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B.Sc. => Solid-State Physics
Chapter - 2
Elementary Lattice Dynamics

Elementary Lattice Dynamics

> **Syllabus:** Linear Monoatomic and Diatomic Chains. Acoustical and Optical Phonons. Qualitative Description Phonon Spectrum in Solids. Dulong and Petit's Law, Einstein and Debye theories of specific heat of solids. T^3 law.

Q.1. What are Lattice vibrations Discuss it for Monoatomic and Diatomic Linear chain?

Ans. Lattice Vibrations: The oscillations of atoms in a solid about their equilibrium positions. In a crystal, these positions form a regular lattice. Because the atoms are bound not to their average positions but to the neighboring atoms, vibrations of neighbors are not independent of each other. In a regular lattice with harmonic forces between atoms, the normal modes of vibrations are lattice waves. These are progressive waves, and at low frequencies they are the elastic waves in the corresponding an isotropic continuum. The spectrum of lattice waves ranges from these low frequencies to frequencies of the order of $10^{13}Hz$, and sometimes even higher. The wavelengths at these highest frequencies are of the order of interatomic spacings.

At room temperature and above, most of the thermal energy resides in the waves of highest frequency. Because of the short wave length, the motion of neighboring atoms is essentially uncorrected, so that for many purposes the vibrations can be regarded as those of independently vibrating atoms, each moving about its average position in three dimensions with average vibrational energy of $3kT$, where k is the Boltzmann constant and T the absolute temperature.

1D monatomic chain: The 1D monatomic chain is comprised of a single-atom basis and an infinite 1D lattice with basis vector $\vec{a}$. If we only consider atomic displacements along the chain direction there are $N = 1$ degrees of freedom per atom – a translational normal mode of an isolated atom. Assuming a classical model with a harmonic potential, it can be shown that the vibrational normal modes of a crystal (long-range pattern of atomic displacements) correspond to a set of travelling waves: $u_{r,\,k} = e^{i(k.r - \omega t)}$

where k is the propagation vector or wave vector ($|k| = 2\pi/\lambda$), is the angular frequency, A_k is the k dependent amplitude of the mode, and the atom in the n the unit cell is reached by the vector $r = na$.

Diatomic ID lattice

Now we consider a one-dimensional lattice with two non-equivalent atoms in a unit cell. It appears that the diatomic lattice exhibit important features different from the monoatomic case. Fig.3 shoes a diatomic lattice with the unit cell composed of two atoms of masses M_1 and M_2 with the distance between two neighboring atoms a.
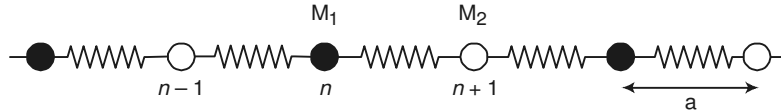
We can that the motion of this lattice in a similar fashion as for monoatomic lattice. However, in this case because we have two different kinds of atoms, we should write two equations of motion.

$$M_1 \frac{d^2 u_n}{dt^2} = -C(2u_n - u_{n+1} - u_{n-1}) \qquad (5.13)$$

$$M_2 \frac{d^2 u_{n+1}}{dt^2} = -C(2u_{n+1} - u_{n+2} - u_n)$$

Q.2. What are Acoustic phonons?

Ans. Acoustic phonons are coherent movements of atoms of the lattice out of their equilibrium positions. If the displacement is in the direction of propagation, then in some areas the atoms will be closer, in others farther apart, as in a sound wave in air (hence the name acoustic). If the wavelength of acoustic phonons goes to infinity, this corresponds to a simple displacement of the whole crystal, and this costs zero deformation energy.

Longitudinal and transverse acoustic phonons are often abbreviated as *LA* and *TA* phonons, respectively. Optical phonons are out-of-phase movements of the atoms in the lattice, one atom moving to the left, and its neighbour to the right. This occurs if the lattice basis consists of two or more atoms. They are called optical because in ionic crystals, like sodium chloride, they are excited by infrared radiation. The electric field of the light will move every positive sodium ion in the direction of the field, and every negative chloride ion in the other direction, sending the crystal vibrating.

Optical phonons that interact in this way with light are called infrared active. Optical phonons that are Raman active can also interact indirectly with light, through Raman scattering. Optical phonons are often abbreviated as *LO* and *TO* phonons, for the longitudinal and transverse modes respectively.

Q.3. What is Dulong and petit's Theory also find its expression?

Ans. Classical Theory of Specific heat due to Vibrating Lattice

(or classical theory of Dulong & petit's law)

We know that in a solid, atoms are assumed to be free to vibrate their mean position called atomic oscillators. The classical assumes that each atom is a classical three-dimensional harmonic oscillator which vibrates independently of all other atoms in the crystal, or in other way we can say that the atoms of the crystal behave as independent classical harmonic oscillators. Thus, one can calculate the heat capacity simply by finding the average thermal energy of one oscillator, multiplying it by N, and finally using equation for C_v.

Let us consider the energy of a three-dimensional harmonic oscillator of mass m and angular frequency ω_o. The energy of harmonic oscillator is given

by
$$E = \frac{p^2}{2m} + \frac{1}{2}m\omega_o(x^2 + y^2 + z^2)$$ Support by Donating

or
$$E = \frac{p^2}{2m} + \frac{1}{2}m\omega^2_o q^2 \qquad \text{...(1)}$$

Where p is the momentum and q the displacement from its equilibrium position. According to Boltzmann distribution law, the average energy of each harmonic oscillator is given by

$$\bar{E} = \frac{\int E \exp\left(-\frac{E}{kT}\right) de}{\int \exp\left(-\frac{E}{kT}\right) de} \qquad \text{...(2)}$$

where k is Boltzmann constant.
Putting equation (1) in eq. (2), we get alllabexperiments.com

$$\bar{E} = \frac{\iint\limits_{p\,q}\left(\frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 q^2\right)\exp\left(-\frac{p^2}{2mkT}\right)\exp\left(-\frac{m\omega_0^2 q^2}{2kT}\right)dp\,dq}{\iint\limits_{p\,q}\exp\left(-\frac{p^2}{2mkT}\right)\exp\left[-\frac{m\omega_0^2 q^2}{2kT}\right]dp\,dq}$$

$$= \frac{\iint\limits_{p\,q}\frac{p^2}{2m}\exp\left[-\frac{p^2}{2mkT}\right]\exp\left[-\frac{m\omega_0^2 q^2}{2kT}\right]dp\,dq}{\iint\limits_{p\,q}\exp\left[-\frac{p^2}{2mkT}\right]\exp\left[-\frac{m\omega_0^2 q^2}{2kT}\right]dp\,dq}$$

$$+\frac{\iint\limits_{p\,q}\frac{1}{2}m\omega_0^2q^2\exp\left[-\frac{p^2}{2mkT}\right]\exp\left[-\frac{m\omega_0^2q^2}{2kT}\right]dp\,dq}{\iint\limits_{p\,q}\exp\left[-\frac{p^2}{2mkt}\right]\exp\left[-\frac{m\omega_o^2q^2}{2kT}\right]dp\,dq}$$

$$=\frac{\int\limits_\infty^\infty\frac{p^2}{2m}\exp\left[-\frac{p^2}{2mkT}\right]dp}{\int\limits_\infty^\infty\exp\left[-\frac{p^2}{2mkT}\right]dp}+\frac{\int\limits_\infty^\infty\frac{m\omega_0^2q^2}{2}\exp\left[-\frac{m\omega_0^2q^2}{2kT}\right]dq}{\int\limits_\infty^\infty\exp\left[-\frac{m\omega_0^2q^2}{2kt}\right]dq}$$

as all other terms cancel, numerator against denominator.

Let $\dfrac{p^2}{2mkT}=\alpha^2$ and $\dfrac{m\omega_0^2q^2}{2kT}=\beta^2$

So, we get

$$\bar{E}=\frac{kT\int\limits_\infty^\infty\alpha^2\exp(-\alpha^2)d\alpha}{\int\limits_\infty^\infty\alpha^2\exp(-\alpha^2)d\alpha}+\frac{kT\int\limits_\infty^\infty\beta^2\exp(-\beta^2)d\beta}{\beta^2\exp(-\beta^2)d\beta}$$

Using standard integral,

$$\int\limits_\infty^\infty\alpha^2\exp(-\alpha^2)d\alpha=\frac{\sqrt{x}}{2}$$

and $$\int\limits_\infty^\infty\alpha^2\exp(-\alpha^2)d\alpha=\sqrt{x}$$

We have

$$\bar{E}=\frac{kT\sqrt{\dfrac{x}{2}}}{\sqrt{x}}\frac{kT\cdot\dfrac{\sqrt{x}}{2}}{\sqrt{x}}$$

$$=\frac{kT}{2}+\frac{kT}{2}=kT$$

Hence, total vibrational energy of a crystal having N independent harmonic oscillators in three dimensions for a gram molecule of a substance will be

$$E = 3N\bar{E} = 3N\,kT$$

Where crystal is being treated in terms of 3 N one dimensional harmonic oscillator. If we suppose that the atoms in a solid behave as free classical harmonic oscillator about their equilibrium positions, then we see that the classical theory predicts the lattice contribution to the molar heat capacity at constant volume, which is given by

$$C_v = \left[\frac{\partial E}{\partial T}\right] = 3Nk = 3R$$

or $\qquad\qquad C_v = 5.96\ cal\ mol^{-1}K^{-1}\ [\therefore\ Nk = R]$

This is called Dulong and Petit's which states that the capacity of all solids is constant and is independent of the temperature and for one mole of any solid element it is equal to about 6 calories.

Q.4. Show that in Einstein model of specific heat $C_v = 3R\left(\dfrac{\theta_E}{T}\right)^2 e^{\frac{\theta_E}{T}}$

Where symbols have their usual meaning. [Important]

Ans. Einstein Theory of Lattice Specific Heat of Solids.

In the classical explanation of specific heat, the atoms in the solid were considered as simple harmonic oscillators vibrating independently and having continuous energy between zero to infinity. This theory could not explain the experimental fact that heat capacity of all solids approaches zero at low temperatures. This discrepancy was explained by Einstein by assuming that

(i) the atoms are again considered identical independent harmonic oscillator as in classical theory.

(ii) all the oscillators have same natural frequency 'v' because of their assumed identical oscillators.

(iii) a solid element containing N atoms, in equivalent to $3N$ one dimensional harmonic oscillators.

(iv) the theory spectrum of oscillators is not continuous but discrete continuous energy values but regarded as quantum harmonic oscillator which of not have Planck's hypothesis, an oscillator of frequency v has discrete units of energy as multiples of hv, where h is Plank's constant. The possible energy levels of an oscillator may thus be represented by

$$\in_n = nhv,\ n = 0,1,2 \qquad\qquad ...(1)$$

where n is any positive integer called the quantum number, v is the frequency and h is Plank's constant, Eqn.(1) may be written as

$$\epsilon_n = n\frac{h}{2\pi}2\pi v$$

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$$= n\hbar\omega \qquad \qquad ...(2)$$

where w is angular frequency and $\hbar = \dfrac{h}{2\pi}$. An energy level is labelled by the value of this integer. Originally, Einstein used the above Planck's result but later the wave mechanical result

$$\epsilon_n = \left(n+\frac{1}{2}\right)\hbar\omega \qquad \qquad ...(3)$$

was used which takes into account the term $\hbar\omega(1/2)$ for the temperature independent zero point energy contribution to the internal energy and shifts all energy levels by the constant amount $\hbar\omega/2$.

As these quantised oscillator from an assembly of systems, which are distinguishable or identifiable by virtue of their location at separate and distinct lattice sites and since any number of these may be in the same energy state of system, so the Maxwell Boltzmann distribution law is still applicable for the description of their behavior. Since the energy is quantised that is discontinuous, hence the average of the oscillator may be obtained by replacing the integrals in Eqn. summation i.e.

$$<\epsilon> = \frac{\sum\limits_{n=0}^{\infty}\epsilon_n e^{-\epsilon_n l k_n T}}{\sum\limits_{n=0}^{\infty}\epsilon_n\, e^{-\epsilon_n l k_n T}} \qquad \qquad ...(4)$$

Putting the value of ϵ_n from eqn. (3) we have

and putting $x = -\dfrac{\hbar\omega}{k_B T}$, we have   alllabexperiments.com

$$<\epsilon> = \frac{\hbar\omega}{e^{\hbar\omega/k_B T-1}} \qquad \qquad ...(5)$$

The first term of the R.H.S. of the eqn. is temperature independent

zero point energy of the oscillator $<\epsilon> = \hbar\omega/2$ for $T = 0$. Thus according to quantum mechanics, the atoms have vibrational energy event at absolute zero. But this term does not make any contribution to heat capacity, because C_v is determined by the derivative of $<\epsilon>$ w.r.t. T. Further from eqn. (5) we note denominator of R.H.S. can be expanded as

$$e^{\hbar\omega/kT_B T} - 1 = 1 + \frac{\hbar\omega}{k_B t} + \frac{1}{2!}\left(\frac{\hbar\omega}{k_B t}\right)^2 + \ldots - 1 = \frac{\hbar\omega}{k_B t} \text{ (neglecting higher terms)}$$

So that $<\in> \cong k_B T$

Thus at higher temperature the average energy as obtained using Plank's Einstein distribution law for harmonic oscillator by the number of oscillator 3N in it, hence

$$E = 3N <\in> \frac{3N\hbar\omega}{2} + \frac{3N\hbar\omega}{e^{\hbar\omega/k_B T - 1}}$$

and

$$C_v = \left(\frac{\partial E}{\partial T}\right) = 3Nk_B \left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{(e^{\hbar\omega/k_B T})}{(e^{\hbar\omega/k_B T} - 1)^2} \qquad \ldots(6)$$

The above expression (6) for C_v can be written in a simpler form by defining characteristic temperature θ_E called "Einstein temperature" such that

$$\hbar\omega = k_B \theta_E$$

Substituting this in eqn. (4.14), we get

$$C_v = 3N k_B \left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_v/T}}{(e^{\theta_E/T} - 1)^2} \qquad \ldots(7)$$

Using eqn. if a plot is drown between C_v versus (T/θ_E), a general curve for diamond of the form shown in Fig is obtained which indicates that theoretical values of C_v agree fairly well with the experimental values over a wide range of temperature in which heat capacity varies appreciably with temperature. The figure shows the agreement of the experimental values of the heat capacity for diamond (dots) with values calculated on the Einstein's model using
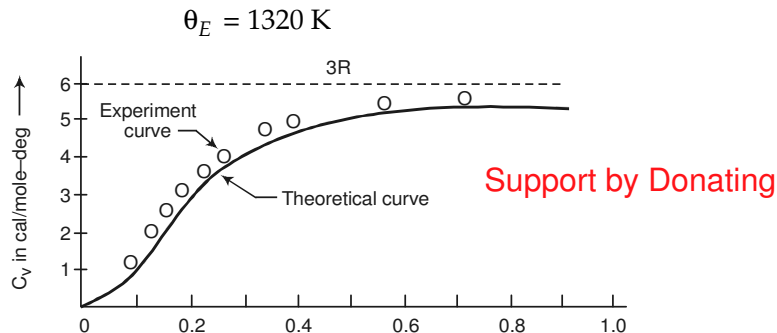
$$\theta_E = 1320 \text{ K}$$

Figure. Comparison of experimental values of heat capacity for diamond with that theoretical values obtained Einstein using model (θ_E = 1320 K).

The temperature θ_E is an adjustable parameter chosen to produced the best fit to the measured values over the whole temperature range. Let us now examine the behaviour of C_v as calculated by eqn.(4.15) for extreme temperature limits.

(i) When temperature are high enough such that $T \gg \theta_E$. becomes very small and therefore Binomial expansion gives

$$e^{\theta_E/T} \cong 1 + \frac{\theta_E}{T}$$

and

$$(e^{\theta_E/T} - 1)^2 \cong \left(1 + \frac{\theta_E}{T} + \frac{1}{2!}\left(\frac{\theta_E}{T}\right)^2 \dots - 1\right)^2$$

$$= \left(\frac{\theta_E}{T}\right)^2 \qquad \text{(Neglecting higher order terms)}$$

Substituting the above values in eqn.(4.15), we get

$$C_v \simeq \frac{3Nk_B\left(1 + \frac{\theta_E}{T}\right)\left(\frac{\theta_E}{T}\right)^2}{\left(\frac{\theta_E}{T}\right)^2} = 3Nk_B\left(1 + \frac{\theta_E}{T}\right)^2$$

$$\cong 3Nk_B \qquad \left(\therefore As\, T \to \infty, \frac{\theta_E}{T} \to 0\right)$$

$$\cong 3R$$

Thus, in this limit heat capacity approaches the classical value $3R$ which is Dulong and Pett's law. So the Einstein model is satisfactory at the high temperature limit because at this temperature quantum concept becomes irrelevant.

(ii) When temperature are low such that $T \ll \theta_E$, or when $T \to 0$, $\theta_E/T \to \infty$, therefore $e^{\theta_E/T \gg 1}$, so $(e^{\theta_E/T} - 1)^2 \approx (e^{\theta_E/T})^2$ neglecting 1 in this expression. Therefore eqn. (7) becomes

$$C_v \cong 3Nk_B \frac{e^{\theta_E/T}}{(e^{\theta_E/T})^2}\left(\frac{\theta_E}{T}\right)^2$$

$$\cong 3Nk_B\left(\frac{\theta_E}{T}\right)^2 e^{-\theta_E/T}$$

Thus in this limit, heat capacity is proportional to the dominating exponential factor $e^{-\theta_E/T}$ and approaches zero as T approaches zero. Thus specific heat of a solid decreases exponentially with temperature and vanishing at absolute zero temperature. Although the fact that specific heat decrease with fall – in temperature and that $C_v \to 0$ when $T \to 0$ K agree with the experiment but the manner in which it approaches zero does not, Experimentally it is found to vary as T^3 for most of the solids. From the fig. It is seen that the Einstein curve fits the experimentally observed value fairly well at all temperature except at very low temperature where it falls off more rapidly than it should and thus deviating from the experimental behaviours $(C_v \infty T^3)$ in this range of temperature.

Q.5. Derive an expression for specific heat of solids on the basis of Debye model. How does Debye model differ from Einstein model? Discuss the variation of specific heat with Temperature.

Ans. In Debye model the following simplifying assumptions are made:

1. In Einstein theory of specific heat of solids, each atom is supposed to vibrate as a single unit/oscillator independently of its neighboring atoms. But the situation is not so simple because each atom is under the influence of the field of force of a number of other vibrating atoms.

   Debye took into account the effect of coupling between neighboring atom s and considered the solid as a continuous elastic body.

2. According to Debye the internal energy of a solid instead of residing in the vibrations of individual atoms was present in the elastic standing waves being produced because of the vibrations of individual atoms.

3. Further Debye assumed that the energy of these elastic standing waves was not continuous but quantised. A quantum vibrational energy is called phonon analogous to photon in e.m. waves. A phonon has energy hv similar to that of a photon where v is frequency of vibration and h is Plank's constant. A phonon travels with the velocity of sound waves are elastic waves in nature. Support by Donating

4. The number of vibrational modes of any kind in the frequency range v and $(v + dv)$ is given by $Z(v)dv = \dfrac{4\pi V}{v^3}v^2 dv$ where $Z(v)$ is number of vibrational modes per unit frequency range and is known as density of modes, $V = L^3$ is the volume of the solid taken in the form of a cube having each side $= L$ and v is the velocity of propagation of the wave through the medium.

$$Z(v)dv = 4\pi v\left(\frac{1}{v_1^3} + \frac{2}{v_t^3}\right)v^2 dv$$

5. Debye further assumed that the phonon gas behaves like a boson gas which obeys Bose-Einstein statistics and the averages energy $<\epsilon>$ per standing wave at a temperature T is given by

$$<\epsilon> = \frac{hv}{e^{hv/k_BT-1}}$$

If a quantum oscillator is associated with each vibrational mode of the same frequency, the vibrational frequency of the crystal is given by

$$E = \int_0^{v_D} <\epsilon> D(v)dv$$

Substituting the values of (v) from eqn. (4.29), we have

$$E = \int_0^{v_D} 4\pi V \left[\frac{1}{v_t^3} + \frac{2}{v_t^3} \right] \frac{hv^3}{e^{hv/k_BT-1}} dv$$

$$= 4\pi V \left[\frac{1}{v_t^3} + \frac{2}{v_t^3} \right] \int_0^{v_D} \frac{hv^3}{e^{hv/k_BT-1}} dv \qquad ...(4.31)$$

From eqn. (4.30)

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

Substituting in eqn. (4.31), we have

$$E = \frac{9N}{v_D^3} \int_0^{v_D} \frac{hv^3}{e^{hv/k_BT-1}} dv \qquad ...(4.32)$$

Substituting $x = \frac{hv}{k_BT}$ and $x_D \frac{k_BT}{h}$, we get

$$v = \frac{xk_BT}{h} \ or \ dv = \frac{k_Bt}{h}dx$$

Equation (4.32) therefore becomes

$$E = \frac{9Nh}{v_D^3} \int_0^{x_D} \frac{x^3 k_B^3 T^3}{h^3} \frac{k_bT \ dx}{h} \frac{1}{e^x - 1}$$

$$= 9N \left(\frac{k_bT}{hv_D} \right)^3 k_BT \int_0^{x_D} \frac{x^3}{e^x - 1} dx \qquad ...(4.33)$$

As in Einstein model, it is convenient here also to introduce a characteristic temperature, θ_D, called Debye temperature and defined as

$$\theta_D = \frac{h v_D}{k_B}$$

so that upper limit $\quad x_D = \frac{h v_D}{k_B T} = \frac{\theta_D}{T}$

Thus eqn. (4.33) can be written as

$$E = 9 N k_B T \left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_B/T} \frac{x^3}{e^x - 1} dx \qquad ...(1)$$

The value of heat capacity or specific heat is obtained by differentiating this energy expression w.r.t. absolute temperature.

$$C_v = \left(\frac{\partial E}{\partial T}\right)_v = 9 N k_B \left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{e^x x^4 dx}{(e^x - 1)^2}$$

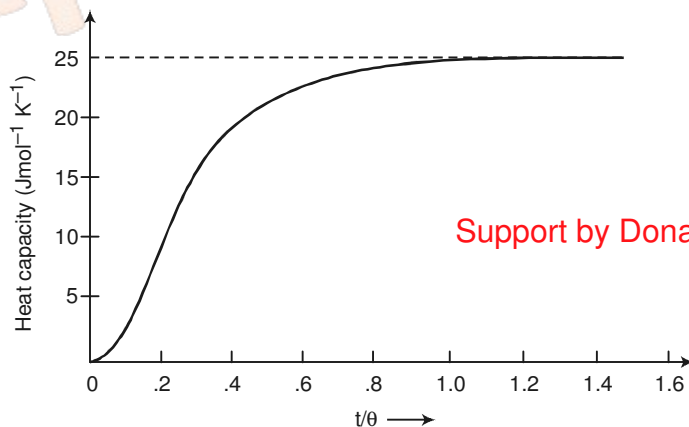or $\qquad C_v = 3 R F_D \times \left(\frac{T}{\theta_D}\right) \qquad ...(2)$

where $\qquad R = N k_B$ for one mole of the substance

and $\qquad F_D = 3 \left(\frac{T}{\theta_D}\right)^4 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx$

is called Debye function.

Expression. (2) gives the specific heat for one mole of the substance and is called the Debye formula. If we plot heat capacity as a function of T/θ, (fig),

it is seen from this plot that the heat capacity the classical value $3Nk_B$ at high temperatures and zero at low temperatures. Now we examine below the heat capacities at these temperature ranges more closely.

(i) For high temperatures i.e. for $T \gg \theta_D$, x is small as compared with unity for the whole range of integration. In that case, the denominator of the integrand in eqn. (1) i.e. $e^x - 1 \approx x$, in first approximation, then we get

$$E = 9\text{N} \frac{1}{x_m^3} k_B T \int_0^{x_D} \frac{x^3}{x} dx$$

$$= 9N \frac{1}{x_m^3} k_B T \frac{x_m^3}{3}$$

$$E = 3Nk_B T \qquad \qquad \text{Support by Donating}$$

and the specific heat

$$C_v = \frac{dE}{dT} = 3Nk_B = 3R \text{ which is Dulong Petit's law.}$$

This specific heat is identical as obtained both by classical theory and Einstein theory at high temperatures. Physically this means that the quantum consideration are of almost no significance at high temperatures.

(ii) For very low temperatures i.e. for $T \gg \theta_D$, the upper limit of integration of eqn. (1) becomes infinity, $\left(\because x_D = \frac{\theta_D}{T} \to \infty \right)$ thus

$$E = 9Nk_B T \left(\frac{k_B T}{h v_d} \right)^3 \int_0^\infty \frac{x^3 dx}{e^x - 1}$$

where

$$\int_0^\infty \frac{x^3 dx}{e^x - 1} = 6\xi(4) = 6\sum_1^\infty \frac{1}{n^4} = \frac{\pi^4}{15}$$

where $\xi(4)$ is Riemann Zeta function.

$$\therefore \qquad \qquad E = 9Nk_B T \left(\frac{k_B T}{h v_D} \right)^3 \times \frac{\pi^4}{15}$$

or

$$E = \frac{3}{5} \pi 4 Nk_B \frac{T^4}{\theta_D^3} \qquad \qquad \qquad ...(3)$$

Thus the energy of vibration is proportional to T^4 at low temperature. The specific heat is then given by

$$C_v = \frac{\partial E}{\partial T} = \frac{12}{5}\pi^4 N k_B \left(\frac{T}{\theta_D}\right)^3 \text{ for } T << \theta_D$$

$$= 77.94 \times 3R\left(\frac{T}{\theta_D}\right)^3 \qquad \ldots(4)$$

This law is analogous to Stefan's law Black body radiation. The phonons (quantum of energy in elastic wave is called phonon) and photons (quantum of energy of electromagnetic waves) obey the same statistics with the difference that phonons obey T^3 law at temperatures while the photons obey T^4 law at all temperatures.

Thus we find that specific heat is directly proportional to T^3 at extremely low temperature because θ_D is constant for the substance. This is called the famous Debye's T^3 Law.

Comparison of C_v from Einstein and Debye Theory. Plots of value of heat capacity obtained form Einstein and Debye models Vs T/θ are shown in fig. The Debye curve lies above the Einstein curve. The reason is that in Debye model, the lower frequency modes are taken into account and at low temperature these have a higher average energy and temperature derivative than the relatively high frequency Einstein oscillators.
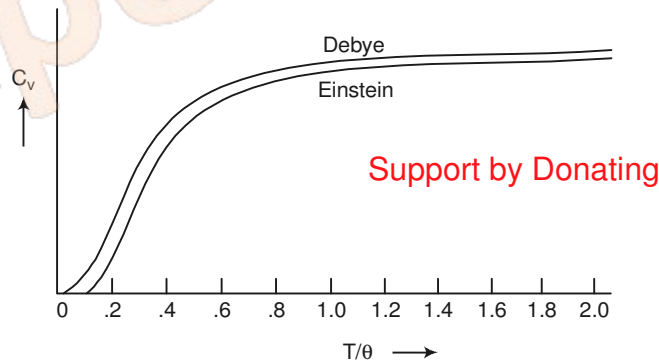

Figure. Comparison for *Cv* obtained form Einstein and Debye models.

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