243(8): Debye Correction to the Einstein Theory

In the Planck Einstein theory the total energy density of black body radiation is:

$$U = \frac{\hbar}{\pi^2 c^3} \int_0^\infty \frac{\omega^3}{e^{\hbar\omega/kT} - 1} d\omega \quad -(1)$$

in units of joules per cubic metre. The Debye correction changes this to:

$$U = \hbar V F \int_0^{\tilde{\omega}_m} \frac{\tilde{\omega}^3}{e^{\hbar\omega/kT} - 1} d\omega \quad -(2)$$

$$= \frac{\hbar V F}{8\pi^3} \int_0^{\tilde{\omega}_m} \frac{\omega^3}{e^{\hbar\omega/kT} - 1} d\omega$$

There is only a slight difference between the Einstein and Debye theories of specific heat but the derivations of the two theories are completely different. The Debye model is the solid state equivalent of Planck's law of black body radiation. In the Debye theory the wavenumber is restricted to:

$$\kappa_n = \frac{n\pi}{L}, \quad \lambda_n = \frac{2L}{n} \quad -(3)$$

and the energy of the phonon is:

$$E_n = \hbar\omega_n \quad -(4)$$

$$= \frac{\hbar c_s}{\lambda_n} = \frac{\hbar c_s n}{2L}$$

2) If p_n is the magnitude of the three dimensional momentum then:

$$E_n^2 = p_n^2 c_s^2 = \left(\frac{h c_s}{2L}\right)^2 (n_x^2 + n_y^2 + n_z^2). \quad -(5)$$

These are accurate approximations for low energy phonons. The total energy is:

$$E = \sum_n E_n \bar{N}(E_n) \quad -(6)$$

where $\bar{N}(E_n)$ is the number of phonons with energy E_n. Therefore the fundamental idea is similar to the Planck law, the energy of phonons is quantized. In 3-D:

$$U = \sum_{n_x} \sum_{n_y} \sum_{n_z} E_n \bar{N}(E_n) \quad -(7)$$

Unlike the Planck law there is a finite number of phonon energy states because a phonon cannot have infinite frequency.

There are N atoms in the solid, and if the solid is a cube there are $N^{1/3}$ atoms per edge separated by $L / N^{1/3}$, where L is the length of the edge. The minimum wavelength is:

$$\lambda = \frac{2L}{N^{1/3}} \quad -(8)$$

so the maximum mode number is:

$$n_{max} = N^{1/3} \quad -(9)$$

3) Therefore in eq. (7):

$$\bar{U} = \sum_{n_x}^{N^{1/3}} \sum_{n_y}^{N^{1/3}} \sum_{n_z}^{N^{1/3}} E_n \bar{N}(E_n). \quad -(10)$$

In the Thomas Fermi approximation the sum can be replaced by an integral:

$$U \sim \int_0^{N^{1/3}} \int_0^{N^{1/3}} \int_0^{N^{1/3}} E(n) \bar{N}(E(n)) \, dn_x \, dn_y \, dn_z \quad -(11)$$

By Bose Einstein statistics:

$$\langle N \rangle_{BE} = \frac{1}{e^{E/kT} - 1} \quad -(12)$$

The phonons have three states of polarization so:

$$\bar{N}(E) = \frac{3}{e^{E/kT} - 1} \quad -(13)$$

so:

$$U = 3 \int_0^{N^{1/3}} \int_0^{N^{1/3}} \int_0^{N^{1/3}} \frac{E(n)}{e^{E(n)/kT} - 1} \, dn_x \, dn_y \, dn_z \quad -(14)$$

Debye used spherical coordinates:

$$(n_x, n_y, n_z) = (n \cos\theta \cos\phi, n \cos\theta \sin\phi, n \sin\theta) \quad -(15)$$

4) and approximate the cube with an eighth of a sphere:

$$U \sim 3 \int_0^{\pi/2} \int_0^{\pi/2} \int_0^{R} \frac{n^2 E(n)}{e^{E(n)/kT} - 1} \sin\theta \, dn \, d\theta \, d\phi \quad -(16)$$

where the radius R is found from:

$$N = \frac{1}{8}\left(\frac{4}{3}\pi R^3\right) \quad -(17)$$

where N is a unit cell volume. Therefore:

$$R = \left(\frac{6N}{\pi}\right)^{1/3}. \quad -(18)$$

this calculation leads to:

$$\frac{U}{Nk} = 9T\left(\frac{T}{T_D}\right)^3 \int_0^{T_D/T} \frac{x^3}{e^x - 1} dx \quad -(19)$$

where the Debye temperature is:

$$T_D = \frac{h c_s R}{2Lk} \quad -(20)$$

and where

$$x = \frac{h c_s n}{2LkT} \quad -(21)$$

Finally the specific heat is given by:

$$\frac{C_V}{Nk} = 9\left(\frac{T}{T_D}\right)^3 \int_0^{T_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad -(22)$$

and is the Debye equation.

5) In Debye's original theory he considered the number n of vibrational states with frequency less than a given value ω_m chosen so that there are $3N$ vibrational states:

$$3N = \frac{1}{3} \omega_m^3 \bar{V} F \quad -(23)$$

so

$$U = \hbar \bar{V} F \int_0^{\omega_m} \frac{\omega^3}{e^{\hbar\omega/kT} - 1} d\omega$$

$$= \frac{\hbar \bar{V} F}{8\pi^3} \int_0^{\omega_m} \frac{\omega^3}{e^{\hbar\omega/kT} - 1} d\omega \quad -(24)$$

Arguing in analogy with eq. (8) of note 243(7) the mean square photon mass can be defined as:

$$\boxed{\langle m^2 \rangle_{phon} = \frac{\hbar^2}{c^4} \left(\frac{\omega^2}{e^{\hbar\omega/kT} - 1} \right)} \quad -(25)$$
