1D monoatomic chain

- long wavelength $\omega = v_s q$
- short wavelength can't ignore the lattice is discrete

phonon: $E = \hbar\omega$, $p = \hbar q$.

$\langle n \rangle = \frac{E}{\hbar\omega} = \frac{1}{e^{\hbar\omega/kT} - 1}$

* chain of identical atoms of mass m, separated by distance a

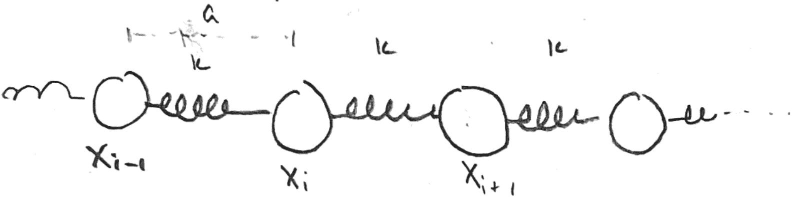
X_n = position of n^{th} atom

X_n^{eq} = equillibrium position of n^{th} atom $= na$

$\delta X_n = X_n - X_n^{eq}$ = deviation of atom from eq position

Generally: the $\frac{1}{2}kx^2$ or kx "x" is just difference in displacements from eq atoms in neighboring atoms :)

$V_{spring} = \frac{1}{2}kx^2$



how stretched spring is, bead deviation of

$$V_{tot} = \underbrace{\sum_i}_{\text{sum all springs}} V\underbrace{(X_{i+1} - X_i)}_{\text{total length of the spring}} = \sum_i \frac{1}{2}k\overbrace{(X_{i+1} - X_i - a)}^{}{}^2 = \sum_i \frac{k}{2}(\delta X_{i+1} - \delta X_i)^2$$

$\delta X_{i+1} = X_{i+1} - 2a \rightarrow X_{i+1} = \delta X_{i+1} + 2a \rightarrow \delta X_{i+1} + 2a - \delta X_i + a - a$

$\delta X_i = X_i - a \qquad X_i = \delta X_i + a \qquad = \delta X_{i+1} - \delta X_i$

how stretched right spring is — how stretched left spring is

$$F_n = -\frac{\partial V_{tot}}{\partial X_n} = k\underbrace{(\delta X_{n+1} - \delta X_n)}_{\text{force of atom to its right}} - k\underbrace{(\delta X_n - \delta X_{n-1})}_{\text{force of atom to its left}}$$

← pulling it the other way or pushing it too hmm...

$\delta X_{n+1} - \delta X_n = X_{n+1} - X_n - a$ = how stretched right spring is

$\delta X_n - \delta X_{n-1} = X_n - X_{n-1} - a$ = how stretched left spring is

} only add displacements from equillibrium to get this x *makes sense* :)

$F_n = m\,\delta\ddot{X}_i = k(\delta X_{n+1} + \delta X_{n-1} - 2\delta X_n)$, given $\delta X_n = A e^{i\omega t - ikX_n^{eq}} = A e^{i\omega t - ikna}$

$\omega \geq 0$, $k = \pm$

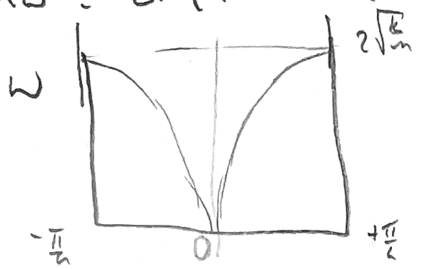
plug in: $-m\omega^2 A e^{i\omega t - ikna} = kAe^{i\omega t}\left(e^{-ika(n+1)} + e^{-ika(n-1)} - 2e^{-ikan}\right)$

$\hookrightarrow m\omega^2 = k(e^{-ika} + e^{+ika})$

$\hookrightarrow m\omega^2 = 2k(1 - \cos(ka)) = 4k\sin^2\left(\frac{ka}{2}\right) \rightarrow$

k spring, q wave

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



Chain

EOM:

$$M_1\, \delta \ddot{X}_n = k(\delta X_{n+1} - \delta X_n) - k(\delta X_n - \delta X_{n-1})$$
$$M_2\, \delta \ddot{X}_{n+1} = k(\delta X_{n+2} - \delta X_{n+1}) - k(\delta X_{n+1} - \delta X_n)$$

Guess: $\delta X_n = A_1 e^{-i\omega t - iqna}$

$$-M_1 \omega^2 A_1 e^{-iqna} = k\left(A_2 e^{-iq(n+1)a} - A_1 e^{-iqna}\right) - k\left(A_1 e^{-iqna} - A_2 e^{-iq(n-1)a}\right)$$
$$-M_2 \omega^2 A_2 e^{-iq(n+1)a} = k\left(A_1 e^{-iq(n+2)a} - A_2 e^{-iq(n+1)}\right) - k\left(A_2 e^{-iq(n+1)a} - A_1 e^{-iqna}\right)$$

$$-M_1\omega^2 A_1 = kA_2 e^{-iqa} \overbrace{- A_1 k - kA_1}^{2A_1 k} + A_2 k e^{iqa}$$
$$-M_2\omega^2 A_2 = kA_1 e^{-iqa} - kA_2 - kA_2 + kA_1 e^{iqa}$$

$$\begin{bmatrix} 2k - M_1\omega^2 & -ke^{-iqa} - ke^{iqa} \\ -ke^{-iqa} - ke^{iqa} & 2k - M_2\omega^2 \end{bmatrix} \begin{bmatrix} A_1 \\ A_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

$e^{-iqa} + e^{iqa} = 2\cos(qa)$

$$(2k - M_1\omega^2)(2k - M_2\omega^2) - k^2\left(e^{-iqa} + e^{iqa}\right)^2 = 0$$
$$M_1 M_2 \omega^4 - 2k\omega^2(M_1 + M_2) + 4k^2 - 4k^2\cos^2(qa) = 0$$
$$\omega^4 - 2k\omega^2 \frac{M_1 + M_2}{M_1 M_2} + \frac{4k^2}{M_1 M_2}\left(1 - \cos^2(qa)\right) = 0$$
$$\omega^2 = k\left(\frac{1}{M_1} + \frac{1}{M_2}\right) \pm \sqrt{4k^2\left(\frac{1}{M_1} + \frac{1}{M_2}\right) - \frac{4k^2}{M_1 M_2}\left(1 - \cos^2(qa)\right)}$$

Density of States

$\boxed{\omega = k_q v \ , \ f = \frac{v}{\lambda} \ , \ \frac{2\pi}{\lambda} v = k}$

*think of vibrations in a solid as sound waves,

↳ $u(x) = A e^{i(qx - \omega t)}$ w/ periodic boundary conditions $u(0) = u(L)$

$e^{iqL} = 1 = e^{i2\pi n} \rightarrow q = n\frac{2\pi}{L}$, $n = 0, \pm 1, \pm \ldots$

Meaning of density of states:

(total number of oscillation modes between $\omega, \omega + d\omega$) $= g(\omega)\, d\omega$ $(q, q+dq)$ ✓

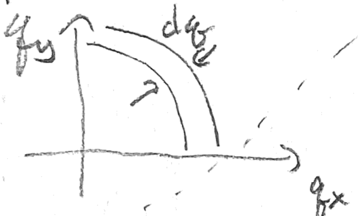
1D $\frac{q}{2\pi/L} = n \rightarrow \underset{\uparrow}{\overset{\downarrow}{2}}\left[\left(\frac{q}{2\pi/L} + \frac{dq}{2\pi/L}\right) - \frac{q}{2\pi/L}\right] = g(\omega)\, d\omega$

[1 longitudinal mode but 1 for each q]

$\rightarrow 2\frac{L}{2\pi} dq = g(\omega)\, d\omega \longrightarrow \frac{L}{\pi}\overbrace{\frac{dq}{d\omega}}^{\frac{1}{v_s}} = g(\omega) \rightarrow \boxed{g(\omega) = \frac{L}{\pi}\frac{1}{v_s}}$

2D $e^{iq_xL + iq_yL} = 1 \longrightarrow \begin{matrix} q_x = n\frac{2\pi}{L} \\ q_y = m\frac{2\pi}{L} \end{matrix}$ → Area in q space corresponds to width in ω space

modes in width dq → ring



$\frac{2\pi q\, dq}{\left(\frac{2\pi}{L}\right)^2}$ = [how many unit area's fit in ring, for each area (atom) there's 2 modes] $\rightarrow 2\frac{2\pi q\, dq}{\left(\frac{2\pi}{L}\right)^2} = \underset{\text{\# of modes in unit area of solid}}{\overset{\text{density of stg}}{g(\omega)\, d\omega}}$

$\left(\frac{2\pi}{L}\right)^2$ ↖ unit area

↳ $\frac{L^2}{\pi} q \frac{dq}{d\omega} = \boxed{g(\omega) = \frac{L^2}{\pi}\frac{\omega}{v^2}}$

3D # modes in dq → shell

$\underbrace{\frac{4\pi q^2\, dq}{\left(\frac{2\pi}{L}\right)^3}}_{\downarrow}\underset{\uparrow}{(3)} = g(\omega)\, d\omega \rightarrow g(\omega) = 3\frac{L^3}{2\pi^2}\left(\frac{\omega}{v}\right)^2 \cdot \frac{1}{v}$

$\frac{2\pi}{L}$ for same reason but 3D now

3 modes of oscillation

How many unit volumes fit in shell, each unit volume (atom) has [3 modes]

$\boxed{g(\omega) = \frac{3L^3}{2\pi^2}\frac{\omega^2}{v^3}}$

Specific Heat of Solids

→ tells you → $Q = C\Delta T$ → $C_p = \lim_{Q\to 0} \frac{Q}{\Delta T}\Big|_{P=\text{constant}}$, $C_v = \lim_{Q\to 0} \frac{Q}{\Delta T}\Big|_{V=\text{const}}$

then using $Q = \Delta U + W$ or ΔU = heat is transfered to sys by work = $Q - W$

$C_p = \left(\frac{\partial H}{\partial T}\right)_P$, $H_f = U_f + PV_f$, $C_v = \left(\frac{\partial U}{\partial T}\right)_V$ since $W = 0$, $Q = \Delta U$

bec/ $PV = nRT$, $H = U + \underset{nRT}{PV}$

$C_p - C_v = \left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V = \frac{dU}{dT} + nR - \frac{dU}{dT} = nR$ *for ideal gas*

For solids:

$C_p - C_v = \alpha_v^2 \beta_T TV \approx 0$ so $C_p \approx C_v \approx 3R$ or $3k_B$ per atom

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Maxwell Boltzmann Distribution

area under curve gives total # particles

* air molecules around us are moving at different velocities (fast, moderate, slow)

→ cont app what is the speed of an air molecule of a gas

↳ [So we ask what is the distribution of velocities (therefore energy)] → $f(v)$ = probability density as a function of speed v $= \sqrt{\left(\frac{m}{2\pi kT}\right)^3}\, 4\pi v^2 e^{\frac{-mv^2}{2kT}}$ a weight of how many there.

[Probability of being in state A] $= P_A = \frac{e^{-E_A/kT}}{\sum_i e^{-E_i/kT}}$ ← like a prob density func ← [Sum of all all states to normalize it] $= Z$ = partition function $\Big|$ $E_{avg} = \frac{\sum E_i P_i}{Z}$

Einstein Model

• atoms treated as quantum harmonic oscillators w/ $E_n = \hbar\omega(n + \frac{1}{2})$

$$\langle E\rangle = \frac{\sum_n^{\infty} E_n e^{-E_n/k_BT}}{\sum_n e^{-E_n/k_BT}}$$, [where the denominator is the partition func, to normalize the numerator] → [numerator is probability density of each state weighted by the corresponding energy]

in QM, we want this one, its norm factor

$\beta = \frac{1}{kT}$

$$\langle E\rangle = -\frac{\partial}{\partial\beta}\ln\left(\sum_n e^{-\beta E_n}\right) = \frac{-\partial}{\partial\beta}\ln\left(\sum e^{-n\hbar\omega\beta}\, e^{-\frac{\hbar\omega}{2}\beta}\right) = \frac{-\partial}{\partial\beta}\ln\left(e^{-\frac{\hbar\omega}{2}\beta}\underbrace{\sum e^{-n\hbar\omega\beta}}_{\frac{1}{1-e^{-\hbar\omega\beta}}}\right)$$

$$= \frac{-\partial}{\partial\beta}\ln\left(\frac{e^{\frac{\hbar\omega\beta}{2}}}{e^{\hbar\omega\beta} - 1}\right) = \boxed{\frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} + \frac{\hbar\omega}{2}}$$ ← [average energy of a atom in quantum SHO]

3 deg of freedom, $\langle E_x\rangle = \langle E_y\rangle = \langle E_z\rangle = \langle E\rangle$ so tot energy per mole , $3N_A k_B = 3R$

avogadro

$$\boxed{U = 3N_A\langle E\rangle \qquad C_v = \left(\frac{\partial U}{\partial T}\right)_V = 3R\left(\frac{\hbar\omega}{k_BT}\right)^2 \frac{e^{\hbar\omega/k_BT}}{\left(e^{\frac{\hbar\omega}{kT}} - 1\right)^2}}$$

• at $kT \gg \hbar\omega$ recover $3k_B$ (high T)

• at low T, too low, C vanishes rapidly which is bad.

Debye's Calculation

- at low temps $C \propto T^3$ Einstein's doesn't do that

↳ solid had waves w/ $\boxed{\omega(\vec{k}) = v|\vec{k}|}$ for each direction of $\vec{k}$ theres 3 modes of oscill

- since energy is related to ω and thus the number of modes, we need to add all the energies for every mode, still using Einsteins eq for $\langle E(\omega)\rangle$

*recall: $g(\omega)\,d\omega$ = # of modes between $\omega, \omega + d\omega$

$$\langle E\rangle = \int_0^\infty g(\omega)\langle E(\omega)\rangle\, d\omega,$$

↳ for each mode we multiply by $\langle E(\omega)\rangle$ bec each one contributes to energy.

let $nL^3 = N$, n = density of atoms

$\omega_d^3 = 6\pi^2 n v^3$

$\beta = \frac{1}{kT}$

$$= \int_0^\infty \frac{3L^3}{2\pi^2}\frac{\omega^2}{v^3}\left(\hbar\omega\left[\frac{1}{e^{\hbar\omega/kT}-1} + \frac{1}{2}\right]\right) d\omega,$$

(will be taking derivative)

$$= \frac{9N\hbar}{\omega_d^3}\int_0^\infty \frac{\omega^3}{e^{\beta\hbar\omega}-1}\, d\omega + [T \text{ ind constant}]$$

← is actually infinite but will be handled later by a cutoff frequency

let $x = \beta\hbar\omega$

$$\langle E\rangle = \frac{9N\hbar}{\omega_d^3(\beta\hbar)^4}\overbrace{\int_0^\infty \frac{x^3}{e^x - 1}\, dx}^{\pi^4/15} \rightarrow \langle E\rangle = 9N\frac{(k_B T)^4\,\pi^4}{(\hbar\omega_d)^3\, 15} + [T.\text{ ind}]$$

$$\boxed{C = \frac{\partial\langle E\rangle}{\partial T} = N k_B\left(\frac{k_B T}{\hbar\omega_d}\right)^3\frac{12\pi^4}{5} = N k_B\frac{T^3}{(T_{Debye})^3}\frac{12\pi^4}{5}, \quad T_{debye} = \frac{\hbar\omega_d}{k_B}}$$

*still can drop zero-point energy bec/ temp ind.

Cutoff freq

*at low T cut-off ≈ ∞ bec the $e^{\hbar\omega/kT} \rightarrow \infty$, so $\langle E\rangle \rightarrow 0$ at ω well below $\omega_{cut\text{-}off}$

$$3N = \int_0^{\omega_{cut\text{-}off}} g(\omega)\, d\omega \rightarrow \langle E\rangle = \int_0^{\omega_{cutoff}} g(\omega)\langle E(\omega)\rangle\, d\omega$$

↳ if you evaluate cutoff w/ $g(\omega)$ you find → $\boxed{\omega_{cutoff} = \omega_d}$