

# Mineral Physics I

## Chapter 3. Lattice vibration

### Section 7. Debye model

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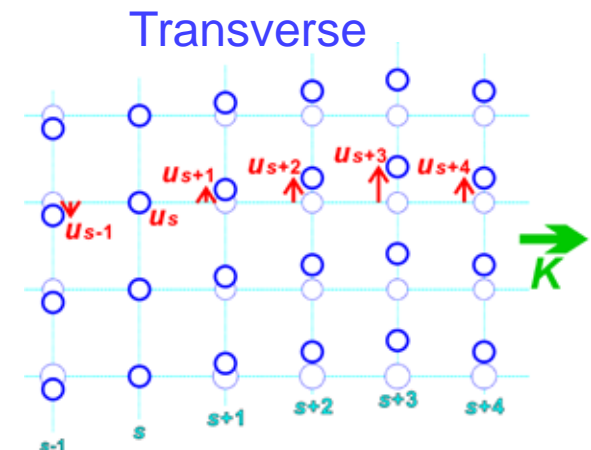
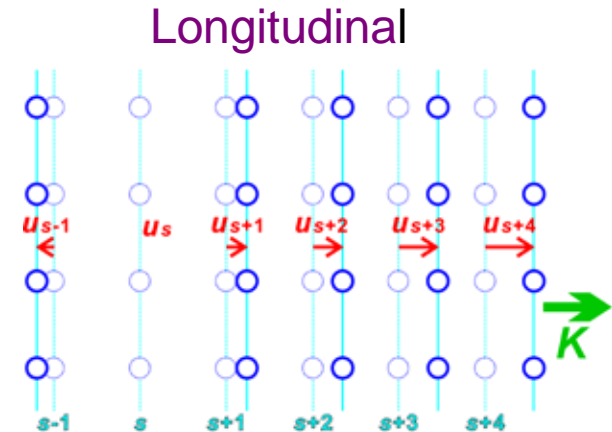
# Debye model

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- q A model of lattice vibration to consider the **frequency dependence** of the **number of modes** as a function of temperature
  - ü **Mode**: any of patterns of lattice waves in a crystal
  - Ø At low  $T$ : the limited number of modes are excited
  - Ø At high  $T$ : all available modes are excited
  - ü The number of modes was constant in the Einstein model

# Longitudinal and transverse waves

- q Lattice vibration: in general propagates in any direction
  - ∅ Propagation direction: expressed using a wave vector  $\vec{K}$
  - ∅ Displacement of an atom from its equilibrium position:  $\vec{u}$
  - ∅ Longitudinal wave:  $\vec{u} \parallel \vec{K}$ 
    - ü P-wave, compressional wave
  - ∅ Transverse wave:  $\vec{u} \perp \vec{K}$ 
    - ü Two directions of oscillation (polarity)
    - ü S-wave, shear wave



# The number of modes in 1D crystals

q How many modes in  $N$ -atom 1D-crystal?

∅ Dimension of the crystal,  $L$ :

$$\ddot{L} = (N - 1)a \approx Na, \quad (a: \text{interval of atoms})$$

∅ Wave length,  $\lambda$ :

$$\ddot{\lambda}_{\max} = L = Na, \quad \frac{L}{2} = \frac{Na}{2}, \dots, \lambda_{\min} = 2a = \frac{Na}{N/2} = \frac{L}{N/2}$$

∅ Angular wave number,  $k$ :

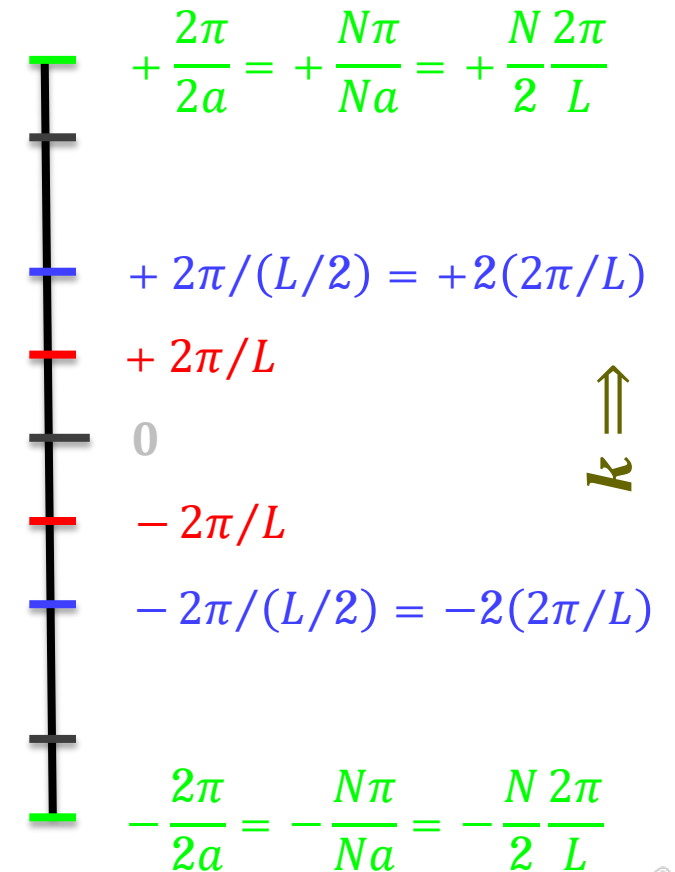
$$\ddot{k}_{\min} = \pm \frac{2\pi}{L}, \pm \frac{2\pi}{(L/2)} = \pm 2 \frac{2\pi}{L}, \pm 3 \frac{2\pi}{L}, \dots, k_{\max} = \pm \frac{2\pi}{2a} = \pm \frac{N 2\pi}{2 Na} = \pm \frac{N 2\pi}{2 L}$$

aligned in the constant interval  $\frac{2\pi}{L}$

∅  $k$  is limited in a discrete lattice!

§ The number of modes:  $2 \times \frac{N}{2} = N$

∅ number of modes = number of atoms



# Density of states in 1D lattice

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q Density of state: the number of modes,  $n_m$ , at a given  $\omega$

$$\emptyset D(\omega)d\omega = \frac{dn_m}{d\omega} d\omega = \frac{dn_m}{dk} \frac{dk}{d\omega} d\omega \quad (3.7.1)$$

q (The number of modes per unit  $k$ ) =  $1 /$  (the interval in  $k$  space)

$$\emptyset \frac{dn_m}{dk} = \frac{1}{dk/dn_m} = \frac{1}{2\pi/L} = \frac{L}{2\pi} \quad (3.7.2)$$

q Assuming a linear relation of  $\omega$  to  $k$ , in the majority of the  $k$  space

$$\emptyset \omega = \sqrt{4C/m} \sin(ka/2) \cong \sqrt{4C/m} ka/2 = \sqrt{C/m} ak \quad (3.7.3)$$

$$\emptyset \text{ Group velocity: } v_g = d\omega/dk \cong \omega/k = \sqrt{C/m} a = v_p \quad (3.7.4)$$

$$\emptyset \frac{dk}{d\omega} = \frac{1}{d\omega/dk} = \frac{1}{v_g} \cong \frac{1}{v_p} = \frac{1}{\sqrt{C/ma}}$$

q The density of state in the 1D lattice is

$$\emptyset D(\omega) = \frac{dn_m}{dk} \frac{dk}{d\omega} = \frac{L}{2\pi} \frac{1}{v_g} \cong \frac{L}{2\pi} \frac{1}{v_p} = \frac{L}{2\pi} \frac{1}{\sqrt{C/ma}} = \text{constant, independent of } \omega \quad (3.7.5)$$



# Density of state in 3D crystals - 1

q Consider the density of states in a 3D  $k$ -space (i.e., reciprocal lattice)

∅  $k$ -points: aligned with a  $2\pi/L$  interval

∅ one  $k$ -point every cubic space of  $(2\pi/L)^3$

$$\dot{\cup} (2\pi/L)^3 = 8\pi^3/L^3 = 8\pi^3/V$$

q The number of mode  $n_m$  with  $|k| \leq k_{\max}$

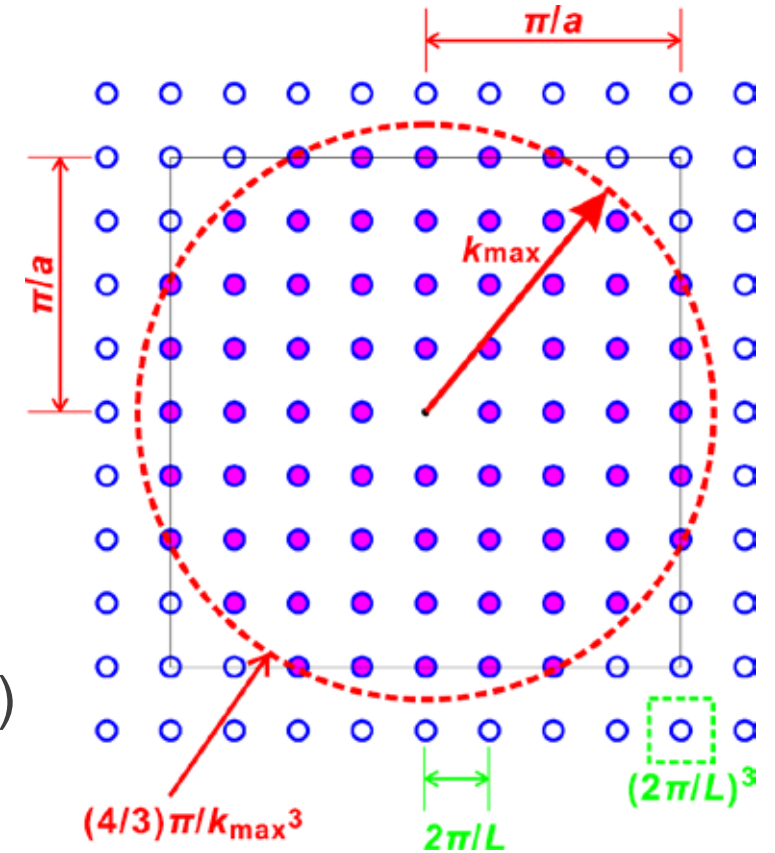
∅ The  $k$ -points within the  $k_{\max}$  sphere

$$\dot{\cup} V_{k \leq k_{\max}} = (4/3)\pi k_{\max}^3$$

$$\dot{\cup} n_m = \left( (4/3)\pi k_{\max}^3 \right) / \left( 8\pi^3/V \right) = V k_{\max}^3 / 6\pi^2 \quad (3.7.6)$$

∅ larger crystal  $V \rightarrow$  more  $n_m$

∅ smaller  $a \rightarrow$  larger  $k \rightarrow$  more  $n_m$



## Density of state in 3D crystals -2

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q Density of states in a 3D crystal with assumption of  $v_g \approx v_p$

$$\text{Ø } D(\omega) = \frac{dn_m}{d\omega} = \frac{dn_m}{dk} \frac{dk}{d\omega} = \frac{d}{dk} \left( \frac{Vk^3}{6\pi^2} \right) \frac{1}{v_g} = \frac{Vk^2}{2\pi^2 v_g} \approx \frac{V(\omega/v_p)^2}{2\pi^2 v_p} = \frac{V\omega^2}{2\pi^2 v_p^3} \quad (3.7.7)$$

$$\text{ü } D(\omega) \propto \omega^2$$

$$\text{§ 1D crystal: } D(\omega) = \frac{dn_m}{dk} \frac{dk}{d\omega} = \frac{L}{2\pi} \frac{1}{v_p}$$

◦ Independent from  $\omega$

q Sum of density of states for **one longitudinal**, **two transverse waves**:

$$\text{Ø } D(\omega) = \frac{1V\omega^2}{2v_L^3\pi^2} + \frac{2V\omega^2}{2v_T^3\pi^2} = \frac{3V\omega^2}{2v_D^3\pi^2} \quad (3.7.8)$$

ü  $v_L$ : the velocity of the longitudinal wave,  $v_T$ : the velocity of the **transverse waves**

$$\text{ü Debye velocity: } \frac{3}{v_D^3} \equiv \frac{1}{v_L^3} + \frac{2}{v_T^3} \quad (3.7.9).$$



# Total energy of lattice vibration - Debye model

q Section 5 à the energy of the lattice vibration

$$\emptyset E_{vib} = \int D(\omega) \frac{\hbar\omega}{\exp(\hbar\omega/k_B T) - 1} d\omega \quad (3.5.6)$$

q By substituting the density of states,  $D(\omega)$ ,  
obtained as Eq. (3.7.9)  $D(\omega) = \frac{3V\omega^2}{2v_D^3\pi^2}$  to Eq. (3.5.6)

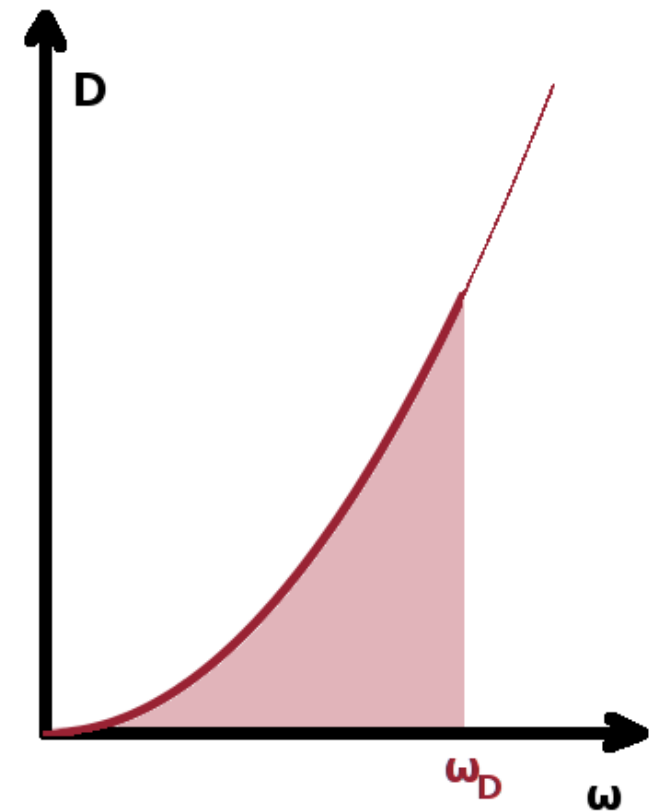
$$\emptyset E_{vib} = \int_0^{\omega_D} \frac{3V\omega^2}{2v_D^3\pi^2} \frac{\hbar\omega d\omega}{\exp(\hbar\omega/k_B T) - 1} \quad (3.7.10)$$

## ü Debye model

Ø The upper bound of the integration: not  $\infty$  but  $\omega_D$

ü  $\omega_D = v_D k_{max}$ : **Debye (cut-off) frequency**

§ The maximum  $\omega$  in a lattice due to discreteness of atoms





# Simpler formula of the Debye model -1

q (The number of modes with  $k < k_{\max}$ ) = (the number of atoms,  $N$ ).  
From Eq. (3.7.6)

$$\text{Ø } N = n_m = \frac{V k_{\max}^3}{6\pi^2} = \frac{V \omega_D^3}{6\pi^2 v_D^3} \quad \text{à} \quad \omega_D = v_D \sqrt[3]{\frac{6\pi^2 N}{V}} \quad (3.7.11)$$

q Define  $x = \frac{\hbar\omega}{k_B T}$  à  $\omega = \frac{k_B T x}{\hbar}$  (3.7.12)

ü for (3.7.10)  $E_{vib} = \int_0^{\omega_D} \frac{3V\omega^2}{2v_D^3\pi^2} \frac{\hbar\omega d\omega}{\exp(\hbar\omega/k_B T) - 1}$

$$\text{Ø } \omega_D \quad \text{à} \quad x_D = \frac{\hbar\omega_D}{k_B T} = \frac{\hbar\omega_D}{k_B} \frac{1}{T} = \frac{\Theta_D}{T},$$

$$\text{ü } \Theta_D \equiv \frac{\hbar\omega_D}{k_B} \quad (3.7.13)$$

§  $\Theta_D$ : Debye temperature



## Simpler formula of the Debye model -2

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$$\omega = \frac{k_B T}{\hbar} x, \quad d\omega = \frac{k_B T}{\hbar} dx, \quad x_D = \frac{\hbar \omega_D}{k_B T}$$

q The total energy of the lattice vibration,  $E_{\text{vib}}$ , from (3.7.10)

$$\begin{aligned} \emptyset E_{\text{vib}} &= \int_0^{\omega_D} \frac{3V\omega^2}{2v_D^3\pi^2} \frac{\hbar\omega d\omega}{\exp(\hbar\omega/k_B T) - 1} = \int_0^{x_D} \frac{3V\left(\frac{k_B T}{\hbar}x\right)^2}{2v_D^3\pi^2} \frac{\hbar\frac{k_B T}{\hbar}x\frac{k_B T}{\hbar}dx}{\exp\left(\hbar\frac{k_B T}{\hbar}x/k_B T\right) - 1} \\ &= \frac{3Vk_B^4 T^4}{2\pi^2 v_D^3 \hbar^3} \int_0^{\Theta_D/T} \frac{x^4 dx}{\exp(x) - 1} \end{aligned} \quad (3.7.14)$$

$$\S x_D = \frac{\Theta_D}{T}, \quad \Theta_D = \frac{\hbar\omega_D}{k_B}$$



# Debye temperature -1

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q Debye temperature:

$$\Theta_D = \frac{\hbar\omega_D}{k_B} = \frac{\hbar}{k_B} v_D \sqrt[3]{\frac{6\pi^2 N}{V}} = \frac{\hbar v_D}{k_B} \sqrt[3]{\frac{6\pi^2 N}{V}} \quad (3.7.15)$$

$$\circ (3.7.11) \quad \omega_D = v_D \sqrt[3]{\frac{6\pi^2 N}{V}}$$

ü At low  $T$ , low  $\omega$  states, i.e. low  $E$  states, are filled, but high  $\omega$  states are not excited.

ü Higher  $\omega$  states are filled with increasing  $T$

§ However, there is the limitation of frequency,  $\omega_D$

ü At  $\Theta_D$ , the excited  $\omega$  reaches  $\omega_D$

ü Above  $\Theta_D$ , all modes of lattice vibration are excited.



# Debye temperature -2

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q Debye temperature: material constant

$$\Theta_D = \frac{\hbar\omega_D}{k_B} = \frac{\hbar v_D}{k_B} \sqrt[3]{\frac{6\pi^2 N}{V}}$$

ü Two parameters intrinsic for materials:  $v_D$  and  $\frac{N}{V}$

ü Sound velocity: high  $v_D \Rightarrow$  high  $\Theta_D$

ü Lattice spacing  $a = \sqrt[3]{\frac{V}{N}}$ ,  $\frac{N}{V} = \frac{1}{a^3}$ : smaller  $a$  (denser phase)  $\Rightarrow$  higher  $\Theta_D$

ü Allowing normalization of the  $T$ -dependence of the vibrational properties of different velocity and density

§ Plotting against  $T/\Theta_D$



# Debye heat capacity -1

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q The density of state of the Debye model  $D(\omega) = \frac{3V\omega^2}{2v_D^3\pi^2}$  is applied to the expression of

heat capacity (3.7.14) 
$$C_{\text{vib}} = \int D(\omega) \frac{\hbar^2 \omega^2 \exp(\hbar\omega/k_B T)}{k_B T^2 (\exp(\hbar\omega/k_B T) - 1)^2} d\omega$$

$$\begin{aligned} \text{Ø } C_{\text{vib}} &= \int_0^{\omega_D} \frac{3V\omega^2}{2v_D^3\pi^2} \frac{\hbar^2 \omega^2 \exp(\hbar\omega/k_B T)}{k_B T^2 (\exp(\hbar\omega/k_B T) - 1)^2} d\omega \\ &= \frac{3V\hbar^2}{2\pi^2 v_D^3 k_B T^2} \int_0^{\omega_D} \frac{\omega^4 \exp(\hbar\omega/k_B T)}{(\exp(\hbar\omega/k_B T) - 1)^2} d\omega \quad (3.7.16) \end{aligned}$$

q By applying the variable,  $x$  by  $\omega = \frac{k_B T x}{\hbar}$  to (3.7.16), we have

$$\text{Ø } C_{\text{vib}} = \frac{3V\hbar^2}{2\pi^2 v_D^3 k_B T^2} \int_0^{x_D} \frac{\left(\frac{k_B T}{\hbar}\right)^5 x^4 \exp(x)}{(\exp(x) - 1)^2} dx \quad (3.7.17)$$



# Debye heat capacity -2

$$q \quad C_{\text{vib}} = \frac{3V\hbar^2}{2\pi^2 v_D^3 k_B T^2} \int_0^{x_D} \frac{\left(\frac{k_B T}{\hbar}\right)^5 x^4 \exp(x)}{(\exp(x)-1)^2} dx = \frac{9Nk_B}{6\pi^2} \frac{1}{N/V} \left(\frac{k_B T}{\hbar v_D}\right)^3 \int_0^{x_D} \frac{x^4 \exp(x)}{(\exp(x)-1)^2} dx$$

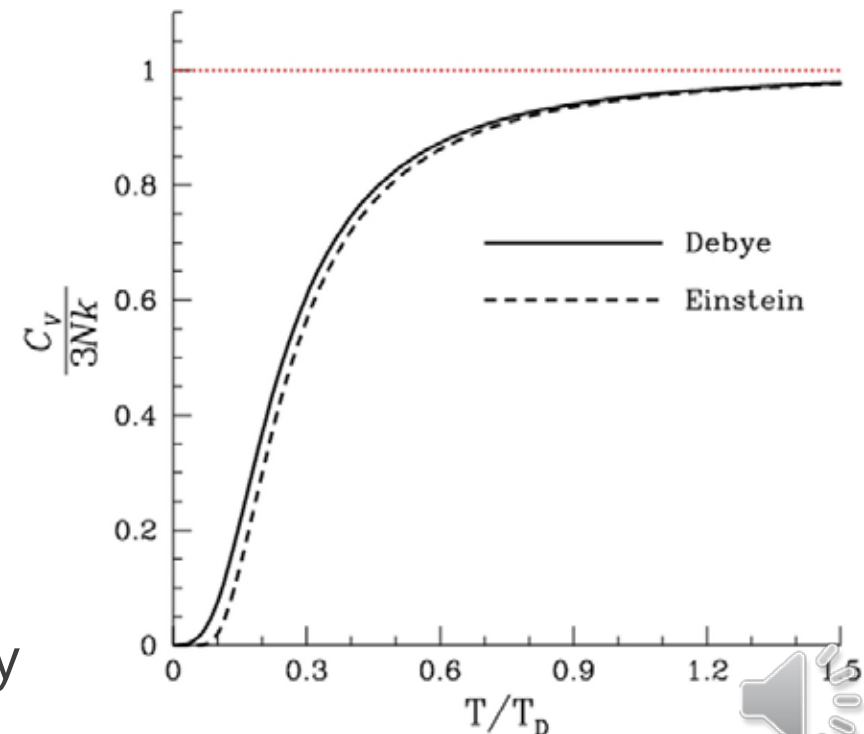
$$= 9Nk_B \left( \frac{k_B T}{\hbar v_D \sqrt[3]{\frac{6\pi^2 N}{V}}} \right)^3 \int_0^{x_D} \frac{x^4 \exp(x)}{(\exp(x)-1)^2} dx$$

$$= \frac{9Nk_B}{x_D^3} \int_0^{x_D} \frac{x^4 \exp(x)}{(\exp(x)-1)^2} dx \quad (3.7.18)$$

$$= 9Nk_B \left( \frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^4 \exp(x)}{(\exp(x)-1)^2} dx \quad (3.7.18')$$

ü Debye heat capacity

§ Higher at lower  $T$  than the Einstein heat capacity



# High $T$ limits of Debye heat capacity

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q HT Limit:  $T \rightarrow \infty$

$$\emptyset x = \hbar\omega/k_B T \rightarrow 0$$

$$\emptyset \exp(x) \rightarrow 1 + x \rightarrow 1, \exp(x) - 1 \rightarrow 1 + x - 1 \rightarrow x$$

$\emptyset$  From (3.7.18)

$$\frac{1}{x_D^3} \int_0^{x_D} \frac{x^4 \exp(x)}{(\exp(x)-1)^2} dx \rightarrow \frac{1}{x_D^3} \int_0^{x_D} \frac{x^4 \cdot 1}{x^2} dx = \frac{1}{x_D^3} \int_0^{x_D} x^2 dx \rightarrow \frac{1}{3} \quad (3.7.19)$$

$$x_D = \hbar\omega_D/k_B T = \Theta_D/T$$

$$\emptyset C_{\text{vib}} = \frac{9Nk_B}{x_D^3} \int_0^{x_D} \frac{x^4 \exp(x)}{(\exp(x)-1)^2} dx \rightarrow 9Nk_B \times \frac{1}{3} \rightarrow 3Nk_B \quad (3.7.20)$$

ü Dulong-Petit law

$\emptyset C_{\text{vib}}$  at HT: nearly constant of  $3Nk_B$  because all modes are excited



# Low $T$ limits of Debye heat capacity

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q LT Limit:  $T \rightarrow 0$

$$\emptyset \quad x_D = \frac{\hbar\omega_D}{k_B T} = \frac{\theta_D}{T} \xrightarrow{T \rightarrow 0} \infty \quad \text{è} \quad \int_0^{x_D} \frac{x^4 \exp(x)}{(\exp(x)-1)^2} dx \xrightarrow{x_D \rightarrow \infty} \frac{\pi^4}{15} \quad (3.7.21)$$

$$\emptyset \quad C_{\text{vib}} = \frac{9Nk_B}{x_D^3} \int_0^{x_D} \frac{x^4 \exp(x)}{(\exp(x)-1)^2} dx \xrightarrow{T \rightarrow 0} 9Nk_B \left(\frac{T}{\theta_D}\right)^3 \frac{\pi^4}{15} = \frac{3}{5} Nk_B \pi^4 \left(\frac{T}{\theta_D}\right)^3 \quad (3.7.22)$$

ü Heat capacity proportional to  $T^3$  at low  $T$

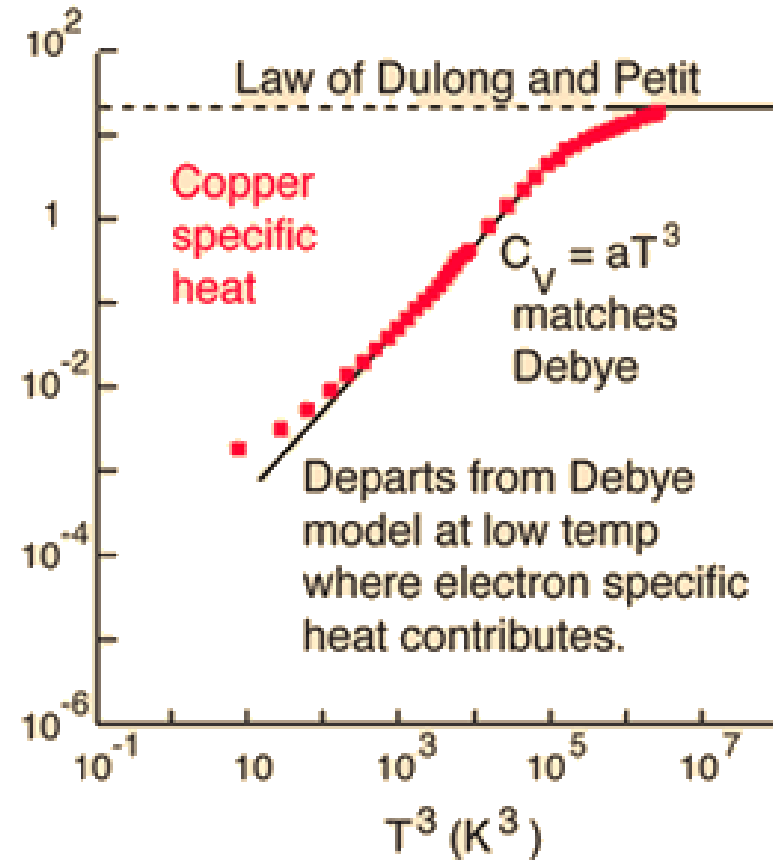
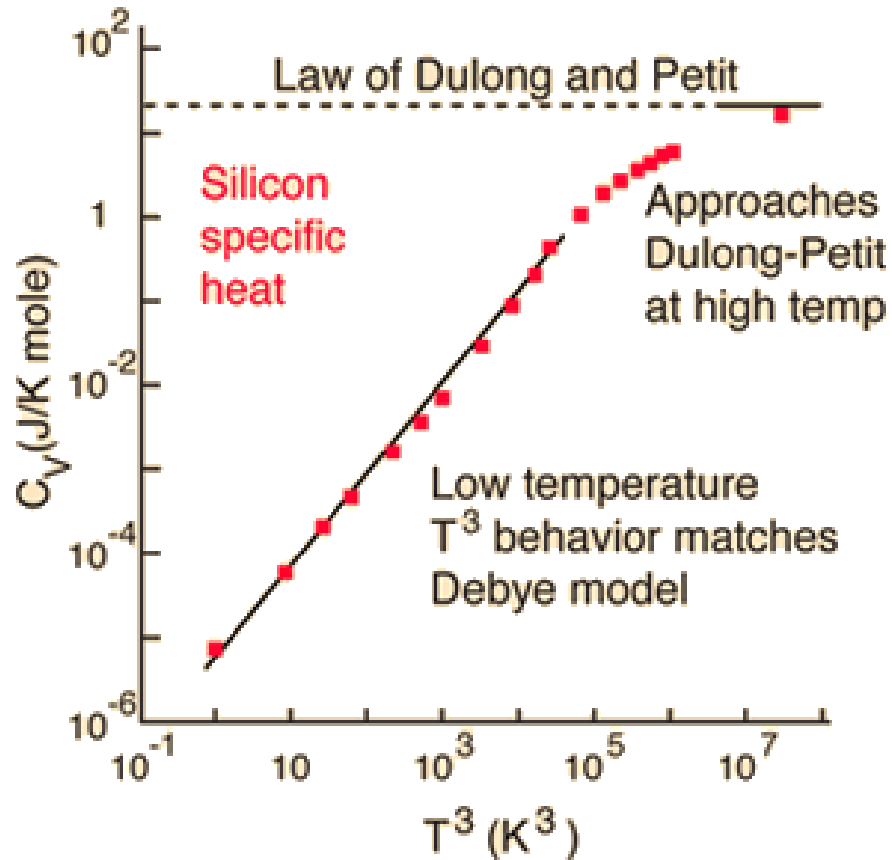
Ø The Debye  $T^3$  law, because the lattice is 3D

ü The mode increase in the three directions with increase  $T$





# Debye $T^3$ law



after Rohlf



# Comparison of the Debye and Einstein models -1

q Debye Model

$$\emptyset C_V = \frac{9Nk_B}{x_D^3} \int_0^{x_D} \frac{x^4 \exp(x)}{(\exp(x)-1)^2} dx \quad (3.7.18)$$

q Einstein Model

$$\emptyset C_V = 3Nk_B \left(\frac{T_\alpha}{T}\right)^2 \frac{\exp(T_\alpha/T)}{[\exp(T_\alpha/T)-1]^2} \quad (3.5.14)$$

q The Debye model provides higher  $C_V$  at lower  $T$

∅ Einstein model:

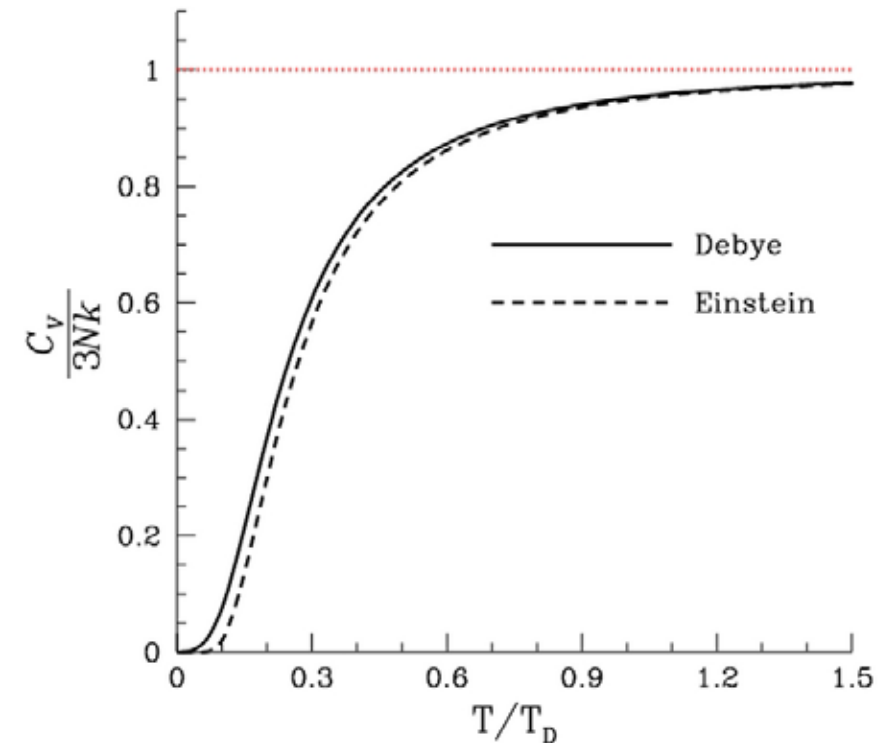
ü Presence of only one frequency

§ Difficult to excite at low temperatures

∅ Debye model:

ü Lattice vibration frequency starts from almost zero

§ Easy to excite even at low temperatures



# Comparison of the Debye and Einstein models -2

q Cu

ü Debye  $T$ : 343 K

§  $\omega \leq \omega_D = 4.5 \times 10^{13}$  Hz

ü Einstein  $T$ : 240 K

§  $\omega = \omega_\alpha = 3.1 \times 10^{13}$  Hz

◦ One frequency

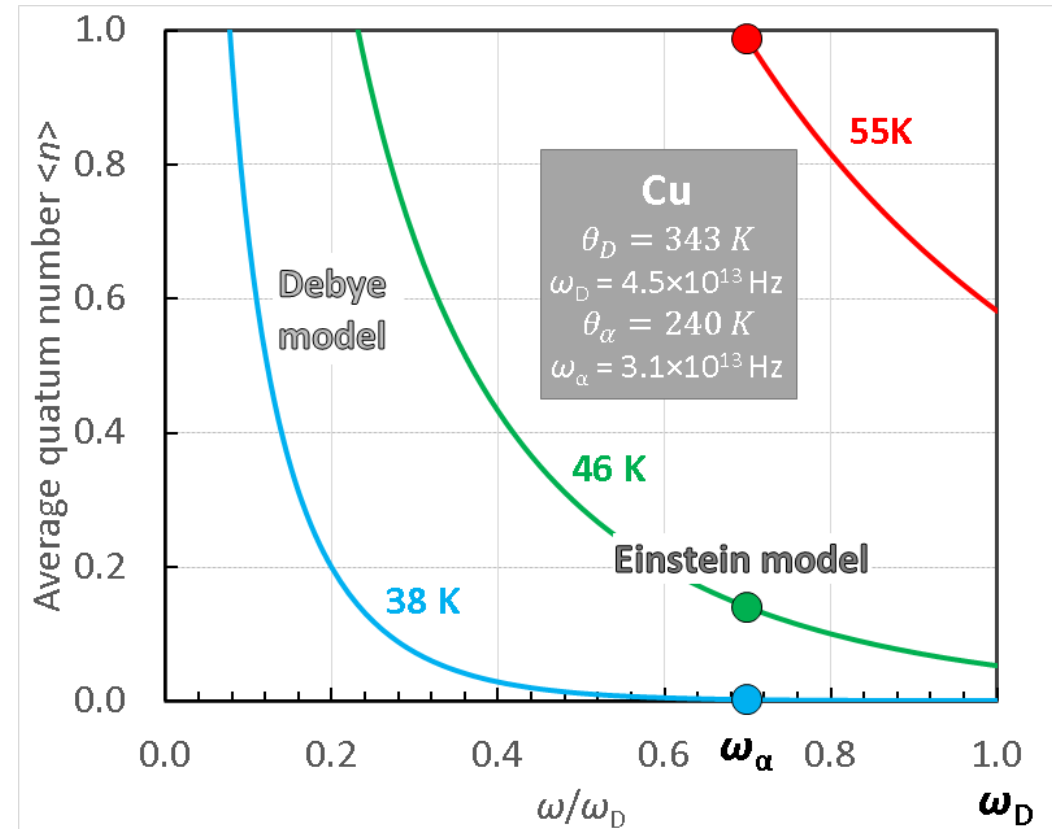
∅ Comparison of quantum number  $\langle n \rangle$

ü At low  $T$ :

§  $\langle n \rangle \approx 0$  in the Einstein model

◦ very low  $C_V$  at low  $T$

§  $\langle n \rangle$ : very large at small  $\omega$



# Comparison of the Debye and Einstein models -2

q Cu

ü Debye  $T$ : 343 K

§  $\omega \leq \omega_D = 4.5 \times 10^{13}$  Hz

ü Einstein  $T$ : 240 K

§  $\omega = \omega_\alpha = 3.1 \times 10^{13}$  Hz

q Number of modes:  $D(\omega)\langle n \rangle d\omega$

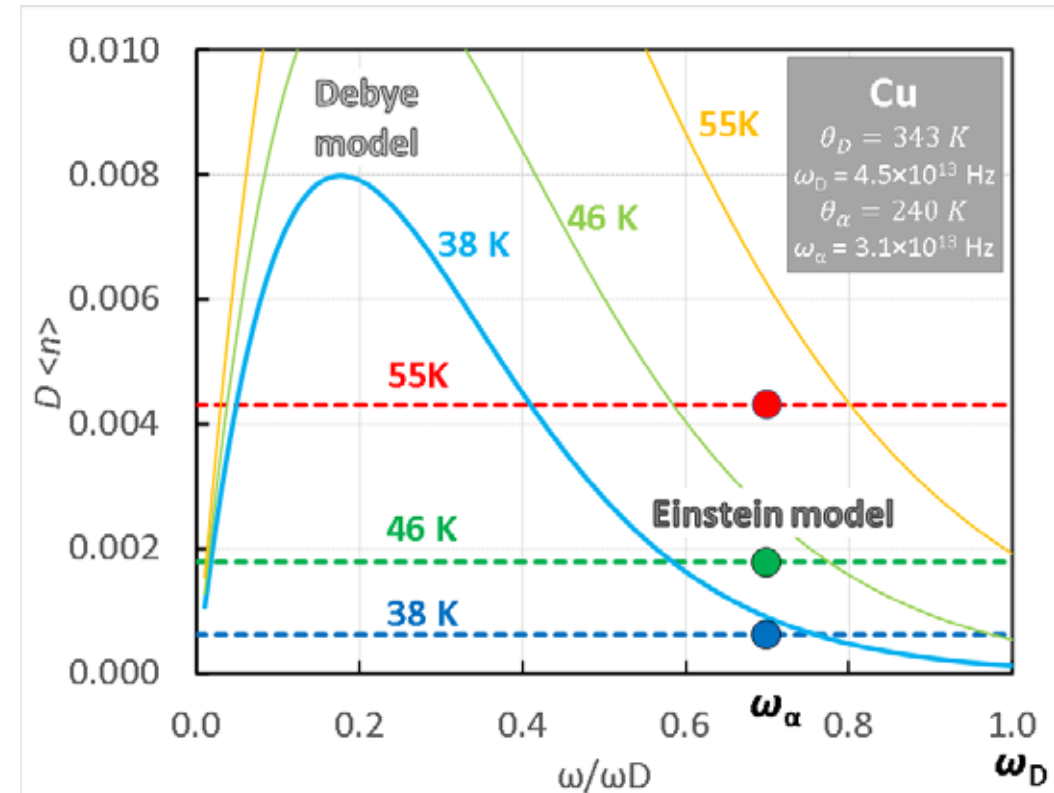
Ø Debye model  $D(\omega) \propto \omega^2$

ü Regions lower than the solid curves

Ø Einstein model  $D(\omega) = \text{const.}$

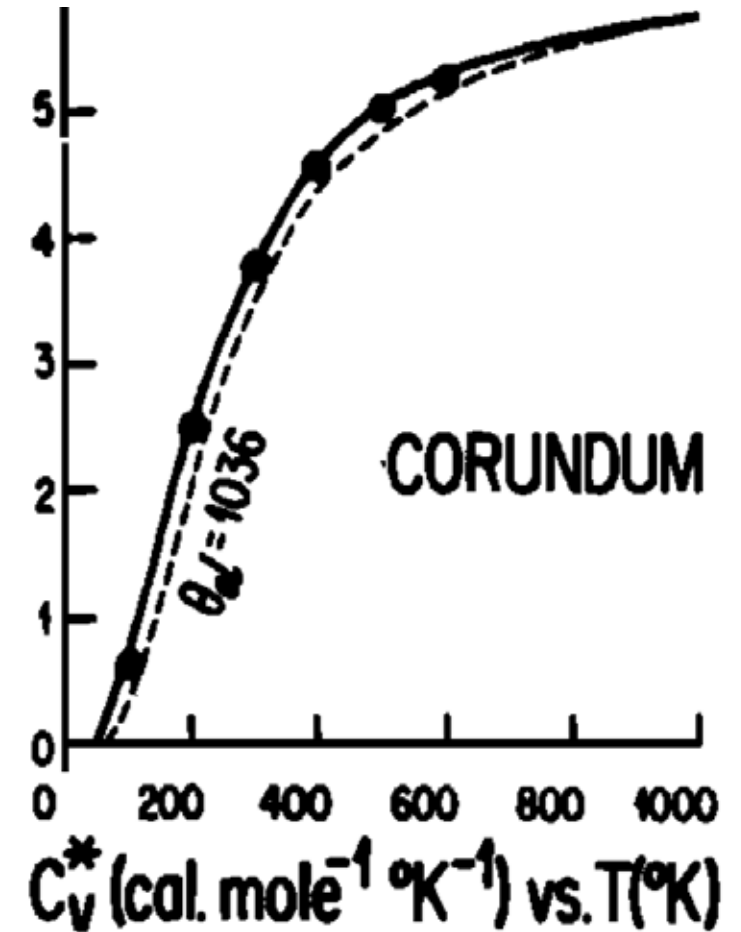
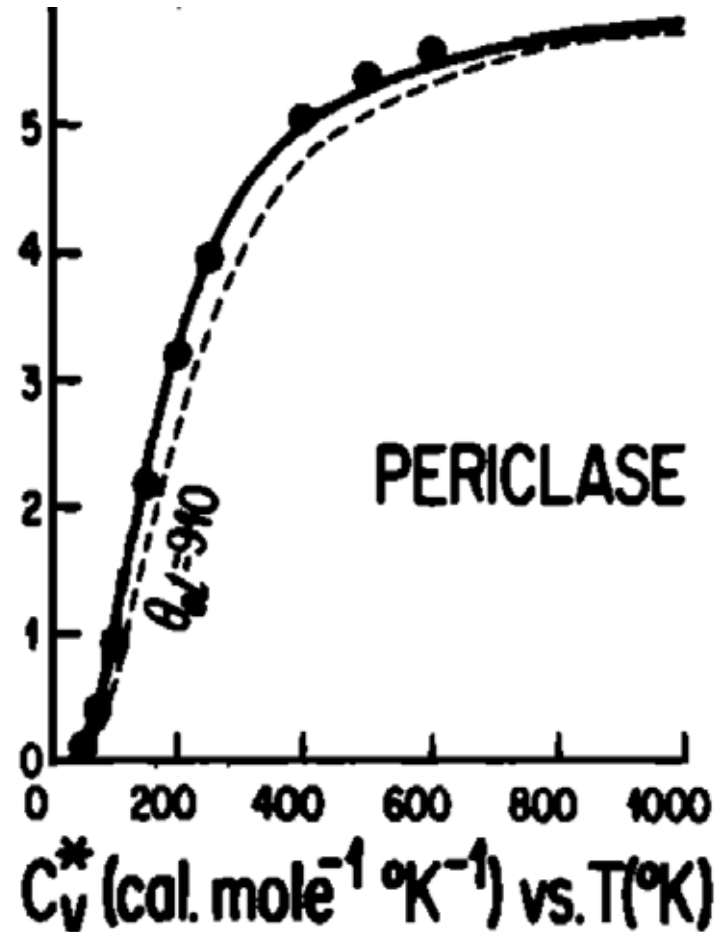
ü Regions lower than the broken lines

Ø The number of modes in the Einstein model is much smaller than the Debye model at low  $T$ .



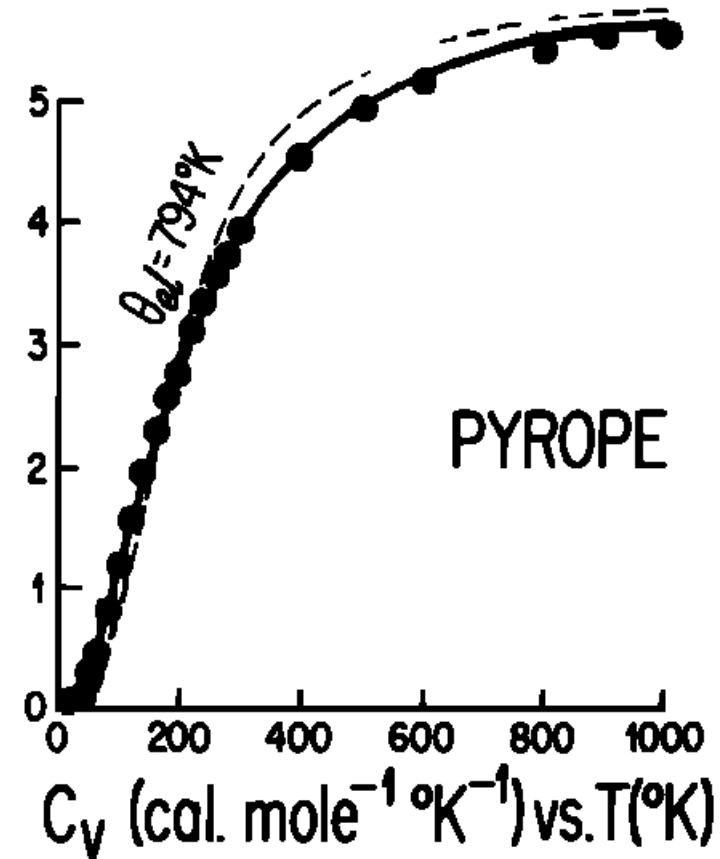
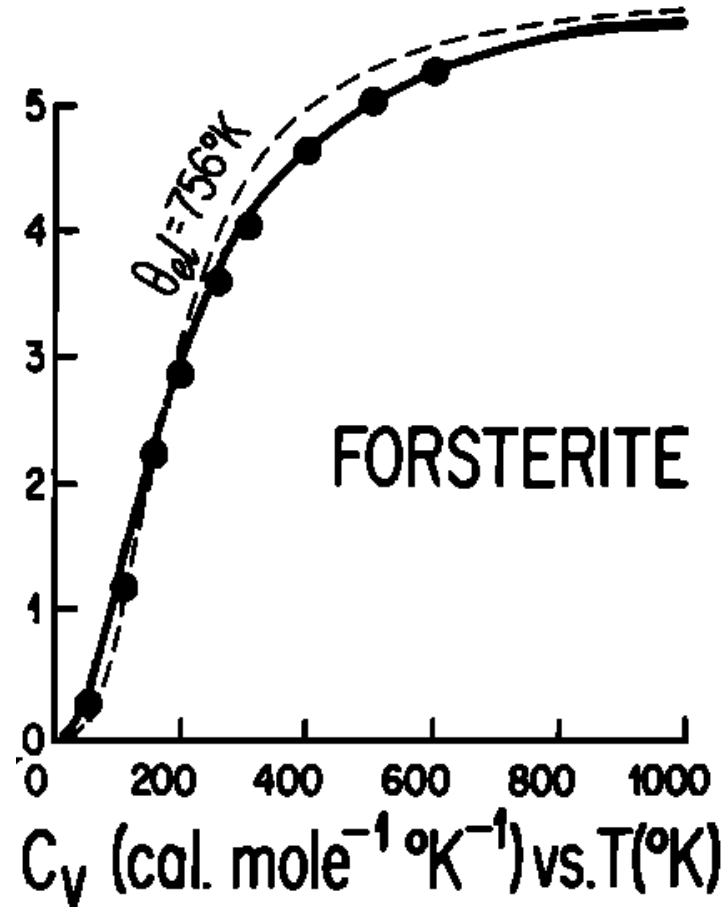
# Debye and real heat capacities: Simple oxides

- The Debye model generally agrees to measurement.
  - Only slight underestimation
  - All modes are excited at  $\theta_D$ .
  - More excited than predicted from the Debye model



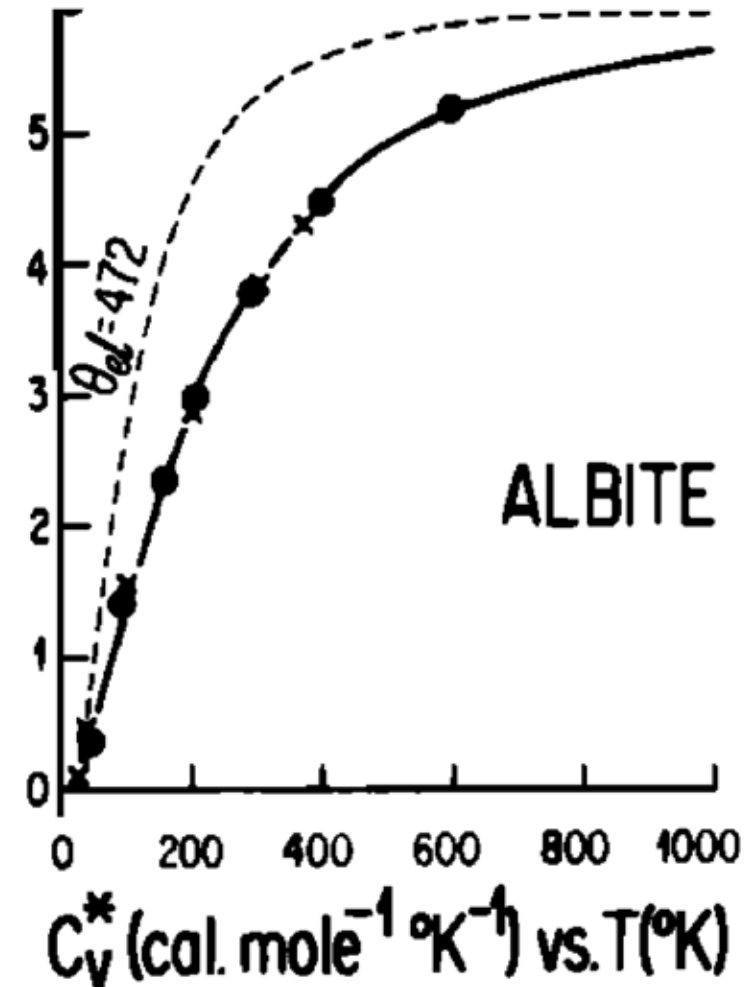
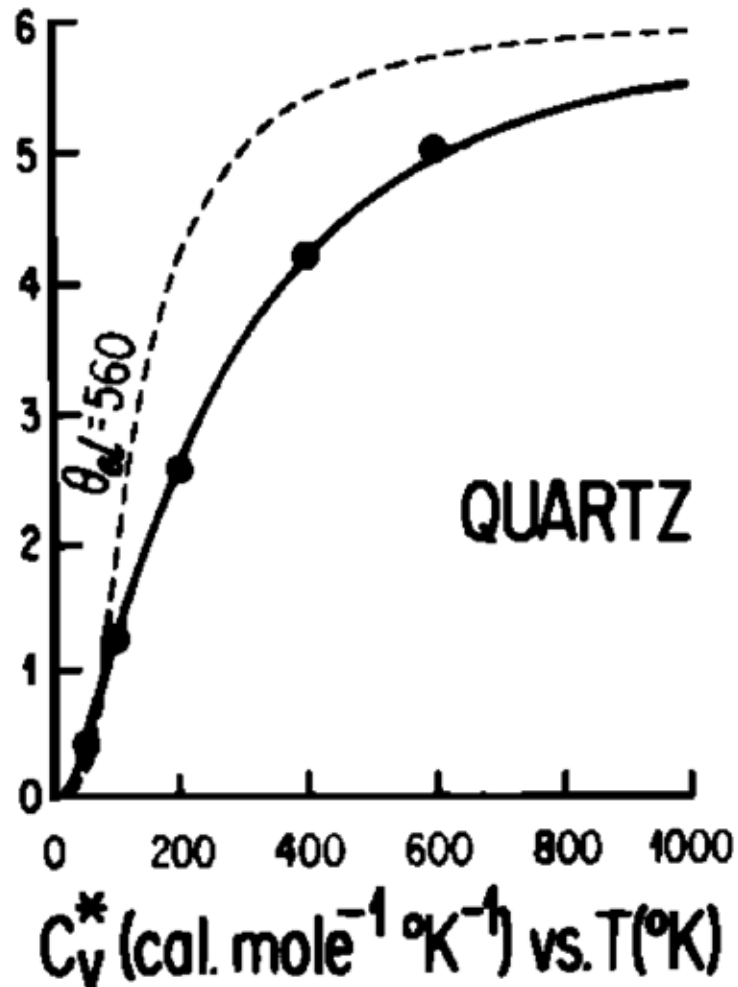
# Debye and real heat capacities: Orthosilicates

- The Debye model agrees to measurement,
  - only slightly overestimates  $C_V$ .
  - All modes are excited at  $\theta_D$ .



# Debye and real heat capacities: Tectosilicates

- The Debye model largely overestimates  $C_V$ 
  - Even above  $\theta_D$ , a large proportion of modes are not excited.
- More energy is necessary to excite lattice vibration than expected from elasticity.



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Section 7. Debye model

End

