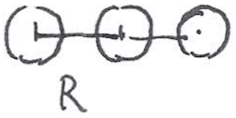
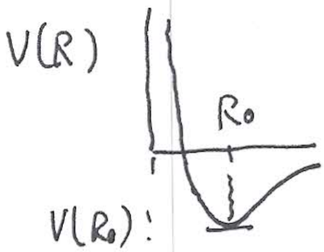
Lattice vibration : Normal modes

Harmonic Model (approximation)





$V(R) = V(R_0) + V'(R_0)\,\delta + \frac{1}{2}V''(R_0)\,\delta^2 + O(\delta^3)$

$R = R_0 + \delta$

$V'(R_0) = 0$ (Minimum)

$$V(R) = V(R_0) + \tfrac{1}{2}V''(R_0)\,\delta^2 + r_1\delta^3 + r_2\delta^4 + \cdots$$

$$\simeq V(R_0) + \tfrac{1}{2}V''(R_0)\,\delta^2 \qquad \text{(Harmonic approx)}$$

Valid : $\underline{\delta/R_0 \ll 1}$

When $\delta/R_0 \gtrsim 0.1 \Rightarrow$ anharmonic effects become important

Lattice expansion
phonon - phonon scattering

HARMONIC MODEL

1d:

$K = 2\pi/\lambda$

$\vec{u}_s$ = displacement of atom at site s.

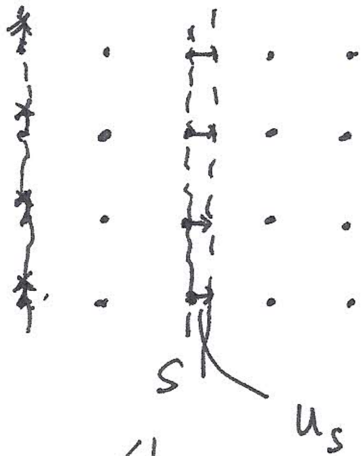
Longitudinal $\quad \vec{u}_s = \hat{x}\,u_s$

Transverse $\quad \vec{u}_s = \hat{y}\,u_s$ or $\hat{z}\,u_s$

For a given $\vec{K} = K\hat{x}$ there are 3 branches

$\omega_{\vec{K}j} \qquad j = 1,2,3 \ (L, T_1, T_2)$

2d $\vec{K}$ along symmetry direction

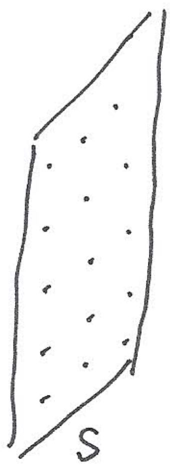


$\longrightarrow \vec{K} = K\hat{x}$

All atoms on axis perpendicular to $\hat{x}$ move exactly same way.

s^{th} chain

3d



$\longrightarrow \vec{K} = Kx$

All atoms on the s^{th} plane move exactly the same.

only nearest neighbor interact.

u_{s-1} u_s u_{s+1}

$$F_s = C[u_{s+1} - u_s] + C[u_{s-1} - u_s]$$

$F_s = 0$ if $u_s = u_{s+1}$

$F_s = 0$ if $u_{s-1} = u_s$

$$F_s = C[u_{s+1} + u_{s-1} - 2u_s]$$

Consider force/atom. , C is also per atom.

$$\boxed{F_s = M\frac{d^2u_s}{dt^2} = C[u_{s+1} + u_{s-1} - 2u_s]}$$

$s = 1, 2, \ldots N$

1d: N atoms

2d: N chains

3d: N planes.

$$u_{s,s\pm 1}(t) = u_{s,s\pm 1}e^{-i\omega t} \quad \text{(Harmonic dynamics)}$$

$$-M\omega^2 u_s = C[u_{s+1} + u_{s-1} - 2u_s]$$

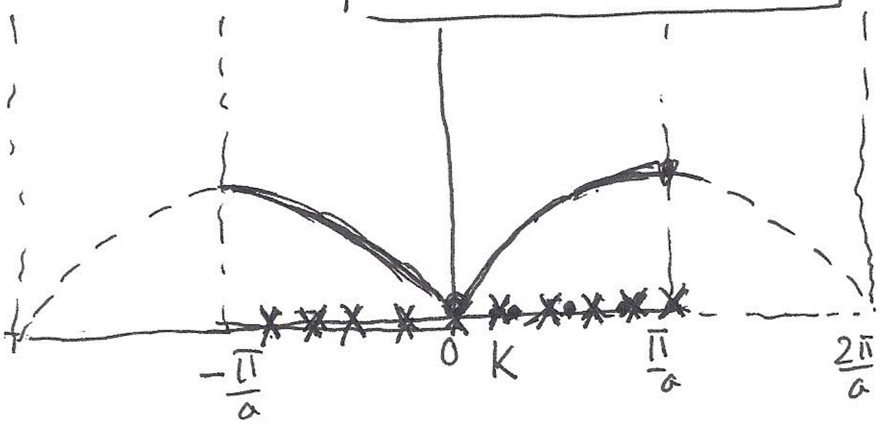
Next: $u_s = u\,e^{iKsa}$

$$-M\omega^2 u\,e^{iKsa} = C\left[e^{iK(s+1)a} + e^{iK(s-1)a} - 2e^{iKsa}\right]u$$

$$-M\omega^2 u = C\left[e^{iKa} + e^{-iKa} - 2\right] = -2C\left[1-\cos Ka\right]$$

$$\therefore\ \omega^2 = \frac{2C}{M}(1-\cos Ka) = \frac{4C}{M}\sin^2\frac{Ka}{2} \geq 0$$

$$\boxed{\omega_K = \sqrt{\frac{4C}{M}}\left|\sin\frac{Ka}{2}\right|}$$



$\boxed{\begin{array}{l}\omega_K \to 0 \text{ as } K \to 0\\ \text{Translational Invariance}\\ * \text{ Goldstone mode}\end{array}}$

Physical modes:

$-\frac{\pi}{a} < K \leq \frac{\pi}{a}$

Inside 1st Brillouin Zone

Allowed: K values: N

$$K = \cancel{0} \pm \frac{2\pi}{Na} n \qquad n = 0, 1, \ldots, \frac{N}{2}$$

$\underline{\underline{N = 10}} \Rightarrow K = 0, \pm\frac{2\pi}{10a}, \pm\frac{4\pi}{10a}, \pm\frac{6\pi}{10a}, \pm\frac{8\pi}{10a}$

$+\frac{10\pi}{10a}$

$-\frac{\pi}{a} < K \leq \frac{\pi}{a}$

$-\frac{10\pi}{10a} = -\frac{\pi}{a}$ is not included.

& $+\frac{\pi}{a}$ is included

of course N very large $\underline{-\frac{\pi}{a} < K \leq +\frac{\pi}{a}}$

<u>Important.</u>

① $K \to 0$ $\quad \omega_K = \sqrt{\frac{4C}{M}}\,\frac{Ka}{2} = \left(\sqrt{\frac{C}{M}}\,a\right)K = V_s K \to$ <u>Sound wave</u>

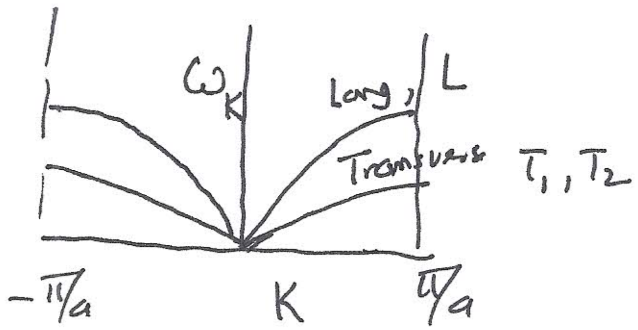
V_s = Sound wave velocity: $\sqrt{C/M}\,a$

② $\omega_K \leq \omega_{max} = \sqrt{\frac{4C}{M}} \propto \frac{1}{M^{1/2}}$

Transverse & Longitudinal modes

$C \equiv C_{Long} = C_L$

$C \equiv C_{trans.} = C_T$



usually $C_{trans} < C_{long}$

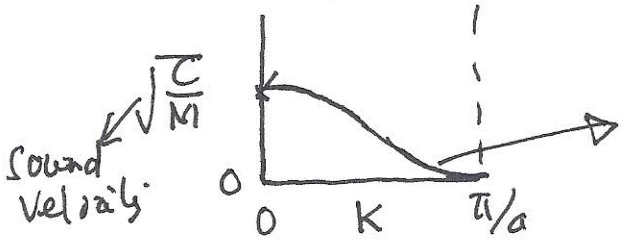
$$\omega_{K,L} = \sqrt{\frac{4C_L}{M}}\left|\sin\frac{Ka}{2}\right|$$

$$\omega_{K,T_1,T_2} = \sqrt{\frac{4C_T}{M}}\left|\sin\frac{Ka}{2}\right|$$

Group Velocity of Lattice vibrational waves

$$v_{gK} = \frac{d\omega_K}{dK} \underset{Long.}{=} \sqrt{\frac{4C_L}{M}}\frac{a}{2}\cos\frac{Ka}{2} = \sqrt{\frac{C}{M}}\cos\frac{Ka}{2}$$

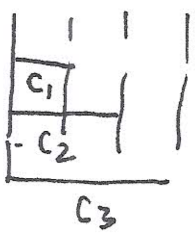
$K > 0$



$0 \Rightarrow$ these waves don't carry any energy.

In 3d. $\boxed{\vec{v}_{g\vec{K}} = \nabla_{\vec{K}}\,\omega_{\vec{K}}}$

Force constant from experimental ω_K



$$-M\omega^2 u e^{iKsa} = \sum_{p>0} C_p\left(e^{iK(s+p)a} + e^{iK(s-p)a} - 2e^{iKsa}\right)u$$

$$= 2\sum_{p>0} C_p(\cos Kpa - 1)$$

$$\boxed{\omega_K^2 = \frac{2}{M}\sum_{p>0} C_p(1-\cos Kpa)} \longrightarrow 0 \text{ as } K \to 0$$

Gold stone mode

$$M \int_{-\pi/a}^{+\pi/a} \omega_K^2 \cos rKa \; dK = 2 \sum_{p>0} C_p \int_{-\pi/a}^{+\pi/a} (1-\cos pKa) \cos rKa$$

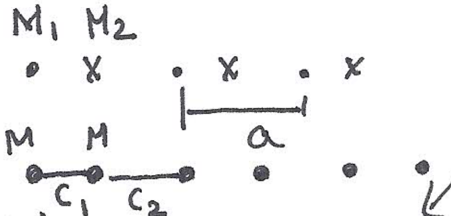
$$= -2\pi C_r/a$$

$$\therefore \quad \boxed{C_r = -\frac{Ma}{2\pi} \int_{-\pi/a}^{+\pi/a} \omega_K^2 \cos rKa \; dK}$$

$r = 1, 2, \ldots$

Normal modes in systems with more than 1 atom/BL unit cell.

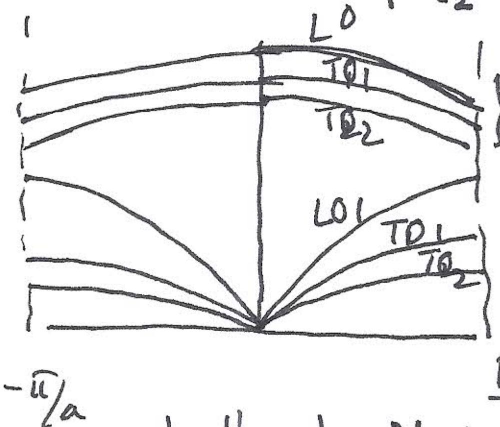
1d



N BL sites

2N atoms.

K : N K value.



} optic For each K, $(2\times3) = 6$ modes.

} Acoustic

$-\pi/a$ $\frac{\pi}{a}$

u_{s-1} v_{s-1} u_s v_s u_{s+1}

Let's do $M_1 \neq M_2$: Same C

$$M_1 \frac{d^2 u_s}{dt^2} = C\left[v_s + v_{s-1} - 2u_s\right]$$

$$M_2 \frac{d^2 v_s}{dt^2} = C\left[u_{s+1} + u_s - 2v_s\right]$$

$u_s = u e^{-i\omega t} e^{iKsa}$

$v_s = v e^{-i\omega t} e^{iKsa}$

$$-M_1\omega^2 u = C\left[v(1+e^{-iKa}) - 2u\right]$$

$$-M_2\omega^2 v = C\left[u(1+e^{+iKa}) - 2v\right]$$

$$(2C - M_1\omega^2)u - C(1+e^{-iKa})v = 0$$

$$-C(1+e^{+iKa})u + (2C - M_2\omega^2)v = 0$$

Eigen values are obtained by making the determinant

$$\det\begin{pmatrix} (2C - M_1\omega^2) & -C(1+e^{-iKa}) \\ -C(1+e^{+iKa}) & (2C - M_2\omega^2) \end{pmatrix} = 0$$

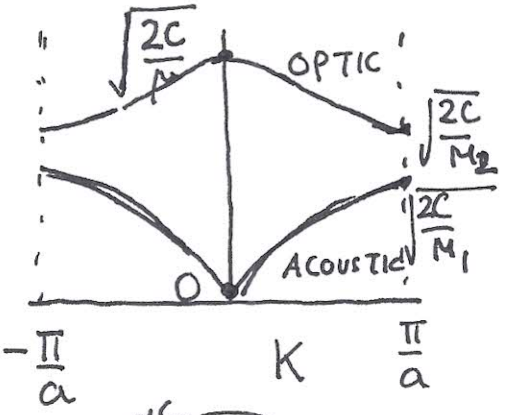
$$\boxed{(2C - M_1\omega^2)(2C - M_2\omega^2) - C^2(1+e^{-iKa})(1+e^{+iKa}) = 0}$$

Define reduced mass μ: $\frac{1}{\mu} = \frac{1}{M_1} + \frac{1}{M_2}$

$$\omega_\pm^2 = \frac{C}{\mu}\left[1 \pm \sqrt{1 - \frac{4\mu^2}{M_1 M_2}\sin^2\frac{Ka}{2}}\right] \Leftarrow \text{2 modes.}$$

Look at $K=0$: $\omega_+^2 = \frac{2C}{\mu}$, $\omega_+ = \sqrt{\frac{2C}{\mu}}$

$\omega_-^2 = 0$ $\qquad \omega_- = 0$ (Goldstone mode)

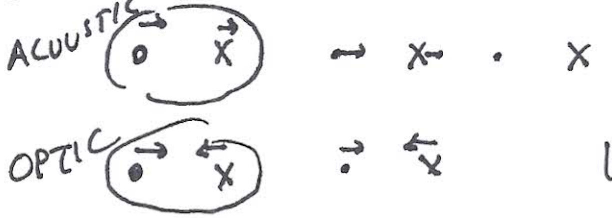


$K = \frac{\pi}{a}$: $\omega_\pm^2 = \frac{C}{\mu}\left[1 \pm \sqrt{1 - \frac{4\mu^2}{M_1 M_2}}\right]$

Let $M_1 > M_2$

$$\omega_+ = \sqrt{\frac{2C}{M_2}}$$

$$\omega_- = \sqrt{\frac{2C}{M_1}}$$



Why ACOUSTIC & OPTIC ?

| M_1 M_2 | M_1 M_2 | .   . |

| +e   −e | +e   −e |

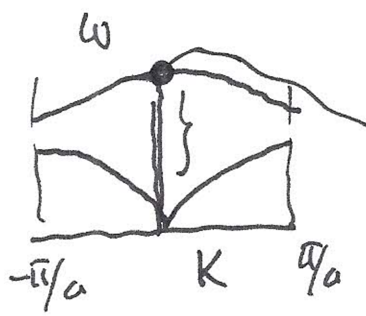
unit cell: Charge neutral, No electric dipole

Acoustic mode: +e and −e move in the same direction
no local dipole created

optic mode: +e and −e move towards each other

$\vec{p}$

$+\!\!\rightarrow\!\cdot \quad +\!\!\rightarrow\!\cdot \quad +\!\!\rightarrow\!\cdot$



local dipole created which can couple to external electric field $-\vec{p}\cdot\vec{E}(t)$

→ can excite this mode by ~~light~~ Electromagnetic wave

Now to thermal properties of lattice vibrations (phonons)

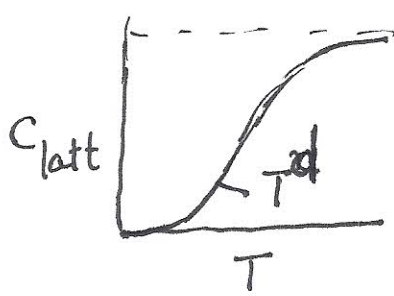
Consider a simple mono-atomic solid → only Acoustic Modes.

explain later

Expt: Electrons Vs phonons

↓ metals

independent of dimension
1d, 2d, 3d



d is the dimensionality

$\sim T$ (1d)
$\sim T^2$ (2d)
$\sim T^3$ (3d)

WHY?

Thermal physics of Lattice Vibration.

N atoms: 3d : 3N normal modes : freq. $\omega_{\vec{k}j}$ (Book uses $j = p$)
(independent) $\downarrow$ Harmonic Approx.

Model:

Each normal mode $\Leftrightarrow$ 1 harmonic oscillator
3N normal modes $\Leftrightarrow$ 3N harmonic oscillators.

Classical picture

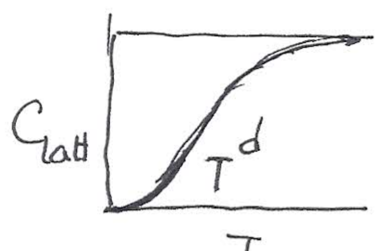
$$U_1 = \frac{p^2}{2m} + \frac{1}{2} k x^2 \quad , \quad \omega = \sqrt{\frac{k}{m}}$$

Average energy at temp T

$$\langle U_1 \rangle = \frac{\langle p^2 \rangle}{2m} + \frac{1}{2} k \langle x^2 \rangle$$
$$= \frac{1}{2} k_B T + \frac{1}{2} k_B T = k_B T$$

(Equipartition theorem) — indep. of ω

$\therefore$ $U = 3N k_B T$
$C_V = 3N k_B \equiv C_{latt}$



$3Nk_B$ (Classical theory)

FAILS AT LOW T

Quantum picture

$$U_1 = (n + \tfrac{1}{2})\hbar\omega \qquad n = 0, 1, 2, \ldots \infty$$

Discrete energy

$$= n\hbar\omega + \underbrace{\tfrac{1}{2}\hbar\omega}$$

Constant (zero point energy) Doesn't Contribute to T-dependence

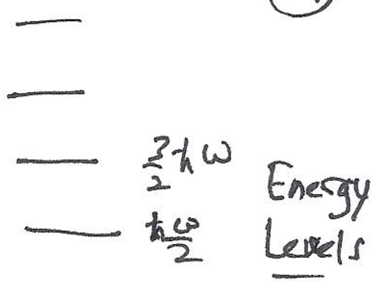
$$\langle U_1 \rangle = \langle n \rangle \hbar\omega + \frac{1}{2}\hbar\omega$$

$$\langle n \rangle = \frac{1}{e^{\hbar\omega/k_B T} - 1}$$

Planck distribution

n = # of phonons ~~in~~ with freq. ω

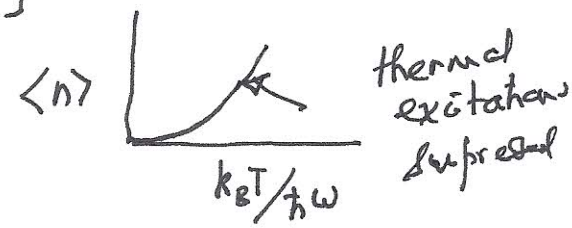
For lattice with 3N normal modes



Drop $\langle\,\rangle$ and zero-point energy (follow Book)

$$U = \sum_{\vec{K}} \sum_{j} \left[\frac{\hbar\omega_{\vec{K}j}}{e^{\frac{\hbar\omega_{\vec{K}j}}{k_B T}} - 1} \right]$$

Imp. physics : (a)



(b) Each mode contributes different amount to U.

Let's follow book notation (with some corrections)

$(j \Rightarrow p)$

$$\boxed{U = \sum_{p} \int D_p(\omega)\, d\omega \left[\frac{\hbar\omega}{e^{\frac{\hbar\omega}{k_B T}} - 1} \right]} \qquad (1)$$

$D_p(\omega)\, d\omega$: # of Normal modes of polarization p with freq. $\omega_{\vec{K}p}$ lying between ω and $\omega + d\omega$

Density of states (vib)

Eqn. (1) separates "Statistics" and "mechanics"

How to find $D_p(\omega)$?

① what are allowed values of $\vec{K}$ (Boundary condn. Geometry)

② How $\omega_{\vec{K}p}$ depends on $\vec{K}$ (Force constants, Interatomic interaction).

① Allowed $\vec{K}$ values

Depends on what boundary conditions we choose.

Two types: - Fixed boundary conditions (not common)

Periodic boundary condition (Common)

Let's look at 1d example

BOUNDARY CONDITIONS

FOR LARGE N DON'T MATTER

Fixed

x x

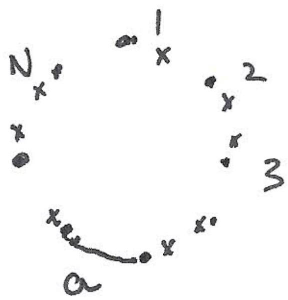
0 1 2 N

$\boxed{u_s = 0\ ,\ s = 0 \text{ and } s = N}$

Fix 0 and N atom

N-1 modes (Read Kittel)

Periodic



• Eq. position

x Displaced position

$\boxed{u_s = u_{N+s}}$

$u_1 = u_9$

$u_3 = u_{11}$

$N = 8$

N modes

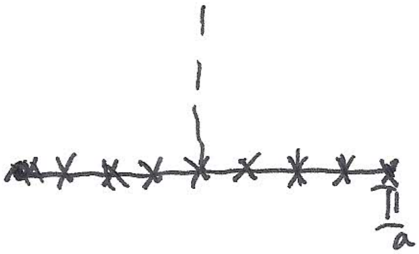
Since $u_s = u e^{iKsa} = u_{N+s} = u e^{iK(N+s)a}$

We need $e^{iKNa} = 1 \Rightarrow K = \pm \frac{2\pi}{Na} \cdot n$ ← integer

For N = 8, allowed K values are:

$$K = 0,\ \pm\frac{2\pi}{8a},\ \pm\frac{4\pi}{8a},\ \pm\frac{6\pi}{8a},\ +\frac{8\pi}{8a} = \frac{\pi}{a}$$

$K = -\frac{\pi}{a}$ is not included (same physics as $+\pi/a$)



$\Delta K/\text{mode} = \frac{2\pi}{Na} = \frac{2\pi}{L}$ (1 dimension)

<u>2 dimension</u> Area in $\vec{K}$ space/mode $= \left(\frac{2\pi}{L}\right)^2$

3 dimension Volume in $\vec{K}$ space/mode $= \left(\frac{2\pi}{L}\right)^3$

Now to Density of vibrational states $D_p(\omega)$

(Similar to what we did for electrons).

We need how $\omega_{\vec{K}p}$ depends on $\vec{K}$.

In general, complicated. Sound wave approx.

Consider only Acoustic Modes

$$\omega_{\vec{K}p} = v_p |\vec{K}|$$

(isotropic, linear, ok for $|\vec{K}|$ small)

But assume OK for large $|\vec{K}| \sim \pi/a$

<u>1d</u>

$$D_p(\omega) d\omega = 2 \cdot \frac{dK}{\left(\frac{2\pi}{L}\right)} \quad \text{with } \omega_{Kp} = \omega$$

$$= 2\left(\frac{L}{2\pi}\right) \cdot \frac{dK}{d\omega_{\vec{K}p}} \cdot d\omega = 2\left(\frac{L}{2\pi}\right) \cdot \frac{1}{v_p} d\omega$$

$$\therefore D_p(\omega) = 2 \cdot \left(\frac{L}{2\pi}\right) \cdot \frac{1}{v_p}$$

<u>2d</u>

$$D_p(\omega) d\omega = 2\pi K \frac{dK}{\left(\frac{2\pi}{L}\right)^2} = \left(\frac{L}{2\pi}\right)^2 \cdot 2\pi K \frac{dK}{d\omega_{Kp}} \cdot d\omega$$

$$= \frac{A}{2\pi} \cdot \frac{\omega}{v_p} \cdot \frac{1}{v_p} d\omega$$

$$\boxed{D_p(\omega) = \frac{A}{2\pi v_p^2} \omega}$$

<u>3d</u>

$$\boxed{D_p(\omega) = \frac{V}{2\pi^2 v_p^3} \omega^2}$$

Show this.

~~Xett~~

Focus on 3d

Make a further simplifying approximation.

$v_p = v$ (~~all~~ three acoustic modes have same speed v).

$$D(\omega) = \frac{V}{2\pi^2 v^3}\,\omega^2 \qquad \text{for } \underline{L, T_1, T_2} \qquad \underline{\text{3N modes}} \quad \text{N for each.}$$

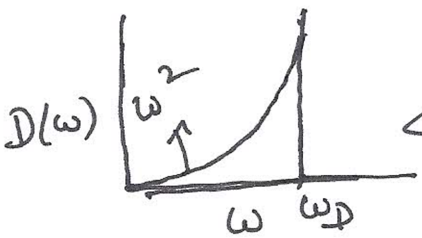
<u>Question.</u> Is there a maximum ω? ω_D

$$\int_0^{\omega_D} D(\omega)\,d\omega = N = \frac{V}{2\pi^2 v^3}\int_0 \omega^2 d\omega = \frac{V}{2\pi^2 v^3}\cdot \omega_D^3/3$$

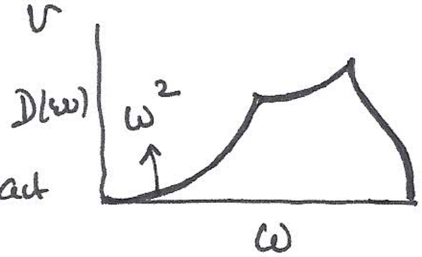
$$\omega_D^3 = 6\pi^2 \frac{N}{V} v^3 \Rightarrow \boxed{\omega_D = \left(6\pi^2\frac{N}{V}\right)^{1/3} v}$$

$$\omega_D = \text{Debye frequency} \propto (N/V)^{1/3}$$
$$\propto v$$

<u>Debye model</u>



⟺ Exact



Heat Capacity in Debye model

$$U = \sum_p \int D_p(\omega)\,\frac{\hbar\omega}{e^{\hbar\omega/k_BT}-1}\,d\omega$$

Exact eqn. to Calculate U

$$\underset{\text{Debye model}}{=} 3\cdot\frac{V}{2\pi^2 v^3}\int_0^{\omega_D}\frac{\hbar\omega}{\underbrace{e^{\hbar\omega/k_BT}-1}_{\text{Bose statistics}}}\,\omega^2\,d\omega$$

Fermions

$$\left[U = \int \frac{D(\epsilon)\,d\epsilon}{\underbrace{e^{(\epsilon-\mu)/k_BT}+1}_{\text{Fermi statistics}}}\right]$$

$D(\epsilon) \propto \epsilon^{1/2}$

Scale: $\hbar\omega/k_BT = x$

$$x_D = \hbar\omega_D / k_B T$$

$$U = \frac{3V k_B^4}{2\pi^2 v^3 \hbar^3} \underset{\sim T^4}{T^4} \left[\int_0^{x_D} \frac{x^3\,dx}{e^x - 1} \right]$$

depends on T indirectly through x_D

Guess 2d: $\underline{\omega^2}\ \underline{\omega}\ \underline{d\omega}$

$\omega\,\omega\,d\omega \sim T^3$

1d $\omega^0\,\omega\,d\omega \sim T^2$

3d If $k_B T \ll \hbar\omega_D$ then $x_D \gg 1$

$\hbar\omega_D = k_B\theta$ ↑ Debye Temp.

$$U \simeq C\,T^4 \underbrace{\int_0^\infty \frac{x^3\,dx}{e^x - 1}}_{\pi^4/15}$$

OK for $0 \lesssim T \lesssim 10\sim 50$ K

Typically $\theta \gtrsim 100$ K

$$U = N \cdot \frac{9\pi^4}{15} \cdot k_B T \left(T/\theta\right)^3$$

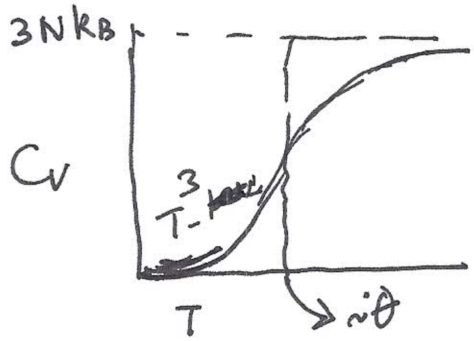
[Eliminate $V, v \ldots$ in favor of θ]

$$\therefore \boxed{C_V = \frac{12\pi^4}{5} \cdot N k_B \left(T/\theta\right)^3}$$

Classical model: $C_V = 3Nk_B$

⇓

3 is replaced by $\frac{12\pi^4}{5} \cdot \left(T/\theta\right)^3$



Debye T^3-Law

In d-dimension. T^d law

Typical θ Values: Li 344, Be 1440, C 2230 ~ spring constants.