Phonons and Thermal Properties: (Specific heat capacity)

We want to discuss the phonon heat capacity at a constant volume $C_v = (\frac{\partial U}{\partial T})_V$, where U is the energy at temperature T. The contribution of the phonons to the total heat capacity of a crystal is called the lattice heat capacity. The determination of C_V can be obtained using three different models, namely

1. Dulong-Petit model
2. Einstein Model
3. Debye model

The experimental data of the relation of C_V versus absolute temperature illustrates a specific behavior shown in the Figure 67. The best competing model is the one which reproduce well the values of in the whole range of temperatures.

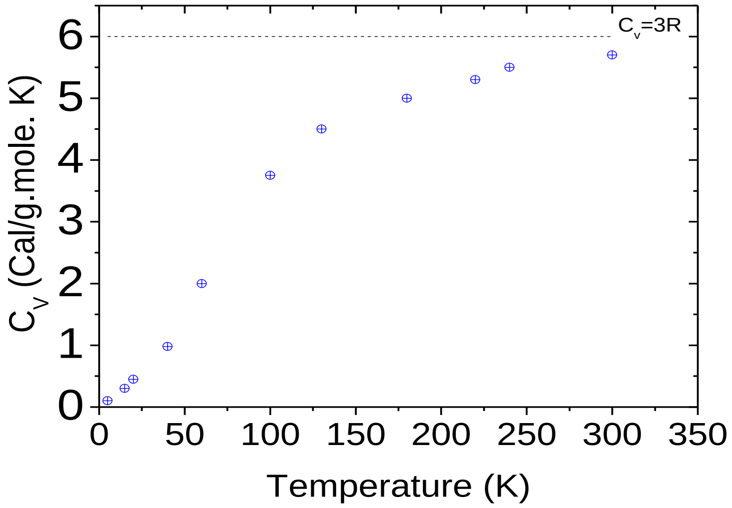

Figure 67: The plot of specific heat capacity, C_v, versus temperature. Experimental data (symbols) is taken from copper sample. The dashed line represents the prediction of C_v from classical theory (Dulong-Petit model).

It is necessary to explain the meaning of density of normal modes (or states) in a continuous medium and tackles its approach as this latter approach will be used in some of the above mentioned models.

The Approach of Density of Normal Modes (or States) in a Continuous Medium:

Density of States in One-Dimension:

For a linear array of N atoms located along x-axis, the vibration of the atoms manifests itself in an elastic wave traveling along x-axis. When the linear chain of atoms has a length $L=Na$, where a is the separation distance between successive atoms, we found that the periodic boundary condition requires that $u(0) = u(L)$. This means that $e^{ikNa} = 1$ which implies that $k = \frac{2\pi n}{L}$ or $k = \frac{2\pi n}{Na}$. Here, in such Born-von Karman periodic boundary condition, the atom at the right end of the linear chain is constrained in such a way that it is in the same state of vibration as the atom at the left end. Each atom, shown in Figure 63, exhibits a mode of vibration for each k-value. When a large number of atoms are considered in the linear chain of length L, the discrete linear atomic chain becomes sort of a quasi-continuous linear medium. In such case, in k-space an arbitrary interval of length dk can be chosen in order to find the number of modes where k lies in the length dk, shown in Figure 68.

Here in this k-space the separation distance between two successive atoms is $\frac{2\pi}{L}$. One can simply say that the number of modes in this quasi-continuous medium of length L is equal $\frac{dq}{(2\pi/L)}$. Using the dispersion curve , shown in Figure 62, one can deduce that the number of modes in length dk lying between dk and $k + dk$ must correspond to the number of modes in the frequency length $d\omega$ lying between ω and $d\omega$, namely:

$$D_o(\omega)d\omega = \frac{Ldq}{2\pi}.$$

Here, $D_o(\omega)$ represents density of states. Since density of states include modes lying in both positive and negative regions of k, in Figure 68, a factor of two must multiply the previous relation because the right mode is due to waves traveling to right and left mode is attributed to waves traveling to the left. Thus one can get:

$$D_o(\omega) = \frac{L}{\pi \frac{d\omega}{dq}}.$$

It can be shown that the velocity of wave v is equal to the group velocity $v_g = \frac{d\omega}{dq}$. Thus the density of states for the continuous linear chain medium is written as:

$$D_o(\omega) = \frac{L}{\pi v}$$

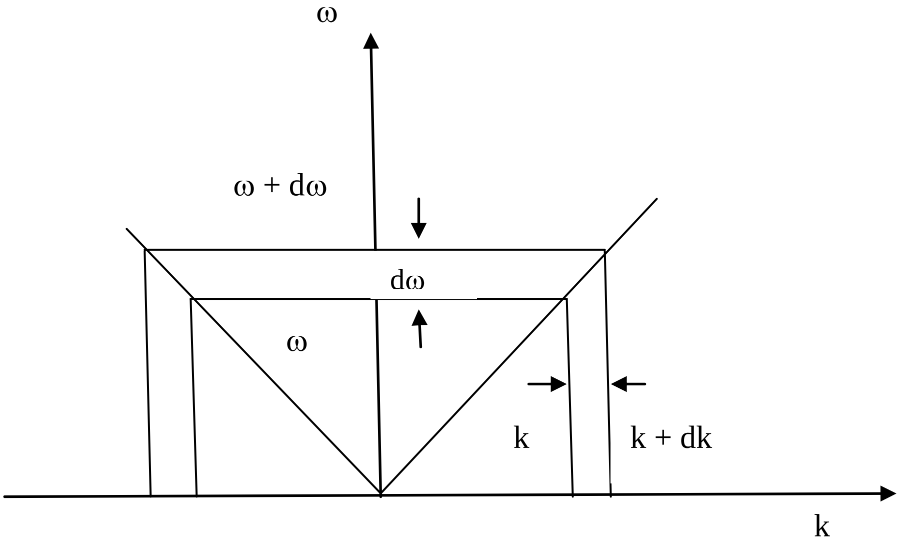

Figure 68: Dispersion relation of ω versus k. The number of modes in length dk is lying between dk and $k + dk$ and corresponds to the number of modes in the length dω of frequency lying between ω and dω.

Density of States in Three Dimensions:

The problem of one dimensional continuous linear chain studied earlier for N primitive cells can be extended to three dimensions $N \times N \times N$ (or N^3) primitive cells. For the three dimensional picture in k-space, the periodic boundary condition requires $e^{i(k_x+k_y+k_z)} = 1$. This, however, implies that $k_x = \frac{2\pi n}{L}, k_y = \frac{2\pi m}{L}$ and $k_z = \frac{2\pi s}{L}$, where $n=m=s=0, \pm2, \pm4,$ …..etc. This three dimensional picture in k-space can be represented by a sphere of radius k with volume $\frac{4\pi k^3}{3}$ that contains a number of cubes where each cube represents a mode of volume $(\frac{2\pi}{L})^3$.

One can get the number of modes per volume as:

$$= \frac{\frac{4\pi k^3}{3}}{(\frac{2\pi}{L})^3}.$$

The derivative of latter expression with respect to k can be defined as the number of modes (or states) per volume in the spherical shell between radii dk and $k + dk$, as shown in Figure 69, or called density of states $D(k)\,dk$, namely:

$$D(k)dk = \frac{4\pi k^2 dk}{(\frac{2\pi}{L})^3}$$

If one makes the change of variables from k to ω using the dispersion relation, shown in Figure 68, and the fact that at low values of k the frequency $\omega = k\,v$, the density of states $D(\omega)$ can be obtained from the number of modes $D(\omega)d\omega$ whose frequencies exist in the range $d\omega$ between ω and $\omega + d\omega$. The latter number of modes can be found from the spherical shell whose radii are ω and $\omega + d\omega$, seen in Figure 70. Thus the density of states $D(\omega)d\omega$ can be expressed by:

$$D(\omega)d\omega = \frac{L^3}{(2\pi)^3}\frac{4\pi\omega^2 d\omega}{(v)^3}.$$

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

, where, the volume of sample is $\tau = L^3$.

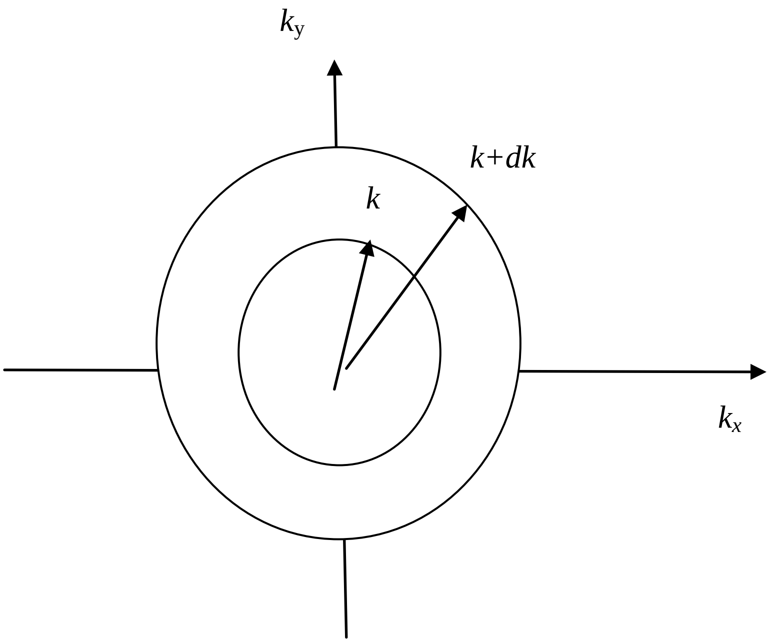

Figure 69: The Spherical shell of radii dk and $k + dk$ in k-space.

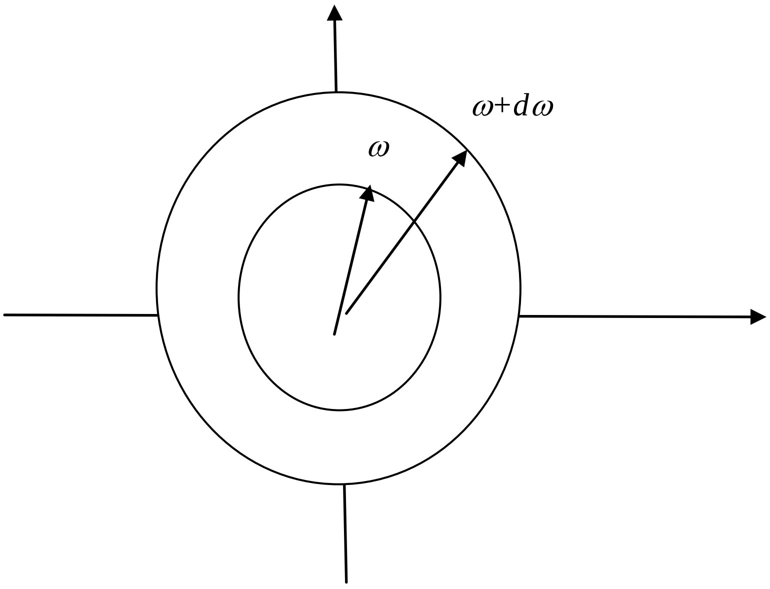

Figure 70: The Spherical shell of radii $d\omega$ and $\omega + d\omega$ in k-space.

The last relation of $D(\omega)$ versus ω is plotted in Figure 71.

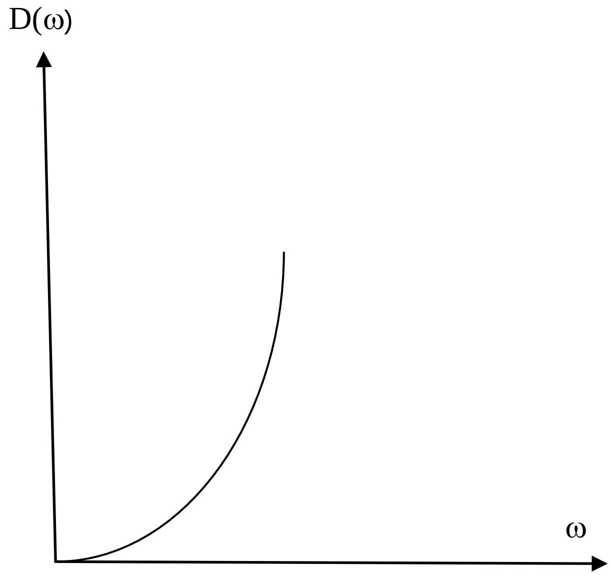

Figure 71: The plot of $D(\omega)$ versus ω in continuous medium.

Important Remark:

The above obtained expression of $D(\omega)$ implies the existence of a single mode for each value of k. This expression must be multiplied by a factor of 3, because there are actually three different modes (one longitudinal and two transverse) are associated with the same value of k. Here, an assumption is made that the velocity in each mode is considered the same (i.e. $v_{\text{longitudinal}} = v_{\text{transverse}} = v$). The final expression of $D(\omega)$ becomes:

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

Specific Heat Capacity and Dulong-Petit Model:

This model is based on the classical theory where it describes the solid as a set of atoms bound to their sites by ideal harmonic forces. When thermal energy is transferred to the solid all atoms start to vibrate around their sites as harmonic oscillators. The average energy of a one-dimensional harmonic oscillator is given by:

$$U_{ave.} = k_B T \, .$$

Here, k_B is Boltzmann constant and T is the absolute temperature. Furthermore, the average energy of a three-dimensional harmonic oscillator per mole is defined as:

$$U = 3N_A k_B T \, .$$

The product of Avogadro's number N_A=6.023×10^{23} mole^{-1} and Boltzmann constant k_B= 1.38×10^{-23} J/K gives R which has the value of 8.31J/mole.K. The heat capacity at constant volume, $C_v = (\frac{\partial U}{\partial T})_V$, may have the expression:

$$C_V = 3R$$

Conclusion:

The obtained result agrees with the experimental data, shown in Figure 67; at high values of temperature but it severely disagree at low values of temperature. The experiment shows, however, that C_V decreases and then vanishes completely as $T \to$ 0K.

Specific Heat Capacity and Einstein Model

The failure of the classical theory to reproduce a correct expression for C_V in the whole range of temperatures motivated other scientist to use a better treatment. In his treatment Einstein assumes that the atoms are independent isolated oscillators where the energy of each oscillator was found from quantum mechanics as:

$$U = (n + \frac{1}{2})\hbar\omega$$

The term $\frac{1}{2}\hbar\omega$ can be neglected because it is irrelevant to the derivation of specific heat capacity. The expression of isolated energy suggests that energy is quantized. The frequency of each oscillator ω is considered the same for each oscillator. However, the adopted expression of energy cannot correctly express the actual behavior of oscillating atoms in solid because oscillating atoms are not isolated but actually exchanging energy with their surroundings. Here the ambient thermal bath provides energy to oscillating atoms. Thus, it is better finding the average energy at thermal equilibrium, namely:

$$U_{ave.} = \frac{\sum_{n=0}^{\infty} U_n e^{-\frac{U_n}{k_B T}}}{\sum_{n=0}^{\infty} e^{-\frac{U_n}{k_B T}}}.$$

Here, the Boltzmann factor $e^{-\frac{U_n}{k_B T}}$ gives the probability for an energy state U_n to be occupied. The sum in the denominator is introduced for the purpose of making correct normalization. Combining the last two equations to get:

$$U_{ave.} = \frac{\sum_{n=0}^{\infty} n\hbar\omega e^{-\frac{n\hbar\omega}{k_B T}}}{\sum_{n=0}^{\infty} e^{-\frac{n\hbar\omega}{k_B T}}} .$$

The above equation can be reduced to the expression:

$$U_{ave.} = \frac{\hbar\omega}{e^{\frac{\hbar\omega}{k_B T}} - 1}$$

Each atom is represented by three oscillators and for Avogadro's number of atoms N_A we should have a total of $3N_A$ oscillators. Thus the last expression of energy must be multiplied by $3N_A$ to get the total energy as:

$$U = 3N_A \frac{\hbar\omega_E}{e^{\frac{\hbar\omega_E}{k_B T}} - 1}$$

It must be noted here that Einstein frequencyω_E replaces ω to indicate the existence of common frequency for all oscillators. The heat capacity may finally have the expression:

$$C_V = 3N_A k_B (\frac{\hbar\omega_E}{k_B T})^2 \frac{e^{\frac{\hbar\omega_E}{k_B T}}}{(e^{\frac{\hbar\omega_E}{k_B T}} - 1)^2} .$$

Put $R = N_A k_B$ and introduce the Einstein temperature Θ_E such that $\hbar\omega_E = \Theta_E k_B$, the above expression becomes

$$C_V = 3R(\frac{\Theta_E}{T})^2 \frac{e^{\frac{\Theta_E}{k_B T}}}{(e^{\frac{\Theta_E}{k_B T}} - 1)^2} .$$

Using the last derived formula of Einstein, plot C_V versus T and compare the results with experimental data in Figure 72, we notice that the general features of the curve are reproduced. In particular, the results from Einstein model agree with the experimental values of C_V over the whole range of temperatures, especially for $C_V \rightarrow$o when $T \rightarrow$oK. It is interesting to note that the fitting of experimental data for copper, for example, using Einstein model gives Θ_E =240K. Here, Θ_E is used as the only adjustable parameter in such fitting process, over a wide range of temperature. Moreover, knowing Θ_E enable us to determine ω_E =2.5 × 10^{13} Hz, where $\omega_E = \frac{\Theta_E k_B}{\hbar}$.

Low and high temperature limits in Einstein Model:

In high temperature limit where T >> Θ_E , we can expand $e^{\frac{\Theta_E}{T}}$ in a power series of $\frac{\Theta_E}{T}$. Retaining the largest terms in the series $e^{\frac{\Theta_E}{T}}$ ≈1- $\frac{\Theta_E}{T}$ +…the approximated expression of C_V becomes

$$C_V \approx 3R\left(\frac{\Theta_E}{T}\right)^2 \frac{1-\frac{\Theta_E}{T}}{\left(1-\frac{\Theta_E}{T}-1\right)^2} = 3R\left(1-\frac{\Theta_E}{T}\right)$$

Ignoring $\frac{\Theta_E}{T}$ in last expression, one can get $C_V \approx 3R$. This final result agrees with the classical result of Dulong-Petit, as shown in Figure 72.

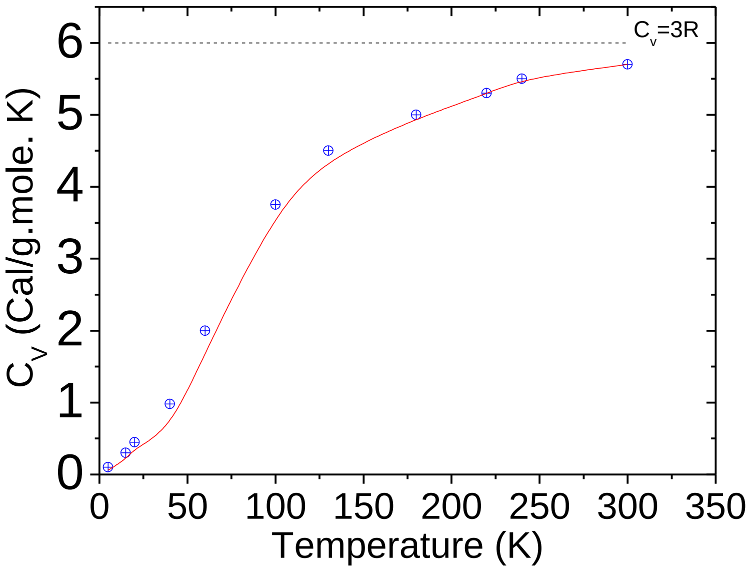

Figure 72: The plot compares the experimental data (symbols) of specific heat capacity, C_v, versus temperature taken from copper sample to both the corresponding Einstein results (solid line) and the prediction of C_v from classical theory (Dulong-Petit model) (dashed line).

In the low-temperature limit, where T<< Θ_E, the exponential $e^{\frac{\Theta_E}{T}}$ in the Einstein expression of C_v is larger than unity. This makes the approximated expression to be as

$$C_V \approx 3R(\frac{\Theta_E}{T})^2 \frac{e^{\frac{\Theta_E}{k_B T}}}{e^{\frac{2\Theta_E}{k_B T}}} = 3R(\frac{\Theta_E}{T})^2 e^{-\frac{\Theta_E}{T}}$$

The exponential term $e^{-\frac{\Theta_E}{T}}$ in last expression is more sensitive to temperature than the term $(\frac{\Theta_E}{T})^2$. This implies that C_V approaches zero exponentially, while the experiment shows that C_V approaches zero as T^3. Thus the decrease found by last expression is much faster than that found by experiment.

Disadvantages of Einstein Model:

1. One of the main pitfalls of Einstein model is the assumption of independence of harmonic oscillators of atoms. The motion of an atom in soild actually affects its neighbors and these neighbors, in turn, affect their neighbors and so on. In this case we cannot ignore the interaction between atoms as harmonic oscillators and another assumption that considers the motion of whole lattice rather than that of a single atom is actually more important.
2. Einstein model assumed that at low temperature, each independent oscillator is essentially unexcited, and hence C_V approaches zero and the oscillator in such case may be considered as "frozen" in its ground state. This "freezing" scenario is also the reason why the vibrational modes in diatomic molecules such as H2, do not contribute to specific heat, except at high temperatures. The inaccurate results obtained at low temperature become evident now. The reason is that the model ignores the existence of very low frequency modes which can absorb heat even at very low temperatures. This is because their energies of quantization are very small and this consequently may lead to smaller values of specific heat than experimental one as seen in Figure 72.