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Ques : Deduce Debye's theory of specific heat of solids and discuss how it agrees with experiment? (2012, 2014, 2016)

Ans : The discrepancies present in Einstein's theory of specific heat of solids are mostly removed by Debye's theory of specific heat of solids. Debye's theory is in excellent agreement with experiment over the whole observable temperature range.

There are following assumptions made by Debye.

(1) Any solid is capable of vibrating elastically in many different modes and frequency of their vibration changes from one mode to another mode.

(2) The number of modes of vibrations of solids is limited.

(3) When a solid is subjected to continuous elastic vibration then these vibrations in solids set up two types of waves in the solid.

(a) Transverse vibration with velocity C_t

(b) Longitudinal vibration with velocity C_l

Theory : Suppose V be volume of one gram atom of a particular solid.

The number of modes of longitudinal vibration with frequencies between ν and $\nu + d\nu$ is

$$n_1 = \frac{4\pi V \nu^2 d\nu}{C_l^2}$$

The number of modes of transverse vibration with frequencies between ν and $\nu + d\nu$ is

$$n_2 = \frac{8\pi V \nu^2 d\nu}{C_t^2}$$

(The expression is doubled because each transverse vibration is equivalent to two waves polarised at right angle)

Total number of independent modes of vibration with frequencies between ν and $\nu + d\nu$ is

$$n = n_1 + n_2 = 4\pi V\left(\frac{1}{C_l^2} + \frac{2}{C_t^2}\right)\nu^2 d\nu$$

Thus total number of independent modes of vibration in one gram atom of the solid is

$$= \int_0^{\nu_m} 4\pi V\left(\frac{1}{C_l^2} + \frac{2}{C_t^2}\right)\nu^2 d\nu \quad \text{..........................(1)}$$

According to Debye, the upper limit of frequency is ot infinte but a defenite limit ν_m. This limit is choosen so that tyhe total number of possible independent vibration is equal to the number of vibrations of separate atoms taken together in solid. Let N be number of atoms in volume V of the solid then total number of modes of vibration = 3N because each atom has three degree of feedom.

$$\int_0^{\nu_m} 4\pi V\left(\frac{1}{C_l^2} + \frac{2}{C_t^2}\right)\nu^2 d\nu = 3N \Rightarrow 4\pi V\left(\frac{1}{C_l^2} + \frac{2}{C_t^2}\right)\left(\frac{\nu^3}{3}\right)_0^{\nu_m} = 3N$$

$$\Rightarrow 4\pi V\left(\frac{1}{C_l^2} + \frac{2}{C_t^2}\right) = \frac{9N}{\nu_m^3} \quad \text{..........................(2)}$$

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From quantum theory, the enrgy associated with each degree of freedom = $\frac{h\nu}{e^{h\nu/kT}-1}$

The thermal energy of 1 gram atom of solid for frequencies between ν and $\nu + d\nu$ is

$$dE = \frac{h\nu}{e^{h\nu/kT}-1}\cdot 4\pi V\left(\frac{1}{C_l^2}+\frac{2}{C_t^2}\right)\nu^2 d\nu \Rightarrow dE = \frac{h\nu}{e^{h\nu/kT}-1}\cdot\frac{9N}{\nu_m^3}\cdot\nu^2 d\nu \quad \text{(using equation 2)}$$

$$\Rightarrow dE = \frac{9N}{\nu_m^3}\cdot\frac{h\nu^3}{e^{h\nu/kT}-1}d\nu \qquad \text{.......................} \ (3)$$

Total thermal energy of 1 gram atom of the solid will be

$$E = \int dE = \int_0^{\nu_m}\frac{9N}{\nu_m^3}\cdot\frac{h\nu^3}{e^{h\nu/kT}-1}d\nu \Rightarrow E = \frac{9N}{\nu_m^3}\int_0^{\nu_m}\frac{h\nu^3}{e^{h\nu/kT}-1}d\nu \qquad \text{....................} \ (4)$$

Put $\frac{h\nu}{kT} = x$ then $\nu = \frac{kT}{h}x \Rightarrow d\nu = \frac{kT}{h}dx$ if $\nu = 0$ then $x = 0$ and if $\nu = \nu_m$ then $x = \frac{h\nu_m}{kT} = \frac{\theta}{T}$

where $\frac{h\nu_m}{kT} = \frac{\theta}{T} \Rightarrow \theta = \frac{h\nu_m}{k}$ or $\nu_m = \frac{k\theta}{h}$, in equation (4)

$$E = \frac{9Nh^3}{k^3\theta^3}\int_0^{\theta/T}\frac{hk^3T^3}{(e^x-1)h^3}x^3\frac{kT}{h}dx \Rightarrow E = \frac{9NkT^4}{\theta^3}\int_0^{\theta/T}\frac{x^3}{e^x-1}dx \qquad \text{....................} \ (5)$$

The specific heat of one gram atom at constant volume is

$$C_V = \frac{dE}{dT} = \frac{d}{dT}\left(\frac{9NkT^4}{\theta^3}\int_0^{\theta/T}\frac{x^3}{e^x-1}dx\right) \Rightarrow C_V = 9NK\left[4\frac{T^3}{\theta^3}\int_0^{\theta/T}\frac{x^3}{e^x-1}dx + \frac{T^4}{\theta^3}\frac{d}{dT}\left(\int_0^{\theta/T}\frac{x^3}{e^x-1}dx\right)\right]$$

$$\Rightarrow C_V = 9NK\left[4\frac{T^3}{\theta^3}\int_0^{\theta/T}\frac{x^3}{e^x-1}dx - \frac{\theta}{T}\cdot\frac{1}{e^{\theta/T}-1}\right] \qquad \text{.......................} \ (6)$$

(Since $\frac{T^4}{\theta^3}\frac{d}{dT}\left(\int_0^{\theta/T}\frac{x^3}{e^x-1}dx\right) = \frac{T^4}{\theta^3}\frac{d}{dT}\left(\int_0^{\theta/T}\frac{\theta^3/T^3}{e^{\theta/T}-1}\cdot\left(-\frac{\theta}{T^2}\right)dT\right) \because x = \frac{\theta}{T} \Rightarrow dx = -\frac{\theta}{T^2}dT$

$\frac{T^4}{\theta^3}\frac{d}{dT}\left(\int_0^{\theta/T}\frac{x^3}{e^x-1}dx\right) = \frac{T^4}{\theta^3}\frac{\theta^3/T^3}{e^{\theta/T}-1}\cdot\left(-\frac{\theta}{T^2}\right) = -\frac{\theta}{T}\cdot\frac{1}{e^{\theta/T}-1}$)

Thus $C_V = 9NK\left[4\left(\frac{T}{\theta}\right)^3\int_0^{\theta/T}\frac{x^3}{e^x-1}dx - \frac{\theta}{T}\cdot\frac{1}{e^{\theta/T}-1}\right] = 3NK\left[12\left(\frac{T}{\theta}\right)^3\int_0^{\theta/T}\frac{x^3}{e^x-1}dx - \frac{\theta}{T}\cdot\frac{3}{e^{\theta/T}-1}\right]$

$$\Rightarrow C_V = 3R\left[12\left(\frac{T}{\theta}\right)^3\int_0^{\theta/T}\frac{x^3}{e^x-1}dx - \frac{\theta}{T}\cdot\frac{3}{e^{\theta/T}-1}\right] \qquad \text{.........} \ (7) \quad \because NK = R = \text{Gas constant}$$

Equation (7) is called Debye's equation for specific heat of monoatomic solid.

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The term in the square bracket of equation (7) is a function of θ/T and it may be denoted by $f(\theta/T)$ known as Debye's function.

Here the parameter $\theta = h\nu_m / K$ varies from element to element known as Debye's temperature.

Equation (7) in terms of Debye's function may be written as $C_V = 3Rf(\theta/T)$

Case I : At high temperature, $x = \frac{h\nu_m}{kT} = \frac{\theta}{T}$ is very small so $e^x = 1 + x \Rightarrow e^{\theta/T} = 1 + \frac{\theta}{T}$ using these in equation (7), we get

$$C_V = 3R\left[12\left(\frac{T}{\theta}\right)^3 \int_0^{\theta/T} \frac{x^3}{1+x-1}dx - \frac{\theta}{T}\cdot\frac{3}{1+\theta/T-1}\right] = 3R\left[12\left(\frac{T}{\theta}\right)^3 \int_0^{\theta/T} x^2 dx - \frac{\theta}{T}\cdot 3\frac{T}{\theta}\right]$$

$$\Rightarrow C_V = 3R\left[12\left(\frac{T}{\theta}\right)^3 \frac{1}{3}\left(\frac{\theta}{T}\right)^3 - 3\right] = 3R(4-3) \Rightarrow C_V = 3R$$

It means , atomic heat of all solid substances tends to maximum value equal to zero.

Case II : At very low temperature near absolute temperature: $x = \frac{h\nu_m}{kT} = \frac{\theta}{T} \to \infty$ since $T \to 0$

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

$$\Rightarrow C_V = 3R\left[12\left(\frac{T}{\theta}\right)^3 \int_0^{\infty} \frac{x^3}{e^x-1}dx - \frac{\theta}{T}\cdot\frac{3}{1+\frac{\theta}{T}+\frac{1}{2}\left(\frac{\theta}{T}\right)^2+\frac{1}{3}\left(\frac{\theta}{T}\right)^3+\ldots-1}\right]$$

$$\Rightarrow C_V = 3R\times 12\left(\frac{T}{\theta}\right)^3 \int_0^{\infty} \frac{x^3}{e^x-1}dx - 3R\times\frac{3}{1+\frac{1}{2}\left(\frac{\theta}{T}\right)+\frac{1}{3}\left(\frac{\theta}{T}\right)^2+\ldots} = 36R\left(\frac{T}{\theta}\right)^3\cdot\frac{\pi^4}{15} - \frac{9R}{\infty}$$

$$\left(\because \int_0^{\infty} \frac{x^3}{e^x-1}dx = \frac{\pi^4}{15} \quad \text{and} \quad \frac{\theta}{T} = \infty\right)$$

$\Rightarrow C_V = \frac{36\pi^4 R}{15}\left(\frac{T}{\theta}\right)^3 \Rightarrow C_V \propto T^3$ Thus at low temperature, the atomic heat of solid is directly proportional to cube of its absolute temperature. It is known as Debye's T^3 law.

Atomic (specific) heat of solid substance decreases with decrease in temperature and tends to become zero as absolute temperature tends to zero.

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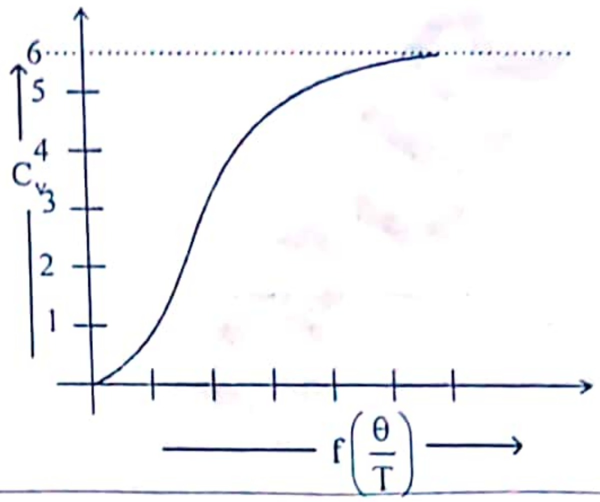
According to Debye, the atomic of solid substance at absolute temperature T is $C_V = 3R \cdot f\left(\frac{\theta}{T}\right)$ where $f\left(\frac{\theta}{T}\right)$ is the function which is same for all the elements. A graph between atomic heat (C_V) and function $f\left(\frac{\theta}{T}\right)$ is plotted as per Debye's theory as shown in figure which is same for all elements which agrees with experiment.



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