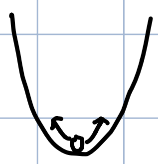
Chapter 2 Specific Heat of Solids: Boltzmann, Einstein and Debye.

Solid: $C = 3k_B$ (per atom) $\left(C_p \approx C_v \text{ because } C_p - C_v = \frac{VT\alpha^2}{\beta} \right)$ small for solid. **Dulong-Petit Theorem**

↓

Boltzmann:



p_x, p_y, p_z — kinetic

x, y, z — potential

equipartition theorem

↓ not hold at low temperature

Einstein: Boltzmann's Model + QM

1-D: $E_n = \hbar\omega(n + \frac{1}{2})$ $\quad \omega = \sqrt{k/m}$ Einstein frequency

partition function: $Z_1 = \sum \exp(-\beta\hbar\omega(n+\frac{1}{2})) = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} = \frac{1}{2\sinh(\beta\hbar\omega/2)}$

$\langle E \rangle = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \frac{\hbar\omega}{2}\coth\left(\frac{\beta\hbar\omega}{2}\right) = \hbar\omega\left(n_B(\beta\hbar\omega) + \frac{1}{2}\right)$

Bose occupation factor $\quad n_B(x) = \frac{1}{e^x - 1}$

$$C = \frac{\partial \langle E \rangle}{\partial T} = k_B(\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}$$

3-D: $E = \hbar\omega(n_x + n_y + n_z + 3/2)$

$Z = Z_1^3$

$$C = 3k_B(\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2} \longrightarrow \lim_{\beta \to 0} C = 3k_B \quad \text{high } T$$

$$\lim_{\beta \to \infty} C = 0 \quad \text{low } T$$

The temperature is less than the space between the eigenstates, so freeze at the bottom state.

Most cases: ω < room temperature

diamond: ω > room temperature $\quad$ Reason: 1° Bonding is strong.

2°. atomic mass is small (carbon) $\quad \omega = \sqrt{k/m}$

↓ At very low temperature, $C \sim T^3$ rather than exponentially small (Einstein predicted)

Debye: the oscillation of atoms is the same thing as sound (wave, interaction)

Handle the wave just like Planck quantized light.

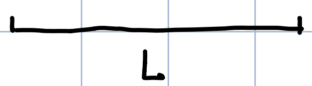
Difference: light: 2 polarizations, transverse modes.

sound: 3 polarizations, longitudinal modes.

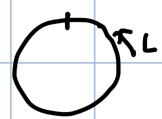
Assumption: The transverse and longitudinal modes have the same velocity.

i.e. V_{sound} is independent of direction. isotropic.

Periodic Boundary Conditions (Born-von Karman)



$\sin \frac{n\pi x}{L} \longrightarrow$



$e^{ik\cdot x}$

$$e^{ikx} = e^{ik(x+L)} \Rightarrow k = \frac{2\pi n}{L}$$

spacing between allowed ks is $\frac{2\pi}{L}$.

$$E_{tot} = \sum_k \hbar\omega\left(n_B(\beta\hbar\omega) + \tfrac{1}{2}\right) \longrightarrow \text{3-D: } \sum_{\vec{k}} \rightarrow \frac{L^3}{(2\pi)^3}\int d\vec{k} = V\int \frac{d^3\vec{k}}{(2\pi)^3}$$

$\frac{L}{2\pi}\int_{-\infty}^{+\infty} dk \cdots$

most physical quantities we measure can be measured far from the boundaries of the sample anyway and would then be independent of what we do with the boundary conditions.

Debye: $$\sum_{\text{modes}} = 3\sum_k = 3V\int \frac{d^3\vec{k}}{(2\pi)^3} \overset{\text{isotropic}}{=} \frac{3V}{(2\pi)^3}\int_0^\infty 4\pi k^2 dk$$

$$\underset{k=v\omega}{=} \frac{3V\cdot 4\pi}{(2\pi)^3\cdot v^3}\int_0^\infty \omega^2 d\omega \equiv \int_0^\infty g(\omega)d\omega$$

$$g(\omega) = \frac{12\pi}{(2\pi)^3 v^3}\,\frac{N}{N/V}\,\omega^2 = N\frac{9\omega^2}{\omega_d^3}$$

= Density of states

$g(\omega)d\omega$ = # of modes with frequency between ω & $\omega+d\omega$

$\omega_d = 6\pi^2 (\frac{N}{V}) v^3$ Debye frequency.

$$\langle E\rangle = 3\sum \hbar\omega(\vec{k})(n_B(\beta\hbar\omega(\vec{k}))+\frac{1}{2})$$
$$= 3\frac{L^3}{(2\pi)^3}\int d\vec{k}\ \hbar\omega(\vec{k})\ (n_B+\frac{1}{2})$$
$$= 3\frac{L^3}{(2\pi)^3}\int 4\pi k^2 dk\ \hbar\omega(\vec{k})(n_B+\frac{1}{2})$$
$$= \frac{3L^3\cdot 4\pi}{(2\pi)^3}\int \omega^2 d\omega\ (\frac{1}{v^3})\ \hbar\omega\,(n_B+\frac{1}{2})$$
$$= \int_0^\infty d\omega\ g(\omega)\ \hbar\omega\,(n_B(\beta\hbar\omega)+\frac{1}{2})$$

Cause infinity but temperature independent

so doesn't influence $C = \frac{\partial\langle E\rangle}{\partial T}$

$$= \frac{9N\hbar}{\omega_d^3}\int_0^\infty \frac{\omega^3}{e^{\beta\hbar\omega}-1}d\omega + T \text{ independent constant}$$
$$= \frac{9N\hbar}{\omega_d^3(\beta\hbar)^4}\int_0^\infty \frac{x^3}{e^x-1}dx + T \text{ independent constant}$$
$$= 9N\frac{(k_BT)^4}{(\hbar\omega_d)^3}\cdot\boxed{\frac{\pi^4}{15}} + T \text{ independent constant}$$

zero-point energy

$\langle E\rangle \sim T^4 + \text{constant} \Rightarrow C = \frac{\partial\langle E\rangle}{\partial T} \sim T^3$

The important thing is that there is $\boxed{\text{NO FREE PARAMETER}}$!

$k_B T_{Debye} = \hbar\omega_d$ $\qquad C = \frac{\partial\langle E\rangle}{\partial T} = Nk_B\frac{T^3}{T_D^3}\frac{12\pi^4}{5}$

Theoritically: $\lim_{T\to\infty} C = 3k_B$. controdictory!!! Introduce ω_{cutoff}.

$$\int_0^\infty g(\omega)d\omega = \text{infinity}.$$

$\langle E\rangle = \int_0^{\omega_c} d\omega\ g(\omega)\hbar\omega\ n_B(\beta\hbar\omega)$ drop $\frac{1}{2}$ because temperature independent

$$\lim_{T\to\infty} \langle E \rangle = k_B T \int_0^{\omega_c} d\omega \; g(\omega)$$
$$= 3N k_B T$$
$\Rightarrow$

$$3N = \int_0^{\omega_c} g(\omega)\, d\omega = \frac{9\omega}{\omega_d^2} \int_0^{\omega_c} \omega^2 d\omega = 3N \frac{\omega_c^2}{\omega_d^2} \Rightarrow \omega_c = \omega_d$$

Shortcomings: 1° the introduction of ω_c : ad hoc

2° $\omega = vk$ no longer holds at high T

3° The Debye theory is not exact at intermediate T (exp.)

4° $C = \gamma T + \alpha T^3$ at low T.