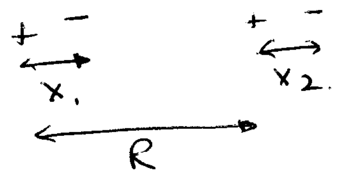
Qu 2.1 This problem closely follows the discussion in Kittel. Chapter 3.

$$\mathcal{H}_0 = \underbrace{\frac{1}{2m}p_1^2 + \frac{1}{2}Cx_1^2 + \frac{1}{2m}p_2^2 + \frac{1}{2}Cx_2^2}_{\text{SHO.}}$$



Each S.H.O. has frequency ω_0

$\Rightarrow C = m\omega_0^2$

[from Q.M. course]

$$\mathcal{H}_1 = \frac{e^2}{R} + \frac{e^2}{R+(x_1-x_2)} - \frac{e^2}{R+x_1} - \frac{e^2}{R-x_2}.$$

$$\simeq -\frac{2e^2x_1x_2}{R^3}. \quad (\text{in CGS})$$

in SI $\quad e^2 \to e^2/4\pi\varepsilon_0 \quad \Rightarrow$ Eq. (2.4)

Make the transformation to symm. & antisymm normal modes (notice that we know the eigenstates by symmetry)

$$\Rightarrow \quad x_1 = \frac{1}{\sqrt{2}}(x_s + x_a) \qquad x_2 = \frac{1}{\sqrt{2}}(x_s - x_a)$$

$$p_1 = \frac{1}{\sqrt{2}}(p_s + p_a) \qquad p_2 = \frac{1}{\sqrt{2}}(p_s - p_a)$$

then elementary algebra gives (2.5)

$$\mathcal{H}_0 = \frac{1}{2m}p_s^2 + \frac{1}{2}m\omega_0^2x_s^2 + \frac{1}{2m}p_a^2 + \frac{1}{2}m\omega_0^2x_a^2$$

$$\mathcal{H}_1 = -\frac{e^2}{2\pi\varepsilon_0R^3}\cdot\frac{1}{2}(x_s^2 - x_a^2)$$

Thus $\omega_s, \omega_a = \sqrt{\left[\omega_0^2 \pm \frac{e^2}{2\pi\varepsilon_0R^3m}\right]}$

$$= \omega_0\left[1 \pm \frac{e^2}{4\pi\varepsilon_0R^3m} - \frac{1}{2}\left(\frac{e^2}{4\pi\varepsilon_0R^3}\cdot\frac{1}{m\omega_0^2}\right)^2 + \dots\right]$$

giving the required answer.

Qu 2.2

This question follows the general prescription for solution of any stationary problem in QM. by matrix methods.

i.e with an orthonormal basis of states $|\varphi_n\rangle$, expand the solution to

$$H|\psi\rangle = E|\psi\rangle \quad \text{as}$$

$$|\psi\rangle = \sum_n a_n|\varphi_n\rangle.$$

Then
$$\langle\varphi_m|H|\psi\rangle = \sum_n \langle\varphi_m|H|\varphi_n\rangle a_n$$

$$= \langle\varphi_m|E|\psi\rangle$$

$$= \sum_n E\, a_n \langle\varphi_m|\varphi_n\rangle$$

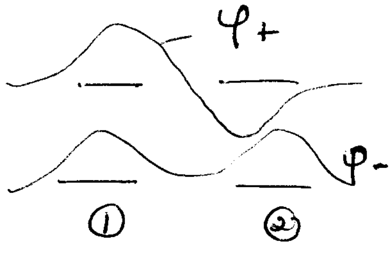
$$= E\, a_m.$$

$$\Rightarrow \sum_n \left\{ (H_{mn} - E\delta_{mn}) a_n \right\} = 0$$

Eigenvalues: $E_\pm = \frac{E_1+E_2}{2} \pm \frac{1}{2}\sqrt{\left[(E_1-E_2)^2 + 4|t|^2\right]}$

$$\left(\frac{a_2}{a_1}\right)_\pm = \frac{E_1-E_2}{|t|} \mp \sqrt{\left[\left(\frac{E_1-E_2}{2|t|}\right)^2 + 1\right]}$$

(a) Identical atoms $E_\pm = \pm|t|$ 2t



(b) Ionic limit. $E_+ = E_1$, $E_- = E_2$

$(a_2/a_1)^+ \to 0$ $\quad \left(\frac{a_1}{a_2}\right)^- \to 0$

+ wfn on atom ①

− wfn on atom ②

3.3

$$\hat{p}\cdot e^{i\underline{k}\cdot\underline{r}} = (-i\hbar\vec{\nabla})\, e^{i\underline{k}\cdot\underline{r}}$$

$$= (-i\hbar)(i\vec{k})\, e^{i\underline{k}\cdot\underline{r}}$$

$$= (\hbar\vec{k})\, e^{i\underline{k}\cdot\underline{r}}$$

For future use, note that the operator

$$\hat{T}_R = e^{-i\hat{\underline{p}}\cdot\underline{R}/\hbar}$$

generates translations:

ie $\hat{T}_R \cdot f(\underline{r}) = f(\underline{r}+\underline{R})$.

Proof:

$$\hat{T}_R \cdot f(r) = e^{\underline{R}\cdot\underline{\nabla}} f(r)$$

$$= \left[1 + \underline{R}\cdot\underline{\nabla} + \frac{1}{2}(\underline{R}\cdot\underline{\nabla})^2 \ldots\right.$$

$$= f(r) + \underline{R}\cdot\nabla f(r) \ldots$$

$\in$ (Taylor series expansion of $f(r)$)

$$= f(r+R).$$

Question 4

Density of states in k-space $= \dfrac{V}{(2\pi)^3}$ $\quad d=3$

area of sample $\longrightarrow \dfrac{A}{(2\pi)^2}$ $\quad d=2$

length $\longrightarrow \left(\dfrac{L}{2\pi}\right)$ $\quad d=1$

Thus

$g(E)\,dE$ = # of states in energy range dE

= # of states in k-space with energy between E and $E+dE$

$$= 2\,\frac{V}{(2\pi)^3}\cdot 4\pi k^2\,dk$$

spin   d.o.s. in k-space   volume in k space with same energy.

Thus $g(E) = 2\cdot\dfrac{V}{(2\pi)^3}\cdot 4\pi k^2\,\dfrac{dk}{dE}$ $\quad$ 3D

$= 2\cdot\dfrac{A}{(2\pi)^2}\cdot 2\pi k\,\dfrac{dk}{dE}$ $\quad$ 2D

$= 2\cdot\dfrac{L}{(2\pi)}\cdot\dfrac{2\,dk}{dE}$ $\quad$ 1D

Rest follows from $E = \dfrac{\hbar^2 k^2}{2m}$.

Question 5

Free electron formulae.

$$E_F = \frac{\hbar^2 k_F^2}{2m}$$

$$k_F = \left(3\pi^2 \frac{N}{V}\right)^{1/3} \qquad \text{eq}^n \ (3.9).$$

$$g(E) = \left(\frac{mV}{\pi^2\hbar^2}\right)\left(\frac{2mE}{\hbar^2}\right)^{1/2} \qquad (\text{see prob } 4).$$

$$N = \int_0^{E_F} g(E)\, dE$$

$$\bar{E} = \int_0^{E_F} g(E) . E . dE$$

Since $g(E) = c . E^{1/2}$. $\qquad c = \text{const}^t$.

$$N = c \frac{2}{3} E_F^{3/2}$$

$$\bar{E} = c . \frac{2}{5} E_F^{5/2}$$

$$\therefore \bar{E} = \frac{3}{5} N . E_F$$

$$P = -\frac{d\bar{E}}{dV} = \frac{2}{5}\frac{NE_F}{V}$$

$$B = -V\frac{dp}{dV} = V\frac{d^2P}{dV^2} = \frac{2}{3}\frac{NE_F}{V}.$$

Potassium: $\frac{N}{V} = 1.4 \times 10^{28} m^{-3} \Rightarrow E_F = 3.4 \times 10^{-19} J.$

$\Longrightarrow B = 0.32 \times 10^{10} N m^{-2}$. — close.

Mg: $k_F = 1.4 \times 10^{10} m^{-1}$.

$$\frac{g(E_F)}{V} = \frac{mk_F}{\pi^2\hbar^2} = 1.1 \times 10^{47} m^{-3} J^{-1}$$

$$C_V = \frac{\pi^2}{3} k_B^2 \frac{g(E_F)}{V} . T = 71 . (T/K) J m^{-3} K^{-1}$$

$$= 1.0 \, (T/\text{Kelvin}) \, mJ \, mol^{-1} K^{-2}.$$

Question 6

$$m\frac{\partial^2 u_n}{\partial t^2} = K\left[(u_{n+1}-u_n)+(u_{n-1}-u_n)\right]$$

Ansatz: $u_n(t) = u_0 \cos(q x_n - \omega t)$

$$\therefore\ -m\omega^2 \cos(q x_n - \omega t) = K\left[\left(\cos(q x_{n+1}-\omega t) - \cos(q x_n - \omega t)\right) + \left(\cos(q x_{n-1}-\omega t) - \cos(q x_n-\omega t)\right)\right]$$

$$= -2K\sin\left(\frac{qa}{2}\right)\left[\sin\left(q\frac{x_{n+1}+x_n}{2}-\omega t\right) - \sin\left(q\frac{x_n+x_{n-1}}{2}-\omega t\right)\right]$$

$$= -4K\sin^2\left(\frac{qa}{2}\right)\cos\left(q x_n - \omega t\right).$$

Hence $\omega^2 = \frac{4K}{m}\sin^2\left(\frac{qa}{2}\right).$

Question 8

$$U_D = \frac{V\hbar}{2\pi^2 v^3} \int_0^{\omega_D} \frac{d\omega\, \omega^3}{e^{\hbar\omega/kT} - 1} \times 3 \quad (1)$$

# of branches.

$$= \frac{3V(k_B T)^4}{2\pi^2 v^3 \hbar^3} \int_0^{x_D} \frac{dx\, x^3}{(e^x - 1)}$$

where $x = \hbar\omega/kT$ $\quad x_D = \hbar\omega_D/kT = \theta_D/T$

$$C_V = \frac{\partial U_D}{\partial T} = \frac{3V}{2\pi v^3} k_B \left(\frac{k_B T}{\hbar}\right)^3 \int_0^{x_D} \frac{dx\, x^4 e^x}{(e^x - 1)^2}$$

(easiest to get by differentiating 1).

Use $\omega_D^3 = \dfrac{6\pi^2 v^3 N}{V}$

$$\Rightarrow C_v = 9Nk_B \left(\frac{T}{\theta_D}\right)^3 \underbrace{\int_0^{\theta_D/T} \frac{dx\, x^4 e^x}{(e^x - 1)^2}}_{I}$$

High ~~Low~~ temperatures

$\theta_D/T \ll 1$. Approximate integral by linearising

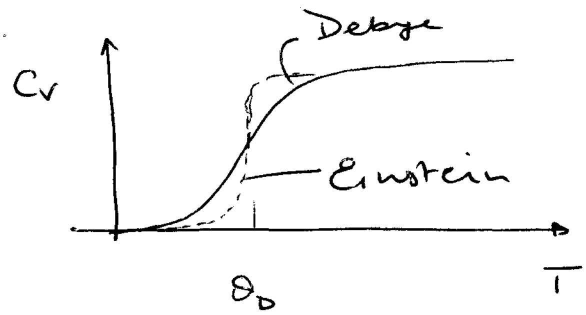
$$I \simeq \int_0^{\frac{\theta_D}{T}} dx \frac{x^4 \cdot 1}{(1 + x - 1)^2} \sim \int_0^{\frac{\theta_D}{T}} dx\, x^2 = \frac{1}{3}\left(\frac{\theta_D}{T}\right)^3$$

$\Rightarrow C_V \to 3Nk_B$ (Classical result)

Low temperatures: replace $\theta_D/T \to \infty$, $I = \dfrac{4\pi^4}{15}$

$$C_V = \frac{12\pi^4}{5} N k_B \left(\frac{T}{\theta_D}\right)^3$$

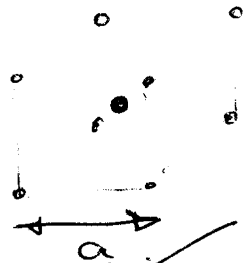
$C_V(\text{Einstein}) \sim 3N\hbar\omega_0 e^{-\frac{\hbar\omega_0}{kT}}$ at low T



Question 9

BCC:

Primitive lattice vectors



cubic lat. const.

$$\vec{a}_1 = \frac{a}{2}(\hat{y} + \hat{z} - \hat{x}) = \frac{a}{2}(\bar{1},1,1)$$

$$\vec{a}_2 = \frac{a}{2}(\hat{z} + \hat{x} - \hat{y}) = \frac{a}{2}(1,\bar{1},1)$$

$$\vec{a}_3 = \frac{a}{2}(\hat{x} + \hat{y} - \hat{z}) = \frac{a}{2}(1,1,\bar{1})$$

Chosen for symmetry — others will do.

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{a_1 \cdot (\vec{a}_2 \times \vec{a}_3)} \quad \text{etc.}$$

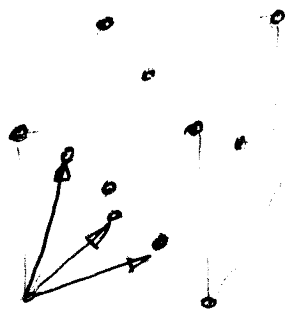
Volume of unit cell

$$\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3 = a^3/2$$

$$\vec{b}_1 = 2\pi \frac{\frac{a^2}{2}(0,1,1)}{a^3/2} = \frac{2\pi}{a}(0,1,1)$$

$$\vec{b}_2 = \frac{2\pi}{a}(1,0,1)$$

$$\vec{b}_3 = \frac{2\pi}{a}(1,1,0)$$



FCC unit cell

Primitive lattice vectors.

$$\vec{a}_1 = \frac{a}{2}(0,1,1)$$

$$\vec{a}_2 = \frac{a}{2}(1,0,1) \quad \Rightarrow \quad \vec{b}_1 = \frac{2\pi}{a}(\bar{1},1,1)$$

$$\vec{a}_3 = \frac{a}{2}(1,1,0)$$

etc.

Question 10

Vol of recip. latt. unit cell

$$\Omega_{R.cell} = \vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3)$$

Substitute $\vec{b}_1 = \dfrac{2\pi \, \vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}$ (but not $\vec{b}_2$ or $\vec{b}_3$)

$$\Omega_{cell} = \vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3$$

$$\Omega_{R.cell} = \frac{2\pi}{\Omega_{cell}} (\vec{a}_2 \times \vec{a}_3) \cdot (\vec{b}_2 \times \vec{b}_3)$$

$$= \frac{2\pi}{\Omega_{cell}} \vec{b}_3 \times (\vec{a}_2 \times \vec{a}_3) \cdot \vec{b}_2$$

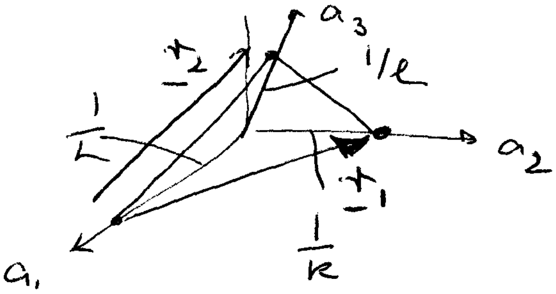
– using cyclic properties of $a \cdot b \times c$

$$= \frac{2\pi}{\Omega_{cell}} \left[(\vec{b}_3 \cdot \vec{a}_3)\vec{a}_2 - \underbrace{(\vec{b}_3 \cdot \vec{a}_2)}_{=0}\vec{a}_3 \right] \cdot \vec{b}_2$$

$$= \frac{2\pi}{\Omega_{cell}} (\vec{b}_3 \cdot \vec{a}_3)(\vec{a}_2 \cdot \vec{b}_2)$$

$$= \frac{(2\pi)^3}{\Omega_{cell}}$$

Question 11



(a) h, k, l plane intersects a_1, a_2, a_3 axes at $\frac{1}{h}, \frac{1}{k}, \frac{1}{l}$.

Consider 2 vectors lying in plane

— e.g. $\underline{t}_1 = \frac{1}{h}\underline{a}_1 - \frac{1}{k}\underline{a}_2$

and $t_2 = \frac{1}{h}\underline{a}_1 - \frac{1}{l}\underline{a}_3$

$$\underline{G}.\underline{t}_1 = \frac{h}{h}\underline{b}_1.\underline{a}_1 - \frac{k}{k}\underline{b}_2.\underline{a}_2 = 0.$$

$$\underline{G}.\underline{t}_2 = \frac{h}{h}\underline{b}_1.\underline{a}_1 - \frac{l}{l}\underline{b}_3.\underline{a}_3 = 0$$

— hence for any vector lying in the plane.

(b). Points $\underline{r}$ in the plane with a unit normal $\hat{n}$ and a perpendicular distance d from the origin obey $\hat{n}.\underline{r} = d$.

Two adjacent $(h,k\,l)$ planes.

$$\frac{1}{h}\underline{a}_1 + \frac{1}{k}\underline{a}_2 + \frac{1}{l}\underline{a}_3 \qquad (1)$$

$$\frac{2}{h}\underline{a}_1 + \frac{2}{k}\underline{a}_2 + \frac{2}{l}\underline{a}_3 \qquad (2)$$

Pick the point $\underline{r}$ to be $\frac{1}{h}\underline{a}_1$ in plane (1)

$$\hat{n} = \frac{1}{|G|}\underline{G}$$

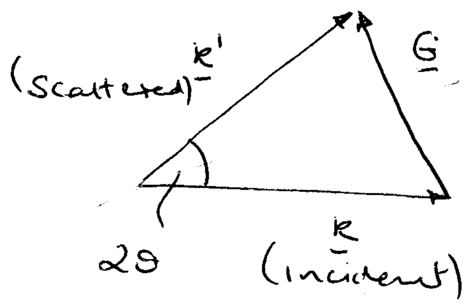
$$\hat{n}.\underline{r} = \frac{1}{|G|}\frac{1}{h}\underline{G}.\underline{a}_1 = \frac{2\pi}{|G|}.$$

For the second plane

$$\hat{n}.\underline{r} = \frac{1}{|G|}.\frac{2}{h}\underline{G}.\underline{a}_1 = \frac{4\pi}{|G|}$$

Difference $= 2\pi/|G|$.

4.10 (c) Ewald Construction



$\underline{k}\cdot\underline{G} = \frac{1}{2}G^2$ or $\frac{|G|}{2} = |k|\sin\theta$

$|G| = \frac{2\pi}{d}$. $|k| = \frac{2\pi}{\lambda}$. $\Rightarrow \frac{\pi}{d} = \frac{2\pi}{\lambda}\sin\theta$

$\Rightarrow \boxed{\lambda = 2d\sin\theta}$

Bragg's Law.