Chapter 4: Vibrations in crystals

Heat capacity

$$C = \frac{\partial Q}{\partial T}$$

in solids $C_p \approx C_V$

$$C_p - C_V = \frac{V T \alpha^2}{\beta}$$

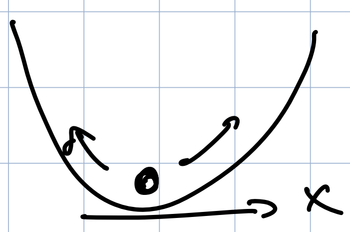
small ← thermal expansion

isothermal compressibility

monatomic gas $\frac{C_V}{N} = \frac{3}{2} k_B$

Solids $\frac{C}{N} = 3 k_B$ Law of Dulong-Petit 1819

Boltzmann model of solids 1896



equipartition theorem: For each degree of freedom

$$E \sim \frac{1}{2} k_B T$$

P_x, P_y, P_z, x, y, z

$$E \sim 6 \times \frac{1}{2} k_B T \times N$$

$$\frac{1}{N} C \sim \frac{1}{N} \frac{\partial E}{\partial T} \sim 3 k_B$$

Problem: Law of D–P does not hold at low T for most materials

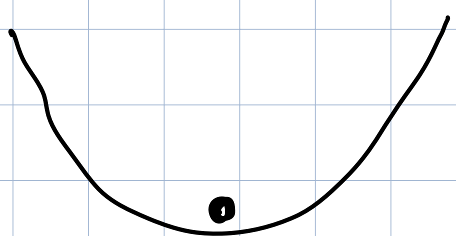
$$T \lll T_{Room} \longrightarrow \frac{C}{N} \ll 3 k_B$$

For some materials (diamond)

$$\frac{C}{N} \ll 3 k_B T \quad \text{even @ } T_{Room}$$

Einstein model of solids 1907

= Boltzmann model + Quantum mechanics



$$\rightarrow E_n = \hbar \omega \left(n + \frac{1}{2}\right) \quad (1)$$

$$n \in \{0, 1, 2, \ldots\}$$

Partition function:

$$Z = \sum_{n=0,1,\ldots} e^{-\beta E_n} \quad (2)$$

$$\beta = \frac{1}{k_B T}$$

$$\langle E \rangle = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}$$

(3)

$$Z = ? = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+\frac{1}{2})}$$

$$= e^{-\beta\hbar\omega/2} \sum_{n=0}^{\infty} \underbrace{\left(e^{-\beta\hbar\omega}\right)^n}_{x}$$

$$1 + x + x^2 + x^3 + \cdots = \frac{1}{1-x}$$

$$\boxed{Z = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}}$$

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

$$\longrightarrow n_B(\omega) = \frac{1}{e^{\beta\hbar\omega} - 1}$$

$$\langle E \rangle = \hbar\omega\left(\# + \frac{1}{2}\right)$$

→ Heat capacity

$$\frac{1}{N} C_{1D} = \frac{1}{N}\frac{\partial \langle E \rangle}{\partial T} = k_B (\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{\left(e^{\beta\hbar\omega}-1\right)^2}$$

for a single atom

In 3D :
$$\frac{C_{3D}}{N} = 3 \cdot C_{1D}$$
$$= 3 k_B \, (\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{\left(e^{\beta\hbar\omega}-1\right)^2}$$

Different limits,

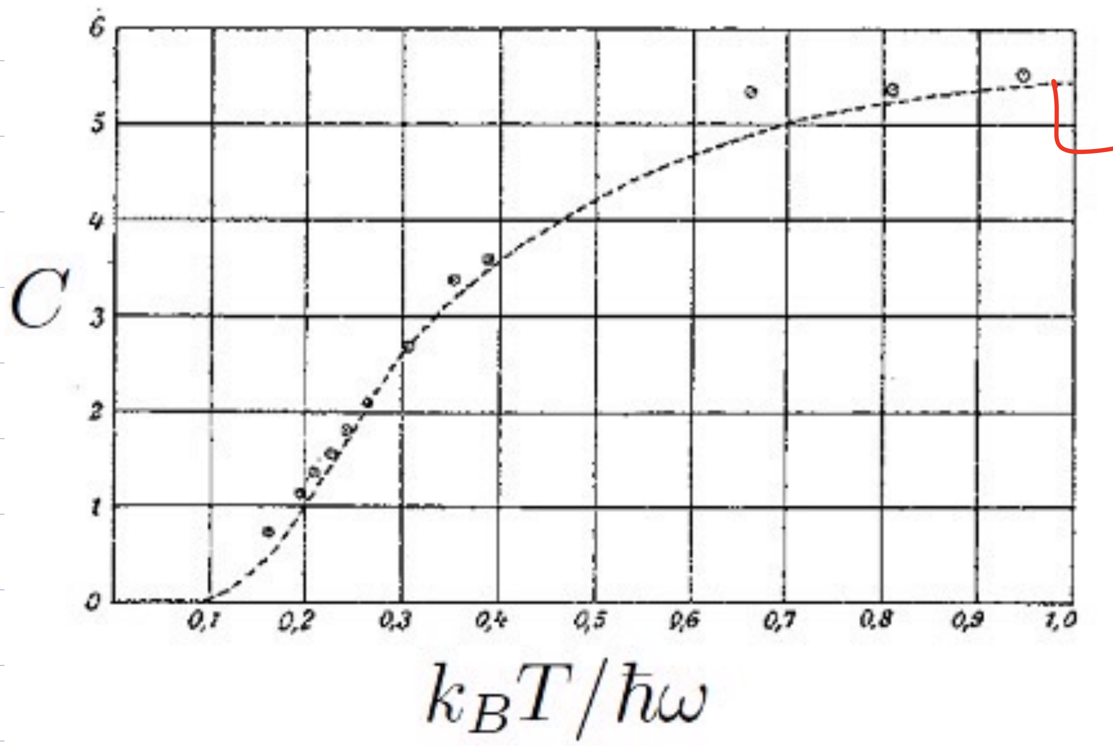
1) High T : small β

$$e^{\beta\hbar\omega} = 1 + \beta\hbar\omega + \cdots$$

$$\frac{C_{3D}}{N} = 3 k_B \quad ✓$$

2) Low T : Large β

$$\frac{C_{3D}}{N} \sim e^{-\beta \hbar\omega}$$



Einstein formula

ω: free parameter

Diamond : $\omega \gg k_B T_{Room}$

Debye 19##

$$C_V \propto T^3$$

✓