Specific Heat Capacity and Debye Model:

In this model, Debye ignores the motion of a single independent atom and considers, instead, the motion of the lattice as a whole. In this case, the motion of atoms is orchestrated in such a way that they all move with the same amplitude and a fixed phase relationship. The sound wave is assumed to propagate in solids when collective lattice modes are considered, because the latter have behavior similar to sound waves where $\omega = kv_s$. This latter dispersion relation is taken as an approximation. However, this assumption actually ignores the discreteness of the lattice for long wavelength or low frequency and means that such approximation does not work for the values of short wavelength when approaching the interatomic distance.

Debye employed the average energy of a single harmonic oscillator of Einstein model to find the total energy of vibration for the whole lattice but by considering the following integration:

$$U = \int U_{ave.} D(\omega) d\omega ,$$

where the integration is taken over all allowed frequencies. The total density of states derived earlier will be used here, namely

$$D(\omega) = \frac{3\tau\omega^2}{2\pi^2 v^3} .$$

Thus, the treatment of Debye considers the vibrating lattice as a set of collective modes which vibrate independently of each other. So, the lattice vibrates as a continuous medium with total energy:

$$U = \frac{3\tau}{2\pi^2 v^3} \int \omega^2 \frac{\hbar\omega}{e^{\frac{\hbar\omega}{k_B T}} - 1} d\omega .$$

The evaluation of the last integral requires knowing the lower and higher limits of frequency spectrum. The lower limit is $\omega_0 =$

0, while the upper limit is the cutoff frequency of Debye ω_D. The latter frequency (called Debye frequency) can be obtained as follows:

Since each atom has three degrees of freedom, the total number of degrees of freedom for the whole solid is $3N_A$. This total number of degrees of freedom must be equal to the total number of modes. However, the total number of modes can be found using the plot of D (ω) versus ω by integrating the former over the range of frequency from ω_o to ω_D, namely

$$\int_0^{\omega_D} D(\omega)d\omega = 3N_A ,$$

or

$$\frac{3\tau}{2\pi^2 v^3} \int_0^{\omega_D} \omega^2 d\omega = 3N_A .$$

The latter expression gives us:

$$\omega_D^3 = \frac{6\pi^2 N_A}{\tau} v^3 ,$$

or,

$$\omega_D = (6\pi^2 n)^{\frac{1}{3}} v ,$$

where $n (= \frac{N_A}{\tau})$ represents the concentration of atoms in solid.

This can be seen as having a sphere of radius k_D which contains a number of k- points (or modes), N_A, where each mode represents a volume of cube $(\frac{2\pi}{L})^3$, namely

$$N_A = \frac{\frac{4}{3} \pi k_D^3}{\frac{(2\pi)^3}{\tau}} .$$

The last relation can simply give us $k_D = (6\pi^2 n)^{\frac{1}{3}}$. The substitution of this expression into $\omega_D = (6\pi^2 n)^{\frac{1}{3}} v$ will give us the dispersion relation $\omega_D = k_D v$.
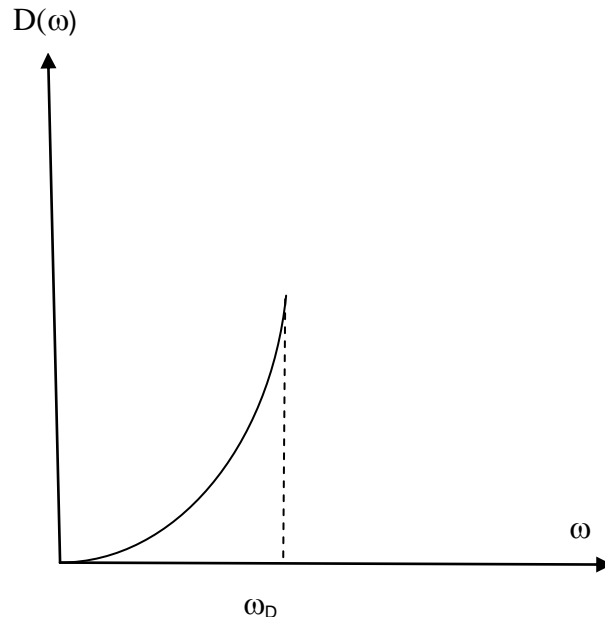
$$D(\omega)$$

Figure 73: The plot of $D(\omega)$ versus ω in a continuous medium. The area under the cure from zero to ω_D represents total number of modes which is equal total number of degrees of freedom.

Thus knowing the lower and upper limits of frequency $\omega_o = 0$ and ω_D, respectively, enable us to determine the total energy as

$$U = \frac{3\tau}{2\pi^2 v^3} \int_0^{\omega_D} \frac{\hbar\omega^3}{e^{\frac{\hbar\omega}{k_BT}} - 1} d\omega .$$

The specific heat at constant volume may have the form:

$$C_V = \frac{3\tau}{2\pi^2 v^3} \frac{\hbar^2}{kT^2} \int_0^{\omega_D} \frac{\omega^4 e^{\frac{\hbar\omega}{k_BT}}}{(e^{\frac{\hbar\omega}{k_BT}} - 1)^2} d\omega .$$

Define Debye temperature as $\Theta_D = \dfrac{\hbar \omega_D}{k_B}$ and make the

change of variables by inserting $x = \dfrac{\hbar \omega}{k_B T}$, the above formula of

C_v becomes:

$$C_V = 9R(\frac{T}{\Theta_D})^3 \int\limits_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx .$$

The final result of C_v obtained by Debye can be compared, now to the available experimental data.

Low and high temperature limits in Debye Model:

In the high temperature limit, when $T \rangle \rangle \Theta_D$, the upper limit of

integration $\dfrac{\Theta_D}{T}$ becomes very small. Since x is getting small over

it full range, an approximation can be conducted by expanding e^x. Thus, $e^x \approx 1 + x$, and by retaining the high terms of expansion only the above integral becomes

$$\int\limits_0^{\Theta_D/T} \frac{x^4(1+x)}{(1+x-1)^2} dx \approx \int\limits_0^{\Theta_D/T} x^2 dx = \frac{1}{3}(\frac{\Theta_D}{T})^3 .$$

This consequently reduces the expression for C_V to:

$$C_V \approx \frac{9R}{3}(\frac{T}{\Theta_D})^3 (\frac{\Theta_D}{T})^3 \approx 3R .$$

Here, the agreement between C_V of Debye model and the corresponding result of Dulong-Petit becomes evident.

When $T \rangle \rangle \Theta_D$, full excitation of each mode of vibration occurs. The energy of each mode of vibration equals the classical energy value of $k_B T$. The average energy of each mode of vibration $U_{ave.} = k_B T$ can be used to find the total energy as follows: $U = \int U_{ave.} D(\omega) d\omega = k_B T \int D(\omega) d\omega$.   This   leads   to

$U = 3N_A k_B T = 3R$. In this case the specific heat becomes $C_V \approx 3R$. The values of Θ_D for several solid materials are close to room temperature. This mean that when $T \approx \Theta_D$ the saturation value of $C_V \approx 3R$ is reached at room temperature, as seen in Figure 73. In the low temperature limit, when $T \langle\langle \Theta_D$, the upper limit of integral $\dfrac{\Theta_D}{T}$ approaches infinity. Thus, the integral becomes

$\displaystyle\int_0^\infty \dfrac{x^4}{(e^x - 1)^2} dx$. The solution of this integral gives the value of

$\dfrac{4\pi^4}{15}$ and the final expression of C_V becomes:

$$C_V \approx \frac{12\pi^4 R}{5}\left(\frac{T}{\Theta_D}\right)^3.$$

The last result indicates that C_V is proportional to T^3 and agrees with the corresponding experimental result. The agreement between values of results obtained from this model and the experimental data is very good, as shown in Figure 73, as those Debye results compared to both Einstein and Dulong-Petit results.
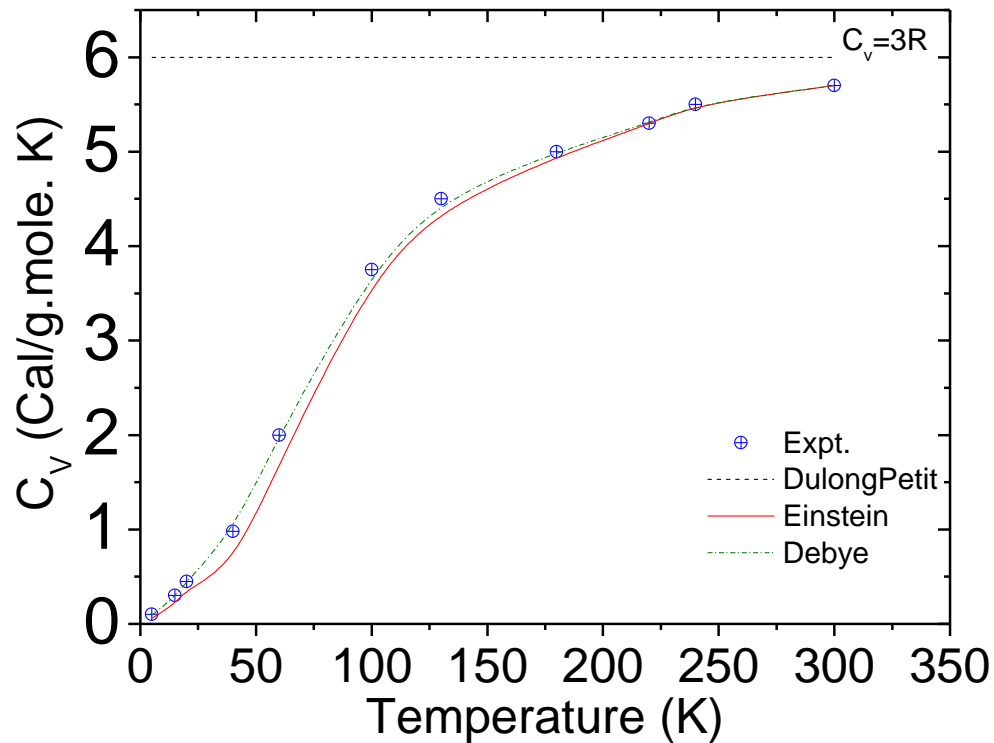
Figure 73: The plot compares the experimental data (symbols) of specific heat capacity, C_v, versus temperature taken from copper sample to both the corresponding Einstein results (solid line), Debye results (Dash-dotted line) and the prediction of C_v from classical theory (Dulong-Petit model) (dashed line).

Disadvantages of Debye model:

The main disadvantage of Debye model, (although it achieves the best results in reproducing the experimental data of C_v over the whole range of temperatures) lies in its approximation of assuming the continuum dispersion relation to hold true for all possible values of excitation. In order to avoid this disadvantage and improve the Debye model, one needs to get rid of the long-wavelength approximation and use, instead, the correct dispersion relation and the corresponding density of states.