Einstein model of heat capacity

EINSTEIN'S THEORY OF LATTICE HEAT CAPACITY:

In 1911 Einstien gave the theory about Lattice heat capacity by applying the plank's Quantum theory. He assumed that harmonic oscillator has discrete energy value. Feature about Einstein theory:

(i) Solids consist 3N one dimensional harmonic oscillator.

(ii) All oscillator vibrate with same natural frequency ω_0. The oscillator are quantum oscillator and have discrete energy spectarum rather than the contineous.

* Discrete energy value of an oscillator is

$$\varepsilon_n = nh\nu =$$

$\times$ 8 $\div$ by 2π

$$\varepsilon_n = n\frac{h}{2\pi}\nu(2\pi)$$

$$= n\hbar(2\pi\nu)$$

$$\boxed{\varepsilon = n\hbar\omega_0} \quad \text{—(A)}$$

$$\hbar = \frac{h}{2\pi}$$

$$\omega = 2\pi\nu$$

where $n = 0, 1, 2, 3, \ldots$

Einstein later used the wave mechanical model $\varepsilon_n = \left(n + \frac{1}{2}\right)h\nu$

which is energy level of harmonic oscillator.

× & ÷ by 2π

$$\varepsilon_n = \left(n+\frac{1}{2}\right)\frac{h}{2\pi}(2\pi\nu)$$

$$\boxed{\varepsilon_n = \left(n+\frac{1}{2}\right)\hbar\omega_0} \quad -①$$

$\omega = 2\pi f$
or $\omega = 2\pi\nu$

$\hbar$ is reduce Plank's constant.

where $\frac{1}{2}\hbar\omega_0$ is the temperature independent zero point energy contribution to the internal energy.

BCZ energy is discrete so $\int \rightarrow \Sigma$

using Maxwell-Boltzmaan distribution of energy:

$$\text{Average energy } \bar{\varepsilon} = \frac{\sum_{n=0}^{\infty} \varepsilon_n e^{\left(\frac{-\varepsilon_n}{K_B T}\right)}}{\sum_{n=0}^{\infty} e^{\left(\frac{-\varepsilon_n}{K_B T}\right)}}$$

Put eq ① in above

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

$$\boxed{\text{let } \frac{-\hbar\omega_0}{K_B T} = x} \quad - Ⓑ$$

$$\bar{\varepsilon} = \frac{\hbar\omega_0 \sum_{n=0}^{\infty} \left(n+\frac{1}{2}\right) e^{\left(\left(n+\frac{1}{2}\right)x\right)}}{\sum_{n=0}^{\infty} e^{\left(\left(n+\frac{1}{2}\right)x\right)}}$$

Put values of $n = 0, 1, 2, 3$

$$\bar{\varepsilon} = \frac{\hbar\omega_0 \left[\left(0+\frac{1}{2}\right)e^{\left(0+\frac{1}{2}\right)x} + \left(1+\frac{1}{2}\right)e^{\left(1+\frac{1}{2}\right)x} + \left(2+\frac{1}{2}\right)e^{\left(2+\frac{1}{2}\right)x} + \cdots\right]}{\left[e^{\left(0+\frac{1}{2}\right)x} + e^{\left(1+\frac{1}{2}\right)x} + e^{\left(2+\frac{1}{2}\right)x} + \cdots\right]}$$

$$\bar{\varepsilon} = \frac{\hbar\omega_0 \left[\frac{1}{2}e^{\frac{x}{2}} + \frac{3}{2}e^{\frac{3x}{2}} + \frac{5}{2}e^{5x/2} + \cdots\right]}{\left[e^{x/2} + e^{\frac{3x}{2}} + e^{\frac{5x}{2}} + \cdots\right]}$$

$$\bar{\varepsilon} = \hbar\omega_0 \left[\frac{d\ln}{dx}\left[e^{\frac{x}{2}} + e^{\frac{3x}{2}} + e^{\frac{5x}{2}} + \cdots\right]\right]$$

$$\frac{d}{dx}\ln\left(e^{\frac{1}{2}x} + e^{\frac{3}{2}x} + \cdots\right)$$

$$= \frac{\frac{1}{2}e^{x} + \frac{3}{2}e^{\frac{3x}{2}} + \frac{5}{2}e^{\frac{5x}{2}} + \cdots}{\left(e^{\frac{1}{2}x} + e^{\frac{3}{2}x} + e^{\frac{5}{2}x} + \cdots\right)}$$

$$\bar{\varepsilon} = \hbar\omega_0 \frac{d}{dx}\ln\left[e^{x/2}\left(1 + e^{x} + e^{2x} + \cdots\right)\right]$$

$\ln(a \cdot b)$

$\ln a + \ln b$

$$= \hbar\omega_0 \frac{d}{dx}\left[\ln e^{\frac{x}{2}} + \ln\left(1+ e^{x} + e^{2x} + \cdots\right)\right]$$

$$= \hbar\omega_0 \left[\frac{d}{dx}\left\{\frac{x}{2} + \ln\left(1+e^{x}+e^{2x}+\cdots\right)\right\}\right]$$

$$= \hbar\omega_0 \left[\frac{d}{dx}\left\{\frac{x}{2} - \ln(1-e^{x})\right\}\right]$$

$\ln(1+e^{x}+e^{2x}+\cdots)$
$= -\ln(1-e^{x})$

$$= \hbar\omega_0 \left[\frac{1}{2} - \frac{d\ln}{dx}(1-e^{x})\right]$$

$$= \hbar\omega_0 \left[\frac{1}{2} - \frac{(-e^{x})}{(1-e^{x})}\right]$$

$$= \hbar\omega_0 \left[\frac{1}{2} + \frac{e^{x}}{1-e^{x}}\right]$$

× & ÷ by e^{x} and term inbracket

$$= \hbar\omega_0 \left[\frac{1}{2} + \frac{e^{x}/e^{x}}{\frac{1}{e^{x}} - e^{x}/e^{x}}\right]$$

$$\bar{\varepsilon} = \hbar\omega_0 \left[\frac{1}{2} + \frac{1}{e^{-x} - 1}\right]$$

$x = \frac{-\hbar\omega_0}{K_B T}$

Put the value of 'x' in above

$$\bar{\varepsilon} = \hbar\omega_0 \left[\frac{1}{2} + \frac{1}{e^{-\left(\frac{-\hbar\omega_0}{K_B T}\right)} - 1}\right]$$

$$\boxed{\bar{\varepsilon} = \frac{1}{2}\hbar\omega_0 + \frac{\hbar\omega_0}{e^{\frac{\hbar\omega_0}{K_BT}} - 1}} \quad -(2)$$

This is average energy of harmonic oscillator.

if we put $T = 0$ then $\bar{\varepsilon} = \frac{1}{2}\hbar\omega_0$
It means At $0^\circ K$ (kelvin) harmonic oscillator have energy.

Total energy:

we have total 3N harmonic oscillator
so $E = 3N\bar{\varepsilon}$ Now put value of $\bar{\varepsilon}$

$$E = 3N\left(\frac{1}{2}\hbar\omega_0 + \frac{\hbar\omega_0}{\left(e^{\frac{\hbar\omega_0}{K_BT}} - 1\right)}\right)$$

$$E = \frac{3}{2}N\hbar\omega_0 + \frac{3N\hbar\omega_0}{e^{\frac{\hbar\omega_0}{K_BT}} - 1}$$

Now SPECIFIC HEAT:

$$C_V = \frac{\partial E}{\partial T} = \frac{dE}{dT}$$

$$C_V = \frac{d}{dT}\left(\frac{3}{2}N\hbar\omega_0 + \frac{3N\hbar\omega_0}{e^{\frac{\hbar\omega_0}{K_BT}} - 1}\right)$$

$$C_V = 0 + 3N\hbar\omega_0\left[\frac{d}{dT}\left(\frac{1}{e^{\frac{\hbar\omega_0}{K_BT}} - 1}\right)\right]$$

$$C_v = 3N\hbar\omega_0\left[\frac{\left(e^{\frac{\hbar\omega_0}{k_BT}}\right)\times 0 - 1\cdot\frac{d}{dT}\left(e^{\frac{\hbar\omega_0}{k_BT}} - 1\right)}{\left(e^{\frac{\hbar\omega_0}{k_BT}} - 1\right)^2}\right]$$

$$C_v = 3N\hbar\omega_0\left[\frac{\left(-e^{\frac{\hbar\omega_0}{k_BT}}\right)\frac{d}{dT}\left(\frac{\hbar\omega_0}{k_BT}\right)}{\left(e^{\frac{\hbar\omega_0}{k_BT}} - 1\right)^2}\right]$$

$$C_v = 3N\hbar\omega_0\left[\frac{\left(-e^{\frac{\hbar\omega_0}{k_BT}}\right)\left(\frac{\hbar\omega_0}{k_B}\right)\left(-\frac{1}{T^2}\right)}{\left(e^{\frac{\hbar\omega_0}{k_BT}} - 1\right)^2}\right]$$

$$C_v = \frac{3N(\hbar\omega_0)^2}{k_BT^2}\left[\frac{e^{\frac{\hbar\omega_0}{k_BT}}}{\left(e^{\frac{\hbar\omega_0}{k_BT}} - 1\right)^2}\right]$$

$\times$ & $\div$ by k_B

$$\boxed{C_v = 3Nk_B\left(\frac{\hbar\omega_0}{k_BT}\right)^2\left[\frac{e^{\frac{\hbar\omega_0}{k_BT}}}{\left(e^{\frac{\hbar\omega_0}{k_BT}} - 1\right)^2}\right]} \quad \text{(3)}$$

$\frac{\hbar\omega_0}{k_B}$ is constant $\theta_E = \frac{\hbar\omega_0}{k_B}$

$$\boxed{C_v = 3Nk_B\left(\frac{\theta_E}{T}\right)^2\frac{e^{\theta_E/T}}{\left(e^{\theta_E/T} - 1\right)^2}} \quad \text{— (4)}$$

Final term:

θ_E is known as Einstein temperature bcz it has temperature dimension.

(i) High temperature Behaviour:

$$\theta_E = \frac{\hbar\omega_0}{K_B}$$

$$K_B T >> \hbar\omega_0$$

$$\text{or } T >> \frac{\hbar\omega_0}{K_B} \Rightarrow T >> \theta_E$$

using eq ③

$$C_v = 3NK_B\left(\frac{\hbar\omega_0}{K_BT}\right)^2 \frac{e^{\frac{\hbar\omega_0}{K_BT}}}{\left(e^{\frac{\hbar\omega_0}{K_BT}}-1\right)^2}$$

θ_E is Einstein temperature:

$$\theta_E = \frac{\hbar\omega_0}{K_B}$$

$$\theta_E = \frac{J \cdot S \cdot S^{-1}}{m^2 \, Kg \, S^{-2} K^{-1}}$$

Joule is unit of work

work has unit

$$W = Fd$$
$$= (ma)(\text{meter})$$
$$= Kg\left(\frac{m}{s^2}\right)(m)$$
$$= m^2 Kg S^{-2}$$

$$\theta_E = \frac{\cancel{m^2}\cancel{Kg}\cancel{S^{-2}}\cancel{S}\cancel{S^{-1}}}{\cancel{m^2}\cancel{Kg}\cancel{S^{-2}}K^{-1}}$$

$$\boxed{\theta_E = K}$$

$$e^{\frac{\hbar\omega_0}{K_BT}} = 1 + \frac{\hbar\omega_0}{K_BT} + \frac{\left(\frac{\hbar\omega_0}{K_BT}\right)^2}{2!} + \text{-- higher term}$$

Higher term can be neglected for larger T

$$e^{\frac{\hbar\omega_0}{K_BT}} = 1 + \frac{\hbar\omega_0}{K_BT}$$

$$C_v = 3NK_B\left(\frac{\hbar\omega_0}{K_BT}\right)^2 \frac{\left(1+\frac{\hbar\omega_0}{K_BT}\right)}{\left(\cancel{1}+\frac{\hbar\omega_0}{K_BT}-\cancel{1}\right)^2}$$

$$C_v = 3NK_B\cancel{\left(\frac{\hbar\omega_0}{K_BT}\right)^2} \frac{\left(1+\frac{\hbar\omega_0}{K_BT}\right)}{\cancel{\left(\frac{\hbar\omega_0}{K_BT}\right)^2}}$$

$$C_v = 3NK_B\left(1 + \frac{\hbar\omega_0}{K_BT}\right)$$

For large T $\frac{\hbar\omega_0}{K_BT} \longrightarrow 0$

$$\Rightarrow \boxed{C_v = 3NK_B} \quad C_v = 3N_AK_B$$

$$\boxed{C_v = 3R}$$

$N_AK_B = R$ universal gas constant.

which is the Dulong and petits law as obtained from classical theory.

(ii) AT Low Temperature:

$$\hbar\omega_0 >> K_BT \qquad \frac{\hbar\omega_0}{K_B} >> T$$

or $\theta_E >> T$

using eq ②

$$\bar{\varepsilon} = \frac{1}{2}\hbar\omega_0 + \frac{\hbar\omega_0}{e^{\frac{\hbar\omega_0}{K_BT}} - 1}$$

$$e^{\frac{\hbar\omega_0}{K_BT}} - 1 \cong e^{\frac{\hbar\omega_0}{K_BT}}$$

$\frac{\hbar\omega_0}{K_B}$ is very greater than T so If we minus 1 from $e^{\frac{\hbar\omega_0}{K_BT}}$, it makes no effect.

$$\Rightarrow \quad \bar{\varepsilon} = \frac{1}{2}\hbar\omega_0 + \frac{\hbar\omega_0}{e^{\frac{\hbar\omega_0}{K_BT}}}$$

Total energy is $\quad E = 3N\bar{\varepsilon}$

$$E = 3N\left(\frac{1}{2}\hbar\omega_0 + \hbar\omega_0 e^{-\frac{\hbar\omega_0}{K_BT}}\right)$$

$$E = \frac{3}{2}N\hbar\omega_0 + 3N\hbar\omega_0 e^{-\frac{\hbar\omega_0}{K_BT}}$$

Energy is exponentionaly decrease with temperature.

Now specific Heat

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \left(\frac{dE}{dT}\right)_V$$

$$C_V = \frac{d}{dT}(0) + \left(3N\hbar\omega_0 \frac{d}{dt}\left(e^{-\frac{\hbar\omega_0}{K_BT}}\right)\right)$$

$$C_V = 3N\hbar\omega_0\, e^{-\frac{\hbar\omega_0}{K_BT}} \cdot \left(\frac{-\hbar\omega_0}{K_B}\right) \cdot \frac{d}{dT}\left(\frac{1}{T}\right)$$

$$C_V = 3N\hbar\omega_0\, e^{-\frac{\hbar\omega_0}{K_BT}} \left(-\frac{\hbar\omega_0}{K_B}\right)\left(-\frac{1}{T^2}\right)$$

$$C_V = \frac{3N(\hbar\omega_0)^2}{K_BT^2} e^{-\frac{\hbar\omega_0}{K_BT}}$$

$\times$ & $\div$ by K_B

$$C_V = 3NK_B\left(\frac{\hbar\omega_0}{K_BT}\right)^2 e^{-\frac{\hbar\omega_0}{K_BT}} \qquad \theta_E = \frac{\hbar\omega_0}{K_B}$$

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

specific heat is decreasing exponential:

graph