

Debye's Theory of Specific Heat of Solids

Einstein's theory could not satisfy the experimentally observed variation of specific heat at low temperatures. Einstein's derivation was based on the hypothesis that the vibrations of single atoms of the solid were independent of each other. However, Debye improved his model by assuming the vibrational modes of the crystal as a whole.

Debye assumptions were:

1. Any solid is capable of oscillating elastically in many different modes, the frequency varying from one mode to other.
2. The number of modes of vibrations of solid is limited.
3. When a solid is subjected to continuous elastic vibrations, two kinds of vibrations (a) Longitudinal and (b) transverse vibrations are set up.

Consider a cube of edge L and assuming the faces of cubes to be fixed, the equations were given by

$$\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} = \frac{1}{c_s^2} \frac{\partial^2 u}{\partial t^2} \quad 1$$

Since the cubefaces are fixed at $u=0$, at $x=y=z=0$ and $x=y=z=L$, solution of above equations is

$$u(x, y, z, t) = ce^{-i\omega t} \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right) \quad 2$$

Substituting u in equation 1, we get

$$\frac{\pi^2}{L^2} (n_x^2 + n_y^2 + n_z^2) = \frac{\omega^2}{c_s^2}$$
$$n_x^2 + n_y^2 + n_z^2 = \frac{\omega^2 L^2}{\pi^2 c_s^2} = \left(\frac{2\nu L}{c_s}\right)^2 = \left(\frac{2L}{\lambda}\right)^2 \quad 3$$

Equation 3 gives the allowed frequencies or modes of vibrations inside the cube for different positive integral values of (n_x, n_y, n_z) . The total number of modes of vibration are specified by the total number of possible sets (n_x, n_y, n_z) .

$$\text{Let } \frac{2L}{\lambda} = n$$

$$n_x^2 + n_y^2 + n_z^2 = n^2 \quad 4$$

n is the radius of sphere in (n_x, n_y, n_z) space and the number of allowed modes can be obtained by plotting (n_x, n_y, n_z) and counting the number of points corresponding to positive integral values.

The total number of allowed modes of vibration will be equal to the volume of the octant in the first quadrant and we can write,

$$N = \frac{1}{8} \left(\frac{4}{3} \pi n^3 \right) = \frac{1}{8} \frac{4}{3} \pi \left(\frac{2L}{\lambda} \right)^3 = \frac{4\pi L^3}{3\lambda^3} \quad 5$$

Number of modes between λ and $\lambda + d\lambda$ is obtained by differentiating equation 5

$$N_\lambda d\lambda = \left| \frac{4\pi V}{3} (-3\lambda^{-4}) d\lambda \right| = \frac{4\pi V}{\lambda^4} d\lambda$$

Number of modes in the frequency range ν and $\nu + d\nu$ is given by

$$N_\nu d\nu = \frac{4\pi V}{c_s^3} \nu^2 d\nu \quad 6$$

Number of modes of longitudinal vibrations with frequencies ν and $\nu + d\nu$ is given by $\frac{4\pi V}{c_l^3} \nu^2 d\nu$.

Since the transverse vibrations have two independent directions of vibrations, therefore they are equivalent to two waves polarised at right angles to each other. Therefore, the number of transverse vibrations between ν and $\nu + d\nu$ is $\frac{8\pi V}{c_t^3} \nu^2 d\nu$.

Therefore, number of modes of vibration between frequencies ν and $\nu + d\nu$ is given by

$$N_\nu d\nu = 4\pi V \left[\frac{1}{c_l^3} + \frac{2}{c_t^3} \right] \nu^2 d\nu \quad 7$$

According to Debye, the upper limit of frequency is not infinite but a maximum frequency ν_D (Debye frequency). This limit is chosen so that the total number of possible independent vibrations is equal to the number of vibrations of separate atoms taken together in the solid.

Let there be N atoms in volume V , the possible number of vibrations will be $3N$, because each atom has 3 degrees of freedom.

$$\therefore \int_0^{v_D} 4\pi V \left[\frac{1}{c_l^3} + \frac{2}{c_t^3} \right] v^2 dv = 3N \quad 8$$

$$4\pi V \left[\frac{1}{c_l^3} + \frac{2}{c_t^3} \right] \frac{v_D^3}{3} = 3N$$

$$4\pi V \left[\frac{1}{c_l^3} + \frac{2}{c_t^3} \right] = \frac{9N}{v_D^3} \quad 9$$

The average energy associated with each oscillator is $\frac{hv}{e^{\frac{hv}{kT}} - 1}$

Therefore, vibrational energy of the crystal is given by

$$E = \int_0^{v_D} \bar{\epsilon} N_v dv = \int_0^{v_D} 4\pi V \left[\frac{1}{c_l^3} + \frac{2}{c_t^3} \right] \frac{v^2 hv}{e^{\frac{hv}{kT}} - 1} dv$$

$$E = \int_0^{v_D} \frac{9N}{v_D^3} \frac{hv^3}{e^{\frac{hv}{kT}} - 1} dv \quad 10$$

$$\text{Let } x = \frac{hv}{kT}, \quad x_m = \frac{hv_D}{kT}, \quad v = \frac{kTx}{h}, \quad dv = \frac{kT}{h} dx$$

$$E = \frac{9N}{v_D^3} \int_0^{x_m} \left(\frac{kT}{h} \right)^3 \frac{x^3}{e^x - 1} \frac{kT}{h} dx$$

$$E = \frac{9N}{v_D^3} \left(\frac{kT}{h} \right)^3 kT \int_0^{x_m} \frac{x^3}{e^x - 1} dx$$

$$\text{Let } \theta_D = \frac{hv_D}{k}$$

$$E = 9Nk \frac{T^4}{\theta_D^3} \int_0^{\frac{\theta_D}{T}} \frac{x^3}{e^x - 1} dx \quad 11$$

For very high temperatures ($T \gg \theta_D$), x is small compared with unity for the whole range of integration. The denominator of the integrand in equation 11 can be replaced by x .

$$\therefore E = 9Nk \frac{T^4}{\theta_D^3} \int_0^{\frac{\theta_D}{T}} \frac{x^3}{x} dx = 9Nk \frac{T^4}{\theta_D^3} \frac{x^3}{3} \Big|_0^{\frac{\theta_D}{T}}$$

$$E = 9Nk \frac{T^4}{\theta_D^3} \frac{1}{3} \left(\frac{\theta_D}{T}\right)^3$$

$$E = 3NkT \tag{12}$$

This results in the specific heat identical with classical theory

$$\boxed{C_V = \frac{\partial E}{\partial T} = 3Nk} \quad \text{for } T \gg \theta_D \tag{13}$$

For very low temperatures, $T \ll \theta_D$, the upper limit of integration of equation 11 can be set to infinity.

$$\int_0^{\infty} \frac{x^3}{e^x - 1} dx = \frac{\pi^4}{15} \tag{14}$$

$$\therefore E = 9Nk \frac{T^4}{\theta_D^3} \frac{\pi^4}{15} = \frac{3}{5} \pi^4 NkT \left(\frac{T}{\theta_D}\right)^3 \quad \text{for } T \ll \theta_D \tag{15}$$

Specific heat can be found by differentiating the above expression with respect to temperature at constant volume.

$$\boxed{C_V = \frac{12}{5} \pi^4 Nk \left(\frac{T}{\theta_D}\right)^3} \tag{16}$$

This is the famous **Debye T³ Law** at low temperatures.

General expression for specific heat as a function of temperature may be obtained by differentiating equation 10 with respect to T.

$$C_V = \frac{dE}{dT} = \frac{d}{dT} \frac{9N}{v_D^3} \int_0^{v_D} \frac{hv^3}{e^{\frac{hv}{kT}} - 1} dv$$

$$C_V = \frac{9N}{v_D^3} \int_0^{v_D} \frac{hv^3 e^{\frac{hv}{kT}}}{(e^{\frac{hv}{kT}} - 1)^2} \frac{hv}{kT^2} dv$$

$$\text{Let } \frac{h\nu}{kT} = x, d\nu = \frac{kT}{h} dx,$$

$$\therefore C_V = \frac{9N}{v_D^3} \int_0^{x_m} \frac{h^2 \left(\frac{kTx}{h}\right)^4 e^x}{(e^x - 1)^2} \frac{1}{kT^2} \frac{kT}{h} dx$$

$$C_V = \frac{9Nk^4 T^3}{v_D^3 h^3} \int_0^{x_m} \frac{x^4 e^x}{(e^x - 1)^2} dx$$

$$C_V = 9Nk \left(\frac{T}{\theta_D}\right)^3 \int_0^{\frac{\theta_D}{T}} \frac{x^4 e^x}{(e^x - 1)^2} dx$$

$$C_V = 3R \cdot 3 \left(\frac{T}{\theta_D}\right)^3 \int_0^{\frac{\theta_D}{T}} \frac{x^4 e^x}{(e^x - 1)^2} dx$$

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This is general expression for specific heat.