Lattice Vibrations, Phonons, Specific Heat Capacity, Thermal Conductivity

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1 Lattice Vibrations, Phonons

1.1 Introduction

The atoms in a solid are executing oscillations about their equilibrium positions with energy governed by the temperature of the solid. Such oscillations in crystals are called lattice vibrations. The lattice vibrations are responsible for the characteristic properties of matter such as specific heat, thermal conductivity, electrical conductivity, optical and dielectric properties, diffusion mechanism, phase change phenomena etc.

In the lattice dynamical treatment, the atoms are considered as point masses averaged in some effective potential, defined by their mutual interactions which determine their motion. This basic formalism of lattice dynamics was originally formulated by Born and von-Karman. The theory of lattice dynamics adopts the basic ingredients such as crystal symmetry, adiabatic approximation and harmonic approximation. Due to the property of crystal symmetry, the properties of entire crystal can be calculated from the knowledge of the behavior of a very small region.

According to Born – Oppenheimer [3], the atomic nuclei being much heavier, move much more slowly than the electrons. At any instant, the electrons see the nuclei fixed in some configuration. As the nuclei moves, the electrons follow the nuclear motion adiabatically in the sense that the electrons state is deformed progressively by the nuclear displacement. This approximation fails to explain the electron–phonon interaction in crystals.

The nuclei in the matter vibrate about their own equilibrium positions under the influence of an effective potential energy, which is the defined by the individual nuclei and all the electrons surrounding them. The potential energy term can be explained in Taylor series. According to harmonic approximation, the series terminates at the quadratic term. Thus, this approximation allows representing a many body problem as a two body problem. The limitation of this approximation is non-accountability of phonon-phonon interaction.

1.2 Lattice Vibrations

Atoms in a crystal are considered to be residing at particular lattice sites. But, in reality they undergo continuous fluctuations in the neighborhood of their regular positions in the lattice. These fluctuations arise from the heat or thermal energy in the lattice, and become more pronounced at higher temperatures.
Since the atoms are bound together by chemical bonds, the movement of one atom about its site causes the neighboring atoms to respond to this motion. The chemical bonds act like springs that stretch and compress repeatedly during oscillatory motion.

The result is that many atoms vibrate in unison, and this collective motion spreads throughout the crystal. Every type of lattice has its own characteristic modes or frequencies of vibration called normal modes, and the overall collective vibrational motion of the lattice is a combination or superposition of many, many normal modes.

With the adiabatic approximation defined, the theory of lattice vibrations can be made. Let the primitive translation vectors be given as $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$. Considering one atom at origin the equilibrium position of the atom in the $l$th unit cell is given as

$$R(l) = l_1 \mathbf{a}_1 + l_2 \mathbf{a}_2 + l_3 \mathbf{a}_3$$

and that of the $s$th atom in the $l$th unit cell is given as

$$R_{(l)}^{(s)} = R(l) + R(s)$$

$s$ can take $r$ values where $r$ is the number of atoms in the unit cell.

---

**Fig. 1. Primitive Cell**

The total kinetic energy of the crystal can be defined as

$$T = \frac{1}{2} \sum_{s} M_s \dot{u}_s^2$$

$$\left(\frac{l}{s}\right)$$

(3)
where $M_s$ is the mass of the $s^{th}$ atom in the $l^{th}$ unit cell, $\alpha$ is the Cartesian component. The potential energy is given as $V(R)$ is a function of instantaneous position of atoms and it can be given as

$$V = V_0 + \sum_{l,s} \Phi(l_s) \cdot u(l_s) + \frac{1}{2} \sum_{l,s,s'} \Phi(l_s l'_s) \cdot u(l_s) u(l'_s) + \ldots \ldots \ldots \ldots \ldots (4)$$

$$= V_0 + V_1 + V_2 + \ldots \ldots \ldots \ldots \ldots (5)$$

The coefficient in the term $V_n$ is a tensor of rank $n$. We have

$$\Phi(l_s) = \left[ \frac{\partial V}{\partial u(l_s)} \right]_o \ldots (6)$$

$$\Phi(l'l'_s) = \left[ \frac{\partial^2 V}{\partial u(l'_s)u(l_s)} \right]_o \ldots (7)$$

where the subscript zero denotes the equilibrium position. All higher terms are neglected. $V_0$ is the static term which can be neglected in the present context. The term $V_1$ vanishes since Eqn. (6) is negative of the force acting on the atom $(l, s)$.

The Hamiltonian for the whole crystal can be given as

$$H = V_0 + \frac{1}{2} \sum_{l,s} M_s \ddot{u}_\alpha(l_s) + \sum_{l,s} \sum_{l',s'} \Phi_{\alpha\beta}(l'_s) u_\alpha(l_s) u_\beta(l'_s) \ldots (8)$$

hence we arrive at the equation of motion for the atom $(l, s)$

$$M_s \ddot{u}(l_s) = \frac{-\partial V}{\partial u(l_s)} = -\sum_{l',s'} \Phi(l'_s) \cdot u(l'_s) \ldots (9)$$

From the Bloch’s theorem, the time dependent displacement $u(l_s)$ can be written as

$$u(l_s) = M_s^{-1} U_s(t) \exp[iq.R(l)] \ldots (10)$$

where $U_s(t)$ is independent of $l$ and contains time dependent factor $e^{-i\omega t}$.

Substituting Eqn. (10) in (9) we then obtain
\[ \omega^2 U_{as} = (M_s M_s')^{\frac{1}{2}} \sum_{\beta s'} D_{\alpha \beta}(ss', q) U_{\beta s}(11) \]

where
\[ D(ss', q) = (M_s M_s')^{\frac{1}{2}} \sum_i \Phi \left( \frac{0l}{ss'} \right) \exp[-iq \cdot R(t)](12) \]

Thus, the problem has been reduced to the solution of 3r equations. The components of D form a 3r * 3r matrix, this is known as the dynamical matrix. The condition that the set of equations given in (10) have a non-trivial solution is given by the usual characteristic equation
\[ |D_{\alpha \beta}(ss', -q) - \omega^2 \delta_{\alpha \beta} \delta_{ss'}| = 0(13) \]

and the 3r values of \( \omega^2 \) obtained for the given q will be distinguished by suffix j. The eigenvalue problem described above has been applied to a single unit cell of a crystal.

1.3 **Force constants and its properties**

According to Eqn. (9), the net force on atom l is a linear function of the displacements \( u \left( \begin{array}{c} l \\ s \end{array} \right) \) and coefficients \( \Phi_{\alpha \beta} \left( \begin{array}{c} l \\ s \\ s' \end{array} \right) \) and are called net atomic force constants. They physically mean that, suppose only one atom l' has a displacement while all other atoms are still at their equilibrium positions, then Eqn. (9) becomes
\[ -\Phi_{\alpha \beta}(l \ l') = \frac{F_{\alpha}(l)}{u_{\beta}(l')}(14) \]

It is clear that \( -\Phi_{\alpha \beta}(l \ l') \) is the direction force acting on atom l when atom l' has moved a distance of unit length in the b direction. The force constants have the following properties.

1. \( \Phi_{\alpha \beta}(l, l') = \Phi_{\beta \alpha}(l', l) \) This is due to the partial derivatives which are independent of the order in which the derivatives are taken.

2. \( \sum_{l'} \Phi_{\alpha \beta}(l, l') = 0 \) This is true because when each \( u \) in Eqn. (9) is replaced by an arbitrary constant \( c \), corresponding to a motion of the crystal as a whole, there
would be no changes in the relative positions of the atoms, total potential energy, and its derivatives.

3. \( \Phi_{\alpha\beta}(l,l') = -\sum_{l\neq l'} \Phi_{\alpha\beta}(l,l') \) which can be directly seen from property 2.

4. \( \Phi_{\alpha\beta}(l,l') = \Phi_{\alpha\beta}(0,l'-l) = \Phi_{\alpha\beta}(l'-l,0) \) which indicates that force constant depends only on the relative position between the atom pair.

5. When the force constants between atoms \( l \) and \( l' \) are represented by a 3x3 matrix, they exhibit certain symmetry properties. When applied to a specific crystal, these symmetry properties can greatly simplify the force constant matrix.

![Fig. 2. Schematic illustration of atomic force constants](image)

### 1.4 Phonons

Lattice vibrational motion can also produce traveling waves in which localized regions of vibratory atomic motion travel through the lattice.

Examples of such traveling waves are sound moving through the air, or seismic waves that start at the epicenter of an earthquake, and travel thousands of miles to reach a seismograph detector that records the earthquake event several minutes later.
Localized traveling waves of atomic vibrations in solids, called phonons, are quantized with the energy $\hbar \omega = \hbar \nu$, where $\nu = \omega / 2\pi$ is the frequency of vibration of the wave. Phonons play an important role in the physics of the solid state.

From quantum mechanics point of view, we know that the energy levels in the harmonic oscillator are quantized. Similarly, the lattice vibrations are quantized. This quantum of vibration is called as phonon analogous to photon which is the quantum of light energy. Phonons play an important role in the physics of the solid state.

The allowed energy levels in the harmonic oscillator are

$$E = \left( n + \frac{1}{2} \right) \hbar \omega$$

(15)

where, $n$ is the quantum number. A normal vibration mode in a crystal of frequency $\omega$ is given by $u = A e^{i(qr-\omega t)}$. If the energy of this mode is given by Eq.(14), we can say that this mode is occupied by $n$ phonons of energy $\hbar \omega$. The term $\frac{1}{2} \hbar \omega$ is the zero point energy of the mode.

Phonons govern the thermal properties in semiconductors and insulators. Their influence on thermal, electrical, optical and other properties of bulk materials is well known.

As we know that the density of states $D(E)$ of conduction electrons are strongly affected by the dimensionality of a material, phonons also have a density of states $D(PH)$ which depends on the dimensionality, and like its electronic counterpart, it influences some properties of solids.

In specific, the specific heat of a solid is the amount of heat that must be added to it to raise its temperature by one degree Celsius. The main contribution to this heat is the amount that excites lattice vibrations, and this depends on the phonon density of states $D(PH)$.

The interactions of phonons are unavoidably altered by the effects of dimensional confinement on phonon modes of nanostructures. These effects are similar to that of electrons confined in a quantum well. The dimensional confinement of phonons results in restrictions in the phase space of the phonon wave vectors, due to which it is certain that carrier-phonon interactions in nanostructures would be modified by the phonon
confinement.

**1.5 Modes of Vibration in a crystal**

To illustrate the modes of vibration, let us consider a linear chain of atoms A and B with spring constants $\chi$ and $\zeta$ between the nearest neighbors only. As there are two degrees of freedom in this problem, we have a dynamical matrix of size $2x2$. We have the force constants between the nearest neighbors as

$$
\Phi_{AA} = -\chi - \zeta = \Phi_{BB}, \quad \Phi_{AB} = \chi, \Phi_{BA} = \zeta \quad (16)
$$

The dynamical matrix equation for the above set of force constants is given by

$$
D_{AB}(k) = \frac{1}{\sqrt{m_A m_B}} (\Phi_{AB} + \Phi_{AB} e^{2ika}) = -\frac{\chi + \zeta e^{2ika}}{\sqrt{m_A m_B}} \quad (17)
$$

Similarly calculating the other terms we finally get the dynamical matrix as

$$
D(k) = \begin{bmatrix}
\frac{\chi + \zeta}{m_A} & -\frac{\chi + \zeta e^{2ika}}{\sqrt{m_A m_B}} \\
-\frac{\chi + \zeta e^{-2ika}}{\sqrt{m_A m_B}} & \frac{\chi + \zeta}{m_B}
\end{bmatrix} \quad (18)
$$

Applying it to the characteristic equation and solving we get the eigenvalues as

$$
\omega^2 = \frac{\chi + \zeta}{m} \pm \frac{1}{m} \sqrt{\chi^2 + \zeta^2 + 2\chi\zeta \cos 2ka} \quad (19)
$$

For simplicity, here masses are considered to be equal.

Here we are interested in their behavior near the zone center at $k = 0$. In this case, we can see that the determinant is zero implying, that one of the eigenvalues is zero. These are called the acoustic modes since the motions of atoms are in phase.

The fact that, this mode is linear in $k$ near $k = 0$ is not always true, but it occurs in most cases where there are no long range forces present in the system, and no peculiar
interactions among the particles. The slope at the origin is the group velocity of that mode and is called the speed of sound, as it is also the speed of propagation of elastic (long wavelength limit) waves.

The other set of modes are called the optical modes, where two atoms in the unit cell are vibrating with a phase difference of \( \pi \). This generally creates a dipole moment and therefore couples to the electromagnetic waves, hence the name optical for these modes.

![Fig. 3. Phonon modes in (a) mono atomic lattice and (b) diatomic lattice](image)

### 2 Specific Heat Capacity, Thermal Conductivity

#### 2.1 Thermal Properties

Heat energy in a solid can be carried by electronic carriers (electrons and holes), lattice waves (phonons), electromagnetic waves, spin waves, or other excitations. In metals, the thermal conductivity is mainly due to the electrons, while in semiconductors and insulators it can be accredited with lattice waves (phonons).

The conductivity can simply be given as

\[
\kappa = \sum \kappa_\alpha \tag{20}
\]

Where, \( \alpha \) is an excitation. Thermal conductivities in solids vary dramatically in magnitude and temperature depending on the material and its dimensions. This is due to
number of parameters such as lattice defects or imperfections, dislocations, anharmonicity of the lattice forces, carrier concentrations, interactions between the carriers and the lattice waves, interactions between magnetic ions and the Lattice waves, etc. due to all these factors studying the thermal properties can reveal a lot about a material.

### 2.2 Lattice Specific heat capacity

Lattice thermal conductivity is a dominant one in non-metals; in fact it is the only one. Normally as discussed above in a crystal we have acoustic phonons and optical phonons. The acoustic phonons are low frequency acoustic branches in which atoms are in phase. While the optical phonons are high frequency braches with atoms out of phase. But optical phonons prove to be ineffective as heat transporters due to their low group velocities. But, they interact with the acoustic phonons which are main contributors of the thermal conductivity.

The specific heat capacity of a solid at a constant volume is generally given as

\[
C_v = \left( \frac{\partial \tilde{E}}{\partial T} \right)_v
\]  

(21)

where \( \tilde{E} \) is the average internal energy of the solid.

The specific heat has two contributions, one from the lattice vibrations i.e., lattice specific heat capacity and the other from the thermal motion of the electrons i.e., electron heat capacity. When temperatures are not too low, the contributions of electrons towards the specific heat can be neglected as it is smaller than that of the lattice specific heat capacity. According to the classical theory, the average energy of each harmonic motion is \( k_B T \). If there are \( N \) atoms in a solid, there will be \( 3N \) harmonic vibrations then the average energy can be given as \( 3N k_B T \).

The specific heat thus obtained is given as

\[
C_v = 3Nk_B
\]  

(22)

From this it can be observed that the lattice specific heat capacity is independent of material properties and temperature. This is known as the Dulong-Petit law. This holds good for higher temperatures but, for lower temperatures \( C_v \) is no longer a constant and
decreases with temperature. This behavior can be explained by quantum mechanical principles.

The average temperature dependent energy is given as

\[ E_T = \sum_{q_j} \frac{k \omega_{q_j}}{\exp(\beta \hbar \omega_{q_j}) - 1} \quad (23) \]

the heat capacity can be now expressed as

\[ C_v = \left( \frac{\partial E_T}{\partial T} \right)_v = k \sum_{q_j} G(\beta \hbar \omega_{q_j}) \quad (24) \]

where

\[ G(x) = \frac{x^2 e^x}{(e^x - 1)^2} \quad (25) \]

For each branch \( j \) the summation over \( q \) may be replaced by integration over the volume of the first Brillouin zone, and this can be transformed into an integration over \( \omega \), the above expression can be represented as

\[ C_v = k \sum_j \int G(\beta \hbar \omega) g_j(\omega) \, d\omega \]

\[ = k \int G(\beta \hbar \omega) g(\omega) \, d\omega \quad (26) \]

Since the total spectral density \( g(\omega) \) is the sum of 3r individual functions \( g_j(\omega) \).

### 2.3 Einstein Model

The first quantum mechanical theory to explain the lattice specific heat was the Einstein model of specific heat for solids. It postulates that all atoms are vibrating independently with same frequency \( \omega_E \). In this theory the correlation between the motions of neighboring atoms were ignored.

The specific heat of the solid can be given as
\[ C_v = 3rNkT \left( \frac{\Theta_E}{T} \right) \]  \hspace{1cm} (27)

Where \( \Theta_E \) is the Einstein characteristic temperature defined by

\[ \hbar \omega_E = k \Theta_E \]  \hspace{1cm} (28)

If the total number of atoms \( rN \), is considered to be Avogadro number \( L \), the high temperature specific can be given as

\[ C_v = 3Lk = 3R(T \gg \Theta_E) \]  \hspace{1cm} (29)

At low temperatures the specific heat of solids can be given as

\[ C_v \approx 3R \left( \frac{\Theta_E}{T} \right)^2 \exp \left( \frac{-\Theta_E}{T} \right) (T \ll \Theta_E) \]  \hspace{1cm} (30)

This tends to zero as \( T \) decreases. Despite this short coming, the Einstein model is useful for high temperature approximations and can also be applied to optical bands.

\section*{2.4 Debye Model}

At low temperatures, the optical branch phonons have energies higher than \( k_B T \), and therefore, optical branch waves are not excited. Only acoustic waves contribute to the heat capacity. For an acoustic branch \( \omega \), as \( q \rightarrow 0 \) and the Einstein model fails to include this feature in its model. The Debye model assumes that the lattice waves are elastic waves (one longitudinal branch and two transverse branches) and the frequency here is not a constant but a specific distribution with a cut off frequency of \( \omega_D \), above which no shorter wave phonons are excited. In the Debye model \( g(\omega) \) can be defined as

\[ g(\omega) = \begin{cases} \frac{3\omega^2}{\omega_D^3} \text{when} \omega < \omega_D \\ 0 \text{when} \omega > \omega_D \end{cases} \]  \hspace{1cm} (31)

We may define \( \Theta_D \) the Debye temperature as
\[ \theta_D = \frac{\hbar \omega_D}{k} \] (32)

we get the Debye specific heat capacity as

\[ C_v = 9Nk \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx = 9Nk f_D(\theta_D/T) \] (33)

Where, \( f_D \) is called the Debye specific heat capacity function. When \( T >> \theta_D \), \( C_v \) approaches the value \( 3Nk \). But, when \( T << \theta_D \), i.e., at low temperatures the Debye specific heat equation becomes as

\[ C_v = \frac{12\pi^4}{5} Nk \left( \frac{T}{\theta_D} \right)^3 \] (34)

Here, \( C_v \) is proportional to \( T^3 \) this is known as the Debye \( T^3 \) law. At lower temperatures the Debye approximation is best suited because almost all excited phonons belong to the long-wavelength waves in the acoustic branches and the crystal behaves like a continuum. The Debye temperature \( \theta_D \) is defined in a temperature-independent parameter.

### 2.5 Thermal Conductivity

If the two ends of a sample of a given material are at two different temperatures \( T_1 \) and \( T_2 \) (\( T_2 > T_1 \)), heat flows from hotter end to cooler end, i.e., down the thermal gradient. Thus the heat current density (\( Q \)) is proportional to the temperature gradient (\( \partial T/\partial x \)). That is

\[ Q = -K \frac{\partial T}{\partial x} \]

The proportionality constant \( K \), known as the thermal conductivity, is a measure of the ease of transmission of heat across the bar and the negative sign indicates the flow of charge.
Heat may be transmitted in the material by several independent factors. In metals, heat is carried by both electrons and phonons among which electron contribution is maximum.

But, in the case of insulators heat is transmitted entirely by phonons. Hence, it is convenient to consider the formation of phonon gas, which moves randomly in all the directions corresponding to the wave vectors in the Brillouin zones.

The thermal conductivity is given by \[ K = \frac{1}{3} \rho C_v v l, \]

where, \( C_v \) is the specific heat per volume, \( v \) is the velocity, \( l \) is the mean free path. Here \( v \) and \( l \) are the average quantities overall occupy modes and the Brillouin zones.

Since mean free path (\( l \)) depends strongly on temperature, let us discuss the dependence of thermal conductivity on temperature. With reference to the kinetic theory of gases (phonon gases), the mean free path (\( l \)) is the average distance travelled by the phonons between two successive collisions. Therefore the mean free path (\( l \)) depends the following the three significant mechanisms:

1. Phonon –phonon interaction
2. Phonon – impurity interaction
3. Phonon – external boundaries of the crystal

Among these mechanisms phonon – phonon collision is dominant at higher temperatures, at which the atomic displacements are large. Therefore at high temperature, mean free path (\( l \)) is inversely proportional to temperature. In other words, more number of phonons participate in the collision at high temperatures reducing mean free path and hence conductivity.
With reference to the second case; when the density of impurities is greater, the greater is the phonon scattering and shorter is the mean free path. Both phonon – phonon and phonon – impurity interactions become ineffective at low temperatures.

In the low temperature region, the primary scattering mechanism is the external boundary of the specimen, which leads to the so called size or geometric effect. This mechanism is very effective because of the comparable size of the specimen and the wavelength of the excited phonon. Therefore, the mean free path (l) is approximately equal to the diameter of the specimen and l is independent of the temperature. Hence, we can conclude the dependence of mean free path of the temperature as follows:

1. At low temperature mean free path (l) is a constant (equal to the diameter of the specimen).
2. At high temperature, mean free path (l) decreases with inverse temperature (as 1/T).

In addition to these factors at low temperatures, the thermal conductivity $K$ is $\sim T^3$, that dependence entirely from the specific heat ($C_v$) point of view and therefore, the thermal conductivity variations with temperature is calculated by using the relation:

$$K = \frac{k_B}{2\pi^2\nu n} \left( \frac{k_B}{\hbar} \right) T^3 \int_0^{\theta_D/T} \tau(x) \frac{x^4 e^x}{(e^x - 1)^2} dx$$

where $\nu$ is the velocity of phonon in solids, $\tau(x)$ is the relaxation time, which is calculated using the mean free path and phonon velocity and $\theta_D$ is the Debye temperature.

### 2.6 Effect of phonons in nanostructures

- The broadening and shift of the Si and Ge Raman lines to lower frequencies as the particle size decreases has been attributed to phonon confinement effects in the nanocrystals.
Acoustic phonons of nanoparticles exhibit Brillouin scattering that depends on particle size.

Acoustic modes shift to higher frequencies with reduced particle size and optical modes shift to lower frequencies as the particle size is reduced.

The temperature variation of the electrical mobility and electrical conductivity for semiconductor nanostructures: Scattering by impurity atoms is important at low temperatures but decreases with increasing temperature. In contrast, scattering by phonons increases with temperature, reflecting the increasing amplitude of the lattice vibrations. The combined effect of these two processes is to give a mobility which, at low temperatures, increases with increasing temperature, followed by a decrease at high temperatures.

In certain semiconductor nanostructures it is possible to turn off the scattering by impurity atoms, resulting in very high carrier mobilities at low temperatures.

4 Solved problems

1. If the unit cell has 3 atoms, thus how many phonon modes are present ____________
   Ans.: 3N modes. Therefore 9 modes.

2. If the velocity of sound in a solid is taken to be $3 \times 10^3$ m/s and interatomic distance as $5 \times 10^{-10}$ m, calculate the value of cutoff frequency assuming a linear lattice.

   **Given value:**
   
   Velocity of sound in a solid ($v$) is $3 \times 10^3$ m/s
   
   Interatomic distance ($a$) is $5 \times 10^{-10}$ m

   **Formula:**
   
   Velocity and frequency related equation
   
   $v = \nu \lambda$
   
   $v = \nu 2a$
\[
\nu = \frac{v}{2a}
\]

**Solution:**

Apply the known values in the equation.

Critical frequency \((\nu) = 3 \times 10^{12} \text{ Hz}\)

3. If the velocity of sound in a solid is of the order \(10^3 \text{ m/s}\), compare the frequency of the sound wave \(\lambda = 20\text{Å}\) for (a) a monoatomic system and (b) acoustic waves and optical waves in a diatomic system containing two identical atoms \((M=m)\) per unit cell of interatomic spacing \(2.2 \text{ Å}\).

**Givenvalue:**

Velocity of sound in a solid \((v_o) = 10^3 \text{ m/s}\)

Frequency of the sound wave \(\lambda = 20 \times 10^{-10} \text{ m}\)

Interatomic spacing \((a) = 2.2 \times 10^{-10} \text{ m}\)

**Solution:**

i. In case of homogenous line, the frequency \(\omega = v_o \frac{2\pi}{\lambda}\)

\[
\omega = \frac{10^3 \times 2\pi}{20 \times 10^{-10}}
\]

\(\omega = 3.14 \times 10^{12} \text{ rad/sec}\)

ii. a. Acoustic wave in a diatomic (identical \(M=m\)) lattice, the frequency varies from

\[
\omega = 0 \text{ at } k = 0 \text{ to } \omega = \left(\frac{2K}{m}\right)^{1/2} \text{ where } k = \frac{\pi}{2a}
\]

Also the velocity expression is given by \(v_o = a \times \left(\frac{2K}{m}\right)^{1/2}\)

Simply \(\omega = \frac{v_o}{a}\)
b. Optical wave, the frequency varies from

\[ \omega = \left( \frac{4K}{m} \right)^{1/2} \quad \text{at} \ k = 0 \quad \omega = \left( \frac{2K}{m} \right)^{1/2} \quad \text{at} \ k = \frac{\pi}{2a} \]

At \ k = 0, \ \omega = \sqrt{2} \times \frac{v_0}{a} \quad \omega = 6.42 \times 10^{12} \ \text{rad/sec}

At \ k = \frac{\pi}{2a}, \ \omega = \frac{v_0}{a} \quad \omega = 4.54 \times 10^{12} \ \text{rad/sec}

4. The unit cell parameter of NaCl is 5.65\text{Å} and the modulus of elasticity along [100] direction is 6 \times 10^{10} \ N/m^2. Estimate the wavelength at which an electromagnetic radiation is strongly reflected by the crystal. At. Wt. of Na = 23 and of Cl = 37.

**Given value:**

- Unit cell parameter (a) = 5.65 \times 10^{-10} \ m
- Modulus of elasticity (Y) = 6 \times 10^{10} \ N/m^2

**Solution:**

The maximum frequency of radiation strongly reflected by the NaCl crystal will be given by

\[ \omega_{max} = \left[ 2K \left( \frac{1}{M} + \frac{1}{m} \right) \right]^{1/2} \]

Let us assume that an extension along [100] direction will have negligible effect on vertical springs. Therefore, we can write

\[ K = aY \]
The frequency expression becomes

$$\omega_{max} = \left[2aY \left(\frac{1}{M} + \frac{1}{m}\right)\right]^{\frac{1}{2}}$$

where $M$ and $m$ be the atomic weight of the crystal, and considered the atomic mass unit.

Atomic weight of chlorine ($M$) = 37

Atomic weight of sodium ($m$) = 23

Atomic mass unit = $1.67 \times 10^{-27} \text{ kg}$

$$\omega_{max} = \left[2 \times 5.65 \times 10^{-10} \times 6 \times 10^{10} \left(\frac{1}{37} + \frac{1}{23}\right)\right]^{\frac{1}{2}}$$

$$\omega_{max} = 5.13 \times 10^{13} \text{ rad/sec.}$$

Hence the wavelength at which this radiation is strongly reflected is

$$\lambda = \frac{c}{\omega} = \frac{2\pi c}{\omega}$$

where $\omega = 5.13\times10^{13} \text{ rad/sec}$, $c$ is the velocity of light

then,

$$\lambda = 3.67 \times 10^{-5} \text{ m}$$
5. Calculate the specific heat for aluminium at 300 K and its Debye temperature 375 K.

**To find:**

Specific heat for aluminium at 300 K \((C_v)\)

**Given value:**

Debye temperature 375 K

**Formula:**

Specific heat of material by Debye method

\[
C_v = \frac{12}{5} \pi^4 N_A k_B \left(\frac{T}{T_D}\right)^3 \; \text{if } T << T_D
\]

**Known values:**

\[
\begin{align*}
\pi \; (\text{pi constant)} & \quad = 3.14 \\
N_A \; (\text{Avogadro number)} & \quad = 6.023 \times 10^{23} \; \text{mol}^{-1} \\
k_B \; (\text{Boltzmann constant)} & \quad = 1.38 \times 10^{-23} \; \text{JK}^{-1} \\
T \; (\text{Temperature)} & \quad = 300 \; \text{K} \\
T_D \; (\text{Debye temperature)} & \quad = 375 \; \text{K}
\end{align*}
\]

**Solution:**

Specific heat for aluminium at 300 K \((C_v) = 995 \; \text{kJ/kmol-K}\)

6. What is the Debye frequency for copper, if it has the Debye temperature of 315 K and finds the Debye specific heat at 10 K and 300 K?

**To find:**

i. Debye frequency for copper \((\nu)\)

ii. Specific heat for copper at 10 K and 300 K \((C_{v(10K)} \text{ and } C_{v(300K)})\)
Given value:

Debye temperature 315 K

Formula:

i. Debye frequency for copper ($\nu$)

$$\nu = \frac{T_D k_B}{\hbar}$$

ii. Specific heat of material by Debye method ($C_v$)

$$C_v = \frac{12}{5} \pi^4 N_A k_B \left(\frac{T}{T_D}\right)^3$$

Known values:

- $\pi$ (pi constant) = 3.14
- $N_A$ (Avogadro number) = 6.023 × 10^{23} mol^{-1}
- $k_B$ (Boltzmann constant) = 1.38 × 10^{-23} JK^{-1}
- $\hbar$ (Planck’s constant) = 6.626068 × 10^{-34} m^2 kg / s
- $T$ (Temperature) = 10 K & 300 K
- $T_D$ (Debye temperature) = 315 K

Solution:

Apply the known values in the equation.

i. Debye frequency for copper ($\nu$)

$$\nu = \frac{(315 \text{ K})(1.38 \times 10^{-23} \text{ JK}^{-1})}{6.626068 \times 10^{-34} \text{ m}^2 \text{ kg} / \text{s}}$$

Debye frequency ($\nu$) = 6.55 × 10^{12} Hz

ii. Specific heat of material by Debye method ($C_v$)

Apply the Known values,
\[ C_v = \frac{12}{5} \pi^4 N_A k_B \left( \frac{T}{T_D} \right)^3 \]

Debye specific heat of copper at 10 K = 62.67 J/kmol-K
Debye specific heat at 300 K = 1.6 \times 10^3 \text{kJ/kmol-K}

7. Find the Debye temperature for sodium chloride at 10, 15 and 20 K and its corresponding specific heat values are 0.066, 0.249 and 0.649 kJ/kmol-K.

**To find:**

Debye temperature \( (T_D) \) for sodium chloride at 10, 15 and 20 K \( (T_D) \)

**Given value:**

Specific heat value:

1. 0.066 kJ/kmol-K at 10 K
2. 0.249 kJ/kmol-K at 15 K
3. 0.649 kJ/kmol-K at 20 K

**Formula:**

Debye Temperature for NaCl \( (T_D) \):

\[ T_D = \sqrt[3]{\frac{12}{5} C_v \pi^4 N_A k_B T^3} \]

**Known values:**

\[
\begin{align*}
\pi \text{ (pi constant)} &= 3.14 \\
N_A \text{ (Avogadro number)} &= 6.023 \times 10^{23} \text{ mol}^{-1} \\
k_B \text{ (Boltzmann constant)} &= 1.38 \times 10^{-23} \text{ JK}^{-1} \\
h \text{ (Planck’s constant)} &= 6.626068 \times 10^{-34} \text{ m}^2 \text{ kg} / \text{s} \\
T \text{ (Temperature)} &= 10 \text{ K, 15 K} \text{ & 20 K} \\
C_v \text{ (Specific heat for NaCl)} &= 0.066, 0.249 \text{ and } 0.649 \text{ kJ/kmol-K}
\end{align*}
\]
**Solution:**

Apply the known values in the equation.

i. At 10 K:

\[ T_{D(10 \text{ K})} = 308 \text{ K} \]

Debye temperature at 10 K = 308 K

ii. At 15 K:

\[ T_{D(15 \text{ K})} = 297 \text{ K} \]

Debye temperature at 15 K = 308 K

iii. At 20 K:

\[ T_{D(20 \text{ K})} = 288 \text{ K} \]

Debye temperature at 20 K = 308 K

**5 References**

2. B. Donovan, J. F. Angress, Lattice Vibrations, Champion & Hall Ltd., 1971
5. Robert W. Kelsall, Ian W. Hamley, Mark Geoghegan, Nanoscale science and technology, John Wiley & Sons Ltd, 2005