

**University of Calcutta**

**Semester 5**

**PHYSICS**

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**ACOUSTICAL AND OPTICAL PHONON**

**DULONG PETIT LAW**

**SOLVED PROBLEMS**

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# PHONON

- *For one-dimensional lattice, the energy for a particular mode of vibration is the same as that of a harmonic oscillator of the same frequency.*
- *The modes of vibration are quantised.*
- *Each quanta is known as a PHONON.*
- *PHONONS are indistinguishable particles.*
- *PHONONS obey Bose-Einstein statistics.*
- *The concept of PHONON can explain successfully many properties of solids, like the SPECIFIC HEAT, ELECTRICAL AND THERMAL CONDUCTIVITY.*

# ACOUSTICAL AND OPTICAL PHONONS

## 5.6. VIBRATIONAL MODES OF A CRYSTAL

The theory given above can be extended to actual crystals. For a linear atomic chain, both longitudinal and transverse waves can exist. The transverse modes consist of two independent vibrations in different planes. In an actual crystal, therefore, two transverse branches which may or may not coincide, occur. Also the longitudinal vibrations are there and the velocity  $c_l$  for the long-wavelength longitudinal waves in a crystal will be different from the corresponding velocity  $c_t$  for the transverse waves. Hence there will be different longitudinal and transverse branches of the  $\omega$  versus  $q$  curves of a crystal (see Fig. 5.6). In the long-wavelength limit, *i.e.* for  $q \rightarrow 0$ , the waves travel with the velocity of sound of corresponding polarisation; these branches are consequently called *acoustic modes*.

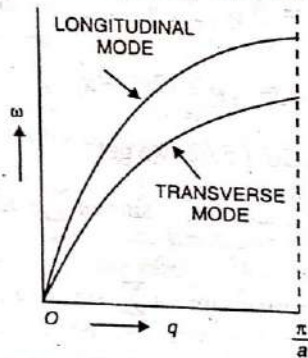


Fig. 5.6:  $\omega$  versus  $q$  curves for the transverse and longitudinal modes.

If the atoms in the linear chain are not identical, *e.g.*, if the alternate atom in the array have different masses, then, in addition to acoustic modes, another branch in the  $\omega - q$  plot appears. The frequencies for this branch are higher and for  $q \rightarrow 0$  the frequency for this branch approaches an angular frequency  $\omega_0 \neq 0$ . The frequency  $\omega_0$  falls in the infra-red range, so that this new mode of vibration is called *optical mode*. The optical modes may be transverse as well as longitudinal. There is a range of forbidden frequencies between the acoustic and optic modes (Fig. 5.7).

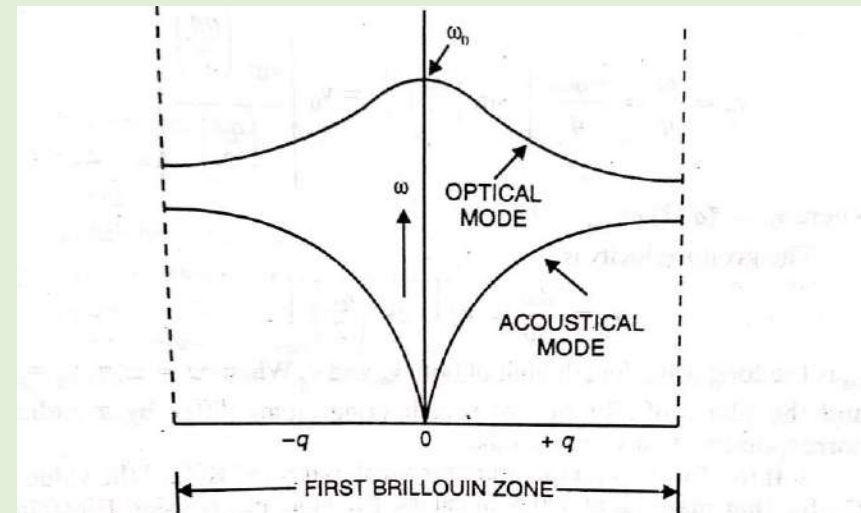
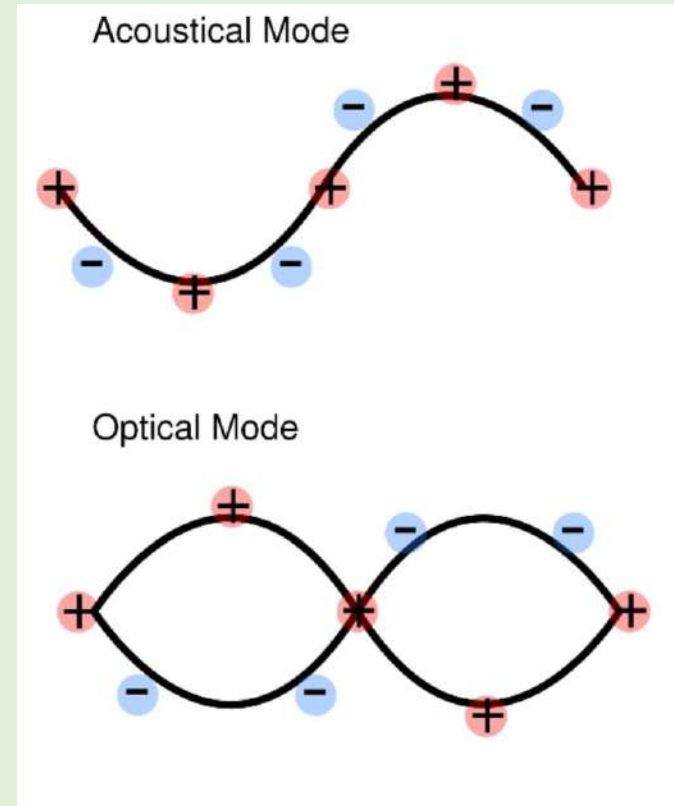
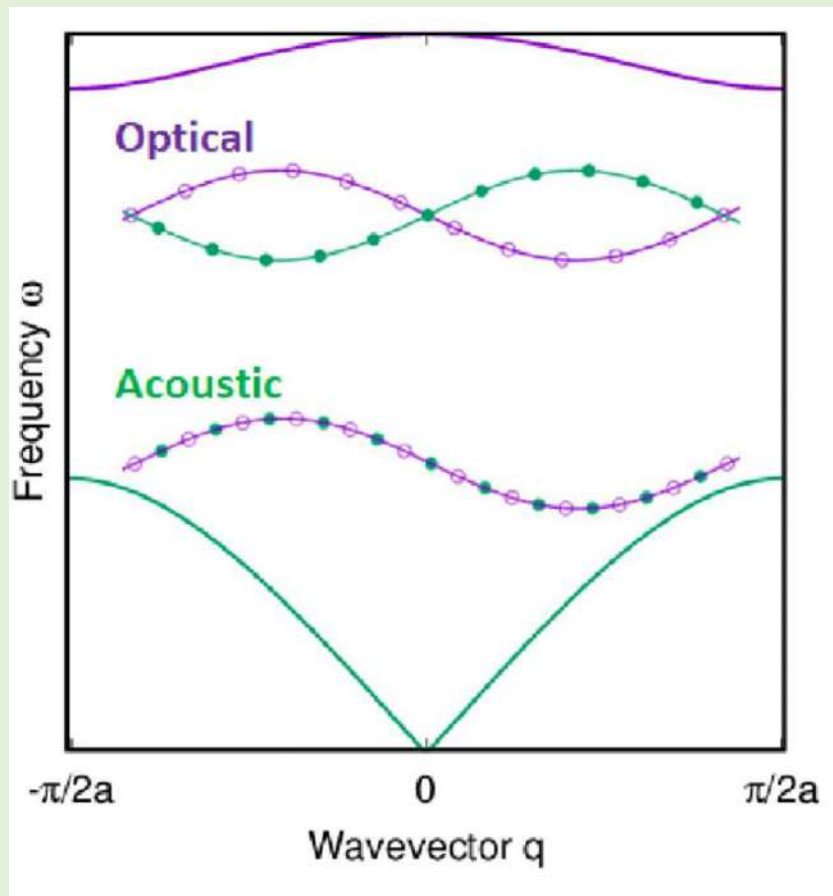


Fig. 5.7: Acoustic and optic vibrational modes for a linear array containing alternate atoms of different masses.



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# DULONG PETIT LAW

The **Dulong–Petit law**, a thermodynamic rule proposed in 1819 by French physicists Pierre Louis Dulong and Alexis Therese Petit, states the classical expression for the molar specific heat capacity of certain chemical elements. Experimentally the two scientists had found that the heat capacity per weight (the mass-specific heat capacity) for a number of elements was close to a constant value, *after* it had been multiplied by a number representing the presumed relative atomic weight of the element. These atomic weights had shortly before been suggested by Dalton



## 5.1. CLASSICAL CALCULATION OF LATTICE SPECIFIC HEAT

We consider a crystal of  $N$  atoms which are free to vibrate about their equilibrium positions. The restoring forces are assumed to obey Hooke's law. The energy of vibration of an atom would be the same as that of three one-dimensional harmonic oscillators, one for each of the three directions of motion. In the classical calculation, each atom is assumed to vibrate independently of the others, so that the total vibrational energy of the crystal is obtained by multiplying the average energy of a one-dimensional oscillator by  $3N$ .

The energy of a one-dimensional harmonic oscillator is given by

$$E = \frac{p_x^2}{2m} + \frac{1}{2} m\omega^2 x^2, \quad \dots(5.1)$$

where  $p_x$  is the momentum,  $m$  is the mass,  $\omega$  is the angular frequency, and  $x$  is the displacement of the atom from the equilibrium position. The first term on the right hand side of Eq. (5.1) is the kinetic energy and the second term is the potential energy.

Assuming that the oscillators obey the Maxwell-Boltzmann distribution law, the distribution function giving the probability of an oscillator to have an energy  $E$  is

$$f(E) = Ae^{-E/k_B T} = Ae^{-\frac{p_x^2}{2mk_B T}} e^{-\frac{m\omega^2 x^2}{2k_B T}} \quad \dots(5.2)$$

where  $A$  is a constant. According to statistical mechanics, the average energy is

$$\begin{aligned} \bar{E} &= \frac{\int_{p_x=-\infty}^{\infty} \int_{x=-\infty}^{\infty} \left( \frac{p_x^2}{2m} + \frac{1}{2} m \omega^2 x^2 \right) e^{-\frac{p_x^2}{2mk_B T}} e^{-\frac{m\omega^2 x^2}{2k_B T}} dp_x dx}{\int_{p_x=-\infty}^{\infty} \int_{x=-\infty}^{\infty} e^{-\frac{p_x^2}{2mk_B T}} e^{-\frac{m\omega^2 x^2}{2k_B T}} dp_x dx} \\ &= \frac{1}{2m} \frac{\int_{-\infty}^{\infty} p_x^2 e^{-p_x^2/2mk_B T} dp_x}{\int_{-\infty}^{\infty} e^{-p_x^2/2mk_B T} dp_x} + \frac{m\omega^2}{2} \frac{\int_{-\infty}^{\infty} x^2 e^{-\frac{m\omega^2 x^2}{2k_B T}} dx}{\int_{-\infty}^{\infty} e^{-\frac{m\omega^2 x^2}{2k_B T}} dx} \quad \dots(5.3) \end{aligned}$$

The first term on the right-hand side of Eq. (5.3) gives the average kinetic energy  $\bar{E}_K$  and the second term gives the average potential energy  $\bar{E}_p$ . Evaluating the integrals by gamma functions we get

$$\bar{E}_K = \bar{E}_p = \frac{1}{2} k_B T, \quad \dots(5.4)$$

so that  $\bar{E} = \bar{E}_K + \bar{E}_p = k_B T$

For a system of  $N$  atoms, the total vibrational energy or the total internal thermal energy is given by

$$U = 3NE = 3Nk_B T. \quad \dots(5.5)$$

If we consider a mole, the number  $N$  is equal to Avogadro's number  $N_0$ , and  $U = 3N_0 k_B T$ . Therefore, the molar specific heat at constant volume is

$$C_v = \left( \frac{\partial U}{\partial T} \right)_v = 3N_0 k_B = 3R, \quad \dots(5.6)$$

where  $R$  is the gas constant. Equation (5.6) gives the **Dulong-Petit** value of the specific heat at constant volume. The classical calculations thus show

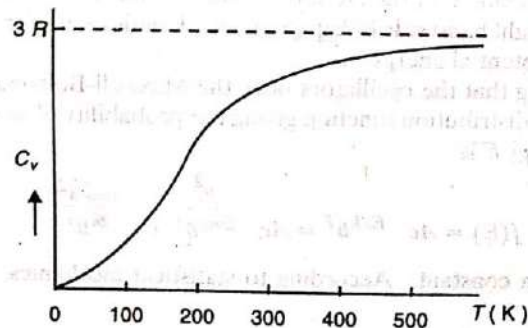
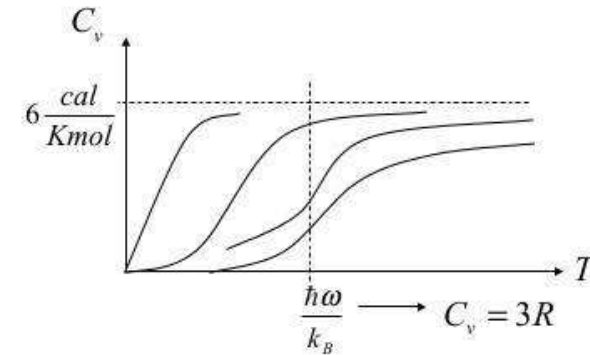


Fig. 5.1: Typical plot of the molar specific heat of a solid as a function of temperature, as observed experimentally.

# DRAWBACK OF DULONG PETIT LAW

that the contribution of the lattice vibration to the specific heat is  $3R$ , i.e.,  $24.9 \text{ JK}^{-1} \text{ mole}^{-1}$ , which is a constant independent of temperature. This result agrees well with the experimental results of the specific heat of many solids at and above room temperature; but serious disagreements occur at low temperatures. As the temperature approaches zero, the specific heat of all solids is found to decrease towards zero (see Fig. 5.1). For insulators the specific heat varies as  $T^3$  as the temperature  $T$  tends to zero, while for metals the specific heat varies as  $T$  as the temperature  $T$  approaches zero.

- At high temperatures, all crystalline solids have a specific heat of  $6 \text{ cal/K}$  per mole; they require  $6 \text{ calories}$  per mole to raise their temperature  $1 \text{ K}$ .
- This arrangement between observation and classical theory **break down** if the temperature **is not high**.
- Observations show that **at room temperatures and below** the specific heat of crystalline solids **is not a universal constant**.



In each of these materials (Pb, Al, Si, and Diamond) specific heat approaches constant value asymptotically at high  $T$ . But at low  $T$ 's, the specific heat decreases towards zero which is in a complete contradiction with the above classical result.

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# SOLVED PROBLEM

## LAW OF DULONG AND PETIT

Q1 Estimate the specific heat of platinum.

Ans. According to the law of Dulong and Petit, the molar heat capacity of Pt (or any other metallic element) is 6 cal/mol·°C. The specific heat is therefore given by

$$\frac{6 \text{ cal}}{\text{mol}\cdot^{\circ}\text{C}} \left( \frac{1 \text{ mol}}{195 \text{ g}} \right) = 0.03 \text{ cal/g}\cdot^{\circ}\text{C}$$

Q2 A 40.0 g sample of a metal at 50.0°C is immersed in 100.0 g of water at 10.0°C. The final temperature of the system is 13.0°C. What is the specific heat of the metal? What is the approximate atomic weight of the metal?

Ans.

$$\begin{aligned} \text{Heat lost} &= -\text{heat gained} \\ (40.0 \text{ g})c(37.0^{\circ}\text{C}) &= (100 \text{ g})(1.0 \text{ cal/g}\cdot^{\circ}\text{C})(3.0^{\circ}\text{C}) \\ c &= 0.20 \text{ cal/g}\cdot^{\circ}\text{C} \end{aligned}$$

According to the law of Dulong and Petit, the metal has a molar heat capacity = 6 cal/mol·°C. Hence the atomic weight is approximately

$$\frac{6 \text{ cal/mol}\cdot^{\circ}\text{C}}{0.20 \text{ cal/g}\cdot^{\circ}\text{C}} = 30 \text{ g/mol} = 30 \text{ u}$$

Q3 Estimate the final temperature of a system after 1.6 mol of an unknown crystalline metal at 60.0°C was immersed in 100 g of water at 20.0°C.

Ans. From the law of Dulong and Petit,  $C = 6 \text{ cal/mol}\cdot^{\circ}\text{C}$

$$\begin{aligned} (1.6 \text{ mol})(6 \text{ cal/mol}\cdot^{\circ}\text{C})(60.0 - t) &= 100 \text{ g} (1.0 \text{ cal/g}\cdot^{\circ}\text{C})(t - 20.0) \\ t &= 24^{\circ}\text{C} \end{aligned}$$

A metallic element whose specific heat is 0.11 cal/g·°C forms an oxide containing 22.27% oxygen. Identify the element.