

Einstein Model of density of state:

The Einstein solid is a model of a solid based on two assumptions:

* Each atom in the lattice is an independent 3D quantum harmonic oscillator.

* All atoms oscillate with the same frequency.

Consider N oscillators with same frequency ω_0 . It is taken as one dimension.

According to Einstein density of state,

$$D(\omega) = N \delta(\omega - \omega_0)$$

$\delta \rightarrow$ Delta function which is centered at ω_0 .

The thermal energy of the system is

$$U = N \langle n \rangle \hbar \omega = \frac{N \hbar \omega}{\exp\left(\frac{\hbar \omega}{T}\right) - 1}$$

Heat capacity of the oscillator is,

$$C_v = \frac{\partial U}{\partial T} = \frac{\partial}{\partial T} \left(\frac{N \hbar \omega}{\exp\left(\frac{\hbar \omega}{T}\right) - 1} \right)$$

$$= \frac{\partial}{\partial T} N \hbar \omega \left[\exp\left(\frac{\hbar \omega}{T}\right) - 1 \right]^{-1}$$

$$= N \hbar \omega (-1) \left[\exp\left(\frac{\hbar \omega}{k_B T}\right) - 1 \right]^{-2} \exp\left(\frac{\hbar \omega}{k_B T}\right)$$

$$= \frac{N \hbar \omega \exp\left(\frac{\hbar \omega}{k_B T}\right) \cdot \left(\frac{+\hbar \omega}{k_B T^2}\right)}{\left[\exp\left(\frac{\hbar \omega}{k_B T}\right) - 1 \right]^2}$$

$$= \frac{N \exp\left(\frac{\hbar \omega}{k_B T}\right) \cdot \frac{\hbar^2 \omega^2}{k_B T^2}}{\left[\exp\left(\frac{\hbar \omega}{k_B T}\right) - 1 \right]^2}$$

$$\left[\exp\left(\frac{\hbar \omega}{k_B T}\right) - 1 \right]^2$$

\times by 2 Divide k_B

$$= \frac{N \exp\left(\frac{\hbar \omega}{k_B T}\right) \cdot \frac{\hbar^2 \omega^2}{k_B T^2} \cdot \frac{k_B}{k_B}}{\left[\exp\left(\frac{\hbar \omega}{k_B T}\right) - 1 \right]^2}$$

$$= \frac{N k_B \exp\left(\frac{\hbar \omega}{k_B T}\right) \cdot \frac{\hbar^2 \omega^2}{k_B T^2}}{\left[\exp\left(\frac{\hbar \omega}{k_B T}\right) - 1 \right]^2}$$

The heat capacity of a solid for N oscillator is identified.

For three dimension, N can be replaced by $3N$. At high temperature limit of C_v is $3Nk_B$ which is said to be Dulong and Petit value.

The Number of states per unit frequency range $D(\omega)$ is found.

$$D(\omega) d\omega = \left(\frac{L}{2\pi}\right)^3 \int_{\text{Shell}} d^3k$$

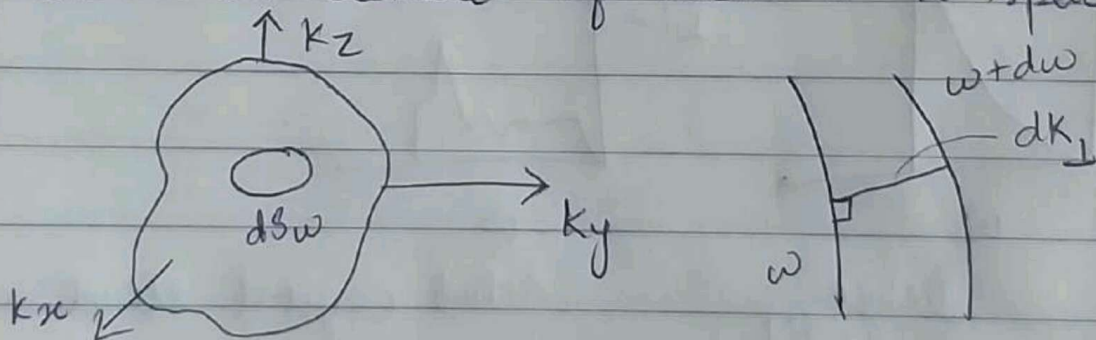
It is the number of allowed values of k for which the phonon frequency is between ω and $\omega + d\omega$.

Integral indicates the volume of the shell in k space.

consider two surface with constant phonon frequency. The frequency of one surface is ω and the other is $\omega + d\omega$.

The volume of the shell $\int_{\text{Shell}} d^3k$ has to be evaluated

let us consider a small surface dS_ω which denotes an element of area in k space with frequency ω



$$\int_{\text{shell}} d^3k = \int_{\text{Surface}} ds_{\omega} dk_{\perp}$$

\downarrow \times L^3 distance.

dk_{\perp} vary for every point. The gradient of ω is $\nabla_{\mathbf{k}}\omega$ which is normal to the surface ω .

$$|\nabla_{\mathbf{k}}\omega| dk_{\perp} = d\omega \Rightarrow dk_{\perp} = \frac{d\omega}{|\nabla_{\mathbf{k}}\omega|}$$

$$ds_{\omega} dk_{\perp} = ds_{\omega} \frac{d\omega}{|\nabla_{\mathbf{k}}\omega|}$$

$$= ds_{\omega} \frac{d\omega}{v_g} \quad (\because v_g = \frac{d\omega}{dk})$$

$$\nabla_{\mathbf{k}}\omega = \frac{d\omega}{dk}$$

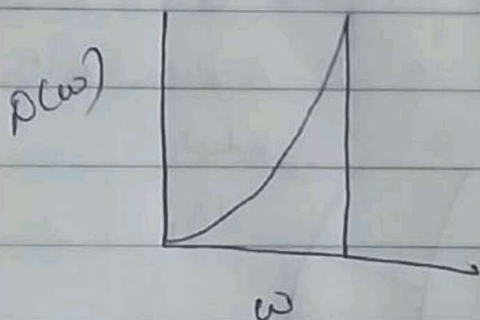
$$D(\omega) d\omega = \left(\frac{L}{2\pi}\right)^3 \int \frac{ds_{\omega} d\omega}{v_g}$$

$$v_g = \text{grad}_{\mathbf{k}} \omega(\mathbf{k})$$

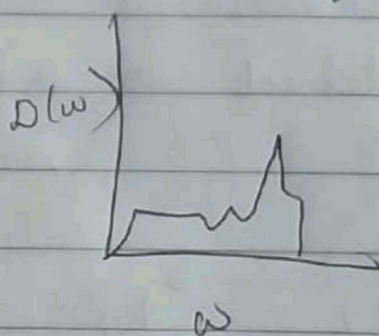
$$V = L^3$$

$$D(\omega) = \frac{V}{(2\pi)^3} \int \frac{ds_{\omega}}{v_g}$$

* This result can be used for electron band



Debye solid



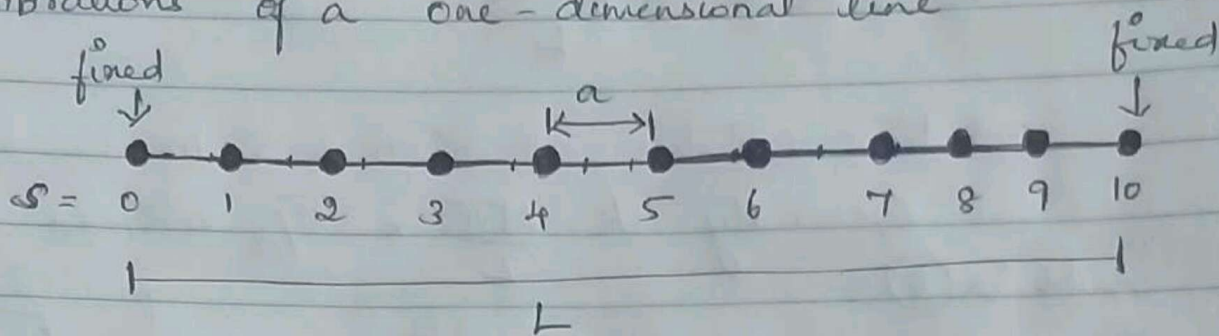
Actual crystal structure.

Density of state in 1D

Density of state :

It is the number of different states at a particular energy level that electrons are allowed to occupy (i.e) no of e^- states per unit volume per unit energy.

* consider a boundary value problem for vibrations of a one-dimensional line.



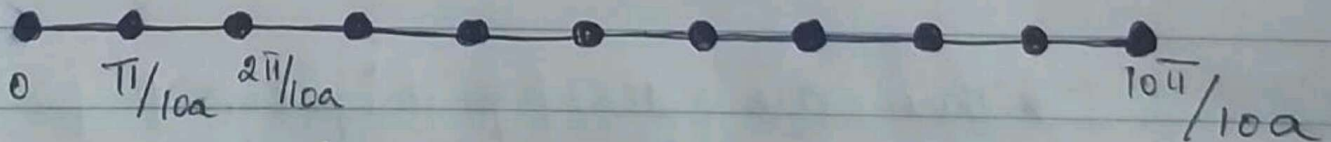
* It carries $N+1$ particles and its separation is "a" & length "L". $s=0$ & $s=N$ (i.e) $s=0$ & $s=10$ are fixed. hence $s=N$.

* Each vibrational mode has the form of standing wave.

$u_s \rightarrow$ Displacement of the particle

$$u_s = u(0) \exp(-i\omega_{k,p} t) \sin sKa \rightarrow \textcircled{1}$$

where $\omega_{k,p}$ related to dispersion relation.



(i.e) wavevector k restricted to a fixed boundary condition.

$$K = \frac{\pi}{L}, \frac{2\pi}{L}, \frac{3\pi}{L}, \dots, \frac{(N-1)\pi}{L}$$

$\begin{matrix} s=1 & s=2 & s=3 & & s=N \end{matrix}$

where $L = 10a$

The solution for $K = \pi/L$ is

$$u_s \propto \sin(ska) \rightarrow (2)$$

$$\boxed{a = L/N}$$

$$u_s \propto \sin \frac{s\pi a}{L}$$

Solution vanishes at $s=0$ & $s=10$

Generally $K = \frac{N\pi}{L} = \frac{\pi}{a} = K_{max}$

subs in (2)

$$u_s \propto \sin s \left(\frac{\pi}{a} \right) a$$

$$\left(\because \frac{\pi}{(L/N)} = \frac{\pi}{a} \right)$$

$$u_s \propto \sin s\pi$$

~~at each atom~~

at $s=0$ & $s=10$

* This shows that no atom moves, because $\sin s\pi$ vanishes at ~~each~~ ^{that} atom.

For 1 Dimensional, $\Delta K = \pi/L$

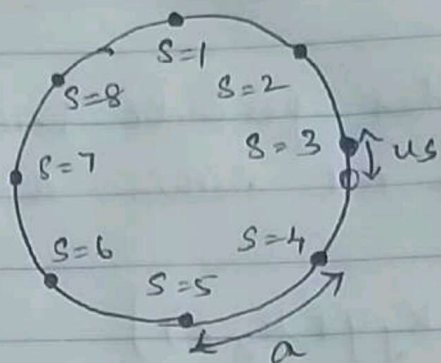
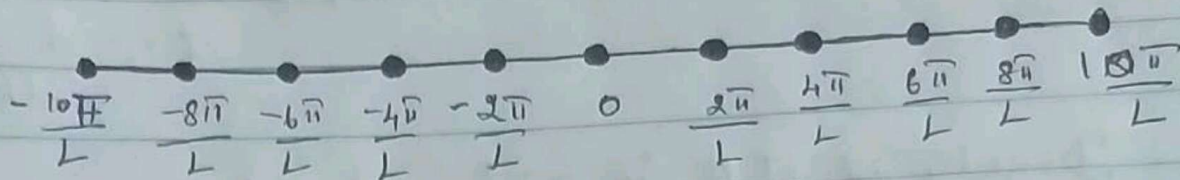
No of modes per unit range $K = L/\pi$ for $K \leq \pi/a$
 $K=0$ for $K > \pi/a$

* There are three polarization P for each value of K . Two of them are transverse and one longitudinal.

Unbounded state:

* consider an unbounded 1D state with distance 'L'.

$$u(sa) = u(sa + L)$$



Solution for unbounded state is

$$u_s = u(0) \exp(i(ska - \omega_k t))$$

Allowed values $k = 0, \pm \frac{2\pi}{L}, \pm \frac{4\pi}{L}, \dots, \pm \frac{N\pi}{L}$

* Since unbounded state has both positive and negative values with interval $\Delta k = \frac{2\pi}{L}$

No of modes per unit range = $L/2\pi$ for $-\pi/a < k < \pi/a$

$D(\omega) \rightarrow$ no of modes per unit frequency range 0 otherwise

$$D(\omega) d\omega = \frac{L}{\pi} \frac{dk}{d\omega} d\omega$$

$$= \frac{L}{\pi} \frac{d\omega}{d\omega/dk}$$

($\because \frac{d\omega}{dk} = \text{group velocity}$)

Density of state in 3 Dimensional:

* Consider periodic boundary condition over N^3 primitive cell within a cube of side L .

$$\exp[i(k_x x + k_y y + k_z z)]$$

$$= \exp[i(k_x (x+L) + k_y (y+L) + k_z (z+L))]$$

$$k_x, k_y, k_z = 0; \pm \frac{2\pi}{L}, \pm \frac{4\pi}{L}, \dots, \pm \frac{N\pi}{L}$$

Allowed values of k per volume $\left(\frac{2\pi}{L}\right)^3$

$$\left(\frac{L}{2\pi}\right)^3 = \frac{V}{8\pi^3} \quad (\because L^3 = V)$$

* Total no of modes with wavevector less than k

$$N = \left(\frac{L}{2\pi}\right)^3 \left(\frac{4\pi k^3}{3}\right)$$

↓
Volume of a sphere of radius k

So, Density of state for each polarization is

$$D(\omega) = \frac{dN}{d\omega} = \frac{d}{d\omega} \left[\left(\frac{L}{2\pi} \right)^3 \frac{4\pi k^3}{3} \right]$$

$$= \frac{V}{8\pi^3} \frac{d}{d\omega} \left[4\pi k^3 \right] \times \frac{dk}{d\omega}$$

$$D(\omega) = \frac{V k}{6\pi^2} \frac{dk}{d\omega} \quad ,,$$

Debye Model for Density of State :-

* Debye Model treats atomic vibrations as phonon in a box. The Debye Model is a method developed by Peter Debye in 1912 for estimating the phonon contribution to the specific heat in a solid.

* This model correctly explains the low temperature dependence of the heat capacity, which is proportional to T^3 .

* In Debye approximation, velocity of sound is taken as constant for each polarization.

The Dispersion relation is $\omega = vK \rightarrow (1)$

$v \rightarrow$ velocity of sound.

$$D(\omega) = \left(\frac{vK^2}{2\pi^2} \right) \left(\frac{dK}{d\omega} \right) \rightarrow (2)$$

from eqn (1), $K = \omega/v \Rightarrow K^2 = \omega^2/v^2$

$$D(\omega) = \frac{v\omega^2}{2\pi^2 v^3} \rightarrow (3)$$

group velocity

$$\left(\because \frac{dK}{d\omega} = \frac{1}{v_g} \right)$$
$$v_g = \frac{d\omega}{dK}$$

For N primitive cell, the total no. of phonon mode is $3N$. A cutoff frequency ω_D is

$$N = \left(\frac{L}{2\pi} \right)^3 \left(\frac{4\pi k^3}{3} \right)$$

$$N = \frac{V}{2\pi^2} \frac{4\pi k^3}{3} \quad (\because V^3 = V)$$

$$= \frac{V k^3}{6\pi^2}$$

$$k^3 = \frac{6\pi^2 N}{V} \rightarrow \textcircled{a}$$

$$\omega = vk \Rightarrow \omega^3 = v^3 k^3$$

Sub eqn (a) in ω^3 :

$$\omega^3 = \frac{v^3 6\pi^2 N}{V}$$

$$\omega = v \left(\frac{6\pi^2 N}{V} \right)^{1/3} \rightarrow \textcircled{4}$$

Its corresponding cutoff wavevector k in space

$$k_D = \frac{\omega_D}{v}$$

$k_D \rightarrow$ cutoff wavevector

Sub eqn (4) we get,

$$= \frac{v \left(\frac{6\pi^2 N}{V} \right)^{1/3}}{v}$$

$$= \left(\frac{6\pi^2 N}{V} \right)^{1/3} \rightarrow \textcircled{5}$$

In Debye Model, we don't allow modes of wavevector larger than k_D .

No. of modes having $k \leq k_D$ gives the number of degrees of freedom of monoatomic lattice.

Thermal energy U is
$$U = \frac{1}{P} \int d\omega \mathcal{D}(\omega) \frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{T}\right) - 1}$$

Sub eqn (3) in U

$$U = \int_0^{\omega_D} d\omega \frac{V\omega^2}{2\pi^2 v^3} \frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{T}\right) - 1} \rightarrow (b)$$

$$= \frac{\hbar V}{2\pi^2 v^3} \int_0^{\omega_D} \frac{\omega^3}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1} d\omega$$

for 3D case:

$$U = \frac{3\hbar V}{2\pi^2 v^3} \int_0^{\omega_D} \frac{\omega^3}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1} d\omega \rightarrow (6a)$$

$$U = \frac{3\hbar V}{2\pi^2 v^3} \int_0^{\omega_D} \frac{x^3 k_B^3 T^3}{\hbar^3 (\exp x - 1)} dx \quad \left(\because x = \frac{\hbar\omega}{k_B T} \right)$$

$$\omega = \frac{x k_B T}{\hbar}$$

$$= \frac{3\hbar V}{2\pi^2 v^3} \int_0^{\omega_D} \frac{x^3 k_B^3 T^3}{\hbar^3 (\exp x - 1)} dx$$

$$= \frac{3NV k_B^3 T^3}{2\pi^2 v^3 h^3} \int_0^{\omega_D} \frac{x^3}{\exp x - 1} dx \rightarrow (7)$$

$$\omega = \frac{k_B T}{h} x \quad ; \quad d\omega = \frac{k_B T}{h} dx \rightarrow (6)$$

Sub (6) eqn in (7), we get

$$= \frac{3V k_B^3 T^3}{2\pi^2 v^3 h^2} \int_0^{\omega_D} \frac{x^3}{\exp x - 1} \left[\frac{k_B T}{h} dx \right]$$

$$= \frac{3V k_B^4 T^4}{2\pi^2 v^3 h^3} \int_0^{\omega_D} \frac{x^3}{\exp x - 1} dx \rightarrow (8)$$

$$x = \frac{h\omega}{k_B T} \Rightarrow x_D = \frac{h\omega_D}{k_B T} = \frac{\theta}{T}$$

$\theta \rightarrow$ Debye Temperature in terms of ω_D

Take ω_D^3 ,

$$\left(\frac{\theta}{T}\right)^3 = \frac{h^3 \omega_D^3}{k_B^3 T^3} = \frac{h^3 6\pi^2 v^3 N}{V k_B^3 T^3}$$

$$\theta^3 = \frac{h^3 6\pi^2 v^3 N}{V k_B^3 T^3}$$

$$\theta = \frac{h v}{K_B} \left(\frac{6\pi^2 N}{V} \right)^{1/3} \rightarrow (9)$$

$$\left(\frac{\theta}{T}\right)^3 = \frac{h^3 6\pi^2 v^2 N}{V k_B^3 T^3}$$

$$k_B^3 T^3 = \frac{h^3 6\pi^2 v^3 N}{V} \left(\frac{T}{\theta}\right)^3 \rightarrow \textcircled{c}$$

Sub in ⑧

$$U = \frac{3V k_B T}{2\pi^2 v^3 h^3} k_B^3 T^3 \int_0^{\omega_D} \frac{x^3}{\exp x - 1} dx$$

Sub ⑨ in U

$$= \frac{3V k_B T}{2\pi^2 v^3 h^3} \left[\frac{h^3 6\pi^2 v^3 N}{V} \left(\frac{T}{\theta}\right)^3 \right]$$

$$\int_0^{\omega_D} \frac{x^3}{\exp x - 1} dx$$

$$= 9N k_B T \left(\frac{T}{\theta}\right)^3 \int_0^{\omega_D} \frac{x^3}{\exp x - 1} dx \rightarrow \textcircled{10}$$

Heat capacity: Taking ⑩

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{\partial}{\partial T} \left[\frac{3V k_B}{2\pi^2 v^3} \int_0^{\omega_D} dw \frac{\omega^3}{\exp\left(\frac{h\omega}{T}\right) - 1} \right]$$

$$= \frac{3V k_B}{2\pi^2 v^3} \int_0^{\omega_D} \frac{\partial}{\partial T} \left[\frac{\omega^3}{\exp\left(\frac{h\omega}{T}\right) - 1} \right] dw$$

$$= \frac{3Vh}{2\pi^2 v^3} \int_0^{\omega_D} \frac{\partial}{\partial T} \omega^3 \left[\exp\left(\frac{h\omega}{T}\right) - 1 \right]^{-1} d\omega$$

$$= \frac{3Vh}{2\pi^2 v^3} \int_0^{\omega_D} \omega^3 (-1) \left[\exp\left(\frac{h\omega}{k_B T}\right) - 1 \right]^{-2} \exp\left(\frac{h\omega}{k_B T}\right) \left(\frac{-h\omega}{k_B T^2}\right) d\omega$$

$$= \frac{3Vh^2}{2\pi^2 v^3 k_B T^2} \int_0^{\omega_D} \omega^4 \left[\exp\left(\frac{h\omega}{k_B T}\right) - 1 \right]^{-2} \exp\left(\frac{h\omega}{k_B T}\right) d\omega$$

$$C_V = \frac{3Vh^2}{2\pi^2 v^3 k_B T^2} \int_0^{\omega_D} \frac{\frac{k_B T^4}{h^4} x^4 \exp(x) \frac{k_B T}{h}}{\left[\exp\left(\frac{h\omega}{k_B T}\right) - 1 \right]^2} d\omega$$

$\omega = \frac{k_B T}{h} x$

$$= \frac{3Vh^2 \frac{k_B^4 T^4}{h^4} \frac{k_B T}{h}}{2\pi^2 v^3 k_B T^2 \frac{k_B^3 T^3}{h^3}} \int_0^{x_D} \frac{x^4 \exp(x) dx}{\left[\exp\left(\frac{h\omega}{k_B T}\right) - 1 \right]^2}$$

$$= \frac{3V k_B^4 T^3}{2\pi^2 v^3 h^3} \int_0^{x_D} \frac{x^4 \exp(x) dx}{\left[\exp\left(\frac{h\omega}{k_B T}\right) - 1 \right]^2}$$

$$= \frac{3V k_B^3 T^3}{2\pi^2 v^3 h^3} \int_0^{x_D} \frac{x^4 \exp(x) dx}{\left[\exp\left(\frac{h\omega}{k_B T}\right) - 1 \right]^2}$$

$$= \frac{3 \cancel{V} k_B}{\cancel{h^3} \cancel{v^3} \cancel{h^3}} \left[\frac{\cancel{h^3} \cancel{v^3} \cancel{h^3} N}{\cancel{V}} \left(\frac{T}{\theta} \right)^3 \right]$$

$$\int_0^{x_D} \frac{x^4 \exp(x) dx}{\left[\exp\left(\frac{\hbar \omega}{k_B T}\right) - 1 \right]^2}$$

$$= 9 N k_B \left(\frac{T}{\theta} \right)^3 \int_0^{x_D} \frac{x^4 \exp(x) dx}{\left[\exp\left(\frac{\hbar \omega}{k_B T}\right) - 1 \right]^2}$$

↳ (ii)

Unit-4

Fermi Electron Gas in three Dimensions:

Any electron that is not attached to an ion, atom or molecule and is free to move under the influence of an applied electric or magnetic field.

According to free-particle Schrodinger equation in 3D

$$H\psi_n = -\frac{\hbar^2}{2m} \frac{d^2\psi_n}{dx^2} = E_n \psi_n \quad (\because \text{for 1D})$$

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi_k(r) = E_k \psi_k(r)$$

$\rightarrow \textcircled{1}$

(\because for 3D)

Consider a cube of length L where the electrons are confined to it. The wave function of standing waves are of the form,

$$\psi_n(x) = A \sin \frac{n\pi x}{L} \quad (\because \text{for 1D})$$



$$\psi_n(r) = A \sin \frac{\pi n_x x}{L} \sin \frac{\pi n_y y}{L} \sin \frac{\pi n_z z}{L}$$

(\because for 3D) $\rightarrow \textcircled{2}$

where n_x, n_y, n_z are positive integers.

The origin of the cube will be at one corner.

where the wavefunction is periodic with period L , then ψ can be represented as,

$$\text{III} \text{ly} \left. \begin{aligned} \psi(x+L, y, z) &= \psi(x, y, z) \\ \psi(x, y+L, z) &= \psi(x, y, z) \\ \psi(x, y, z+L) &= \psi(x, y, z) \end{aligned} \right\} \rightarrow \textcircled{3}$$

If the wavevector of free particle Schrodinger equation and periodicity conditions are of the form of travelling plane wave.

$$\psi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r}) \rightarrow \textcircled{4} \quad (\text{pg: 164 nearly free electron model})$$

$$k_x, k_y, k_z = 0; \pm \frac{2\pi}{L}, \pm \frac{4\pi}{L}, \dots$$

$k = \frac{2n\pi}{L}$. This wavevector satisfies the periodicity condition

$$\exp[ik_x(x+L)] = \exp\left[\frac{i2n_x\pi}{L}(x+L)\right]$$

$$= \exp\left(\frac{i2n_x\pi x}{L}\right) \cdot \exp\left(\frac{i2n_x\pi L}{L}\right)$$

$$= \exp\left(\frac{i2n_x\pi x}{L}\right) \cdot 1$$

$$= \exp(ik_x x) \rightarrow \textcircled{5}$$

sub $\textcircled{4}$ in $\textcircled{1}$

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \exp(i\mathbf{k} \cdot \mathbf{r}) = E_{\mathbf{k}} \exp(i\mathbf{k} \cdot \mathbf{r})$$

$$E_k = \frac{\hbar^2}{2m} k^2 = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2) \rightarrow \textcircled{6}$$

$$k = \frac{2\pi}{\lambda}$$

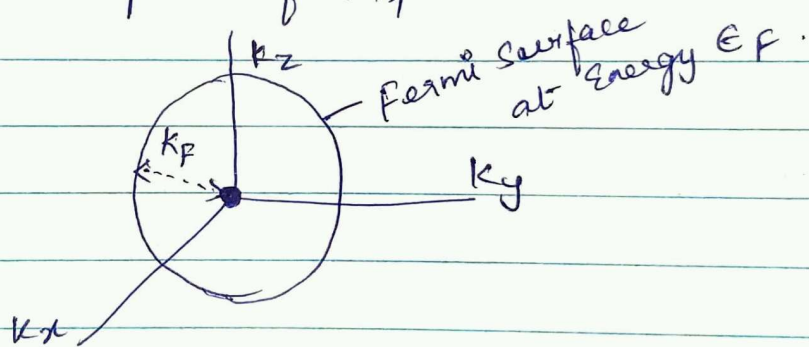
Linear Momentum P can be represented in quantum mechanics as

$$P = -i\hbar \nabla$$

$$P \psi_k(r) = -i\hbar \nabla \psi_k(r) = -i\hbar \nabla (\exp i\mathbf{k} \cdot \mathbf{r}) \\ = \hbar \mathbf{k} \cdot \mathbf{r} = \hbar \mathbf{k} \psi_k(r)$$

$$P = \hbar \mathbf{k} \Rightarrow m\mathbf{v} = \hbar \mathbf{k} \Rightarrow \mathbf{v} = \frac{\hbar \mathbf{k}}{m}$$

Consider a system of N free electrons in ground state, the occupied orbital is represented as a point inside the sphere of k space.



Energy of the Fermi sphere is

$$E_F = \frac{\hbar^2}{2m} k_F^2 \rightarrow \textcircled{7}$$

$$\text{Volume element} = \left(\frac{2\pi}{L} \right)^3$$

The volume of the sphere is $\frac{4\pi R^3}{3} = \frac{4\pi k_F^3}{3}$

Total no. of orbitals

$$N = 2 \cdot \frac{4\pi k_F^3 / 3}{(2\pi/L)^3} = 2 \cdot \frac{4\pi k_F^3}{3} \cdot \frac{L^3}{8\pi^3}$$

$$= \frac{2 \cdot 4\pi k_F^3 \times L^3}{3 \times 8\pi^3}$$

$$= \frac{k_F^3 L^3}{3\pi^2} = \frac{k_F^3 V}{3\pi^2}$$

$$N = \frac{V k_F^3}{3\pi^2} \rightarrow \textcircled{8}$$

The factor 2 is because of two allowed values of the spin quantum number ($+\frac{1}{2}, -\frac{1}{2}$). \downarrow

Rearranging eqn (8)

$$k_F^3 = \frac{3\pi^2 N}{V} \Rightarrow k_F = \left(\frac{3\pi^2 N}{V} \right)^{1/3} \rightarrow \textcircled{9}$$

The k_F depends only on particle concentration

sub eqn (9) in (7)

$$E_F = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V} \right)^{2/3} \rightarrow (10)$$

- This relates E_F to N/V (i.e) Fermi energy to electron concentration.

Then the electron velocity v_F at Fermi surface is

$$v_F = \frac{\hbar k_F}{m} = \frac{\hbar}{m} \left(\frac{3\pi^2 N}{V} \right)^{1/3} \rightarrow (11)$$

The Density of states for free electron gas in 3D is taking eqn (10)

$$\frac{2mE_F}{\hbar^2} \left(\frac{V}{3\pi^2} \right)^{2/3} = N^{2/3}$$

$$\left(\frac{2mE_F}{\hbar^2} \right)^{3/2} \frac{V}{3\pi^2} = N \rightarrow (12)$$

$$D(E) = \frac{dN}{dE} = \frac{d}{dE} \left(\frac{V}{3\pi^2} \left(\frac{2mE_F}{\hbar^2} \right)^{3/2} \right)$$

$$= \frac{V}{3\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \frac{3}{2} E_F^{1/2}$$

$$D(E) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E_F^{1/2} \rightarrow (13)$$

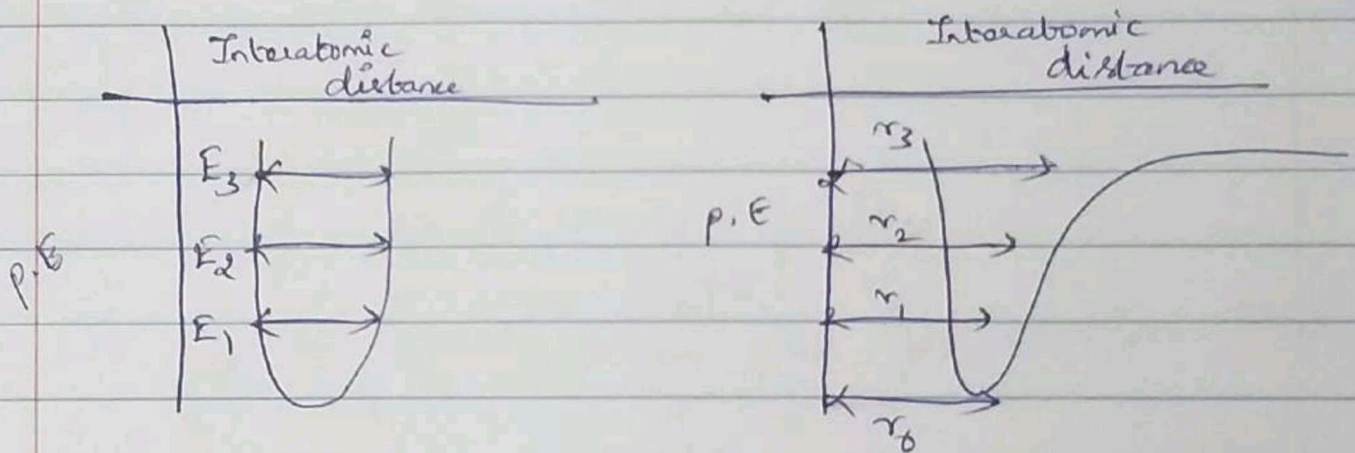
It can be represented simply as

$$D(E) = \frac{dN}{dE} = \frac{3N}{2E}$$

Thermal expansion:

- * Solids expands on heating
- * Thermal expansion corresponds to an increase in the average interatomic distance.
- * Amplitude of lattice vibration increases as temperature increases.
- * If lattice vibrations are harmonic, there is no thermal expansion. They are exactly parabolic
- * If lattice vibrations are anharmonic, the minimum point is parabolic and it deviates from its form as distance increases.
- * The position will not remain constant as potential energy increases.

$$U(x) = \underbrace{cx^2}_{\text{Harmonic}} - \underbrace{gx^3}_{\text{anharmonic}} + \underbrace{fx^4}_{\text{anharmonic}}$$



Thermal Expansion:

* The increase in the dimensions of a body due to increase in its temperature is called Thermal expansion

(a) ^{When} ~~with~~ potential is harmonic:

$$U(x) = cx^2 \rightarrow (1)$$

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} dx x e^{-U(x)/k_B T}}{\int_{-\infty}^{\infty} dx e^{-U(x)/k_B T}} \rightarrow (2)$$

(1)

Sub eqn (1) in (2),

$$= \frac{\int_{-\infty}^{\infty} dx x e^{-cx^2/k_B T}}{\int_{-\infty}^{\infty} dx e^{-cx^2/k_B T}} = 0$$

(b) When potential is anharmonic

$$U(x) = cx^2 - gx^3 - fx^4 \rightarrow (3)$$

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} dx x e^{-U(x)/k_B T}}{\int_{-\infty}^{\infty} dx e^{-U(x)/k_B T}} \rightarrow (4)$$

Sub (3) in (4),

$$= \frac{\int_{-\infty}^{\infty} dx x e^{-(cx^2 - gx^3 - fx^4)/k_B T}}{\int_{-\infty}^{\infty} dx e^{-(cx^2 - gx^3 - fx^4)/k_B T}}$$

$$e^{gx^3+fx^4/k_B T} = 1 + \frac{gx^3+fx^4}{k_B T} + \dots \quad e^{-\frac{cx^2}{k_B T}} \cdot e^{\frac{gx^3+fx^4}{k_B T}}$$

$$= \int_{-\infty}^{\infty} dx \, x \, e^{-\frac{cx^2}{k_B T}} \left(1 + \frac{gx^3+fx^4}{k_B T} \right)$$

$$\frac{\int_{-\infty}^{\infty} dx \, e^{-\frac{cx^2}{k_B T}} \left(1 + \frac{gx^3+fx^4}{k_B T} \right)}{\int_{-\infty}^{\infty} dx \, e^{-\frac{cx^2}{k_B T}}}$$

$$= \int_{-\infty}^{\infty} dx \, x \, e^{-\frac{cx^2}{k_B T}} \left(x + \frac{gx^4+fx^5}{k_B T} \right)$$

$$\int_{-\infty}^{\infty} dx \, e^{-\frac{cx^2}{k_B T}}$$

(\therefore neglecting higher terms in Denominator)

$$\int_{-\infty}^{\infty} dx \, x \, e^{-\frac{cx^2}{k_B T}} = 0, \quad \int_{-\infty}^{\infty} dx \, x^5 \, e^{-\frac{cx^2}{k_B T}} = 0$$

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} dx \, x \, e^{-\frac{cx^2}{k_B T}} \left(\frac{gx^4}{k_B T} \right)}{\int_{-\infty}^{\infty} dx \, e^{-\frac{cx^2}{k_B T}}}$$

$$= \frac{g}{k_B T} \frac{\int_{-\infty}^{\infty} dx \, x^4 \, e^{-\frac{cx^2}{k_B T}}}{\int_{-\infty}^{\infty} dx \, e^{-\frac{cx^2}{k_B T}}}$$

$$= \frac{g}{k_B T} \frac{\int_{-\infty}^{\infty} dx \, x^4 \, e^{-\frac{cx^2}{k_B T}}}{\int_{-\infty}^{\infty} dx \, e^{-\frac{cx^2}{k_B T}}}$$

$$\int_{-\infty}^{\infty} dx \, e^{-\frac{cx^2}{k_B T}}$$

$$\int_{-\infty}^{\infty} dx x^4 e^{-\gamma x^2} = \frac{3}{4\gamma^2} \sqrt{\frac{\pi}{\gamma}}$$

$$\int_{-\infty}^{\infty} dx e^{-\gamma x^2} = \sqrt{\frac{\pi}{\gamma}}$$

$$\gamma = \frac{c}{k_B T}$$

$$\langle x \rangle = \frac{g}{k_B T} \frac{3}{4c^2} \frac{\sqrt{\frac{\pi}{c} k_B T}}{(\frac{k_B T}{c})^2} \frac{\sqrt{\frac{\pi}{c} k_B T}}{c}$$

$$\langle x \rangle = \frac{g}{k_B T} \frac{3(k_B T)^2}{4c^2} \frac{\sqrt{\frac{\pi}{c} k_B T}}{c} \frac{\sqrt{\frac{\pi}{c} k_B T}}{c}$$

$$\Rightarrow \frac{g}{\rho} \frac{3g k_B T}{4c^2}$$

if $\langle x \rangle \propto T$

Thermal expansion coefficient,

$$\alpha = \frac{d\langle x \rangle}{dT} = \frac{3g}{4c^2} k_B$$

ρ is independent of Temperature.

But according to experiments α is Temperature dependent and goes to zero as $T \rightarrow 0$

The classical value of α is quite high than the experimental value for all the solids.