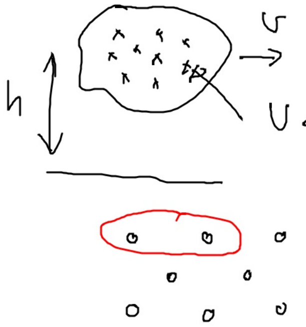
Solid State Physics

Lattice vibrations

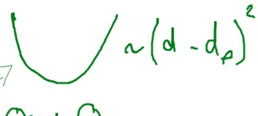
$$\mathcal{E} = \mathcal{E}_{ext.} + \mathcal{E}_{int}$$

kinetic potential U



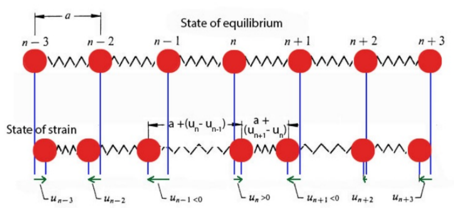
U ~ random internal motion.

$\mathcal{E}_{th} \approx \boxed{k_B T}$



harmonic vibrations

$\frac{1}{2} k_B T \to$ every degree of freedom

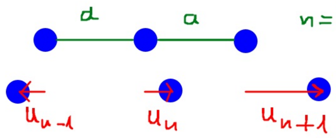


— linear chain → specific heat

let u_n — excursion of the n-th atom from equilibrium position!

then $F_n = -\beta \Delta x_{n,n+1} - \beta \Delta x_{n-1,n}$, where $\Delta x_{n,n+1} \equiv u_n - u_{n+1}$

$\Delta x_{n-1,n} \equiv u_n - u_{n-1}$



$n = 1, \ldots, 10^{23}, \ldots$

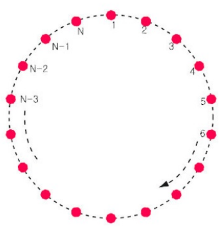
$$F_n = \beta(u_{n+1} - u_n) + \beta(u_{n-1} - u_n) \Rightarrow$$
$$F_n = \beta(u_{n-1} + u_{n+1} - 2u_n)$$

Problem! Chain is not infinite!

Solution: $u_{N+1} = u_1$ periodic boundary condition

$u_{-1} = u_N$

works as N is so large, the effect of the edges is negligible



The $N > 10^{26}$ coupled equations:

$$M \frac{d^2 u_n}{dt^2} = \beta(u_{n+1} - 2u_n + u_{n-1}) \qquad n = 1, 2, \ldots, N$$

Try this!

$$u_n = u_0 e^{i(\omega t + k n a)} \quad N \sim 10^{26}$$

ω — angular frequency; a — lattice constant; $n = 0, 1, 2, \ldots, N-1$

ansatz

then $\dfrac{d^2 u_n}{dt^2} = -\omega^2 \cdot u_n$ and $u_{n\pm1} = e^{\pm ika} \cdot u_n$

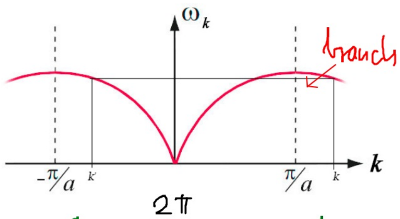
so all of the 10^{26} equations will become the same:

$$-M\omega^2 \cancel{u_n} = \beta\left(e^{ika} + e^{-ika} - 2\right)\cancel{u_n}$$

a single equation to solve for ω $\qquad e^{ika} + e^{-ika} - 2 = 2\cos ka - 2 = 2\cdot 2\cdot \sin^2 \frac{1}{2} ka$

$$\boxed{\omega(k) = 2\sqrt{\frac{\beta}{M}}\,\left|\sin \frac{1}{2} k a\right|}$$ mode

$\omega(k)$ dispersion relation



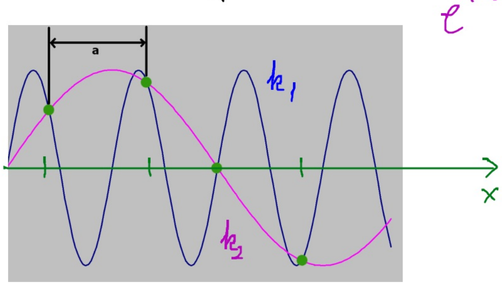
$\dfrac{2\pi}{a}$

reciprocal lattice

$k = \dfrac{2\pi}{\lambda}$ E.M waves

$-\dfrac{\pi}{a} < k < \dfrac{\pi}{a}$ Brillouin-zone

$e^{i(\omega t \pm k x)}$ $\quad x = n \cdot a$



$$\mathcal{E}_{tot} = \sum_{n=1}^{N} \mathcal{E}^{(n)}_{oscill} = \sum_{n=1}^{N} \left(\mathcal{E}^{(n)}_{kin} + \mathcal{E}^{(n)}_{pot}\right)$$

$\frac{1}{2}Mv^2 + \frac{1}{2}\beta x^2$

or $\dfrac{p^2}{2M} + \frac{1}{2}M\omega^2 x^2$

in classical physics for a single oscillator $M\dfrac{d^2x}{dt^2} = -\beta x \Rightarrow \dfrac{d^2x}{dt^2} = -\underbrace{\dfrac{\beta}{m}}_{\omega^2} x$

$\omega \equiv \omega(k)$

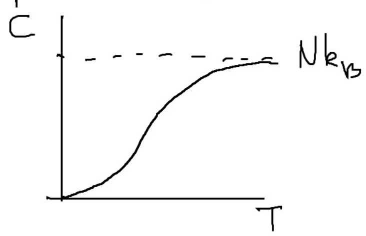
$p \equiv p(k)$

$$\mathcal{E}_{tot} = \sum_k \underbrace{\left(\frac{p^2(k)}{2M} + \frac{1}{2}M\omega^2(k)\, x^2\right)}$$

degree of freedom $= 2N$ (# of coord. on the second power)

$2 \cdot \frac{1}{2} k_B T = k_B T$ $\leftarrow$ equipartition theorem

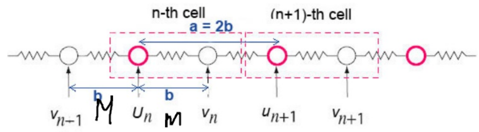
experimental curve



classical physics: $\mathcal{E}_{tot} \equiv U = N k_B T \rightarrow C = \dfrac{\Delta U}{\Delta T} = \dfrac{\Delta \mathcal{E}_{tot}}{\Delta T} = N k_B$

something is wrong with classical physics!

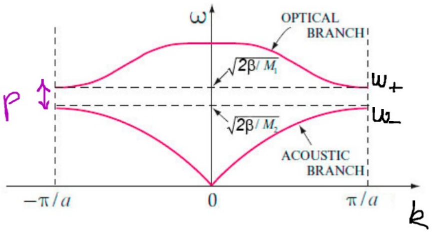
linear chain with 2 atoms

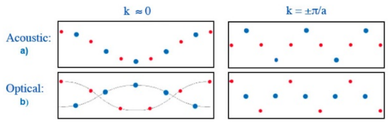


2 atom linear chain
(diatomic)

$$
\left.\begin{aligned}
M\frac{d^2 v_n}{dt^2} &= \beta\left((v_n - u_n) - (u_n - v_{n-1})\right) \\
m\frac{d^2 u_n}{dt^2} &= \beta\left((u_{n+1} - v_n) - (v_n - u_n)\right)
\end{aligned}\right\} \quad 2\times 10^{26}
$$

energy gap ↕

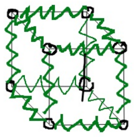




Origin of naming
optical branch: at $k=0$
e.g. ionic crystal, EM-wave (light)

$\underline{E} = \underline{E}_0\, e^{i(\omega t + \underline{k}\,\underline{r})}$

$\underline{F}_+ = Q\underline{E}$ $\quad$ $\underline{F}_- = -Q\underline{E}$



only
closest neighbors

$\hbar\omega$ energy gap

3D crystals

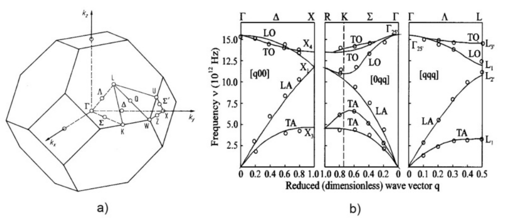
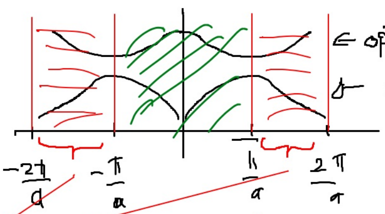


Figure 12.8: High symmetry points and the corresponding dispersion relations in Si. Γ is the origin $(0,0,0)$, $X = (1/2,0,1/2)$, $L = (1/2,1/2,1/2)$, $W = (1/2,1/4,3/4)$, etc are high symmetry points (all coordinates are in units of π/a), Δ, Σ and Λ, etc are the lines connecting them. K, R, U, etc are some special points along the lines

$\omega(\underline{k}) = \omega(k_1, k_2, k_3)$



← optical branch

← acoustic branch

2nd Brillouin zone

1st Brillouin zone

Quantum Mechanics

$\mathcal{E}(\underline{k}) = \hbar\,\omega(\underline{k})$

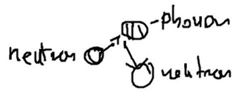
photons

sound waves

$\omega \to \lambda \to$ $\to$ method $\uparrow$ phonons $\leftarrow$ quanta of lattice vibrations

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

λ slow neutrons $p = \frac{h}{\lambda} = \hbar \underline{k}$



linear harmonic oscillator   nodes $\downarrow$ n excitation

$$dn(\nu, \nu + d\nu) = g(\nu)\, d\nu = 4\pi V \frac{\nu^3}{v^3(\nu)}\, d\nu$$

density of states

k discrete, but

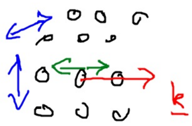
$N \sim 10^{23} - 10^{26} \Rightarrow \Delta k = \frac{2\pi}{Na} \ll 1$

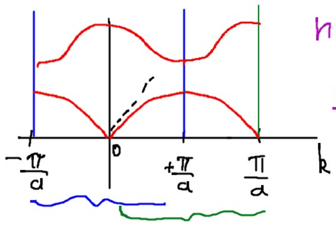
$\Downarrow$ (quasi) continuous quantity

$v_s(k)$ sound waves   2 transversal   wave

$\uparrow$ 1 longitudinal

$s =$ transv. / longit.





n atom basis

3 $(= 1l + 2t)$ acoustic

$3n-3$ $\left(= (n-1)l + 2(n-1)t\right)$ optical branches

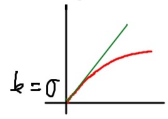
$$g(\nu) = 4\pi V \nu^2 \left(\frac{1}{v_l(\nu)} + \frac{2}{v_t(\nu)}\right)$$

$v_l(\nu)$ longitudinal phonon velocity

$v_t(\nu)$ transversal

$\nu \approx 0 \Rightarrow v_l(0) = v_{sound}^{(l)}$

complicated functions $v_t(0) = v_{sound}^{(t)}$



$$\int_0^\infty g(\nu)\, d\nu = \#\text{ of states if } N \text{ atoms (1 atom basis)} \Rightarrow 3N$$

$$3N = \int_0^\infty 4\pi V \nu^2 \left(\frac{1}{v_l(\nu)} + \frac{2}{v_t(\nu)}\right) d\nu$$

Debye $\Rightarrow$ $\begin{matrix} v_l(\nu) \\ v_t(\nu) \end{matrix} = \begin{cases} v_l, v_t \text{ const} & \nu_{l,t} < \nu_D \\ 0 & \nu_{l,t} > \nu_D \end{cases} \Rightarrow$

$$3N = \underbrace{4\pi V \left(\frac{1}{v_l} + \frac{2}{v_t}\right)}_{\text{const}} \underbrace{\int_0^{\nu_D} \nu^2 d\nu}_{\frac{\nu_D^3}{3}}$$

i.e. the constant is: $\frac{9N}{\nu_D^3} = 4\pi V \left(\frac{1}{v_l} + \frac{2}{v_t}\right)$

$$g(\nu) = \frac{9N}{\nu_D^3}\nu^2$$

phonons are the quanta of the lattice vibrations
(quantums)

photons are — || — of the electromagnetic field
vibrations travels

phonons are Bosons

$$f_{B-E} = \frac{1}{e^{h\nu/k_BT} - 1}$$

$$\langle \mathcal{E} \rangle = \int_0^\infty g(\nu) \cdot f_{B-E}(T,\nu) \cdot \mathcal{E}(\nu,T)\, d\nu$$

$$\Updownarrow$$

$$U = \frac{9N}{\nu_D^3}\int_0^{\nu_D} \nu^2 \frac{1}{e^{h\nu/k_BT} - 1}\,\mathcal{E}(\nu,T)\, d\nu$$

↑ # of phonons is not constant (no chemical potential)

$$\boxed{C_V(T) := \left(\frac{\partial U}{\partial T}\right)}$$

in 1D $\mathcal{E}(\nu,T) = h\nu\left(n+\frac{1}{2}\right) \Rightarrow U = \frac{9Nh}{\nu_D^3}\int_0^{\nu_D} \frac{\nu^3}{e^{h\nu/k_BT} - 1}\, d\nu + \text{const}$

because $\nu \neq \nu(T)$

$$\frac{\partial}{\partial T}\int f(T)\, d\nu = \int \frac{\partial}{\partial T} f(T)\, d\nu$$

$$C_V = \frac{9Nh}{\nu_D^3}\int_0^{\nu_D} \frac{\partial}{\partial T}\frac{\nu^3}{e^{h\nu/k_BT} - 1}\, d \qquad \frac{\partial}{\partial T}\frac{1}{e^{h\nu/k_BT} - 1} = -\frac{e^{h\nu/k_BT}\cdot\frac{h\nu}{k_B}\cdot\left(-\frac{1}{T^2}\right)}{\left(e^{h\nu/k_BT} - 1\right)^2}$$

$$C_V = \frac{9Nh}{\nu_D^3}\cdot\frac{h}{k_BT^2}\int_0^{\nu_D} \frac{\nu^4 e^{h\nu/k_BT}}{\left(e^{h\nu/k_BT} - 1\right)^2}\, d\nu$$

Let $y := \frac{h\nu}{k_BT} \Rightarrow \nu = \frac{k_BT}{h}y \to d\nu = \frac{k_BT}{h}dy$ and $\nu^4 = \left(\frac{k_BT}{h}\right)^4 y^4$

$$C_V = \frac{9Nh^{\cancel{2}}}{\nu_D^3 \cancel{k_B} T^2}\int_0^{\nu_D} \left(\frac{k_BT}{h}\right)^4 \frac{y^4 e^y}{(e^y-1)^2}\cancel{\frac{k_BT}{h}}\, dy = \frac{9N k_B^4 T^3}{h^4 \nu_D^3}\int_0^{\nu_D} \frac{y^4 e^y}{(e^y-1)^2}\, dy$$

Introduce the Θ_D Debye temperature so that $k_B\Theta_D = h\nu_D$

$$C_V = 9N\cdot k_B\left(\frac{T}{\Theta_D}\right)^3\int_0^{\Theta_D/T} \frac{y^4 e^y}{(e^y-1)^2}\, dy$$

let $\underbrace{N = L_A}_{1\,\text{mol}} \Rightarrow 9Nk_B = 9k_BL_A = 9\underbrace{R}_{\text{univ. gas constant}}$ $\quad \left(R = 8.31\frac{J}{\text{mol}K}\right)$

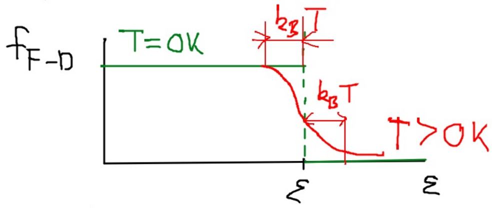
molar heat capacity: $C_V = 9R\left(\frac{T}{\Theta_D}\right)^3 \cdot (\text{constant - integral})$

This corresponds to experimental curve at low temperatures and tends to the classical high temp. value $9R$

Problem: this is only valid for insulators

conductors (metals) need additional terms: $C_V = C_V^{vib.} + C_V^{electrons}$

electrons: Fermi - Dirac stat



$\Delta N_e \sim k_B T \qquad \Delta \mathcal{E}_e \sim k_B T$

$\Downarrow$

$U \sim \Delta N \cdot \Delta \mathcal{E} \sim T^2$

$C_V^{(e)} = \left(\frac{\partial U}{\partial T}\right)_V \sim T$

$\frac{C_V^{(electron)}}{C_V^{(phonon)}} \sim \frac{T}{T^3} \Rightarrow C_V^{(electron)} \sim C_V^{(phonon)} \frac{1}{T^2}$

T (K)	300	10	1	0.1	0.01
$C_V^{(e)}/C_V^{(ph)}$	0.001	0.1	1	100	10 000