Fononi

M. Peressi

Lezione 16/12/2024

slides adattate da Butov e completate
– vedere cap. 22 di A&M -

Attenzione al contesto: in alcuni casi la notazione U è usata per l'energia potenziale totale, in altri per il potenziale di coppia

VIBRAZIONI RETICOLARI

Assumiamo che

- la posizione di eq. di ogni ione sia un sito di un reticolo di Bravais
- Lo spostamento di ogni ione dalla sua posizione di equilibrio sia «piccolo» rispetto alle distanze interatomiche tra primi vicini

VIBRAZIONI RETICOLARI

Assumiamo che

- la posizione di eq. di ogni ione sia un sito di un reticolo di Bravais

  => NO DIFFUSIONE

- Lo spostamento di ogni ione dalla sua posizione di equilibrio sia «piccolo» rispetto alle distanze interatomiche tra primi vicini

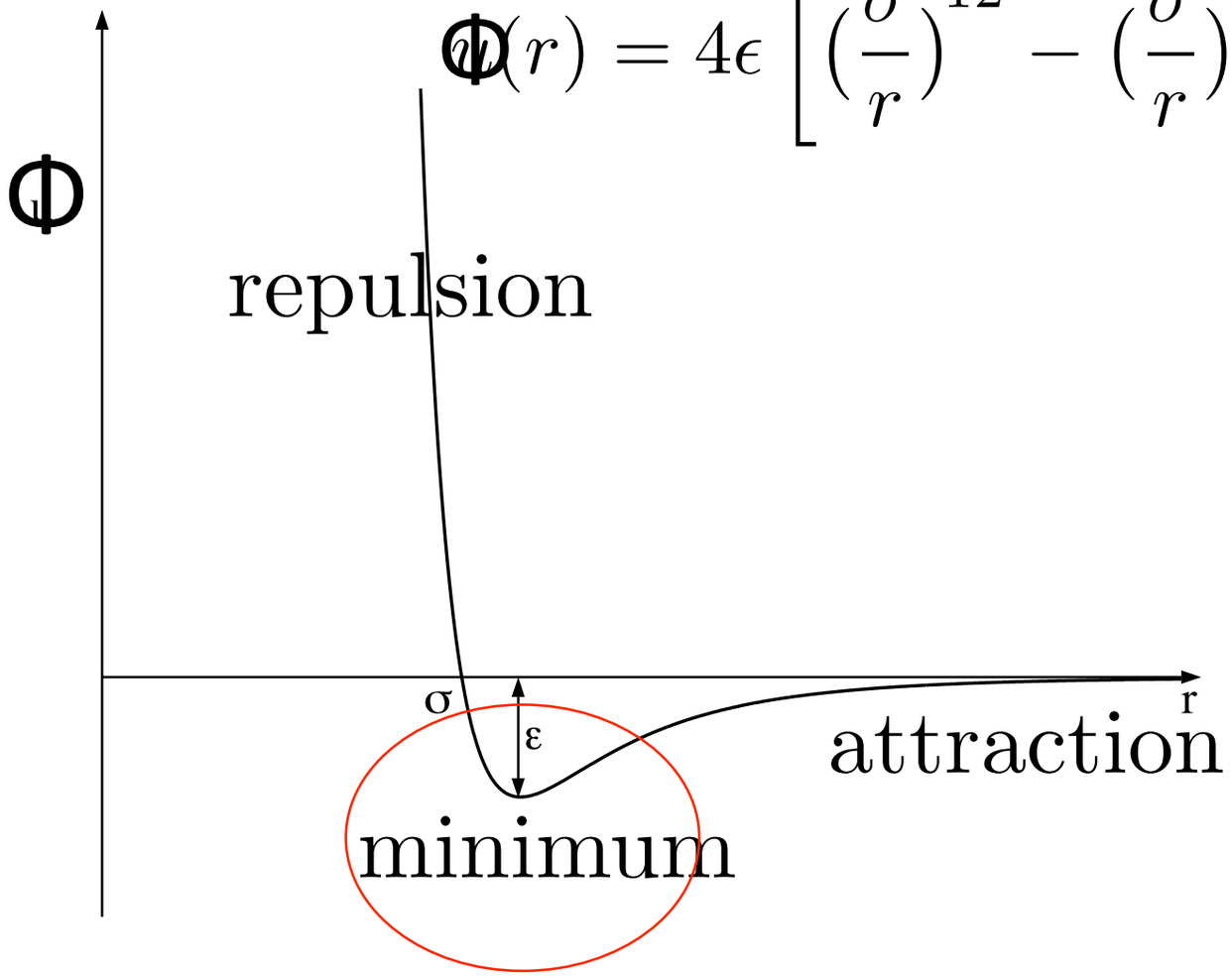
  => APPROSSIMAZIONE ARMONICA

Per ogni ione, ad un dato tempo t :

$$\mathbf{r}(\mathbf{R}) = \mathbf{R} + \mathbf{u}(\mathbf{R})$$

Lennard-Jones potential

$$\Phi(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$



U(r) è un potenziale di coppia effettivo

Energia totale = somma di potenziali di coppia

$$U_{TOT} = \frac{1}{2}\sum_{RR'} \Phi(\boldsymbol{r}(\boldsymbol{R}) - \boldsymbol{r}(\boldsymbol{R'}))$$

$$U_{TOT} = \frac{1}{2}\sum_{RR'} \Phi(\boldsymbol{r}(\boldsymbol{R}) - \boldsymbol{r}(\boldsymbol{R'}))$$

$\mathbf{r(R) = R + u(R)}$

the harmonic approximation

the mean equilibrium position of each atom is a Bravais lattice site
typical displacements of each ion are small compared to interatomic spacing

the pair potential energy of the Lennard-Jones form $\Phi(r) = \frac{B}{r^{12}} - \frac{A}{r^6}$

is approximated by the quadratic term $\Phi = \Phi_{eq} + \Phi_{harm}$

$\Phi_{harm} \propto (r - r_{eq})^2$

Le

van der Waals attraction dominating at large r

repulsion due to the Pauli exclusion principle dominating at small r

$$U_{eq} = \frac{1}{2}\sum_{RR'} \Phi(\boldsymbol{R} - \boldsymbol{R'})$$

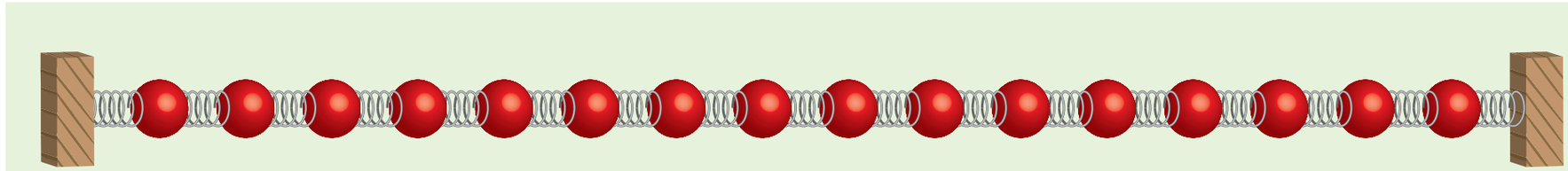
$$U_{harm} = \frac{1}{2}\sum_{RR'} [u(\boldsymbol{R}) - \boldsymbol{u}(\boldsymbol{R'})]\boldsymbol{D}(\boldsymbol{R} - \boldsymbol{R'})[u(\boldsymbol{R}) - \boldsymbol{u}(\boldsymbol{R'})]$$

Dynamical matrix

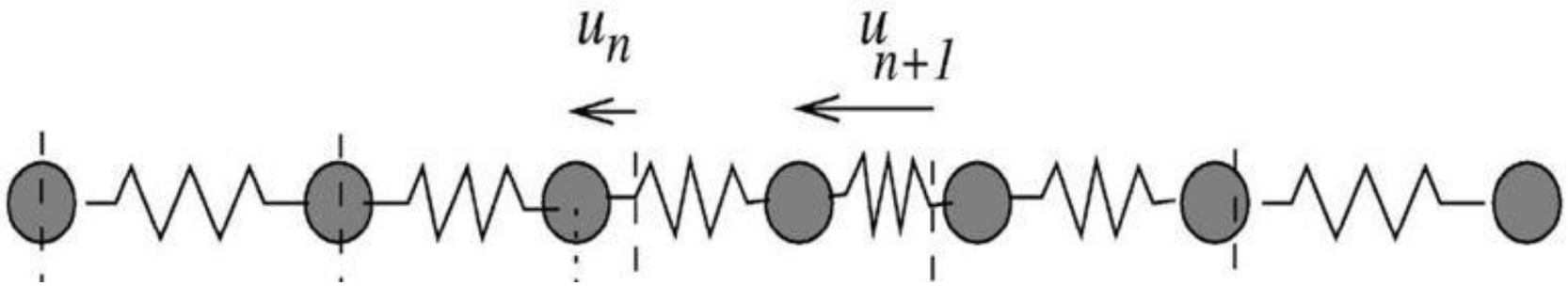
$$D_{\mu\nu}(\mathbf{r}) = \frac{1}{2}\frac{\partial^2 \Phi(\mathbf{r})}{\partial r_\mu \partial r_\nu}$$

Step by step we now face:

- Normal modes of a 1D monoatomic Bravais lattice
- Normal modes of a 1D Bravais lattice with basis
- Generalization



A chain of N particles linked by springs
(one-dimensional analogue of atoms in a crystal)



Linear interaction (Hooke's law):
(force)

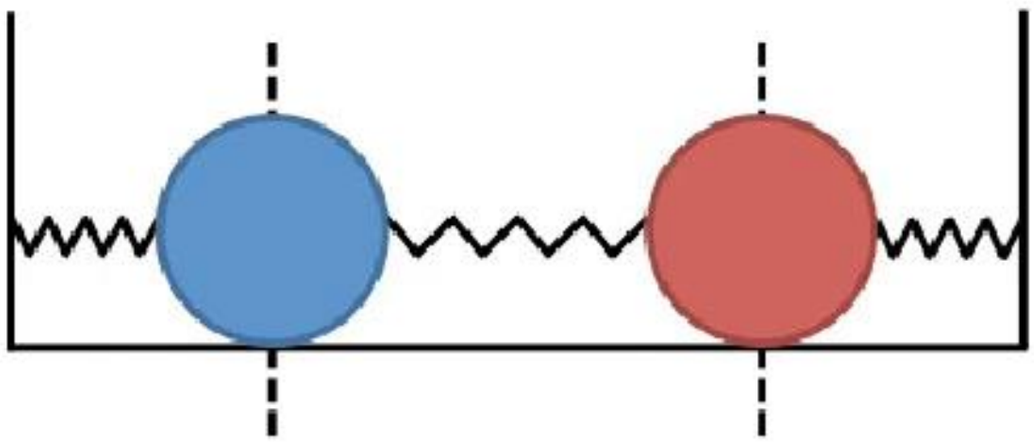
- There are N 'normal' modes

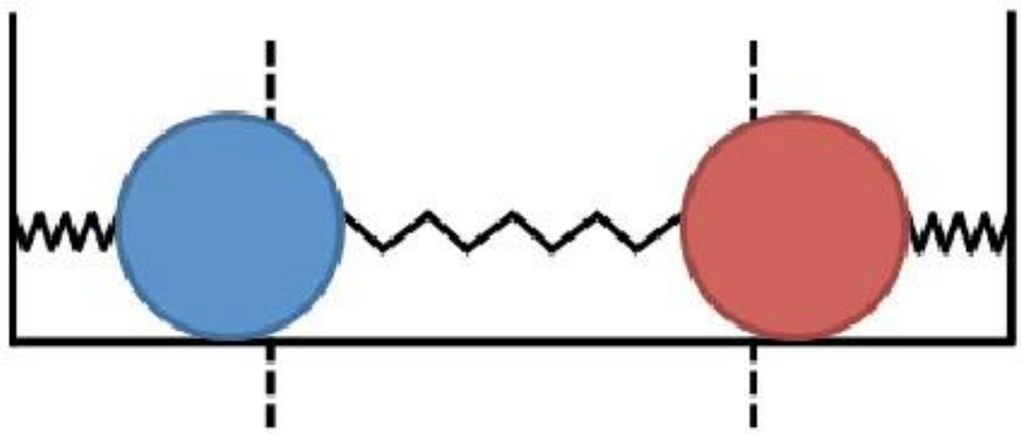
(i.e., patterns of motion in which all parts of the system oscillate with the same frequency and with a fixed phase relation)

- The energy given to a single 'normal' mode

always remains in that mode.

Example with 2 oscillators:
'normal' modes





http://fisicaondemusica.unimore.it/Oscillatori_accoppiati.html

More on: https://fisicaondemusica.unimore.it/Catena_di_Fermi-Pasta-Ulam.html

normal modes of a 1D monoatomic lattice

assume that only neighbor atoms interact

$u(na)$ is displacement of atom about na

$$U_{harm} = \frac{1}{2} K \sum_n \left[u(na) - u([n+1]a) \right]^2$$

force from left spring — force from right spring

$$M \frac{d^2 u(na)}{dt^2} = -\frac{\partial U}{\partial u(na)} = -K\left[u(na) - u([n-1]a)\right] - K\left[u(na) - u([n+1]a)\right] =$$

$$= -K\left[2u(na) - u([n-1]a) - u([n+1]a)\right]$$

$$u(na,t) \propto e^{i(kna - \omega t)}$$

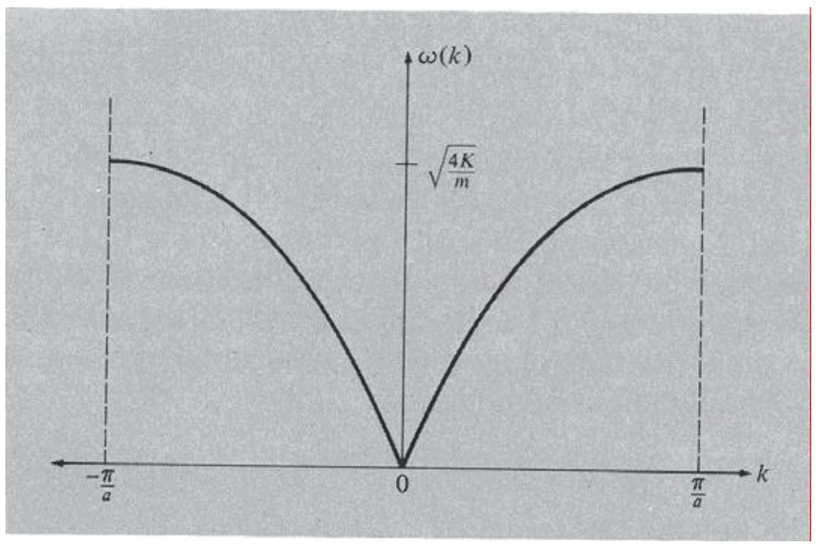
$$-M\omega^2 e^{i(kna-\omega t)} = -K\left[2 - e^{-ika} - e^{ika}\right] e^{i(kna-\omega t)}$$

sin(α/2)^2=(1-cos α)

$$\omega(k) = 2\sqrt{\frac{K}{M}} \left| \sin \frac{1}{2} ka \right|$$

← dispersion of waves propagating along the chain

$$\sin\frac{\alpha}{2} = \pm\sqrt{\frac{1-\cos\alpha}{2}}$$



if k is changed by $m2\pi/a$ ➡ $u(na,t)$ does not change

$-\pi/a < k < \pi/a$ covers all independent values of k

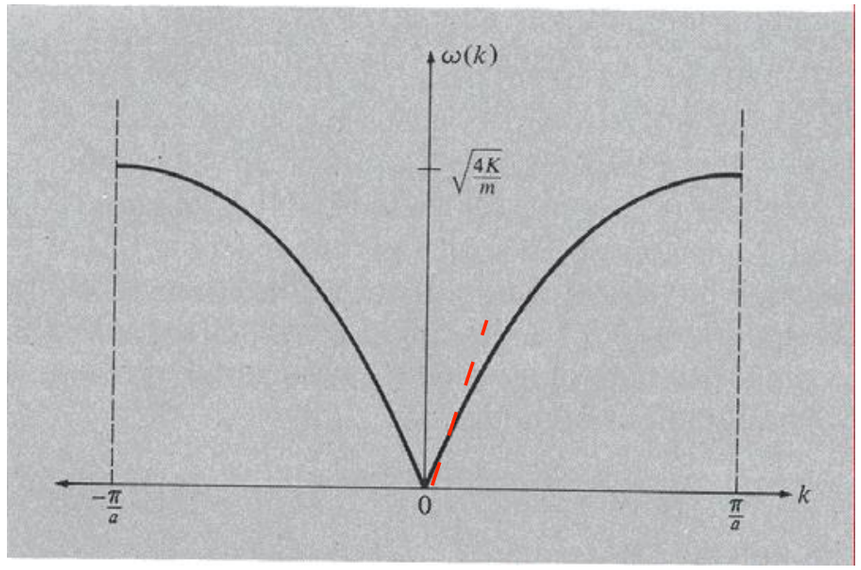
k and $k + m2\pi/a$ are equivalent

periodic boundary conditions for N atoms $u([N+1]a) = u(a)$

$$e^{ikNa} = 1$$

allowed values of k $\quad k = \frac{2\pi}{a}\frac{j}{N}$, $\quad j$ is an integer

there are N values of k that yield distinct solutions



$$\omega(k) = 2\sqrt{\frac{K}{M}}\sin\left|1/2\,ka\right|$$

$v = \partial\omega/\partial k$ the group velocity – the transmission velocity of a wave packet, the velocity of energy propagation

---

$k << \pi/a \qquad (\lambda >> a)$ long wavelength limit

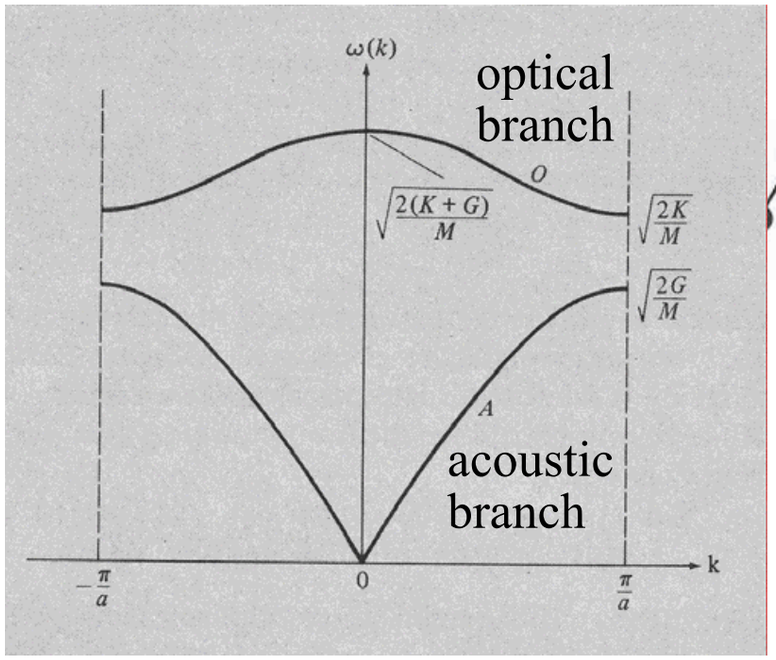
$$\omega(k) = a\sqrt{\frac{K}{M}}\,|k|$$ (typical behaviour of a sound wave)

$$v = a\sqrt{\frac{K}{M}}$$ sound velocity

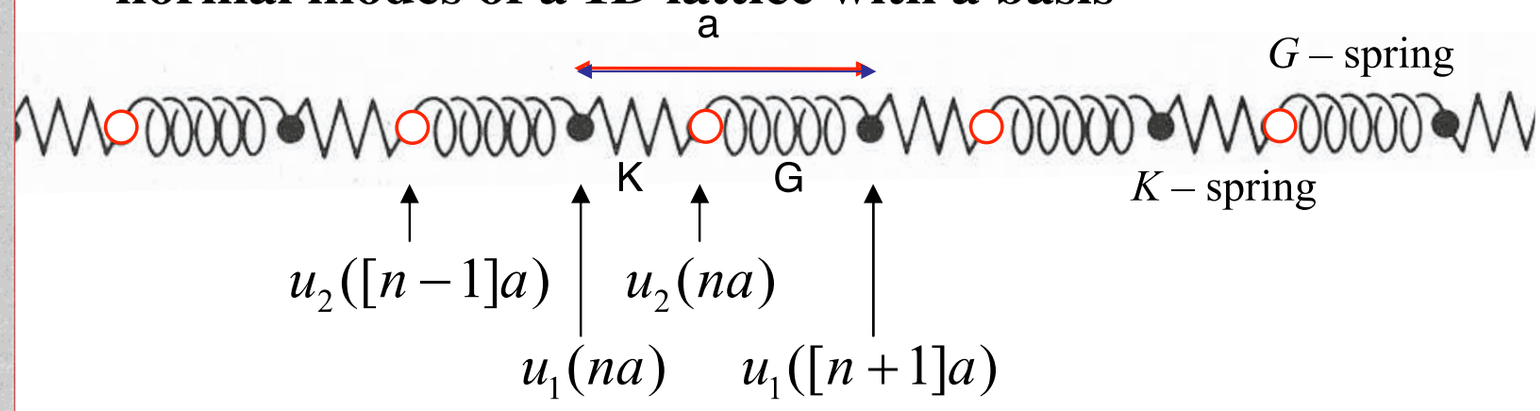
$$k = \pm\pi/a$$

$$\omega(k) = \sqrt{\frac{4K}{M}}$$

$v = 0$ standing wave



normal modes of a 1D lattice with a basis



$$U_{harm} = \frac{K}{2}\sum_n \left[u_1(na) - u_2(na)\right]^2 + \frac{G}{2}\sum_n \left[u_2(na) - u_1([n+1]a)\right]^2$$

$$M\frac{d^2u_1(na)}{dt^2} = -\frac{\partial U_{harm}}{\partial u_1(na)} = -K\left[u_1(na) - u_2(na)\right] - G\left[u_1(na) - u_2([n-1]a)\right]$$

$$M\frac{d^2u_2(na)}{dt^2} = -\frac{\partial U_{harm}}{\partial u_2(na)} = -K\left[u_2(na) - u_1(na)\right] - G\left[u_2(na) - u_1([n+1]a)\right]$$

$$u_1(na,t) \propto \varepsilon_1 e^{i(kna-\omega t)}$$

$$u_2(na,t) \propto \varepsilon_2 e^{i(kna-\omega t)}$$

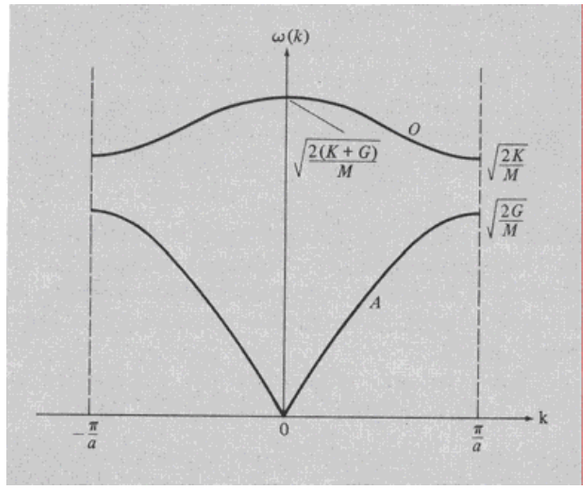
Substituting and setting to 0 the determinant of the homogeneous system :

$$\omega^2 = \frac{K+G}{M} \pm \frac{1}{M}\sqrt{K^2 + G^2 + 2KG\cos ka}$$

$$\frac{\varepsilon_2}{\varepsilon_1} = \mp\frac{K + Ge^{ika}}{\left|K + Ge^{ika}\right|}$$

Two solutions for each value of k => 2N normal modes:

$$\omega^2 = \frac{K+G}{M} \pm \frac{1}{M}\sqrt{K^2+G^2+2KG\cos ka}$$

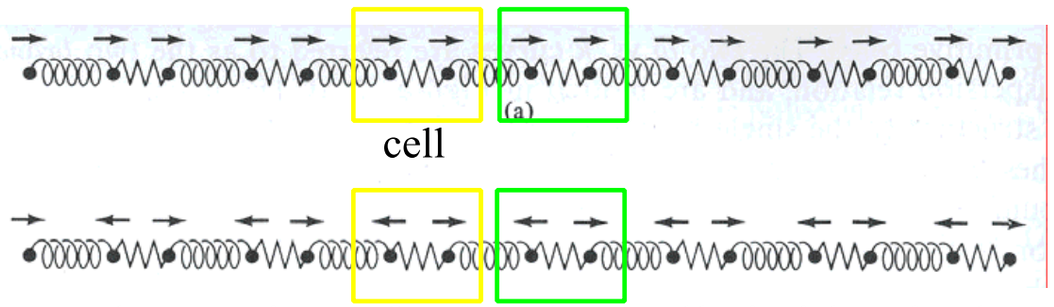


$k << \pi/a$

$$\cos ka \approx 1-(ka)^2/2$$

$$\omega = \sqrt{\frac{KG}{2M(K+G)}}(ka) \qquad \varepsilon_1 = \varepsilon_2 \qquad \text{acoustic}$$

$$\omega = \sqrt{\frac{2(K+G)}{M} - O(ka)^2} \qquad \varepsilon_2 = -\varepsilon_1 \qquad \text{optical}$$

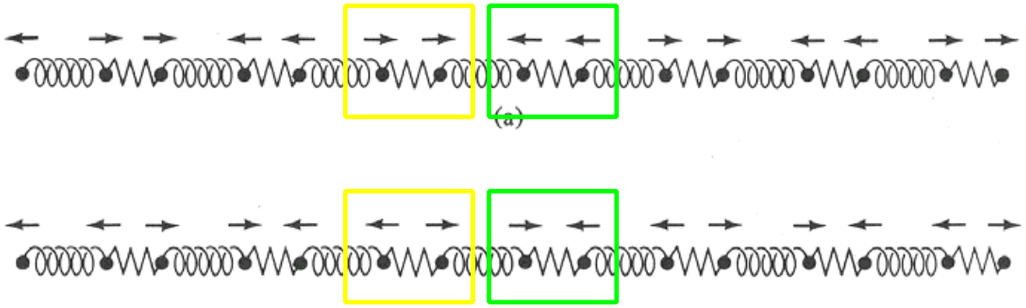


the motion of primitive cells is identical

$k = \pi/a$

$$\omega = \sqrt{\frac{2G}{M}} \qquad \varepsilon_1 = \varepsilon_2 \qquad \text{acoustic}$$

$$\omega = \sqrt{\frac{2K}{M}} \qquad \varepsilon_2 = -\varepsilon_1 \qquad \text{optical}$$



the motion changes by 180^0 from cell to cell

in the acoustic mode the atoms within a cell move together
in the optical mode the atoms within a cell move 180^0 out of phase

Monoatomic 3D Bravais lattice:

$$U^{harm} = \frac{1}{2}\sum_{\mathbf{R}\mathbf{R}'}\sum_{\mu\nu} u_\mu(\mathbf{R}) D_{\mu\nu}(\mathbf{R}-\mathbf{R}') u_\nu(\mathbf{R}')$$

Exploiting symmetry properties of the dynamical matrix:

1) $D_{\mu\nu}(\mathbf{R}-\mathbf{R}') = D_{\nu\mu}(\mathbf{R}'-\mathbf{R})$

2) $D_{\mu\nu}(\mathbf{R}-\mathbf{R}') = D_{\mu\nu}(\mathbf{R}'-\mathbf{R})$ $\qquad \mathbf{D}(\mathbf{R}) = \mathbf{D}(-\mathbf{R})$

3) $\sum_{\mathbf{R}} D_{\mu\nu}(\mathbf{R}) = 0$ $\qquad \sum_{\mathbf{R}} \mathbf{D}(\mathbf{R}) = 0$

These symmetries allow to simplify the eqs.

$$M\ddot{\mathbf{u}}(\mathbf{R}') = -\sum_{\mathbf{R}'} \mathbf{D}(\mathbf{R}-\mathbf{R}')\mathbf{u}(\mathbf{R}')$$

We seek for a solution of the form:

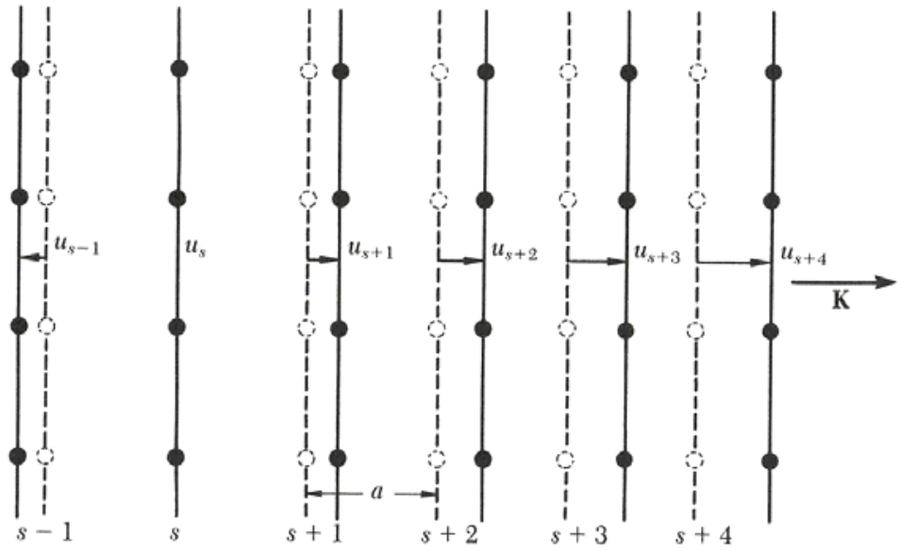
$$\mathbf{u}(\mathbf{R},t) = \vec{\epsilon} e^{i(\mathbf{k}\cdot\mathbf{R}-\omega t)}$$

Polarization vector of the normal mode
(the direction in which the ion moves)

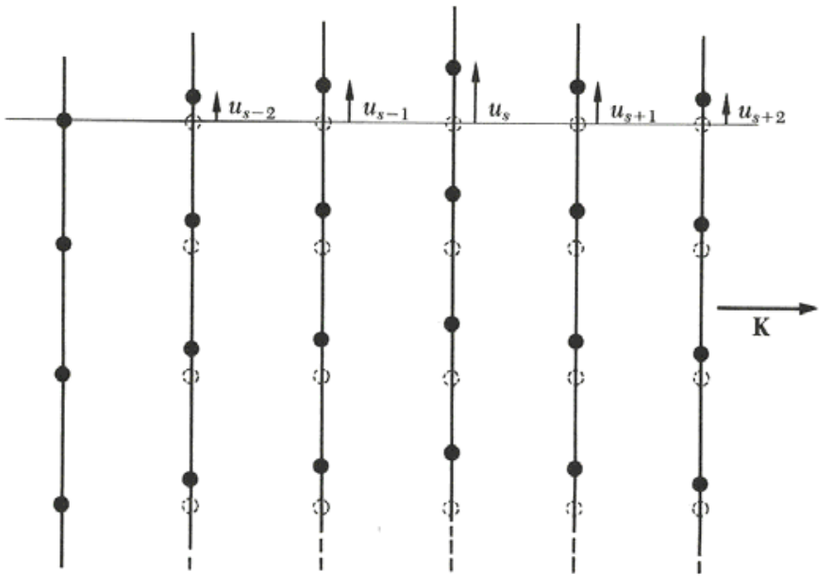
Substituting we obtain:

$$M\omega^2\vec{\epsilon} = \mathbf{D}(\mathbf{k})\vec{\epsilon} \quad \text{with} \quad \mathbf{D}(\mathbf{k}) = \sum_{\mathbf{R}} \mathbf{D}(\mathbf{R})e^{-i\mathbf{k}\cdot\mathbf{R}}$$

normal modes of a 3D lattice



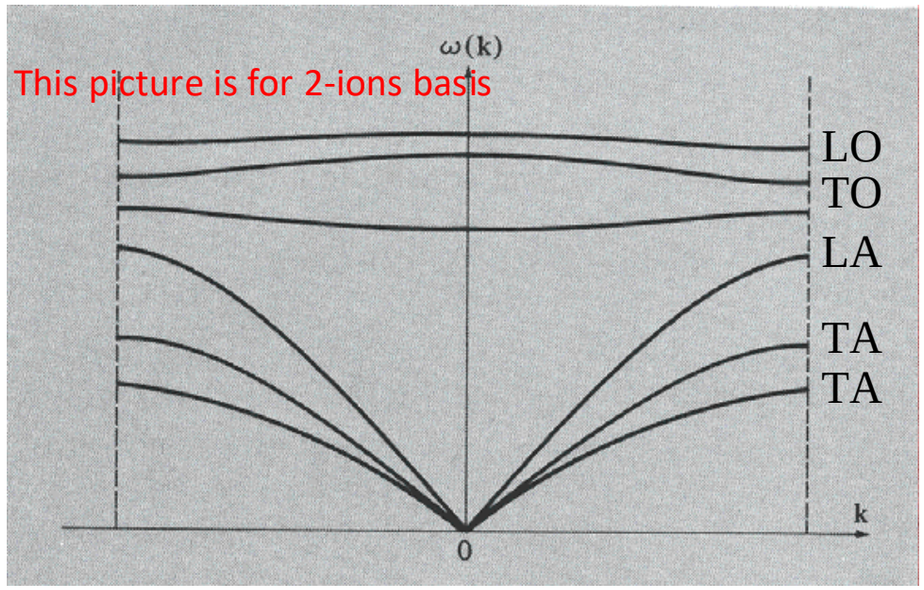
longitudinal wave



transverse wave

3D lattice with monoatomic basis:
for each k there are 3 acoustic modes
1 longitudinal and 2 transverse

3D lattice with p atoms in the basis:
for each k there are $3p$ modes
3 branches are acoustic
and $3p$ F 3 branches are optical

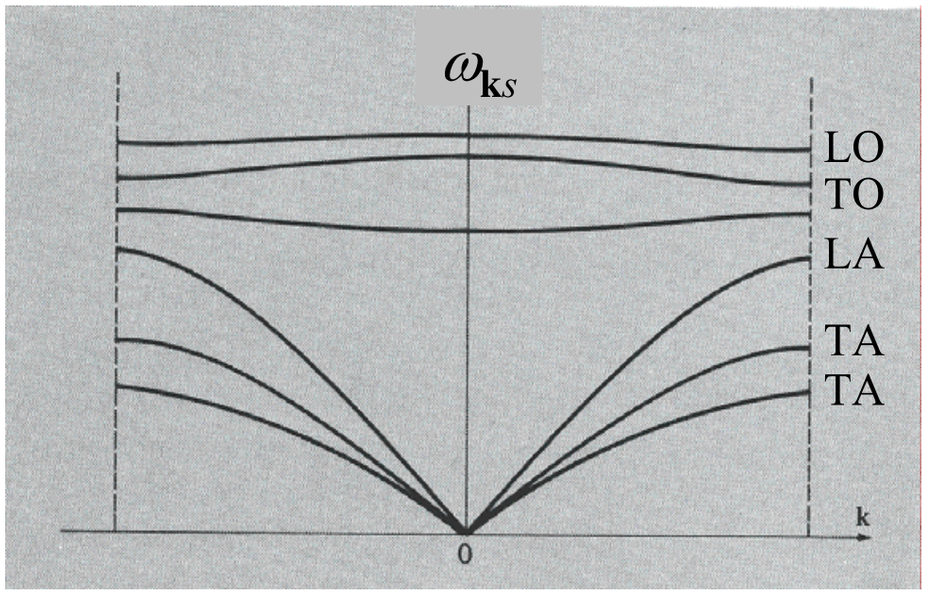


correspond to 3 translational and $3p$ F 3 vibrational degrees of freedom of a p atomic molecule

with p atoms per primitive cell and N primitive cells
there are pN atoms
3 degrees of freedom for each atom, one for each direction:
a total $3pN$ degrees of freedom for the crystal

the number of allowed k in a single branch
for one Brillouin zone is N:
$3p$ phonon branches accommodate $3pN$ degrees of freedom

phonons



vibration of N-ion harmonic crystal correspond to
$3N$ independent oscillators whose frequencies are
those of the $3N$ normal modes
energy vibrations are quantized:
$\omega_{\mathbf{k}s}$ can have only the discrete set of values

$$\varepsilon_{\mathbf{k}s} = \left(n_{\mathbf{k}s} + \frac{1}{2} \right) \hbar \omega_{\mathbf{k}s}$$

$n_{\mathbf{k}s} = 0, 1, 2 \ldots$ is the excitation number of the normal mode

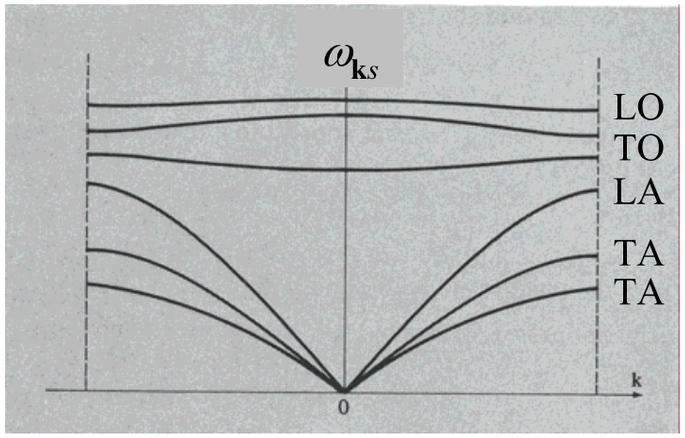
equivalent corpuscular description of the normal modes:
phonon – the quanta of the ionic displacement field ⟵ similar to photon – the quanta of the radiation field

the normal mode of branch s with wave vector k is in its $n_{\mathbf{k}s}$th excited state

↕

there are $n_{\mathbf{k}s}$ phonons of type s with wave vector $\mathbf{k}$ present in a crystal

thermal vibrations in a crystal are thermally excited phonons



lattice specific heat

$$\varepsilon_{\mathbf{k}s} = \hbar\omega_s(\mathbf{k})\left[n_s(\mathbf{k}) + \frac{1}{2}\right]$$ energy of $n_s(\mathbf{k})$ phonons of type s with wave vector $\mathbf{k}$

$$n_s(\mathbf{k}) = \frac{1}{e^{\beta\hbar\omega_s(\mathbf{k})} - 1}$$ number of phonons of type s with wave vector $\mathbf{k}$ at temperature T

$$\beta = \frac{1}{k_B T}$$

the Planck distribution
= BE distribution with $\mu = 0$ $f_{BE}(E) = \frac{1}{e^{\beta(E-\mu)} - 1}$
(Bose-Einstein)

$$u = u^{eq} + \frac{1}{V}\sum_{\mathbf{k}s}\hbar\omega_s(\mathbf{k})\left[n_s(\mathbf{k}) + \frac{1}{2}\right]$$ the energy density of a harmonic crystal

$$c_v = \frac{1}{V}\sum_{\mathbf{k}s}\frac{\partial}{\partial T}\hbar\omega_s(\mathbf{k})\frac{1}{e^{\beta\hbar\omega_s(\mathbf{k})} - 1}$$ the specific heat of a harmonic crystal

$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$
$F = E - TS$
$S = \ln(\text{number of states})$

---

high temperature specific heat

$$x = \beta\hbar\omega = \frac{\hbar\omega}{k_B T} << 1$$

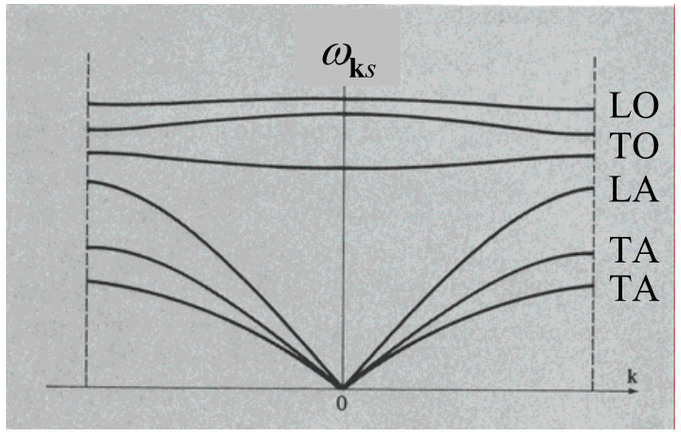
$$\frac{1}{e^x - 1} \approx \frac{1}{x}$$

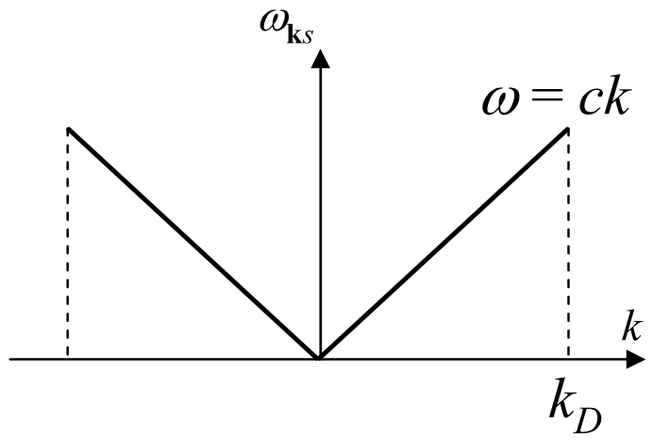
$$c_v \approx \frac{1}{V}\sum_{\mathbf{k}s}\frac{\partial}{\partial T}\hbar\omega_s(\mathbf{k})\frac{k_B T}{\hbar\omega_s(\mathbf{k})} = \frac{1}{V}3N_{atoms}k_B$$

$\boxed{c_v = 3nk_B}$ the classical law of Dulong and Petit

additional terms in the expansion yield the high-temperature quantum corrections to the Dulong and Petit law

specific heat at low temperatures





$$c_v = \frac{1}{V}\sum_{\mathbf{k}s}\frac{\partial}{\partial T}\frac{\hbar\omega_s(\mathbf{k})}{e^{\beta\hbar\omega_s(\mathbf{k})}-1} \rightarrow \frac{\partial}{\partial T}\sum_s\int\frac{d\mathbf{k}}{(2\pi)^3}\frac{\hbar\omega_s(\mathbf{k})}{e^{\beta\hbar\omega_s(\mathbf{k})}-1}$$

integration over the 1st Brillouin zone

$$\downarrow \quad d\mathbf{k} = k^2 dk d\Omega$$

$$c_v = \frac{\partial}{\partial T}\frac{3\hbar c}{2\pi^2}\int_0^{k_D}\frac{k^3 dk}{e^{\beta\hbar ck}-1}$$

the Debye model:

1. all branches of the vibrational spectrum are replaced with 3 branches with $\omega = ck$
2. the integral over the 1st Brillouin zone is replaced by an integral over a sphere of radius k_D chosen to contain N allowed wave vectors

volume in k-space per wave vector is $(2\pi)^3/V$

for N atoms

$$3N\frac{(2\pi)^3}{V} = 3\frac{4}{3}\pi k_D^3$$

$$k_D = \left(6\pi^2 n\right)^{1/3}$$

$\omega_D = k_D c$ Debye frequency

$k_B\Theta_D = \hbar\omega_D$ Debye temperature – a measure of the temperature above which all modes begin to be excited, and below which modes begin to be "frozen out"

$$\Theta_D = \frac{\hbar c}{k_B}(6\pi^2 n)^{1/3}$$

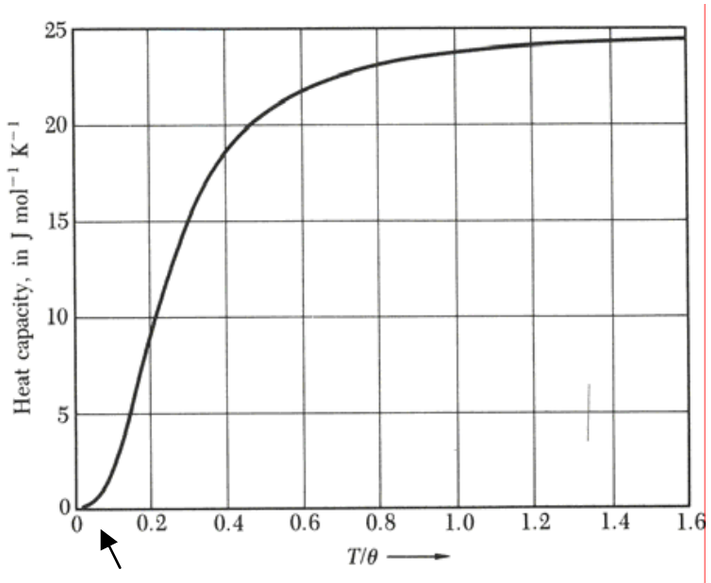
without equilibrium energy and the energy of the zero-point vibrations

phonon density of states

$$u = \int_0^{\omega_D} \hbar\omega D(\omega) n(\omega) d\omega$$

$$u = 9nk_B T \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^3 dx}{e^x - 1}$$

$$c_v = 9nk_B \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x dx}{(e^x - 1)^2} \rightarrow$$



at low temperatures $c_v \sim T^3$

at low temperatures $T << \Theta_D$

$$u = 9nk_B T \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^3 dx}{e^x - 1} \rightarrow 9nk_B T \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\infty} \frac{x^3 dx}{e^x - 1} = 9nk_B T \left(\frac{T}{\Theta_D}\right)^3 \frac{\pi^4}{15}$$

$$c_v = \frac{12\pi^4}{5} nk_B \left(\frac{T}{\Theta_D}\right)^3 = 234nk_B \left(\frac{T}{\Theta_D}\right)^3$$

$\longrightarrow$ fit to T^3 at low temperatures $\rightarrow \Theta_D$

	Θ_D, K
Li	400
Na	150
K	100

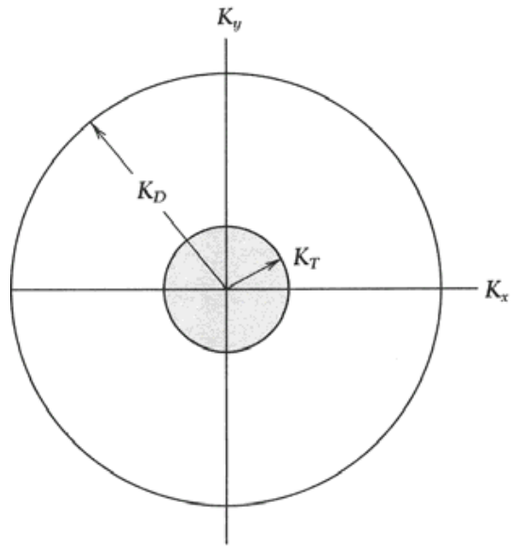
at low temperatures $c_v \sim T^3$

at high temperatures $c_v \sim 3nk_B$ Dulong an Petit result

understanding T^3 law

$$\hbar c k_T = k_B T$$

suppose that
all phonon modes with wavevector less than k_T
have the classical thermal energy $k_B T$
and modes with $k > k_T$ are not excited
of the $3N$ possible modes, the fraction excited is $(k_T / k_D)^3 = (T / \Theta_D)^3$
the energy density is $u \approx k_B T \cdot 3n(T / \Theta_D)^3$
and the specific heat is $c_v = \partial u / \partial T \approx 12 n k_B (T / \Theta_D)^3$



$$c_v = \frac{12\pi^4}{5} n k_B \left(\frac{T}{\Theta_D} \right)^3 = 234 n k_B \left(\frac{T}{\Theta_D} \right)^3$$

the phonon contribution to specific heat $c_v = \frac{12\pi^4}{5} n k_B \left(\frac{T}{\Theta_D} \right)^3$

the electronic contribution to specific heat $c_v = \frac{\pi^2}{2} \frac{k_B T}{E_F} n k_B$

contributions to specific heat

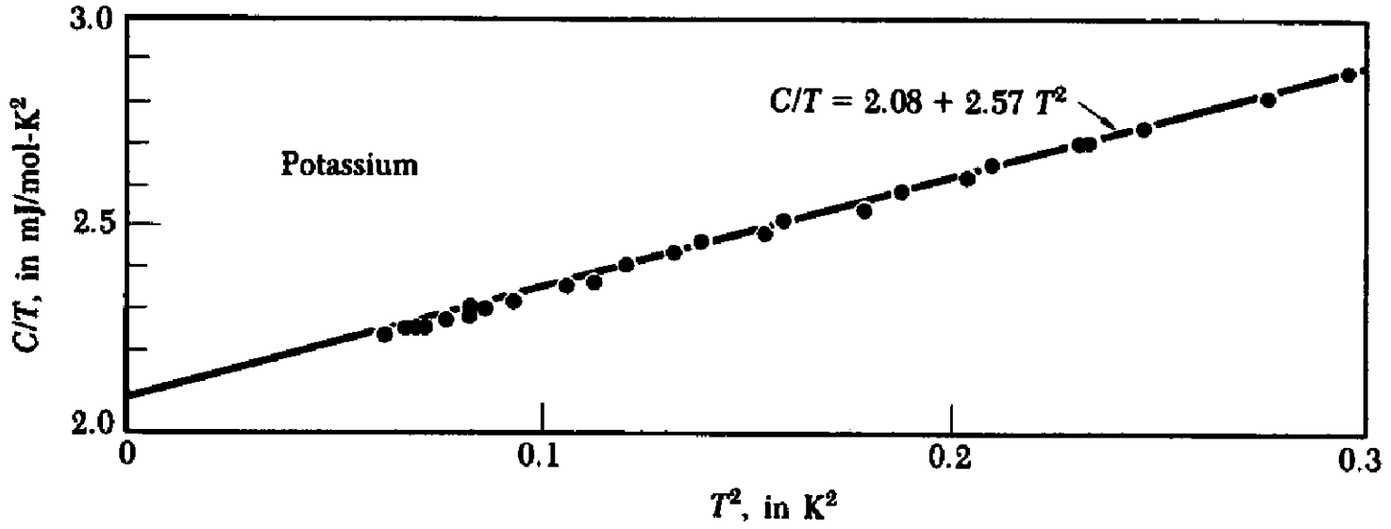
electrons phonons

$$c_v = \gamma T + A T^3$$

$c_{electron} \approx c_{phonon}$ at

$$T_0 = 0.145 \left(\frac{Z\Theta_D}{T_F} \right)^{1/2} \Theta_D$$

~ a few degrees Kelvin



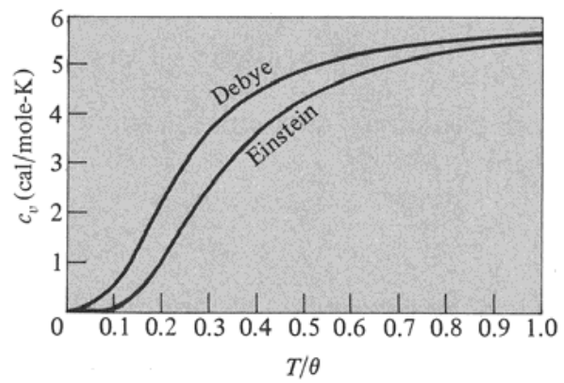
the Einstein model

the Einstein approximation replaces the frequency of each optical branch by a frequency ω_E

each optical branch will contribute to the thermal energy density and to the specific heat

$$u = \frac{n\hbar\omega_E}{e^{\hbar\omega_E/k_BT} - 1}$$

$$c_v = nk_B \left(\frac{\hbar\omega_E}{k_BT}\right)^2 \frac{e^{\hbar\omega_E/k_BT}}{\left(e^{\hbar\omega_E/k_BT} - 1\right)^2}$$



at low T the contribution of the optical modes to c_v drops exponentially $c_v \approx nk_B \left(\frac{\hbar\omega_E}{k_BT}\right)^2 e^{-\hbar\omega_E/k_BT}$

it is difficult to excite thermally optical modes at low T