Einstein theory of lattice heat Capacity

To resolve the discrepancies of classical results, Einstein came forward in 1911 to explain the lattice sp. heat in solids.

He used planck's quantum theory & proposed that energy of H.O are not continuous but they can have only discrete energy values. He replaced the classical ~~HO~~ harmonic oscillators with quantum Harmonic oscillators.

The keypoints of Einstein's theory are:

① A crystal consist of atoms, which are regarded as independent H.Os.

② A solid composed of N atoms (H.Os) vibrating in 3-D is equivalent to 3N - 1-D Harmonic oscillators.

③ All the HOs vibrate with same natural frequency.

1.Imp ④ The oscillators are quantum oscillators and have discrete energy levels.

⑤ Any no. of oscillators may be present in same energy state.

⑥ The atomic oscillators are distinguishable and obey Maxwell - Boltzman distribution law of energies.

Acc to planck's quantum theory, the discrete energy values of an oscillator are given by

$$\epsilon_n = nh\nu = n\hbar\omega_0$$

ν = frequency of oscillator.

$n = 0, 1, 2 3$ --- quantum No.

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

Later on '$\frac{1}{2}\hbar\omega_0$' factor is added to the expression of energy, known as zero point energy.

$$\epsilon_n = \left(n + \frac{1}{2}\right)\hbar\omega_0 \quad \text{—①} \qquad n = 0, 1, 2, ---$$

The average energy of an oscillator can be expressed as

$$\bar{\epsilon} = \frac{\sum_{n=0}^{\infty} \epsilon_n \exp\left(\frac{-\epsilon_n}{K_B T}\right)}{\sum_{n=0}^{\infty} \exp\left(-\frac{\epsilon_n}{K_B T}\right)}$$

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

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

$$\bar{\epsilon} = \frac{~~or~~ \; \hbar\omega_0 \sum_{n=0}^{\infty} \left(n+\frac{1}{2}\right) \exp\left[\left(n+\frac{1}{2}\right)x\right]}{\sum_{n=0}^{\infty} \exp\left[\left(n+\frac{1}{2}\right)x\right]}$$

$$\bar{\epsilon} = \frac{\hbar\omega_0 \left(\frac{1}{2} e^{x/2} + \frac{3}{2} e^{3x/2} + \frac{5}{2} e^{5x/2} + ---\right)}{\left(e^{x/2} + e^{3x/2} + e^{5x/2} + ----\right)}$$

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

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

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

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

$$\left[\because \ln\left(1 + e^{x} + e^{2x} + \cdots\right) = -\ln\left(1 - e^{x}\right)\right]$$

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

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

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

$$\boxed{\bar{\varepsilon} = \frac{\hbar\omega_0}{2} + \underbrace{\frac{\hbar\omega_0}{\exp\left(\frac{\hbar\omega_0}{k_BT}\right) - 1}}_{\text{freq \& Temp dependent term.}}} \quad \text{—②}$$

At $T=0$, $\bar{\varepsilon} = \frac{1}{2}\hbar\omega_0$ & is temperature independent zero point energy. Acc. to quantum mechanics, the atoms are not at rest even at 0K. and each atom possesses the vibrational energy of $\frac{1}{2}\hbar\omega_0$.

The Total internal energy of crystal containing 3N atoms

$$E = 3N\bar{E}$$

$$\boxed{E = \frac{3}{2} N\hbar\omega_0 + \frac{3N\hbar\omega_0}{e^{\hbar\omega_0/k_BT} - 1}} \quad -③$$

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

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

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

$$C_V = \frac{3Nk_B \left(\frac{\hbar\omega_0}{k_BT}\right)^2 e^{\hbar\omega_0/k_BT}}{\left(e^{\hbar\omega_0/k_BT} - 1\right)^2}$$

NOTE

⇒ Let $\theta_E = \frac{\hbar\omega_0}{k_BT}$ = Einstein temperature

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

Now, we can consider two cases:

i) High temperature case

$$k_B T >> \hbar \omega_0 \quad \text{or}$$
$$T >> \theta_E$$

$$e^x = 1 + x + \frac{x^2}{2} ---$$

$$e^{\frac{\hbar\omega_0}{k_BT}} = 1 + \frac{\hbar\omega_0}{k_BT} + \overset{0}{\cancel{\frac{1}{2}\left(\frac{\hbar\omega_0}{k_BT}\right)^2}} + ---$$

Neglecting higher order terms.

$$\therefore e^{\frac{\hbar\omega_0}{k_BT}} - 1 \cong \cancel{1} + \frac{\hbar\omega_0}{k_BT} + --- \cancel{-1} = \frac{\hbar\omega_0}{k_BT}$$

$$\therefore e^{\frac{\hbar\omega_0}{k_BT}} - 1 = \frac{\hbar\omega_0}{k_BT} = \frac{\theta_E}{T}$$

Putting in eq ②

$$\bar{E} = \frac{1}{2}\hbar\omega_0 + k_BT \simeq k_BT$$

∴ at high temp, the avg vibrational energy is same as that obtained from classical theory
& eq ④ becomes

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

$$C_V = 3Nk_B\left(1 + \frac{\theta_E}{T}\right)$$

for large T, $\frac{\theta_E}{T} \longrightarrow 0$ ∴

$$C_V = 3Nk_B$$

⑤ — $\boxed{C_V = 3R}$ (for $N = N_a$)
→ same as Dulong & Petit's law.

2) Low temperature case :

$$k_B T << \hbar\omega_0 \quad \text{or} \quad T << \theta_0$$

$$\therefore e^{\frac{\hbar\omega_0}{k_B T}} - 1 \simeq e^{\hbar\omega_0/k_B T} \Rightarrow \left\{ \begin{array}{l} T \rightarrow \text{v. small} \\ \therefore \frac{1}{T} \rightarrow \text{v. large} \\ e^{\text{large qty}} = \text{large qty} \\ \therefore 1 \text{ can be neglected in comparison} \end{array} \right.$$

eq ② becomes

$$\bar{\epsilon} = \frac{1}{2}\hbar\omega_0 + \hbar\omega_0 e^{-\hbar\omega_0/k_B T}$$

$\Downarrow$

This shows that, at low temp., the avg. vibrational energy decreases exponentially with decrease in temperature.

eq ④ becomes, $\boxed{C_V = 3Nk_B\left(\frac{\theta_E}{T}\right)^2 e^{-\theta_E/T}}$ —⑥

∴ for low temp, the heat capacity is proportional to $e^{-\theta_E/T}$, which is the dominating factor.

Experimentally, it is observed that at low temp., C_V vary as T^3 for most of the solid. This is not observed in Einstein's theory. Therefore, this theory fails to account for the values of specific heat at ~~to~~ very low temp.

- Further, it was proposed that in classical & Einstein theory, it was assumed that HOs vibrate independently with natural freq ω_0, but infact these oscillators are coupled together & there may be no. of possible vibrational frequencies, & those should be taken into account. —x—