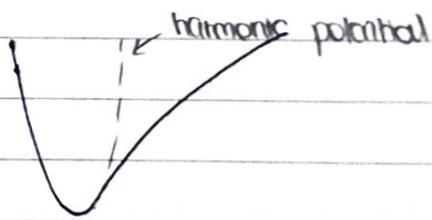
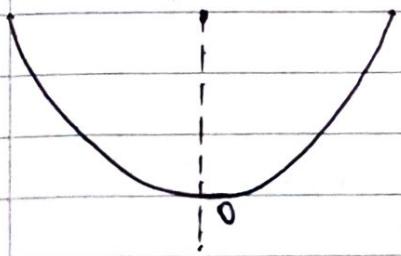
### Thermal Expansion from Interatomic Potential

↗ increasing Energy  $\rightarrow$

- ↗ increasing  $T \rightarrow$  giving  $E$  to atoms  $\rightarrow$  vibrating about equil position
- ↗ move apart from one another (not towards each other)  $\leftarrow$  shape of  $V(r)$

⊗ harmonic potential

shape of Lennard Jones potential



thermal expansion is due to ANTHARMONISITY OF THE WELL

### Cohesive Energy

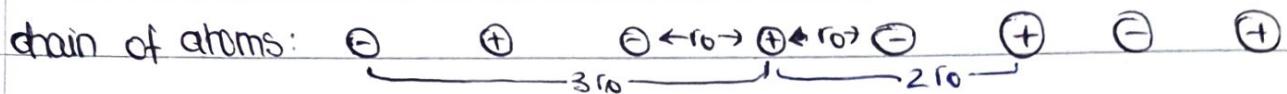
Cohesive energy = energy required to separate all the atoms to infinity  
 - it is always positive

- ↳ this value (but negative) is normally written as  $U$
- related to melting / boiling temp.

## Cohesive energy calculations (example)

$$V(r) = \frac{B}{r^12} + \left( \frac{q_1 q_2}{4\pi \epsilon_0 r} \right)$$

For a pair of ions, cohesive energy,  $U = -V(r) \approx -\left(\frac{q_1 q_2}{4\pi \epsilon_0 r}\right)$   
 as  $1/r^{12}$  is a small correction at  $r_0$ .



$$q_1 = +, q_2 = -$$

$$\Rightarrow U = -\frac{e \cdot e}{4\pi \epsilon_0 r_0} \times 2 + \frac{e \cdot e}{4\pi \epsilon_0 (2r_0)} \times 2 - \frac{e \cdot e}{4\pi \epsilon_0 (3r_0)} \times 2 + \dots$$

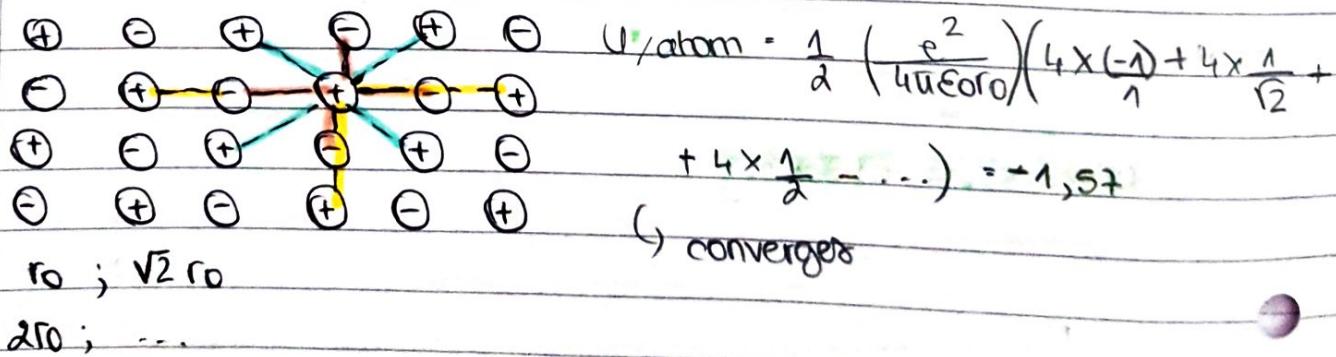
$$U = \left( \frac{2e^2}{4\pi \epsilon_0 r_0} \right) \left( -1 + \frac{1}{2} - \frac{1}{3} + \dots \right)$$

BUT FOR 1 atom:  $U/\text{atom} = \frac{1}{2} \left( \frac{2e^2}{4\pi \epsilon_0 r_0} \right) \left( -1 + \frac{1}{2} - \frac{1}{3} + \frac{1}{4} - \dots \right)$   
 ↳ to avoid doublecounting

Taylor expansion of  $\frac{1}{x}$ :  $\ln(1+x) = (x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \dots)$   
 ↳ where  $x=1$

$$U/\text{atom} = -\ln 2 \left( \frac{1}{2} \left( \frac{2e^2}{4\pi \epsilon_0 r_0} \right) \right)$$

Cohesive energy per atom: SQUARE LATTICE SPACING  $r_0$



# CHAPTER II: MECHANICAL PROPERTIES

## STRESS AND STRAIN

> Applying a force to the end of a rod induces a STRESS

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

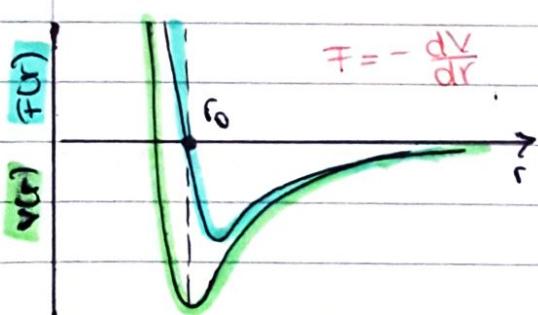
> For a tensile force (pulling apart) we induce a STRAIN  $\epsilon$

$$\epsilon = \frac{\Delta L}{L}$$

> Young's modulus = a measure of the ability of a material to withstand changes in length under tension (or compression)

$$E = \frac{\sigma}{\epsilon}$$

## INTERATOMIC POTENTIALS



> the steeper the gradient of  $V(r)$  the more force is required to deform the atoms from their equilibrium positions  $r_0 \rightarrow$  higher the Young's modulus

$$E \propto \frac{d^2V}{dr^2} \quad \text{at } r_0$$

② for cubic lattice:

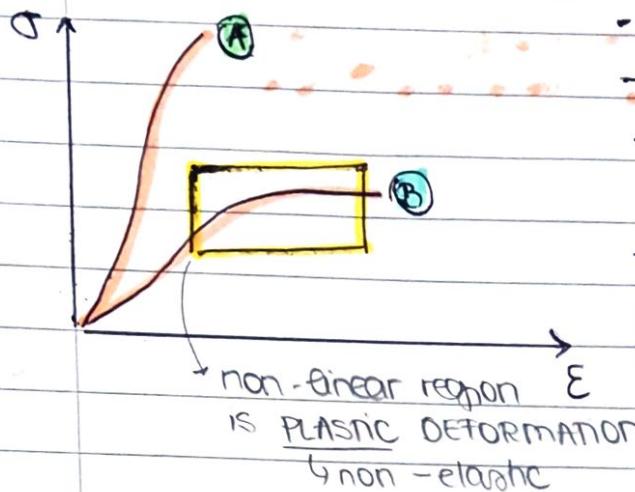
$$E = \frac{1}{a} \frac{d^2V}{dr^2} \Big|_a$$

Young's modulus is proportional to the 2nd derivative of the interatomic potential curve at equilibrium separation

## EXAMPLES

| BOND TYPE     | E <sub>calc</sub> | E <sub>exp</sub>        |
|---------------|-------------------|-------------------------|
| COVALENT      | 200-1000 GPa      | diamond: 1000 GPa       |
| METALLIC      | 60-300 GPa        | aluminium: 69 GPa       |
| IONIC         | 30-100 GPa        | sodium chloride: 40 GPa |
| VAN DER WAALS | 2-4 GPa           | nylon: ~3 GPa           |

## STRESS-STRAIN CURVES



- linear relationship in low stress regime
- gradient = Young's modulus :  $E = \sigma / \epsilon$
- A COVALENT Bonding  
↳ stiff material, large E, brittle
- B METALLIC Bonding  
↳ initially linear  $\Rightarrow$  shape changes

ELASTIC ENERGY - the potential energy stored in a material as work is performed to distort its shape

Apply a force  $\rightarrow$  stretch bonds do work on material  $\rightarrow$  tensile stress

$$\text{F}\Delta\text{L} = FdL$$

↳ work done on material

$$V = A\epsilon$$

↳ volume

$$dE = dL \quad [\epsilon = \frac{\Delta L}{L}]$$

$$\rightarrow W = \frac{F}{V} \cdot V dL = \frac{F}{A} \frac{d\epsilon}{\epsilon} \cdot V$$

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

$$\int W = V \sigma dE$$

$$dU = Q + W$$

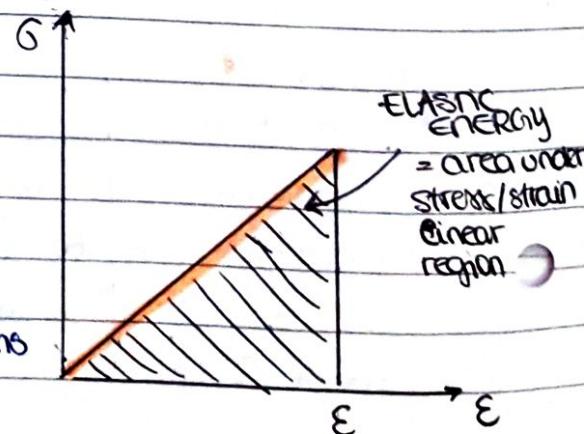
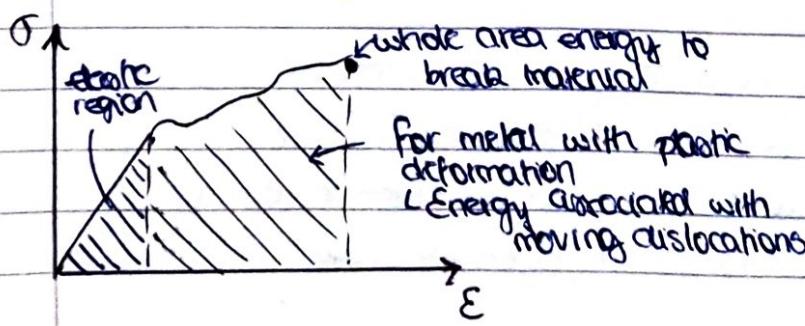
Assume work is all going into ~~internal~~ internal energy (no Q)

$$\Rightarrow dU = V \sigma dE$$

Deform a material from a strain = 0 to strain =  $\epsilon$

$$\begin{aligned} \frac{U}{V} &= \int_0^\epsilon \sigma dE = \epsilon \int_0^\epsilon \sigma dE = \\ &= E \left[ \frac{1}{2} \epsilon^2 \right]_0^\epsilon = \frac{1}{2} E \epsilon^2 = \frac{1}{2} \sigma \epsilon \end{aligned}$$

$$\frac{U}{V} = \frac{1}{2} \sigma \epsilon \rightarrow \text{elastic energy stored per unit volume}$$

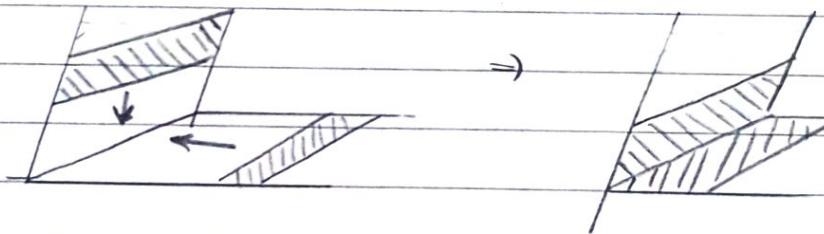


## Mechanism of Plastic Deformation : microscopic picture of deformation

- > metals stretch and bend (and stay bent)
- > real materials have defects
- > dislocations = 'LINE DEFECTS'
  - extra plane of atoms in crystal
- > metallic bonding is prone to dislocations
- > dislocation moves through the crystal lattice (caterspurs, ruts)

## WORK HARDENING

- > dislocations move through material and meet at grain boundaries, different directions
- > They pile up / get stuck  $\rightarrow$  the material is work hardened
  - ? can hardening certain metals (Al, Cu, Steel) at low T



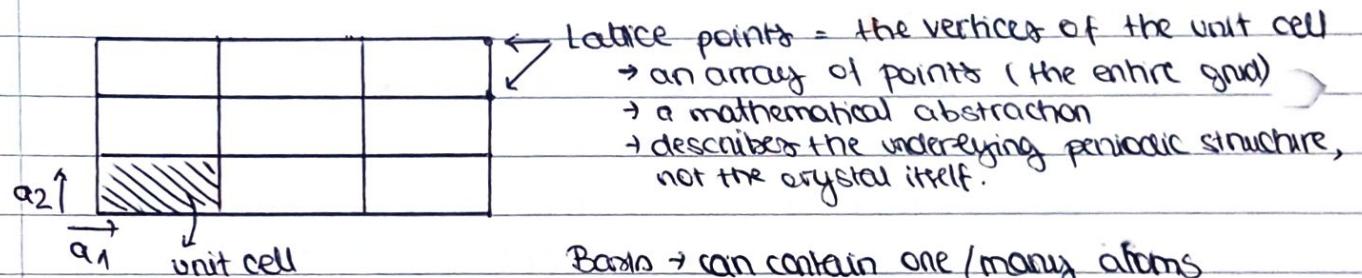
# CHAPTER 11 CRYSTALS

**CRYSTAL** = solid in which the comprising atoms / ions / molecules form a periodic arrangement

**LATTICE** = an infinite set of identical points within the crystal (a grid of points)

**UNIT CELL** = is the repeat unit (lego brick)

**BASIS** = content of a unit cell



Basis → can contain one / many atoms

↑ constituents of basis ∈ "fractional coordinates"

⇒ CRYSTAL STRUCTURE = convolution of basis and lattice



**LATTICE POINTS** = points of the lattice

→ if lattice point is at the origin =)

$$2D: \underline{\Gamma} = l\underline{a}_1 + m\underline{a}_2$$

$$3D: \underline{\Gamma} = l\underline{a}_1 + m\underline{a}_2 + n\underline{a}_3$$

**BRAVAI'S LATTICE** = an infinite periodic lattice that displays translational invariance (it looks the same from every lattice point)

→ only certain shapes that can tile without gaps

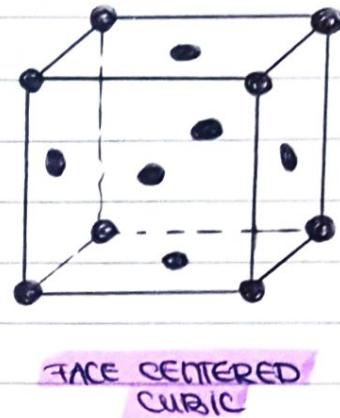
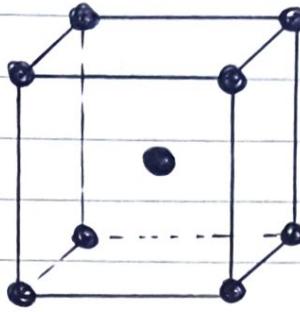
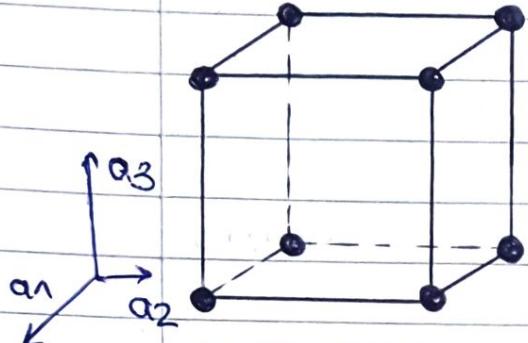
→ 2D: 5 distinct Bravais lattices

→ 3D: 14 distinct Bravais lattices

↳ arranged into 7 "classes" / "systems" that reflect their symmetry

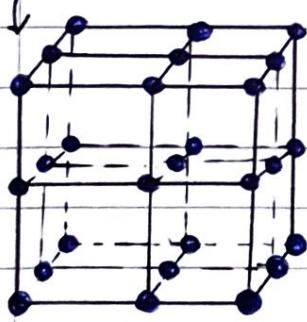
## CUBIC LATTICES

$$a=b=c; \alpha=\beta=\gamma=90^\circ$$



|                             | simple cubic | body-centered | face-centered |
|-----------------------------|--------------|---------------|---------------|
| No. of lattice sites        | 1            | 2             | 4             |
| Coord no./nearest neighbour | 6 / 12       | 8 / 6         | 12 / 6        |
| Packing fraction            | 0,52         | 0,68          | 0,74          |

ALPHA-POLONIUM = only known element with a simple cubic with a single atom basis.



PRIMITIVE UNIT CELL = minimum area/volume that when translated by all Bravais lattice vectors just fills space.

→ not uniquely defined

→ each primitive unit cell contains one and only one lattice site.

→ does not always reflect the symmetry of the lattice

→ each primitive unit cell has the same area.

## PACKING FRACTION

= unitless number of the amount of volume compared with its volume.

→ calculation for cubic calc: the ratio of the total volume of objects packed into space to the volume of that space.

APF = atomic packing fraction

$$\boxed{\text{APF} = \frac{N_a \cdot V_a}{V_u}}$$

$$N_a = \text{no. of atoms in unit cell}$$

$$V_a = \text{volume of 1 atom}$$

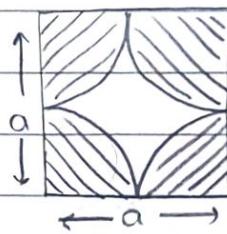
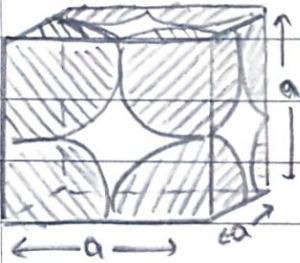
$$= \frac{4}{3} \pi r^3$$

→ fill unit cells with hard spheres

$$V_u = \text{volume of unit cell}$$

$$= a^3$$

### 1) SIMPLE CUBIC



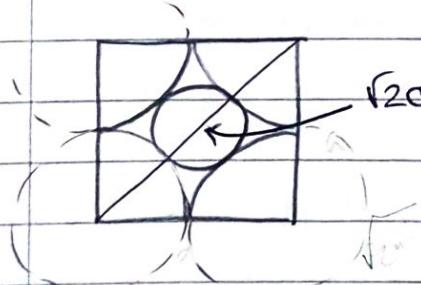
radius of 1 sphere

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

1 atom for simple cubic

$$\rightarrow \text{APF} = \frac{1 \times \frac{4}{3} \pi \left(\frac{a}{2}\right)^3}{a^3} = \frac{\frac{4}{3} \pi \frac{a^3}{8}}{a^3} - \frac{\pi}{6} = 0,52$$

### 2) FACE CENTERED CUBIC



4 atoms in unit cell

radius of 1 sphere

$$r = \frac{\sqrt{2}a}{4}$$

$$\rightarrow \text{APF} = \frac{4 \times \frac{4}{3} \pi \left(\frac{\sqrt{2}a}{4}\right)^3}{a^3} = 0,74$$

### 3) BODY CENTERED CUBIC → PSC

## PLANES AND MILLER INDICES

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

$$\vec{t} = u\vec{a}_1 + v\vec{a}_2 + w\vec{a}_3$$

$$\hookrightarrow [u, v, w]$$

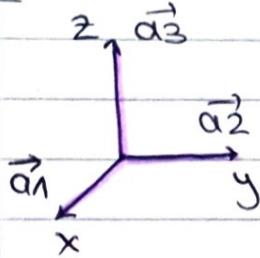
$$\Rightarrow \text{volume of unit cell: } a_1 \cdot a_2 \times a_3$$

MILLER INDICES  $\rightarrow$  defined such that the plane closest to the

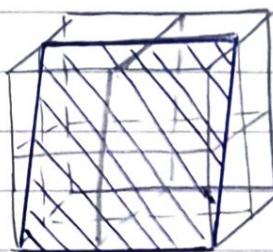
$(h k l)$  origin has the intercepts  $\frac{a_1}{h}, \frac{a_2}{k}, \frac{a_3}{l}$

↑ no common

$\rightarrow$  used to describe planes in crystals

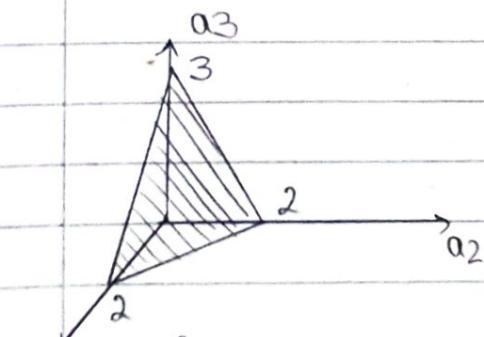


Lattice vector defined:  $\vec{t} = u\vec{a}_1 + v\vec{a}_2 + w\vec{a}_3$

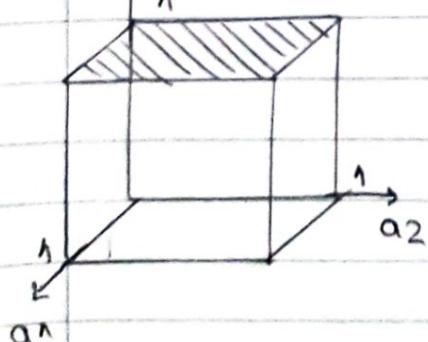


Define any plane in the crystal

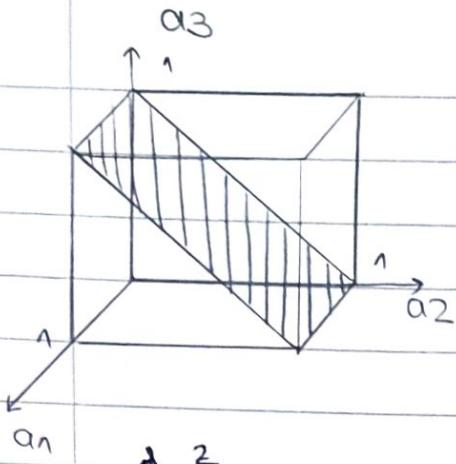
MILLER INDICES METHOD - understand & use



|                | $a_1$ | $a_2$ | $a_3$ |  |
|----------------|-------|-------|-------|--|
| intercepts     | 2     | 2     | 3     | 1. Write down intercepts with axis   |
| reciprocal     | $1/2$ | $1/2$ | $1/3$ | 2. take reciprocal $\frac{1}{\text{number}}$                                       |
| Miller indices | 3     | 3     | 2     | 3 Remove fraction e.g. multiplying with lowest common denominator<br>this case - 6 |

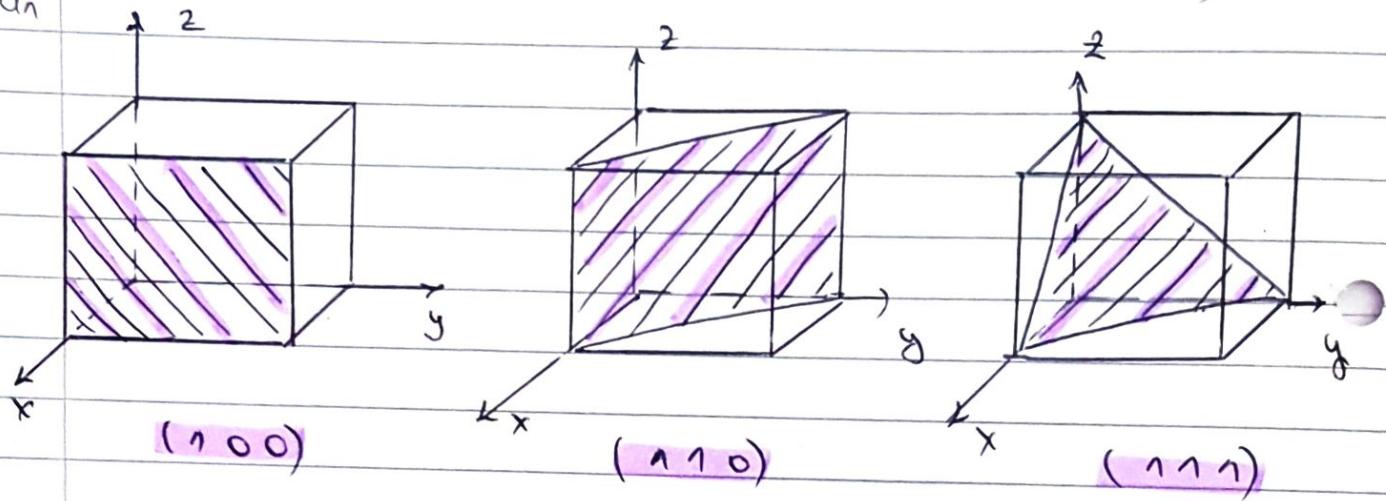


|                | $a_1$    | $a_2$    | $a_3$ |                                 |
|----------------|----------|----------|-------|---------------------------------|
| intercepts     | $\infty$ | $\infty$ | 1     |                                 |
| reciprocal     | 0        | 0        | 1     |                                 |
| Miller indices | 0        | 0        | 1     | $\Rightarrow$ Miller is (0 0 1) |



|            | $a_1$ | $a_2$ | $a_3$ |
|------------|-------|-------|-------|
| intercept  | 0     | 1     | 1     |
| recipr.    | 0     | 1     | 1     |
| miller ind | 0     | 1     | 1     |

$\Rightarrow$  Miller is  $(011)$



Families of planes and negative miller indices

$$\begin{matrix} \downarrow h100 \\ (001) \rightarrow (00\bar{1}) \end{matrix}$$

### Notations:

- miller planes  $(hkl)$
- lattice points  $x, y, z$
- directions within lattice points  $[u, v, w]$
- Reflections  $h\bar{k}\ell$
- Families of equivalent miller planes  $h\bar{h}\bar{k}\ell$
- Negative values  $(00\bar{1})$

# CHAPTER VI: CRYSTALLOGRAPHY

DIFFRACTION = Interference of waves (typically after encountering an obstacle or slit that is comparable with their wavelength)

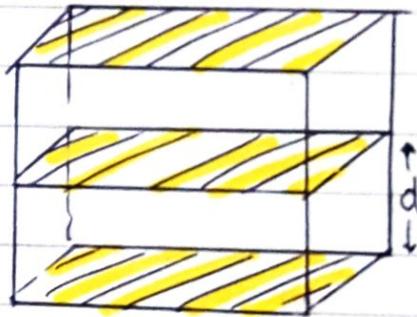
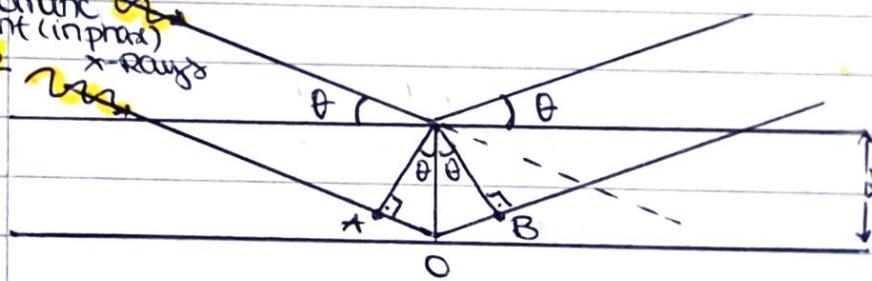
BRAGG'S LAW (know how to derive!)

→ assumed PERFECT REFLECTION\* of x-rays from crystal planes

Beam 1 → actually x-rays are elastically scattered

monochromatic  
coherent (in phase)  
Beam 1

Beam 2  
x-rays

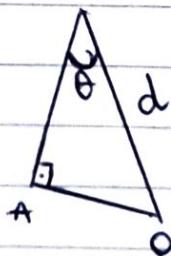


Beam 1: Scatters off top plane

Beam 2: Scatters off 2<sup>nd</sup> plane

Beam 2: travels AO + OB extra

$AO = OB \Rightarrow$  travels  $2 \times AO$  extra than Beam 1



$$\rightarrow \sin \theta = \frac{AO}{d} \Rightarrow AO = d \sin \theta$$

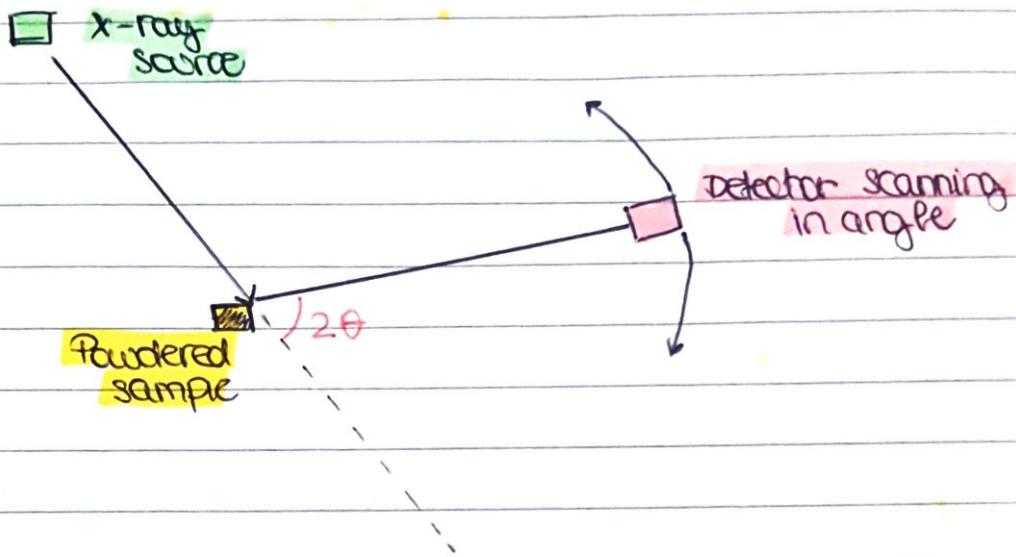
→ Beam 2 travels  $2AO = 2d \sin \theta$  more  
For constructive interference the distance must be an integer number of  $\lambda$

$$2d \sin \theta = n\lambda \rightarrow \text{Bragg's law}$$

Spectrum of planes in crystal wavelength of x-rays

• 'd-spacing' = the distance between a particular set of planes

## POWDER X-RAY DIFFRACTION EXPERIMENT



d<sub>hkl</sub> distance for cubic lattices:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

put this in Bragg's formula

$$n\lambda = 2d\sin(\theta)$$

convention!

[n=1] for x-Rays

we calculate

$$[2\theta]^\circ$$

$$h, k, l = 0 \text{ or } 1$$

Exam question:

The 1<sup>st</sup> order Bragg reflection for a cubic crystal with lattice parameter 0.3639 nm, was observed at  $2\theta$  equal to  $43^\circ$ . The x-ray wavelength was 0.154 nm. Calculate the interplanar spacing and the Miller indices of the lattice planes responsible for this reflection.

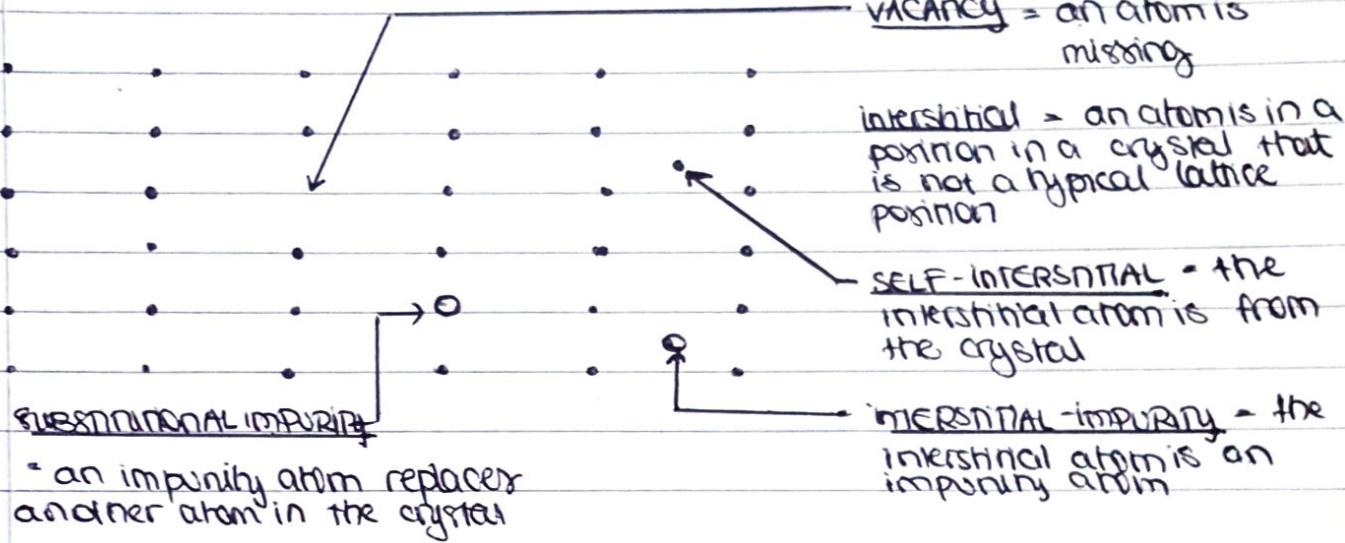
$$n\lambda = 2d\sin\theta \rightarrow d = \frac{n\lambda}{2\sin\theta} = \frac{1 \times 0.154 \times 10^{-9}}{2\sin(43^\circ)} = 2.1 \times 10^{-10} \text{ m} = 0.2101 \text{ nm.}$$

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \rightarrow \sqrt{h^2 + k^2 + l^2} = \frac{a}{d_{hkl}} = \frac{0.3639}{0.2101} = 1.732$$

$$\rightarrow h^2 + k^2 + l^2 \approx 3 \rightarrow h = k = l = 1 \rightarrow \text{Miller index is } (111)$$

## POINT DEFECTS

A point defect is a 0-dimensional defect as the crystal is disrupted at a point in the lattice. There are several types



## 0D DEFECTS

### *INTERSTITIAL DEFECTS (examples)*

*Carbon in iron – steel*

- Carbon atoms stops dislocation movement

*Some Al replaced with Mg (substitutional)*

- Aid dislocation- enhance ductility/Corrosion resistance

*Hydrogen storage:* design materials that can store high density of H<sub>2</sub> for fuel cells

- However hydrogen interstitials weakens iron/steel – need new pipe infrastructure.

### *SUBSTITUTIONAL DEFECTS (examples)*

Creating single spins for quantum computing

- E.g. 31P in Si

*Hope diamond*

Rubies (Al<sub>2</sub>O<sub>3</sub> with Cr replacing Al)

Sapphire (Al<sub>2</sub>O<sub>3</sub> with Fe or Ti replacing Al)

Amethyst (SiO<sub>2</sub> with Fe replacing Si)

## 1D DEFECTS

*Elastic energy* is the potential energy stored in a material as work is performed to distort its shape.

- Metals bend and stay bent
- Dislocation moves through the crystal lattice
- Since one plane is slipping at a time only small fraction of bonds broken at one time
- See caterpillars, ruts (Egon Orowan) and bubble rafts

Different planes have different *packing densities*

- Metals have close packed planes
- *Bonding is strongest within close packed planes*
- Bonding weakest normal to close packed planes
- Dislocations move in close packed directions – called slip planes

## 2D DEFECTS (GRAIN BOUNDARIES)

- Most materials are *polycrystalline*
- Grain boundaries (crystallites) are 2D joins of different crystallites
- Crystallites form upon crystallisation
- *Can trap impurities* - structural weakness ☹
- Scatter electrons (reduce conductivity) ☹
- Arrest dislocations – need fine grains to stop dislocations moving ☺