

Fononi

M. Peressi

Lezione 15/12/2023

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

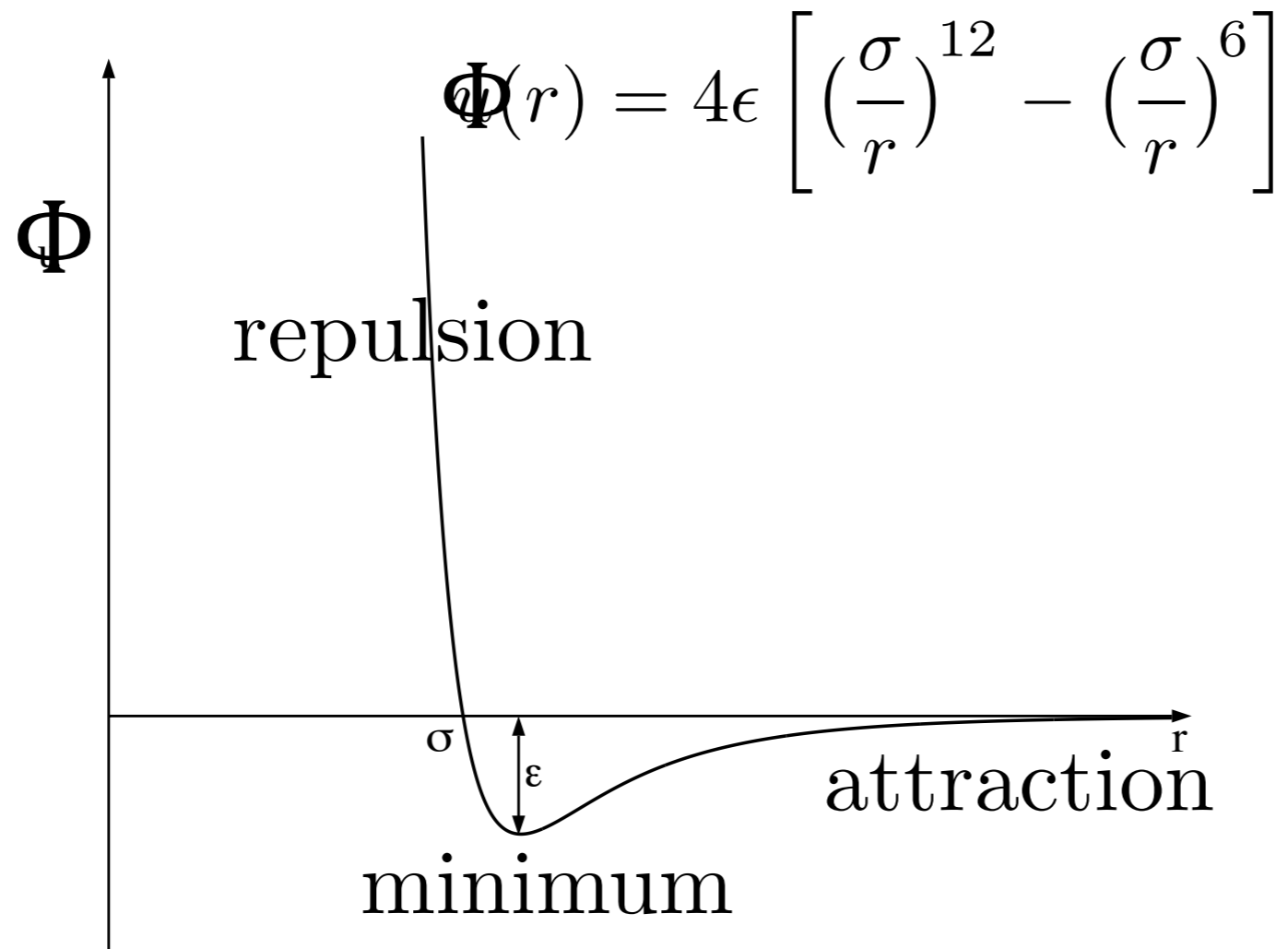
Assumiamo che

- 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



$U(r)$ è un potenziale di coppia effettivo

Energia totale = somma di potenziali di coppia

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

$$U_{TOT} = \frac{1}{2} \sum_{RR'} \Phi(\mathbf{r}(\mathbf{R}) - \mathbf{r}(\mathbf{R}')) \quad \mathbf{r}(\mathbf{R}) = \mathbf{R} + \mathbf{u}(\mathbf{R})$$

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 $\Phi = \Phi_{eq} + \Phi_{harm}$

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

van der Waals attraction
 dominating at large r

repulsion due to the
 Pauli exclusion principle
 dominating at small r

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

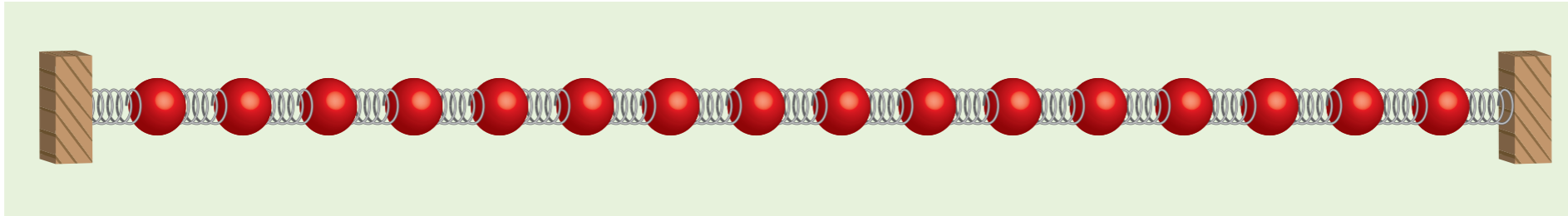
$$U_{harm} = \frac{1}{2} \sum_{RR'} [\mathbf{u}(\mathbf{R}) - \mathbf{u}(\mathbf{R}')] \mathbf{D}(\mathbf{R} - \mathbf{R}') [\mathbf{u}(\mathbf{R}) - \mathbf{u}(\mathbf{R}')]$$

Dynamical matrix

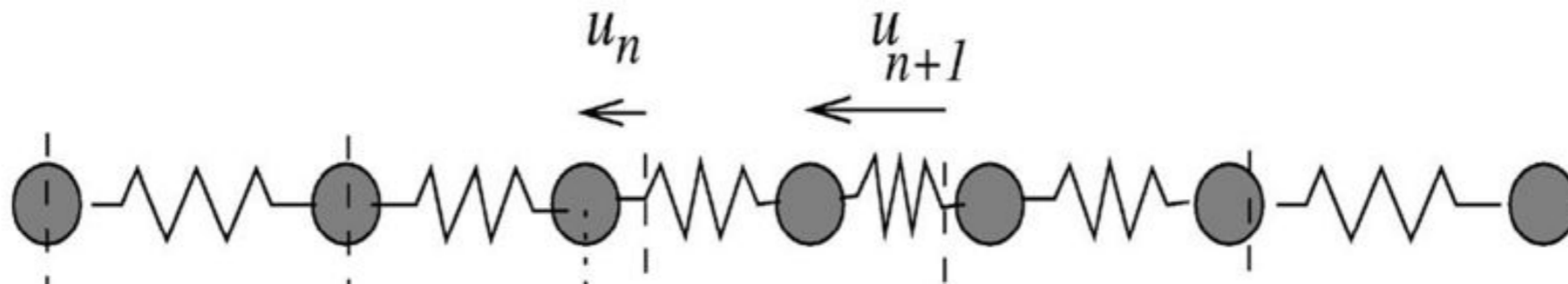
$$D_{\mu\nu}(\mathbf{r}) = \frac{1}{2} \frac{\partial^2 \Phi(\mathbf{r})}{\partial r_\mu \partial r_\nu}$$

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)



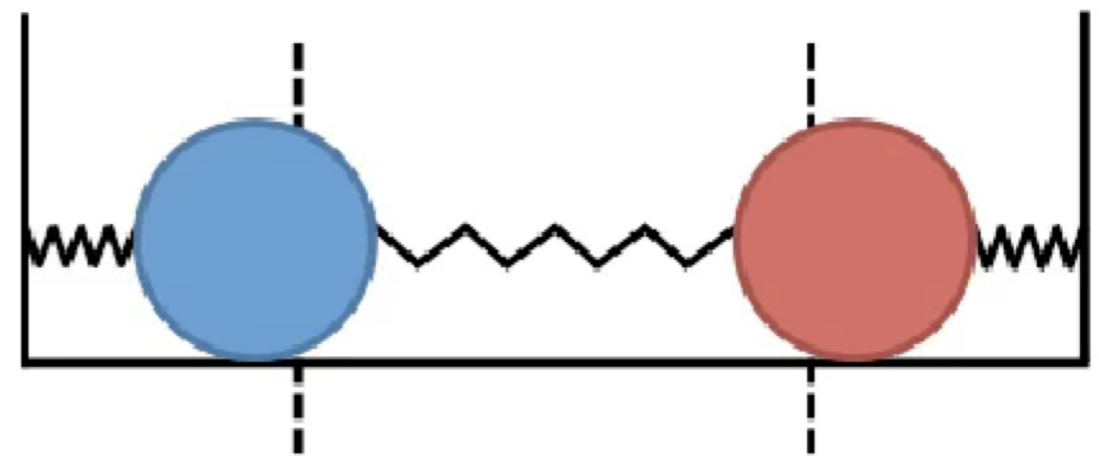
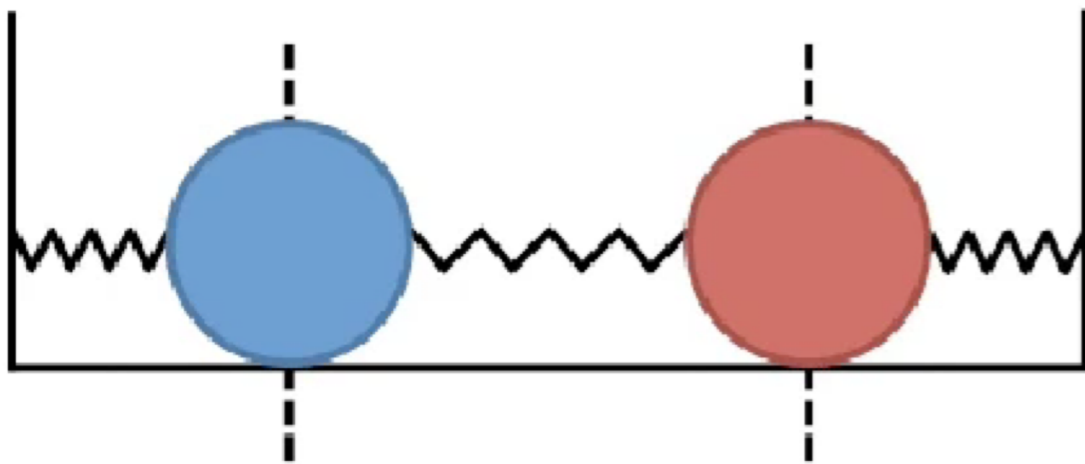
Linear interaction (Hooke's law):
(force)

- 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

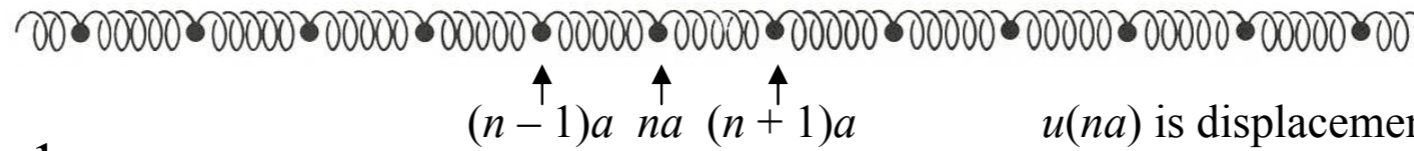


http://fisicaondemusica.unimore.it/Oscillatori_accoppiati.html

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

assume that only neighbor atoms interact

normal modes of a 1D monoatomic lattice



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

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

force from left spring

force from right spring

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

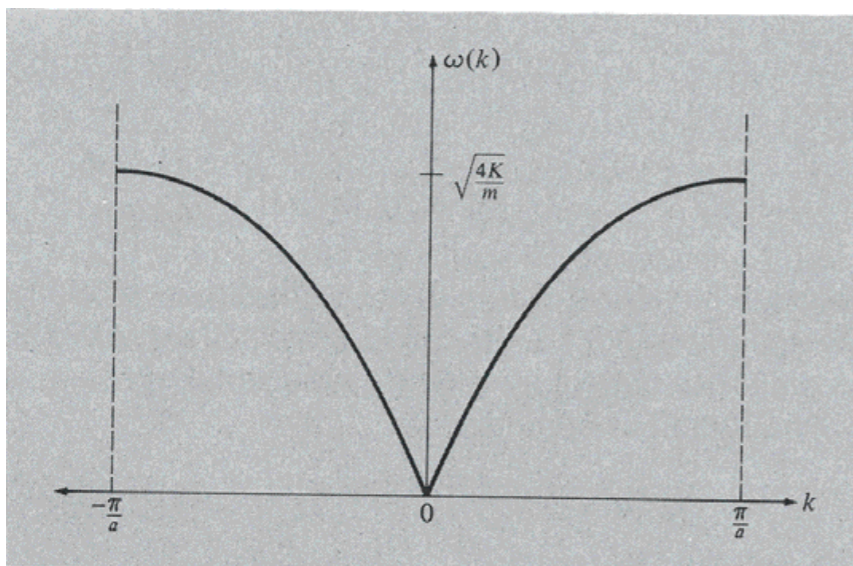
$$= -K [2u(na) - u([n-1]a) - u([n+1]a)]$$

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

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

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

← dispersion of waves propagating along the chain



if k is changed by

$$-\pi/a < k < \pi/a$$

$$m2\pi/a$$



covers all independent values of k

$u(na, t)$ does not change

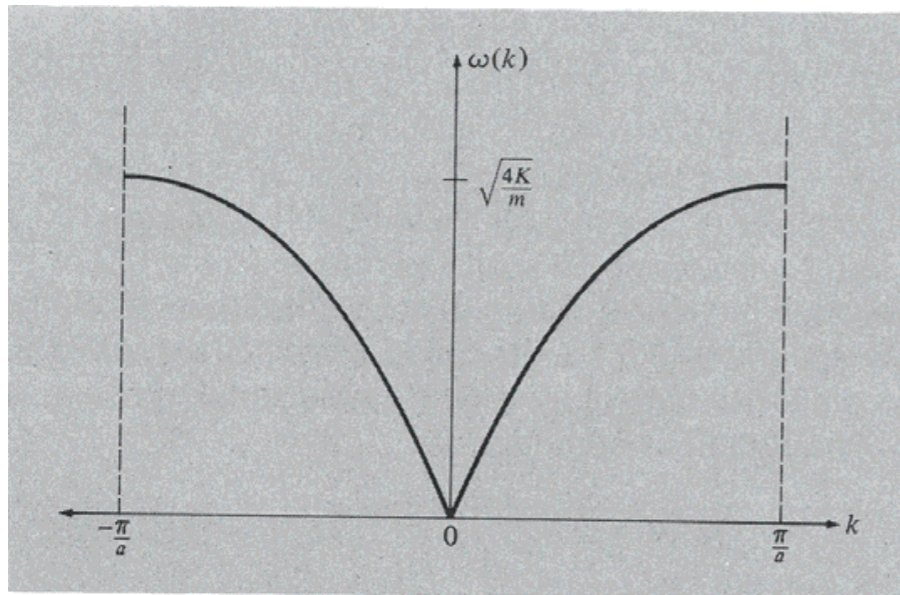
k and $k + m2\pi/a$ are equivalent

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

$$e^{ikNa} = 1$$

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

there are N values of k that yield distinct solutions



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

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

$k \ll \pi/a$ ($\lambda \gg a$) long wavelength limit

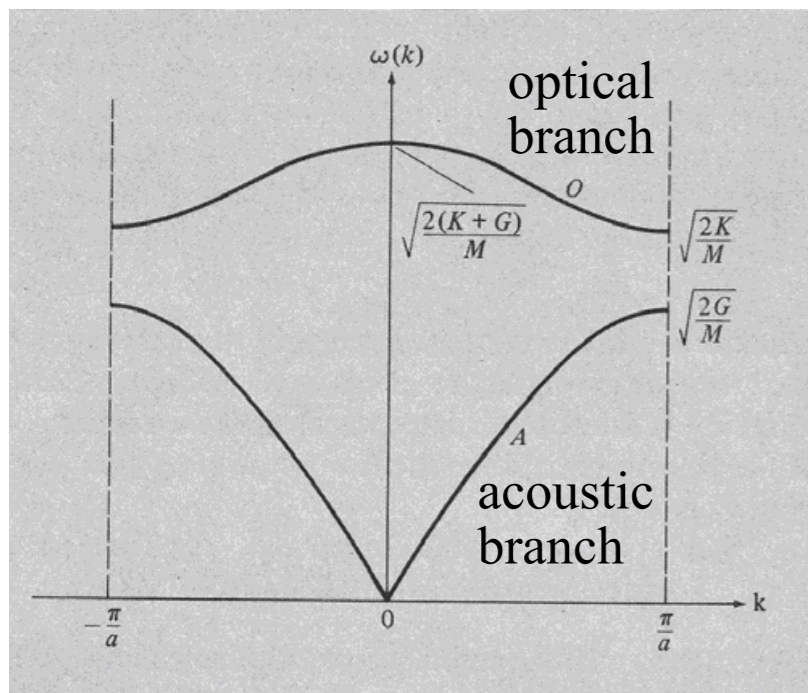
$$\omega(k) = a\sqrt{\frac{K}{M}} |k| \quad (\text{typical behaviour of a sound wave})$$

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

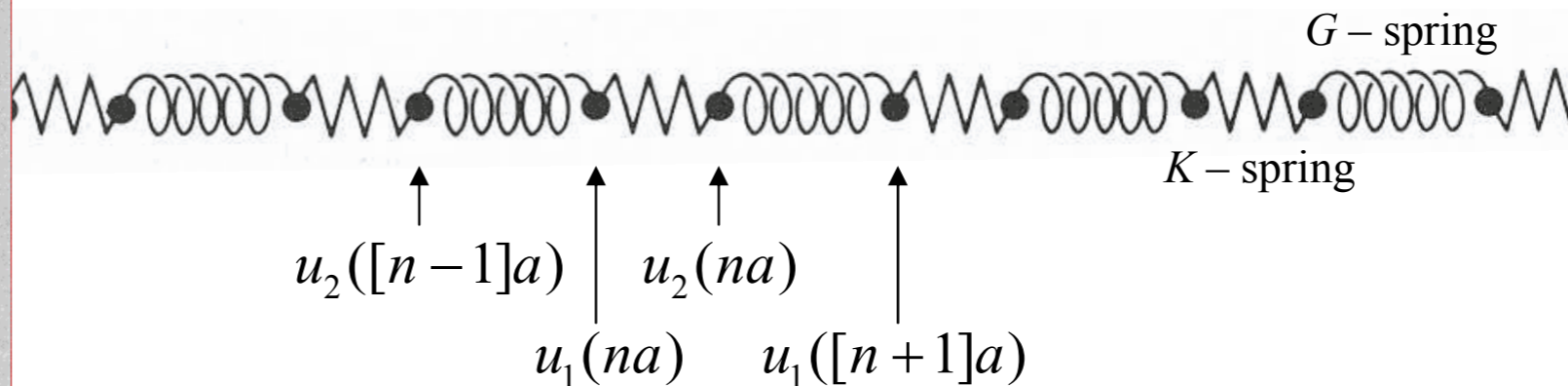
$$k = \pm \pi/a$$

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

$$v = 0 \quad \text{standing wave}$$



normal modes of a 1D lattice with a basis



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

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

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

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

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

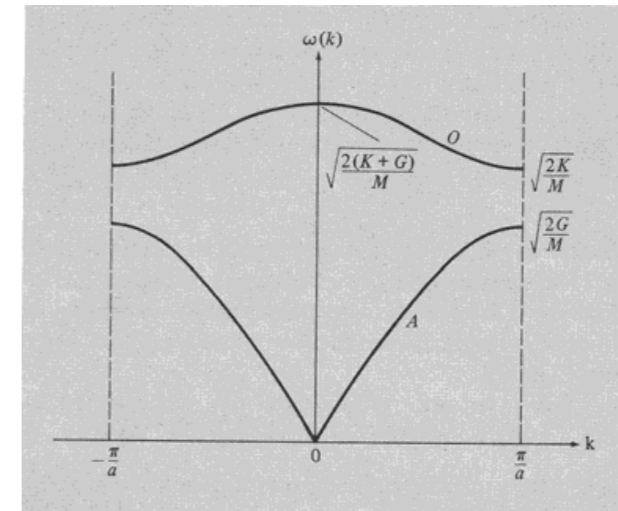
Substituting and setting to 0 the determinant of the homogeneous system :

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

$$\frac{\varepsilon_2}{\varepsilon_1} = \mp \frac{K + Ge^{ika}}{K + Ge^{-ika}}$$

Two solutions for each value of $k \Rightarrow 2N$ normal modes:

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

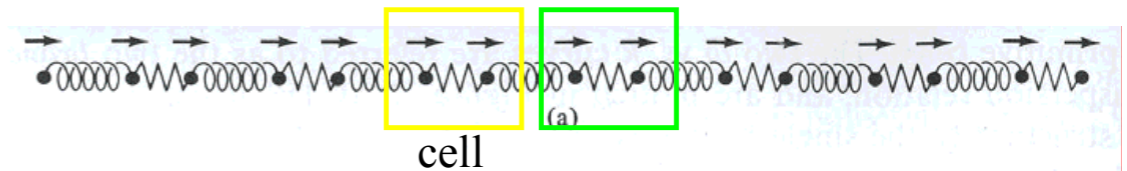


$$k \ll \pi/a$$

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

$$\omega = \sqrt{\frac{KG}{2M(K+G)}} (ka)$$

$\varepsilon_1 = \varepsilon_2$ acoustic



$$\omega = \sqrt{\frac{2(K+G)}{M}} - O(ka)^2$$

$\varepsilon_2 = -\varepsilon_1$ optical

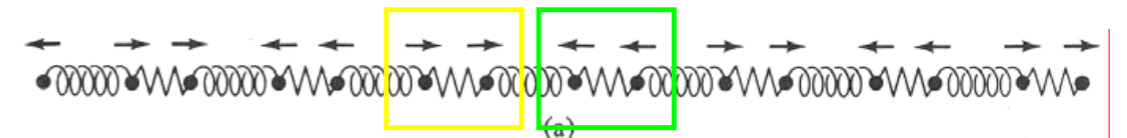


the motion of primitive cells is identical

$$k = \pi/a$$

$$\omega = \sqrt{\frac{2G}{M}}$$

$\varepsilon_1 = \varepsilon_2$ acoustic



$$\omega = \sqrt{\frac{2K}{M}}$$

$\varepsilon_2 = -\varepsilon_1$ optical



the motion changes by 180° 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° 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:

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

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

$$\mathbf{D}(\mathbf{R}) = \mathbf{D}(-\mathbf{R})$$

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

$$\sum_{\mathbf{R}} \mathbf{D}(\mathbf{R}) = 0$$

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:

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

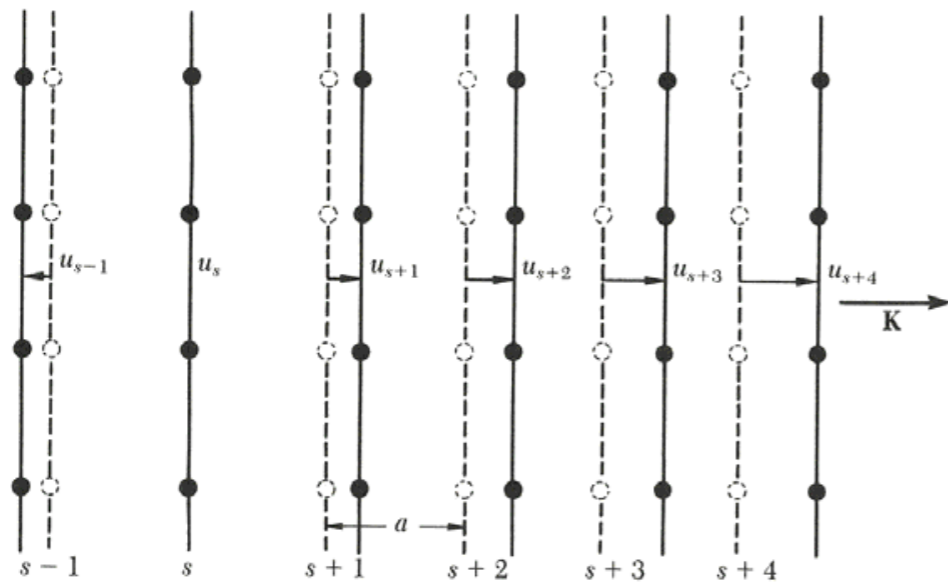


Polarization vector of the normal mode
(the direction in which the ion moves)

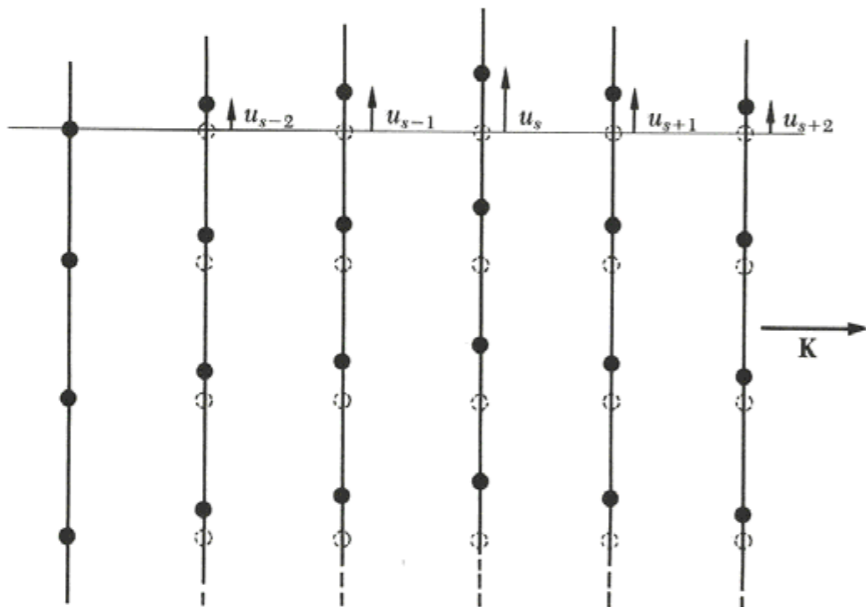
Substituting we obtain:

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

normal modes of a 3D lattice



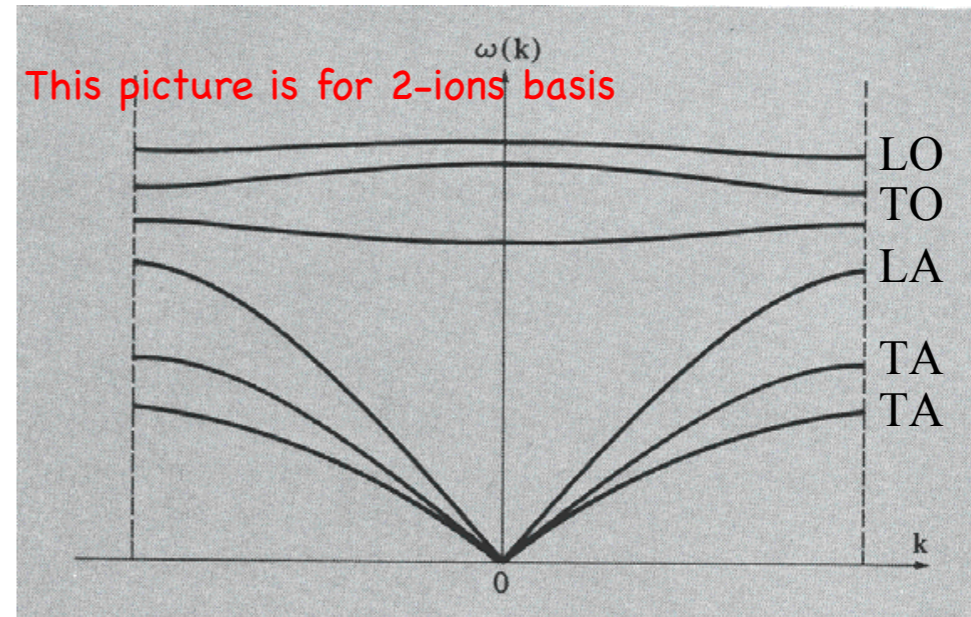
longitudinal wave



transverse wave

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

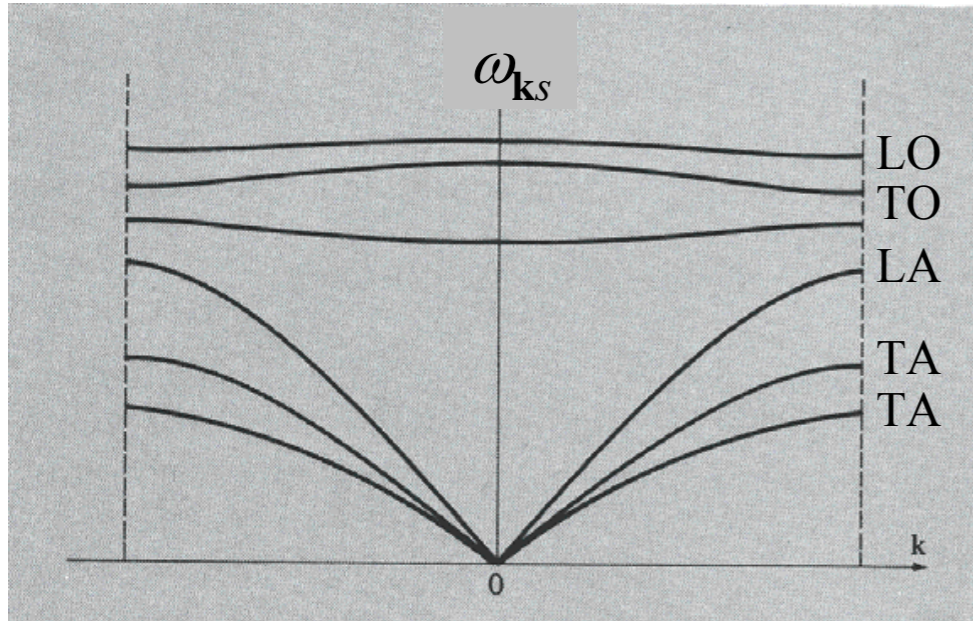
3D lattice with p atoms in the basis:
for each k there are $3p$ modes
3 branches are acoustic
and $3p - 3$ branches are optical



correspond to 3 translational and $3p - 3$ 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:

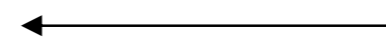
$\omega_{\mathbf{k}s}$ can have only the discrete set of values

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

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

equivalent corpuscular description of the normal modes:

phonon – the quanta of the ionic displacement field



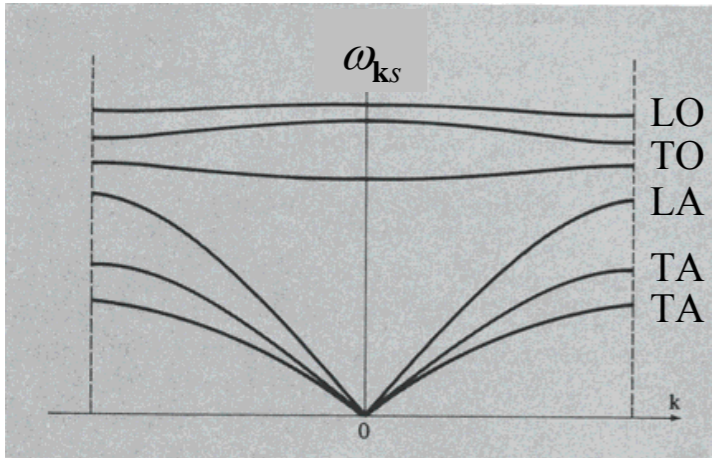
similar to photon – the quanta of the radiation field

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 $\mu = 0$

$$f_{BE}(E) = \frac{1}{e^{\beta(E-\mu)} - 1}$$

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V}$$

$$F = E - TS$$

$$S = \ln(\text{number of states})$$

$$u = u^{eq} + \frac{1}{V} \sum_{\mathbf{k}s} \hbar\omega_s(\mathbf{k}) \left[n_s(\mathbf{k}) + \frac{1}{2} \right]$$

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

high temperature specific heat

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

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

↑

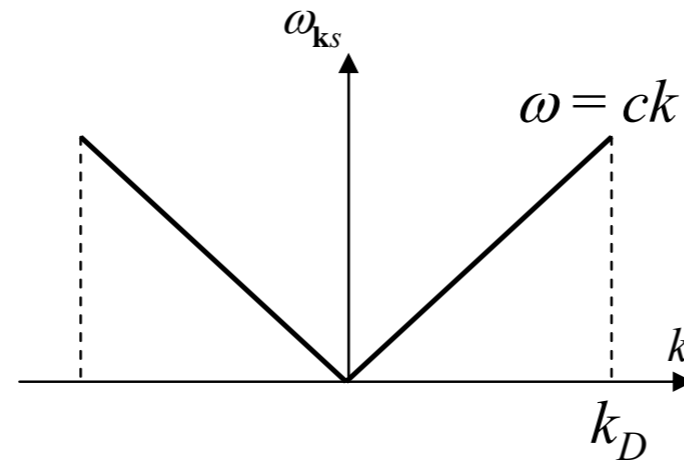
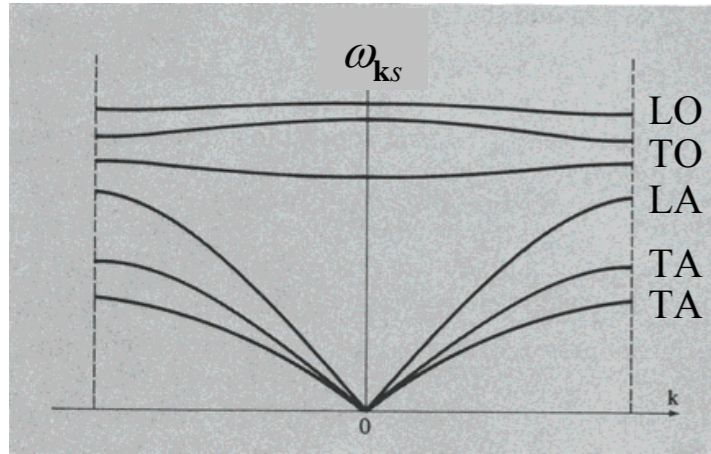
$$c_v \approx \frac{1}{V} \sum_{\mathbf{k}s} \frac{\partial}{\partial T} \hbar\omega_s(\mathbf{k}) \frac{k_B T}{\hbar\omega_s(\mathbf{k})} = \frac{1}{V} 3N_{atoms} k_B$$

$$c_v = 3nk_B$$

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



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

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

integration over the 1st Brillouin zone

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

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

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

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

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

$\omega_D = k_D c$ 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”

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

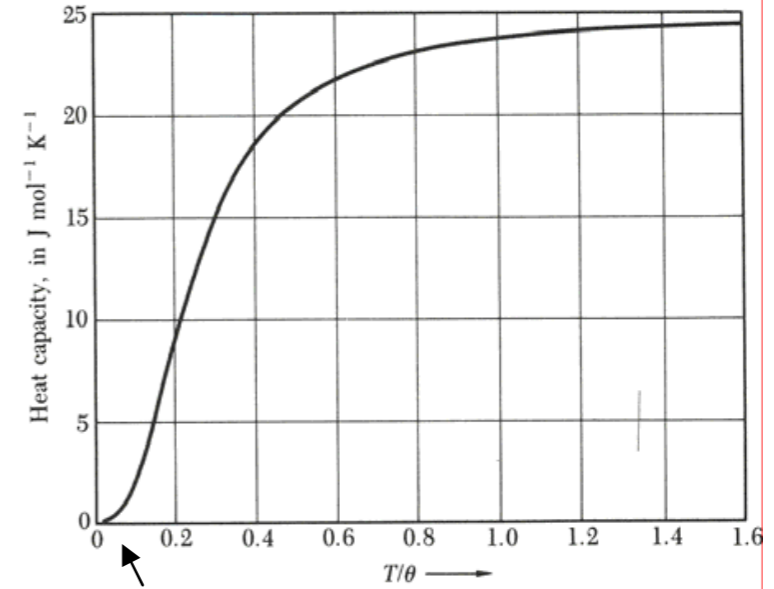
without equilibrium energy and the energy of the zero-point vibrations

phonon density of states

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

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

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



at low temperatures $c_v \sim T^3$

at low temperatures $T \ll \Theta_D$

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

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

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

suppose that

all phonon modes with wavevector less than k_T

have the classical thermal energy $k_B T$

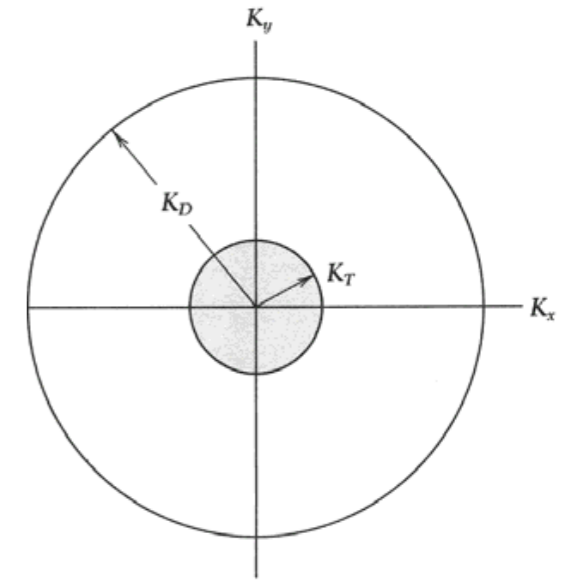
and modes with $k > k_T$ are not excited

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 $c_v = \partial u / \partial T \approx 12nk_B (T / \Theta_D)^3$

$$\hbar c k_T = k_B T$$



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

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

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

contributions to specific heat

electrons phonons

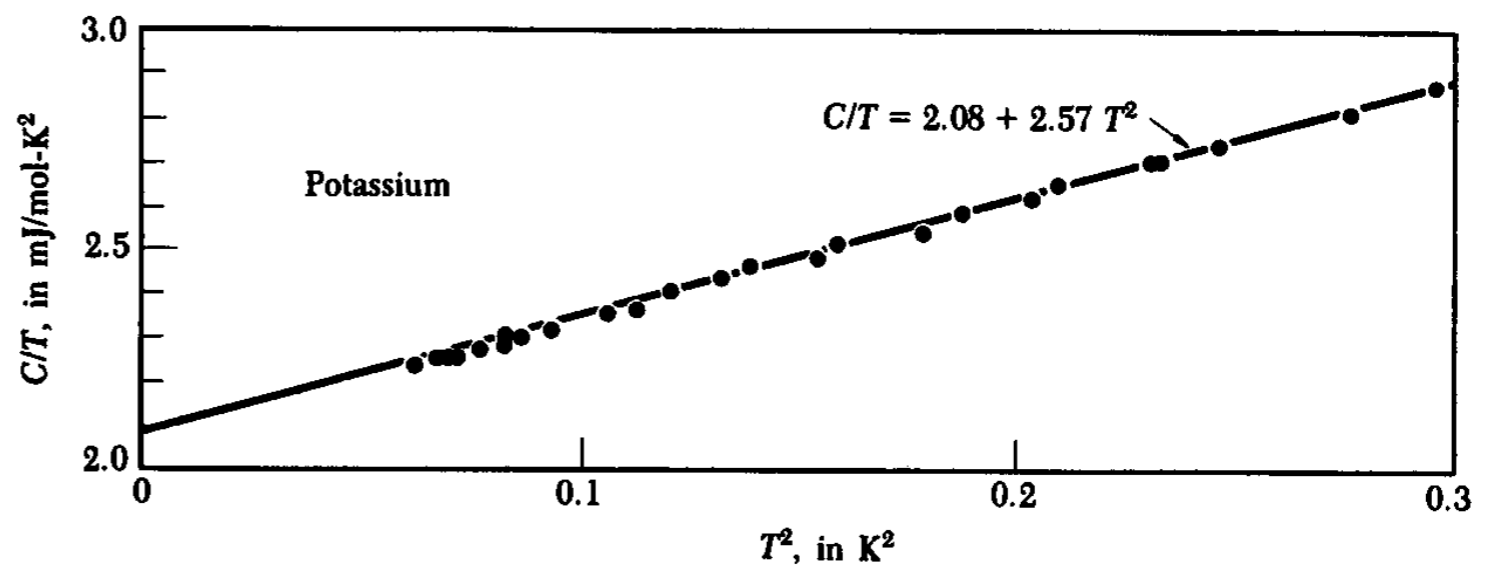


$$c_v = \gamma T + AT^3$$

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

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

~ a few degrees Kelvin



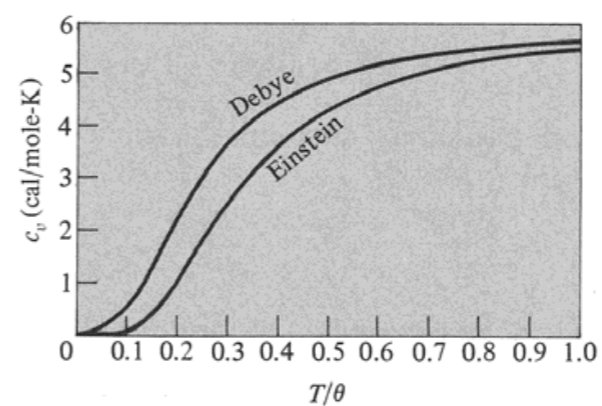
the Einstein model

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

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

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



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