



# Intro. to Electro-physics

**Crystal vibration (3<sup>rd</sup>)**

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# Thermal property of solids

- Phonon heat capacity

- Definition: the contribution of phonons to the heat capacity of a solid

$$C_V \triangleq \left( \frac{\partial U}{\partial T} \right)_V$$

- The total energy of phonons

$$U = \sum_k \langle n_k \rangle \hbar \omega_k$$

- $\langle n_k \rangle$ : The average number of phonons with wavevector  $k$  at  $k_B T$  ( $\triangleq \tau$ )

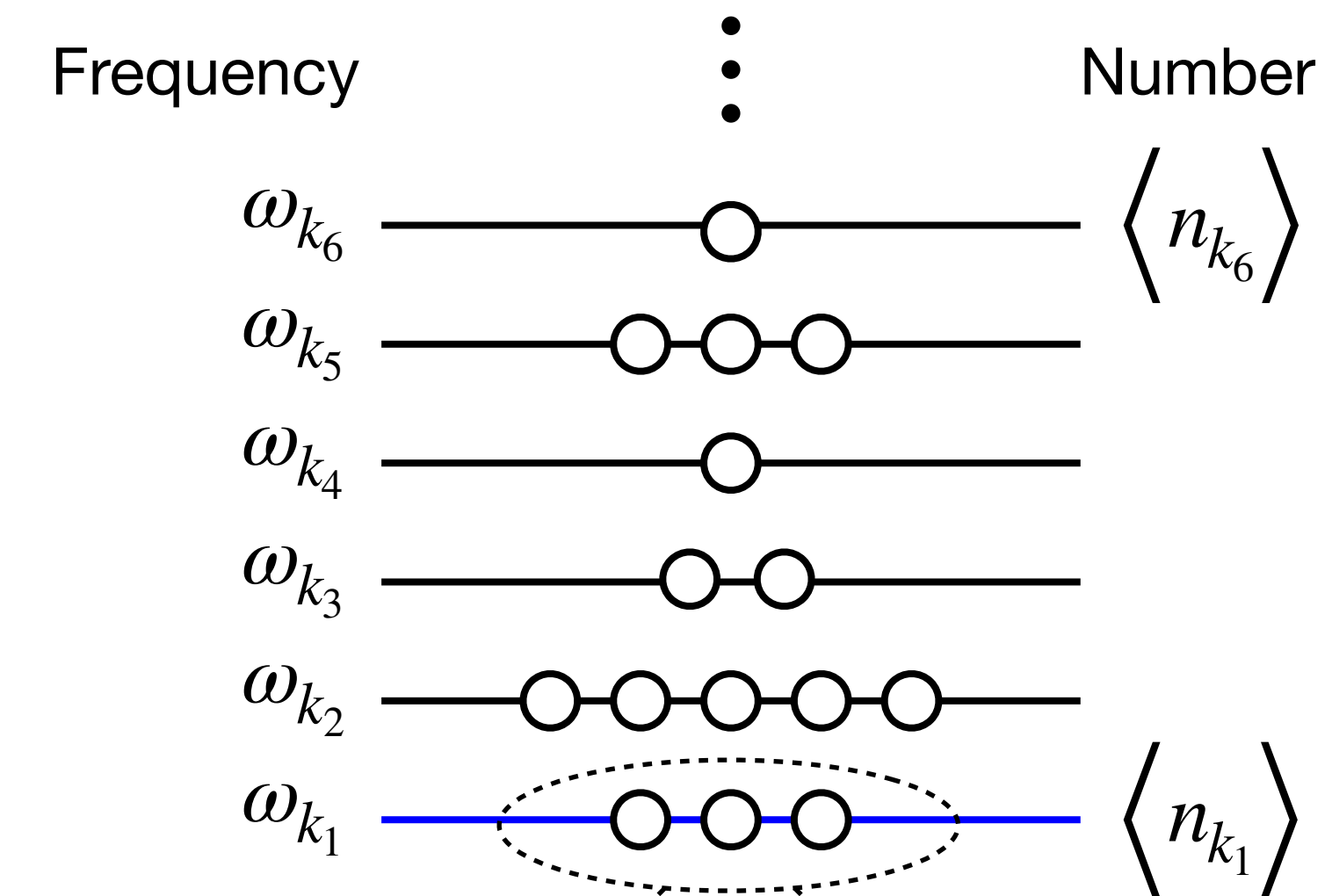
$$\langle n \rangle = \frac{1}{\exp \frac{\hbar \omega}{k_B T} - 1} = \frac{1}{\exp \frac{\hbar \omega}{\tau} - 1}$$

**Planck distribution**

- A special case of Bose-Einstein distribution for the boson particles which...

(1) have an energy quantized in units of  $\hbar \omega$

(2) do not have a fixed number in a system ( $\rightarrow$  lack of chemical potential  $\mu$ )



$$E_k = \hbar \omega_k \left( \langle n \rangle + \frac{1}{2} \right)$$

# Planck distribution

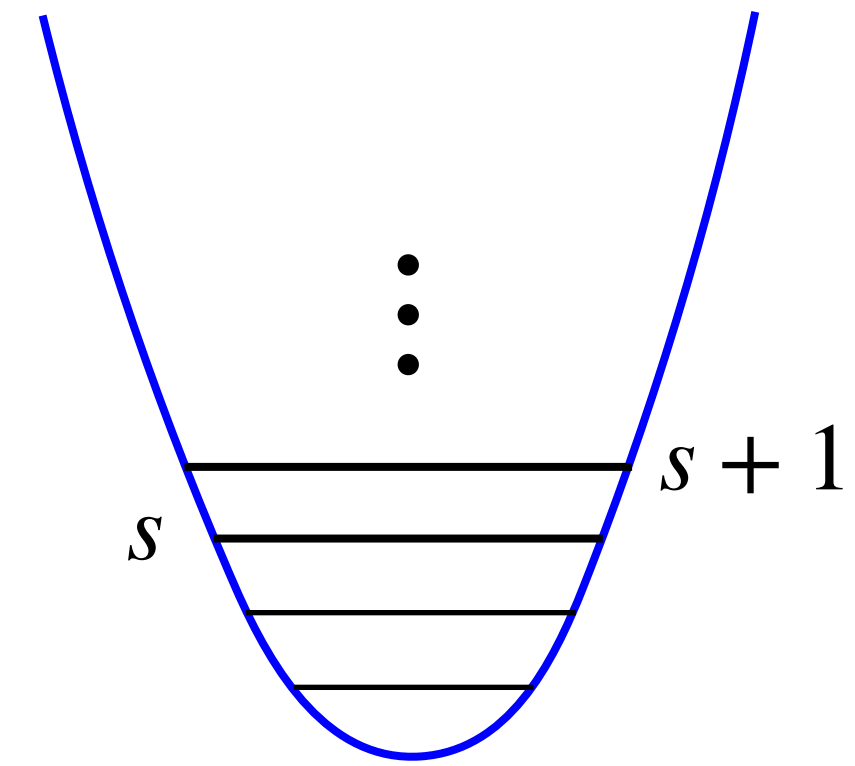
- Derivation

- At a given  $\tau$  and  $\omega$ , the ratio of the number of oscillators in their  $(s + 1)$  vs.  $(s)$ -th quantum levels :

$$\frac{N_{s+1}}{N_s} = \exp \left( \frac{E_{s+1} - E_s}{\tau} \right) = \exp \left( -\frac{\hbar\omega}{\tau} \right) \longrightarrow N_s \sim \exp \left( -\frac{\hbar\omega}{\tau} s \right)$$

- The fraction of the total number of oscillators in the  $(s)$ -th level :

$$\frac{N_s}{\sum_{a=1}^{\infty} N_a} = \frac{\exp(-s\hbar\omega/\tau)}{\sum_{a=1}^{\infty} \exp(-a\hbar\omega/\tau)}$$



- The average quantum number of oscillators :

$$\langle n \rangle = \frac{\sum_{a=1}^{\infty} a \exp(-a\hbar\omega/\tau)}{\sum_{a=1}^{\infty} \exp(-a\hbar\omega/\tau)} \xrightarrow{\exp(-\frac{\hbar\omega}{\tau}) \triangleq x} \begin{cases} \sum_{a=1}^{\infty} x^a = \frac{1}{1-x} \\ \sum_{a=1}^{\infty} ax^a = x \frac{d}{dx} \sum_{a=1}^{\infty} x^a = \frac{x}{(1-x)^2} \end{cases}$$

$$\langle n \rangle = \frac{x}{1-x} = \frac{1}{\exp\left(\frac{\hbar\omega}{\tau}\right) - 1} \quad \blacksquare$$

# Phonon heat capacity and density of states

- Phonon heat capacity (contd.)

- Total energy = The sum for the energy of oscillators with frequency  $\omega_k$  over all  $k$

$$U = \sum_k \langle n_k \rangle \hbar \omega_k = \sum_k \frac{\hbar \omega_k}{\exp\left(\frac{\hbar \omega_k}{\tau}\right) - 1}$$

- It is convenient to replace  $\sum_k \longrightarrow \int d\omega$  such that  $U = \int d\omega D(\omega) \frac{\hbar \omega}{\exp(\hbar \omega / \tau) - 1}$

- $D(\omega) d\omega$  : **Number of modes in the frequency range  $[\omega, \omega + d\omega]$ ;  $D(\omega) \triangleq$  Density of states**

- The phonon heat capacity

$$C = \left( \frac{\partial U}{\partial T} \right)_V = k_B \int d\omega D(\omega) \frac{x^2 \exp x}{(\exp x - 1)^2}, \text{ where } x = \frac{\hbar \omega}{\tau}$$

**Finding the D.O.S ( $D(\omega)$ ) is a central problem!**

# Density of states in 3D

- General expression for DOS in 3D
  - Allowed  $\mathbf{k}$ -vectors : integer multiples of  $2\pi/L$  along three axes

$$\mathbf{k} = (k_x, k_y, k_z) = \left( \frac{2\pi}{L}n_x, \frac{2\pi}{L}n_y, \frac{2\pi}{L}n_z \right)$$

- Number of allowed  $\mathbf{k}$ -values in the unit volume of  $\mathbf{k}$ -space :

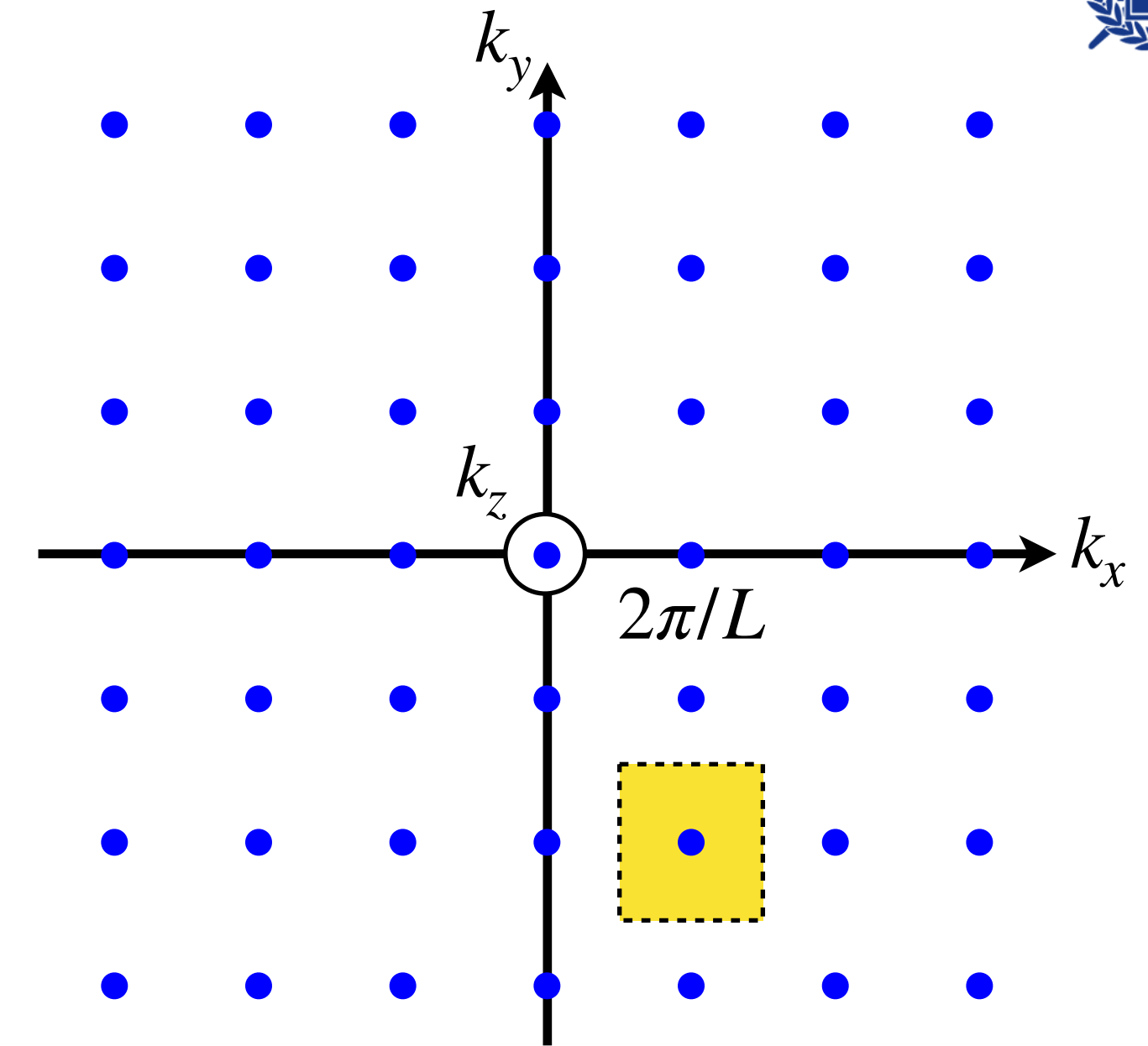
$$\frac{1}{(2\pi/L)^3} = \frac{L^3}{8\pi^3} = \frac{V}{8\pi^3} \text{ (i.e., a density per unit volume)}$$

- Number of allowed  $\mathbf{k}$ -values within the  $\mathbf{k}$ -sphere :

$$N = \frac{V}{8\pi^3} \cdot \frac{4}{3}\pi k^3 = \frac{V}{6\pi^2} k^3$$

- Density of states

$$D(\omega) = \frac{dN}{d\omega} = \frac{V}{6\pi^2} \cdot 3k^2 \frac{dk}{d\omega} = \frac{Vk^2}{2\pi^2} \frac{1}{\frac{d\omega}{dk}}$$



$$\therefore D(\omega) = \frac{Vk^2}{2\pi^2} \frac{1}{\frac{d\omega}{dk}}$$



# Einstein model of D.O.S.

- Density of states by Einstein

- There are  $N$ —oscillators of the same frequency  $\omega_0$  :

$$D(\omega) = N\delta(\omega - \omega_0)$$

- Thermal energy of the system :

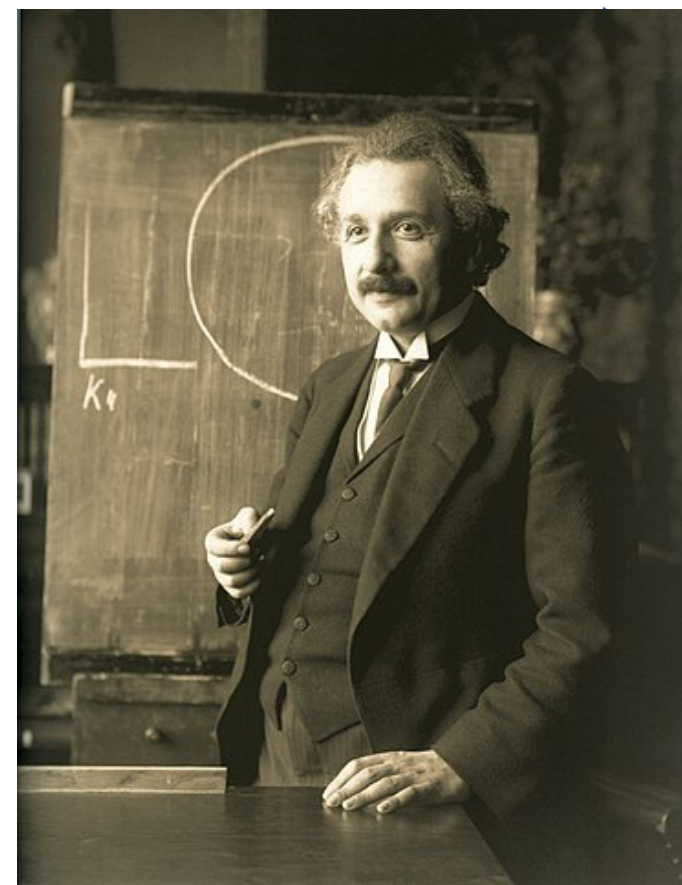
$$U = \int d\omega D(\omega) \frac{\hbar\omega}{\exp(\hbar\omega/\tau) - 1} \rightarrow U = \frac{N\hbar\omega_0}{\exp(\hbar\omega_0/\tau) - 1}$$

- The heat capacity of the system :

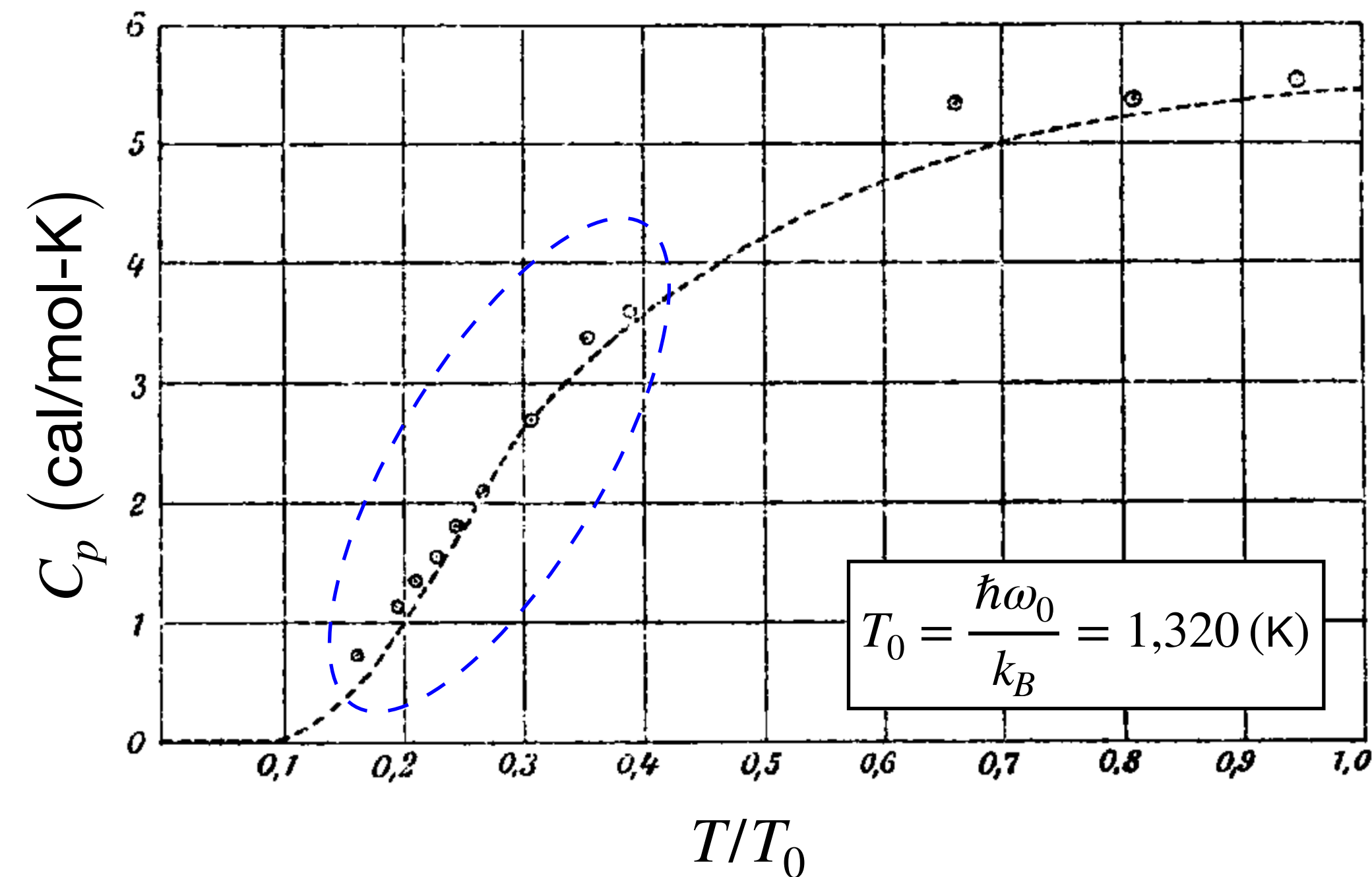
$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = Nk_B \left( \frac{\hbar\omega_0}{\tau} \right)^2 \frac{\exp(\hbar\omega_0/\tau)}{\left( \exp(\hbar\omega_0/\tau) - 1 \right)^2}$$

▸ In 3D :  $N \longrightarrow 3N$  (i.e., three modes per oscillator)

▸ At high temperatures,  $\lim_{T \rightarrow \infty} C_V = 3Nk_B$



Albert Einstein  
(Germany)  
1879-1955



**The heat capacity of diamond**

A. Einstein, Ann. Phys., 22, 180 (1907)

# Debye's model of D.O.S.

- Debye's approximation

- The velocity of crystal wave is assumed constant :

$$\omega = vk \longrightarrow D(\omega) = \frac{Vk^2}{2\pi^2} \frac{1}{\frac{d\omega}{dk}} = \frac{V\omega^2}{2\pi^2 v^3}$$

- The upper limit of the frequency = **Debye's frequency** ( $\omega_D = vk_D$ )

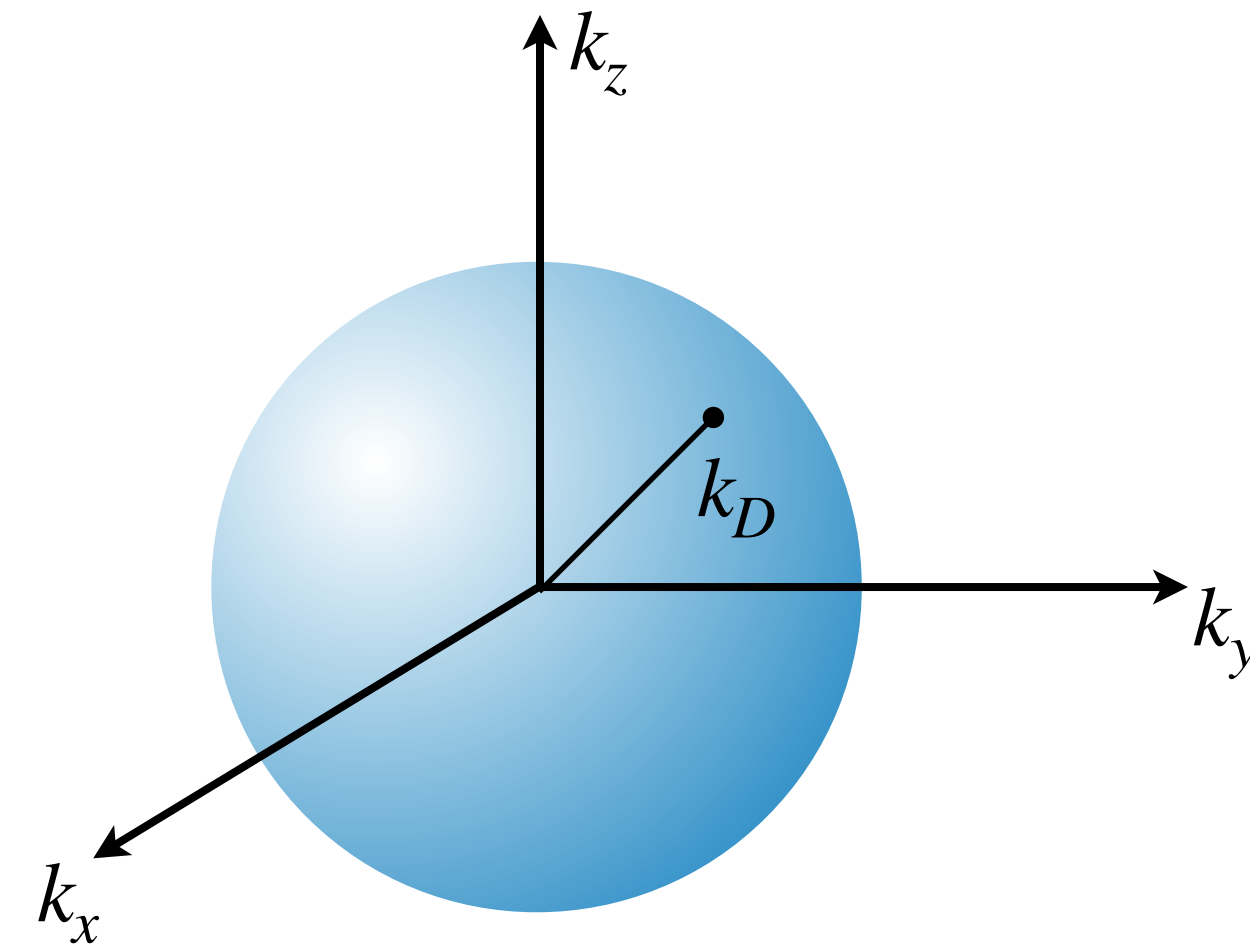
- If there are  $N$  unit cells in the solid,

the total number of acoustic phonon modes is  $N$

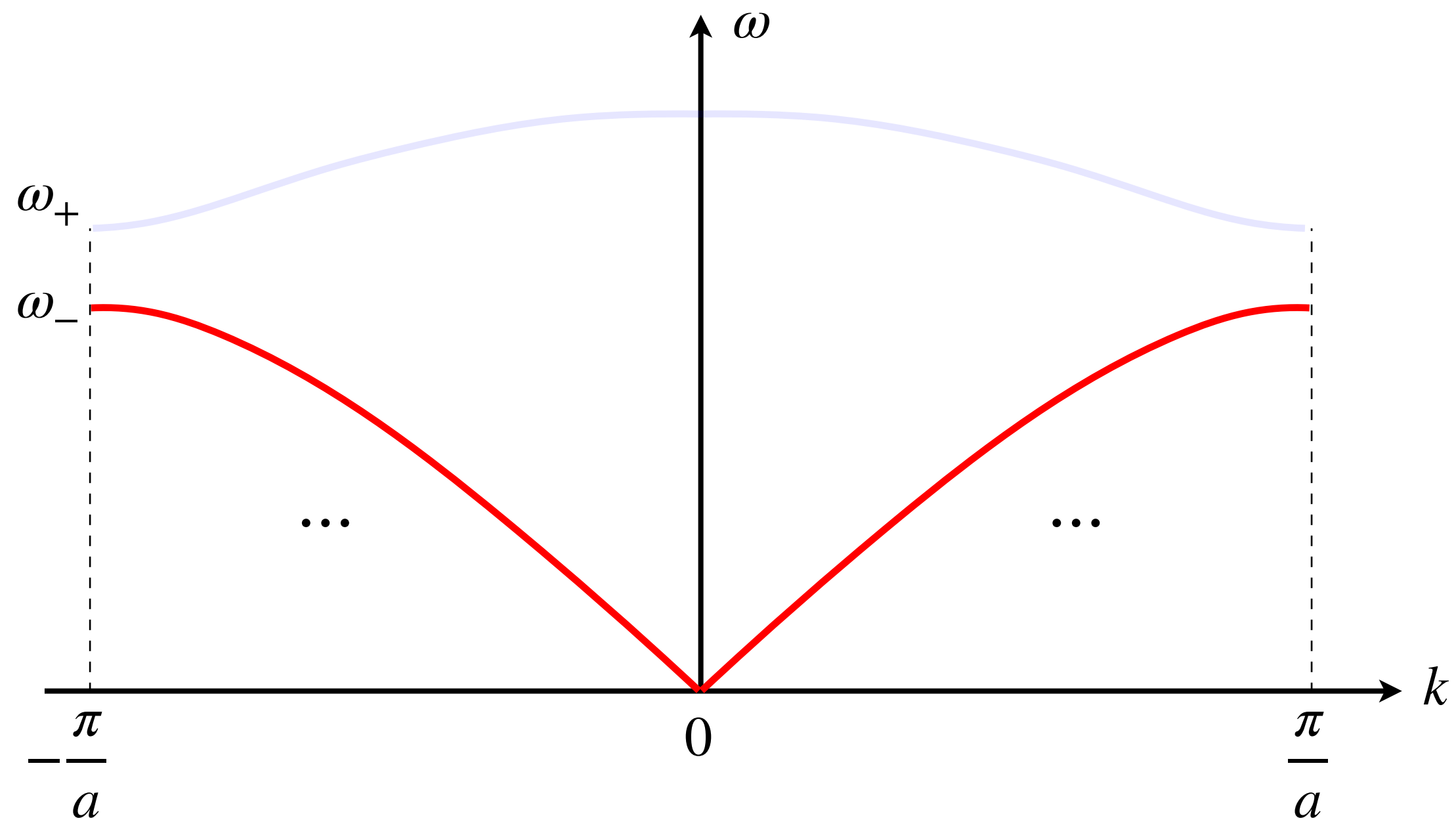
- Such  $N$  modes confined within the sphere of radius  $k_D$

$$\text{For } k < k_D : N = \frac{V}{8\pi^3} \cdot \frac{4}{3}\pi k_D^3 = \frac{V}{6\pi^2} \left( \frac{\omega_D}{v} \right)^3$$

For  $k > k_D$  : No modes are allowed!



Peter Debye  
(Netherlands)  
1884-1966



# Total phonon energy in Debye's model

- The total energy of the system:

$$U = \int d\omega D(\omega) \frac{\hbar\omega}{\exp(\hbar\omega/\tau) - 1} \rightarrow U = \int_0^{\omega_D} d\omega \left( \frac{V\omega^3}{2\pi^2v^3} \right) \frac{\hbar\omega}{\exp(\hbar\omega/\tau) - 1}$$

- $1D \rightarrow 3D$  : For simplicity, assume that the phonon velocity is independent of direction  
(i.e.,  $v_x = v_y = v_z = v$ )

$$U = \frac{3V\hbar}{2\pi^2v^3} \int_0^{\omega_D} d\omega \frac{\omega^3}{\exp(\hbar\omega/\tau) - 1} = \frac{3Vk_B^4T^4}{2\pi^2v^3\hbar^3} \int_0^{x_D} dx \frac{x^3}{e^x - 1}, \text{ where } \begin{cases} x = \frac{\hbar\omega}{k_BT} \\ x_D = \frac{\hbar\omega_D}{k_BT} \end{cases}$$

- Now, let  $\hbar\omega_D = k_BT_D$ , where  $T_D$  : Debye temperature. Then,  $U$  in terms of  $T_D$  is given by :

$$T_D = \frac{\hbar v}{k_B} \left( \frac{6\pi^2N}{V} \right)^{\frac{1}{3}} \rightarrow U = 9Nk_BT \left( \frac{T}{T_D} \right)^3 \int_0^{x_D} dx \frac{x^3}{e^x - 1}$$

## Debye's DOS

$$D(\omega) = \frac{Vk^2}{2\pi^2} \frac{1}{\frac{d\omega}{dk}} = \frac{V\omega^2}{2\pi^2v^3}$$

## Debye frequency

$$\omega_D = v \left( \frac{6\pi^2N}{V} \right)^{\frac{1}{3}}$$



# The Debye's $T^3$ law

- Heat capacity

$$U = 9Nk_B T \left( \frac{T}{T_D} \right)^3 \int_0^{x_D} dx \frac{x^3}{e^x - 1}$$

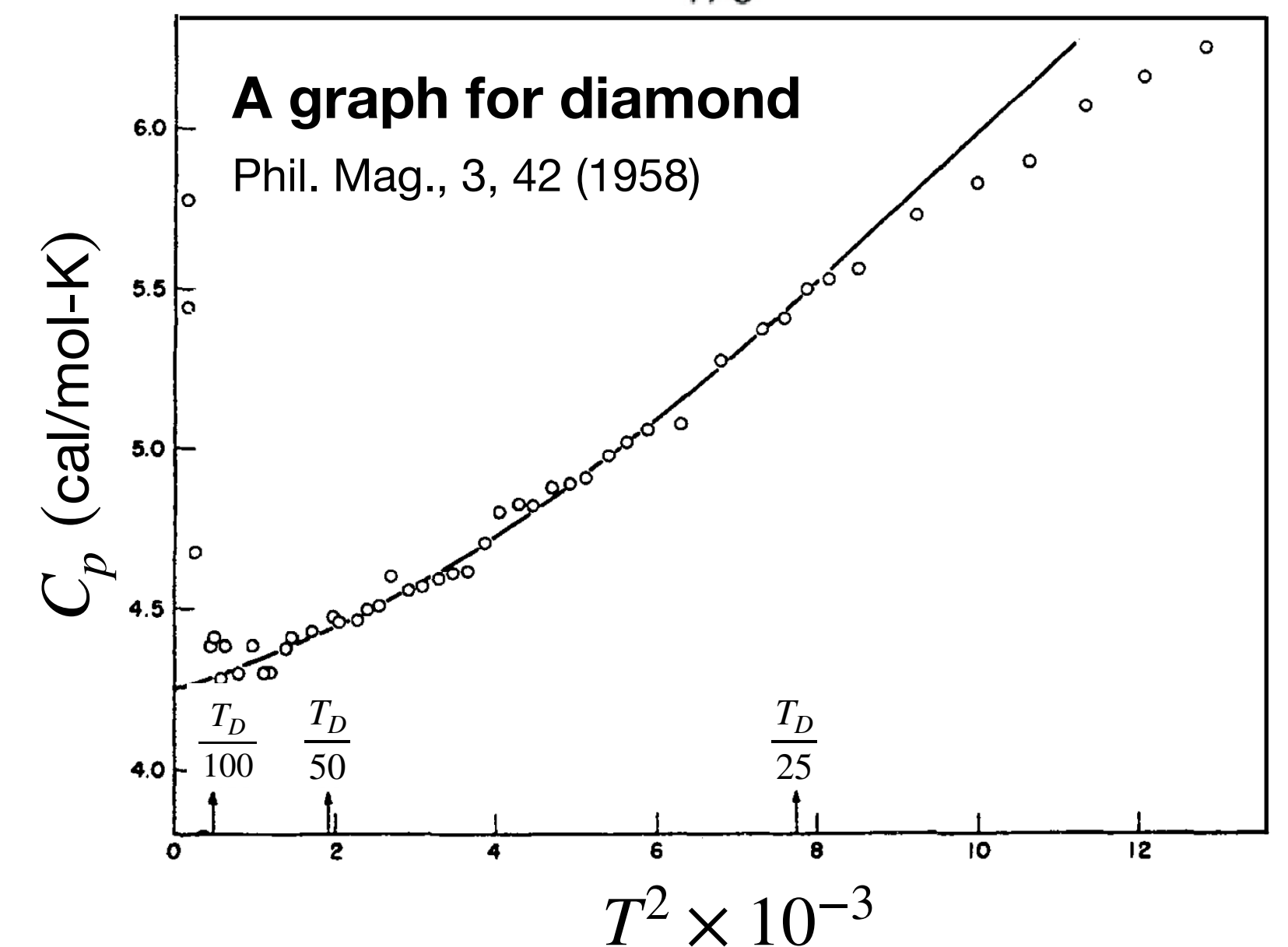
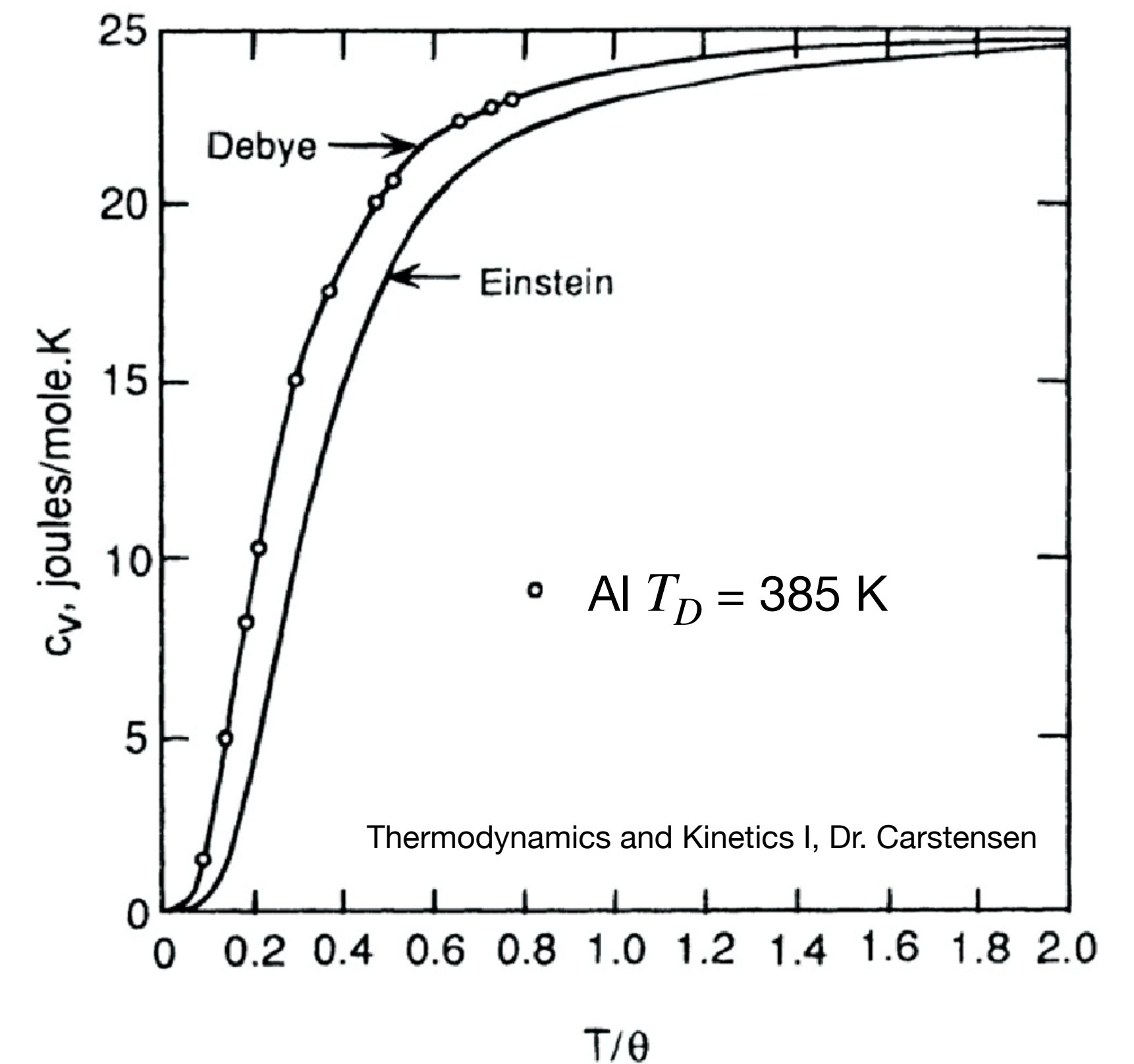
$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = 9Nk_B \left( \frac{T}{T_D} \right)^3 \int_0^{x_D} dx \frac{x^4 e^x}{(e^x - 1)^2}$$

- For  $T \gg T_D$  :  $C_V \approx 3Nk_B$

- For  $T \ll T_D$  :

$$\lim_{x_D \rightarrow \infty} \int_0^{x_D} dx \frac{x^4 e^x}{(e^x - 1)^2} = \frac{\pi^4}{15} \rightarrow C_V \approx \frac{12\pi^4}{5} Nk_B \left( \frac{T}{T_D} \right)^3$$

- At low  $T < T_D/50$  when only the acoustic modes are thermally excited, the  $T^3$  approximation is quite good!



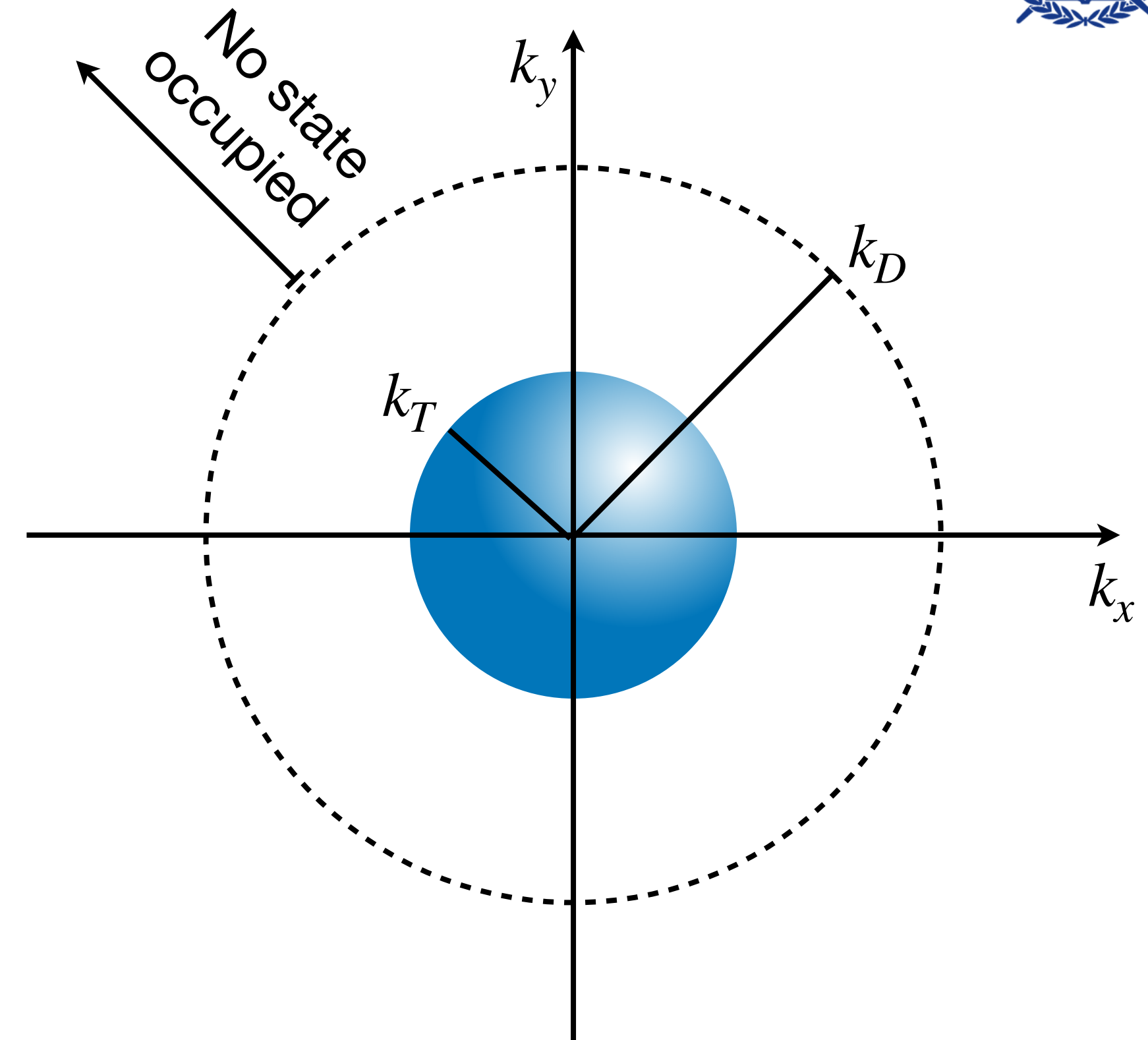
# Qualitative understanding of $T^3$ law

- Only those modes with  $\mathcal{E} = \hbar\omega < k_B T$  will be excited at low  $T$ 's
- Assume that  $\mathcal{E}$  of such modes are  $\mathcal{E} = \hbar\omega \approx k_B T$  at low  $T$ 's

$$\begin{cases} \hbar\omega_T = \hbar(vk_T) = k_B T, & k_T : \text{thermal wavevector} \\ \hbar\omega_D = \hbar(vk_D) = k_B T_D, & k_D : \text{Debye's cutoff wavevector} \end{cases}$$

- The fraction of oscillators excited at  $T \sim \left(\frac{T}{T_D}\right)^3$
- The number of excited modes (in 3D) :  $\sim 3N \left(\frac{T}{T_D}\right)^3$
- Total energy of the excited modes :  $\sim 3Nk_B T \left(\frac{T}{T_D}\right)^3$
- Heat capacity :  $C_V = \left(\frac{\partial U}{\partial T}\right)_V \sim Nk_B T \left(\frac{T}{T_D}\right)^3$

$$\text{c.f.) } C_V \approx \frac{12\pi^4}{5} Nk_B \left(\frac{T}{T_D}\right)^3$$



# Shortcomings of the Debye theory

- The introduction of the cutoff frequency ( $\omega_D = \hbar k_D$ ) is “ad hoc”  
(Although it physically makes sense)
- The failure of linear dispersion at high  $k$ —values ( $\omega \neq vk$ )
- At intermediate temperatures, the Debye’s prediction fails
- At extremely low  $T$  for metals, the Debye’s prediction fails

**The specific heat = Phonon contribution + electronic contribution**

$$C_V = \gamma T + AT^3$$

Without  $\gamma T$ , the curve ( $C_V/T$  vs.  $T^2$ ) would have intercepted the origin!

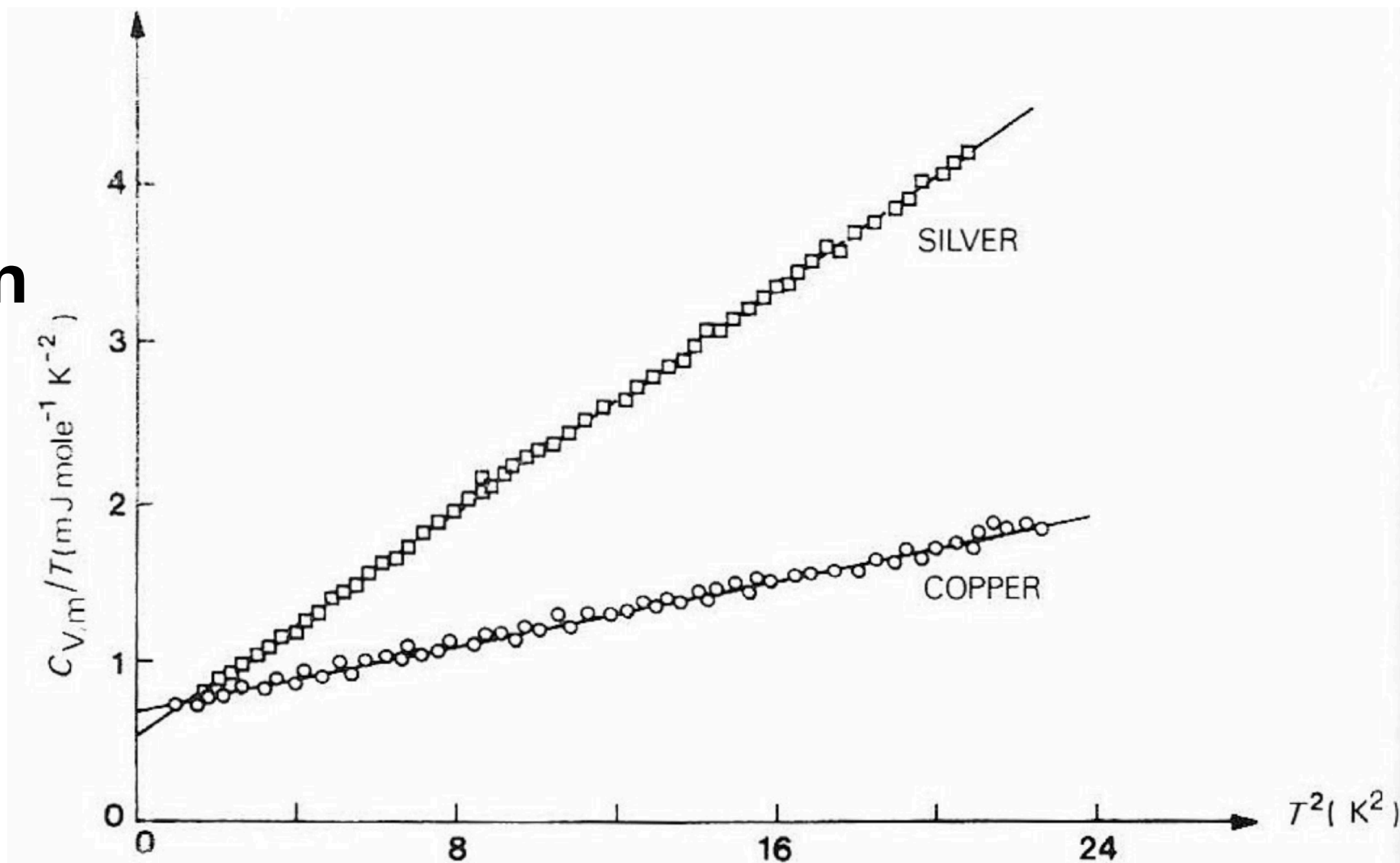
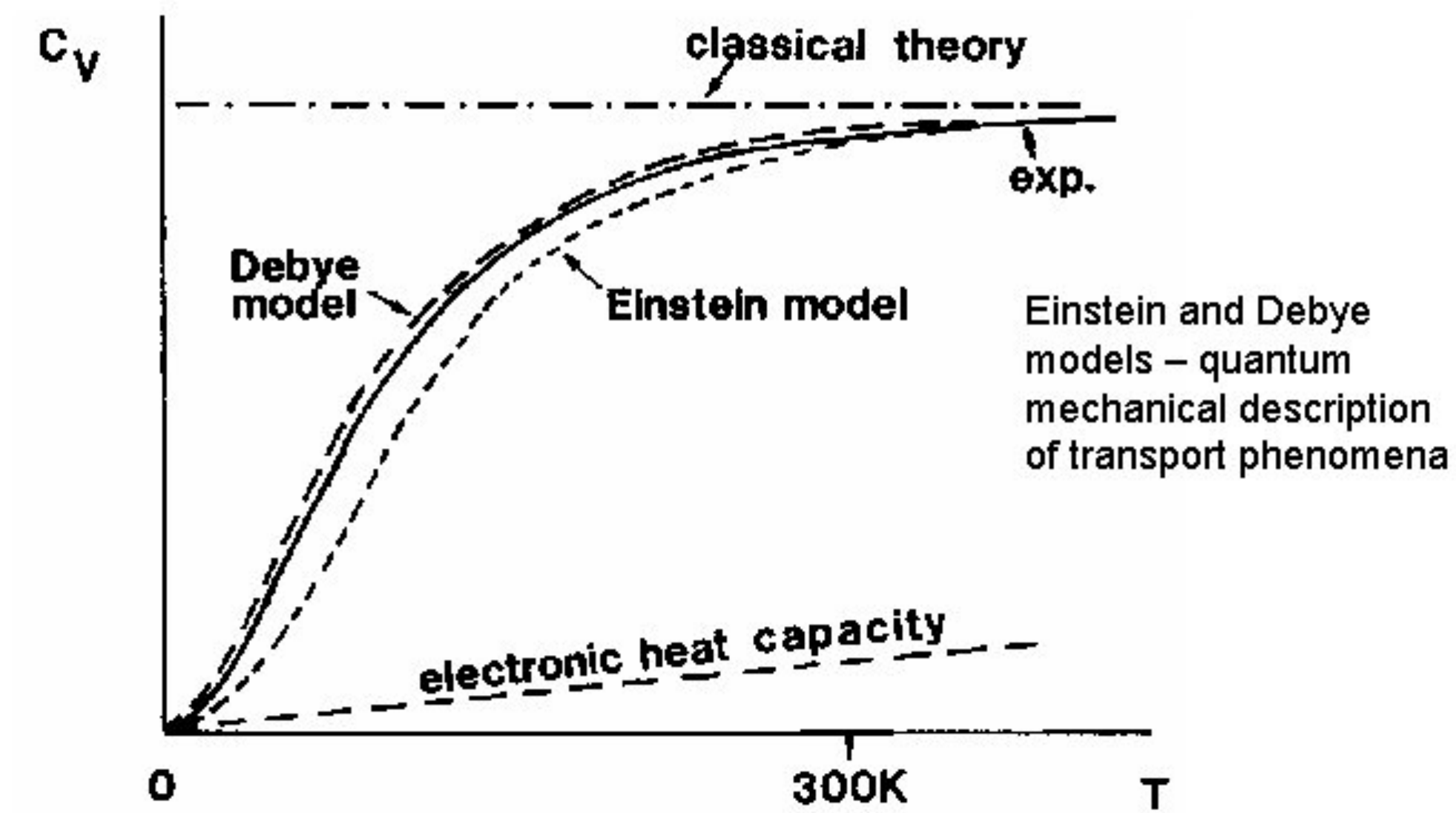


Figure 12.7—Low temperature molar heat capacity of metals;  $C_{V,m}/T$  is plotted against  $T^2$ . The results are consistent with equation (12.29), according to which  $C_{V,m}$  is equal to  $\gamma T + AT^3$ . The intercepts give the values of  $\gamma$ . The values of  $A$  can be determined from the slopes. (Reproduced with permission from *Statistical Mechanics and Properties of Matter* by E. S. R. Gopal, Ellis Horwood Ltd., Chichester.)

# Limitation of our discussion

- The theory of crystal vibrations so far...
  - Limited in the potential energy to terms quadratic in the interatomic spacing (i.e., harmonic potential)

$$F = -\kappa x \rightarrow U = -\frac{1}{2}\kappa x^2$$

- Consequences
  - Two lattice waves do not interact; A single wave do not decay or change its form with time
  - No thermal expansion considered
  - Adiabatic & isothermal elastic constants ( $\kappa$ ) are equal
  - The elastic constants are independent of pressure and temperature
  - The heat capacity becomes constant at high  $T > T_D$
- In real crystals none of these consequences is accurately satisfied!

***(Further reading : Kittel, Chap. 5, pp. 120-128)***