Specific Heat of Solids: Einstein's Theory

Thermodynamics of Specific Heat

The First Law of Thermodynamics:

$$\boxed{\Delta U = \Delta Q + \Delta W}$$

(Energy Conservation)

$\Delta U \to$ Internal Energy.
$\Delta Q \to$ Heat exchanged.
$\Delta W \to$ Work done.

For a Hydrostatic System: $\boxed{\Delta W = -P\Delta V}$

$P \to$ Pressure, $V \to$ Volume in (P, V, T).
(thermodynamic variables)

Now $\boxed{U \equiv U(V, T)}$, because an equation of state connects $\boxed{(P, V, T)}$ in a single relation at thermodynamic equilibrium.

Eg. $\boxed{PV = nRT}$ $\to$ The ideal gas equation of state.

Hence only two variables are independent.

For U we choose V and T. $\therefore \boxed{U \equiv U(V, T)}$.

$$\Rightarrow \boxed{\Delta U = \left(\frac{\partial U}{\partial V}\right)_T \Delta V + \left(\frac{\partial U}{\partial T}\right)_V \Delta T}$$

$\to$ Variation of U, with change of V and T.

(P.T.O.)

Now $\boxed{\Delta Q = \Delta U - \Delta W = \Delta U + P\Delta V}$

$$\Rightarrow \Delta Q = \left(\frac{\partial U}{\partial T}\right)_V \Delta T + \left(\frac{\partial U}{\partial V}\right)_T \Delta V + P\Delta V$$

$$\Rightarrow \boxed{\frac{\Delta Q}{\Delta T} = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\frac{\Delta V}{\Delta T}}$$

When $\boxed{\Delta V = 0}$ (at constant volume),

$$\boxed{\frac{\Delta Q}{\Delta T} \equiv C_V = \left(\frac{\partial U}{\partial T}\right)_V} \rightarrow \text{Specific heat at constant volume.}$$

Appropriate for solids (constant volume).

The Classical Theory

In a solid (a metal), the metallic lattice is made up of ordered arrays of atoms. The atoms vibrate about their equilibrium position. The energy of vibration is like that of three (3) independent harmonic oscillators, each corresponding to a coordinate axis. Hence, the vibration of N atoms is the equivalent of 3N harmonic oscillators.

(P.T.O.)

For a harmonic oscillator,

$$\boxed{m\frac{d^2x}{dt^2} = F(x) = -kx} \quad \text{(Hooke's law)}.$$

Now, $\boxed{F(x) = -\frac{dV}{dx}}$ $\boxed{V \equiv V(x)}$ $V \to$ Potential energy.

$$\therefore \boxed{V = -\int F(x)\,dx = -\int (-kx)\,dx = \frac{kx^2}{2}}.$$

$$\boxed{\text{Kinetic energy} = \frac{1}{2}mv^2 = \frac{m^2v^2}{2m} = \frac{p^2}{2m}}$$

$\boxed{\text{momentum } p = mv}$

Hence total energy $\boxed{\epsilon = \frac{p^2}{2m} + \frac{kx^2}{2}}$ (for an oscillator).

Since there are two quadratic degrees of freedom in ϵ, by the equipartition of energy, $\boxed{\langle\epsilon\rangle = \frac{1}{2}k_BT + \frac{1}{2}k_BT = k_BT}$.

By the Boltzmann principle the probability of having an energy state of value ϵ is $\boxed{e^{-\epsilon/k_BT}}$.

$$\therefore \boxed{\langle\epsilon\rangle = \frac{\int_0^\infty \epsilon\, e^{-\epsilon/k_BT}\,d\epsilon}{\int_0^\infty e^{-\epsilon/k_BT}\,d\epsilon}}$$

The average energy of an oscillator.

(P.T.O.)

(continued)

$$\boxed{\langle \epsilon \rangle = \frac{N}{D}} \quad D = \int_0^\infty e^{-\epsilon/k_B T} d\epsilon = \int_0^\infty e^{-x} dx \,(k_B T)$$

$$\boxed{x = \epsilon / k_B T}$$

$$\Rightarrow D = k_B T \left. \frac{e^{-x}}{-1} \right|_0^\infty = \frac{k_B T}{-1} \left[e^{-\infty} - e^{-0} \right] = k_B T .$$

$$N = \int_0^\infty \epsilon\, e^{-\epsilon/k_B T} d\epsilon = (k_B T)^2 \int_0^\infty x\, e^{-x} dx$$

$$\Rightarrow N = (k_B T)^2 \left[x \int_0^\infty e^{-x} dx - \int_0^\infty \left\{ \left(\frac{dx}{dx}\right) \int e^{-x} dx \right\} dx \right]$$

$$\Rightarrow N = (k_B T)^2 \left[x \left. \frac{e^{-x}}{-1} \right|_0^\infty - \int_0^\infty \left\{ \frac{e^{-x}}{-1} \right\} dx \right]$$

$$\Rightarrow N = (k_B T)^2 \left[0 + \left. \frac{e^{-x}}{-1} \right|_0^\infty \right] = (k_B T)^2$$

$$\Rightarrow \boxed{\langle \epsilon \rangle = \frac{N}{D} = \frac{(k_B T)^2}{k_B T} = k_B T}$$

Agrees with the Equipartition Theorem

Since, the total number of harmonic oscillators is $3N$, total internal energy

$$\boxed{U = 3N\langle \epsilon \rangle \Rightarrow U = 3N k_B T} \quad \therefore \boxed{C_V = \frac{dU}{dT} = 3N k_B}$$

Since $\boxed{k_B = \frac{R}{N_A}}$ when $\boxed{N = N_A}$ $\boxed{C_V = 3R}$

$$\boxed{R = 8.31\ J\,mol^{-1}\,k^{-1}} \Rightarrow \boxed{C_V \simeq 25\ J\,mol^{-1}\,k^{-1}}$$

Dulong-Petit Law.

Einstein's Quantum Solution

Experimental observation is $\boxed{C_V \to 0}$ as $\boxed{T \to 0}$, contrary to the Dulong-Petit Law.

Einstein: $\boxed{\epsilon_n = nh\nu}$ (using Planck's Quantum Concept). $(n = 0, 1, 2, 3, \ldots)$

This implies that the oscillators do not have a continuous energy spectrum.

The oscillator energy is quantised.

$$\therefore \boxed{\langle \epsilon \rangle = \frac{\sum_{n=0}^{\infty} \epsilon_n e^{-\epsilon_n/k_B T}}{\sum_{n=0}^{\infty} e^{-\epsilon_n/k_B T}}}$$

For discrete energy the integral is replaced by a summation.

(Average energy of oscillators)

The denominator (geometric series) $\boxed{D = \sum_{n=0}^{\infty} e^{-nh\nu/k_B T}}$.

$\Rightarrow \boxed{D = a + ar + ar^2 + \cdots}$ where $\boxed{a = 1}$ $\boxed{r = \frac{1}{e^{h\nu/k_B T}}}$

$$\therefore \boxed{D = 1 + e^{-h\nu/k_B T} + e^{-2h\nu/k_B T} + \cdots \text{ (up to infinity)}}$$

The sum in $\boxed{D = \frac{a}{1-r}}$ $\boxed{r = \frac{1}{e^{h\nu/k_B T}} < 1}$. (since $r < 1$)

$$\Rightarrow \boxed{D = \frac{1}{1 - e^{-h\nu/k_B T}} = \left(1 - e^{-h\nu/k_B T}\right)^{-1}}$$

The sum of the geometric series.

(P. T. O.)

$$\frac{\partial D}{\partial(1/k_BT)} = -\left(1-e^{-h\nu/k_BT}\right)^{-2} \times -e^{-h\nu/k_BT} \times (-h\nu)$$

$$\Rightarrow \boxed{\frac{\partial D}{\partial(1/k_BT)} = -\frac{h\nu\, e^{-h\nu/k_BT}}{\left(1-e^{-h\nu/k_BT}\right)^2}}.$$

Also since $\boxed{D = \sum_{n=0}^{\infty} e^{-nh\nu/k_BT}}$, we see that

$$\frac{\partial D}{\partial(1/k_BT)} = \sum_{n=0}^{\infty} e^{-nh\nu/k_BT} \times (-nh\nu).$$

$$\therefore \boxed{\frac{\partial D}{\partial(1/k_BT)} = -\sum_{n=0}^{\infty} nh\nu\, e^{-nh\nu/k_BT}}.$$

Now in $\boxed{\langle\epsilon\rangle = \frac{N}{D}}$, the numerator N is

$$\boxed{N = \sum_{n=0}^{\infty} \epsilon_n\, e^{-\epsilon_n/k_BT} = \sum_{n=0}^{\infty} nh\nu\, e^{-nh\nu/k_BT}}.$$

By comparing we see that $\boxed{N = -\frac{\partial D}{\partial(1/k_BT)}}$.

$$\therefore \boxed{\langle\epsilon\rangle = \frac{N}{D} = \frac{h\nu\, e^{-h\nu/k_BT}}{1-e^{-h\nu/k_BT}} = \frac{h\nu}{e^{h\nu/k_BT}-1}}$$

The total energy for 3N number of oscillators, $\boxed{U = 3N\frac{h\nu}{e^{h\nu/k_BT}-1}}$. This is a quantum result.

(P. T. O.)

$$C_v = \frac{\partial U}{\partial T} = 3Nh\nu \times \frac{-1}{\left(e^{h\nu/k_BT}-1\right)^2} \times e^{h\nu/k_BT} \times \frac{h\nu}{k_B} \times \frac{-1}{T^2}$$

$$\Rightarrow \boxed{C_v = 3Nk_B\left(\frac{h\nu}{k_BT}\right)^2 \times \frac{e^{h\nu/k_BT}}{\left(e^{h\nu/k_BT}-1\right)^2}}.$$

Since $\boxed{k_B = \frac{R}{N_A}}$, for $\boxed{N = N_A}$, we write

$$\boxed{C_v = 3R\left(\frac{h\nu}{k_BT}\right)^2 \times \frac{e^{h\nu/k_BT}}{\left(e^{h\nu/k_BT}-1\right)^2}}$$ (for 1 mole of substance)

i.) When $\boxed{T \to 0}$, $\boxed{h\nu/k_BT \to \infty}$ for very cold conditions.

$$\therefore \boxed{C_v \sim \frac{(h\nu/k_BT)^2}{e^{h\nu/k_BT}} \to \frac{\infty^2}{e^{\infty}} \to 0}$$ The exponential ~~part~~ dominates.

Hence, when $\boxed{T \to 0}$, $\boxed{C_v \to 0}$, in agreement with experimental results.

ii.) When $\boxed{T \to \infty}$, $\boxed{h\nu/k_BT \to 0}$ for hot conditions.

$$\therefore \boxed{C_v \simeq 3R\left(\frac{h\nu}{k_BT}\right)^2 \frac{1}{(h\nu/k_BT)^2}}$$ Using $\boxed{e^x \simeq 1+x}$ for $x \to 0$.

$\Rightarrow \boxed{C_v \simeq 3R}$ in agreement with the (when $\boxed{T \to \infty}$). Dulong and Petit law at high T.

The theory was improved by Debye with a wide frequency spectrum.