

## Einstein's Theory of Specific heat

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The specific heat of all solids drop sharply at low temperatures and approaches 0, as  $T$  approaches 0K, could not be explained satisfactorily on the basis of classical theory.

The first attempt to explain the variation of specific heat of solid at low temperature was made by Einstein in 1907 on the basis of quantum principles related to the thermal vibration of atoms in solids.

Einstein assume that

the atoms of crystal are identical, independent harmonic ~~oscilla~~ oscillators, all of which vibrate independently with the natural frequency, but have discrete energy values. These discrete values are given by Planck's formula

$$E_n = \left(n + \frac{1}{2}\right) h\nu_0 \quad \text{with } n = 0, 1, 2, 3, \dots \quad \text{--- (1)}$$

If  $dN$  oscillators have energies lying between  $E$  and  $E + dE$ , then the mean energy of the atomic oscillator is given by

$$E = \frac{\sum E dN}{\sum dN} \quad \text{--- (2)}$$

From statistical mechanics, we know that the number of atomic oscillators  $dN$ , having energies lying between  $E$  and  $(E + dE)$  at a temperature  $T$ , is

Proportional to  $e^{-E/k_B T}$ . Thus.

$$\bar{E} = \frac{\sum_{n=0}^{\infty} E e^{-E/k_B T}}{\sum_{n=0}^{\infty} e^{-E/k_B T}}$$

$$\bar{E} = \frac{\sum_{n=0}^{\infty} \left(n + \frac{1}{2}\right) \hbar \omega_0 e^{-\frac{\left(n + \frac{1}{2}\right) \hbar \omega_0}{k_B T}}}{\sum_{n=0}^{\infty} e^{-\frac{\left(n + \frac{1}{2}\right) \hbar \omega_0}{k_B T}}}$$

Now putting  $n=0, 1, 2, 3, \dots$

$$\bar{E} = \hbar \omega_0 \left[ \frac{1}{2} e^{-\frac{\hbar \omega_0}{2 k_B T}} + \frac{3}{2} e^{-\frac{3}{2} \frac{\hbar \omega_0}{k_B T}} + \frac{5}{2} e^{-\frac{5}{2} \frac{\hbar \omega_0}{k_B T}} + \dots \right]$$

$$\left[ e^{-\frac{\hbar \omega_0}{2 k_B T}} + e^{-\frac{3}{2} \frac{\hbar \omega_0}{k_B T}} + e^{-\frac{5}{2} \frac{\hbar \omega_0}{k_B T}} + \dots \right]$$

Putting  $\alpha = -\frac{\hbar \omega_0}{k_B T}$ , we have

$$\bar{E} = \hbar \omega_0 \left[ \frac{1}{2} e^{\frac{\alpha}{2}} + \frac{3}{2} e^{\frac{3\alpha}{2}} + \frac{5}{2} e^{\frac{5\alpha}{2}} + \dots \right]$$

$$\left[ e^{\frac{\alpha}{2}} + e^{\frac{3\alpha}{2}} + e^{\frac{5\alpha}{2}} + \dots \right]$$

$$\bar{E} = \hbar \omega_0 \left[ \frac{d}{dx} \log \left( e^{\frac{\alpha}{2}} + e^{\frac{3\alpha}{2}} + e^{\frac{5\alpha}{2}} + \dots \right) \right]$$

$$= \hbar \omega_0 \left[ \frac{d}{dx} \log \left\{ e^{\frac{\alpha}{2}} \left( 1 + e^{\alpha} + e^{2\alpha} + \dots \right) \right\} \right]$$

$$\begin{aligned}
&= \hbar \omega_0 \left[ \frac{d}{dx} \log \left\{ e^{\frac{x}{2}} \left( \frac{1}{1-e^x} \right) \right\} \right] \\
&= \hbar \omega_0 \left[ \frac{d}{dx} \left\{ \log \left( \frac{e^{\frac{x}{2}}}{1-e^x} \right) \right\} \right] \\
&= \hbar \omega_0 \left[ \frac{d}{dx} \left\{ \log e^{\frac{x}{2}} - \log (1-e^x) \right\} \right] \\
&= \hbar \omega_0 \left[ \frac{d}{dx} \left\{ \frac{x}{2} - \log (1-e^x) \right\} \right] \\
&= \hbar \omega_0 \left[ \frac{1}{2} - \frac{(-e^x)}{1-e^x} \right] \\
&= \hbar \omega_0 \left[ \frac{1}{2} + \frac{e^x}{1-e^x} \right] = \hbar \omega_0 \left[ \frac{1}{2} + \frac{1}{e^{-x} - 1} \right] \\
\bar{E} &= \hbar \omega_0 \left[ \frac{1}{2} + \frac{1}{e^{\hbar \omega_0 / k_B T} - 1} \right] \quad \text{--- (3)}
\end{aligned}$$

Now, the internal energy of the crystal is obtained by multiplying the average energy per oscillator by the number of oscillators ( $3N$ ) in it i.e.,

$$U = 3N \bar{E} = 3N \hbar \omega_0 \left[ \frac{1}{2} + \frac{1}{e^{\hbar \omega_0 / k_B T} - 1} \right]$$

Hence, the molar specific heat is

$$\begin{aligned}
C_v &= \left[ \frac{dU}{dT} \right]_v = \frac{d}{dT} \left[ \frac{3N \hbar \omega_0}{e^{\hbar \omega_0 / k_B T} - 1} \right] = 3N \hbar \omega_0 \left[ \frac{d}{dT} \left( e^{\frac{\hbar \omega_0 / k_B T}{-1}} \right) \right] \\
C_v &= 3N \hbar \omega_0 (-1) \left[ \left( e^{\frac{\hbar \omega_0}{k_B T} - 1} \right)^{-2} e^{\frac{\hbar \omega_0}{k_B T}} \cdot \frac{\hbar \omega_0}{k} \left( \frac{-1}{T^2} \right) \right] \\
&= \frac{3N \hbar \omega_0 \hbar \omega_0 e^{\hbar \omega_0 / k_B T}}{k T^2 \left( e^{\hbar \omega_0 / k_B T} - 1 \right)^2} = 3Nk \left( \frac{\hbar \omega_0}{k_B T} \right)^2 \frac{e^{\hbar \omega_0 / k_B T}}{\left( e^{\hbar \omega_0 / k_B T} - 1 \right)^2} \quad \text{--- (4)}
\end{aligned}$$

Let  $h\nu_0 = k_B \theta_E$ , where  $\theta_E$  is called Einstein temperature. we have

$$\frac{h\nu_0}{k_B T} = \frac{k_B \theta_E}{k_B T} = \frac{\theta_E}{T}$$

Putting this in equation (4), we get

$$C_V = 3Nk_B \frac{\left(\frac{\theta_E}{T}\right)^2 e^{\left(\frac{\theta_E}{T}\right)}}{\left[e^{\left(\frac{\theta_E}{T}\right)} - 1\right]^2} \quad \text{--- (5)}$$

Case I. At high temperature  $T \gg \theta_E$ , so that

$$e^{\frac{\theta_E}{T}} \approx 1 + \frac{\theta_E}{T}$$

Hence,

$$C_V = 3Nk_B \left(\frac{\theta_E}{T}\right)^2 \frac{1 + \left(\frac{\theta_E}{T}\right)}{\left[1 + \frac{\theta_E}{T} - 1\right]^2} = \frac{3Nk_B \left(\frac{\theta_E}{T}\right)^2 \left(1 + \frac{\theta_E}{T}\right)}{\left(\frac{\theta_E}{T}\right)^2}$$

$$C_V = 3Nk_B$$

Thus, ~~at~~ for large values of  $T$ , the expression reduces to the classical expression i.e., the Dulong and Petit value ( $3Nk_B$ ).

Case 2. At low temperature,  $T \ll \theta_E$  and hence

$$e^{\left(\frac{\theta_E}{T}\right)} \gg 1, \text{ therefore}$$



$$C_v = 3NK_B \left(\frac{\theta_E}{T}\right)^2 \frac{e^{-\frac{\theta_E}{T}}}{\left[e^{-\frac{\theta_E}{T}}\right]^2}$$

$$= 3NK_B \left(\frac{\theta_E}{T}\right)^2 \frac{1}{\left(e^{\theta_E/T}\right)} = 3NK_B \left(\frac{\theta_E}{T}\right)^2 e^{-\frac{\theta_E}{T}}$$

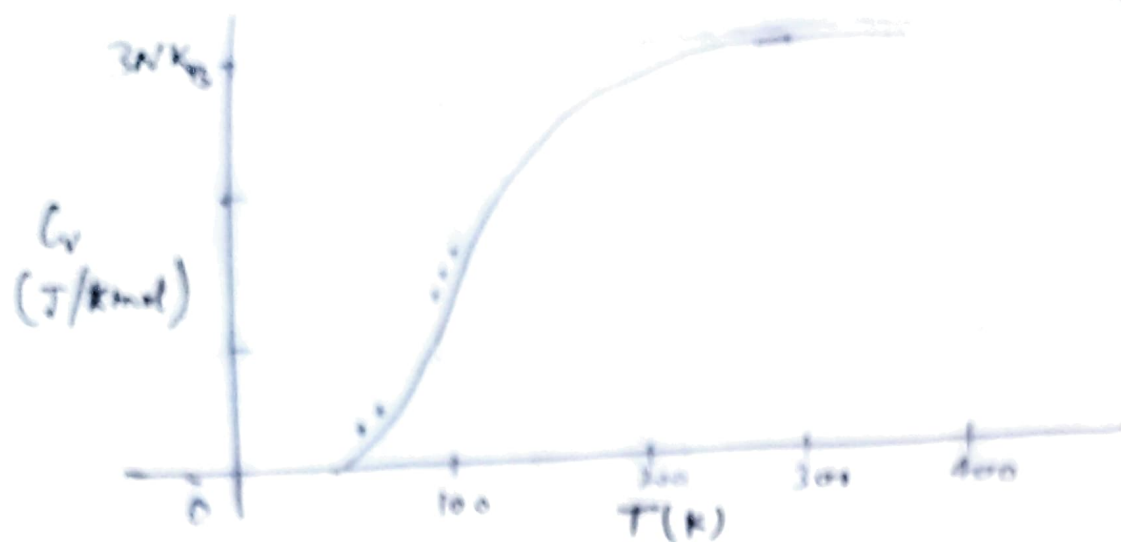
$$C_v = 3NK_B \left(\frac{\theta_E}{T}\right)^2 e^{-\frac{\theta_E}{T}}$$

i.e.,  $C_v \propto e^{-\theta_E/T}$  (6)

Equation (6) indicates that at low temperature, the exponential term is more important than the  $\left(\frac{\theta_E}{T}\right)^2$  term in determining the temperature ~~var~~ variation of  $C_v$ .

Thus, with decreasing temperature,  $C_v$  drops exponentially. Equation (6) is plotted for Al with  $\nu = 6.4 \times 10^{12} \text{ Hz}$ . There is evidently good agreement with data except at very low temperature where  $C_v$  is more nearly proportional to  $T^3$  than to equation (6).

This disagreement is due to the neglect of the mutual force exerted by the atom upon each other. Einstein explained Dulong and Petit law on the basis of quantum theory and said that atomic heat is equal to 6 only at higher temperature and this is max<sup>m</sup> value.



A comparison of specific heat data for aluminium (dots) and the predicted curve from Einstein equation

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