

(2) Einstein Theory (Quantum theory) :-

There is only one change, Einstein made in classical theory.

All the assumption of Einstein theory were same as classical theory. But the only difference was, now the Harmonic oscillators are Quantum Harmonic Oscillators.

& They are oscillating with quantised frequencies.
freq. is Quantised in terms of a Q. No. (n), & n can take values from $n = 0, 1, 2, 3, \dots \infty$.

Energy of one-dim Quantum H.O. is

$$E_n = \left(n + \frac{1}{2}\right) \hbar \omega, \quad n = 0, 1, 2, 3, \dots$$

At temp. T , Average energy of H.O. is

$$\bar{E} = \frac{1}{2} \hbar \omega + \frac{\hbar \omega}{e^{\frac{\hbar \omega}{kT}} - 1}$$

↓
this $\frac{1}{2} \hbar \omega$ is not thermal.

This is the energy of 1 H.O., But Here N , 3D H.O.

N , 3D H.O. is equivalent to $3N$, 1 Dim H.O.

So Energy of $3N$, 1 Dim H.O. is

$$\bar{E} = \frac{3N}{2} \hbar \omega + \frac{3N \hbar \omega}{e^{\frac{\hbar \omega}{kT}} - 1}$$

Specific heat,

$$C_v = \left(\frac{\partial \bar{E}}{\partial T} \right)$$

$$C_v = -3N\hbar\omega \left(e^{\frac{\hbar\omega}{k_B T}} - 1 \right)^{-2} \cdot e^{\frac{\hbar\omega}{k_B T}} \cdot \frac{\hbar\omega}{k_B} \left(-\frac{1}{T^2} \right)$$

$$C_v = 3N \frac{(\hbar\omega)^2}{k_B} \left(\frac{1}{T^2} \right) \frac{e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2}$$

Now put, $\theta_E = \frac{\hbar\omega}{k_B}$ (Einstein temp.)

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

Einstein temp θ_E is reference temp.

Case-1 :- At high temp. $\hbar\omega \ll kT$
 $\Rightarrow \theta_E \ll T$

$e^{\frac{\theta_E}{T}}$ is very-very small. By Binomial expansion,

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

$$C_v = 3R$$

This theory matches with classical theory at high temp. It gives correct results at high temp.

Case-2 :- At low temp. $\hbar\omega \gg kT$
 $\Rightarrow \theta_E \gg T$

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

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

Here exponential term, i.e. $e^{-\theta_E/T}$ is dominating.