Chapter #5:
Thermal Properties of Insulators

Lecture 2: Heat Capacity of Solids: Debye model

Classical Model Failure

The classical model predicts that heat capacity is constant and equal to 3R at all temperatures.
However, experiments show that heat capacity decreases and approaches zero at low temperatures.
This failure occurs because the classical model assumes continuous energy and that all vibrational modes are always excited.

Einstein Model Failure

The Einstein model introduces quantization and correctly predicts that heat capacity decreases at low temperatures.
However, it assumes that all atoms vibrate with a single frequency.
As a result, it predicts an exponential decrease, while experiments show a T^3 behavior.
This is because it neglects low-frequency phonon modes.

Debye Model

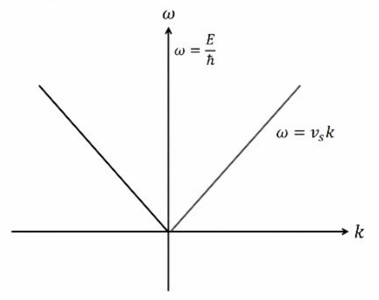
Therefore, we need a model that includes quantum effects and a distribution of vibrational frequencies.
This leads to the Debye model.

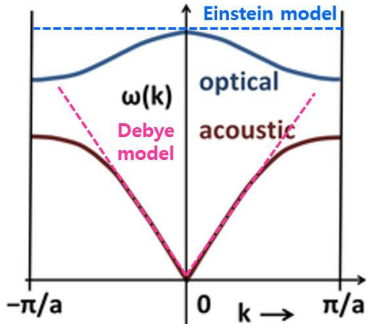
5-3 Debye Model for Specific Heat:

Debye assumed the following:

1. Atoms **interact with each other**, and the motion of any atom affects the rest of the atoms.
2. The collective vibrational modes are **elastic waves** that obey the dispersion relation:

$$\omega = vq \tag{10}$$





This applies when the wavelength of the propagating wave (phonon) inside the crystal is **much larger than the lattice constants**, so the crystal appears as a **continuous medium** from the wave's perspective, and the details of the lattice structure are not resolved.

3. The vibrational frequencies of the lattice span a **wide range of frequencies**, unlike the Einstein model, which assumes a single frequency.
    - The lowest frequency is:

      $\omega = 0$ when $q = 0$

    - The maximum frequency will be determined later using the **density of states**.

5-3-1 Density of States in One Dimension:

Initially, we study the density of states in one dimension.

Assume an elastic wave propagating in a rod of length L. The general solution is:

At $t=0$ $u = Ae^{iqx}$

We apply **periodic boundary conditions**, meaning the displacement at the left end equals that at the right end:

$$u(x=0)=u(x=L)$$

$$A=Ae^{iqL}$$

$$e^{iqL}=1$$

This condition requires:

$$qL=2\pi n$$

$$q=\frac{2\pi n}{L}$$

where n=0,1,2,…

Hence, the spacing between allowed **q** values is:

$$\frac{2\pi}{L}$$

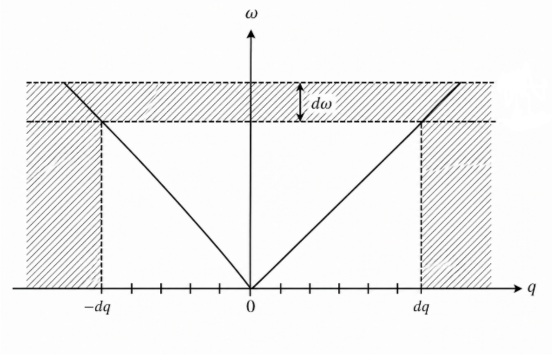
So, the number of vibrational modes in an interval **dq** is:

$$\frac{L}{2\pi}dq$$

Since there is a relation between q and ω, we can find the number of vibrational modes between ω and ω+dω.

Thus:

$$g(\omega)d\omega=\frac{L}{2\pi}dq$$



where g(ω) is the **density of states and given by:**

$$g(\omega)=\frac{L}{2\pi}.\left(\frac{1}{d\omega/dq}\right)$$

Because negative values of q must also be considered, we multiply by 2:

$$g(\omega)=\frac{L}{\pi}.\left(\frac{1}{d\omega/dq}\right)$$

Using:

$$\omega = vq \;\Rightarrow\; \frac{d\omega}{dq} = v$$

So, the density of state becomes:

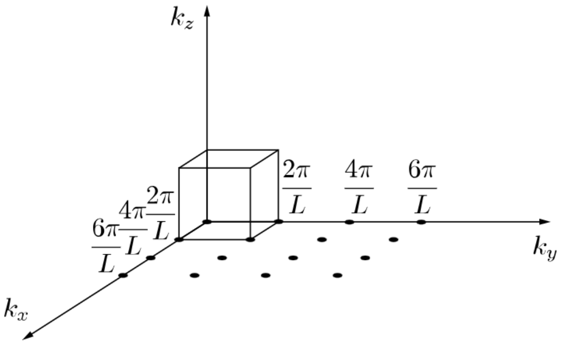
$$g(\omega) = \frac{L}{\pi}.\left(\frac{1}{v}\right)$$

👉 This shows that in one dimension, the density of states is **independent of frequency**.

5-3-2 Density of States in Three Dimensions:

Now consider a cube of side L with a wave propagating in three dimensions:

$$u = Ae^{i(q_x x + q_y y + q_z z)} \qquad (11)$$



Applying periodic boundary conditions:

$$\begin{aligned} q_x x &= 2\pi n \\ q_y y &= 2\pi m \\ q_z z &= 2\pi l \end{aligned} \qquad (12)$$

where *n,m,l* are integers.

Now, if we plot the graphical relationship of these values in **q-space**, as shown in the figure, we obtain a **three-dimensional cubic lattice**.

The volume associated with each point in this space is equal to $\left(\frac{2\pi}{L}\right)^3$.

Note that each point represents a single mode.

5-3-3 Number of Modes in a Sphere

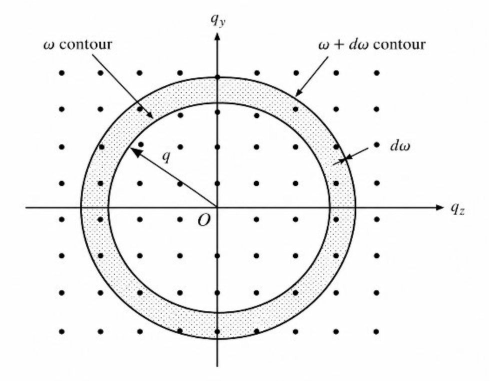
Consider a sphere of radius q and its volume is given by:

$$V = \frac{4}{3}\pi q^3$$

As for the number of modes, it is equal to the total volume of the sphere divided by the volume occupied by each point, as follows:

$$\frac{\frac{4}{3}\pi q^3}{\left(\frac{2\pi}{L}\right)^3} = \frac{V}{(2\pi)^3}.\frac{4}{3}\pi q^3 \qquad \text{, where } V=L^3 \qquad (13)$$

Modes in a Shell:



- Between q and q+dq:

If we want the number of modes (or points) within a spherical shell bounded between q and q+dq, we differentiate equation (13) with respect to q to obtain the following:

$$\frac{V}{(2\pi)^3}.4\pi q^2 dq \qquad (14)$$

- Convert to Frequency:

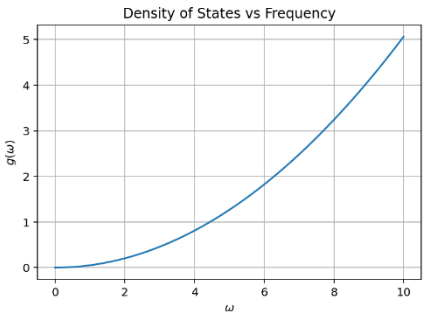
Now, using the same method as before, we can determine the number of modes whose frequencies lie within the interval between ω and ω+dω by changing variables from q to ω, using the dispersion relation ω=vq, as follows:

$$q = \frac{\omega}{v}$$

$$g(\omega)d\omega = \frac{V}{(2\pi)^3}.4\pi\left(\frac{\omega}{v}\right)^2 d\left(\frac{\omega}{v}\right) = \frac{V}{(2\pi)^3}.4\pi\frac{\omega^2}{v^3}d\omega \qquad (15)$$

Thus, the density of states is given by:

$$g(\omega)=\frac{V}{2\pi^2}\cdot\frac{\omega^2}{v^3} \tag{16}$$

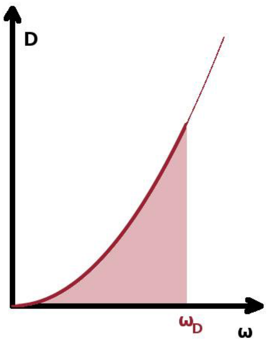


Since each q has **3 modes** (1 longitudinal + 2 transverse) and by assuming that the longitudinal and transverse waves have the same velocity v, the total density of states becomes:

$$g(\omega)=\frac{3V}{2\pi^2}\cdot\frac{\omega^2}{v^3} \tag{17}$$

👉 Unlike 1D, here: $g(\omega)\propto\omega^2$

- ✓ The number of vibrational modes increases rapidly with frequency. This means high-frequency phonons are much more numerous than low-frequency ones.
- ✓ Each allowed wave corresponds to a point in q-space. Counting modes becomes equivalent to counting points inside a sphere in this space.
- ✓ Larger radius → more modes → higher frequency.



5-3-4 Calculating the heat capacity:

The total energy of the vibrations within the lattice is given by the relation:

$$E_{total}=\int\langle E\rangle\, g(\omega)d\omega \tag{18}$$

where the limits of integration cover all allowed frequency values ($0\le\omega\le\omega_{\max}$). In fact, the upper limit of the frequency—called the cut-off frequency—was determined by Debye by assuming that the total number of vibrational states equals the number of degrees of freedom in the crystal. Since this number is $3N_A$ (because each atom has three degrees of freedom), this condition can be written as follows:

Debye Condition: Total number of modes = total degrees of freedom:

$$\int_0^{\omega_D} g(\omega)d\omega = 3N_A \tag{19}$$

where ω_D is the **Debye cutoff frequency**.

What is ω_D?
It is not a real physical boundary in the crystal, but an **approximation** that ensures the total number of vibrational modes equals the number of degrees of freedom 3N.

Physical interpretation:
Debye replaces the complex phonon spectrum with a simplified one that has a maximum frequency.

Solving to determine the Debye frequency by substituting equation (17) into equation (19), as follows:

$$\int_0^{\omega_D} \frac{3V}{2\pi^2}.\frac{\omega^2}{v^3}d\omega = \frac{3V}{2\pi^2}.\frac{1}{v^3}\int_0^{\omega_D}\omega^2 d\omega = \frac{V}{2\pi^2}.\frac{{\omega_D}^3}{v^3} = 3N_A \qquad (20)$$

$$\omega_D = \left(\frac{6\pi^2 N_A}{V}\right)^{\frac{1}{3}} v \qquad (21)$$

Now, we return to equation (18), which becomes as follows:

$$E_{total} = \frac{3V}{2\pi^2}.\frac{1}{\mathrm{v}^3}\int_0^{\omega_D}\omega^2\frac{\hbar\omega}{e^{\hbar\omega/kT}-1}d\omega \qquad (21)$$

Now, we differentiate this equation with respect to T to obtain the heat capacity:

$$\begin{aligned} C = \frac{\partial E_{total}}{\partial T} &= \frac{3V}{2\pi^2}.\frac{1}{\mathrm{v}^3}\int_0^{\omega_D}\frac{\hbar\omega^3}{(e^{\hbar\omega/kT}-1)^2}(e^{\hbar\omega/kT})(\frac{\hbar\omega}{kT^2})d\omega \\ &= \frac{3V}{2\pi^2}.\frac{\hbar^2}{\mathrm{v}^3.kT^2}\int_0^{\omega_D}\frac{\omega^4.e^{\hbar\omega/kT}}{(e^{\hbar\omega/kT}-1)^2}d\omega \end{aligned} \qquad (22)$$

By performing a change of variables:

Let's assume that:

$$x = \frac{\hbar\omega}{kT} \;➔\; dx = \frac{\hbar}{kT}d\omega \qquad \text{where: } x = \frac{\theta_D}{T}$$

When: $\omega = 0 \Rightarrow x = 0$ and $\omega_{\max} = \frac{kT}{\hbar}x_{\max} = \omega_D \Rightarrow x_{\max} = \frac{\hbar\omega_D}{kT} = \frac{\theta_D}{T}$

After substitution and differentiation:

$$C = 9R\left(\frac{T}{\theta_D}\right)^3\int_0^{\frac{\theta_D}{T}}\frac{x^4.e^x}{(e^x-1)^2}dx \qquad (23)$$

Now, we will study this relation at high and low temperatures.

Temperature Limits

1. High Temperature

This will happen when:

$$x \ll 1 \qquad \frac{\hbar\omega}{kT} \ll 1$$

Using: For small x:

$$e^{x} \approx 1 + x \qquad \text{So,} \quad e^{x} - 1 \approx x$$

Then,

$$\int_0^{\frac{\theta_D}{T}} \frac{x^4.e^x}{(e^x-1)^2}\,dx \approx \int_0^{\frac{\theta_D}{T}} x^2\,dx \approx \frac{1}{3}(\frac{\theta_D}{T})^3$$

$$C \approx 9R\left(\frac{T}{\theta_D}\right)^3 \frac{1}{3}(\frac{\theta_D}{T})^3 \approx 3R$$

- ✓ This result agrees with experimental results, as we also observed in the Einstein model at high temperatures.
- ✓ At high temperatures, all phonon modes are excited.

2. Low Temperature

In this case, it follows that the integral in equation (21) approaches infinity; therefore, the equation can be written in the following form:

$$E_{total} = 9RT\left(\frac{T}{\theta_D}\right)^3 \int_0^{\infty} \frac{x^3}{(e^x-1)}\,dx \tag{24}$$

Since:

$$\int_0^{\infty} \frac{x^3}{(e^x-1)}\,dx = \frac{\pi^4}{15}$$

Then,

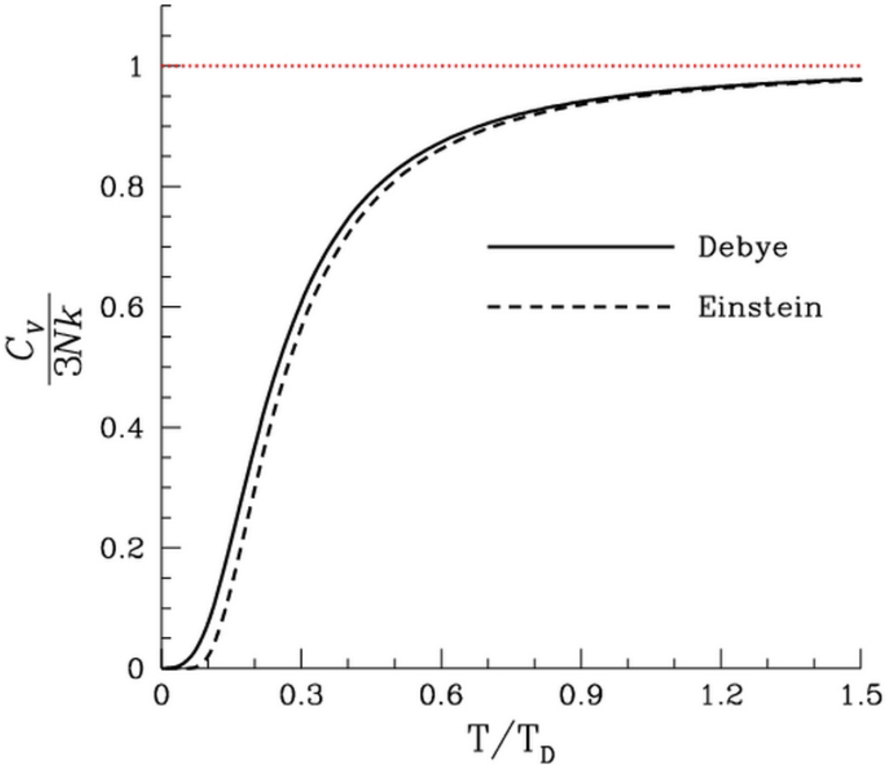
$$E_{total} = 9RT\left(\frac{T}{\theta_D}\right)^3 (\frac{\pi^4}{15}) = \frac{3}{5}R\pi^4 T\left(\frac{T}{\theta_D}\right)^3$$

As a result, the heat capacity is given by:

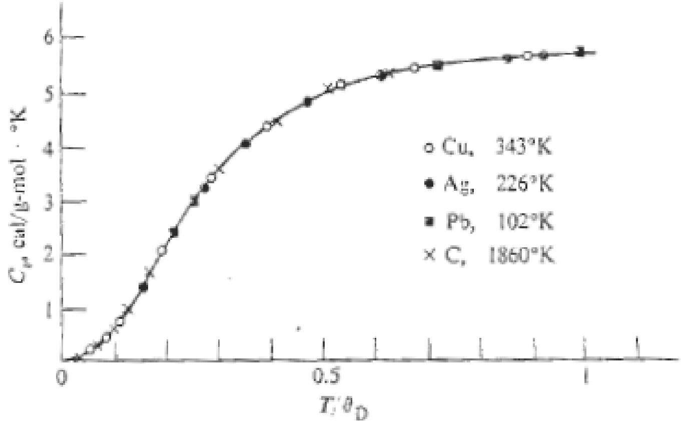
$$C = \frac{\partial E_{total}}{\partial T} = \frac{12}{5}\frac{R\pi^4 T^3}{\theta_D{}^3} \tag{25}$$

$C \propto T^3$ This is the famous **Debye** T^3 **law.**

That is, the heat capacity (at low temperatures) decreases as the temperature decreases, which is in complete agreement with experimental results, as shown in the following figure:



The following relation illustrates the experimental results along with the Debye curve.



At low temperatures:

- Only low-frequency phonons are excited
- Number of modes $\propto \omega^2$
- Energy per mode $\propto T$

Model	Assumption	Result
Classical	Continuous energy	(3R)
Einstein	Single frequency	exponential decay
Debye	Spectrum	(T^3) law

👉

Why the Einstein model fails:
It assumes all atoms vibrate at the same frequency, thereby ignoring low-frequency modes.

What Debye fixes:
It introduces a continuous range of frequencies, especially low-frequency phonons that dominate at low temperatures.

- Heat capacity depends on **how many phonon modes are excited**
- Low T: few modes → small C
- High T: all modes → 3R
- Debye model captures this correctly.