

I MSC PHYSICS
SOLID STATE PHYSICS
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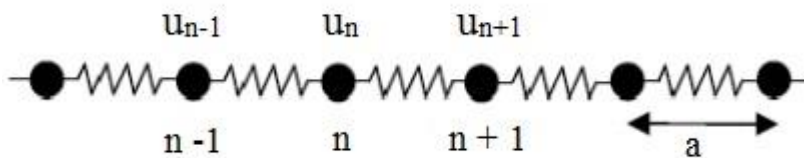
UNIT 1

MONATOMIC LATTICE VIBRATIONS

For monatomic gases we can model heat energy as the kinetic energy of the atoms. This model leads to the ideal gas law, and the model can be expanded to include other gas molecules. For solids, we can model heat energy as the energy in lattice vibrations. This model should then lead to predictions about heat capacity, thermal conductivity, and thermal expansion of solids.

We first look at longitudinal oscillations (oscillations in the direction of the wave). Homework problems will look at transverse oscillations (oscillations perpendicular to the direction of the wave).

For simplicity we consider first a one dimensional crystal lattice and assume that the forces between the atoms in this lattice are proportional to relative displacements from the equilibrium positions.



Lattice Vibration

The wave-like solution is

$$u(x) = A \cdot \exp[i(qx - \omega t)] \quad (3)$$

ω is the angular frequency
 q is the wavevector

$$\begin{aligned} \rightarrow P &= h/2\pi \times q \\ E &= h/2\pi \times \omega \end{aligned}$$

The vibrational motion in the crystal is regarded as a kind of wave propagation. Because of the finite extent of the crystal, the wave motion is often regarded as a **standing wave system**. the **phonon** is defined to be the quantised energy of elastic waves in a crystal. The phonons are similar to the photons in electromagnetic waves in many respects. Both of these two excitations exhibit the duality property, namely possessing both wave-like and particle-like behaviour.

We assume that the elastic response of the crystal is a linear function of the forces. That is equivalent to the assumption that the elastic energy is a quadratic function of the relative displacement of any two points in the crystal. Terms in the energy that are linear in the displacements will vanish in equilibrium—see the minimum in Fig. 3.6. Cubic and higher-order terms may be neglected for sufficiently small elastic deformations.

We assume that the force on the plane s caused by the displacement of the plane $s + p$ is proportional to the difference $u_{s+p} - u_s$ of their displacements. For brevity we consider only nearest-neighbor interactions, with $p = \pm 1$. The total force on s from planes $s \pm 1$:

$$F_s = C(u_{s+1} - u_s) + C(u_{s-1} - u_s) . \quad (1)$$

This expression is linear in the displacements and is of the form of Hooke's law.

The constant C is the **force constant** between nearest-neighbor planes and will differ for longitudinal and transverse waves. It is convenient hereafter to regard C as defined for one atom of the plane, so that F_s is the force on one atom in the plane s .

The equation of motion of an atom in the plane s is

$$M \frac{d^2 u_s}{dt^2} = C(u_{s+1} + u_{s-1} - 2u_s) , \quad (2)$$

where M is the mass of an atom. We look for solutions with all displacements having the time dependence $\exp(-i\omega t)$. Then $d^2 u_s / dt^2 = -\omega^2 u_s$, and (2) becomes

$$-M\omega^2 u_s = C(u_{s+1} + u_{s-1} - 2u_s) . \quad (3)$$

This is a difference equation in the displacements u and has traveling wave solutions of the form:

$$u_{s\pm 1} = u \exp(isKa) \exp(\pm iKa) , \quad (4)$$

where a is the spacing between planes and K is the wavevector. The value to use for a will depend on the direction of K .

With (4), we have from (3):

$$-\omega^2 M u \exp(isKa) = C u \{ \exp[i(s+1)Ka] + \exp[i(s-1)Ka] - 2 \exp(isKa) \} . \quad (5)$$

We cancel $u \exp(isKa)$ from both sides, to leave

$$\omega^2 M = -C [\exp(iKa) + \exp(-iKa) - 2] . \quad (6)$$

With the identity $2 \cos Ka = \exp(iKa) + \exp(-iKa)$, we have the **dispersion relation** $\omega(K)$.

$$\omega^2 = (2C/M)(1 - \cos Ka) . \quad (7)$$

The boundary of the first Brillouin zone lies at $K = \pm \pi/a$. We show from (7) that the slope of ω versus K is zero at the zone boundary:

$$d\omega^2/dK = (2Ca/M) \sin Ka = 0 \quad (8)$$

at $K = \pm \pi/a$, for here $\sin Ka = \sin(\pm \pi) = 0$. The special significance of phonon wavevectors that lie on the zone boundary is developed in (12) below.

By a trigonometric identity, (7) may be written as

$$\omega^2 = (4C/M) \sin^2 \frac{1}{2} Ka ; \quad \omega = (4C/M)^{1/2} \left| \sin \frac{1}{2} Ka \right| . \quad (9)$$

A plot of ω versus K is given in Fig. 4.

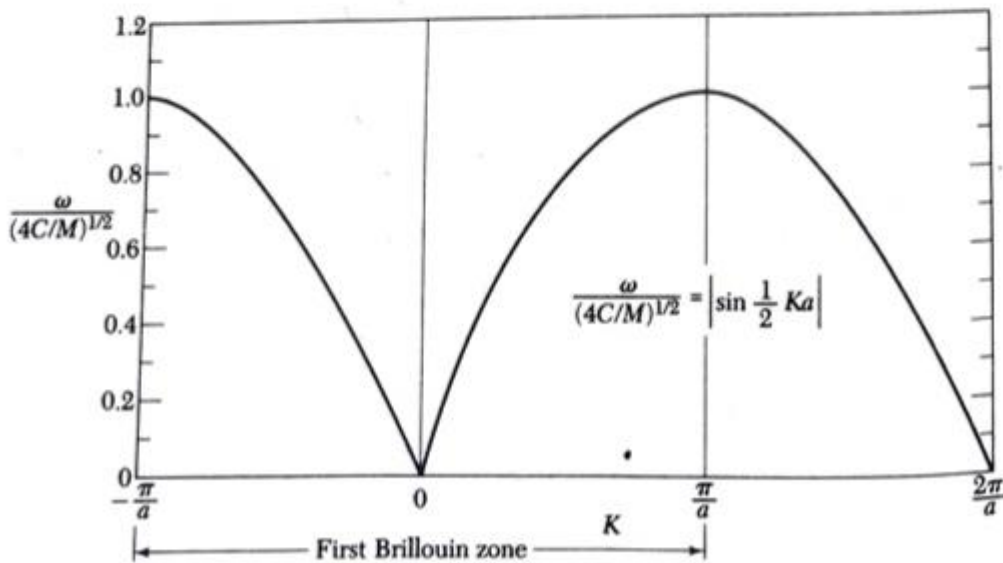


Figure 4 Plot of ω versus K . The region of $K \ll 1/a$ or $\lambda \gg a$ corresponds to the continuum approximation; here ω is directly proportional to K .

First Brillouin Zone

What range of K is physically significant for elastic waves? Only those in the first Brillouin zone. From (4) the ratio of the displacements of two successive planes is given by

$$\frac{u_{s+1}}{u_s} = \frac{u \exp[i(s+1)Ka]}{u \exp(isKa)} = \exp(iKa) . \quad (10)$$

The range $-\pi$ to $+\pi$ for the phase Ka covers all independent values of the exponential.

The range of independent values of K is specified by

$$-\pi < Ka \leq \pi , \quad \text{or} \quad -\frac{\pi}{a} < K \leq \frac{\pi}{a} .$$

This range is the first Brillouin zone of the linear lattice, as defined in Chapter 2. The extreme values are $K_{\max} = \pm\pi/a$. Values of K outside of the first Brillouin zone (Fig. 5) merely reproduce lattice motions described by values within the limits $\pm\pi/a$.

We may treat a value of K outside these limits by subtracting the integral multiple of $2\pi/a$ that will give a wavevector inside these limits. Suppose K lies outside the first zone, but a related wavevector K' defined $K' = K - 2\pi n/a$ lies within the first zone, where n is an integer. Then the displacement ratio (10) becomes

$$u_{s+1}/u_s = \exp(iKa) \equiv \exp(i2\pi n) \exp[i(Ka - 2\pi n)] \equiv \exp(iK'a) , \quad (11)$$

because $\exp(i2\pi n) = 1$. Thus the displacement can always be described by a wavevector within the first zone. We note that $2\pi n/a$ is a reciprocal lattice vector because $2\pi/a$ is a reciprocal lattice vector. Thus by subtraction of an appropriate reciprocal lattice vector from K , we always obtain an equivalent wavevector in the first zone.

At the boundaries $K_{\max} = \pm\pi/a$ of the Brillouin zone the solution $u_s = u \exp(isKa)$ does not represent a traveling wave, but a standing wave. At the zone boundaries $sK_{\max}a = \pm s\pi$, whence

$$u_s = u \exp(\pm is\pi) = u (-1)^s . \quad (12)$$

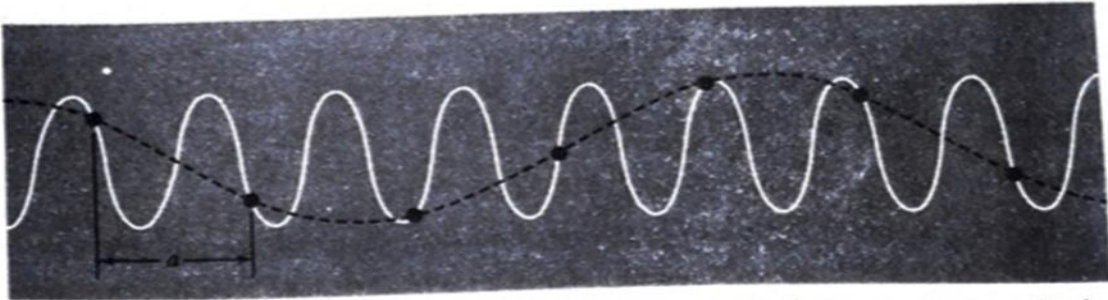


Figure 5 The wave represented by the solid curve conveys no information not given by the dashed curve. Only wavelengths longer than $2a$ are needed to represent the motion.

This is a standing wave: alternate atoms oscillate in opposite phases, because $u_s = \pm 1$ according to whether s is an even or an odd integer. The wave moves neither to the right nor to the left.

This situation is equivalent to Bragg reflection of x-rays: when the Bragg condition is satisfied a traveling wave cannot propagate in a lattice, but through successive reflections back and forth, a standing wave is set up.

The critical value $K_{\max} = \pm \pi/a$ found here satisfies the Bragg condition $2d \sin \theta = n\lambda$: we have $\theta = \frac{1}{2}\pi$, $d = a$, $K = 2\pi/\lambda$, $n = 1$, so that $\lambda = 2a$. With x-rays it is possible to have n equal to other integers besides unity because the amplitude of the electromagnetic wave has a meaning in the space between atoms, but the displacement amplitude of an elastic wave usually has a meaning only at the atoms themselves.

Group Velocity

The transmission velocity of a wave packet is the **group velocity**, given as

$$v_g = d\omega/dK ,$$

or

$$\mathbf{v}_g = \text{grad}_{\mathbf{K}} \omega(\mathbf{K}) , \quad (13)$$

the gradient of the frequency with respect to \mathbf{K} . This is the velocity of energy propagation in the medium.

With the particular dispersion relation (9), the group velocity (Fig. 6) is

$$v_g = (Ca^2/M)^{1/2} \cos \frac{1}{2} Ka . \quad (14)$$

This is zero at the edge of the zone where $K = \pi/a$. Here the wave is a standing wave, as in (12), and we expect zero net transmission velocity for a standing wave.

Long Wavelength Limit

When $Ka \ll 1$ we expand $\cos Ka \equiv 1 - \frac{1}{2}(Ka)^2$, so that the dispersion relation (7) becomes

$$\omega^2 = (C/M)K^2a^2 . \quad (15)$$

The result that the frequency is directly proportional to the wavevector in the long wavelength limit is equivalent to the statement that the velocity of sound is independent of frequency in this limit. Thus $v = \omega/K$, exactly as in the continuum theory of elastic waves—in the continuum limit $Ka \ll 1$.

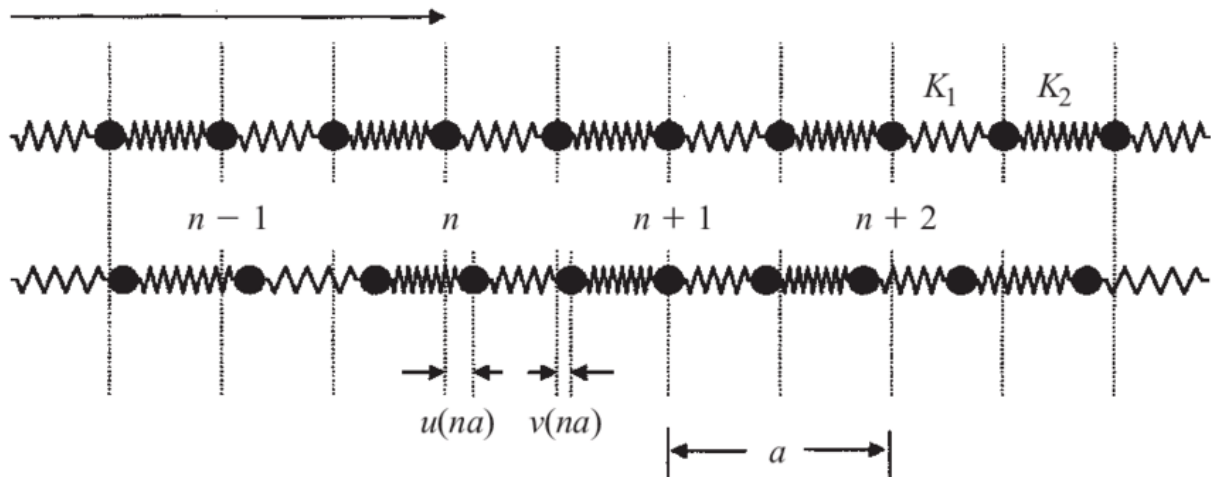
Derivation of Force Constants from Experiment

In metals the effective forces may be of quite long range and are carried from ion to ion through the conduction electron sea. Interactions have been found between planes of atoms separated by as many as 20 planes. We can make a statement about the range of the forces from the observed experimental

Lattices with two atoms per primitive cell

Lattice with 2 atoms per primitive cell

1. Let's look at a plane that contains only one kind of atom (say the 100 plane in the SC lattice of CsCl, or the 111 plane in the FCC lattice of NaCl both of which contain only one kind of atom). Let's call the displacement from its equilibrium position of this plane, u_n . Let's call the displacement from its equilibrium position of the next plane which contains only the other kind of atom, v_n



2. Let's consider only nearest neighbor interactions, and call the spring constant between these $C_{12} = C$. Let's also call the mass of the one atom, M_1 , and the mass of the other atom, M_2 , where $M_1 > M_2$.

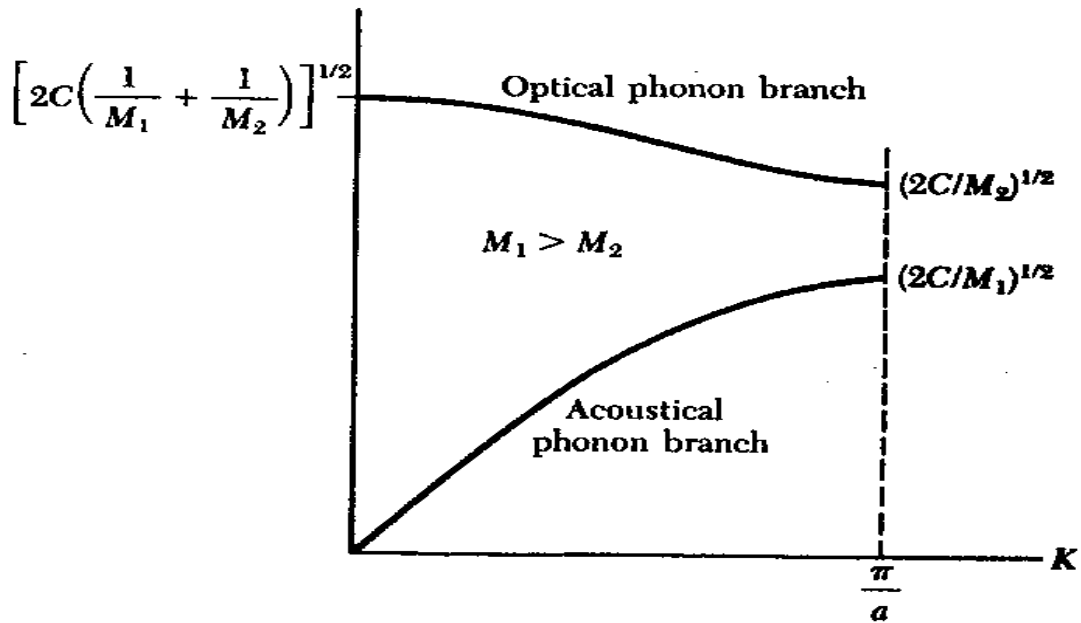
(Cl has a mass of 35.4 amu; Na has a mass of 23.0 amu; Cs has a mass of 132.9 amu.)

Note: If we put one kind of atom at a lattice point and the other in the hole, we have the same kind of lattice if we consider the other atom as at the lattice point and the first atom in the hole. In other words, it doesn't matter if we put the Cl atom at the lattice point and Na in the hole, or put Cs at the lattice point and Cl in the hole.

3. Since we have two different atoms, we will have two different equations from Newton's Second Law:

$$M_1 \frac{d^2 u_n}{dt^2} = C(v_n - u_n) + C(v_{n-1} - u_n), \text{ and}$$

$$M_2 \frac{d^2 v_s}{dt^2} = C(u_{s+1} - v_s) + C(u_s - v_s)$$



Latent Heat

Latent heat, energy absorbed or released by a substance during a change in its physical state (phase) that occurs without changing its temperature. The latent heat associated with melting a solid or freezing a liquid is called the heat of fusion; that associated with vaporizing a liquid or a solid or condensing a vapour is called the heat of vaporization. The latent heat is normally expressed as the amount of heat (in units of joules or calories) per mole or unit mass of the substance undergoing a change of state.

Specific Latent Heat
Heat Energy

$$L = \frac{Q}{m}$$

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Mass

Density of States

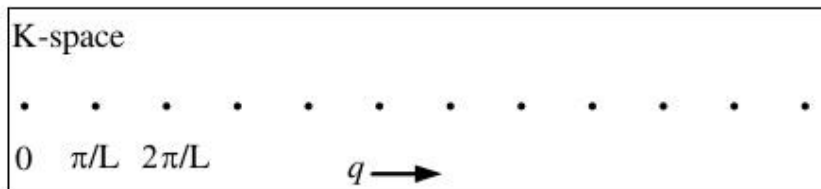
In solid state physics and condensed matter physics, the density of states (DOS) of a system describes the proportion of states that are to be occupied by the system at each energy. The density of states is defined as $\rho(E)$, where $N(E)$ is the number of states in the system of volume whose energies lie in the range E to $E + dE$. It is mathematically represented as a distribution by a probability density function, and it is generally an average over the space and time domains of the various states occupied by the system. The density of states is directly related to the dispersion relations of the properties of the system. High DOS at a specific energy level means that many states are available for occupation.

Generally, the density of states of matter is continuous. In isolated systems however, such as atoms or molecules in the gas phase, the density distribution is discrete, like a spectral density. Local variations, most often due to distortions of the original system, are often referred to as local densities of states (LDOSs).

Density of states

The wavevector q

$$q = \frac{\pi}{L}, \frac{2\pi}{L}, \frac{3\pi}{L}, \frac{4\pi}{L}, \dots, \frac{(M-1)\pi}{L}$$



There are $M-1$ allowed independent value of q , thus

$$N = \frac{Lq}{\pi} \qquad D(\omega) = \frac{dN}{d\omega} = \frac{L}{\pi} \frac{dq}{d\omega}$$

We shall now determine the possible modes of vibration (i.e., the independent solutions of the wave equation which satisfy a given set of boundary conditions) in one dimensional atomic lattice of finite length L . Let there be $(N + 1)$ atoms in length L at separation a and numbered $n = 0$ to $n = N$ as shown in fig. 15. Suppose the atoms at the two ends are fixed.

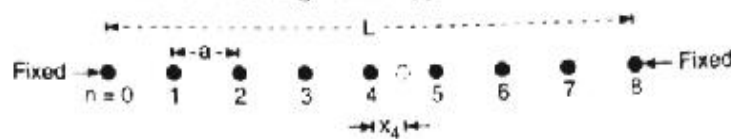


Fig. 15. Elastic line of $(N + 1)$ atoms with $N = 8$ for fixed boundary conditions.

When a wave is moving in the lattice, it is reflected from the fixed end and a standing wave is generated. This standing wave is represented as :

$$x_n = x_0 \sin kna \sin \omega t \quad \dots(14)$$

If this equation satisfies the boundary condition, which at the two ends are

$$x_n = x_0 = 0. \quad \dots(15)$$

This requires that

$$\sin kna = \sin kNa = 0$$

$$\text{or} \quad k = \frac{\pi}{Na}, \frac{2\pi}{Na}, \frac{3\pi}{Na}, \frac{4\pi}{Na}, \dots, \frac{N\pi}{Na}$$

$$\text{or} \quad k = \frac{\pi}{L}, \frac{2\pi}{L}, \frac{3\pi}{L}, \frac{4\pi}{L}, \dots, \frac{N\pi}{L}, \quad \dots(16)$$

where $Na = L$. Here $k = 0$ is excluded as it corresponds to all the atoms at rest. Further for $k = \frac{N\pi}{L}$, we have

$$x_n = x_0 \sin n\pi \sin \omega t = 0.$$

The value also corresponds to all the atoms at rest hence this value is also excluded. We thus conclude that

$$k = \frac{\pi}{L}, \frac{2\pi}{L}, \frac{3\pi}{L}, \dots, \frac{(N-1)\pi}{L} \quad \dots(17)$$

Thus there are $(N - 1)$ allowed independent values of k . This number represents the number of atoms allowed to move. Hence there are $(N - 1)$ normal modes. So there is one normal mode of vibration corresponding to every atom which is mobile.

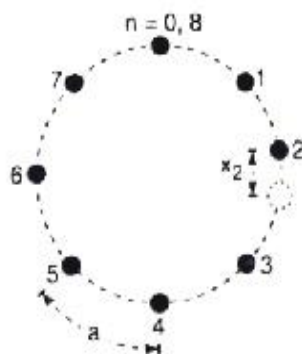


Fig. 16. Lattice bent with a ring by joining zeroth atom with eighth atom.

We have shown above that under fixed boundary conditions (atoms at the boundary are fixed), the number of possible vibrational modes of a lattice is equal to the number of atoms which are mobile. Now we shall derive the same result when the two ends of the lattice are free and suffer exactly the same displacement, when a vibrational motion is excited. Actually this happens for a lattice of length L inside in an infinitely long lattice. In this case, we assume that the lattice has been bent into circular form with zeroth atom joined to N^{th} atom to form a close lattice as shown in fig. 16.

$$x_n = x_0 \exp [i (\omega t - k n a)] \quad \dots(18)$$

This equation will be valid when the displacement x_n at the two ends of the lattice must be the same, *i.e.*,

$$x_0 = x_{0+N} \quad \dots(19)$$

This condition corresponds to the repetition of same amplitude conditions after every set of N atoms. In another words, we can say that the conditions correspond to the periodic repetition of amplitude, of course, periodicity being of the lattice $L = N a$. In general,

$$x_n = x_{n+N} \quad \dots(20)$$

The above conditions were proposed by Born and Von Kurman and are called as cyclic or periodic boundary conditions.

Applying the boundary conditions to eq. (18), we get

$$\exp [-i k N a] = 1 \quad \dots(21)$$

or
$$k = 0, \pm \frac{2\pi}{Na}, \pm \frac{4\pi}{Na}, \pm \frac{6\pi}{Na}, \dots, \pm \frac{N\pi}{Na}$$

or
$$k = 0, \pm \frac{2\pi}{L}, \pm \frac{4\pi}{L}, \pm \frac{6\pi}{L}, \dots, \pm \frac{N\pi}{L} \quad \dots(22)$$

So, the total number of independent k values is equal to N . This is also equal to the number of atoms which are free to move. So, under this condition too, the number of possible vibrational modes of a lattice is equal to the number of atoms which are mobile.

DENSITY OF k -STATES

The number of modes per unit range of k is defined as the density of k -states. This is denoted by $D(k)$. For one-dimensional lattice, with lattice constant a , there is one mode for each interval and hence

$$\Delta k = \frac{\pi}{L} \quad (\text{for fixed boundary conditions})$$

$$= \frac{2\pi}{L} \quad (\text{for periodic boundary conditions})$$

So we have

$$D(k) = \frac{L}{\pi} \quad (\text{for fixed boundary conditions})$$

$$= \frac{L}{2\pi} \quad (\text{for periodic boundary conditions})$$

For fixed boundary conditions, k ranges from 0 to $\frac{\pi}{a}$ while for periodic boundary conditions, k ranges from $-\frac{\pi}{a}$ to $\frac{\pi}{a}$. This accounts for the difference of a factor 2 in the two expressions of $D(k)$; of course, the total number of vibrational modes being the same for the two representations.

INELASTIC SCATTERING OF NEUTRONS BY PHONONS

Consider that a neutron impinges on a solid crystal and is scattered inelastically. In this process, the neutron will lose or gain the energy and momentum. Let loss or gain corresponds to creation or annihilation of one phonon. The conservation of wave vector is given by the relation

$$\mathbf{k} = \mathbf{k}' + \mathbf{G} \pm \mathbf{K} \quad \dots(1)$$

Here \mathbf{k} is the wave vector of incident neutron and \mathbf{k}' that of the scattered neutron, \mathbf{G} is the wave vector of reciprocal lattice and \mathbf{K} is the wave vector of the phonon. Positive and negative signs are used for the cases when a phonon is created (+) or when a phonon is absorbed (-) respectively.

Let M_n be the mass of the neutron, then

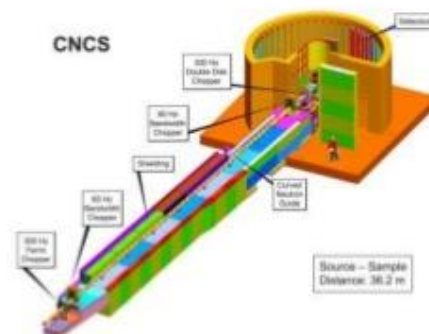
$$\text{kinetic energy of the incident neutron} = \frac{p^2}{2M_n}$$

$$\text{momentum of the incident neutron} = \hbar \mathbf{k}$$

$$\text{kinetic energy of incident neutron} = \frac{\hbar^2 k^2}{2M_n}$$

Inelastic scattering by phonons

- One way to determine the dispersion relation of phonons in a solid is to use the technique of inelastic neutron scattering.



Let \mathbf{k}' be the wave vector of scattered neutron, then

$$\text{kinetic energy of the scattered neutron} = \frac{\hbar^2 k'^2}{2M_n}$$

Applying the law of conservation of energy, we have

$$\frac{\hbar^2 k^2}{2M_n} = \frac{\hbar^2 k'^2}{2M_n} \pm \hbar \Omega \quad \dots(2)$$

or

$$E = E' \pm \hbar \Omega.$$

The plus sign is used when phonon is created and negative sign is used when phonon is absorbed. $\hbar \Omega$ is the energy of phonon created.

In order to determine the dispersion relation using equations (1) and (2), it is necessary to find the gain or loss of energy of scattered neutrons which will give $\hbar \Omega$ and hence Ω . Secondly, we have to determine the corresponding scattering direction which will give $\mathbf{k} - \mathbf{k}'$. Knowing the value of \mathbf{G} from $\mathbf{k} - \mathbf{k}' = \mathbf{G}$ for the elastically scattered neutrons, one can obtain \mathbf{K} . This vector is shown in fig. 26. We distinguish elastically scattered neutrons from inelastically scattered neutrons by the fact that they are more numerous and produce a peak in the intensity curve at Bragg angle.

A time of flight method is used for inelastic neutron scattering. The experimental set up is shown in fig. 27. A pulse of mono-energetic neutrons of proper energy E and wave

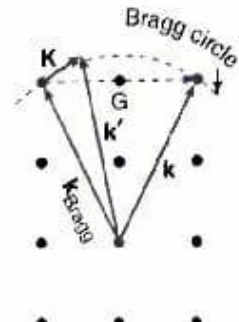


Fig. 26. Ewald construction for inelastic scattering of neutrons.

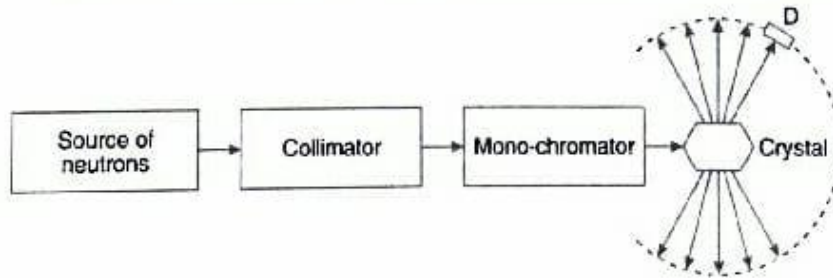


Fig. 27. The time of flight method of neutron scattering.

vector \mathbf{k} is allowed to fall on the crystal. The detector D measures the time of flight from the initiation of the pulse. The time of flight gives the value of E' and the position of detector gives the direction of \mathbf{k}' . Now $\hbar \Omega$ can be calculated. The neutron scattering occurs at many possible angles corresponding to different possible \mathbf{k} vector of the lattice vibrations and hence the detector is moved to another positions around the crystal. In this way different sets of E' and \mathbf{k}' are obtained.

The accurate determination of phonon spectra for sodium is shown in fig. 28. The figure shows the dispersion curves for sodium when phonons are propagated in [100], [110] and [111] directions at 90 K.

The neutron scattering is an ideal method for the determination of phonon spectra. This method is only applicable when the absorption of neutrons by nuclei of the crystal is not high. In some cases, considering the angular width of scattered neutron beam, some important data about the phonon life-time can be obtained.

DEBYE'S MODEL OF LATTICE SPECIFIC HEAT

The Debye approximation : The crystals are made up of atoms, *i.e.*, discrete "mass points". The reason is as follows : consider an elastic wave propagated in a crystal. As long as the wavelength of the wave is large compared with the interatomic distances, the crystal can be regarded as a continuum from the point of view of wave. Hence according to Debye the continuum model may be employed for all possible vibrational modes of crystal. The total number of vibrations in a crystal spectrum can be obtained by integrating $Z(\nu) d\nu$ within the proper limits. The lower limit of integration may be taken as $\nu = 0$ because the density of states in the frequency spectrum increases *very rapidly* with increasing frequency. In case of a crystal having N atoms the number of vibrations cannot exceed $3N$ because each atom vibrates with the three degrees of freedom, hence the upper limit ν_D must be defined in such a way as to satisfy the relation,

$$\int_0^{\nu_D} Z(\nu) d\nu = 3N, \quad \dots(11)$$

where ν_D is called the Debye cut off frequency. The situation is shown in figure (4).

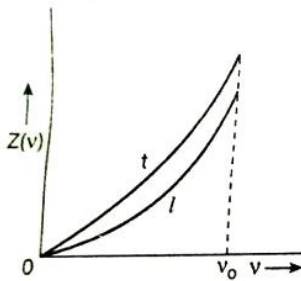


Fig. 4. Showing the cut-off frequency.

$$\therefore \int_0^{\nu_D} Z(\nu) d\nu = \int_0^{\nu_D} 4\pi V \left(\frac{2}{C_t^3} + \frac{1}{C_l^3} \right) \nu^2 d\nu = 3N$$

or

$$4\pi V \left(\frac{2}{C_t^3} + \frac{1}{C_l^3} \right) \int_0^{\nu_D} \nu^2 d\nu = 3N.$$

or

$$4\pi V \left(\frac{2}{C_t^3} + \frac{1}{C_l^3} \right) \frac{\nu_D^3}{3} = 3N.$$

$$\therefore \nu_D^3 = \frac{9N}{4\pi V} \left(\frac{2}{C_t^3} + \frac{1}{C_l^3} \right)^{-1} \quad \dots(12)$$

Taking $\left(\frac{N}{V}\right) = 10^{28}$ per m^3 and velocity of sound as 1000 m/s, we have

$$\nu_D^3 = \frac{9 \times 10^{28}}{4 \times 3.14} \times \left[\frac{2}{(1000)^3} + \frac{1}{(1000)^3} \right]^{-1}$$

or

$$\nu_D^3 = \frac{9 \times 10^{28}}{4 \times 3.14} \times \left[\frac{3}{(1000)^3} \right]^{-1} \quad \text{or} \quad \nu_D \approx 10^{13} \text{ Hz.}$$

The corresponding minimum wavelength is given by

$$\nu = \nu_D \lambda_m \quad \text{or} \quad \lambda_m = \frac{\nu}{\nu_D} = (1000) \times 10^{-13} \times 0.1 \text{ nm}$$

This shows that wavelengths are greater than inter-atomic distances. So the continuum theory may not work, especially in high frequency region.

The internal energy E can be calculated by the formula

$$E = \int_0^{\nu_D} \bar{E} Z(\nu) d\nu$$

$$E = \int_0^{\nu_D} Z(\nu) d\nu \times \left[\frac{h\nu}{\exp\left(\frac{h\nu}{K_B T}\right) - 1} \right], \quad \dots(13)$$

where $\frac{h\nu}{\exp\left(\frac{h\nu}{K_B T} - 1\right)}$ is the average energy (\bar{E}) of an oscillator having frequency ν .

$$\begin{aligned} \therefore E &= \int_0^{\nu_D} 4\pi V \left(\frac{2}{C_t^3} + \frac{1}{C_l^3} \right) \nu^2 d\nu \times \left[\frac{h\nu}{\exp\left(\frac{h\nu}{K_B T} - 1\right)} \right] \\ C_v = \left(\frac{\partial E}{\partial T} \right)_v &= \int_0^{\nu_D} 4\pi V \left(\frac{2}{C_t^3} + \frac{1}{C_l^3} \right) \nu^2 d\nu \frac{h\nu (-1) \exp\left(\frac{h\nu}{K_B T}\right) \left(\frac{-h\nu}{K_B T^2}\right)}{\left[\exp\left(\frac{h\nu}{K_B T} - 1\right) \right]^2} \\ &= \int_0^{\nu_D} 4\pi V \left(\frac{2}{C_t^3} + \frac{1}{C_l^3} \right) \nu^2 d\nu \frac{\exp\left(\frac{h\nu}{K_B T}\right) \left[\frac{(h\nu)^2}{K_B T^2} \right]}{\left[\exp\left(\frac{h\nu}{K_B T} - 1\right) \right]^2} \\ &= K_B \int_0^{\nu_D} 4\pi V \left(\frac{2}{C_t^3} + \frac{1}{C_l^3} \right) \nu^2 d\nu \times \frac{\exp\left(\frac{h\nu}{K_B T}\right)}{\left[\exp\left(\frac{h\nu}{K_B T} - 1\right) \right]^2} \times \left(\frac{h\nu}{K_B T} \right)^2 \end{aligned}$$

Putting $\left(\frac{h\nu}{K_B T}\right) = x$ and $\left(\frac{h\nu_D}{K_B T}\right) = x_m$ and using equation (12), we get

$$C_v = 9 N K_B \frac{1}{x_m^3} \int_0^{x_m} \frac{x^4 e^x dx}{(e^x - 1)^2} \quad \dots(14)$$

Let us define Θ_D , as the Debye temperature given by the relation

$$\Theta_D = \frac{h\nu_m}{K_B} \quad \dots(15)$$

In terms of Θ_D , the expression for C_v becomes

$$C_v = 9 N K_B \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{e^x x^4 dx}{(e^x - 1)^2} \quad \dots(16)$$

$$= 3 R F_D \frac{\Theta_D}{T} \quad \because N K_B = R \quad \dots(17)$$

where

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

and is known as Debye function. Eq. (16) is known as Debye formula for heat capacities of solids.

Debye's result for silver at $\Theta_D = 225$ K is shown in fig. (5). It is observed from the graph that heat capacity approaches classical value at high temperatures and zero value at low temperatures.

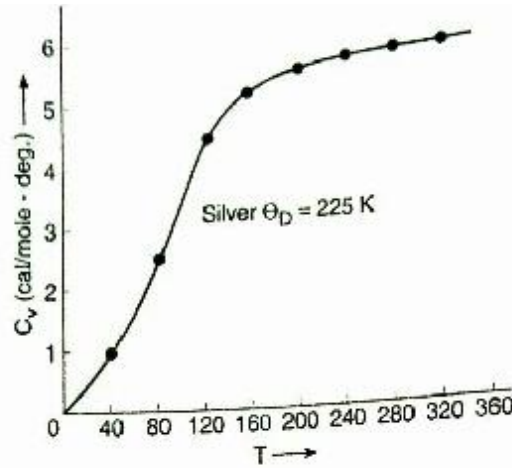


Fig. 5.

Now we shall consider the value of C_v for high and low temperatures.

(i) **At high temperatures** : For high temperatures $T \gg \Theta_D$ and x is small as compared with unity. Hence from equation (13),

$$E = \int_0^{\nu_D} Z(\nu) \left[\frac{h \nu d\nu}{\exp\left(\frac{h \nu}{K_B T}\right) - 1} \right] = 9 N \left(\frac{K_B T}{h \nu_D} \right)^3 K T \int_0^{x_m} \frac{x^3 dx}{e^x - 1} \quad \dots(18)$$

where $x = \frac{h \nu}{K_B T}$ and $x_m = \frac{h \nu_D}{K_B T}$

At high temperature $e^x - 1 \approx x$

$$\therefore E = 9 N \frac{1}{x_m^3} K_B T \int_0^{x_m} x^2 dx = 3 N K_B T \quad \dots(19)$$

and

$$C_v = \frac{\partial E}{\partial T} = 3 N K_B. \quad \dots(20)$$

The result is in accordance with classical results.

(ii) **At low temperatures** : At low temperatures, i.e., for $T \ll \Theta_D$, the upper limit of integration will be infinity, hence from equation (16), we have

$$\begin{aligned} C_v &= 9 N K_B \left(\frac{T}{\Theta_D} \right)^3 \int_0^\infty \frac{e^x x^4 dx}{(e^x - 1)^2} \\ &= 9 N K_B \left(\frac{T}{\Theta_D} \right)^3 \cdot \frac{4}{15} \pi^4 \\ \therefore C_v &= \frac{12}{5} \pi^4 N K_B \left(\frac{T}{\Theta_D} \right)^3. \quad \dots(21) \end{aligned}$$

This is well known "Debye T^3 law" and is in good agreement with the experimental data for many substances. The curve is shown in fig. 2.

$$E = 9 N K_B T \left(\frac{K_B T}{h v_D} \right)^3 \int_0^{x_m} \frac{x^3 dx}{e^x - 1}$$

i.e.,

$$E \propto T^4$$

...(22)

This result is analogous to Stefan's law for the density of black body radiation. Thus we can say that phonons and photons obey the same statistics with the difference that phonons obey T^4 law only at low temperatures, while photons only T^4 law at all temperatures. The table shows the Debye temperatures for a number of solids.

| DEBYE TEMPERATURE IN DEGREES ABSOLUTE FOR A NUMBER OF SOLIDS | | | | | |
|--|------------|-------|------------|------------------|------------|
| Solid | Θ_D | Solid | Θ_D | Solid | Θ_D |
| Na | 150 | Fe | 420 | NaCl | 281 |
| K | 100 | Co | 385 | KCl | 230 |
| Ag | 215 | Al | 390 | AgCl | 183 |
| Au | 170 | Sn | 260 | AgBr | 144 |
| Zn | 250 | Pt | 225 | CaF ₂ | 474 |

Although the Debye approximation met a great success but accurate measurements show deviations from theoretical predictions in low temperature region. According to Debye, the T^3 law should hold in the temperature region $T \leq 0.1 \Theta_D$ but Blackman's paper showed that this is not always true but T^3 law holds for temperature region $T \leq \Theta_D/50$, *i.e.*, at considerably lower temperatures than predicted by Debye.

UNIT 4

Dielectric Constant

When we use the dielectric constant we often are referring to a solvent. A refractive index refers to speed of light. For a bulk material we describe the polarization density in a material. Instead of looking at a single molecule, we can look at the polarizability of the entire bulk material induced by an electric field.

In bulk materials, the linear polarization is given by:

$$P_i(\omega) = \sum_{ij} \chi_{ij}(\omega) E_j(\omega) \quad (4)$$

where

$\chi_i(\omega)$ is the polarization density in direction i .

ω is the frequency

$\chi_{ij}(\omega)$ is the linear susceptibility tensor of an ensemble of molecules.

Note that the vectorial and tensor aspects of E and χ have been ignored to simplify notation.

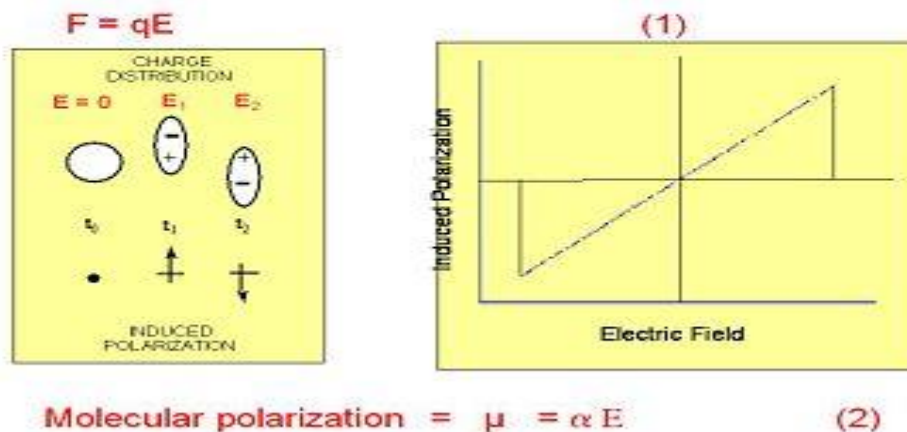
The total electric field (the "displaced" field, D) within the material becomes:

$$D = E + 4\pi P = (1 + 4\pi\chi)E \quad (5)$$

$P = \chi E$ (Equation (4)),

$4\pi\chi E$ is the internal electric field created by the induced displacement (polarization) of charges.

Polarizability: A Microscopic View



MACROSCOPIC ELECTRIC FIELD

One contribution to the electric field inside a body is that of the applied electric field, defined as

$$\mathbf{E}_0 \equiv \text{field produced by fixed charges external to the body} . \quad (3)$$

The other contribution to the electric field is the sum of the fields of all charges that constitute the body. If the body is neutral, the contribution to the average field may be expressed in terms of the sum of the fields of atomic dipoles.

We define the average electric field $\mathbf{E}(\mathbf{r}_0)$ as the **average field over the volume of the crystal cell** that contains the lattice point \mathbf{r}_0 :

$$\mathbf{E}(\mathbf{r}_0) = \frac{1}{V_c} \int dV \mathbf{e}(\mathbf{r}) , \quad (4)$$

where $\mathbf{e}(\mathbf{r})$ is the microscopic electric field at the point \mathbf{r} . The field \mathbf{E} is a much smoother quantity than the microscopic field \mathbf{e} . We could well have written the dipole field (2) as $\mathbf{e}(\mathbf{r})$ because it is a microscopic unsmoothed field.

We call \mathbf{E} the **macroscopic electric field**. It is adequate for all problems in the electrodynamics of crystals provided that we know the connection between \mathbf{E} , the polarization \mathbf{P} , and the current density \mathbf{j} , and provided that the wavelengths of interest are long in comparison with the lattice spacing.¹

To find the contribution of the polarization to the macroscopic field, we can simplify the sum over all the dipoles in the specimen. By a famous theorem of electrostatics² the macroscopic electric field caused by a uniform polarization is equal to the electric field in vacuum of a fictitious surface charge

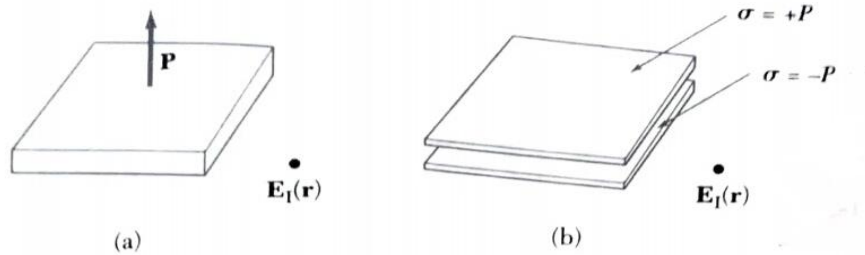


Figure 3 (a) A uniformly polarized dielectric slab, with the polarization vector \mathbf{P} normal to the plane of the slab. (b) A pair of uniformly charged parallel plates which give rise to the identical electric field \mathbf{E}_1 as in (a). The upper plate has the surface charge density $\sigma = +P$, and the lower plate has $\sigma = -P$.

density $\sigma = \hat{\mathbf{n}} \cdot \mathbf{P}$ on the surface of the body. Here $\hat{\mathbf{n}}$ is the unit normal to the surface, drawn outward from the polarized matter.

We apply the result to a thin dielectric slab (Fig. 3a) with a uniform volume polarization \mathbf{P} . The electric field $\mathbf{E}_1(\mathbf{r})$ produced by the polarization is equal to the field produced by the fictitious surface charge density $\sigma = \hat{\mathbf{n}} \cdot \mathbf{P}$ on the surface of the slab. On the upper boundary the unit vector $\hat{\mathbf{n}}$ is directed upward and on the lower boundary $\hat{\mathbf{n}}$ is directed downward. The upper boundary bears the fictitious charge $\sigma = \hat{\mathbf{n}} \cdot \mathbf{P} = P$ per unit area, and the lower boundary bears $-P$ per unit area.

The electric field \mathbf{E}_1 due to these charges has a simple form at any point between the plates, but comfortably removed from their edges. By Gauss's law

$$\text{(CGS)} \quad E_1 = -4\pi|\sigma| = -4\pi P ; \quad \text{(SI)} \quad E_1 = -\frac{|\sigma|}{\epsilon_0} = -\frac{P}{\epsilon_0} . \quad (4a)$$

We add \mathbf{E}_1 to the applied field \mathbf{E}_0 to obtain the total macroscopic field inside the slab, with $\hat{\mathbf{z}}$ the unit vector normal to the plane of the slab:

$$\text{(CGS)} \quad \mathbf{E} = \mathbf{E}_0 + \mathbf{E}_1 = \mathbf{E}_0 - 4\pi P \hat{\mathbf{z}} ; \quad (5)$$

$$\text{(SI)} \quad \mathbf{E} = \mathbf{E}_0 + \mathbf{E}_1 = \mathbf{E}_0 - \frac{P}{\epsilon_0} \hat{\mathbf{z}} .$$

We define

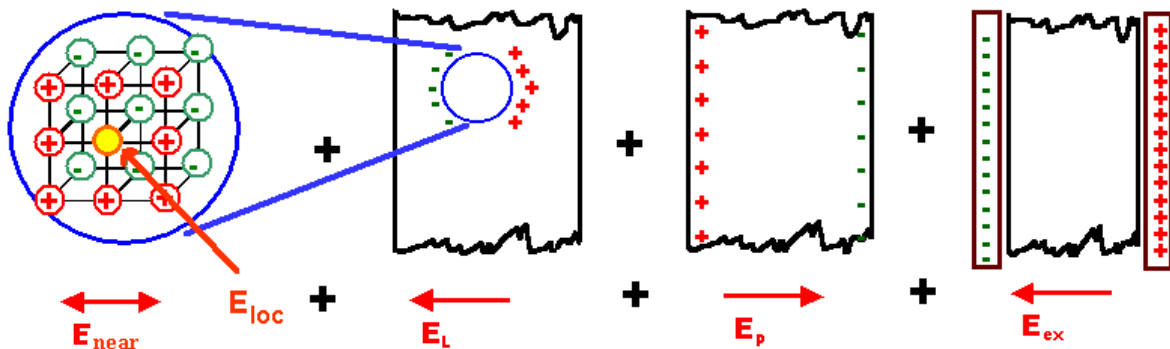
$$\mathbf{E}_1 \equiv \text{field of the surface charge density } \hat{\mathbf{n}} \cdot \mathbf{P} \text{ on the boundary .} \quad (6)$$

This field is smoothly varying in space inside and outside the body and satisfies the Maxwell equations as written for the macroscopic field \mathbf{E} . The reason \mathbf{E}_1 is a smooth function when viewed on an atomic scale is that we have replaced the discrete lattice of dipoles \mathbf{p}_j with the smoothed polarization \mathbf{P} .

Local electric field at an atom

In dielectric solids, the atoms or molecules experience not only the external applied electric field but also the electric field produced by the dipoles. The resultant electric field acting on the atoms or molecules of dielectric substance is called the local field or an internal field.

To find an expression for local electric field on a dielectric molecule or an atom, we consider a dielectric material in the electric field of intensity E , between the capacitor plates so that the material is uniformly polarized, as a result opposite type of charges are induced on the surface of the dielectric near the capacitor plates. The local field is calculated by using the method suggested by Lorentz.



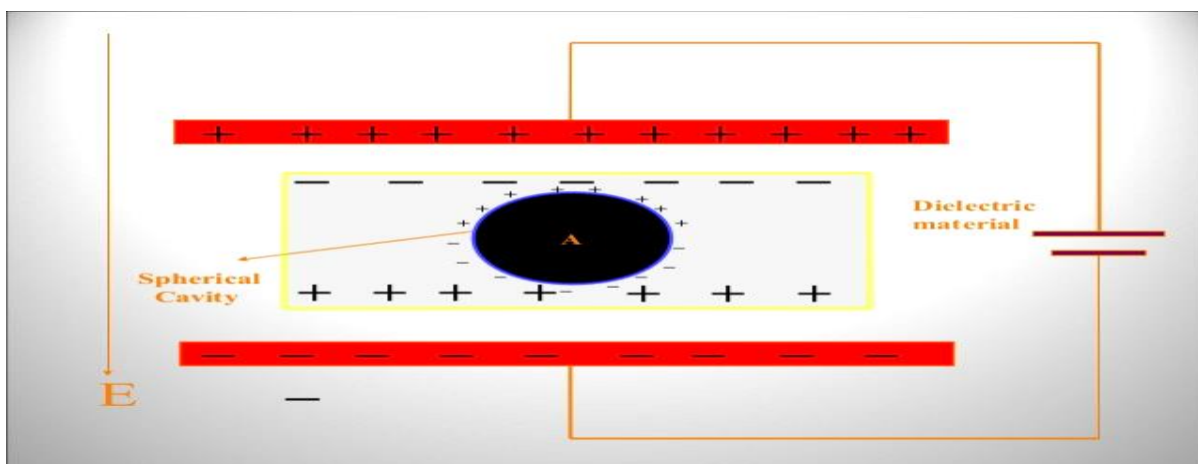
Internal fields or local fields

Local field or internal field in a dielectric is the space and time average of the electric field intensity acting on a particular molecule in the dielectric material.

In other words, the field acting at the location of an atom is known as local or internal field "E".

The internal field E_i must be equal to the sum of applied field plus the field produced at the location of the atom by the dipoles of all other atoms.

$$E_i = E + \text{the field due to all other dipoles}$$



Field E_1 :

1) This is due to polarized charges on the surface of the spherical cavity.

$$dA = 2\pi \cdot pq \cdot qR$$

$$dA = 2\pi \cdot r \sin \theta \cdot r d\theta$$

$$dA = 2\pi \cdot r^2 \sin \theta d\theta$$

Where dA is Surface area between θ & $\theta+d\theta$...

Field E_2 :

E_2 is the field intensity at A due to the charge density induced on the two sides of the dielectric.

$$E_2 = \frac{-P}{\epsilon_0} \dots\dots\dots(2)$$

Field E_3 :

E_3 is the field intensity at A due to the atoms contained in the cavity, we are assuming a cubic structure, so $E_3 = 0$.

2) The total charge present on the surface area dA is...

$dq = (\text{normal component of polarization}) \times (\text{surface area})$

$$dq = p \cos \theta \times dA$$

$$dq = 2\pi r^2 p \cos \theta \cdot \sin \theta \cdot d\theta$$

3) The field due to this charge at A, denoted by dE_4 , is given by

$$dE_4 = \frac{1}{4\pi\epsilon_0} \frac{dq}{r^2}$$

The field in $\theta = 0$ direction

$$dE_4 = \frac{1}{4\pi\epsilon_0} \frac{dq \cos \theta}{r^2}$$

$$dE_4 = \frac{1}{4\pi\epsilon_0 r^2} (2\pi r^2 p \cos \theta \cdot \sin \theta \cdot d\theta) \cos \theta$$

$$dE_4 = \frac{P}{2\epsilon_0} \cos^2 \theta \cdot \sin \theta \cdot d\theta$$

4) Thus the total field E_4 due to the charges on the surface of the entire cavity is

$$E_4 = \int_0^\pi dE_4$$

$$= \int_0^\pi \frac{P}{2\epsilon_0} \cos^2 \theta \sin \theta \cdot d\theta$$

$$= \frac{P}{2\epsilon_0} \int_0^\pi \cos^2 \theta \sin \theta \cdot d\theta$$

$$\text{let } x = \cos \theta \rightarrow dx = -\sin \theta d\theta$$

$$= \frac{P}{2\epsilon_0} \int_1^{-1} x^2 \cdot dx$$

$$= \frac{-P}{2\epsilon_0} \left(\frac{x^3}{3} \right)_1^{-1} \Rightarrow \frac{-P}{2\epsilon_0} \left(\frac{-1-1}{3} \right)$$

$$E_4 = \frac{P}{3\epsilon_0}$$

The internal field or Lorentz field can be written as

$$E_i = E_1 + E_2 + E_3 + E_4$$

$$E_i = \left(E + \frac{P}{\epsilon_0}\right) - \frac{P}{\epsilon_0} + 0 + \frac{P}{3\epsilon_0}$$

$$E_i = E + \frac{P}{3\epsilon_0}$$

$$P = N\alpha_e E_i$$

$$P = N\alpha_e \left(E + \frac{P}{3\epsilon_0}\right)$$

$$P = N\alpha_e E + N\alpha_e \frac{P}{3\epsilon_0}$$

$$P - N\alpha_e \frac{P}{3\epsilon_0} = N\alpha_e E$$

$$P \left(1 - \frac{N\alpha_e}{3\epsilon_0}\right) = N\alpha_e E$$

$$P = \frac{N\alpha_e E}{\left(1 - \frac{N\alpha_e}{3\epsilon_0}\right)} \dots\dots\dots(1)$$

We know that the polarization vector

$$P = \epsilon_0 E (\epsilon_r - 1) \dots \dots \dots (2)$$

from eqⁿs (1) & (2)

$$\frac{N\alpha_e E}{(1 - \frac{N\alpha_e}{3\epsilon_0})} = \epsilon_0 E (\epsilon_r - 1)$$

$$1 - \frac{N\alpha_e}{3\epsilon_0} = \frac{N\alpha_e E}{\epsilon_0 E (\epsilon_r - 1)}$$

$$1 = \frac{N\alpha_e}{3\epsilon_0} + \frac{N\alpha_e E}{\epsilon_0 E (\epsilon_r - 1)}$$

$$1 = \frac{N\alpha_e}{3\epsilon_0} + \frac{N\alpha_e}{\epsilon_0 (\epsilon_r - 1)}$$

$$1 = \frac{N\alpha_e}{3\epsilon_0} \left(1 + \frac{3}{\epsilon_r - 1}\right)$$

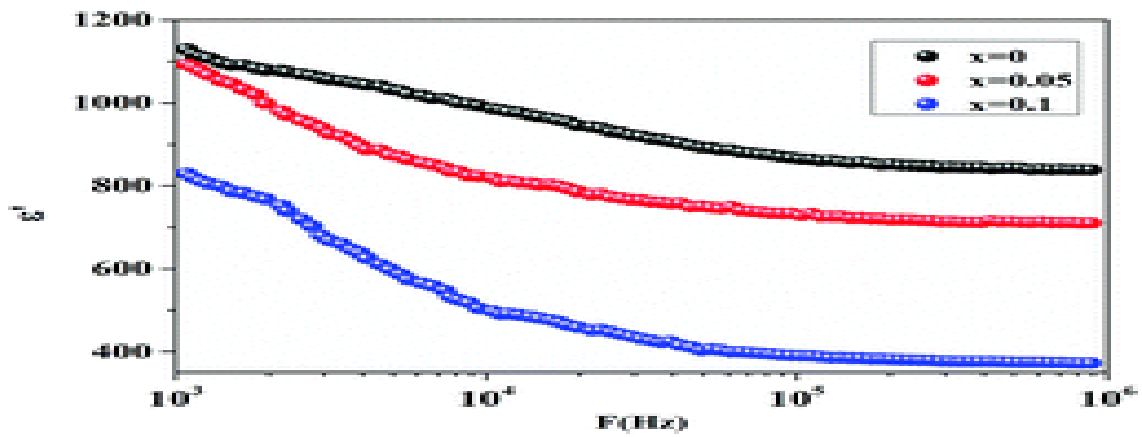
$$\frac{N\alpha_e}{3\epsilon_0} = \frac{1}{\left(1 + \frac{3}{\epsilon_r - 1}\right)}$$

$$\frac{N\alpha_e}{3\epsilon_0} = \frac{\epsilon_r - 1}{\epsilon_r + 2} \dots \dots \rightarrow \text{Classius Mosotti relation}$$

Where “N” is the number of dipoles per unit volume

This is the **Clausius - Mosotti equation**, it relates the *microscopic* quantity α on the left hand side to the *macroscopic* quantity ϵ_r (or, if you like that better, $\chi = \epsilon_r - 1$) on the right hand side of the equation

Temperature and frequency dependency



Experimental Interpretation

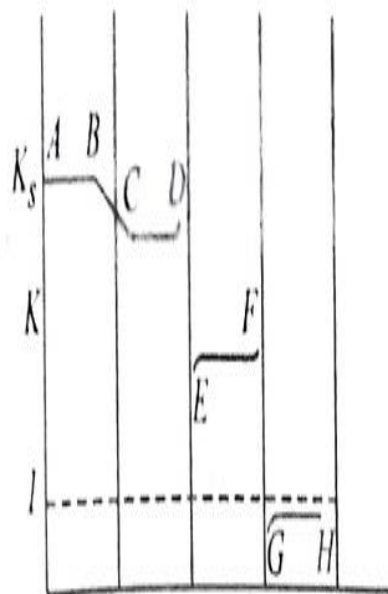


Fig. 18.

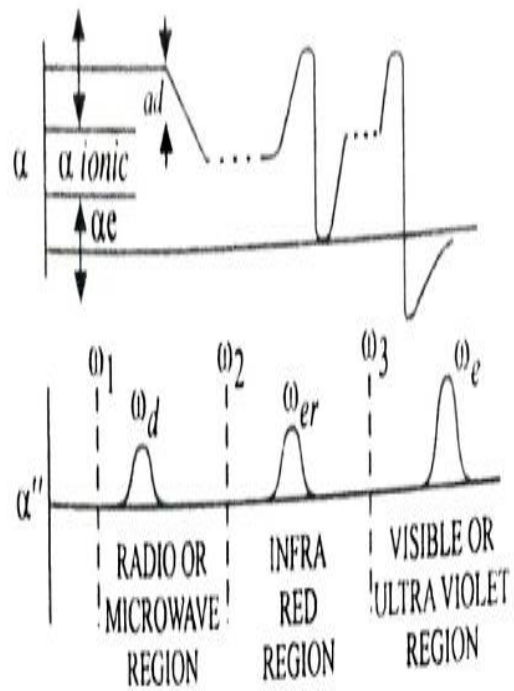


Fig. 19.

higher frequency the dielectric constant falls because orientation polarization cannot follow such rapidly varying fields.

However, there is still distortion polarisation. This may be of two kinds. One in the displacement of electrons relative to the nucleus fig (20) i.e. from the deformation of the electronic shell about a nucleus. The other is the displacement of the nuclei relative to each other within the molecule. The first is called the electronic polarization.

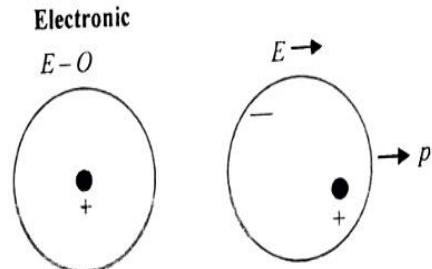


Fig. 20

Since electrons have relatively small mass, it is very rapid mechanism when its natural frequency is in the visible or ultra violet region. An alternative name may, therefore, be given as optical polarization.

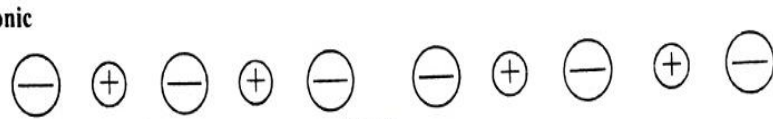


Fig. 21.

The second is a less rapid process which ceases to be operative about frequency in the "infrared", it is called atomic or infrared polarization. A special case of infrared polarization occurs in ionic crystals. Here the positive and the negative ions are pulled apart by a field and the whole lattice is polarized fig. (21).

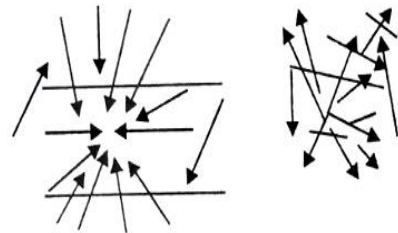


Fig. 22.

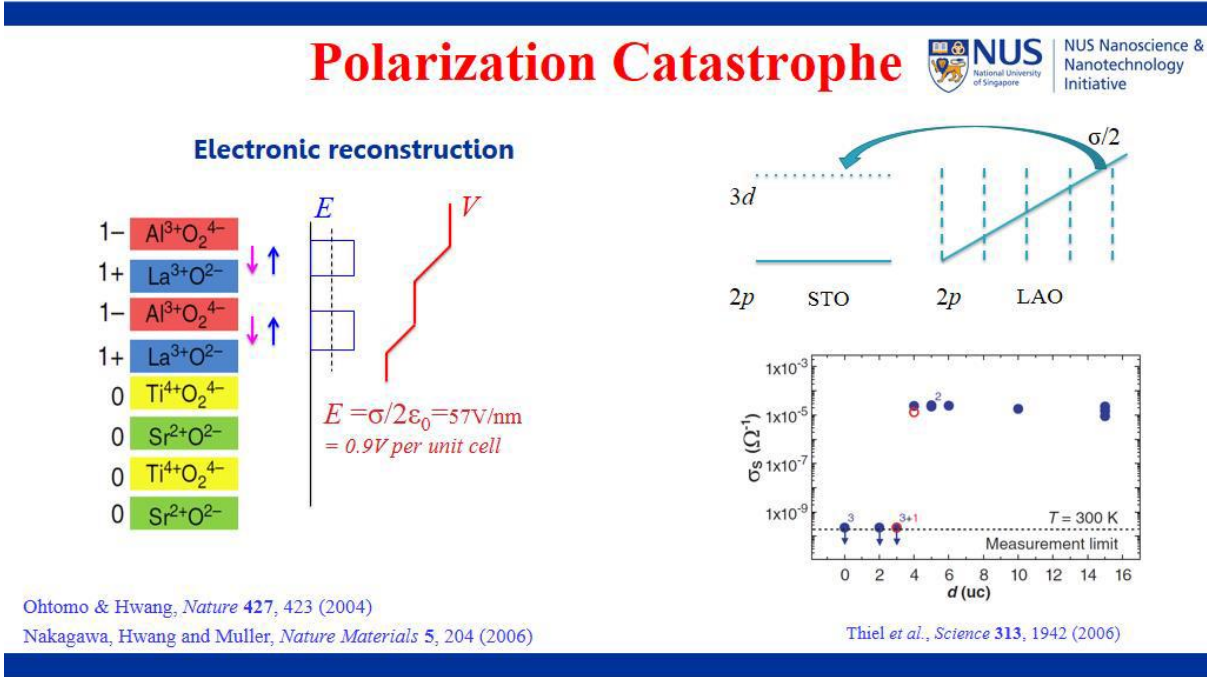
The ionic contribution comes from the displacement and deformation of a charged ion with respect to other ions. The orientational or dipolar polarizability fig. (22) arises when the Dipolar substance is built up of molecules possessing a permanent electrical dipole moment which may be more or less free to change orientation in the applied electric field. The ionic and dipolar contributions are seldom both large in the same substance. In ordinary ionic crystals there is no dipolar contribution. One way to separate them is shown in the schematic diagram.

In the optical frequency range the dielectric constant arises entirely from electronic polarizability. The dipolar and the ionic contributions are small or almost negligible because of the inertia of molecules and ions. Electric polarizability on an ion may depend slightly on the environment in which it is placed. Notice that the negative ions have high value of polarizability. D-E shows another fall at the infrared frequency at which the moment of the nuclei ceases to be operative. Optical polarization is the sole remaining effective mechanism. At F the ultra violet dielectric constant and refractive index both approach unity.

At frequencies $\omega_d, \omega_r, \omega_e$ there will be absorption peaks corresponding to the maxima of ϵ''

$$\epsilon = \epsilon' + i\epsilon'' \quad \dots (12.1)$$

POLARIZATION CATASTROPHE



In terms of a polarization catastrophe in which for some critical condition the polarization becomes very large ; or we may speak in terms of a transverse optical phonon of very low frequency. In a polarization catastrophe the local electric field caused by the polarization increases faster than the elastic restoring force on an ion in the crystal , thereby leading to an asymmetrical shift in ionic positions . The shift is limited to a finite displacement by higher order re-storing forces . The occurrence of ferro electricity in an appreciable number of crystals with the perovskite structure suggests that this structure is favourably disposed to a polarizability catastrophe. Calculations of local fields have made clear the physical reason for the favoured position of the perovskite structure.

We gave first the simple form of the catastrophe theory , supposing that the local field at all atoms is equal to $E + 4\pi P/3$ in CGS or $E+P/3\epsilon_D$ in SI. The theory

given now leads to a second-order transition ; the physical ideas can be carried over to a first order transition . In a second-order transition there is no latent heat ; the order parameter (in this instance , the polarization) is not discontinuous at the transition temperature . In a first order transition there is a latent heat ; the order parameter changes discontinuously at the transition temperature .

We rewrite (24) for the dielectric constant in the form

$$\text{CGS} \quad \epsilon = \frac{1 + 8\pi/3 \sum N_i \alpha_i}{1 - 4\pi/3 \sum N_i \alpha_i}$$

Where α_i is the electronic plus ionic polarizability of an ion of type i and N_i is the number of ions i per unit volume . The dielectric constant becomes infinite and permits a finite polarization in zero applied field when $\sum N_i \alpha_i$ comes infinite and permits a finite polarization in zero applied field when

$$\text{(CGS)} \quad \sum N_i \alpha_i = 3/4\pi.$$

This is the condition for a polarization catastrophe. The value of ϵ in (30) is sensitive to small departure of $\sum N_i \alpha_i$ from the critical value $3/4\pi$. If we write

$$\text{(CGS)} \quad (4\pi/3) \sum N_i \alpha_i = 1 - 3s,$$

Where $s \ll 1$, the dielectric constant in (30) becomes

$$\epsilon \approx 1/s .$$

suppose near the critical temperature s varies linearly with temperature :

$$s \approx (T - T_c) / \xi ,$$

where ξ is a constant . such a variation of s or $\sum N_i \alpha_i$ might come from normal thermal expansion of the lattice . The dielectric constant has the form

$$\epsilon \approx \xi / T - T_c ,$$

close to the observed temperature variation in the paraelectric state.