

Name of the Teacher-Chitra

Guest lecturer, Department of physics and Electronics

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Applied Physics

Lecture-15 & 16

Unit III-Thermal Properties of solids

Topics to be discussed in this lecture:

- Specific heat
- Specific heat of solids (**Dulong and Petit's law**)
- **Einstein Quantum theory of specific heat of solids**
- **Debye theory of Specific heat of solids**

Specific heat

The specific heat of any substance is defined as the quantity of heat energy required to raise the temperature of unit mass of substance through 1°C. The specific heat of substance is expressed in C.G.S system in unit erg/gm/ °C and in M.K.S. system in unit Joule/kg/ °C. In terms of old unit of heat, i.e., Calorie (=4.2× 10⁷ ergs), it is expressed in unit Cal/gm/ °C. The specific heat of substance varies with temperature. The specific heat determined experimentally is the mean specific heat of the substance. For different substances of heat capacity is also different. If ΔQ represents the quantity of heat energy to a substance m and rise in temperature is $\Delta\theta$, then

Specific heat $\bar{C} = \frac{1}{m} \cdot \frac{\Delta Q}{\Delta\theta}$ (1)

$$\text{And heat capacity} = \frac{\Delta Q}{\Delta \theta} \quad (2)$$

Thus the heat capacity of the substance can be defined as the ratio of heat supplied to the corresponding rise in temperature, i.e., the heat energy required to raise the temperature of the body by 1°C. Clearly its unit will be kilo-Cal/°C or J/°C or Cal/°C in the respective system of units.

Molar or atomic specific heat: It is defined as the quantity of heat energy required to raise the temperature of 1 kg-mole or 1kg-atom of any substance by 1 °C. Its unit in M.K.S system is J×kg/mole/°C. Clearly it is the product of molecular weight or atomic weight with the specific heat. Molar or atomic specific heat is usually denoted by letter C_v .

Specific heat of gases: In case of gases it is necessary to specify the physical conditions such as constant pressure or constant volume. Thus gases has two specific heats, specific heat at constant pressure (C_p) and specific heat at constant volume (C_v).

Specific heat of solids (Dulong and Petit's law)

In 1819, Dulong and Petit established empirically that the atomic specific heat (i.e., the product of atomic weight and specific heat) of all solids is nearly equal to 6 Cal/gm-atom/°C or 6 Cal/kg-atom/ K. this law shows that the atomic specific heat is independent of temperature and depends on the number of molecules or atoms that the solid contains and not the mass of the solid. The value of atomic heat of solids also agrees with the value derived from kinetic molecular theory.

Atomic specific heat of about 60 elements in solid state are found to lie in the range 5.38 to 6.93 Cal/gm-atom/°C with an average of 6.15. However, some light

elements having high melting points deviate considerably from Dulong and Petit's law i.e., Silicon has atomic specific heat 4.95 and diamond has 1.46.

Deduction of Dulong and Petit's law from classical theory

At absolute zero, the atoms in the solid are arranged in a regular crystalline array and are at rest due to mutual interaction between them. When the temperature of the solid is increased, energy of the atoms in solid increases and they start oscillating about their mean positions. If the temperature is not very high, then the vibrations of atoms are nearly simple harmonic and the total energy of the vibration is represented by

$$E = E_x + E_y + E_z \quad (3)$$

$$E_x = \frac{1}{2}m\dot{x}^2 + \frac{1}{2}k_x x^2 \quad (4.1)$$

$$E_y = \frac{1}{2}m\dot{y}^2 + \frac{1}{2}k_y y^2 \quad (4.2)$$

$$E_z = \frac{1}{2}m\dot{z}^2 + \frac{1}{2}k_z z^2 \quad (4.3)$$

Equation 3 has 3 terms on r.h.s showing that the atom has three degrees of freedom of vibration. Here k_x , k_y and k_z are restoring force constants along the three axes. First term in equation 4 represents the kinetic energy and the second term represents potential energy.

If the solid is in thermal equilibrium at absolute temperature T, then by the law of equipartition of energy, the average energy associated with each of the six squared terms in equation 4 for E is $\frac{1}{2}kT$, where k is the Boltzmann constant. Therefore average energy per atom

$$\bar{E} = 6 \times \frac{1}{2}kT = 3kT \quad (5)$$

Now 1 kg-atom of a solid has N atoms in it ($=6.03 \times 10^{26}$ atoms/-kg), where N is the Avogadro number. Thus the total energy of 1 kg-atom of solid is given by

$$U = N \times 3kT = 3RT \quad (6)$$

[Gas constant, $R = 8.4 \times 10^3 \text{ J/kg-atom/K}$]

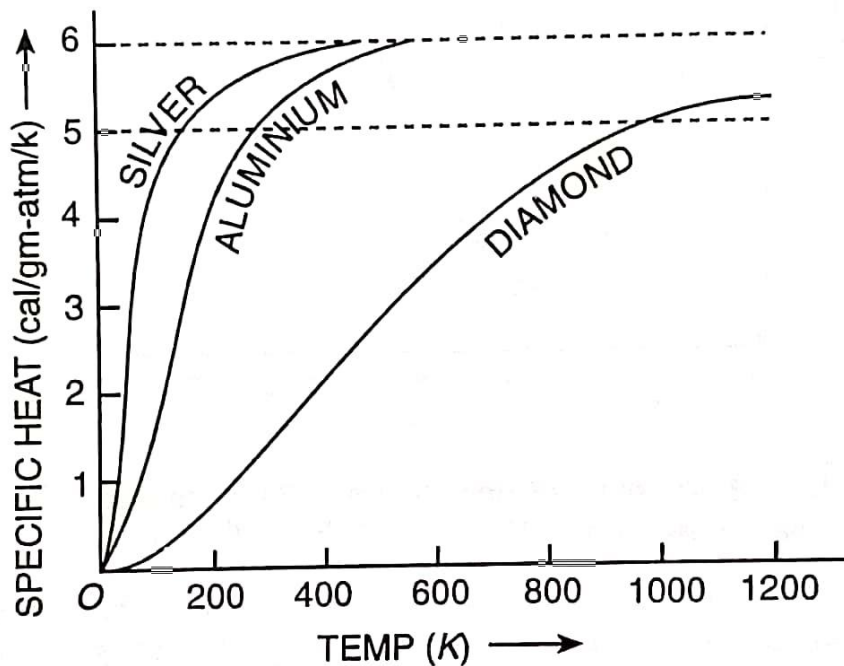
The atomic specific heat of a solid at constant volume is the energy required to raise the temperature of 1-kg-atom of substance by 1°C .

$$C_v = \frac{dU}{dT} = \frac{d}{dT}(3RT) = 3R \quad (7)$$

This is Dulong Petit's Law.

The variation of specific heat with temperature

We have seen that according to the Dulong and Petit's law, the specific heat of all solids must be about 6 and furthermore it should not vary with temperature. However this is not true. Experimental observations reveal that non metallic solids such as Boron, carbon and silicon have specific heat value approach to the value given by Dulong and Petit's law.



Experimental results regarding the specific heats of metallic solids, show that at ordinary temperatures the value of specific heat lies near 6 and changes little with the increase in temperature. Clearly, metallic solids obey Dulong and Petit's law. However, the law completely fails at very low temperatures. Experimental observations indicate that the atomic specific heat at low temperatures is found to decrease with fall in temperature. Below a certain temperature specific heat falls rapidly with decreasing temperature and tends to zero at absolute zero temperature.

The non agreement of results of specific heat of solids obtained from Dulong and Petit's law (classical theory) with experiment led to the belief that classical theory breaks down in this case. Einstein in 1907 successfully applied the quantum theory to the problem.

Einstein quantum theory of specific heat

To explain the variation of specific heat of solids with temperature Einstein assumed

- (1) The atoms of solids are at rest under the action of their mutual forces of attraction at absolute zero temperature i.e., the energy of solid in this state is zero. When the temperature of the solid is increased, the atoms are set into simple harmonic vibrations about their mean positions with a frequency ν , which is characteristic of a solid and is called Einstein's frequency.
- (2) Each atom of a solid has three degrees of freedom just like a molecule of monoatomic gas.
- (3) Each atom of a solid behaves as a plank's oscillator, i.e., its energy is quantized. If ν is the characteristic frequency (differs from solid to solid) then its energy is integral multiple of $h\nu$. The mean energy per degree of freedom is not kT as given by equipartition law but is given by

$$\epsilon = hv/[e^{hv/kT} - 1] \quad (8)$$

Thus the energy associated with each atom having 3 degrees of vibrational freedom = $\frac{3hv}{e^{hv/kT} - 1}$

Therefore, Energy of a gm atom of the solid consisting of N atoms is

$$U = \frac{3N hv}{e^{hv/kT}} \quad (9)$$

Atomic specific heat of solid is given by

$$\begin{aligned} C_v &= \frac{dU}{dT} = 3Nk \left(\frac{hv}{kT}\right)^2 \frac{e^{hv/kT}}{(e^{hv/kT} - 1)^2} \\ &= 3R \left(\frac{hv}{kT}\right)^2 \frac{e^{hv/kT}}{(e^{hv/kT} - 1)^2} \end{aligned}$$

Put $hv/k = \theta_E$, where θ_E is the Einstein's characteristic temperature of a solid. It has dimensions of temperature.

$$C_v = 3R \left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2} \quad (10)$$

Above equation is called the atomic specific heat formula of solids. Therefore, the value of ν gives good fit for a particular solid and is given by ν_E . Equation 10 also shows that C_v is the function of temperature as shown below:

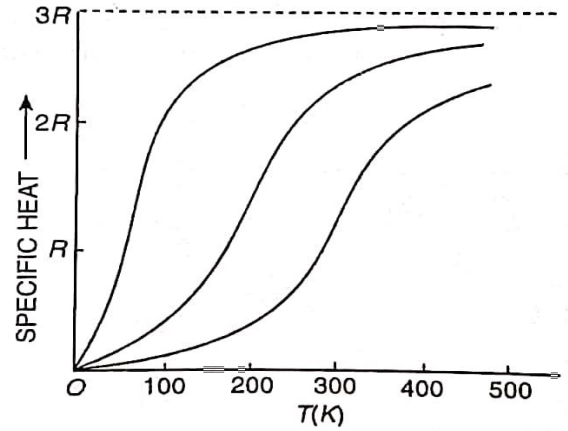


Fig. 8.2. Variation of Specific heat of a solid with temperature according to Einstein's theory.

Now we will discuss the results in different temperature range:

(I) **At high temperature:** $T \gg \theta_E$, $\therefore \frac{\theta_E}{T} \ll 1$ and $\exp\left(\frac{\theta_E}{T}\right) = 1 + \frac{\theta_E}{T} + \dots$

Thus equation 10 takes the form

$$C_v = 3R \left(\frac{\theta_E}{T}\right)^2 \frac{1 + \frac{\theta_E}{T}}{\left(1 + \frac{\theta_E}{T} - 1\right)^2} = \frac{3R \left(\frac{\theta_E}{T}\right)^2 \left(1 + \frac{\theta_E}{T}\right)}{\left(\frac{\theta_E}{T}\right)^2}$$

$$= 3R \left(\frac{\theta_E}{T} \right) = 3R \quad (11)$$

Thus the results at high temperature are in agreement with Dulong Petit's Law as well as with experiments.

(2) At very low temperatures: At very low temperatures we have

$T \ll \theta_E$, i.e., $\frac{\theta_E}{T} \gg 1$, so, $\exp \left(\frac{\theta_E}{T} \right) \gg 1$. This 1 may be neglected in comparison to $e^{\theta_E/T} \rightarrow 0$, hence

$$C_v = 3R \left(\frac{\theta_E}{T} \right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T})^2} = 3R \left(\frac{\theta_E}{T} \right)^2 e^{-\theta_E/T} \quad (12)$$

As $T \rightarrow 0$, $\frac{h\nu}{kT} = \frac{\theta_E}{T} \rightarrow \infty$; $e^{-\theta_E/T} \rightarrow 0$, hence

$$C_v = 0$$

This shows that as $T \rightarrow 0$, the atomic specific heat also approaches to zero, a conclusion in general agreement with experiments.

Theoretical curves showing the variation of C_v with temperature (shown above), one can see that the $C_v \rightarrow 0$ and $C_v \rightarrow 3R$ as $T \rightarrow 0$ and $T \rightarrow \infty$ respectively.

However, this theory has certain limitations:

- (a) Einstein's theory gives qualitative account of the experimental results; there is no quantitative agreement between specific heat curves and theory. Atomic specific heat, C_v of some solids like copper, iron, aluminum etc. decreases more rapidly than predicted by this theory. The theory fails at very low temperatures where C_v is found to be nearly proportional to T^3 rather than as represented by equation 12.
- (b) Value of Einstein's characteristic frequency ν_E for a solid has to be chosen arbitrarily to fit with the experimental value. Attempts to relate this with other properties of solids such as compressibility, melting point etc. were not very successful.

The above disagreement between theory and operational results is due to the neglect of mutual forces exerted by atoms in a solid on each other. Taking this into consideration, Debye in 1912 modified Einstein's theory which gives excellent agreement over the whole temperature range.

Debye theory of specific heat of solids

Debye treated the solid as a continuous elastic body in which the vibrations of the atoms generate stationary waves. According to Debye, the atoms in a solid do not vibrate independently with same frequency. The oscillations belong to the entire solid and frequencies of various modes of oscillation vary from 0 to a certain maximum value ν_m which is characteristic of a substance and one can express it in terms of elastic constants.

Let us consider a unit volume of continuous solid subjected to elastic vibrations. There are two kind of elastic vibrations that can occur in solid: (i) *longitudinal vibrations* with speed C_l and (ii) *transverse vibrations* with speed C_t . The number of longitudinal modes of vibration per unit volume in frequency range in ν and $\nu+d\nu$ is given by $4\pi\nu^2 d\nu / C_l^3$. Since transverse vibrations are polarized in two

perpendicular directions and hence the number of transverse mode of vibration per unit volume in the given frequency range ν and $\nu+d\nu$ is given by $8\pi\nu^2 d\nu / C_t^3$.

Therefore the total number of independent modes of vibrations in the given frequency range ν and $\nu+d\nu$ in volume V is given by

$$= 4\pi V \left[\frac{1}{C_l^3} + \frac{2}{C_t^3} \right] \nu^2 d\nu \quad (14)$$

Since the total number of independent modes of vibrations is equal to the total number of degree of freedom of all atoms of the solid, i.e., $3N$ and hence

$$4\pi V \int_0^{v_m} \left[\frac{1}{c_l^3} + \frac{2}{c_t^3} \right] v^2 dv = 3N$$

or
$$4\pi V \left[\frac{1}{c_l^3} + \frac{2}{c_t^3} \right] \frac{v_m^3}{3} = 3N$$

$$\therefore v_m^3 = \frac{9N}{4\pi V \left[\frac{1}{c_l^3} + \frac{2}{c_t^3} \right]} \quad (15)$$

Knowing elastic constant of given solid one can find v_m from equation 15.

Energy of the solid: According to plank's quantum hypothesis, the mean energy per mode of vibration is given by

$$\bar{E} = hv / (\exp\left(\frac{hv}{kT}\right) - 1)$$

Therefore the total energy of a gm atom (having N atoms) of the solid is

$$\begin{aligned} U = \bar{E}N &= 4\pi V \left[\frac{1}{c_l^3} + \frac{2}{c_t^3} \right] \int_0^{v_m} \frac{hv^3 dv}{e^{hv/kT} - 1} \\ &= \frac{9N}{v_m^3} \int_0^{v_m} \frac{hv^3 dv}{e^{hv/kT} - 1} \end{aligned}$$

Let's put $\frac{hv}{kT} = x$ then $v = \frac{kTx}{h}$ and $dv = \frac{kT}{h} dx$

$$\begin{aligned} \therefore U &= \frac{9N}{v_m^3} \left(\frac{kT}{h}\right)^3 kT \int_0^{x_m} \frac{x^3}{e^x - 1} dx \\ &= 9Nk \left(\frac{k}{hv_m}\right)^3 T^4 \int_0^{x_m} \frac{x^3}{e^x - 1} dx \quad (16) \end{aligned}$$

Now let us introduce new characteristic temperature Θ , called as Debye temperature as

$$\Theta = \frac{h\nu_m}{k}, \text{ so that } x_m = \frac{h\nu_m}{kT} = \frac{\Theta}{T} \quad (17)$$

From equation 16 and 17, we have

$$U = 9Nk\left(\frac{T^4}{\Theta^4}\right) \int_0^{\Theta/T} \frac{x^3}{e^x - 1} dx \quad (18)$$

\therefore Atomic specific heat

$$C_v = \frac{dU}{dT} = 3R \left[12 \left(\frac{T}{\Theta}\right)^3 \int_0^{\Theta/T} \frac{x^3}{e^x - 1} dx - \left(\frac{\Theta}{T}\right) \frac{3}{e^{\Theta/T} - 1} \right] \text{ since, } Nk=R \quad (19)$$

$$= 3RD\left(\frac{\Theta}{T}\right) \quad (20)$$

This is called Debye's formula for atomic specific heat of solids. $D\left(\frac{\Theta}{T}\right)$ is called Debye function and it denotes the expression within square brackets in equation 19 and 20 reveals the following facts:

(i) At high temperature: $C_v \approx 3R$, as both x and $\left(\frac{\Theta}{T}\right)$ are very small so that $e^x = 1 + x + \dots$ and $e^{\left(\frac{\Theta}{T}\right)} = 1 + \left(\frac{\Theta}{T}\right) + \dots$ using these expansions in equation 19 we get,

$$\begin{aligned} C_v &= 3R \left[12 \left(\frac{T}{\Theta}\right)^3 \int_0^{\Theta/T} x^2 dx - \left(\frac{\Theta}{T}\right) \frac{3}{\left(\frac{\Theta}{T}\right)} \right] \\ &= 3R \left[12 \left(\frac{T}{\Theta}\right)^3 \frac{1}{3} \left(\frac{\Theta}{T}\right)^3 - 3 \right] \cong 3R \end{aligned}$$

Which is Dulong-Petit's result in excellent agreement with experiment at high temperatures.

(ii) **At low temperatures:** At very low temperatures $\left(\frac{\theta}{T}\right) \rightarrow \infty$ and hence the second term in the square bracket of eq. 19, becomes negligible. Therefore one can replace the upper limit of the integration in the first term by ∞ , thus we have,

$$C_v = 3R \left[12 \left(\frac{T}{\theta}\right)^3 \int_0^\infty \frac{x^3}{e^x - 1} dx \right]$$

$$\cong 3R \left(\frac{T}{\theta}\right)^3 \frac{\pi^4}{15} \approx \frac{12\pi^4 R}{5\theta^3} T^3 \quad (21)$$

Since θ is a constant of a solid and hence one obtains

$$C_v \propto T^3 \quad (22)$$

This is *Debye's T^3 law*. Thus the specific heat at extremely low temperatures varies as the cube of absolute temperature and fits experimentally.

(iii) **At intermediate temperatures:** The Debye's formula (eq. 19) has been evaluated numerically for many solids at intermediate temperatures. The results are in good agreements.

A graph between C_v and $D\left(\frac{\theta}{T}\right)$ is shown here further reveals:

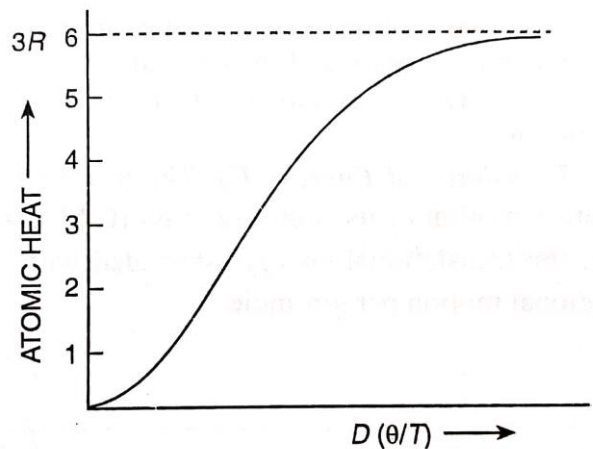


Fig. 8-3. C_v Vs $D(\theta/T)$ graph.

- (a) The atomic sp. Heat of all solids decreases with decrease in temperature and tends to zero as the temperature tends to zero.
- (b) The variation of C_v with temperature is same for all substances