

## 7. Debye Model

### 1. What is the Debye Model?

In *crystallography*, crystal structure is a description of the ordered arrangement of *atoms, ions* or *molecules* in a *crystalline material* – the crystal lattice. If the crystal lattice is composed of atoms, it can be referred to as *atomic lattice*. If heat is applied to the atomic lattice, *vibrations* occur – known as lattice vibrations. Several models were developed to explain the effect lattice vibrations, such as the *Einstein model* and the Debye model. We are looking at the Debye model. The Debye model was developed by Peter Debye in 1912.

In *thermodynamics* and *solid state physics*, the Debye model is a method for estimating the *phonon* contribution to the *specific heat* (heat capacity) in a *solid*. A phonon is a collective *excitation in a periodic, elastic* arrangement of atoms or molecules in *condensend matter*, specifically in solids – phonons can be thought of as quantized *sound waves*. In other words, the Debye model is a model of lattice vibration that considers the *frequency dependence* of the number of *modes* as a function of temperature (T). The term mode describes any of the patterns of lattice waves in a crystal. At low temperature, a limited number of modes are excited, whereas all available modes are excited at high temperature. In contrast to the Debye model, the Einstein model treats a solid as many individual, non-interacting *quantum harmonic oscillators* and the number of modes is considered to be constant.

The Debye model correctly predicts the low temperature (T) dependence of heat capacity: heat capacity is proportional to  $T^3$ , known as the Debye  $T^3$  law.

### 2. Waves in the crystal lattice

In general, lattice vibration propagates in any direction. The propagation direction is expressed using a wave vector  $\vec{K}$  and the displacement of an atom from its equilibrium position is expressed as vector  $\vec{u}$ . If the displacement vector is parallel to the wave vector ( $\vec{u} \parallel \vec{K}$ ), the wave is called compressional or *P-wave* (Fig. 1, left). If the displacement vector is perpendicular to the wave vector ( $\vec{u} \perp \vec{K}$ ), the wave is called transverse or *S-wave* and it has two directions of oscillation (polarity) (Fig. 1, right).

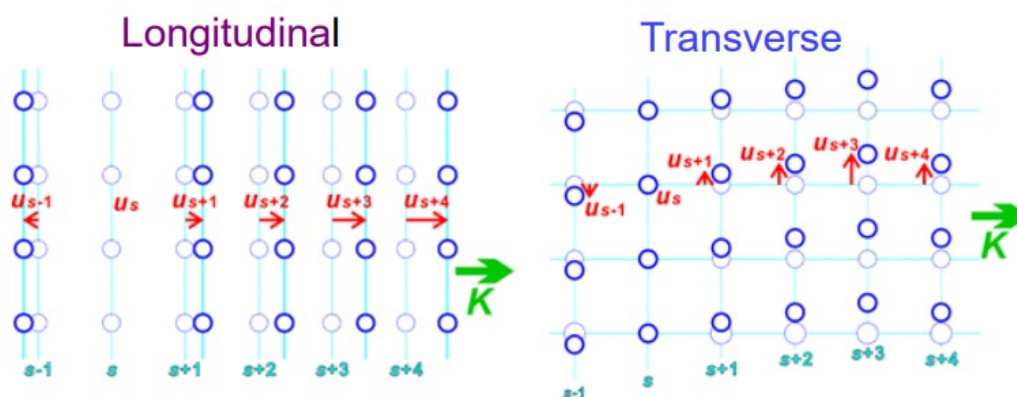


Fig. 1. Conceptual diagram of longitudinal waves (left) and transverse waves (right) propagation through a crystal lattice. Wave vector (green) and displacement vectors (red) are indicated.

### 3. The number of modes in a 1D crystal

The *Debye model* treats atomic vibrations as phonons in a box – the box being the crystal. Consider a 1 dimensional (1D) crystal with the dimensions  $L$  and atoms located in specific intervals ( $a$ ), then  $L$  can be expressed as:

$$L = (N - 1)a \quad (3.7.1)$$

The resonating modes of the sonic disturbances inside the crystal (considering for now only those aligned with one axis) have wavelengths ( $\lambda$ ) given by:

$$\lambda_{max} = L = Na \quad (3.7.2)$$

$$\frac{L}{2} = \frac{Na}{2} \text{ etc.} \quad (3.7.3)$$

$$\lambda_{min} = 2a = \frac{Na}{N/2} = \frac{L}{N/2} \quad (3.7.4)$$

The angular wave number  $k$ , aligned in the constant interval  $\frac{2\pi}{L}$ , is calculated as (Fig. 2):

$$k_{min} = \pm \frac{2\pi}{L} \quad (3.7.5)$$

$$k_{max} = \pm \frac{2\pi}{2a} = \pm \frac{N}{2} \frac{2\pi}{Na} = \pm \frac{N}{2} \frac{2\pi}{L} \quad (3.7.6)$$

This shows that  $k$  is limited in a discrete lattice. The number of modes is calculated as:

$$2 \times \frac{N}{2} = N \quad (3.7.7)$$

which means that the number of modes equals the number of atoms in the crystal lattice.

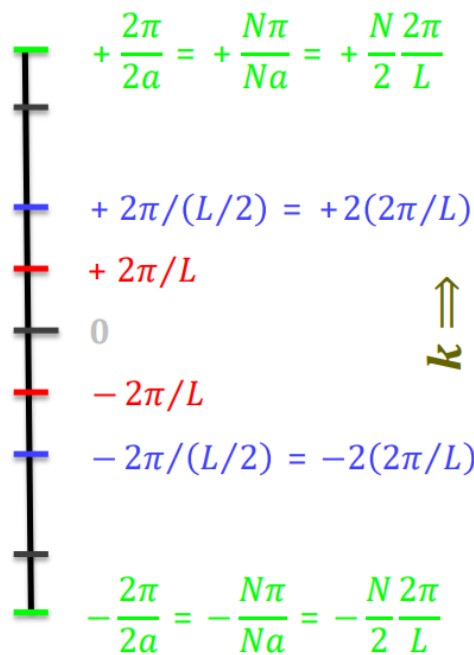


Fig. 2. Conceptual illustration of calculating the angular wave number at different points in the crystal lattice.

#### 4. Densities of states in 1D lattice

The density of state ( $D$ ) is the number of modes ( $n_m$ ) at a given frequency ( $\omega$ ):

$$D(\omega)d\omega = \frac{dn_m}{d\omega} d\omega = \frac{dn_m}{dk} \frac{dk}{d\omega} d\omega \quad (3.7.8)$$

The number of modes per unit  $k$  is equal to the reciprocal of the interval in  $k$  space:

$$\frac{dn_m}{dk} = \frac{1}{dk/dn_m} = \frac{1}{2\pi/L} = \frac{L}{2\pi} \quad (3.7.9)$$

If we assume a linear relation of  $\omega$  to  $k$  in the majority of the  $k$  space, frequency  $\omega$  can be calculated as:

$$\omega = \sqrt{4C/m} \sin(ka/2) \cong \sqrt{4C/m} ka/2 = \sqrt{C/m} ak \quad (3.7.10)$$

Group velocity can be expressed as:

$$v_g = d\omega/dk \cong \omega/k = \sqrt{C/m} a = v_p \quad (3.7.11)$$

$$\frac{dk}{d\omega} = \frac{1}{d\omega/dk} = \frac{1}{v_g} \cong \frac{1}{v_p} = \frac{1}{\sqrt{C/m} a} \quad (3.7.12)$$

By combining the equations, density of state in a one dimensional lattice can be calculated as:

$$D(\omega) = \frac{dn_m}{dk} \frac{dk}{d\omega} = \frac{L}{2\pi} \frac{1}{v_g} \cong \frac{L}{2\pi} \frac{1}{v_p} = \frac{L}{2\pi} \frac{1}{\sqrt{C/m} a} \quad (3.7.13)$$

This means that density of state in a one dimensional lattice is constant and independent of frequency  $\omega$ .

## 5. Densities of states in 3D crystals

Let's consider the density of state in three dimensional crystals (3D  $k$ -space) (Fig. 3), meaning in a reciprocal lattice.  $K$ -points are aligned with a  $2\pi/L$  interval, so there is one  $k$ -point for every cubic space of  $(2\pi/L)^3$ . This can be expressed as:

$$(2\pi/L)^3 = 8\pi^3/L^3 = 8\pi^3/V \quad (3.7.14)$$

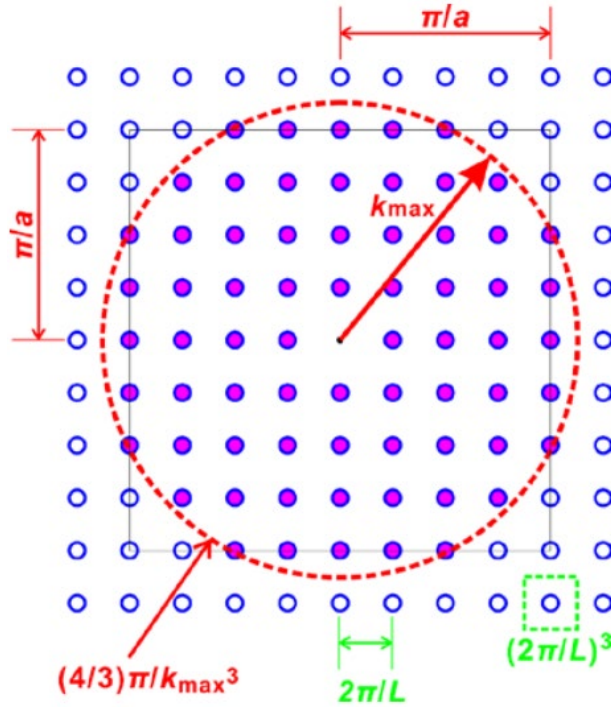


Fig. 3. Conceptual illustration of calculating the density of states in a three dimensional crystal, which shows the relevant parameters.

To calculate the volume ( $V$ ) of a sphere with diameter  $k$ , the number of modes ( $n_m$ ) with  $|k| \leq k_{\max}$  and  $k$ -points within the  $k_{\max}$  sphere, we need:

$$V_{k \leq k_{\max}} = (4/3) \pi k_{\max}^3 \quad (3.7.15)$$

$$n_m = ((4/3) \pi k_{\max}^3) / 8\pi^3 / V = V k_{\max}^3 / 6\pi^2 \quad (3.7.16)$$

That means that the number of modes  $n_m$  increases with a larger crystal volume  $V$ , smaller specific intervals  $a$  and larger unit  $k$ . Let's continue our calculation of density of states in a 3D crystal assuming that  $v_g \approx v_p$ :

$$D(\omega) = \frac{dn_m}{d\omega} = \frac{dn_m}{dk} \frac{dk}{d\omega} = \frac{d}{dk} \left( \frac{Vk^3}{6\pi^2} \right) \frac{1}{v_g} = \left( \frac{Vk^2}{2\pi^2 v_g} \right) \approx \frac{V(\omega/v_p)^2}{2\pi^2 v_p} = \frac{V\omega^2}{2\pi^2 v_p^3} \quad (3.7.17)$$

This means that  $D(\omega)$  is proportional to  $\omega^2$ . In a one dimensional crystal

$$D(\omega) = \frac{dn_m}{dk} \frac{dk}{d\omega} = \frac{L}{2\pi} \frac{1}{v_p} \quad (3.7.13)$$

which means that it is independent from  $\omega$ . The sum of density of states for one longitudinal and two transverse waves is calculated as:

$$D(\omega) = \frac{1V\omega^2}{2v_L^3\pi^2} + \frac{2V\omega^2}{2v_T^3\pi^2} = \frac{3V\omega^2}{2v_D^3\pi^2} \quad (3.7.18)$$

where  $v_L$  is the velocity of the longitudinal wave and  $v_T$  is the velocity of the transverse waves. The Debye velocity can be deduced from that equation as:

$$\frac{3}{v_D^3} = \frac{1}{v_L^3} + \frac{2}{v_T^3} \quad (3.7.19)$$

## 6. Total energy of lattice vibration – Debye model

To calculate the total energy of lattice vibration using the Debye model, we need the energy of lattice vibration as calculated in section 5:

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

By substituting the density of states  $D(\omega)$ , obtained as equation (9.3.18) (3.7.18)

$$D(\omega) = \frac{3V\omega^2}{2v_D^3\pi^2}$$

to equation (3.5.6), we obtain the total energy of lattice vibration of the Debye model:

$$E_{vib} = \int_0^{\omega_D} \frac{3V\omega^2}{2v_D^3\pi^2} \frac{\hbar\omega d\omega}{\exp(\hbar\omega/k_B T) - 1} \quad (3.7.19)$$

The upper bound of the integration is not limitless but  $\omega_D$  with  $\omega_D = v_D k_{\max}$  known as the *Debye (cut-off) frequency*. The maximum  $\omega$  in a lattice is due to the discreteness of atoms.

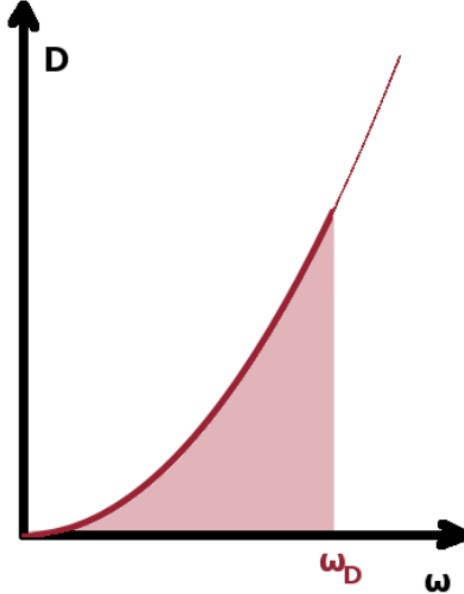


Fig. 4. Conceptual illustration of the relationship between  $D$  and  $\omega_D$ .

## 6. Simpler formula of the Debye model

Let's simplify the formula of the Debye model. We know that the number of modes with  $k < k_{max}$  is equal to the number of atoms  $N$  from equation 3.7.16. This gives us:

$$N = n_m = \frac{V k_{max}^3}{6\pi^2 v_D^3} \rightarrow \omega_D = v_D \sqrt[3]{\frac{6\pi^2 N}{V}} \quad (3.7.20)$$

When we define  $x$  as  $x = \frac{\hbar\omega}{k_B T}$  it gives us:

$$\omega = \frac{k_B T x}{\hbar} \quad (3.7.21)$$

To calculate the *Debye temperature*  $\Theta$ , we need equation (3.7.19):  $E_{vib} = \int D(\omega) \frac{\hbar\omega}{\exp(\hbar\omega/k_B T) - 1} d\omega$  and  $\omega_D \rightarrow x_D = \frac{\hbar\omega_D}{k_B T} = \frac{\hbar\omega_D}{k_B} \frac{1}{T} = \frac{\Theta_D}{T}$ , which gives us:

$$\Theta = \frac{\hbar\omega_D}{k_B} \quad (3.7.22)$$

To further simplify the formula of the *Debye model*, we need the following formulas:

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

The total energy of lattice vibration  $E_{vib}$  from equation (3.7.19) can then be calculated as:

$$\begin{aligned} E_{vib} &= \int_0^{\omega_D} \frac{3V\omega^2}{2v_D^3\pi^2} \frac{\hbar\omega d\omega}{\exp(\hbar\omega/k_B T) - 1} = \frac{3V \frac{k_B T^2}{\hbar}}{2v_D^3\pi^2} \frac{\hbar \frac{k_B T}{\hbar} \frac{\hbar\omega_D}{k_B T}}{\exp(\hbar \frac{k_B T}{\hbar} / k_B T) - 1} \quad (3.7.23) \\ &= \frac{3Vk_B^4 T^4}{2\pi^2 v_D^3 \hbar^3} \int_0^{\Theta_D/T} \frac{x^4 dx}{\exp(x) - 1} \end{aligned}$$

This means that  $x_D = \frac{\Theta_D}{k_B}$  and  $\Theta_D = \frac{\hbar\omega_D}{k_B}$ .

## 7. Debye temperature

The *Debye temperature* is calculated with  $\omega_D = v_D \sqrt[3]{\frac{6\pi^2 N}{V}}$  from equation (3.7.20) as:

$$\theta_D = \frac{\hbar\omega_D}{k_B} = \frac{\hbar}{k_B} v_D \sqrt[3]{\frac{6\pi^2 N}{V}} = \frac{\hbar v_D}{k_B} \sqrt[3]{\frac{6\pi^2 N}{V}} \quad (3.7.24)$$

Therefore, at low temperature  $T$  we have low  $\omega$  states, which means that low energy  $E$  states are filled, but high  $\omega$  states are not excited. Higher  $\omega$  states are filled with increasing temperature  $T$ , but frequency  $\omega_D$  is a limitation. At  $\theta_D$ , the excited  $\omega$  reaches  $\omega_D$  and above  $\theta_D$  all modes of lattice vibration are excited.

The Debye temperature is a material constant. From equation (3.7.24) we see that two parameters are intrinsic for materials - sound velocity  $v_D$  and  $\frac{N}{V}$ . Therefore, if the sound velocity is high, the Debye temperature is high. If lattice spacing  $a = \sqrt[3]{\frac{N}{V}}$  is solved to  $\frac{N}{V} = \frac{1}{a^3}$  it becomes apparent that Debye temperature  $\theta_D$  is higher with smaller  $a$ , i.e. a denser phase. This allows the normalization of the temperature dependence of the vibrational properties of different velocities and densities against  $T/\theta_D$ .

## 8. Debye heat capacity

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 (equation 3.7.23) and gives:

$$\begin{aligned} & C_{vib} \quad (3.7.23) \\ &= \int_0^{\omega_D} \frac{3V\omega^2}{2v_D^3\pi^2} \frac{\hbar^2\omega^2 \exp(\hbar\omega/k_B T)}{k_B T^2 \exp(\hbar\omega/k_B T) - 1} d\omega \\ &= \frac{3V\hbar^2}{2v_D^3\pi^2 k_B T^2} \int_0^{\omega_D} \frac{\omega^4 \exp(\hbar\omega/k_B T)}{(\exp(\hbar\omega/k_B T) - 1)^2} d\omega \end{aligned}$$

By applying the variable  $x$  by  $\omega = \frac{k_B T}{\hbar} x$  to (3.7.24) we have:

$$C_{vib} = \frac{3V\hbar^2}{2v_D^3\pi^2 k_B T^2} \int_0^{x_D} \frac{\left(\frac{k_B T}{\hbar}\right)^5 x^4 \exp(x)}{(\exp(x) - 1)^2} dx \quad (3.7.25)$$

Simplifying equation (3.7.25) gives us the *Debye heat capacity*:

$$C_{vib} = \frac{9Nk_B}{x_D^3} \int_0^{x_D} \frac{x^4 \exp(x)}{(\exp(x) - 1)^2} dx \quad (3.7.26)$$

$$C_{vib} = 9Nk_B \left(\frac{T}{\theta_D}\right) \int_0^{\theta_D/T} \frac{x^4 \exp(x)}{(\exp(x) - 1)^2} dx \quad (3.7.27)$$

This equation shows that the Debye heat capacity is higher at lower temperatures than the *Einstein heat capacity* (Fig. 5).

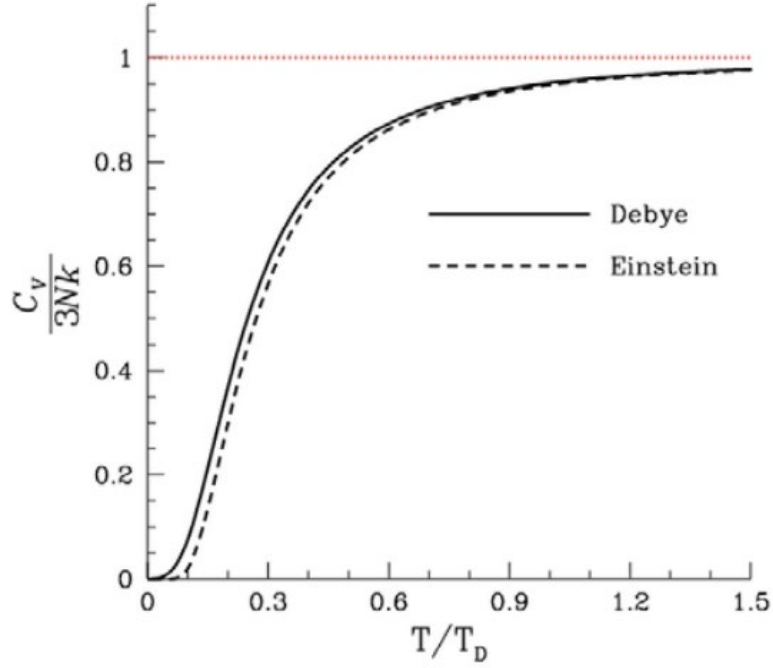


Fig. 5. Schematic illustration of the comparison between the heat capacity calculated using the Debye and Einstein model.

## 9. High temperature limits of Debye heat capacity

To calculate the Debye heat capacity at high temperatures, we set the high temperature limit to  $T \rightarrow \infty$  and  $x = \hbar\omega/k_B T \rightarrow \infty$  and  $\exp(x) \rightarrow 1 + x \rightarrow 1$ ,  $\exp(x) - 1 \rightarrow 1 + x - 1 \rightarrow x$ . Applying this to equation (3.7.27) gives:

$$\frac{1}{x_D^3} \int_0^{x_D} \frac{x^4 \exp(x)}{(\exp(x) - 1)^2} dx \rightarrow \frac{1}{x_D^3} \int_0^{x_D} \frac{x^4 \cdot 1}{x^2} dx = \frac{1}{x_D^3} \int_0^{x_D} x^2 dx \rightarrow \frac{1}{3} \quad (3.7.28)$$

with  $x_D = \hbar\omega_D/k_B T = \theta_D/T$  we get

$$C_{\text{vib}} = \frac{9Nk_B}{x_D^3} \left(\frac{T}{\theta_D}\right) \int_0^{x_D} \frac{x^4 \exp(x)}{(\exp(x) - 1)^2} dx \rightarrow 9Nk_B \times \frac{1}{3} \rightarrow 3Nk_B \quad (3.7.29)$$

This formula is called *Dulong-Petit law*. It states that at high temperature  $C_{\text{vib}}$  is nearly a constant of  $3Nk_B$  because all modes are excited.

## 10. Low temperature limits of Debye heat capacity

To calculate the Debye heat capacity at low temperatures, we set the low temperature limit to  $T \rightarrow 0$  and  $x_D = \frac{\hbar\omega_D}{k_B T} = \frac{\theta_D}{T} \xrightarrow{T \rightarrow 0} \infty$ . Applying this gives:

$$\int_0^{x_D} \frac{x^4 \exp(x)}{(\exp(x) - 1)^2} dx \xrightarrow{x_D \rightarrow \infty} \frac{\pi^4}{15} \quad (3.7.30)$$

This allows calculation of Debye heat capacity at low temperatures as:

$$C_{\text{vib}} = \frac{9Nk_B}{x_D^3} \int_0^{x_D} \frac{x^4 \exp(x)}{(\exp(x) - 1)^2} dx \xrightarrow{T \rightarrow 0} 9Nk_B \left(\frac{T}{\theta_D}\right)^3 \frac{\pi^4}{15} = \frac{3}{5} Nk_B \pi^4 \left(\frac{T}{\theta_D}\right)^3 \quad (3.7.31)$$

The above equation shows that heat capacity is proportional to  $T^3$  at low temperatures. This is called the Debye  $T^3$  law because the lattice is in 3D and it shows that the mode increases in the three directions with increasing temperature (Fig. 6).

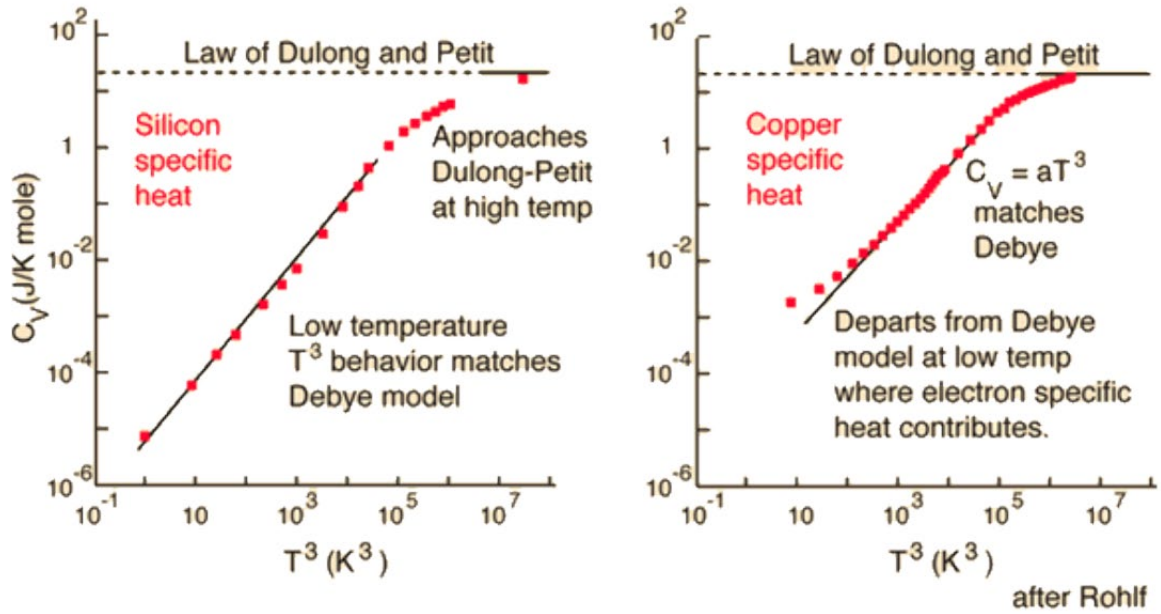


Fig. 6. Schematic illustration of the Debye  $T^3$  law after Rohlif.

## 11. Comparison of the Debye and Einstein models

Heat capacity is calculated using the Debye model as

$$C_{\text{vib}} = \frac{9Nk_B}{x_D^3} \int_0^{x_D} \frac{x^4 \exp(x)}{(\exp(x) - 1)^2} dx \quad (3.7.29)$$

and using the Einstein model equation (3.5.14) as

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

Comparison shows that the Debye model provides higher  $C_{\text{vib}}$  at lower temperatures than the Einstein model (Fig. 5). This is because the Einstein model only uses one frequency, which makes excitation at low temperatures difficult – whereas in the Debye model lattice vibration frequency starts from almost zero and thus makes excitation at low temperatures easy.

Let's look at the Einstein and Debye models using the example copper (Cu) (Fig. 7). In the Debye model at a temperature  $T = 343 \text{ K}$   $\omega \leq \omega_D = 4.5 \times 10^{13} \text{ Hz}$  and in the Einstein model at  $T = 240 \text{ K}$   $\omega = \omega_\alpha = 3.1 \times 10^{13} \text{ Hz}$  using one frequency for calculation. Comparing the quantum number  $\{n\}$  at low temperature gives  $\{n\} \approx 0$  in the Einstein model with a very low  $C_v$  at low temperature, and a very large  $\{n\}$  at small  $\omega$ .

Comparing the number of nodes ( $D(\omega)\{n\}d\omega$ ) in the Einstein and Debye models shows that in the Debye model  $D(\omega) \propto \omega^2$  and the regions are lower than the solidus curves. In the Einstein model  $D(\omega)$  is constant and the regions are lower than the broken lines. This means that the number of modes in the Einstein model is much smaller than the number of modes in the Debye model at low temperature.



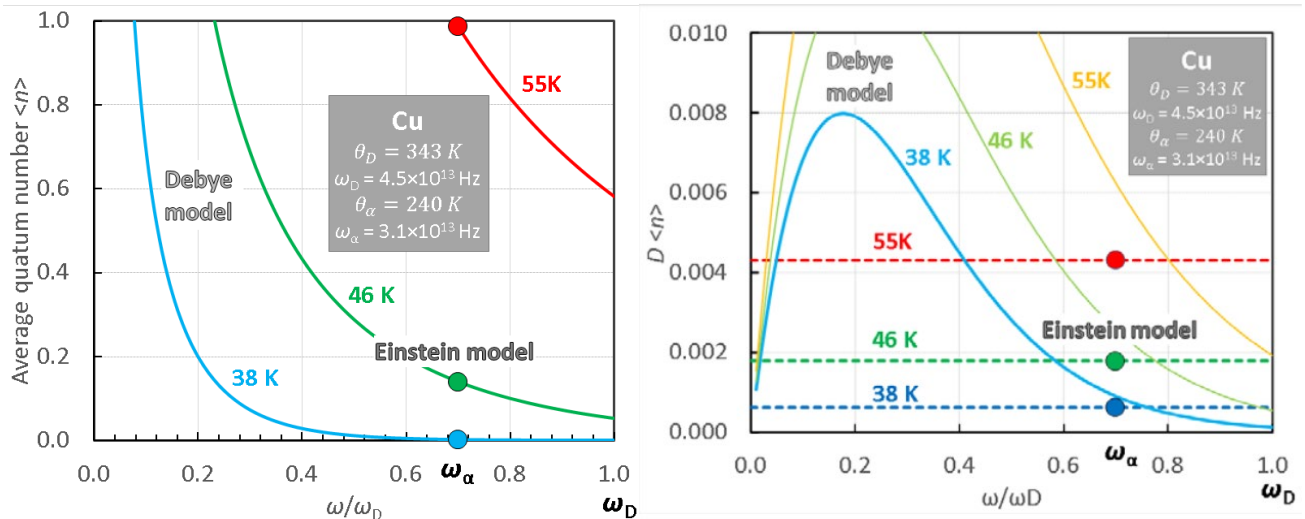


Fig. 7. Comparison of Debye and Einstein models using copper as an example.

## 12. Debye model and real heat capacities

In the last section, we will look at real heat capacities from real minerals and compare them to those calculated using the Debye model (Fig. 8).

### 12.1 Simple oxides

The Debye model generally agrees with the measurements and only slightly underestimates them. All modes are excited at  $\Theta_D$ . In fact, they are more excited than predicted from the Debye model.

### 12.2 Orthosilicates

The Debye model generally agrees with the measurements and only slightly overestimates them. All modes are excited at  $\Theta_D$ .

### 12.1 Tectosilicates

The Debye model largely overestimates the heat capacity. Even above  $\Theta_D$ , a large proportion of modes are not excited. This means that more energy is necessary to excite lattice vibration than expected from elasticity.

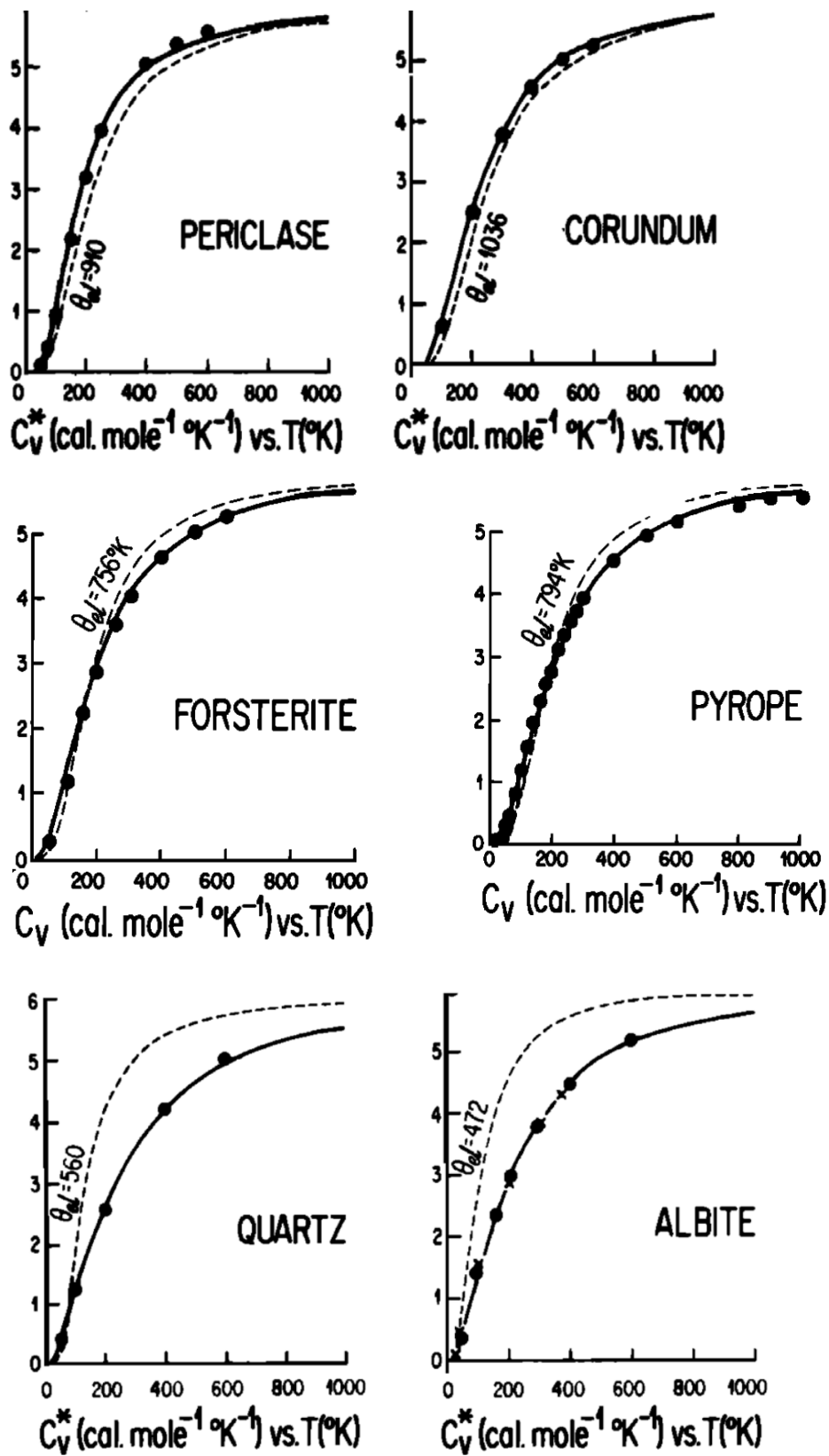


Fig. 7. Comparison of the Debye model with real heat capacities measured on real minerals: top – simple oxides, middle – orthosilicates, bottom - tectosilicates.