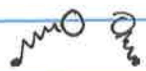
21-1

We had a problem in the last problem set on solids (i.e. Einstein's model):



← each atom is pinned to a lattice site with springs

This is equivalent to 3N independent harmonic oscillators each with frequency ω:

$$q_{HO} = \frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}}$$ ← partition function for one oscillator

$$Q(N,V,T) = \left(\frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}}\right)^{3N}$$ ← no factorial because the lattice sites are distinguishable

Helmholtz free energy:

$$A(T,N) = -k_B T \ln Q = -3Nk_BT\left[-\frac{\beta\hbar\omega}{2} - \ln\left[1-e^{-\beta\hbar\omega}\right]\right]$$

$$= \frac{3N}{2}\hbar\omega + 3Nk_BT\ln\left(1-e^{-\beta\hbar\omega}\right)$$

$$\langle E\rangle = -\frac{\partial \ln Q}{\partial\beta} = 3N\left[\frac{-\partial}{\partial\beta}\left(-\frac{\beta\hbar\omega}{2} - \ln\left(1-e^{-\beta\hbar\omega}\right)\right)\right]$$

$$= 3N\left(\frac{\hbar\omega}{2} + \frac{\hbar\omega\, e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}\right)$$

$$C_V = \frac{\partial\langle E\rangle}{\partial T} = 3Nk_B\left(\frac{\hbar\omega}{k_BT}\right)^2\frac{e^{-\hbar\omega/kT}}{\left(1-e^{-\hbar\omega/kT}\right)^2} = 3Nk\left(\frac{\Theta_v}{T}\right)^2\frac{e^{-\Theta_v/T}}{\left(1-e^{-\Theta_v/T}\right)^2}$$

This works well as $T\to\infty$ ($C_V \to 3R$), but at low T

$$C_V \approx 3Nk\left(\frac{\Theta_v}{T}\right)^2 e^{-\Theta_v/T}$$ ← This falls much more rapidly than the experimentally observed T^3

The Debye model:

include couplings between oscillators

$$\mathcal{H} = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + \sum_{j,i} A_{ij} q_i q_j$$

includes q_i^2 terms!

If we change variables to new coordinates (Q_k, P_k) such that matrix $\underline{\underline{A}}$ is diagonal, $\underline{\underline{U}}$ is a unitary transform:

mass weighted force constant matrix.

$$\underline{\underline{\omega}}^2 = \left(\underline{\underline{U}}^T \underline{\underline{A}}\, \underline{\underline{U}}\right) \qquad \underline{\underline{U}}^T \underline{\underline{U}} = \underline{\underline{I}}$$

identity matrix

frequency matrix

Then:

$$\mathcal{H}(\vec{Q}, \vec{P}) = \sum_k \frac{P_k^2}{2m} + \sum_k \frac{m\omega_k^2}{2} Q_k^2$$

ω is not the same for each oscillator

single sum

P_k & Q_k describe phonons or the normal modes of an extended solid.

Each ω_k is different, but the overall form of the Hamiltonian is preserved:

$$\mathcal{H} = \sum_k \left(\frac{P_k^2}{2m} + \frac{m\omega_k^2}{2} Q_k^2\right) \longleftarrow \text{classical}$$

$$\hat{\mathcal{H}} = \sum_k \hbar\omega_k \left(\hat{n}_k + \frac{1}{2}\right)$$

each oscillator has a quantum number

$$E = E_{mode1} + E_{mode2} + E_{mode3} + \cdots$$

$$= \hbar\omega_1\left(n_1 + \tfrac{1}{2}\right) + \hbar\omega_2\left(n_2 + \tfrac{1}{2}\right) + \hbar\omega_3\left(n_3 + \tfrac{1}{2}\right) + \cdots$$

$$E = \sum_k (\hbar\omega_k)(n_k + \tfrac{1}{2})$$

$$Q_N = \sum_{\text{states}} e^{-\beta E_{\text{state}}} = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \cdots e^{-\beta \sum_{k=1}^{3N} \hbar\omega_k (n_k + \frac{1}{2})}$$

this can't move out front this time!

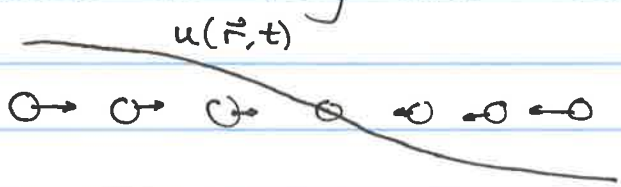
$$A(T,V,N) = \frac{\hbar}{2} \sum_{k=1}^{3N} \omega_k + k_B T \sum_{k=1}^{3N} \ln\left[1 - e^{-\beta\hbar\omega_k}\right]$$

If we have many modes, with closely-spaced frequencies:

$$= \frac{\hbar}{2} \int_0^{\infty} g(\omega)\,d\omega + k_B T \int_0^{\infty} g(\omega) \ln\left[1 - e^{-\beta\hbar\omega}\right] d\omega$$

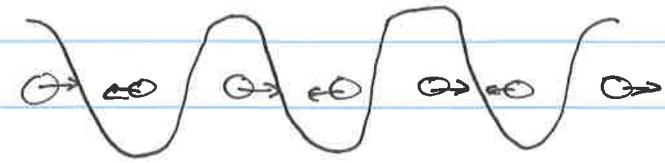
$g(\omega)\,d\omega$ = the number of modes with frequency between ω & $\omega + d\omega$, or the degeneracy of phonons with frequency ω. What does $g(\omega)$ look like?

Phonons are really waves moving through a crystal:



low frequency

$u(\vec{r},t)$ measures the displacement of atom at $\vec{r}$ at time t due to this phonon.



high frequency

$$u(\vec{r},t) = A e^{i(\vec{k}\cdot\vec{r} - \omega t)}$$

wave with amplitude A travelling in $\vec{k}$ direction with frequency $\omega = 2\pi\nu$

$$|\vec{k}| = \frac{2\pi}{\lambda}$$

wavelength

Useful relations: $$\boxed{|\vec{k}| = \frac{2\pi}{\lambda} \qquad \lambda = \frac{V_p}{\nu} \qquad \nu = \frac{V_p}{\lambda} \qquad \omega = 2\pi\nu}$$

A standing wave:

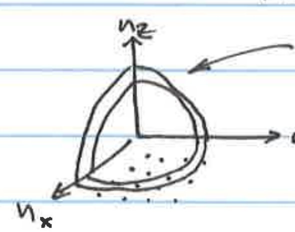
$$u(\vec{r},t) = 2A\, e^{i\vec{k}\cdot\vec{r}} \cos\omega t$$

Since the wave must vanish at the edges of the crystal, we really have particle-in-a-box boundary conditions:

$$\vec{k} = \frac{\pi}{L}\vec{n} \leftarrow \text{vector of positive integers} \quad \begin{pmatrix} n_x \\ n_y \\ n_z \end{pmatrix}$$

$$|\vec{k}|^2 = \left(\frac{\pi^2}{L^2}\right)\left(n_x^2 + n_y^2 + n_z^2\right)$$

$|\vec{k}|^2$ is like the radius^2 of a sphere



\# of standing waves between k & $k+dk$
= \# of <u>dots</u> between r & $r+dr$

Volume of the sphere: $$V = \frac{4}{3}\pi r^3 \cdot \underbrace{\frac{1}{8}}_{\text{one octant only}} = \frac{\pi}{6} r^3$$

$$r = \sqrt{n_x^2 + n_y^2 + n_z^2} = \frac{|k|L}{\pi} \Longrightarrow r^3 = \frac{k^3L^3}{\pi^3} = \left(\frac{kL}{\pi}\right)^3$$

So:

$$\Phi(k) = \frac{\pi}{6}\left(\frac{Lk}{\pi}\right)^3 = \frac{L^3k^3}{6\pi^3} = \frac{\overset{\text{volume}}{V}\, k^3}{6\pi^3}$$

$\uparrow$ number of <u>dots</u> contained within sphere defined by $|k|$

But # between k & $k+dk$ = surface area of shell * dk

$$g(k)\,dk = \frac{d\Phi(k)}{dk} * dk$$

$$g(k)\,dk = \frac{Vk^2}{2\pi^2}\,dk$$

But we want $g(\omega)$ or $g(\nu)$: $\nu = \frac{V_p}{\lambda} = \frac{V_p k}{2\pi}$ ← speed of propagation

So : $$g(\nu)\,d\nu = \frac{4\pi V \nu^2}{V_p^3}\,d\nu$$

There are 2 kinds of transverse waves

There is 1 kind of longitudinal wave

$$g(\nu)\,d\nu = \left(\frac{2}{V_T^3} + \frac{1}{V_l^3}\right) 4\pi V \nu^2 d\nu$$

These waves have an average velocity: $\frac{3}{V_0^3} \simeq \frac{2}{V_t^3} + \frac{1}{V_l^3}$

$$\therefore \quad g(\nu)\,d\nu = \frac{12\pi V}{V_0^3}\,\nu^2 d\nu$$

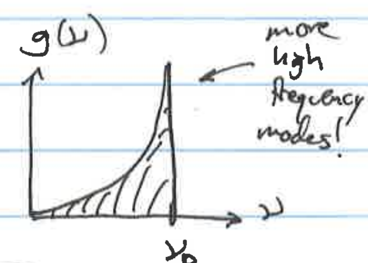
$\omega = 2\pi\nu$
$d\omega = 2\pi\, d\nu$

$$\therefore \quad g(\omega)\,d\omega = \frac{6V}{4\pi^2 V_0^3}\,\omega^2 d\omega$$

Normalization : Total # of frequencies = $3N$

$$\int_0^{\nu_D} g(\nu)\,d\nu = 3N$$

$$\nu_D = \left(\frac{3N}{4\pi V}\right)^{1/3} V_0$$



$$\boxed{g(\nu)\,d\nu = \begin{cases} \frac{9N}{\nu_D^3}\,\nu^2 d\nu & \nu \le \nu_D \\ 0 & \nu > \nu_D \end{cases}}$$

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

$$\Theta_D = \frac{h\nu_D}{k_B} \qquad x = \frac{h\nu}{k_B T}$$

The Debye model gives almost perfect agreement with experiments!

$$C_V(T \to \infty) = 3R$$

$$C_V(T \to 0) = \frac{12\pi^4}{5} N k_B \left(\frac{T}{\Theta_D}\right)^3$$