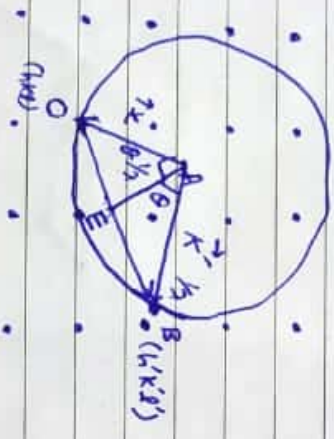


Bragg's law in reciprocal lattice



$k' = nh$
 $k = nk$
 $k' = nk$
 n common factor
 $(h'k'l') \rightarrow (nh nk nl)$

$|OB| = \frac{n}{d_{hkl}}$

$|OB| = \frac{n}{d_{hkl}}$

$|OE| = |EB|$

$OA \sin \theta = OA \sin \theta$

$|OB| = |OE| + |EB|$

$|OB| = 2 |OE|$

$|OB| = 2 |OA| \sin \theta$

$|OB| = \frac{2 \sin \theta}{\lambda}$

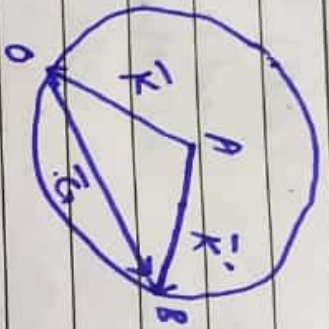
$|OA| = \frac{1}{\lambda}$

radius of the circle

~~$\frac{n}{d_{hkl}} = \frac{2 \sin \theta}{\lambda}$~~

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

n order of reflection



$$\vec{K} = \vec{K} + \vec{G}$$

square on both sides

$$|\vec{OB}| = \frac{a}{d} = \vec{G}$$

$$A^2 = \vec{A} \cdot \vec{A} \quad (\vec{K})^2 = (\vec{K} + \vec{G})^2$$

$$\vec{K} \cdot \vec{K} = (\vec{K} + \vec{G}) \cdot (\vec{K} + \vec{G})$$

$$K^2 = K^2 + \vec{K} \cdot \vec{G} + \vec{G} \cdot \vec{K} + G^2$$

$$K^2 = K^2$$

$$\cancel{K^2} = \cancel{K^2} + 2\vec{K} \cdot \vec{G} + G^2$$

$$0 = \underline{2\vec{K} \cdot \vec{G} + G^2}$$

Brillion Zone (simple cubic) - 2D

gives information of order of diffraction

1st BZ \rightarrow 1st order diff

2nd BZ \rightarrow 2nd order diff

and so on

$$2\bar{K} \cdot \bar{G} + G^2 = 0$$

$$\bar{G} = a^*h + b^*k + c^*l \quad (3D)$$

$$\bar{G} = a^*h + b^*k \quad (2D)$$

20

$$\bar{K} = K_x \hat{i} + K_y \hat{j}$$

$$2\bar{K} \cdot \bar{G} + G^2 = 0$$

$$G^2 = \bar{G} \cdot \bar{G}$$

$$2 \left[(K_x \hat{i} + K_y \hat{j}) \cdot (a^* h \hat{i} + b^* k \hat{j}) \right] + (a^* h \hat{i} + b^* k \hat{j}) \cdot (a^* h \hat{i} + b^* k \hat{j}) = 0$$

$$2 \left[h K_x a^* + K_y b^* \right] + (a^{*2} h^2 + b^{*2} k^2) = 0$$

as $a^* = \frac{2\pi}{a}$ $b^* = \frac{2\pi}{a}$ for SC $a = b$

$$2 \left[h K_x \frac{2\pi}{a} + K_y \frac{2\pi}{a} \right] + \left(\frac{4\pi^2}{a^2} h^2 + \frac{4\pi^2}{a^2} k^2 \right) = 0$$

$$\frac{4\pi}{a} \left[h K_x + K_y \right] = - \frac{4\pi^2}{a^2} (h^2 + k^2)$$

$$hK_x + K K_y = -\frac{\pi}{a} (h^2 + K^2)$$

$$K_x = ? \quad K_y = ?$$

put $K = 0$
 $h = \pm 1$

$$K K_x = -\frac{\pi}{a} h^2$$

$$K_x = -\frac{\pi}{a} h$$

$$\boxed{K_x = -\frac{\pi}{a}}$$

$$h = +1$$

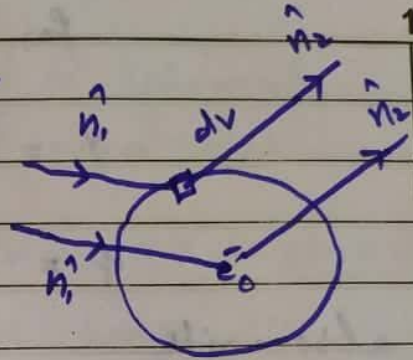
$$K_x = -\frac{\pi}{a} (-1)$$

$$h = -1$$

$$\boxed{K_x = \frac{\pi}{a}}$$

atomic scattering factor

Scattering factor = f



$f = \frac{\text{amplitude of wave scattered from charge}}{\text{amplitude of wave scattered from electron}}$

$$p = \frac{q}{v}$$

wave

$$y = A \sin(kx - \omega t)$$

$$p = \frac{dq}{dv}$$

initial phase is zero

$$p dv = dq$$

also write $y = A e^{i(kx - \omega t)}$

$$f = \iiint e^{i\phi} 2\pi r^2 dr \sin\theta d\theta$$

in spherical coordinates

we know

$$|N| = 2\pi \sin\theta$$

$$\phi = \frac{2\pi}{\lambda} (\vec{r} \cdot \vec{N})$$

$$= \frac{2\pi}{\lambda} (rN \cos\phi)$$

$$\phi = \frac{4\pi}{\lambda} r \sin\theta \cos\phi$$

$$\phi = u r \cos\phi$$

$dv = 2\pi r^2 dr \sin\theta d\theta$
 as charge is distributed spherically

put $N = 2\pi \sin\theta$

$$u = \frac{4\pi}{\lambda} \sin\theta$$

$$f = \int_0^{\infty} 2\pi r^2 \rho(r) dr \left[\frac{2}{4r} \left(\frac{e^{iur} - e^{-iur}}{2} \right) \right]$$

$$= \int 2\pi r^2 \rho(r) dr \frac{2}{4r} \sin ur$$

$$f = 4\pi \int_{r=0}^{\infty} r^2 \rho(r) \frac{\sin ur}{ur} dr$$

$$\lim_{\theta \rightarrow 0} \frac{\sin \theta}{\theta} = 1$$

$$f = 4\pi \int_0^{\infty} r^2 \rho(r) dr$$

$$\lim_{ur \rightarrow 0} \frac{\sin ur}{ur} = 1$$

Geometrical structure factor

$$F(h'k'l') = \sum_j f_j e^{i\Phi_j} \quad \text{--- (i)}$$

$$\Phi_j = \frac{2\pi}{\lambda} (\bar{r}_j \cdot \bar{N}) \quad \text{--- (ii)}$$

$$\bar{r}_j = u_j \bar{a} + v_j \bar{b} + w_j \bar{c}$$

$$\bar{a} \cdot \bar{N} = h' \lambda$$

$$\bar{b} \cdot \bar{N} = k' \lambda$$

$$\bar{c} \cdot \bar{N} = l' \lambda$$

u_j , v_j and w_j are integers

$$\bar{r}_j \cdot \bar{N} = \lambda [h' u_j + k' v_j + l' w_j]$$

put in eq (ii) and in eq (i)

$$F(h'k'l') = \sum_j f_j e^{i \frac{2\pi}{\lambda} (\bar{r}_j \cdot \bar{N})}$$

$$= \sum_j f_j e^{i \frac{2\pi}{\lambda} (\lambda (u_j h' + v_j k' + w_j l'))}$$

$$F(h'k'l') = \sum_j f_j e^{i 2\pi (u_j h' + v_j k' + w_j l')}$$

for identical atoms f_j 's = f

$$S = \sum_j e^{i 2\pi (u_j h' + v_j k' + w_j l')}$$

↓
geometrical structure factor

$$F(h'k'l') = f \sum_j e^{i2\pi(u_j h' + v_j k' + w_j l')}$$

$$= f_j \sum_j e^{i2\pi(u_j h' + v_j k' + w_j l')}$$

we know that Intensity is proportional to the square of Scattering amplitude

$$I(\text{scattering}) = \text{Scattering Intensity}$$

$$I(\text{scattering}) = F(h'k'l') * F(h'k'l')$$

$$= F^2$$

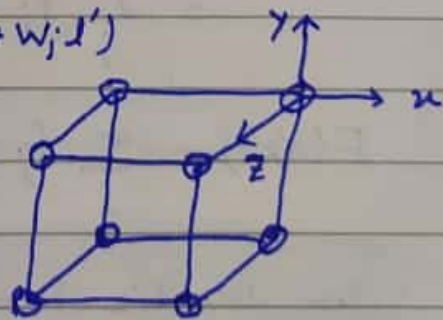
for Simple cubic structure (Sc)

$$S = \sum_j e^{i2\pi(u_j h' + v_j k' + w_j l')}$$

$$S = \sum_j e^{i2\pi(0)}$$

$$S = \sum_j 1$$

$$S = 1$$



(0,0,0)

(h' k' l')

$$F(h'k'l') = f(1)$$

relation b/w force and $\frac{dU}{dr}$

page
3

$\frac{dU}{dr}$ = gradient of
energy

$$\frac{d}{dr} \left(K \frac{q^2}{r} \right)$$

$$U = K \frac{q^2}{r}$$

$$K q^2 \frac{d}{dr} \left(\frac{1}{r} \right)$$

$$\frac{dU}{dr} = K q^2 \left(-\frac{1}{r^2} \right)$$

$$= -K \frac{q^2}{r^2}$$

$$F = K \frac{q_1 q_2}{r^2}$$

$$\frac{dU}{dr} = -F$$

$$F = K \frac{q^2}{r^2}$$

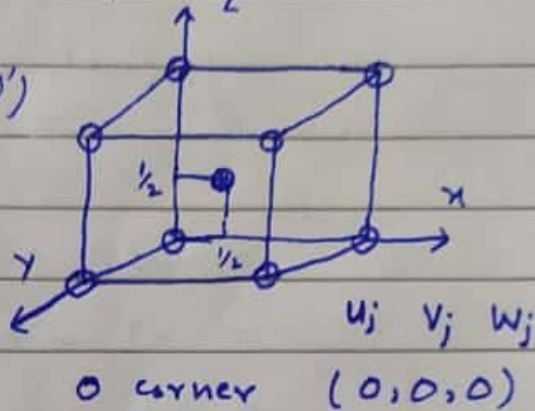
$$F = -\frac{dU}{dr}$$

$$F(h'k'l') = f$$

$$\text{intensity} = F^2 = f^2$$

For BCC (structure factor)

$$S = \sum_j e^{i2\pi(u_j h' + v_j k' + w_j l')}$$



corners
↓

● body centre (1/2, 1/2, 1/2)

$$S \neq \left[e^{i2\pi(0)} + e^{i2\pi(\frac{1}{2}u_j + \frac{1}{2}v_j + \frac{1}{2}w_j)} \right]$$

$$= \left[e^0 + e^{i2\pi \frac{1}{2}(u_j + v_j + w_j)} \right]$$

$$= \left[1 + e^{i\pi(u_j + v_j + w_j)} \right]$$

$$S = \left[e^{i2\pi(0)} + e^{i2\pi(\frac{1}{2}h' + \frac{1}{2}k' + \frac{1}{2}l')} \right]$$

$$= \left[e^0 + e^{i2\pi \frac{1}{2}(h' + k' + l')} \right]$$

$$S = \left[1 + e^{i\pi(h' + k' + l')} \right]$$

$$F(h'k'l') = fS$$

$$F(h'k'l') = f \left[1 + e^{i\pi(h'+k'+l')} \right]$$

for odd values of $h'+k'+l' = \text{odd}$

$$e^{i\pi(\text{odd})} = -1$$

$$\begin{aligned} e^{i\pi(1)} &= \cos \pi + i \sin \pi && 1 \text{ is odd} \\ &= -1 + 0 \\ &= -1 \end{aligned}$$

$$\begin{aligned} e^{i\pi(3)} &= \cos 3\pi + i \sin 3\pi \\ &= -1 + 0 \\ &= -1 \end{aligned}$$

$$F(h'k'l') = f [1 + (-1)] = 0$$

$(001), (111), (210), \dots$

Scattering amplitude is zero from

these planes

for $h' + k' + l' = \text{even}$

$$F_{(h'k'l')} = f S$$

$$S = f e^{i2\pi(\dots)}$$

$$S = \left[1 + e^{i\pi(h'+k'+l')} \right]$$

$$e^{i\pi(\text{even})} = 1$$

$$\begin{aligned} e^{i\pi(2)} &= \cos 2\pi + i \sin 2\pi \\ &= 1 + 0 \\ &= 1 \end{aligned}$$

scattering amplitude

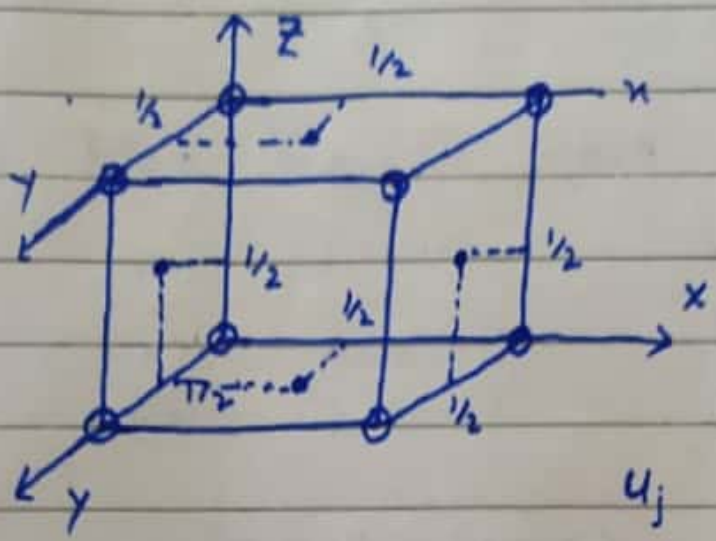
$$F_{(h'k'l')} = f [1 + 1] = 2f$$

$$\text{intensity } I = 4f^2 = F_{(h'k'l')}^2$$

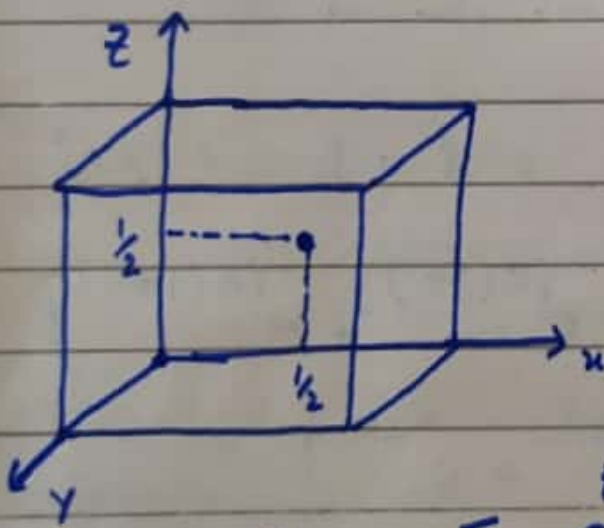
(110), (200), (222) ...

scattering is allowed

FCC structure factor



	u_j	v_j	w_j
corner	0	0	0
face	0	$\frac{1}{2}$	$\frac{1}{2}$
face	$\frac{1}{2}$	$\frac{1}{2}$	0
face	$\frac{1}{2}$	0	$\frac{1}{2}$



$$S = \sum_j e^{i2\pi(u_j h' + v_j k' + w_j l')}$$

$$S = \left[e^{i2\pi(0)} + e^{i2\pi(0 + \frac{1}{2}k' + \frac{1}{2}l')} \right. \\ \left. + e^{i2\pi(\frac{1}{2}h' + \frac{1}{2}k' + 0)} + e^{i2\pi(\frac{1}{2}h' + 0 + \frac{1}{2}l')} \right] \\ = \left[1 + e^{i2\pi \frac{1}{2}(k'+l')} + e^{i2\pi \frac{1}{2}(h'+k')} \right. \\ \left. + e^{i2\pi \frac{1}{2}(h'+l')} \right]$$

$$S = \left[1 + e^{i\pi(h'+k')} + e^{i\pi(k'+l')} + e^{i\pi(h'+l')} \right]$$

for all even or all odd $(h' k' l')$

h' odd

h' even

k' odd

k' even

l' odd

l' even

0 = even

$(111), (200), (222)$

$(313) \rightarrow \dots$

$h' = 1, k' = 1, l' = 1 \quad (111)$

$$S = \left[1 + e^{i\pi(1+1)} + e^{i\pi(1+1)} + e^{i\pi(1+1)} \right]$$

$$= \left[1 + e^{i2\pi} + e^{i2\pi} + e^{i2\pi} \right]$$

$$= [1 + 1 + 1 + 1] = 4$$

$$F_{(h'k'l')} = f S = f(4)$$

$$I = F^2 = 16f^2$$

16

$$h' = 2 \quad k' = 0 \quad l' = 0 \quad (200)$$

$$S = \left[1 + e^{i\pi(2+0)} + e^{i\pi(0+0)} + e^{i\pi(2+0)} \right]$$

$$S = \left[1 + e^{i2\pi} + e^0 + e^{i2\pi} \right]$$

$$= \left[1 + 1 + 1 + 1 \right] = 4$$

$$F = 4f$$

$$I = 16f^2$$

if some are even and odd
combination (mix)

$$(101) \quad (110) \quad (001) \quad (210)$$

+ - - - -

$$S = 0$$

$$h' = 0 \quad k' = 0 \quad l' = 1$$

$$S = (001)$$

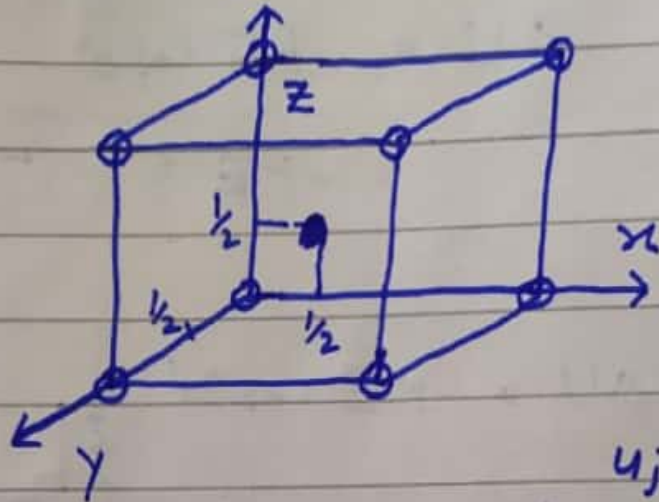
$$S = \left[1 + e^{i\pi(0)} + e^{i\pi(0+1)} + e^{i\pi(0+1)} \right]$$

$$= \left[1 + e^0 + e^{i\pi} + e^{i\pi} \right]$$

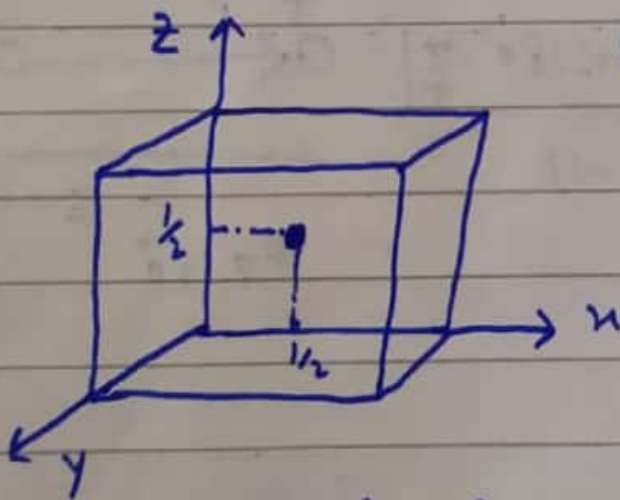
$$= \left[1 + 1 - 1 - 1 \right]$$

$$S = 0$$

BCC structure factor



	u_j	v_j	w_j
corner	0	0	0
body centre	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$



corner	bc
(000)	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$

Binding Energy of ionic crystal

The binding energy of ionic crystals was first calculated by born and Madelung

Two type of interaction.

- 1- Long range columb's electrostatic interaction which may be attractive or Repulsive
- 2- short range repulsive interaction which comes when when interatomic distance becomes so small, electronic cloud of one ion starts overlapping with other ion

columb's interaction energy b/w two ions is

$$U = \pm \frac{q^2}{r}$$

here + sign b/w like (same) charges and -ve sign b/w opposite charges

short range repulsive interaction energy is of the form

$$U_{rep} = \lambda e^{-r/\rho}$$

here λ represents strength and ρ represents the range of repulsive interaction

interaction energy of cohesive energy of an 'i' th ion is

$$U_i = \sum_j U_{ij} \quad \text{--- (i)}$$

U_{ij} is the interaction energy b/w i'th and j'th ion

$$U_{ij} = \lambda e^{-r_{ij}/\rho} \pm q^2/r_{ij}$$

if crystal contained N molecules that is N positive ions and N negative ions then the total binding energy of the lattice become

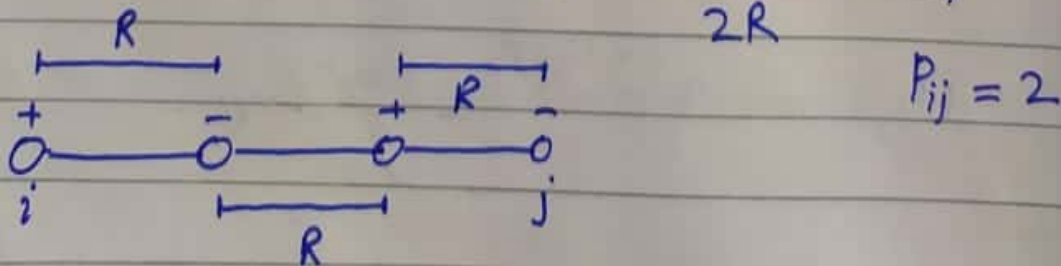
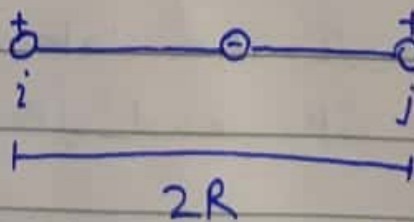
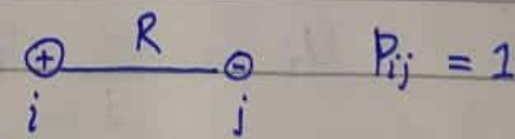
$$U_{tot} = N U_i \quad \text{--- (ii)}$$

Now $r_{ij} = P_{ij} R$

here R is the nearest neighbour distance between the two ions

P_{ij} is one for first nearest neighb and two for second nearest neighbour

' R ' is the distance b/w two consecutive ions



$$P_{ij} = 3$$

$$U_{ij} = \lambda e^{-P_{ij}R/\rho} \pm q^2/P_{ij}R$$

eq (i) become

$$U_i = \sum_j \left[\lambda e^{-P_{ij}R/\rho} \pm q^2/P_{ij}R \right]$$

as repulsive term is very short range we take this repulsive term applicable only for 1st nearest neighbours, if there are 'z' 1st nearest neig then $P_{ij} = 1$

$$U_i = z \lambda e^{-R/\rho} \pm \sum_j q^2/P_{ij}R$$

$$U_i = z \lambda e^{-R/\rho} - \alpha q^2/R \quad \text{--- (iii)}$$

here $\alpha = \sum_j \mp 1/P_{ij}$ is called

Madelung constant

$$\alpha = \sum_j \mp \frac{1}{P_{ij}}$$

we know that

$$F = \frac{dU}{dR}$$

and at $R = R_0$ $F = 0$

So

$$\frac{dU_{\text{tot}}}{dR_0} = 0$$

put the value of U_i from (iii)
into eq (ii)

$$U_{\text{tot}} = N \left[z\lambda e^{-R/\rho} - \alpha q^2/R \right] \text{ --- (iv)}$$

$$\frac{dU_{\text{tot}}}{dR} = N \left[-\frac{z\lambda}{\rho} e^{-R/\rho} + \alpha q^2/R^2 \right]$$

at $R = R_0$

(for 1st nearest nei)

$$\frac{dU_{\text{tot}}}{dR_0} = 0 = -\frac{Nz\lambda}{\rho} e^{-R_0/\rho} + \alpha Nq^2/R_0^2$$

$$\frac{Nz\lambda}{\rho} e^{-R_0/\rho} = \alpha Nq^2/R_0^2$$

$$e^{-R_0/\rho} = \frac{\rho \alpha v^2}{z \lambda R_0^2}$$

put in eq (iv)

$$U_{\text{tot}} = N \left[z \lambda \left(\frac{\rho \alpha v^2}{z \lambda R_0^2} \right) - \alpha v^2 / R_0 \right]$$

$$= N \left[\rho \alpha v^2 / R_0^2 - \alpha v^2 / R_0 \right]$$

$$U_{\text{tot}} = -N \frac{\alpha v^2}{R_0} \left[-\rho / R_0 + 1 \right]$$

$$U_{\text{tot}} = -N \frac{\alpha v^2}{R_0} \left[1 - \rho / R_0 \right]$$

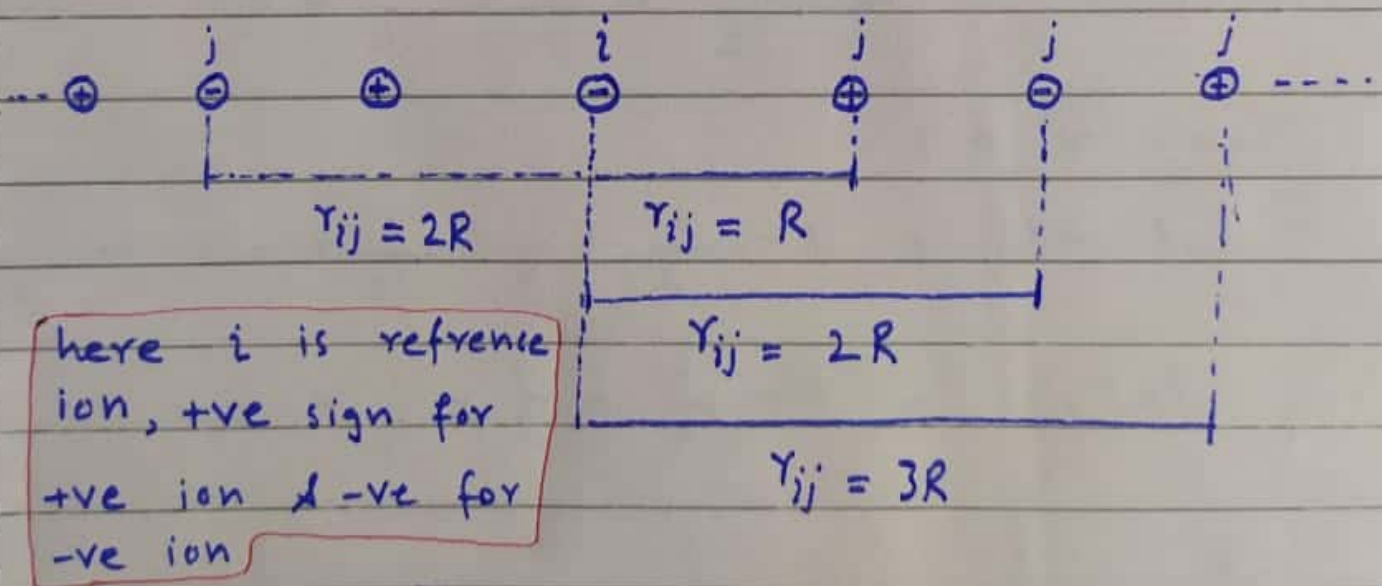
Madelung constant

$$\alpha = \sum_j \mp \frac{1}{P_{ij}}$$

we know that $r_{ij} = P_{ij} R$

so
$$\alpha = \sum_j \mp \frac{R}{r_{ij}}$$

simplest case (Madelung constant for 1D crystal)



$$\alpha = \frac{R}{R} - \frac{R}{2R} + \frac{R}{3R} - \frac{R}{4R} + \dots$$

as there are two ions on each side of reference ion 'i'

So multiply with 2 from each term

$$\alpha = \frac{2R}{R} - \frac{2R}{2R} + \frac{2R}{3R} - \frac{2R}{4R} + \dots$$

take 2 common

$$\alpha = 2 \left[1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \dots \right]$$

the series expansion of $\ln(1+x)$

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

for $x = 1$

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

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

so

$$\alpha = 2 \ln(2) = 1.38$$

Binding energy of crystals of inert gases

inert gases has completely filled last shells

He³ and He⁴ has fcc crystals in solid state

Consider a molecular crystal of N atoms, then cohesive energy is

$$U_i = \sum_j U_{ij}$$

$$U_{\text{tot}} = \frac{N}{2} U_i$$

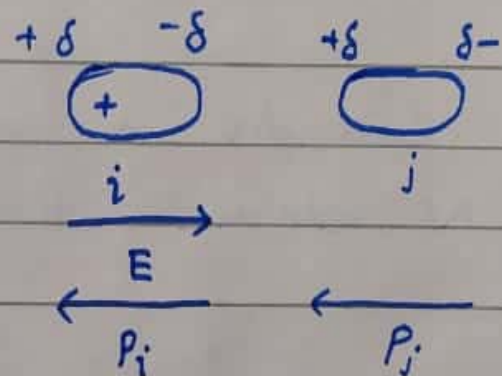
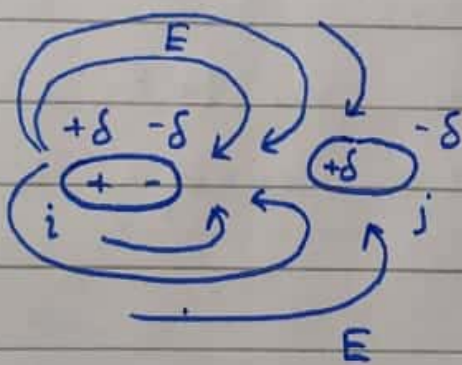
$$U_{\text{tot}} = \frac{N}{2} \sum_j U_{ij}$$

there are two types of interactions

- 1- Van der Waals or London interaction
- 2- Repulsive interaction

Van der Waals interaction is also called dipole induced dipole interaction

Let P_i is ~~the~~ instantaneous dipole moment of i th atom. This dipole produce E field, this field further produces a dipole moment P_j in nearby j th atom



$$E = \frac{2P_i}{r_{ij}^3}$$

$$P_j = \alpha E$$

$$P_j = \alpha \frac{2P_i}{r_{ij}^3}$$

$$U_{att} = -\frac{2P_i P_j}{r_{ij}^3}$$

page 3

put value of P_j in U_{att}

$$U_{att} = -2 \left(\frac{\alpha 2 P_i}{r_{ij}^3} \right) \frac{P_i}{r_{ij}^3}$$

$$U_{att} = \frac{-4 \alpha P_i^2}{r_{ij}^6}$$

$$B = 4 \alpha P_i^2$$

$$U_{att} = -B / r_{ij}^6$$

2 - Repulsive interaction

$$U_{rep} = \lambda e^{-r_{ij}/\rho}$$

here ρ is the range of repulsive interaction

repulsive force is due to overlapping of atomic orbitals.

empirical form of U_{rep}

$$U_{rep} = C / r_{ij}^{12}$$

page 4

$$U_{ij} = -B/r_{ij}^6 + C/r_{ij}^{12}$$

$$U_{ij} = 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right]$$

Here ε and σ are parameters related to B and C

$$4\varepsilon \sigma^6 = B, \quad 4\varepsilon \sigma^{12} = C$$

Above is known as Lennard-Jones potential

put the value of U_{ij} in eq of U_{tot}

$$U_{tot} = \frac{N}{2} \sum_j U_{ij}$$

$$U_{tot} = \frac{N}{2} (4\varepsilon) \sum_j \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right]$$

$$\therefore r_{ij} = P_{ij} R$$

$$U_{tot} = N 2\varepsilon \sum_j \left[\left(\frac{\sigma}{P_{ij} R} \right)^{12} - \left(\frac{\sigma}{P_{ij} R} \right)^6 \right]$$

CH # 04

heat capacity of solids

$$C = \frac{dQ}{dT}$$

C_p is different from C_v

specific heat capacity

$$C = \frac{dQ}{m dT}$$

we are interested in specific heat capacity but we take $m = 1 \text{ kg}$ so

$$C = \frac{dQ}{dT}$$

first law of thermodynamics

$$dQ = dE + PdV$$

$$dQ = dE + PdV$$

at constant volume $dV = 0$

$$dQ = dE$$

$$C_V = \frac{dQ}{dT} = \frac{dE}{dT}$$

in solids most of the heat supplied is used up in increasing internal energy E

$$C_{\text{solid}} = C_{\text{lattice}} + C_{\text{electron}}$$

classical theory of Lattice heat capacity

lattice atoms vibrates in 3 (three) dimension along x , y and z axis

Energy of one dimensional harmonic oscillator (along x -axis)

page 3

$$\epsilon = \frac{p^2}{2m} + V(x) \quad \text{--- (i)}$$

as $V = \frac{1}{2} K x^2$

$$K = \omega^2 m$$

$$V = \frac{1}{2} (\omega^2 m) x^2$$

$$\omega^2 = \frac{K}{m}$$

put value of V in

eq (i)

$$\omega^2 m = K$$

$$\epsilon = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 x^2$$

if there are N atoms then average energy of each harmonic oscillator is

$$\bar{\epsilon} = \frac{\int \epsilon |\psi|^2 dx}{\int |\psi|^2 dx}$$

according to Maxwell energy distribution

$$e^{-\frac{\epsilon}{KT}}$$

$$\bar{\epsilon} = \frac{\int \epsilon e^{-\frac{\epsilon}{KT}} d\epsilon}{\int e^{-\frac{\epsilon}{KT}} d\epsilon} \quad \text{--- (ii)}$$

~~known~~ Now take $\frac{p^2}{2m} = AP^2$

and $\frac{1}{2} m\omega^2 x^2 = Bx^2$

So $\epsilon = AP^2 + Bx^2$

eq (ii) become

$$\bar{\epsilon} = \frac{\iint_{p, x} (AP^2 + Bx^2) e^{-\frac{(AP^2 + Bx^2)}{KT}} dp dx}{\iint_{p, x} e^{-\frac{AP^2}{KT}} e^{-\frac{Bx^2}{KT}} dp dx}$$

$$\bar{\epsilon} = \frac{\iint_{p, x} AP^2 e^{-\frac{AP^2}{KT}} e^{-\frac{Bx^2}{KT}} dp dx + \iint_{p, x} Bx^2 ()}{\iint_{p, x} e^{-\frac{AP^2}{KT}} e^{-\frac{Bx^2}{KT}} dp dx}$$

$$\iint_{p, x} e^{-\frac{AP^2}{KT}} e^{-\frac{Bx^2}{KT}} dp dx$$

for opposite charges

$\overset{+}{0}$ $\overset{-}{0}$

$F = \text{attractive} = -ve$

energy = $U = -ve$ (binding state)

For same charges

$\overset{+}{0}$ $\overset{+}{0}$ or $\overset{-}{0}$ $\overset{-}{0}$

$F = \text{repulsive} = +ve$

energy = $U = +ve$

for fcc structure

$$\sum_j \frac{1}{r_{ij}^{12}} = 12.13$$

$$\sum_j \frac{1}{r_{ij}^6} = 14.45$$

and we know that at $R = R_0$

$$\frac{dU_{tot}}{dR_0} = 0$$

which give $\frac{R_0}{\sigma} = 1.09$

	Ne	Ar	Kr	Xe
$\frac{R_0}{\sigma}$	1.14	1.11	1.10	1.09

~~Now put~~

$$\bar{\epsilon} = \frac{\int_P AP^2 e^{-\frac{AP^2}{KT}} dp \int_n e^{-\frac{Bn^2}{KT}} dn}{\int_P e^{-\frac{AP^2}{KT}} dp \int_n e^{-\frac{Bn^2}{KT}} dn} + \frac{\int_n Bn^2 e^{-\frac{Bn^2}{KT}} dn \int_P e^{-\frac{AP^2}{KT}} dp}{\int_P e^{-\frac{AP^2}{KT}} dp \int_n e^{-\frac{Bn^2}{KT}} dn}$$

$$\bar{\epsilon} = \frac{\int_P AP^2 e^{-\frac{AP^2}{KT}} dp}{\int_P e^{-\frac{AP^2}{KT}} dp} + \frac{\int_n Bn^2 e^{-\frac{Bn^2}{KT}} dn}{\int_n e^{-\frac{Bn^2}{KT}} dn}$$

We know that

$$\int_0^{\infty} u^2 e^{-au^2} du = \frac{1}{4} \sqrt{\frac{\pi}{a^3}}$$

and $\int_0^{\infty} e^{-au^2} du = \frac{1}{2} \sqrt{\frac{\pi}{a}}$

$$= \frac{A \left[\frac{1}{4} \sqrt{\frac{\pi}{(A/KT)^3}} \right]}{\frac{1}{2} \sqrt{\frac{\pi}{(A/KT)}}} + \frac{B \left[\frac{1}{4} \sqrt{\frac{\pi}{(B/KT)^3}} \right]}{\frac{1}{2} \sqrt{\frac{\pi}{(B/KT)}}}$$

$$\bar{\epsilon} = \frac{1}{2A} \left[\frac{(A/KT)^{1/2}}{(A/KT)^{3/2}} \right] + \frac{1}{2B} \left[\frac{(B/KT)^{1/2}}{(B/KT)^{3/2}} \right]$$

$$= \frac{1}{2} A \left[\frac{KT}{A} \right] + \frac{1}{2} B \left[\frac{KT}{B} \right]$$

$$= \frac{1}{2} KT + \frac{1}{2} KT$$

$$\bar{\epsilon} = KT$$

As there are 3-D harmonic oscillations of N atoms, so the total vibrational energy of the crystal is

$$E = 3N \bar{\epsilon}$$

$$E = 3NKT$$

as

$$C_v = \frac{dE}{dT} = 3NK$$

$$C_v = 3NK$$