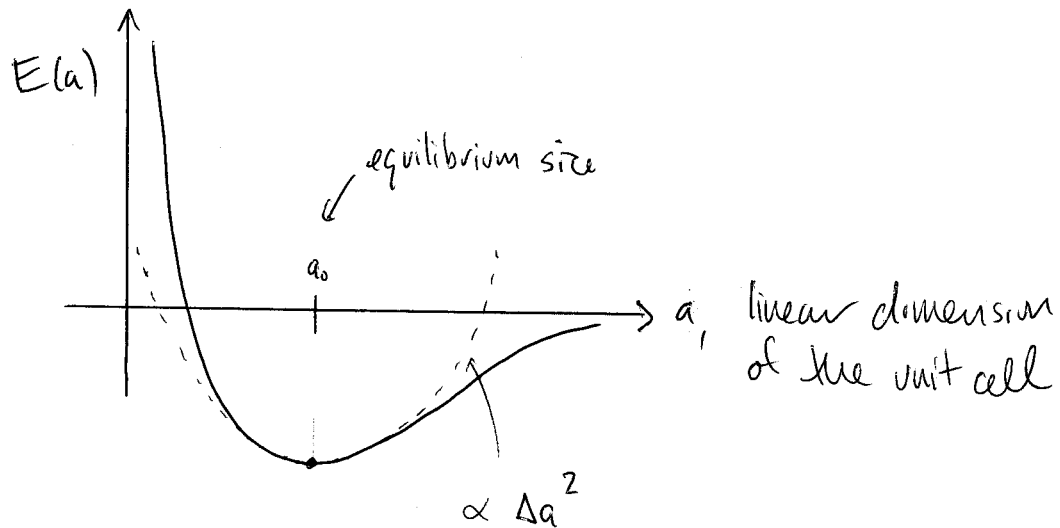* At zero temperature, each ion in a crystal sits motionless (at least classically) in its equilibrium position

→ imagine a uniform compression that leaves the crystal structure in tact but changes its volume
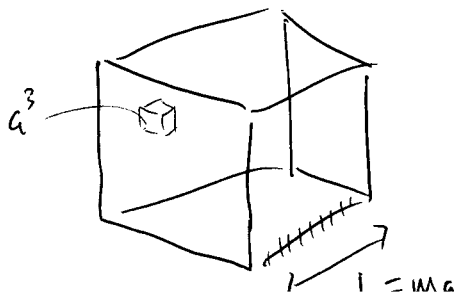

→ equilibrium is at the bottom of an energy well where the forces $\sim -E'(a)$ vanish

→ near equilibrium the well is locally quadratic, so for small deviations $\Delta a = a - a_0$ we can approximate

$$E(a) = E(a_0) + E'(a_0)\overset{0}{\cancel{\Delta a}} + \frac{1}{2} E''(a_0)(\Delta a)^2$$

* For specificity, consider an $L \times L \times L$ cube of conventional a^3 unit cells:

$N_{atoms} = b m^3$

number of atoms in the basis of the unit cell

$\longrightarrow$ suppose that all the elastic energy is stored in a spring-like potential between nearest neighbour atoms:

$$dE = \frac{1}{2} K (\Delta a)^2 N_{bonds}$$

atomic-scale spring constant

$b \left(\frac{z}{2} \right) m^3$, where z is the coordination number of the lattice

$\longrightarrow$ Compression of the crystal is achieved by applying pressure equally to its six faces

$$dE = \frac{1}{2} K (\Delta a)^2 b \frac{z}{2} m^3$$

units force

$$= \frac{bz}{12} \boxed{\frac{K \Delta a}{a^2}} \cdot 3m^3 a^2 \Delta a$$

P

units area

dV

$\longrightarrow$ extract information about microscopic spring constant from bulk elastic measurements

Restoring forces

* forces between ions caused by short-range electronic overlap
and long-range Coulomb and van der Waals interactions

→ estimate: freeze all atoms at crystal positions $\vec{R} = \vec{R}^{(o)}$
except one that is displaced to $\vec{R} = \vec{R}^{(o)} + \vec{u}$;
compute the energy change (by numerical methods)

$$E(\vec{u}) - E(0) = \frac{1}{2} \vec{u} \cdot \overset{\leftrightarrow}{K} \cdot \vec{u} + O(u^3)$$

↑ in general, spring
constant is a tensor
and <u>not</u> isotropic

→ extract from models of the ionic pair potential:

$$V(R_i - R_j) = V(R_{ij}^{(o)} + \vec{u}_{ij})$$

$$= \underset{①}{V(R_{ij}^{(o)})} + \underset{②}{\vec{\nabla} V(R_{ij}^{(o)})} \cdot \vec{u}_{ij}$$

$$+ \underset{③}{\frac{1}{2!} u_{ij}^\alpha \left. \frac{\partial^2 V(\vec{R})}{\partial R_\alpha \partial R_\beta} \right|_{R_{ij}^{(o)}}} \cdot u_{ij}^\beta$$

① contributes to ground state energy but not
the vibrational properties

② $-\vec{\nabla} V$ is the force acting on the ion. It is
exactly zero when summed over all neighbours.

③ harmonic approximation that gives rise to
   independent vibrational modes

* special case of a <u>central</u> potential

$$\frac{\partial}{\partial R_\alpha} V(R) = \frac{R_\alpha}{R} \frac{dV(R)}{dR} \qquad \left(\text{or } \vec{\nabla} V = \hat{R} \, V'(R) \right)$$

$$\frac{\partial^2}{\partial R_\alpha \partial R_\beta} V(R) = \frac{\delta_{\alpha\beta}}{R} \frac{dV(R)}{dR} + \frac{R_\alpha R_\beta}{R^2} \left[\frac{d^2 V}{dR^2} - \frac{1}{R} \frac{dV}{dR} \right]$$

$$\left(\text{or } \vec{\nabla}\vec{\nabla} V = \overleftrightarrow{1} \frac{1}{R} V' + \hat{R}\hat{R} \left(V'' - \frac{1}{R} V' \right) \right)$$

→ when atoms are near equilibrium, the V' term
   is nearly zero, so the V'' term dominates:

$$\overleftrightarrow{K} = V'' \, \hat{R}\hat{R}$$

$$\uparrow \text{ "bond-directed" potential}$$

$$\text{with } V(R_i - R_j) = V(R_{ij}^{(0)})$$

$$+ \frac{1}{2} K \left(\hat{R}_{ij} \cdot \vec{u}_{ij} \right)^2$$

→ may be a good approximation for rare gas solids
   and simple metals, provided that we include
   constants K_1 and K_2 coupling first- and second-nearest
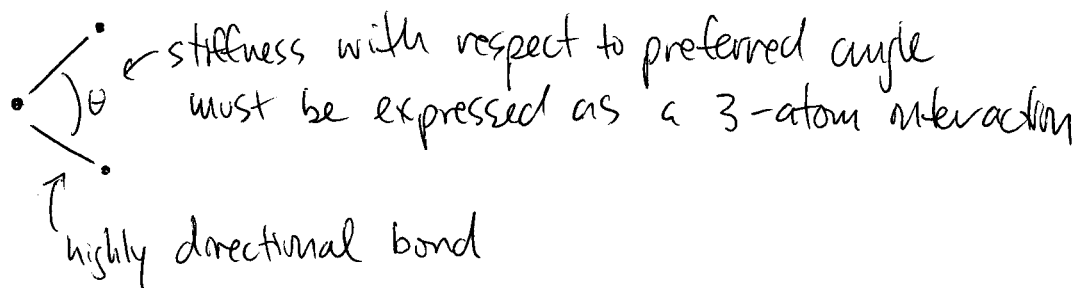   neighbor ions

* The situation is more complicated if there are long-range Coulomb forces

→ in the case of <u>ionic solids</u> (e.g. alkali halides), the vibrating anions and cations create a dipole $q_i^* \vec{u}_i$ when they displace from equilibrium

$\nwarrow \vec{d}_1$

$\nearrow \vec{d}_2$

potential energy due to long-range dipole-dipole interactions

→ for <u>covalently bonded solids</u>, bond bending forces are very important

← stiffness with respect to preferred angle must be expressed as a 3-atom interaction
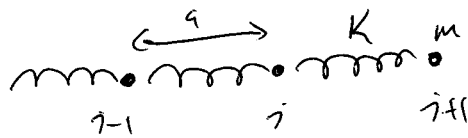
↑ highly directional bond

Oscillating dipoles may also arise in many semiconductors (e.g. GaAs, SiC, CdS but not single-element C, Si, Ge) due to charge transfer between species

Linear chain of atoms

* Classical vibrations of atoms $m_i = m$ at positions $X_i = a \cdot i$

  → consider longitudinal modes

  → hamiltonian for displacements u_i

$$H = \sum_i \left[\frac{P_i^2}{2m} + \frac{1}{2} K (u_{i+1} - u_i)^2 \right]$$

  where $p_i = m\dot{u}_i$ is momentum conjugate to u_i

  → equations of motion describe Hooke's law forces on each atom

$$F_i = m\ddot{u}_i = K(u_{i-1} - u_i) + K(u_{i+1} - u_i)$$

$$= K(u_{i-1} - 2u_i + u_{i+1})$$

  → wave like trial solution (real part)

$$u_j = A\left[e^{i(kja - \omega t)} \right] \text{~~~~~~~~~~~~}$$

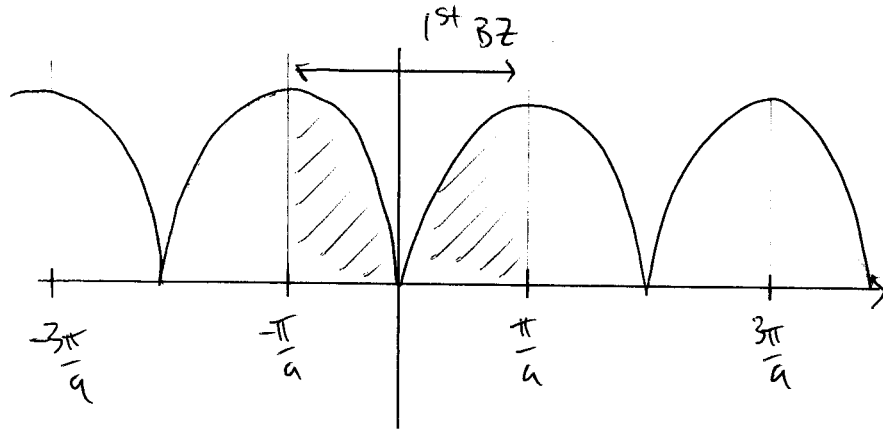 gives

$$-m\omega^2 = -K(2 - e^{ika} - e^{-ika})$$

  NB $\sin\theta = \frac{1}{2i}(e^{i\theta} - e^{-i\theta})$ and $\sin^2\theta = \frac{1}{4}(2 - e^{i2\theta} - e^{-i2\theta})$

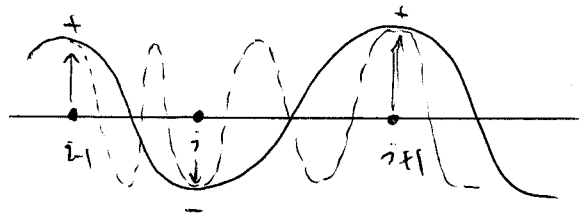$$\Rightarrow \omega^2 = \frac{4K}{m} \sin^2\left(\frac{ka}{2}\right)$$

* We call $\omega = 2\sqrt{\frac{K}{m}}\,|\sin\frac{ka}{2}|$ a dispersion relationship

$\rightarrow$ here, infinite repeating with period $\frac{2\pi}{a} = g$

$\rightarrow$ Solution $u_j^{(\vec{k})} = A e^{i(kja - \omega_k t)}$ unchanged by the substitution $\vec{k} \rightarrow k+G$ for any reciprocal lattice vector $G = $ integer $\times g$

$\rightarrow$ related to issue of aliasing : solutions exist at discrete points and not in an elastic continuum

$k = \frac{\pi}{a}$

and $k = \frac{\pi}{a} + \frac{2\pi}{a} = \frac{3\pi}{a}$

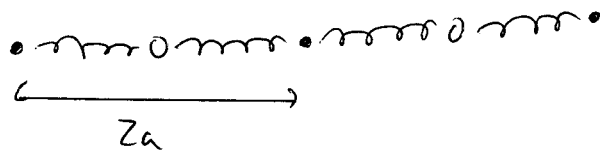are the same solution

$\rightarrow$ must distinguish between phase velocity $\frac{\omega_k}{k}$ and the group velocity $\frac{\partial \omega_k}{\partial k}$:
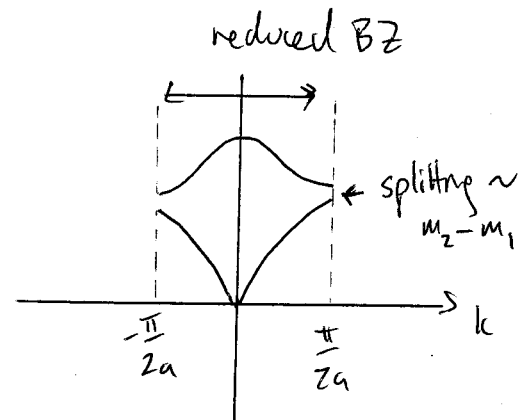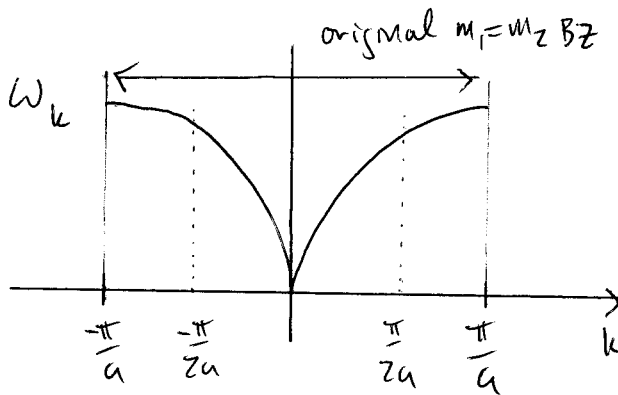
$$v_{group} = \frac{\partial \omega}{\partial k} = a\sqrt{\frac{K}{m}}\,|\cos\frac{ka}{2}| \neq v_{phase} \text{ except near } k=0$$

speed of the propagating wavefront (vanishes at BZ edges)

* What happens if we have two inequivalent masses m_1 and m_2 alternating along the chain?
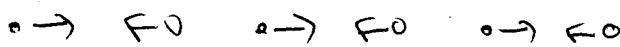

$\quad\quad\quad\quad\quad\quad\quad$ $2a$

→ width of the unit cell has <u>doubled</u> and the length of the reciprocal lattice vector is <u>halved</u>

original $m_1 = m_2$ BZ $\quad\quad\quad\quad$ reduced BZ

ω_k $\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ ← splitting ~ $m_2 - m_1$

$-\frac{\pi}{a}$ $\quad -\frac{\pi}{2a}$ $\quad\quad \frac{\pi}{2a}$ $\quad \frac{\pi}{a}$ $\quad k$ $\quad\quad\quad -\frac{\pi}{2a}$ $\quad \frac{\pi}{2a}$ $\quad k$
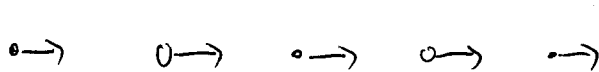
→ dispersion relation develops two branches, an upper "optical" branch in addition to the lower "acoustic" branch

→ the optical branch includes antiphase vibrations of the second atom in the basis:

•→ ←◦ •→ ←◦ •→ ←◦

as opposed to

•→ ◦→ •→ ◦→ •→ } for $q \to 0$ this is pure } translation of the crystal and must have zero energy

→ In general, we have polarizations that are

    ① longitudinal or transverse

    ② optical or acoustic

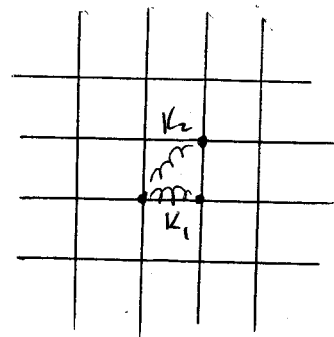   ↑ only in crystals with a basis!

Square lattice of atoms

* Square lattice with one atom per unit cell

    → if there are only bond-directed
        forces between n.n.s, then

$$m\ddot{\vec{u}}_j = -\sum_{\vec{\eta}} K(\vec{\eta})\,\hat{\eta}\hat{\eta}\cdot(\vec{u}_j + \vec{u}_{j+\eta})$$

        ↑ sum over vectors to nn sites

simple spring coupling
and in-plane
vibrations

    → Assuming a wave solution $\vec{u}_j = \vec{A}e^{i(\vec{q}\cdot\vec{R}_j - \omega t)}$, we get

$$m\omega^2 A_x = 2K_1 A_x(1-\cos q_x a) = 4K_1 A_x \sin^2 \frac{q_x a}{2}$$

$$m\omega^2 A_y = 2K_1 A_y(1-\cos q_y a) = 4K_1 A_y \sin^2 \frac{q_y a}{2}$$

    → Slightly pathological model: x and y motions are
        completely uncoupled and the solution does
        not support transverse waves

* Correct this by including K_2 along $\hat{\eta} = \frac{(\pm 1, \pm 1)}{\sqrt{2}}$

→ system of equations now expressed in terms of a __dynamical matrix__ D:

$$D \begin{pmatrix} A_x \\ A_y \end{pmatrix} = \omega^2 \begin{pmatrix} A_x \\ A_y \end{pmatrix}$$

→ in this case

$$D = \begin{pmatrix} \omega_1^2(1-C_x) + \omega_2^2(1-C_xC_y) & \omega_2^2 S_x S_y \\ \omega_2^2 S_x S_y & \omega_1^2(1-C_y) + \omega_2^2(1-C_xC_y) \end{pmatrix}$$

with $C_x = \cos q_x a$ $\quad$ etc. $\quad$ $\omega_j^2 = \frac{2K_j}{m}$
$\quad\quad S_x = \sin q_x a$

→ Solve by determining roots of the characteristic polynomial

$$\det(D - \omega^2 \mathbb{1})$$

$$\Rightarrow \omega_\pm^2 = \omega_2^2(1-C_xC_y) + \omega_1^2\left[(1-\tfrac{1}{2}(C_x+C_y)\right]$$

$$\pm \tfrac{1}{2}\sqrt{\omega_1^4(C_x-C_y)^2 + 4\omega_2^4 S_x^2 S_y^2}$$

→ corresponding __eigenvectors__ determine the vector displacements of the ions

Quantized vibrational excitations

* quantized vibrational excitation is a _phonon_
    → boson carrying definite energy and crystal momentum
    → thermally populated in a crystal at temp T

* simple harmonic oscillator

$$H = \frac{p^2}{2m} + \frac{K}{2} x^2$$

→ x and p are now operators with $[x, p] = xp - px = i\hbar$

→ work in units $x_0 = \sqrt{\frac{\hbar}{m\omega}} = \left(\frac{\hbar^2}{Km}\right)^{1/4}$

→ define raising and lowering operators

$$a = \frac{1}{\sqrt{2} x_0} \left[x + \frac{ip}{m\omega} \right]$$

$$a^\dagger = \frac{1}{\sqrt{2} x_0} \left[x - \frac{ip}{m\omega} \right]$$

$\dagger$ = hermitian conjugate

→ new ~~commu~~ anticommutation relations

$$[a, a] = [a^\dagger, a^\dagger] = 0$$

and $[a, a^\dagger] = \frac{1}{2x_0^2} \left[x + \frac{ip}{m\omega}, x - \frac{ip}{m\omega} \right]$

$$= \frac{-i}{2\hbar} \left([x, p] - [p, x] \right) = 1$$

* Using

$$a^\dagger a = \frac{1}{2x_0^2}\left[x - \frac{ip}{m\omega}\right]\left[x + \frac{ip}{m\omega}\right]$$

$$= \frac{1}{2x_0^2}\left[x^2 + \frac{p^2}{m^2\omega^2} + \frac{i}{m\omega}(x_ip]\right]$$

$$= \frac{1}{2x_0^2}\left[x^2 + \frac{p^2}{m^2\omega^2} - x_0^2\right]$$

we can reexpress the Hamiltonian

$$a^\dagger a + \frac{1}{2} = \frac{1}{2x_0^2}\left[x^2 + \frac{p^2}{m^2\omega^2}\right]$$

$$= \frac{1}{kx_0^2}\left[\frac{k}{2}x^2 + \frac{p^2}{2m}\right] = \frac{1}{\hbar\omega}H \qquad \text{since} \quad k = m\omega^2$$

$$\Rightarrow \quad H = \hbar\omega\left[a^\dagger a + \frac{1}{2}\right]$$

$\rightarrow$ ~~sequence~~ ladder of states ~~to satisfying~~ $|n\rangle = \frac{(a^\dagger)^n}{\sqrt{n!}}|0\rangle$

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

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

$$[a, a^\dagger]|n\rangle = a\sqrt{n+1}\,|n+1\rangle - a^\dagger\sqrt{n}\,|n-1\rangle$$

$$= (n+1-n)|n\rangle = |n\rangle$$

$$\Rightarrow \quad H|n\rangle = \hbar\omega\left[n+\frac{1}{2}\right]|n\rangle = E_n|n\rangle$$

$\rightarrow$ recover the physical picture via

$$X = \frac{X_0}{\sqrt{2}}(a + a^\dagger) \quad \text{and} \quad p = \frac{i\hbar}{\sqrt{2}X_0}(a^\dagger - a)$$

Phonons in 1D

* redo the linear chain in this language

$$H = \sum_{j=1}^{N} \left(\frac{P_j^2}{2m} + \frac{k}{2}(u_j - u_{j+1})^2 \right)$$

$\rightarrow$ collective coordinates

$$P_j = \frac{1}{\sqrt{N}} \sum_k e^{-ikaj} P_k$$

$$u_j = \frac{1}{\sqrt{N}} \sum_k e^{+ikaj} u_k$$

$$[u_j, P_{j'}] = i\hbar \delta_{jj'} \quad \text{and} \quad [u_k, P_{k'}] = i\hbar \delta_{kk'}$$

$\rightarrow$ define $P_k = \frac{\hbar}{i} \frac{\partial}{\partial u_k}$

$$\text{①} \quad \sum_{j=1}^{N} \frac{P_j^2}{2m} = \frac{1}{2mN} \sum_{kk'} P_k P_{k'} \sum_j e^{ija(k+k')} = \sum_k \frac{P_k P_{-k}}{2m}$$

$$\text{②} \quad \frac{k}{2} \sum_j (u_j - u_{j+1})^2 = \frac{k}{2} \sum_j u_j (2u_j - u_{j-1} - u_{j+1}) = k \sum_k u_k u_{-k} (1 - \cos ka)$$

* frequency of collective mode is

$$\omega_k^2 = \frac{2K}{m}(1-\cos ka) = \frac{4K}{m}\sin^2\left(\frac{ka}{2}\right)$$

and $H = \sum_k \left(\frac{P_k P_{-k}}{2m} + \frac{m\omega_k^2}{2} u_k u_{-k} \right)$

$\rightarrow$ solve by introducing $u_k = X_k (a_k + a_{-k}^\dagger)$, $P_k = -i m \omega_k X_k$

$(a_{-k} - a_k^\dagger)$

with $X_k = \frac{\hbar}{2m\omega_k}$

$\rightarrow$ leads to $H = \sum_k \hbar\omega_k \left(a_k^\dagger a_k + \frac{1}{2} \right)$, which

describes a set of independent bosonic modes

$\rightarrow$ populated according to

$$\langle a_k^\dagger a_k \rangle = \frac{1}{e^{\beta\hbar\omega_k} - 1}$$

in thermal equilibrium at ~~their~~ temp $T = \frac{1}{k_B \beta}$

$\rightarrow$ no chemical potential for ~~the~~ phonons, since
their number is not fixed

Thermal expectation values

* total number of phonons

$$n_{ph} = \sum_\lambda \int \frac{d^3q}{(2\pi)^3} \frac{1}{e^{\beta \hbar \omega_q^{(\lambda)}} - 1}$$

integrate over BZ

bosonic occupation factor for each mode

Sum over all polarizations / branches

$$= \int d\omega \, D(\omega) \frac{1}{e^{\beta \hbar \omega} - 1}$$

where

$$D(\omega) = \sum_\lambda \int \frac{d^3q}{(2\pi)^3} \delta(\omega - \omega_q^{(\lambda)})$$

is the <u>phonon density of states</u>

* Similarly, total phonon energy is

$$U(T) = \sum_\lambda \int \frac{d^3q}{(2\pi)^3} \hbar \omega_q^{(\lambda)} \left[\frac{1}{e^{\beta \hbar \omega_q^{(\lambda)}} - 1} + \frac{1}{2} \right]$$

Zero-point energy

$$= \hbar \int d\omega \, \omega D(\omega) \left[\frac{1}{e^{\beta \hbar \omega} - 1} + \frac{1}{2} \right]$$

→ high temperature limit

$$\frac{1}{e^{\beta\hbar\omega}-1} = \frac{k_B T}{\hbar\omega} - \frac{1}{2} + O(\hbar\omega/k_B T)$$

$$\Rightarrow U(T) = k_B T \int d\omega\, D(\omega) + O\left(\frac{1}{k_B T}\right)$$

heat capacity
$$C(T) = \frac{dU}{dT} = k_B \int d\omega\, D(\omega) = \text{const.} \quad \text{(classical equipartition)}$$

→ very low temp limit: acoustic phonons $\omega_q \sim |\vec{q}|$

DoS: $$\lim_{\omega\to 0} D(\omega) \sim \sum_\lambda \int dq \cdot q^{d-1} \delta(\omega - c_\lambda^{(\lambda)} q)$$

$$\propto \omega^{d-1} \sum_{\lambda} \left[c^{(\lambda)}\right]^{-d}$$

or $$\lim_{\omega\to 0} D(\omega) = G\omega^{d-1}$$

$$\lim_{T\to 0} U(T) = U_0 + \hbar G \int_0^\infty d\omega\, \frac{\omega^d}{e^{\beta\hbar\omega}-1} \qquad \text{change } x = \beta\hbar\omega$$

$$= U_0 + \hbar G \left(\frac{k_B T}{\hbar}\right)^{d+1} \int_0^\infty dx\, \frac{x^d}{e^x - 1}$$

$$\lim_{T\to 0} C(T) = k_B G (d+1) \left(\frac{k_B T}{\hbar}\right)^d \int_0^\infty dx\, \frac{x^d}{e^x - 1} \sim T^3 \text{ for bulk solids}$$