LECTURE 5_1

Start with those 3 pages

Phonons as excitations

THE PROBLEM OF QUANTUM MELTING

Second quantization:

Recall from quantum mechanics:

$$[x,p] = xp - px = i\hbar$$

based on this lets introduce 2 operators, which create and annihilate an excitation when applied to the ground state or vacuum.

$$\begin{cases} b = \frac{1}{\sqrt{2\hbar M\omega}}(M\omega x + ip) \\ b^+ = \frac{1}{\sqrt{2\hbar M\omega}}(M\omega x - ip) \end{cases}$$

lets verify that anticommutator is

$$[b, b^+] = 1$$

$$[bb^+] = \frac{1}{2\hbar M\omega}\Big\{ (M\omega^2)\overset{=0}{[xx]} + iM\omega \overset{=-i\hbar}{[px]} -$$

$$- iM\omega \overset{=i\hbar}{[xp]} + \overset{=0}{[pp]}\Big\} = \frac{1}{2\hbar} iM\omega [px]$$

$$= \frac{1}{2\hbar}\left(-2i[xp]\right) = \frac{-2i\hbar i}{2\hbar} = \underline{\underline{1}}$$

inversely we can express x and p as

$$x = \sqrt{\frac{\hbar}{2M\omega}}(b^+ + b) \qquad p = i\frac{\sqrt{2\hbar M\omega}}{2}(b^+ - b)$$

Recall x, p are operators here!
Just a different representation.

For the HARMONIC OSCILLATOR:

Recall $\boxed{\omega = \sqrt{\frac{B}{M}}}$

$$\mathcal{H} = \frac{p^2}{2M} + B\frac{x^2}{2} = -\frac{2\hbar M\omega}{2\,\cancel{4}\,2M}(b^+ - b)^2$$

$$+ \frac{B\hbar}{2M\omega}(b^+ + b)^2 = -\frac{\hbar\omega}{4}(b^+ - b)^2 + \frac{B\hbar}{2M\sqrt{B/M}}(b^+ + b)^2$$

$\hookrightarrow B = \omega^2 M$

$=$

$$\mathcal{H} = \frac{1}{2}\hbar\omega\,(b b^+ + b^+ b) \overset{LS}{=}$$

$$= \hbar\omega\, b^+ b + \frac{1}{2}\hbar\omega = \hbar\omega\,(n + \tfrac{1}{2})$$

$[b b^+] = 1$

where $n = b^+ b$ is the occupation number (the number of particles in the ground state)

for the states with excitations present:

$b|n\rangle = \sqrt{n}\,|n-1\rangle$

$b^+|n\rangle = \sqrt{n+1}\,|n+1\rangle$

the philosophy of bosons the more the merier!

the amplitude grows as $\sim\sqrt{n+1}$!

b - anihilator

b^+ - creation operators.

they increase (decrease) the # of bosons by + (-1).

for $n \equiv b^+ b \Rightarrow n|n\rangle = b^+ b|n\rangle = b^+\sqrt{n}\cdot|n-1\rangle$

$= \sqrt{n}\cdot\sqrt{n}\,|n\rangle = n|n\rangle$

for the groun state: $b|0\rangle = 0$

$|n\rangle = \frac{1}{\sqrt{n!}}\,(b^+)^n\,|0\rangle$.

Now we are ready for something interesting.

Quantum Melting.

Recal that vibration amplitude

$$u \equiv \delta x = \sqrt{\frac{\hbar}{2M\omega}}\,(b^\dagger + b) \quad \text{for 1 phonon mode}$$

The average shift from eq. is $\langle u \rangle = 0$

but for:

$$\langle u^2 \rangle = \frac{\hbar}{2M\omega}\left\langle (b + b)^2 \right\rangle = \frac{\hbar}{2M\omega}\langle b^\dagger b^\dagger + bb + \underbrace{b^\dagger b + b b^\dagger}_{2b\,\cancel{bb}\ \ [b\,b^\dagger] = 1} \rangle = \frac{\hbar}{2M\omega}\left(2\langle b^\dagger b\rangle + 1\right) = \frac{\hbar}{2M\omega}\left(n + \frac{1}{2}\right)$$

and for the highest energy phonons

$\omega = \omega_D$ $\quad \Theta_D \equiv \hbar\omega_D$

$$\langle u^2 \rangle = \frac{\hbar^2}{2M\Theta_D}\left(n + \frac{1}{2}\right) \qquad n = \frac{1}{e^{\hbar\omega/k_BT} - 1} = \frac{1}{e^{\Theta_D/k_BT} - 1}$$

So for

$T \to 0$ $\quad \langle u^2 \rangle \to \dfrac{\hbar^2}{2M\omega_D}$ (zero point oscillations!)

$T \gg \Theta_D$: $\quad \langle u^2 \rangle \sim \dfrac{\hbar^2}{M\Theta_D^2}$

According to the Lindermann criterion when $\langle u^2 \rangle \sim a$ melting occurs. (precisely $\langle u^2 \rangle \sim 0.2a$)

So one can introduce the melting parameter $\Lambda \equiv \dfrac{\langle u^2 \rangle}{a}$ ← De Boer parameter

at $T = 0$ $\quad \langle u^2 \rangle \sim \dfrac{\hbar}{M\omega}$ where $\omega = \sqrt{\dfrac{B}{M}}$ ← bulk modulus or the stiffness of the lattice

Lets estimate B

If we shift an atom from the equilibrium by ~a there will be ~~a~~ change in the pot. energy $\sim Ba^2 \sim V(a)$

$\xleftarrow{\quad}$ the interaction potential between atoms.

so $B \sim \frac{V(a)}{a^2} \Rightarrow \Lambda \approx \frac{\hbar}{a}\frac{1}{\sqrt{MV(a)}}$

and if $\Lambda \gtrsim 0.2-0.3$ the system is unstable against the ~~p~~ zero point motion and the xtal <u>quantum melts</u> !!!

Q: Does it really happen?

Well we need small M and weak $V(a)$

meet ^{4}He   He is very light and He–He interaction is very small.

That's why He is liquid down to $T=0$!

What do you think about H (hydrogen)?

Another way to "encorage" quantum melting is to apply pressure p but of course $a\downarrow$ but $V(a)$ goes up and then $\Lambda \approx V(a)a^2$ may change either way. For He $V(a)$ goes up quick and it becomes SOLID. For electronic liquid it is opposite:

$$V(a) = \frac{e^2}{a} \quad \text{and} \quad \Lambda = \frac{\hbar}{a}\sqrt{\frac{Me^2}{a}} \sim \frac{1}{\sqrt{a}}$$

So as $p\uparrow$ $a\downarrow$ $\Lambda\uparrow$ $\Rightarrow$ cold melting of an electronic crystal (Wigner)

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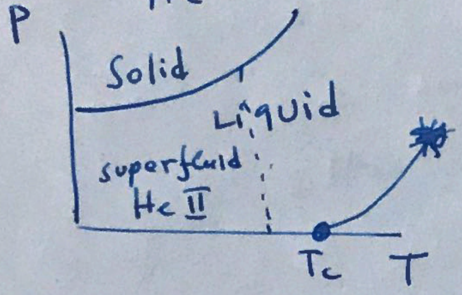
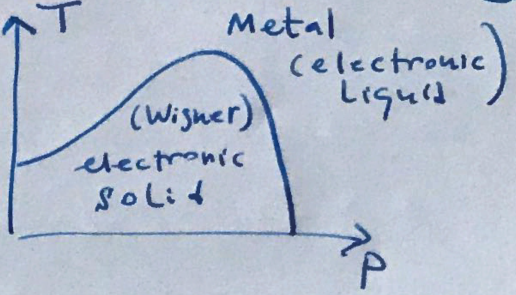


VS.

Wigner xtal



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LECTURE 5

Phonons. The 1st take on collective excitations

Consider a chain of identical atoms: (ions)

→ Motion along the chain //

Define the position of atoms as:

x_n – in the equalibrium $x_n^{eq} = n\cdot a$

If we allow the motion of the atoms:

$$\delta x_n = x_n - x_n^{eq}$$

Note since it is 1D we allow only longitudinal motion.

Let us also assume the potential is quadratic,

Now its getting strange. We technically descibe the motion of balls connected with springs?!

$$V_{total} = \sum V(x_{j-1} - x_j) =$$

$$= \sum_j \frac{k}{2}(\delta x_{j+1} - \delta x_j)$$

The restoring Force on the mass n is

$$F_n = -\frac{\partial V_{tot}}{\partial x_n} \underset{\substack{\uparrow \\ \delta x_n = x_n - \underline{na} \\ x_n^{eq}}}{=} -\frac{\partial}{\partial x_n}\left(\frac{k}{2}(x_{n+1} - x_n - a)\right)^2 =$$

$$= \underbrace{k(\delta x_{n+1} - \delta x_n) + k(\delta x_{n-1} - \delta x_n) = m\cdot \delta\ddot{x}_n}_{\text{Newtonian Law.}}$$

Recap: A normal mode is a collective oscillation where all particles move at the same frequency.

Lets attempt to solve it by assuming that we have a wave propagating through the chain

$$\delta x_n = A e^{i\omega t - ikx_n^{eq}} = A e^{i\omega t - ikna}$$

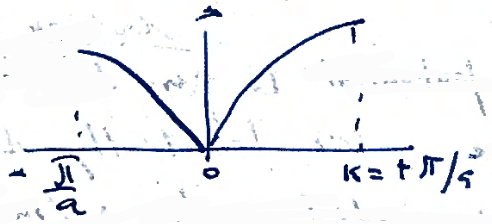
A is the amplitude of the wave

$$-m\omega^2 A e^{i\omega t - ikna} = \kappa A e^{i\omega t}\left[e^{-ika(n+1)} + e^{-ika(n-1)} - 2e^{-ikan}\right]$$

or

$$m\omega^2 = 2\kappa\left[1 - \cos(ka)\right] = 4\kappa \sin^2(ka/2)$$

or $$\omega = 2\sqrt{\frac{\kappa}{m}}\left|\sin\left(\frac{ka}{2}\right)\right|$$



Not too surprizing again b/c of the periodicity of the crystal we end up with the same physics

$$e^{iG\cdot x} = 1 \quad \text{where } G_n = \frac{2\pi}{a}\cdot n$$

Again the same issue as for electrons

k is defined up to $k + G_n = k$

But what k we should use say in

$$v_{phase} = \frac{\omega}{k} = ? = \frac{\omega}{k+G} ?$$

or do we say $\frac{2\pi}{k} \overset{?}{=} \frac{2\pi}{k+G}$?

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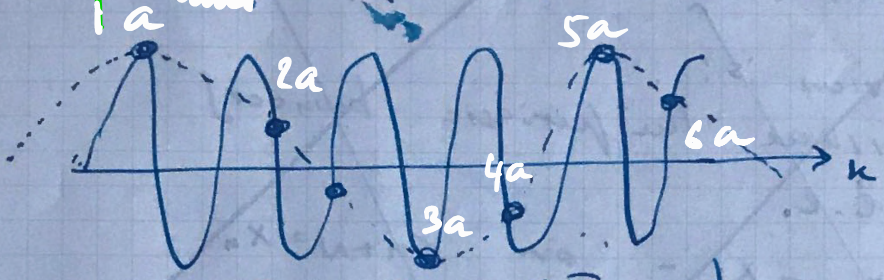
The resolution to this puzzle comes from the fact that:

We can define the wave only at the lattice points $x_n = n \cdot a$



So $k + \frac{2\pi}{a} n$ and k | are the same! as long as we look only at x_n!

This is also known as aliasing of waves.

Properties of 1D chains.

Sound wave: always has λ much larger than a (e.g. human 1 cm – 10 m)

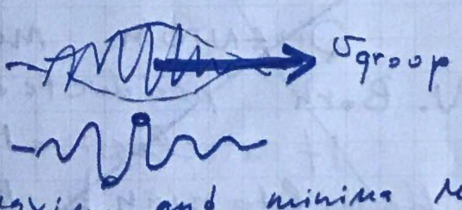
Large l, small k so the dispersinon $\omega = v_{sound} k$

$$\omega = 2\sqrt{\frac{k}{m}} \left|\sin\left(\frac{ka}{2}\right)\right| \cong \cancel{2}\sqrt{\frac{k}{m}} \cdot \frac{ka}{\cancel{2}}$$

$$v_{sound} = \frac{\omega}{k} \cong \sqrt{\frac{k}{m}} \cdot a$$

Large l, Short k: We define the group velocity:

$$\begin{cases} v_{group} = \frac{d\omega}{dk} \\ v_{phase} = \omega/k \end{cases}$$



how individual maxima and minima move.

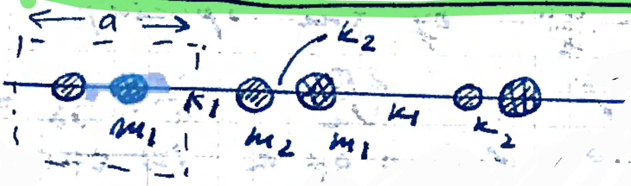
if the dispersion is linear

$v_{group} = v_{phase}$

non-linear they are different.

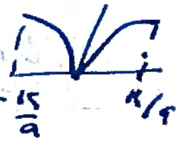
Note at $\pm\pi/a$: $v_{group} = 0$! the dispersion is flat.

Two atoms per unit cell. - PHONON modes.

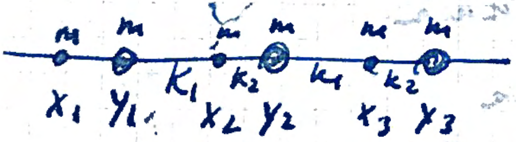


Lets for simplicity assume that $m_1 = m_2$

We are about to repeat the same algebra as for the 1D chain with 1-type of atoms where we found that the system will have the energy dispersion $\omega(k) \sim \left|\sin\frac{ka}{2}\right|$



$$\begin{cases} m\,\delta\ddot{x}_n = k_2(\delta y_n - \delta x_n) + k_1(\delta y_{n-1} - \delta x_n) \\ m\,\delta\ddot{y}_n = k_1(\delta x_{n+1} - \delta y_n) + k_2(\delta x_n - \delta y_n) \end{cases}$$



again we will be looking for a solution of this kind:

$$\delta x_n = A_x\, e^{i\omega t - ikna}$$

$$\delta y_n = A_y\, e^{i\omega t - ikna}$$

We focus our attention on the 1st BZ.

$-\frac{\pi}{a} \leq k \leq \frac{\pi}{a}$, with N unit cells

$L = N\cdot a$

k will be quantized $k = \frac{2\pi}{Na} = \frac{2\pi}{L}$

here we mean N the number of u.c. Not the number of atoms.

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If we devide the range of k values in the 1st BZ $\frac{2\pi}{a}$ by the spacing between neighboring ks $\frac{2\pi}{Na}$: $\frac{2\pi}{a} : \frac{2\pi}{Na} \Rightarrow N$ we obtain N possible values of k or 1 value of k per unit cell.

But Debye states that there is only one more normal mode per degree of freedom and here we have 2 atoms but seemingly one mode!

What to do? Lets go ahead and solve the equations:

$$\begin{cases} -\omega^2 m A_x e^{-i\omega t - ikna} = K_2 A_y e^{i\omega t - ikna} + K_1 A_y e^{i\omega t - ik(n-1)a} - (K_1+K_2) A_x e^{i\omega t - ikna} \\ -\omega^2 m A_y e^{i\omega t - ikna} = K_1 A_x e^{i\omega t - ik(n+1)a} + K_2 A_x e^{i\omega t - ikna} - (K_1+K_2) A_y e^{i\omega t - ikna} \end{cases}$$

$$\begin{cases} -\omega^2 m A_x = K_2 A_y + K_1 A_y e^{ika} - (K_1+K_2) A_x \\ -\omega^2 m A_y = K_1 A_x e^{-ika} + K_2 A_x - (K_1+K_2) A_y \end{cases}$$

or

$$m\omega^2 \begin{pmatrix} A_x \\ A_y \end{pmatrix} = \begin{pmatrix} (K_1+K_2) & -K_2 - K_1 e^{ika} \\ -K_2 - K_1 e^{-ika} & (K_1+K_2) \end{pmatrix} \begin{pmatrix} A_x \\ A_y \end{pmatrix}$$

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The solution is:

$$0 = \begin{vmatrix} (k_1+k_2) - m\omega^2 & -k_2 - k_1 e^{ika} \\ -k_2 - k_1 e^{-ika} & (k_1+k_2) \cdot \quad - m\omega^2 \end{vmatrix} =$$

$$= |(k_1+k_2) - m\omega^2|^2 - |k_2 + k_1 e^{ika}|^2 = 0$$

$$m\omega^2 = (k_1+k_2) \pm |k_1 + k_2 e^{ika}|$$

$$|k_1 + k_2 e^{ika}| = \sqrt{(k_1 + k_2 e^{ika})(k_1 + k_2 e^{-ika})} =$$

$$= \sqrt{k_1^2 + k_2^2 + 2k_1k_2 \cos ka}$$

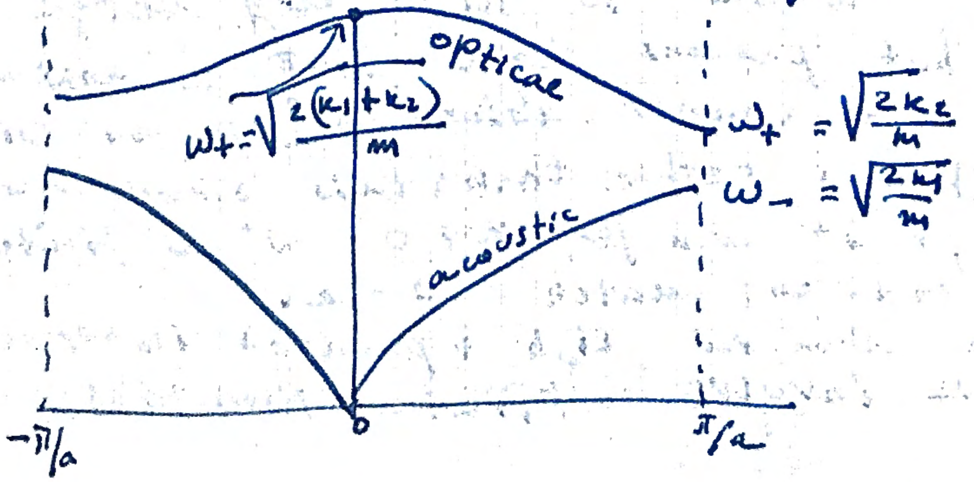
So finaly

$$\omega_\pm = \sqrt{\frac{k_1+k_2}{m} \pm \frac{1}{m}\sqrt{k_1^2+k_2^2+2k_1k_2\cos(ka)}}$$

$$= \sqrt{\frac{k_1+k_2}{m} \pm \frac{1}{m}\sqrt{(k_1+k_2)^2 - 4k_1k_2\sin^2\left(\frac{ka}{2}\right)}}$$

for each k we have 2 solutions ±
or 2 <u>branches of the dispersion</u>

or we have
2N modes! Exactly as Debye predicted
one excitation mode per degree of freedom.



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Long wavelength show linear dispersion = acoustic branch. $= \omega_-(k)$

Def: any mode which $\omega = \alpha k$ for $k \to 0$ is called acoustic

and if we assume $\sin\frac{ka}{2} \sim \frac{ka}{2}$ and $\sqrt{1+x} \cong 1 + x/2$

we get $\omega_- = \sqrt{\frac{k_1+k_2}{m} \cancel{+} - \frac{1}{m}\sqrt{(k_1+k_2)^2 - \frac{-4k_1k_2}{4}(ka)^2}} \Rightarrow$

$$v_{sound} = \frac{d\omega_-}{dk} = \sqrt{\frac{a^2 k_1 k_2}{2m(k_1-k_2)}}$$

The high energy branch is more interesting:

for $k=0$ $\quad \omega_+ = \sqrt{\frac{2(k_1+k_2)}{m}}$

and

$v_{group} = \frac{d\omega}{dk} = 0 \Big|_{at\ k=0}$!

This branch is called OPTICAL.

Here is why.

during the light absorption energy and momentum must be conserved, i.e.

$\omega = ck$ so as is very large

but phonons have $k \sim \frac{\pi}{a}$ as maximum and cannot absorb the photon with anything rather than this small value.

But for ω^+ even for $k \to 0$ ω^+ is finite and can match $\omega = ck$.

So whenever ligh + phonons interact we involve OPTICAL PHONONS.

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Lets look a little more carefully at the opt. and. acoustic mode for k → 0

$$m\omega^2 \begin{pmatrix} A_x \\ A_y \end{pmatrix} = \begin{pmatrix} k_1+k_2 & -k_2-k_1 \\ -k_2-k_1 & k_1+k_2 \end{pmatrix} \begin{pmatrix} A_x \\ A_y \end{pmatrix}$$

or $$\omega^2 \begin{pmatrix} A_x \\ A_y \end{pmatrix} = \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \begin{pmatrix} A_x \\ A_y \end{pmatrix} \cdot \frac{k_1+k_2}{m}$$

For the acoustic mode $\omega=0$ at $k=0$

$$\begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \begin{pmatrix} A_x \\ A_y \end{pmatrix} = 0 \Rightarrow \begin{pmatrix} A_x \\ A_y \end{pmatrix} = \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

masses at position x and y move together

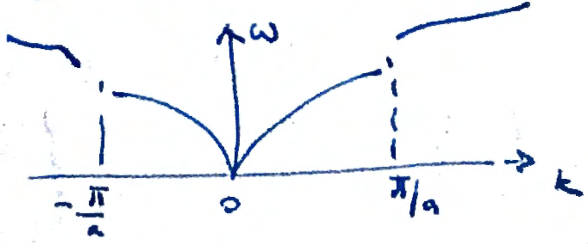
In short the atoms within the unit cell always move together

For optical branch $k=0$ $\omega_+^2(k=0) = \frac{2(k_1+k_2)}{m}$

$$\frac{2\cancel{(k_1+k_2)}}{\cancel{m}} \begin{pmatrix} A_x \\ A_y \end{pmatrix} = \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \begin{pmatrix} A_x \\ A_y \end{pmatrix} \frac{\cancel{k_1+k_2}}{\cancel{m}} \Rightarrow$$

$$\begin{pmatrix} A_x \\ A_y \end{pmatrix} = \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

describes two masses movin in opposite direction within the unitcell.



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Now lets study our modes close to the zone boundary. $\pm \frac{\pi}{a}$

$$\omega_+ = \sqrt{\frac{2k_2}{m}}$$

$$\omega_- = \sqrt{\frac{2k_1}{m}} \qquad \frac{d\omega}{dk} = 0 \text{ at the ZB.}$$

when the phonon k approaches the z.b. the plane wave turns into a standing wave with antiphase motion

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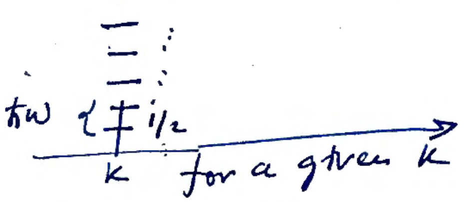
For $n=0$ we get $\hbar\omega(k)/2$

The lowest energy of excitation for $\hbar\omega(k) \Rightarrow n=1$



Phonon is a descrete quantum of vibration (photon is a quantum of light)

All known excitations are bosons except for exotics like spinons, majonas etc.

Temperature shakes atoms and the phonons can occupy higher and higher energ states.

Based on the Bose statistics:

$$n_B(\beta\hbar\omega) = \frac{1}{e^{\beta\hbar\omega}-1} \qquad \beta = \frac{1}{k_B T}$$

Thus the energy expectation:

$$E_k \doteq \hbar\omega(k)\left(n_B + \frac{1}{2}\right) \text{ for finite } T\text{s}$$

From this we can calulate many thermodynamical quantities, including say the heat capacity:

$$U_{total} = \sum_k \hbar\omega(k)\left(n_B + \frac{1}{2}\right)$$

" sum over all normal modes

$$k = \frac{2\pi}{Na}\cdot m \qquad \text{for } -\frac{\pi}{a} \le k \le \frac{\pi}{a}$$

As we did for electrons:

$$\sum_k \to \frac{Na}{2\pi}\int_{-\pi/a}^{\pi/a} dk$$

Note the Total number of modes is

$$\frac{Na}{2\pi}\int_{-\pi/a}^{\pi/a} dk = \underline{N}$$

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Now lets calcula the total internal energy due to phonons

$$U_{total} = \frac{Na}{2\pi}\int_{-\pi/a}^{\pi/a} dk\, \hbar\omega(k)\left(n_B(\beta\hbar\omega(k)) + \frac{1}{2}\right)$$

↳ $\frac{dU}{dT} = C_V$.

Historically, the difference between Debye and what we got is in ω_k for Debye $\omega = v \cdot k$, but in our case $\omega(k) = \sqrt{\frac{\kappa}{m}}\sin\left(\frac{ka}{2}\right)$

In fact what Einstein did he just introduced the same idea stating how ω depends on k.

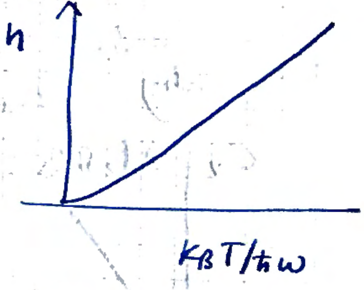
THERMODYMICS OF PHONONS.

We state without a proof that bosons should obey to the Bose-Einshtein statistics:, i.e.

$$n = \frac{1}{e^{\epsilon/k_BT}-1}$$

and if consider the thermal vibrations of the frequency ω (or $E = \hbar\omega$)

$$n(\omega, T) = \frac{1}{e^{\hbar\omega/k_BT}-1}$$



for high temperatures

$k_BT > \hbar\omega$

$$\frac{1}{2} + n = \frac{1}{2} + \frac{1}{e^{\underset{\uparrow = \frac{1}{k_BT}}{\beta}\epsilon}-1} = \frac{e^{\beta\epsilon}+1}{2(e^{\beta\epsilon}-1)} =$$

$$= \frac{(1+\beta\epsilon+\dots)+1}{2(1+\beta\epsilon+(\beta\epsilon)^2/2+\dots)-1} = \frac{2+\beta\epsilon+\dots}{\beta\epsilon(2+\beta\epsilon+\dots)}$$

$$\simeq \frac{1}{\beta\epsilon} = \frac{k_BT}{\hbar\omega}$$

$\Rightarrow$ for high Ts we have

$$E = \hbar\omega\left(\frac{1}{2} + n(\omega,T)\right) = \hbar\omega\left(\frac{1}{2} + \frac{k_BT}{\hbar\omega}\right) =$$

$$= \underset{\uparrow\text{"0" motion}}{\frac{\hbar\omega}{2}} + k_BT = k_BT$$

(This is for 1D)

for 3D $\equiv$ 3 deg. of freedom

$$E = \sum \dots = 3k_BT$$

which is equivalent to the internal energy of a gas.

Heat capacity:

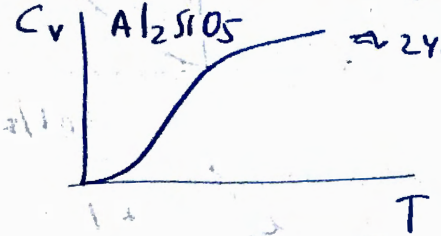
$$c_V = \left(\frac{\partial E}{\partial T}\right)_V = \sum \hbar\omega \frac{\partial n}{\partial T} =$$

$$= \sum k_B \left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{e^{\hbar\omega/k_BT}}{\left(e^{\hbar\omega/k_BT}-1\right)^2}$$

For the high T lim $C_V = 3R$ $(J K^{-1})$

≡ Dulong - Petit

What classical stat. physics cannot explain why the heat capacity → 0 T → 0 ?



≈ 24R JK^{-} per mole (8 atoms per. u.c)

Density of states for phonons

g(ω) the number of vibration mods between ω and ω+dω ⇒ g(ω) dω

$$U = \int \left(n(\omega) + \tfrac{1}{2}\right)\hbar\omega\, g(\omega)\, d\omega$$

$$C_V = \int \frac{dn}{\partial T} h\omega\, g(\omega)\, d\omega$$

Now lets apply the idea of DOS to acoustic phonons:

To determine g(ω) we note

$g(\omega)\, d\omega = g(k)\, dk$ since $\omega = v_{ac}.\bar{k}$

In the xtal with N unit cells, the volume per u.c. $\frac{V}{N}$ and the volume of B.Z. $= \frac{(2\pi)^3 N}{V}$

So in the 1st BZ there will be N avalaible values of the k-vector, and the number of k-values per unit volume of the Reciprocal space

$N / V_{BZ} = V/(2\pi)^3$

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or in Sperical coordinates: $g(\omega)\,d\omega = \frac{V}{(2\pi)^3}\, 4\pi k^2\, dk = \quad k = \omega/v_a \quad dk = \frac{d\omega}{v_a} =$

$$\Rightarrow g(\omega)\,d\omega = 3 \times \frac{V}{(2\pi)^3}\, 4\pi \left(\frac{\omega}{v_a}\right)^2 \frac{d\omega}{v_a} = \frac{3V\omega^2}{2\pi^2 v_a^3}\cdot d\omega$$

3 comes from the fact that there are 3 branches of acoustic waves for 3D.

so $g(\omega) \sim \omega^2$

HEAT CAPACITY

The total energy due to phonons:

$$E = \int_0^{\omega_D} \frac{3V\omega^2}{2\pi^2 v_a} \overbrace{\frac{1}{e^{-\hbar\omega/k_BT} - 1}}^{= n(\omega,T)} d\omega$$

where ω_D is called the Debye frequency, a cut-off parameter.

$$\Rightarrow \frac{dE}{dt} = C_V = \int_0^{\omega_D} \frac{3V\omega^2}{2\pi^2 v_a} \cdot \hbar\omega \frac{dn}{dT}\, d\omega$$

1) Low T limit: At low T only low ω phonons exists since $n(\omega,T) \to 0$ $T \to 0$ also those $\omega \ll \omega_D$ so ω_D looks like ∞:

Substituting $x \equiv \hbar\omega/k_BT$ $\quad \omega^3 d\omega = \left(\frac{k_BT}{\hbar}\right)^4 x^3 dx$

$$E = \frac{3V\hbar}{2\pi^2 v_a} \left(\frac{k_BT}{\hbar}\right) \underbrace{\int_0^\infty x^3 (e^x - 1)^{-1} dx}_{= \pi^4/15} \Rightarrow$$

$$E = \frac{V\pi^2 (k_BT)^4}{10(v_a\hbar)^3} \Rightarrow E \sim T^4 \Rightarrow C_V = \frac{dE}{dT} \sim T^3$$

or $C_V = \frac{2V\pi^2 k_B}{5(v_a\hbar/k_B)^3}\cdot T^3$ if we introduce the Debye temperature

$\Theta_D = \frac{\hbar\omega_D}{k_B} \Rightarrow \Theta_D = \frac{\hbar c v_a}{k_B}\left(\frac{16\pi N^2}{V}\right)^{1/2}$ (not shown here read A&M)