

Discussions on Einstein's Theory of Specific Heat:-

When the temperature is so high that $T \gg h\nu/K_B$ or $T \gg \Theta_E$, then $x \ll 1$ and the expansion of the Einstein's funⁿ $E(x)$ yields unity.

$$\lim_{x \rightarrow 0} \frac{x^2 e^x}{(e^x - 1)^2} = \lim_{x \rightarrow 0} \frac{x^2 (1 + x + \frac{x^2}{2!} + \dots)}{(1 + x + \frac{x^2}{2!} + \dots - 1)^2} \\ \approx \frac{x^2}{x^2} = 1$$

Thus for $T \gg \Theta_E$, $C_v \rightarrow 3R$.

This is the Law of Dulong and Petit.

Thus, Einstein's theory indicates that the Dulong and Petit's Law is an asymptotic Law valid only in the high temperature range.

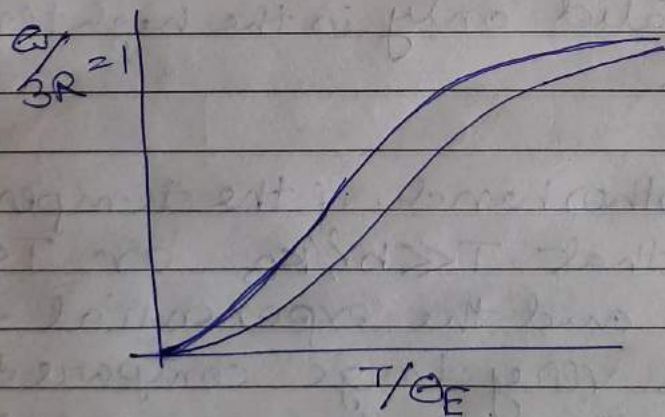
On the other hand, if the temperature is so low that $T \ll h\nu/K_B$ or $T \ll \Theta_E$, then $x \gg 1$ and the exponential factor becomes very large compared to unity. The specific heat then becomes quite small. More precisely, for $T \ll \Theta_E$

$$C_v \rightarrow 3R x^2 e^{-x} \quad \text{i.e.} \quad C_v \rightarrow 3R \left(\frac{\Theta_E}{T} \right)^2 e^{-\Theta_E/T}$$

Thus, the specific heat should approach

zero as $T \rightarrow 0$. This is somewhat in general agreement with experiments. But the specific heat approaches zero exponentially which is faster than what experiments indicate. Experimentally it is observed that for many solids the specific heat contribution from lattice vibration at very low temp. $\propto T^3$, that is, $C_v \propto T^3$ as $T \rightarrow 0$.

On the other hand Einstein's theory shows an exponential dependence of specific heat on temperature $C_v \sim e^{-\Theta_E/T}$ when $T \ll \Theta_E$. Thus this function ~~fails~~ falls off more rapidly at low temperature than what is observed experimentally.



It is observed that the Einstein's expression explains well the specific heat curve upto a certain point, but fails completely at extremely low temperatures. For instance, the value of C_v as calculated from Einstein's

for silver at 14K is 28 times lower than the experimental value. Another drawback of the theory is that there is no other way of verifying the validity of the experimentally determined Θ_E .

The atomic vibration in a crystal are strongly coupled and cannot thus be considered as independent. As a consequence of coupling, the monochromatic character of atomic vibration is lost. The system of $3NA$ coupled oscillators has $3NA$ frequency modes spread around the Einstein frequency ν . Thus we have a spectral picture of the atomic vibration in a solid. That is why although T may be quite small, there are always some modes of oscillations with a frequency so low that $h\nu/k_B \ll T$ and they still contribute appreciably to the specific heat which does not decrease as rapidly as indicated by his eq.

Moreover, solids have a crystalline structure and the very assumption of isotropy is not strictly justified.