

The Dulong-Petit law states that, the specific heat of a solid is independent of temperature. However, as the temperature drops below the room temperature and beyond, the specific heat of all solids starts to decline below the classical value, and eventually is observed to vanish as T^3 in insulators and $AT + BT^3$ in metals. The explanation of this behaviour is one of the earliest triumphs of quantum theory of solids.

In quantum theory of specific heat of a harmonic crystal, the classical expression for the thermal energy density u must be replaced by the general quantum mechanical result,

$$u = \frac{1}{V} \frac{\sum_i E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}$$

where E_i is the energy of the i^{th} stationary state of the crystal, and the sum is over all stationary states. The energies of these stationary states are given by the eigenvalues of the harmonic hamiltonian:

$$H^{\text{harm}} = \sum_{\vec{R}} \frac{\vec{p}(\vec{R})^2}{2M} + \frac{1}{2} \sum_{\substack{\vec{R}, \vec{R}' \\ u, v}} \langle u(\vec{R}) \rangle \nabla_{uv} (\vec{R} - \vec{R}') \langle v(\vec{R}') \rangle$$

The eigenvalues are found by standard procedures of Quantum Mechanics (introducing \hat{a} and \hat{a}^\dagger and the further calculations). We will simply state the result from the calculation. To specify the energy levels of an N-ion harmonic crystal, one regards it as $3N$ independent oscillators, whose frequencies are those of $3N$ classical normal modes. The contribution to the total energy of a particular normal mode with angular frequency $\omega_s(\vec{k})$ can have only discrete values -

$$(n_{ks} + \frac{1}{2})\hbar\omega_s$$

where $n_{ks} = 0, 1, 2, \dots$. A state of the entire crystal is specified by giving the value of n_{ks} for each of the $3N$ normal modes. The total energy is just the sum of the energies of the individual normal mode in that state:

$$E = \sum_{k,s} \left(n_{ks} + \frac{1}{2} \right) \hbar\omega_s(\vec{k})$$

Normal modes vs. Phonons

The total energy in a particular state of the crystal is described in terms of the excitation number n_{ks} of the normal mode with wave

vector \vec{k} in the branch s . Usually, the clumsy nomenclature is replaced by an equivalent corporcular description, which is analogous

to the terminology used in the quantum theory of em field. In that theory, the allowed energies of a normal mode ~~is~~ of the radiation field in a cavity are given by $(n + \frac{1}{2})\hbar\omega$, where ω is the angular frequency of the mode. It is the universal picture practice, however, to speak not of the quantum number of excitation of the mode n , but of the number, n , of photons of that type are present. In precisely the same way, instead of saying that normal mode of branch s with wave-vector \vec{k}_s , is in its n_s^{th} excited state, one says there are n_s phonons of type s with wave-vector \vec{k}_s present in the crystal. Just like the photon ~~describer~~ is the quantum of the radiation field that describes classical light, phonon is the quantum of the ionic displacement field that describes classical sound.

The Einstein model of specific heat

In this model, the atoms/ions are treated as independent oscillators whose energy is given by,

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

with ω being the energy of the oscillator.
For $n=0$,^{that is,} the ground state, the energy is $\frac{1}{2}\hbar\omega$, and is known as the zero-point energy. However, the zero point energy is irrelevant in the discussion of specific heat and we will dis-regard it here and continue our calculation.

using $E_n = n\hbar\omega$.

Now, the oscillators in a crystal is not isolated, and is constantly exchanging energy with the thermal bath surrounding the solid. The average energy is given by,

$$\bar{E} = \frac{\sum_{n=0}^{\infty} E_n e^{-\frac{E_n}{k_B T}}}{\sum_{n=0}^{\infty} e^{-\frac{E_n}{k_B T}}}$$

$$= \frac{\sum_{n=0}^{\infty} E_n e^{-\beta E_n}}{\sum_{n=0}^{\infty} e^{-\beta E_n}}$$

The expression can also be written as -

$$\bar{E} = -\frac{\partial}{\partial \beta} \ln \left[\sum_{n=0}^{\infty} e^{-\beta E_n} \right]$$

You can explicitly calculate the logarithm of the sum to find the previous expression of \bar{E} . Note that, the \bar{E} is the average energy of an independent oscillator connected with a thermal bath. To find the total energy, we will have to multiply this with N , where N is the number of atoms. You can also work out the results using $E_n = (n + \frac{1}{2})\hbar\omega$, and see that you get the same result.

Now, $\bar{E} = \frac{\sum_{n=0}^{\infty} E_n e^{-\beta E_n}}{\sum_{n=0}^{\infty} e^{-\beta E_n}}$

However, it is easy to calculate \bar{E} using the alternate definition.

$$\bar{E} = -\frac{\partial}{\partial \beta} \ln \left[\sum_{n=0}^{\infty} e^{-\beta n \hbar \omega} \right]$$

$$= -\frac{\partial}{\partial \beta} \ln \left[1 + e^{-\beta \hbar \omega} + e^{-2\beta \hbar \omega} + \dots \right]$$

$$= -\frac{\partial}{\partial \beta} \ln \frac{1}{1 - e^{-\beta \hbar \omega}}$$

You can easily work for three-four lines to find that,

$$\bar{E} = \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}$$

If $E_n = (n + \frac{1}{2})\hbar\omega$,

$$\bar{E} = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}$$

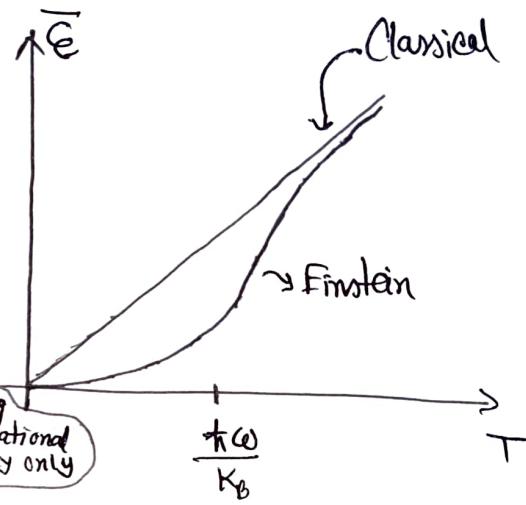
The following figure shows the energy \bar{E} versus temperature as a function of temperature.

The classical one is found from

the Dulong-Petit ~~law~~ calculation

$$(U = V^{eq} + 3Nk_B T)$$

We can see that, at high



temperature the energy $\bar{E} \rightarrow k_B T$, since as $T \rightarrow \infty$, $\beta \rightarrow 0$, and so,

$$\bar{E} \approx \frac{\hbar\omega}{(1 + \beta\hbar\omega + \frac{(\beta\hbar\omega)^2}{2!} + \dots) - 1} = \frac{\hbar\omega}{1/\beta\hbar\omega - 1}$$

$$\therefore \bar{E} \approx 1/\beta = k_B T$$

which is the same as the classical value given by Dulong-Petit calculation. As temperature decreases, \bar{E} decreases as well and at $T=0$, $\bar{E}=0$ (if precise E_n was used, at $T=0$, $\bar{E}=\frac{1}{2}\hbar\omega$). This behaviour of \bar{E} is a consequence of the quantum nature of the motion, and is responsible for classically unexpected decrease in

specific heat in the low temperature region.

We can now find the energy of the solid by noting that, for one mole atom, there is a total of $3N_A$ oscillators (since each atom is equivalent to 3 oscillators). The total energy is then,

$$E = 3N_A \frac{\frac{\hbar\omega_E}{e^{\beta\hbar\omega_E} - 1}}{}$$

where we used ω_E , the Einstein frequency to denote the common frequency of the oscillators. Now, the molar specific heat,

$$C_v^{\text{molar}} = \left(\frac{\partial E}{\partial T} \right)_V = \frac{\partial E}{\partial \beta} \cdot \frac{\partial \beta}{\partial T}$$

$$= \frac{\partial}{\partial \beta} \left[3N_A \frac{\frac{\hbar\omega_E}{e^{\beta\hbar\omega_E} - 1}}{} \right] \frac{\partial}{\partial T} \left(\frac{1}{K_B T} \right)$$

$$= 3N_A \hbar\omega_E (-1) \frac{\frac{1 \times e^{\beta\hbar\omega_E} \times \hbar\omega_E}{(e^{\beta\hbar\omega_E} - 1)^2}}{} \frac{1}{K_B} (-1) \frac{1}{T^2}$$

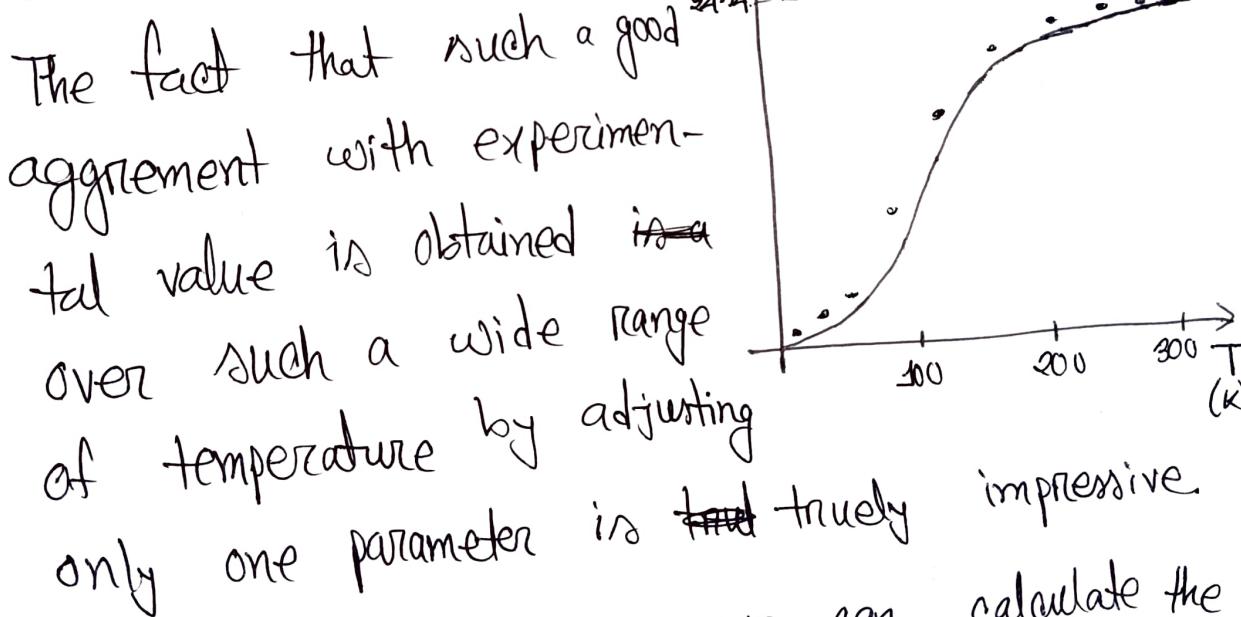
$$= 3N_A \left(\frac{\hbar\omega_E}{T} \right)^2 \frac{1}{K_B} \frac{\frac{e^{\beta\hbar\omega_E}}{(e^{\beta\hbar\omega_E} - 1)^2}}{}$$

$$\boxed{C_v^{\text{molar}} = 3R \left(\frac{\hbar\omega_E}{K_B T} \right)^2 \frac{\frac{e^{\beta\hbar\omega_E}}{(e^{\beta\hbar\omega_E} - 1)^2}}{}}$$

Defining Einstein temperature θ_E as, $\theta_E = \frac{\hbar\omega_E}{k_B}$,

$$C_v^{\text{molar}} = 3R \left(\frac{\theta_E}{T} \right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2}$$

The temperature θ_E is an adjustable parameter, chosen to produce the best fit to the measured values over the whole temperature range. For example, the following figure shows C_v^{molar} vs $T(K)$ for Copper, for which it is found that $\theta_E = 240 \text{ K}$.



The fact that such a good agreement with experimental value is obtained over such a wide range of temperature by adjusting only one parameter is truly impressive.

Once we calculate θ_E , we can calculate the Einstein frequency as, $\omega_E = k_B \hbar \theta_E$, which for Copper is $2.5 \times 10^{13} \text{ s}^{-1}$, which is in the infrared region.

High-temperature limit

$$T \gg \theta_E,$$

$$C_v^{\text{molar}} = 3R \left(\frac{\theta_E}{T}\right)^2 \frac{1 + \left(\frac{\theta_E}{T}\right) + \frac{1}{2!} \left(\frac{\theta_E}{T}\right)^2 + \dots}{\left(1 + \frac{\theta_E}{T} + \frac{1}{2!} \left(\frac{\theta_E}{T}\right)^2 + \dots - 1\right)^2}$$

$$\approx 3R \left(\frac{\theta_E}{T}\right)^2 \frac{1 + \frac{\theta_E}{T}}{\left(\frac{\theta_E}{T}\right)^2} \approx 3R \left(1 + \frac{\theta_E}{T}\right)$$

\therefore In $T \rightarrow \infty$ limit,

$$C_v^{\text{molar}} \approx 3R$$

Low temperature limit

$$T \ll \theta_E,$$

$$C_v^{\text{molar}} = 3R \left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2}$$

$$e^{\theta_E/T} - 1 \approx e^{\theta_E/T}$$

$$\therefore C_v^{\text{molar}} \approx 3R \left(\frac{\theta_E}{T}\right)^2 e^{-\theta_E/T}$$

$$\approx B(T) e^{-\theta_E/T}$$

Because of the $e^{-\theta_E/T}$ (exponential term), the specific heat approaches zero very rapidly. As $T \rightarrow 0$, $C_v^{\text{molar}} \rightarrow 0$. However, in Einstein model C_v^{molar} approaches to zero exponentially, where experiments shows that it approaches zero as T^3 .

Hence, despite its remarkable success, Einstein's results are not in good agreement with the experimental values at low temperatures. These disagreements are removed by the Debye model.

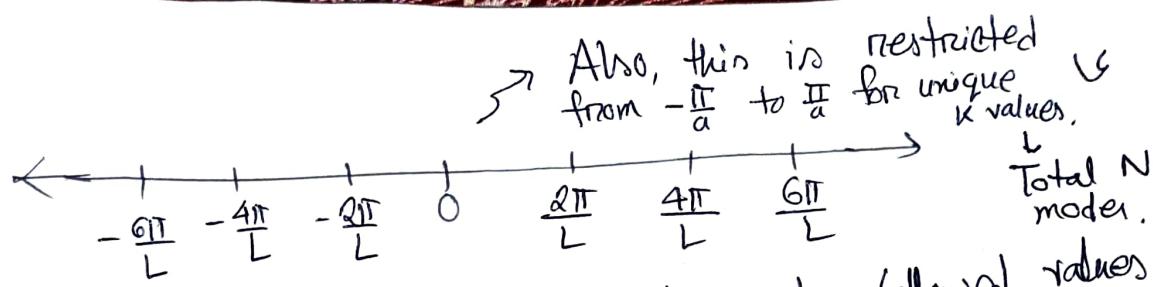
The Debye model

We start the Debye model by introducing the density of state. The density of state $g(\omega)$ is defined such that $g(\omega) \Delta\omega$ gives the number of modes between the frequency range ω and $\omega + \Delta\omega$. One can also define the density of states in the K space where $g(\vec{k}) d^3k$ gives the density of number of states that lie between k_x and $k_x + dk_x$, k_y and $k_y + dk_y$, k_z and $k_z + dk_z$.

In one dimension, it's just $g(k) \Delta k$ gives the number of modes between frequency k and $k + \Delta k$. For example, in 1D monoatomic Bravais lattice, $k = \frac{2\pi}{aN} l$, where a is the interatomic spacing, N is the number of atoms and l is integers. So,

$$k = \frac{2\pi}{L} l \quad \text{with}$$

$L = aN = \text{length of the crystal.}$



So, we get an evenly spaced points (allowed values of k). If the length of the bar L is large, the spacing $\Delta k = \frac{2\pi}{L}$ becomes small and the points form a quasi-continuous mesh. In theory, the 1D crystal should be in the limit $L \rightarrow \infty$, so that $\Delta k \rightarrow 0$. Since the spacing between the points is $\frac{2\pi}{L}$, the number of modes between k and $k + dk$ is,

$$\frac{L}{2\pi} dk \quad \left| \text{Density} = \frac{1}{\text{Spacing}} = \frac{L}{2\pi} \right.$$

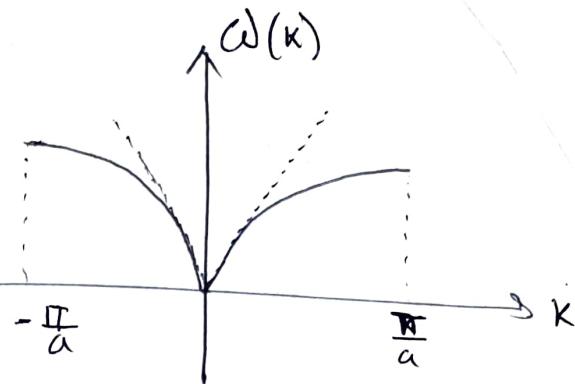
But, k and ω are related by dispersion relation, and the equivalent number of modes should be in the region between corresponding ω and $\omega + d\omega$ (since we have a ω value for a particular k value).

$$\therefore g(\omega) d\omega = g(k) dk = \frac{L}{2\pi} dk$$

$$\Rightarrow g(\omega) = \frac{L}{2\pi} \left(\frac{dk}{d\omega} \right)$$

$$\therefore g(\omega) = \left(\frac{L}{2\pi} \right) \frac{1}{V_g}$$

If you ~~free~~ recall from crystal vibration with monoatomic basis, the dispersion graph looks ~~like~~



like this and in the limit $k \rightarrow \pm \frac{\pi}{a}$, $\omega = \frac{dk\omega}{dk} \rightarrow 0$. So, $\rho(\omega) \rightarrow \infty$ in the limit $k \rightarrow \pm \frac{\pi}{a}$.

However, in the Debye model, he used an approximation. According to the definition of density of states, we should get the total number of modes if we integrate over all possible k values, that is,

$$\int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} g(k) dk = \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} \frac{L}{2\pi} dk = \frac{L}{2\pi} \left[\frac{\pi}{a} + \frac{\pi}{a} \right] = \frac{L}{a} = N$$

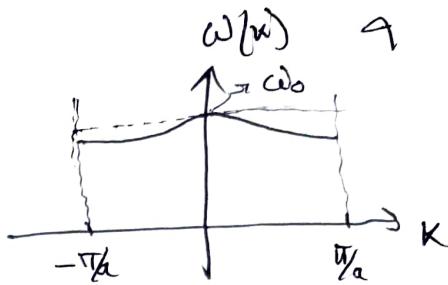
And, N is the total number of ~~no~~ distinct modes, as expected. Similarly,

$$\int_0^{\omega_{\max}} g(\omega) d\omega = N$$

Now, in Einstein theory, he considered ω to be a constant for all possible modes. This have

resemblance with optical modes.

The density of modes can be chosen as,



$$g(\omega) = N \frac{\delta(\omega - \omega_0)}{\omega_{\max}}$$

so that, $\int_0^{\omega_{\max}} g(\omega) d\omega = \int_0^{\omega_{\max}} N \delta(\omega - \omega_0) d\omega = N$

In Debye model, only the linear portion of the dispersion relation (in the previous page) is considered. So, in Debye model

$$\omega(k) = v_s k \quad \text{with} \quad v_s = \frac{d\omega}{dk}, \text{ the speed of acoustic waves (sound)}$$

$$\therefore g(\omega) = \left(\frac{L}{2\pi}\right) \frac{1}{v_s}$$

Also, the maximum frequency at $k = +\frac{\pi}{a}$ is denoted by the Debye frequency, which is found from the normalization condition,

$$\int_0^{\omega_D} g(\omega) d\omega = \frac{N}{2} \Rightarrow \int_0^{\omega_D} \left(\frac{L}{2\pi}\right) \frac{1}{v_s} d\omega = \frac{N}{2}$$

$$\Rightarrow \omega_D = \frac{2\pi N v_s}{L}$$

Here, we wrote $\frac{N}{2}$ since we are only dealing with the modes on the positive k axis. One can equivalently define $g(\omega)$

~~is~~ to twice as before so that the integration from 0 to ~~w~~ ω_0 gives N.

Three dimensional case

In three dimensional case, the wave solution is given by,

$$U(\vec{r}, t) = A e^{i(\vec{k} \cdot \vec{r} - \omega t)}$$

If we consider a cubic sample for simplicity, whose edge lengths are L, the periodic boundary conditions are given by,

$$U(\vec{r} + L\hat{x}, t) = U(\vec{r}, t) \Rightarrow e^{i k_x L} = 1$$

$$U(\vec{r} + L\hat{y}, t) = U(\vec{r}, t) \Rightarrow e^{i k_y L} = 1$$

$$U(\vec{r} + L\hat{z}, t) = U(\vec{r}, t) \Rightarrow e^{i k_z L} = 1$$

$$\therefore k_x = n_x \frac{2\pi}{L}, \quad k_y = n_y \frac{2\pi}{L}, \quad k_z = n_z \frac{2\pi}{L} \quad \text{with}$$

n_x, n_y, n_z being integers. If we plot the allowed k values in k -space, we get a

3D cubic structure, whose ~~is~~ $k_x k_y$ cross

section is shown in the figure here.
 Notice here, if you have a cube of edge $\frac{2\pi}{L}$,

that is with volume $(\frac{2\pi}{L})^3$,

you can place it such that each corner has a point in the k-space. Since 8 such cubes

will share a particular point,

the $\frac{1}{8}$ th of a point is assigned to a particular

cube. So, a cube of volume $(\frac{2\pi}{L})^3$ contains one point in k-space. So, density of modes

$$\text{in k-space} = \frac{1}{(\frac{2\pi}{L})^3} = \frac{L^3}{8\pi^3}$$

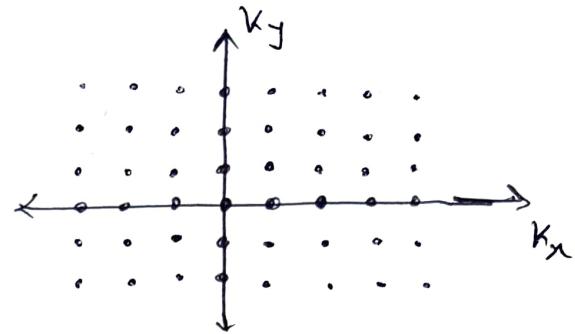
$$\therefore g(k) = \frac{L^3}{8\pi^3}$$

So, number of modes between

k and $k+dk$ is,

$$g(k) dk = \frac{L^3}{8\pi^3} dk$$

However, we have to find the number of density of states $g(v)$.



Now, Debye considered the dispersion relation as the dispersion relation for sound (which is true for 3D crystals in long wavelength limit, $k \rightarrow 0$), which is given by,

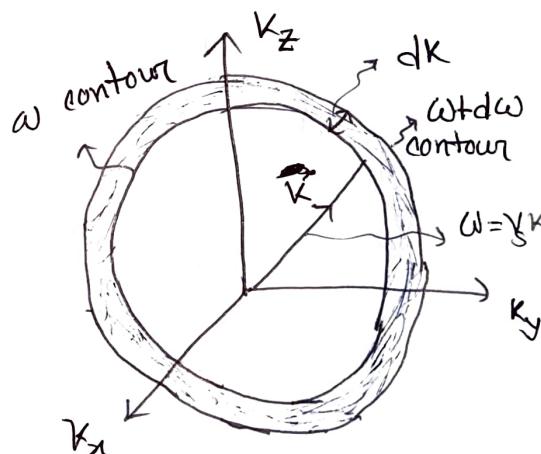
$$\omega = v_s k \quad | \quad v_s = \frac{d\omega}{dk} = \frac{\Delta\omega}{\Delta k}$$

Now, for a wavevector \vec{k} where the propagation ~~is~~ direction of the wave is \hat{k} , the frequency depends only on the magnitude of \vec{k} . So, things are isotropic here.

The volume of this shaded region $= 4\pi k^2 dk$

\therefore The number of modes between k and $k+dk$ is

$$g(k) dk = (4\pi k^2 dk) \times \frac{L^3}{8\pi^3} = (4\pi k^2 dk) \frac{V}{8\pi^3}$$



$$\text{Now, } g(k) dk = 4\pi \left(\frac{\omega}{v_s}\right)^2 \frac{d\omega}{v_s} \times \frac{V}{8\pi^3} = \left[\left(\frac{\omega^2}{v_s^3}\right) \frac{V}{2\pi^2}\right] d\omega$$

But since $g(k) dk = g(\omega) d\omega$

$$\therefore g(\omega) d\omega = \frac{\omega^2}{v_s^3} \frac{V}{2\pi^2} d\omega$$

This expression gives the number of points between the surface of constant frequency at ω and

at $\omega + d\omega$. The density of states is then,

$$g(\omega) = \frac{V}{2\pi^2} \frac{\omega^2}{\sqrt[3]{\omega}}$$

We just need one more modification. In 1D, each point in k-space is associated with one mode. However, in 3D, each value of \vec{k} can be associated with one longitudinal and two transverse modes. Hence, we should multiply by 3 to get the accurate density of state -

$$g(\omega) = \frac{3V}{2\pi^2} \frac{\omega^2}{\sqrt[3]{\omega}}$$

Now, let us calculate the specific heat.

Like before, the average energy of a mode is given by,

$$\bar{E}(\omega) = \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}$$

which has a frequency ω . But now, the frequency is not a constant for all modes. So, just multiplying by $3N_A$ won't give us the total energy of 1 mole solid.

We have to integrate over the density of states now, which will give the total energy

as —

$$E = \int \bar{E}(\omega) g(\omega) d\omega$$

$$= \frac{3V}{2\pi^2 v_s^3} \int \omega^2 \frac{\frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}}{d\omega}$$

Before evaluating the integral, we have to find the lower and upper limit, that is lower and upper frequency ends of the frequency spectrum.

The lower limit is zero. ($\omega=0$). There should be some upper limit as well which is not infinity, since the K values are only unique in some range. Hence, there should be unique ω values as well, up to some maximum ω . The upper cut-off frequency was determined by Debye, by requiring that the total number of modes must be $3N_A$ for 1 mole solid. This means,

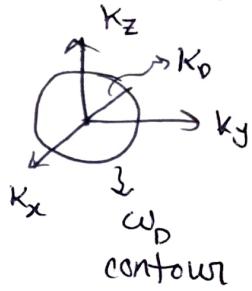
$$\int_0^{\omega_D} g(\omega) d\omega = 3N_A$$

$$\Rightarrow \frac{3V}{2\pi^2 v_s^3} \int_0^{\omega_D} \omega^2 d\omega = 3N_A$$

$$\therefore \omega_D = \left(\frac{(6N_A \pi^2 v_s^3)^{1/3}}{V} \right) = v_s (6\pi^2 n)^{1/3}$$

where $n = \frac{N_A}{V}$ is the concentration of atoms in the solid.

One can also find the result in another way. We consider a contour corresponding to the frequency $\omega = \omega_D$ in the k -space. There will be all the points (N_A in total) present inside the sphere of radius K_D that corresponds to $\omega_D = v_s K_D$, where K_D is called the Deby sphere. Then,



$$\text{Density of states} \times \text{volume} = N_A$$

$$\rightarrow \frac{V}{(2\pi)^3} \times \frac{4}{3}\pi K_D^3 = N_A$$

$$\therefore K_D = \left(\frac{3N_A \times 8\pi^3}{4V\pi} \right)^{1/3} = (6n\pi^2)^{1/3}$$

$$\therefore \omega_D = v_s K_D = v_s (6n\pi^2)^{1/3}$$

Now,

$$E = \frac{3V}{2\pi^2 v_s^3} \int_0^{\omega_D} \frac{\hbar\omega^3}{e^{\beta\hbar\omega} - 1} d\omega$$

Let,

$$x = \beta\hbar\omega$$

$$\Rightarrow \frac{dx}{d\omega} = \beta\hbar$$

$$\therefore dx = \beta\hbar d\omega$$

$$\text{For } \omega=0, x=0$$

$$\omega = \omega_D, x = \beta\hbar\omega_D = \frac{\hbar\omega_D}{k_B T}$$

We define, $\Theta_D = \frac{\hbar\omega_D}{k_B T}$ as the Debye temperature. Typically $\omega_D \approx 10^{13} \text{ rad s}^{-1}$ and $\Theta_D \approx 300 \text{ K}$ which you can calculate using $v_s \approx 1000 \text{ m s}^{-1}$ and $n \approx 6 \times 10^{29} \text{ /m}^3$.

$$\begin{aligned}\therefore E &= \frac{3V\hbar}{2\pi^2 v_s^3} \int_0^{\Theta_D/T} \frac{\frac{k_B T^3}{\hbar^3} x^3}{e^x - 1} \frac{k_B T}{\hbar} dx \\ &= \frac{3V\hbar}{2\pi^2 v_s^3} \left(\frac{k_B T}{\hbar} \right)^4 \int_0^{\Theta_D/T} \frac{x^3}{e^x - 1} dx \\ &= \frac{3V\hbar k_B^4 T^4}{2\pi^2 v_s^3 \hbar^3} \int_0^{\Theta_D/T} \frac{x^3}{e^x - 1} dx\end{aligned}$$

Low temperature limit : $T \rightarrow 0$

$$E = \frac{3V k_B^4 T^4}{2\pi^2 v_s^3 \hbar^3} \int_0^\infty \frac{x^3}{e^x - 1} dx$$

You can evaluate the integral to find it to be equal to $\frac{\pi^4}{15}$.

$$\therefore E = \frac{3V k_B^4 T^4}{2\pi^2 v_s^3 \hbar^3} \cdot \frac{\pi^4}{15} = \frac{V k_B^4 T^4}{10 v_s^3 \hbar^3}$$

$$\therefore C_V = \left(\frac{\partial E}{\partial T} \right)_V = \frac{4V k_B^4 T^3}{10 v_s^3 \hbar^3}$$

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$\therefore C_v \propto T^3$ in the low temperature limit, matching nicely with experimental results. Here, the limit is that $T \ll \theta_D$.

High temperature limit: $T \rightarrow \infty$

$$E = \frac{3V k_B^4 T^4}{2\pi^2 v_s^3 \hbar^3} \int_0^{\theta_D/T} \frac{x^3}{e^x - 1} dx$$

But now, $x = \frac{\hbar \omega}{k_B T}$ and since $T \rightarrow \infty$, it's a very small number.

$$\frac{x^3}{e^x - 1} \approx \frac{x^3}{1 + x + \dots - 1} \approx x^2$$

$$\therefore E = \frac{3V k_B^4 T^4}{2\pi^2 v_s^3 \hbar^3} \int_0^{\theta_D/T} x^2 dx$$

$$\rightarrow E = \frac{3V k_B^4 T^4}{2\pi^2 v_s^3 \hbar^3} \frac{\theta_D^3}{3T^3}$$

$$\therefore E = \frac{3V k_B^4 \theta_D^3}{2\pi^2 v_s^3 \hbar^3} T$$

$$\therefore C_v = \left(\frac{\partial E}{\partial T} \right)_V = \frac{3V k_B^4 \theta_D^3}{2\pi^2 v_s^3 \hbar^3} \quad \text{which is a constant of temperature, as expected.}$$

Here,

$$C_V = \frac{V K_B^4}{2\pi^2 V_s^3 \hbar^3} \frac{\hbar^3 \omega_0^3}{K_B^3}$$

$$\omega_0 = V_s (6n\pi^2)^{1/3}$$

$$\Rightarrow C_V = \frac{V \omega_0^3}{2\pi^2 V_s^3} K_B = \frac{K_B V}{2\pi^2 V_s^3} \times V_s^3 \times 6 \frac{N_A}{V} \pi^2$$

$$\Rightarrow C_V = 3 \cdot K_B$$

$$\therefore C_V^{\text{molar}} = 3R$$

which is exactly what is the Dulong-Petit law.

