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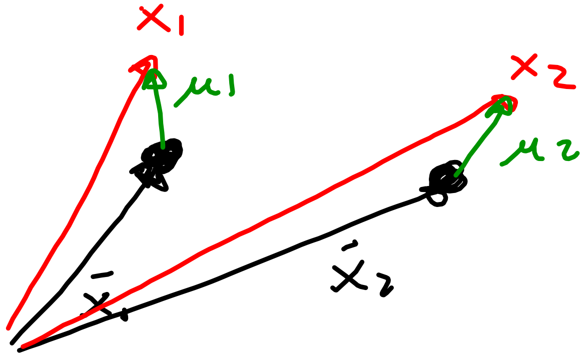


$$H = \phi_0 + \left\{ \sum_i \tfrac{1}{2} m \dot{u}_i^2 + \sum_{ij} \alpha_{ij} u_i u_j \right\}$$

$$\alpha_{ij} = \frac{1}{2} \frac{\partial^2 \phi}{\partial x_i \partial x_j} \Big|_{\{x_i = \bar{x}_i\}}$$

This is non diagonal.

We can change basis so that H is diagonal.

We will get

$$q_i = \sum_{j=1}^{3N} \gamma_j u_j$$

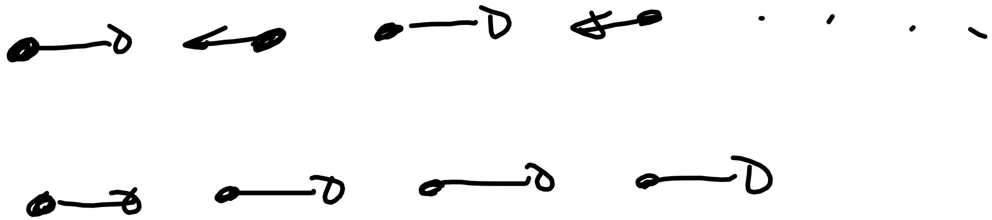
new eigenvectors are linear combinations of the u's.

ω_i: are the 3N frequencies of the collective vibrations and are the eigenvalues of H.

ω_i: are called the "normal" frequencies

q_i: are the normal modes.

Examples of normal modes:



Now

$$H = \phi_0 + \sum_{i=1}^{3N} \frac{1}{2} m \left(\dot{q}_i^2 + \omega_i^2 q_i^2 \right)$$

ω_i $(i = 1, 2, \ldots 3N)$ frequencies of the normal modes.

ϕ_0 is the energy of the solid at $T=0$ (cohesion energy) but the remaining energy corresponds to the energy of $3N$ 1D harmonic oscillators.

classically : lattice vibrations

quantum: harmonic oscillators populated by quasiparticles called phonons.

We know that:

$$E\{n_i\} = \phi_0 + \sum_i \left(n_i + \frac{1}{2}\right)\hbar\omega_i$$

occupation number of the phonon levels.

1

$$\therefore \; U(T) = \underbrace{\left\{ \phi_0 + \sum_i \frac{1}{2}\hbar\omega_i \right\}}_{T=0 \text{ energy of the solid.}} + \sum_i \frac{\hbar\omega_i}{e^{\hbar\omega_i/kT} - 1}$$

n_i for bosons.

Notice that classically equipartition is valid and $c_V = 3Nk$ constant for all T.

However, in the lab. it was noticed that $c_V \to 0$ for $T \to 0$. Quantum mech. solved this:

1

$$c_V = \left.\frac{\partial U}{\partial T}\right|_V = k \sum_{i=1}^{3N} \frac{(\hbar\omega_i/kT)^2 \, e^{\hbar\omega_i/kT}}{(e^{\hbar\omega_i/kT}-1)^2} \quad (2)$$

To study this we need to know $\{\omega_i\}$.

They can be measured or they can be modelled.

First "model" was proposed by Einstein.
It was not really realistic but the goal was to show that $\lim_{T \to 0} c_V = 0$.

$$\omega_i = \omega_E \quad \forall i \quad \text{(Einstein's model).}$$

Replacing in 2:

$$c_V = \frac{3Nk \left(\frac{\hbar \omega_E}{kT} \right)^2 e^{\frac{\hbar \omega_E}{kT}}}{\left(e^{\frac{\hbar \omega_E}{kT}} - 1 \right)^2}$$

Define: $x = \frac{\hbar \omega_E}{kT} = \frac{\theta_E}{T} \qquad \theta_E = \frac{\hbar \omega_E}{k}$

Then:

$$C_V(T) = 3Nk\,\mathcal{E}(x) \quad \text{with} \quad \mathcal{E}(x) = \frac{x^2 e^x}{(e^x - 1)^2}$$

Now we see that

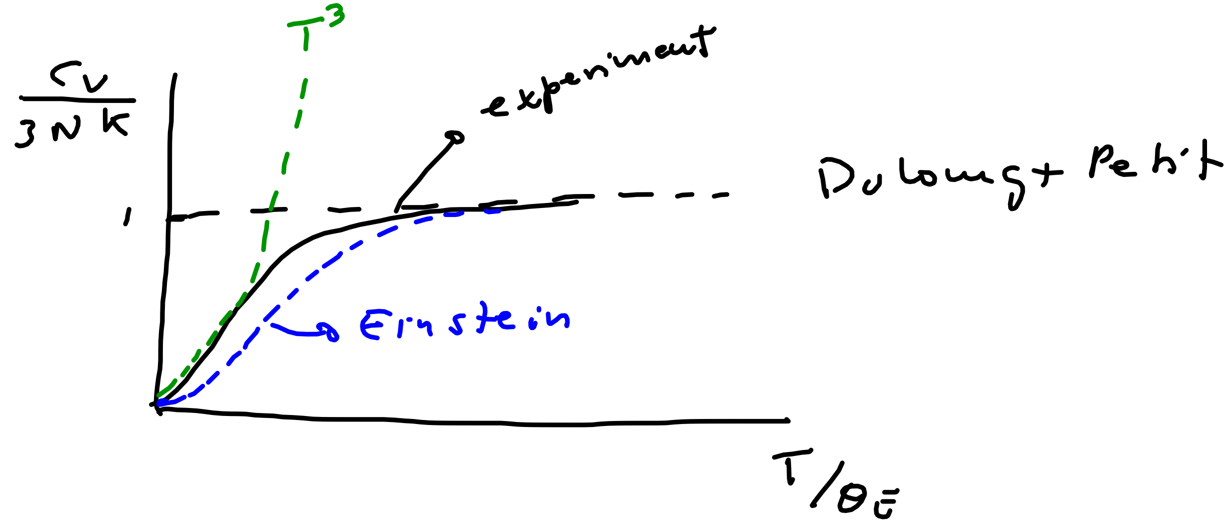
$$x = \frac{\hbar\omega_E}{kT}$$

$$\lim_{\substack{x\to 0 \\ (T\to\infty)}} \mathcal{E}(x) = \frac{x^2}{(\cancel{1}+x-\cancel{1})^2} = 1$$

$\therefore\; C_V(T\to\infty) = 3Nk$ Dulong + Petit. (classical)

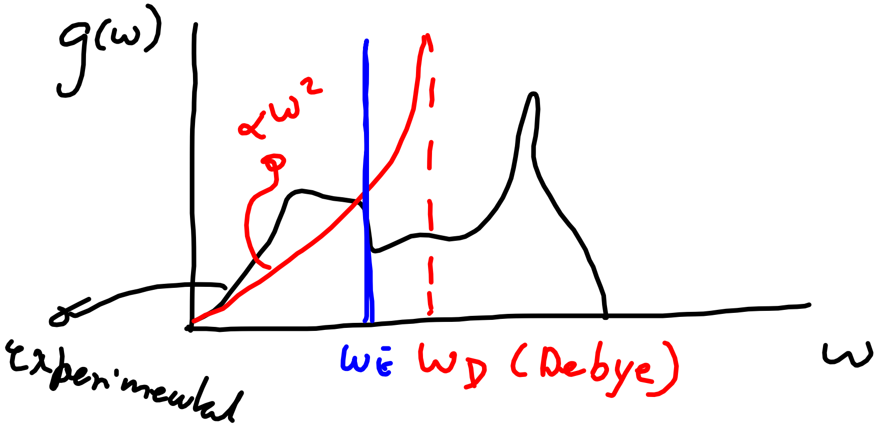
$$\lim_{\substack{x\to\infty \\ (T\to 0)}} \mathcal{E}(x) = x^2\frac{e^x}{e^{2x}} = x^2 e^{-x} \longrightarrow 0$$

goes to 0 exponentially.
But experimentally it went like T^3.



A more refined model for $g(\omega)$ was proposed by Debye.

Experimentally:



Beyond a certain ω the solid cannot produce the wavelength.

Debye compared phonons to photons realizing that the only difference is that photons have 2 polarizations while phonons can have 3: 2 transversal + 1 longitudinal acoustic phonons have a cut frequency since $\int_0^\infty g(\omega)\, d\omega = 3N$.

Debye said that $g(\omega)$ will be given by the same expression as for photons but replacing 2 by 3:

$$g(\omega)\, d\omega = 3 \frac{V}{2\pi^2 c_s^3} \omega^2 d\omega \qquad c_s = c_\ell = c_t$$

also we can assume that $c_\ell \neq c_t$ (more refined)

$$\int_0^{\omega_D} g(\omega)\, d\omega = 3N$$

from here we find ω_D which depends on c_ℓ and c_t.

Notice that c_ℓ and c_t are material dependent.

C_s: sound velocity.

If $c_\ell \neq c_t$:

$$\int_0^{\omega_D} V \left(\frac{\omega^2 d\omega}{2\pi^2 C_L^3} + \frac{2\,\omega^2 d\omega}{2\pi^2 C_T^3} \right) = 3N$$

$$3N = \frac{1}{3}\,\omega_D^3 \frac{V}{\pi^2} \left(\frac{1}{2C_L^3} + \frac{1}{C_T^3} \right)$$

$$\therefore \boxed{\omega_D^3 = 18\pi^2 \frac{N}{V} \left(\frac{1}{C_L^3} + \frac{2}{C_T^3} \right)^{-1}}$$

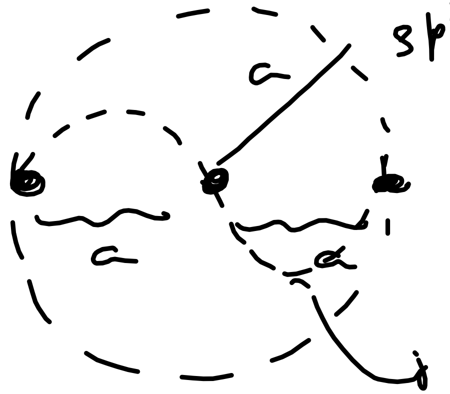
Then:

$$g(\omega) = \begin{cases} \dfrac{9 N \omega^2}{\omega_D^3} & \text{for } \omega \leq \omega_D \\ 0 & \text{for } \omega > \omega_D \end{cases} \quad (3)$$

Notice that to be more refined one can try to find ω_D^L and ω_D^T:

$$\int_0^{\omega_D^L} \frac{V \omega^2 d\omega}{2\pi^2 c_L^3} = N \quad \text{and} \quad \int_0^{\omega_D^T} \frac{V \omega^2 d\omega}{\pi^2 c_T^3} = 2N$$

Both frequencies are associated to the same minimum λ allowed by the solid.



$$\frac{V}{N} = a^3$$

; $\lambda \sim 2a$ minimum wavelength.

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

$$\lambda = \frac{2\pi c}{\omega}$$

ω and c depend on being l or t but λ is fixed.

Now

$$c_V = k \int g(\omega) \frac{\left(\frac{\hbar\omega}{kT}\right)^2 e^{\hbar\omega/kT}}{\left(e^{\hbar\omega/kT}-1\right)^2} d\omega \overset{c_L = c_T}{=}$$

3

$$= \frac{k\,9N}{\omega_D^3} \int_0^{\omega_D} \frac{\omega^2 \left(\frac{\hbar\omega}{kT}\right)^2 e^{\hbar\omega/kT}}{\left(e^{\hbar\omega/kT}-1\right)^2} d\omega =$$

$$x = \hbar\omega/kT \qquad x_D = \hbar\omega_D/kT$$

$$= \frac{9kN}{\omega_D^3} \int_0^{x_D} \frac{(kT)^3}{\hbar^3} \frac{x^4 e^x}{\left(e^x-1\right)^2} dx =$$

$$= \frac{9kN}{\omega_D^3} \frac{(kT)^3}{\hbar^3} \int_0^{\omega_D} \frac{x^4 e^x}{\left(e^x-1\right)^2} dx = 3kN \frac{3}{x_D^3} \int_0^{x_D} \frac{x^4 e^x}{\left(e^x-1\right)^2} dx$$

$$\therefore \quad C_V(T) = 3kN\,D(x_D)$$

$$D(x_D) = \frac{3}{x_D^3}\int_0^{x_D} \frac{x^4 e^x\,dx}{(e^x-1)^2}$$ Debye's function

$$x = \frac{\hbar\omega}{kT}$$

$$x_D = \frac{\hbar\omega_D}{kT} = \frac{\Theta_D}{T}$$ $\Theta_D = \frac{\hbar\omega_D}{k}$ Debye's temperature

If $T \gg \Theta_D \Rightarrow x_D \ll 1$

$$D(x_D) \approx 1 - \frac{x_D^2}{20} \longrightarrow 1$$

$C_V(T\to\infty) = 3kN$ Dulong + Petit

$T << \Theta_D \qquad T \to 0$

instead of x_D because x_D is very large in this limit.

$$D(x_D) = \frac{3}{x_D^3} \int_0^{\infty} \frac{x^4 e^x \, dx}{(e^x - 1)^2} = \frac{3}{x_D^3} \frac{4\pi^4}{5}$$

$$c_V = \frac{12\pi^4}{5} N k \left(\frac{T}{\Theta_D}\right)^3 \propto T^3$$ as in the experiments.