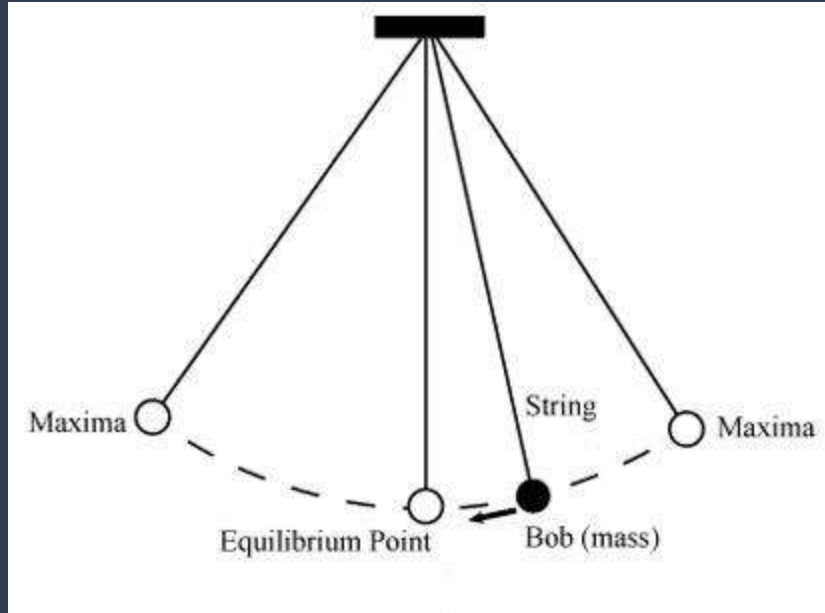# DEBYE THEORY OF SPECIFIC HEAT SOLVED PROBLEMS

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# WHAT IS SIMPLE HARMONIC OSCILLATOR ?

Maxima — String — Maxima
Equilibrium Point — Bob (mass)

https://youtu.be/5o1kFtaAx1Q

A physical system in which some value oscillates above and below a mean value at one or more characteristic frequencies. Such systems often arise when a contrary force results from displacement from a force-neutral position, and gets stronger in proportion to the amount of displacement. For example, pulling or pushing the end of a spring from its rest position results in a force pushing back toward the rest position. Letting the spring go from a position of tension results in harmonic motion of the spring; the spring is now a harmonic oscillator. Other examples include a swinging pendulum, a vibrating violin string, or an electronic circuit that produces radio waves.

WHAT IS COUPLED HARMONIC OSCILLATOR
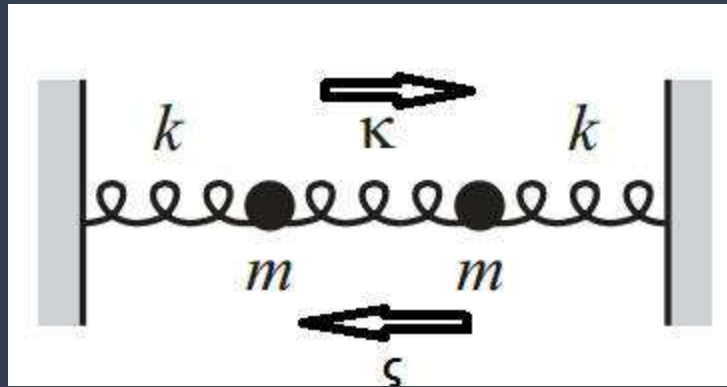
Coupled Oscillations occur when two or more oscillating systems are connected in such a manner as to allow motion energy to be exchanged between them. Coupled oscillators occur in nature (e.g., the moon and earth orbiting each other) or can be found in man-made devices (such as with the pacemaker).

https://youtu.be/YyOUJUOUvso

ASSUMPTIONS OF DEBYE MODEL

- The vibration of the crystal as a whole is considered equivalent to the vibrational motion of a system of coupled harmonic oscillator.
- The coupled harmonic oscillators can propagate a range of frequencies rather than one.
- The crystals can propagate elastic waves of low frequencies like sound wave to high frequencies.
- The number of vibrational modes per unit frequency range is called the DENSITY OF STATES.

DEBYE SPECIFIC HEAT THEORY

The possible number of modes of elastic standing waves of any kind with frequencies lying between ν and $\nu + d\nu$ is given by

$$g(\nu)d\nu = \left(\frac{4\pi V}{v_s^3}\right) \nu^2 d\nu \qquad (5.7.1)$$

where V is the volume of a mole of the solid cube, and v_s is the wave speed.

In general, the elastic waves propagating in a solid are of two types—*longitudinal*, of speed v_l and *transverse*, of speed v_t. Also, there are two perpendicular directions of polarisation for a given transverse wave.

$\therefore$ The total number of vibrational modes of frequencies lying between ν and $\nu + d\nu$ is

$$g(\nu)d\nu = 4\pi V \left(\frac{1}{v_l^3} + \frac{2}{v_t^3}\right) \nu^2 d\nu \qquad (5.7.2)$$
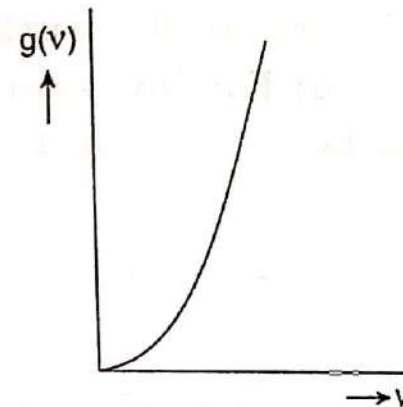

Fig. 5.10 Frequency spectrum

● A curve between the density of states $g(\nu)$ and ν, as given in Fig. 5.10, shows that $g(\nu)$ increases as ν^2. The function $g(\nu)$ is also called the *spectral distribution function.*

The average energy $\bar{\varepsilon}$ of an oscillator of frequency ν at temperature T is

$$\bar{\varepsilon} = \frac{h\nu}{e^{h\nu/kT} - 1} \qquad (5.7.3)$$

Associating a harmonic oscillator of the same frequency with each vibrational mode, the vibrational energy of the crystal is

$$E = \int_0^{\nu_D} 4\pi V \left(\frac{1}{v_l^3} + \frac{2}{v_t^3}\right) \frac{h\nu^3}{e^{h\nu/kT} - 1} d\nu \qquad (5.7.4)$$

Here the upper limit of integration is some *maximum frequency*, called *Debye frequency* ν_D or *Debye cut-off frequency*. There cannot thus be an infinite number of standing waves. Debye *assumed* that if there are N number of atoms in a solid, the total number of vibrational modes is limited to $3N$. So, using (5.7.2),

$$\therefore \int_0^{\nu_D} 4\pi V \left(\frac{1}{v_l^3} + \frac{2}{v_t^3}\right) \nu^2 d\nu = 3N$$

$$\text{or,} \quad 4\pi V \left(\frac{1}{v_l^3} + \frac{2}{v_t^3}\right) \frac{\nu_D^3}{3} = 3N$$

$$\text{or,} \quad \nu_D^3 = \frac{9N}{4\pi V} \left(\frac{1}{v_l^3} + \frac{2}{v_t^3}\right)^{-1} \qquad (5.7.5)$$
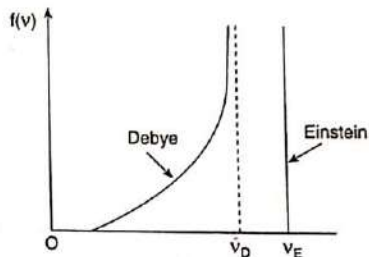
which can be used to determine the Debye frequency, ν_D. It is interesting to note the frequency spectrum according to Debye and Einstein models, as are illustrated in Fig. 5.11.

Fig. 5.11 Frequency spectrum according to Debye model and Einstein model

From (5.7.4), using (5.7.5), we obtain

$$E = \frac{9Nh}{v_D^3} \int_0^{\nu_D} \frac{\nu^3 d\nu}{e^{h\nu/kT} - 1}, \quad \text{in terms of } \nu_D. \qquad (5.7.6)$$

Putting $h\nu/kT = x$ and $h\nu_D/kT = x_D$, $\nu = xkT/h \Rightarrow d\nu = (kTdx)/h$.

$\therefore$ Equation (5.7.6) becomes,

$$E = \frac{9Nh}{v_D^3} \left(\frac{kT}{h}\right)^4 \int_0^{x_D} \frac{x^3 dx}{e^x - 1} = 9N \left(\frac{kT}{h\nu_D}\right)^3 kT \int_0^{x_D} \frac{x^3 dx}{e^x - 1} \qquad (5.7.7)$$

Defining, as in Einstein's theory, the *Debye (characteristic) temperature*

$$\Theta_D = \frac{h\nu_D}{k} \Rightarrow x_D = \frac{\Theta_D}{T}, \quad \text{we have from (5.7.7)}$$

$$E = 9NkT \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^3 dx}{e^x - 1} \qquad (5.7.8)$$

which does not depend explicitly on the volume.

$\therefore$ Molar specific heat, $C_V = \left(\frac{\partial E}{\partial T}\right)_V = 9N_A k \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{e^x x^4}{(e^x - 1)^2} dx$

$$= 3R \left(\frac{\Theta_D}{T}\right) F_D \qquad (5.7.9)$$

The function F_D is called the **Debye function** and is expressed as

$$F_D = 3 \left(\frac{T}{\Theta_D}\right)^4 \int_0^{\Theta_D/T} \frac{e^x x^4}{(e^x - 1)^2} dx \qquad (5.7.10)$$

Let us now consider the following two *limiting cases*.

(i) **High temperature case**: For $T \gg \Theta_D$, x is small compared to unity for the entire range of integration so that we have $e^x - 1 \simeq x$. The equation (5.7.8) reduces to

$$E = 9NkT \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} x^2 dx = 3NkT$$

$$\therefore C_V = \left(\frac{\partial E}{\partial T}\right)_V = 3Nk = 3R$$

in complete agreement with *Dulong and Petit's law*. It means, in fact, that quantum consideration has hardly any significance at high temperatures for when $T \gg \Theta_D$, every mode of oscillation is completely excited and has an average energy $\bar{\varepsilon} = kT$, the classical value.

(ii) **Low temperature case**: For $T \ll \Theta_D$, $x_D = \Theta_D/T \to \infty$ and the equation (5.7.8) reduces to the form

$$E = 9NkT \left(\frac{T}{\Theta_D}\right)^3 \int_0^\infty \frac{x^3 dx}{e^x - 1}$$

$$= 9NkT \left(\frac{T}{\Theta_D}\right)^3 \times \frac{\pi^4}{15} \qquad \left[\because \int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{\pi^4}{15}\right]$$

$$= \frac{3}{5}\pi^4 Nk \frac{T^4}{\Theta_D^3} \qquad (5.7.11)$$

which shows that the *vibrational energy is proportional to* T^4, analogous to Stefan's law of black radiation. This implies that *both phonons and photons obey the same statistics* with the difference that while photons obey T^4-law at all temperatures, phonons do so only at low temperatures.

$$\therefore \text{ Molar specific heat, } C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{12}{5}\pi^4 N_A k \left(\frac{T}{\Theta_D}\right)^3$$

$$= \frac{12}{5}\pi^4 R \left(\frac{T}{\Theta_D}\right)^3 \qquad (5.7.12)$$

Thus, *at very low temperatures, $C_V \propto T^3$* and this is the famous expression known as *Debye's T^3-law* for specific heat. According to this law, $C_V \to 0$ as $T \to 0$ (the law
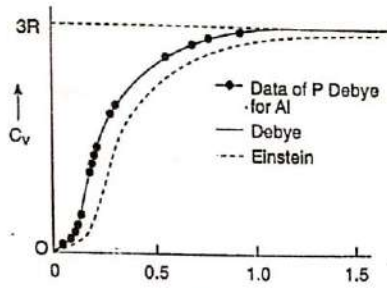
Fig. 5.12 Various specific heat curves of a solid

holds for $T \leq \Theta_D/10$). There is an *excellent agreement* between the experimental values of C_V at various temperatures with those calculated from Debye's model (Fig. 5.12) for Al and Cu validating the Debye-approximation at sufficiently low temperatures. Fig. 5.12 gives a typical Debye plot along with measured data, Einstein's plot and the classical value.

(iii) **Intermediate temperature case:** Debye's model agrees remarkably well at the two extremes of temperatures, i.e., in the range $T \leq \Theta_D/50$ and $T \geq 0.2\Theta_D$. But at temperatures intermediate between the above two, where a gradual transition of T^3-law to the classical one occurs, the agreement is not satisfactory.

This is because a solid cannot be treated as a continuum at frequencies near ν_D as assumed by Debye. In fact, this frequency corresponds to a wavelength of atomic spacing. The frequency spectrum of Debye model is different from that expected from
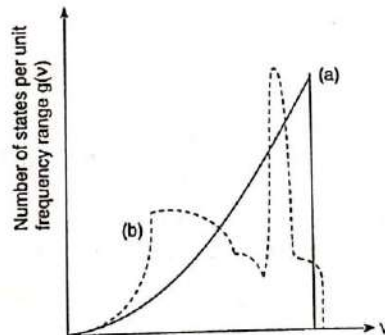

Fig. 5.13 Frequency spectrum (a) according to Debye model, (b) behaviour as expected from a real crystal

a real crystal, as illustrated in Fig. 5.13. But, interestingly, the area under the two curves are equal. To improve Debye's model, the correct dispersion relation and the corresponding density of states are to be used.

We conclude the section by summarising the different limitations of Debye's model.

https://youtu.be/JbsIEOnpfQ8

IMPORTANCE OF DEBYE THEORY

Most important, the theory put a cut-off to the frequency distribution at highest frequency of vibration corresponds to the nearest inter-atomic distance. This indicates that modes having wavelength smaller than inter-atomic distance is not possible, which is true.
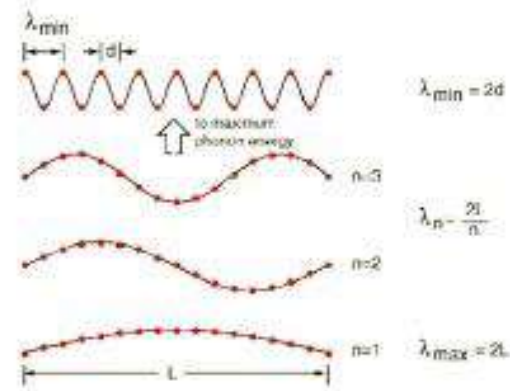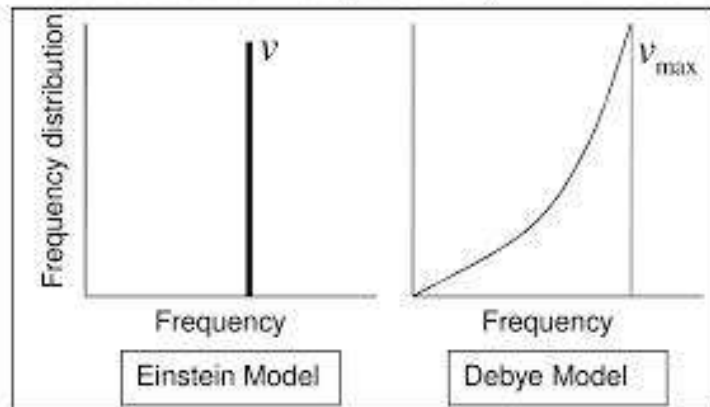
For most of the metals the Debye temperature lies in the range 300 to 400K. Since the Debye temperature is directly proportional to the maximum lattice frequency, a high value of the frequency implies that we are dealing with a lattice which has very strong inter-atomic forces and light atoms. e.g., for diamond

SUMMARY AND RECALL

https://youtu.be/1Ht1QLRcn_A

For $T >> \Theta_D$ $\qquad c = \dfrac{1}{V} 3Nk$

Same as a classical non-interacting gas

For $T << \Theta_D$ $\qquad c(T) = \dfrac{1}{V} 3Nk \dfrac{4\pi^4}{5} \left(\dfrac{T}{\Theta} \right)^3$

Quantum effects important

The assumptions of Debye theory are:
• the crystal is harmonic
• elastic waves in the crystal are non-dispersive
• the crystal is isotropic (no directional dependence)
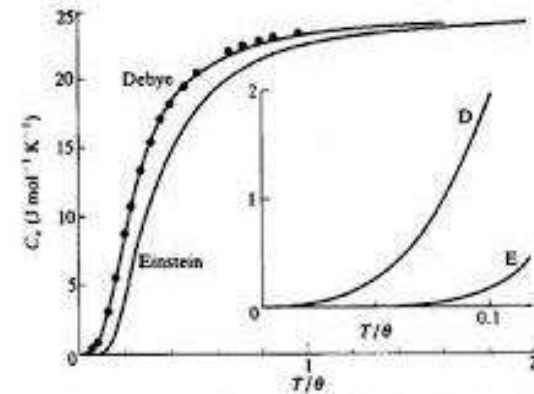• there is a high-frequency cut-off determined by the number of degrees of freedom

Figure 5.3 The Debye expression for the heat capacity fitted to data for Ag with $\theta_D = 215$ K. Here we also compare the Einstein and the Debye expressions when $\theta_E = \theta_D$. In particular, the inset diagram shows the failure of the Einstein values near the absolute zero of temperature.

SOLVED PROBLEMS

▶ **Example 8.** *For aluminium, the Debye temperature Θ_D is 400 K. Calculate its specific heat at constant volume at a temperature 40 K. Assume R = 2 calorie.*

Solution : Since 40 K is quite low a temperature, we may apply Debye's T^3-law.

$$\therefore \quad C_V = 77.9 \times 3R(T/\Theta_D)^3$$

$$= 77.9 \times 3 \times 2 \times (40/400)^3$$

$$= 0.467 \text{ cal.}$$

▶ **Example 9.** *Estimate the Debye temperature of gold if its atomic weight is 197, the density is 1.9×10^4 kg/m³ and the velocity of sound in it is 2100 m/s.*

Solution : At. wt. of Au = 197, density $\rho = 1.9 \times 10^4$ kg/m³, $v_s = 2100$ m/s, $\theta_D =$?

$$\therefore \quad \text{Volume, } V = \frac{M}{\rho} = \frac{197}{1.9 \times 10^4} = 103.68 \times 10^{-4} \text{ m}^3$$

$$\text{The Debye temperature, } \Theta_D = \frac{hv_s}{k} \left(\frac{9N_A}{12\pi V} \right)^{1/3}$$

$$= \frac{6.62 \times 10^{-34} \times 2100}{1.38 \times 10^{-23}} \left(\frac{9 \times 6.02 \times 10^{26}}{12\pi \times 103.68 \times 10^{-4}} \right)^{1/3}$$

$$= 240 \text{ K}$$