Neutron Scattering for Condensed Matter Studies

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Week 10: Lecture 26A

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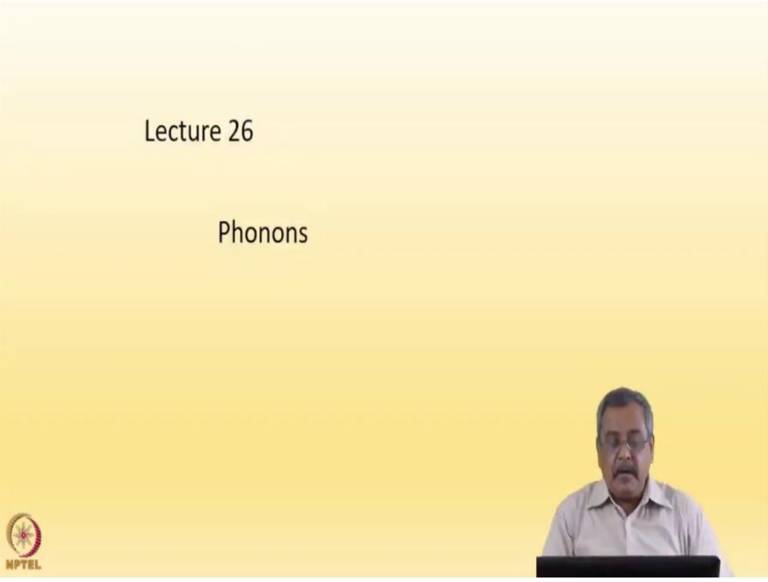

In this lecture, I will continue with Inelastic Scattering of Neutrons by Phonons. As I told you earlier, we have discussed elastic neutron scattering for all structure related studies at various length scales. Now we have come to inelastic neutron scattering, in which phonons form a very important part of the experimental studies for understanding collective oscillations in crystalline solids known as phonons.

I will discuss phonons first and later I will also discuss stochastic motions. And towards the end, I will come to molecular vibrations and extremely slow motions (~nanoseconds). Now, we will continue our discussion on phonons.

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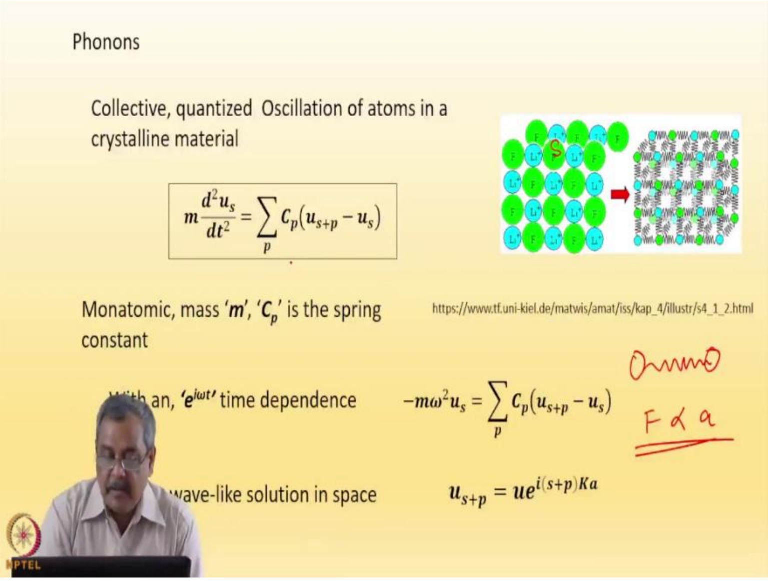

Phonons are collective oscillations in a solid. We assume that atoms constituting solid have springs connecting them or rather the force behaves like a spring. That means the force is proportional to displacement in the first order and behaves like a simple harmonic oscillator.

This is a picture I have borrowed from the source given here, where it is a lithium fluoride crystal, which actually is shown as springs connecting the ions in this crystal. And this picture remains valid for all crystalline materials, in which we will discuss the phonons. Now, the equation of motion for the, say, s^{th} ion will be given by the force summed over all neighbors and second differential of the displacement.

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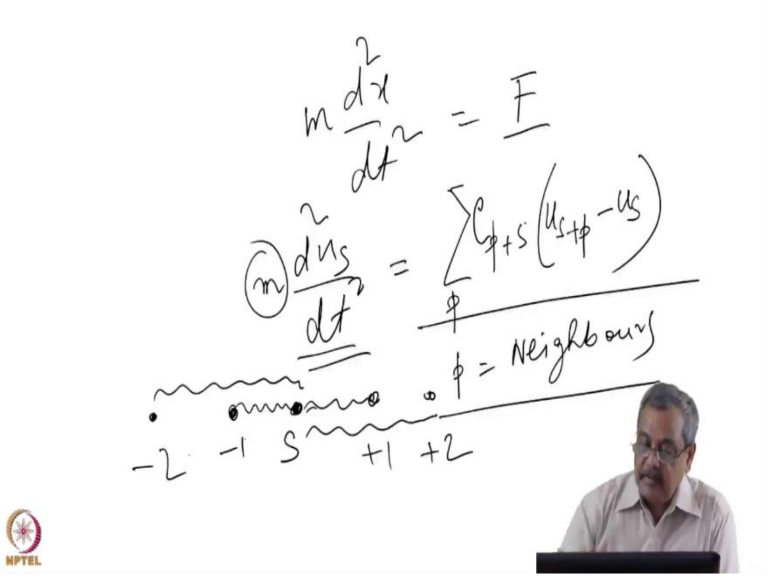

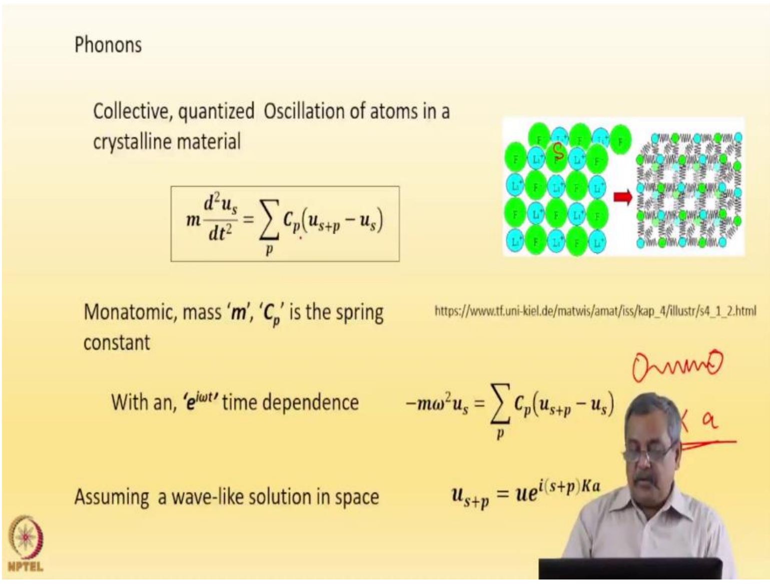

So, basically it is the Newtonian equation of $m\frac{d^2x}{dt^2} = F$ that translates here as

$$m\frac{d^2u_s}{dt^2} = \sum_p C_p\left(u_{s+p} - u_s\right)$$

Here, m is the mass of the ion and the force is a spring constant. So, this is a simple harmonic force, which depends on the relative displacement of the p^{th} neighbor. Let me just take a linear chain so that there is a spring here, there is also a spring here between the atoms, there is a spring here and also spring between the next nearest neighbors. So, if this is the s^{th} atom, this is s-1, this is s-2, this is s+1, this is s+2 and so on. And in ideal case, I should sum up over all the neighbors and then we get the equation of motion for the s^{th} atom. I have started with a monatomic lattice; C_p is the spring constant and then the sum is over all the neighbors of the s-th atom.

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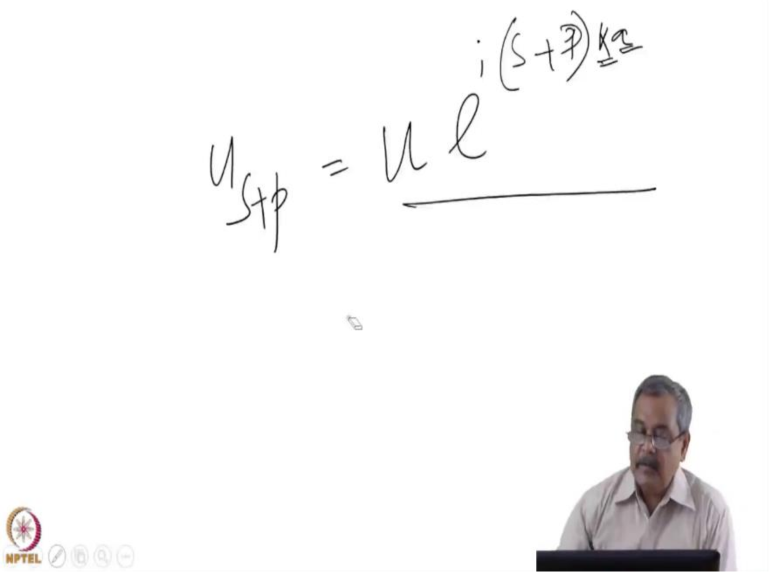

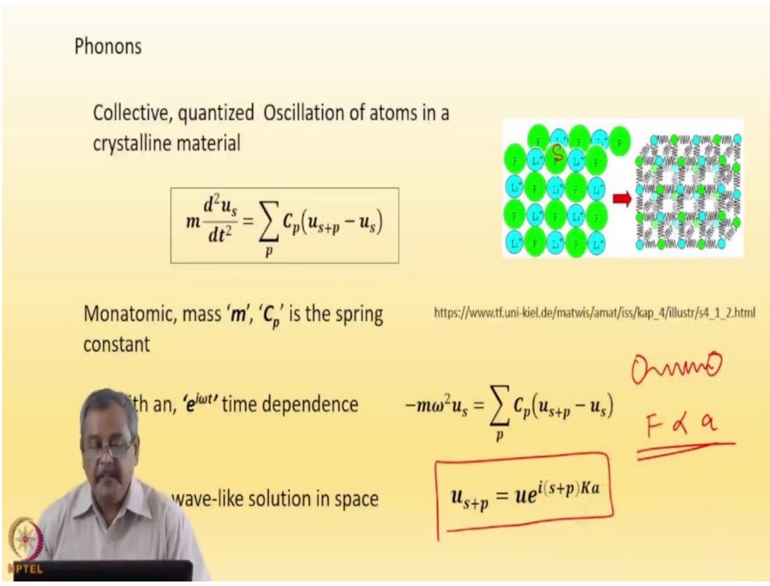

For this particular case, the concept of phonon is that, I consider a wave like solution (in space) where the displacement of u_{s+p} is given in terms of $u_{s+p} = ue^{i(s+p)Ka}$, where u is a constant and K is a wave vector (of the propagating wave) and a is the lattice spacing. Please note that here a wave vector is associated with the displacement and I have taken the displacement as a traveling wave in space and this is a very general solution. And what are the solutions? Let us get into that.

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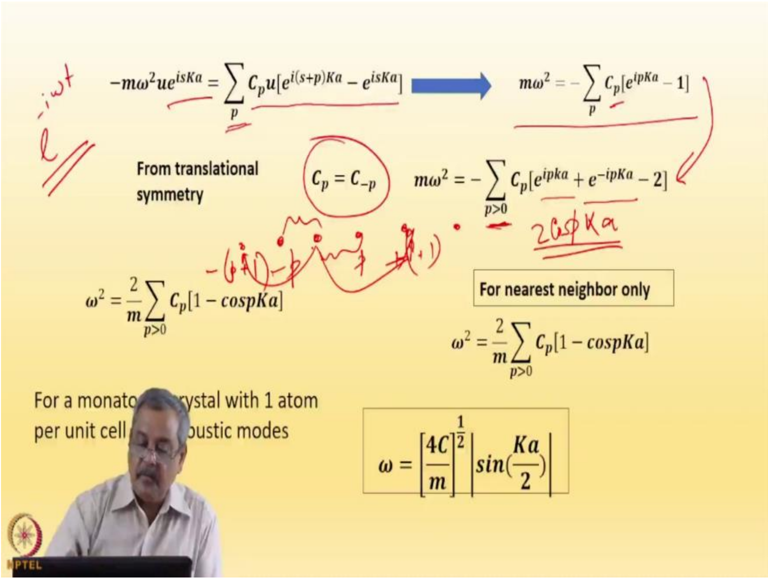

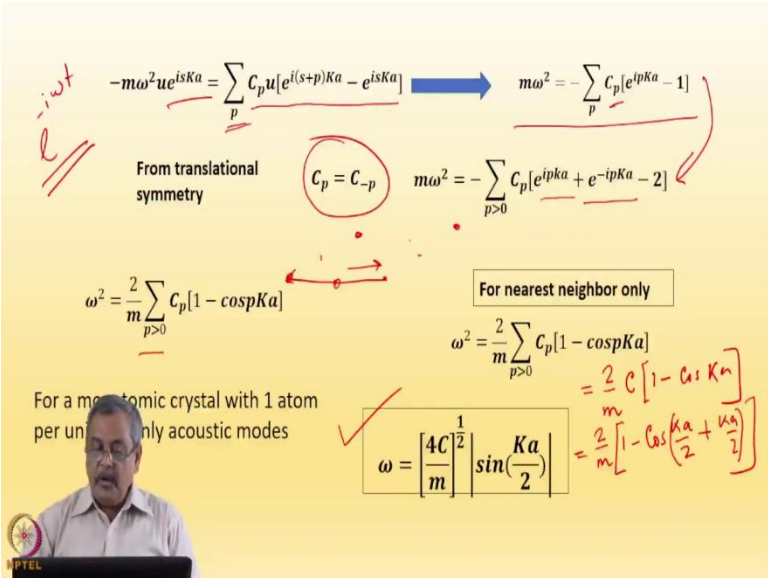

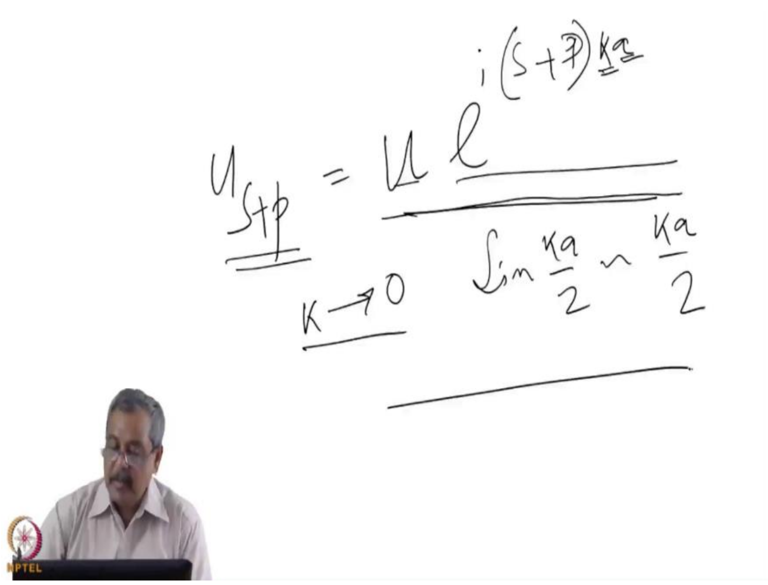

I consider the time dependence in form of $e^{-i\omega t}$ where ω is the temporal frequency, and e^{isKa} gives the spatial frequency. Substituting this we get the equation of motion as, $-m\omega^2 u e^{isKa} = \sum_p C_p u\left(e^{i(s+p)Ka} - e^{isKa}\right)$ or $m\omega^2 = -\sum_p C_p\left(e^{ipKa} - 1\right)$. This is summing over all neighbors.

I am discussing it as a linear chain, but it can be easily translated into three dimensional that is also. Fact is that, if this for a central atom *'s'*, if I consider the p^{th} neighbor then I also have a neighbor at -p^{th} position and likewise. So, the C_p and the force constants are symmetric, because the force between these two are same as force between these two. Similarly, the force between this and this one is same as force between this and the next nearest neighbor. So, $C_p = C_{-p}$ and then this summation series instead of summing over all atoms, I can do it over $p > 0$. Then we have relation reduced to, $m\omega^2 = -\sum_{p>0} C_p\left(e^{ipKa} + e^{-ipKa} - 2\right)$ or $\omega^2 = \frac{2}{m}\sum_{p>0} C_p(1 - \cos pKa)$.

If I consider only nearest neighbor interaction, then of all the p's we know only the nearest neighbors survive and then we have, $\omega^2 = \frac{2}{m}C(1 - \cos Ka) = \frac{2C}{m}\sin^2\frac{Ka}{2}$ and we have the solution as,

$$\omega = \left[\frac{4C}{m}\right]^{1/2}\left|\sin\frac{Ka}{2}\right|$$

Now, let us look at this solution. We know that as x tends to 0 then $\sin x$ tends to x.

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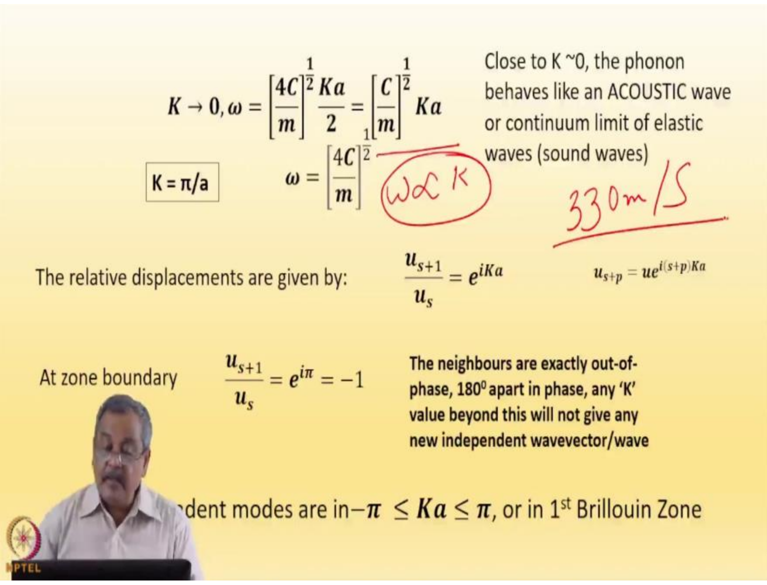

And, hence, in the limit as k tends to 0 the solution can be approximated to,

$$\omega = \left[\frac{4C}{m}\right]^{1/2} \frac{Ka}{2} = \left[\frac{C}{m}\right]^{1/2} Ka$$

So, in this limit $\omega \propto K$ as a linear relationship and that means, when I go to center of the zone, which is at $K = 0$, then the solution rather $\omega\ vs\ K$ relationship, ω goes down 0 linearly. This is similar to a sound wave propagating in a continuous media. We know that sound wave has a velocity of 330 m/sec and in this range, there is no dispersion of the wave.

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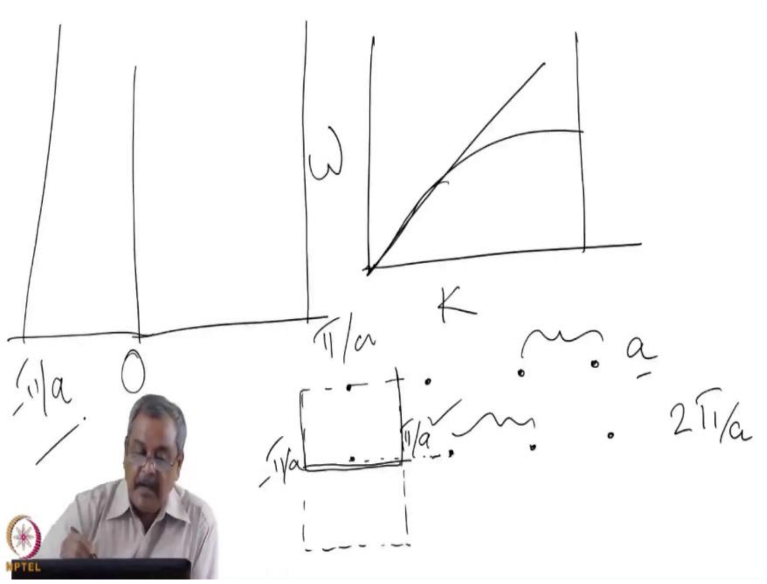

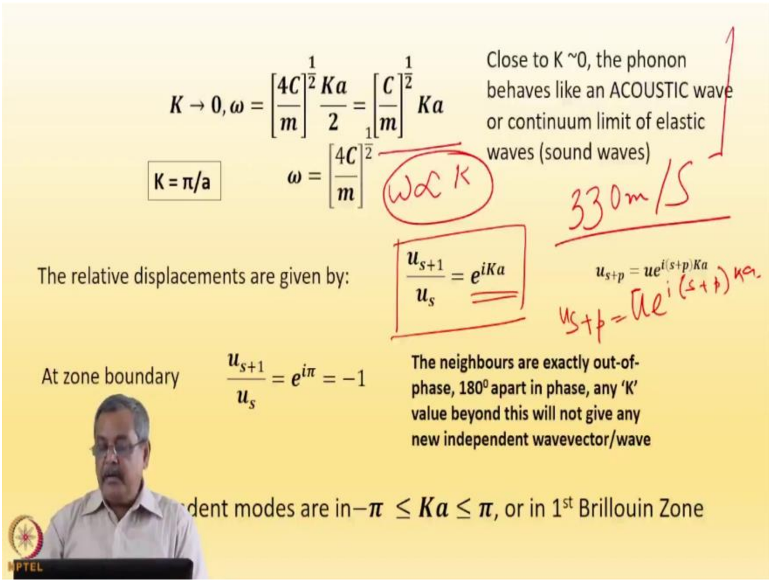

I mean ω $vs.$ K is linear for sound waves. For our case, which is phonons, it is going like this. So, when K goes to 0, it behaves like a sound wave or rather in a continuum limit like a mechanical wave propagating in thae medium.

And that is why $\omega \propto K$, this branch is called acoustic branch because as K goes to 0, ω also goes to 0 like sound wave. And actually speaking, when you tend towards K equal to 0, the acoustic wave or the acoustic phonon goes into sound (wave in a continuous medium). This is (phonon) basically an elastic wave in an elastic medium where we have the microscopic structure of atoms sitting at various sites.

At longer wavelength limit, the whole medium behaves like a continuum, because when the wavelength is so large, it cannot distinguish between the sites and the medium acts like a continuum and what you get are sound waves.

Now, another interesting thing is that, let us consider the relative displacement of the neighbors. From our solution, $\frac{u_{s+1}}{u_s} = e^{iKa}$ derived from $u_{s+p} = ue^{i(s+p)Ka}$ and when we use this value, consider the boundary of the first Brillouin zone. What is the Brillouin zone? Let me just consider a linear lattice of spacing a in real space then its lattice in the reciprocal space is linear with spacing $2\pi/a$. Now for the Brillouin zone we connect the nearest neighbors and draw a perpendicular bisector to the vector connecting the nearest neighbors. In three dimensions, the perpendicular bisectors are planes and they constitute a volume that is called a Wigner Sietz cell in reciprocal space. That is known as the first Brillouin zone. So, the first Brillouin zone boundary in comes at π/a and $-\pi/a$ for a square lattice.

For more complicated cases, for example, if I have other kinds of lattices, then the Brillouin zone shapes will be different, but at Brillouin zone boundary, we will have special properties of the phonon. In this chain, let me see when $K = \pi/a$ that is at zone boundary what we find? In this case, $\frac{u_{s+1}}{u_s} = e^{i\pi} = -1$ that means, at the zone boundary the nearest neighbors are exactly π phase apart in their movement.

Now, once they are π phase away any further difference will not give us a new independent displacement set (of travelling waves), because already they are π phase apart after that they can only repeat something which has happened (at values of wavevector) less than π/a. So, this is the reason we plot for total dispersion curves in the range of $-\pi/a$ to π/a for phonons.

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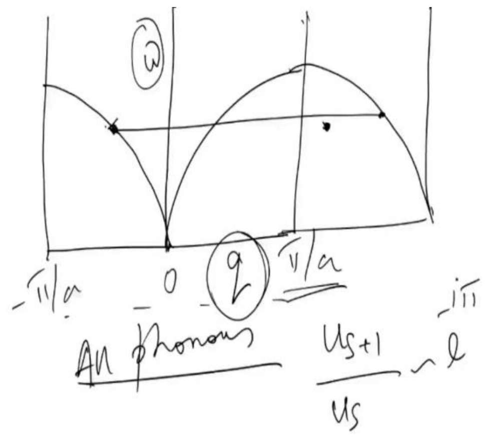

$$K \to 0, \omega = \left[\frac{4C}{m}\right]^{\frac{1}{2}} \frac{Ka}{2} = \left[\frac{C}{m}\right]^{\frac{1}{2}} Ka$$

Close to K ~0, the phonon behaves like an ACOUSTIC wave or continuum limit of elastic waves (sound waves)

K = π/a

$$\omega = \left[\frac{4C}{m}\right]^{\frac{1}{2}}$$

The relative displacements are given by: $\frac{u_{s+1}}{u_s} = e^{iKa}$

$$u_{s+p} = ue^{i(s+p)Ka}$$

At zone boundary $\frac{u_{s+1}}{u_s} = e^{i\pi} = -1$

The neighbours are exactly out-of-phase, 180° apart in phase, any 'K' value beyond this will not give any new independent wavevector/wave

...dent modes are in $-\pi \le Ka \le \pi$, or in 1st Brillouin Zone

$$-m\omega^2 ue^{isKa} = \sum_p C_p u[e^{i(s+p)Ka} - e^{isKa}] \rightarrow m\omega^2 = -\sum_p C_p[e^{ipKa} - 1]$$

From translational symmetry $C_p = C_{-p}$

$$m\omega^2 = -\sum_{p>0} C_p[e^{ipka} + e^{-ipKa} - 2]$$

$$\omega^2 = \frac{2}{m}\sum_{p>0} C_p[1 - cospKa]$$

For nearest neighbor only

$$\omega^2 = \frac{2}{m}\sum_{p>0} C_p[1 - cospKa]$$

For a mona... crystal with 1 atom per unit c... acoustic modes

$$\omega = \left[\frac{4C}{m}\right]^{\frac{1}{2}} \left|sin(\frac{Ka}{2})\right|$$

This is the zone center, say origin, and zone boundary is at $-\pi/a$ and π/a and we will try to evaluate the phonons up to the zone boundary. Because any K beyond zone boundary $-\pi/a$ or π/a can be reflected back to first Brillouin zone. For example, let us assume some dispersion curve in the 1st Brillouin zone then for a point in 2nd B.Z. it will look same as a point if I move it by $-2\pi/a$ and get back to the first Brillouin zone. So, all phonons, by all phones I mean that all the possible displacements, are contained inside the 1st Brillouin zone. And outside the 1st Brillouin zone, whatever we find can be brought back to (an identical displacement wave) in the first Brillouin zone, that is why we tried to get the phonon dispersion curve [plot between phonon frequency (ω) vs. phonon wavevector (q)] within the first Brillouin zone. So, at the zone boundary, we complete the set of possible displacements where any two neighboring atoms are π phase apart and after that we cannot have any new motion pattern that will give us a new phonon. This is already contained in the first Brillouin zone. Here for the solution for a monatomic lattice I showed that as K goes to 0, $\omega \propto K$ which is acoustic.

But at $K = \pi/a$ the frequency $\omega = \left[\frac{4C}{m}\right]^{1/2}$.

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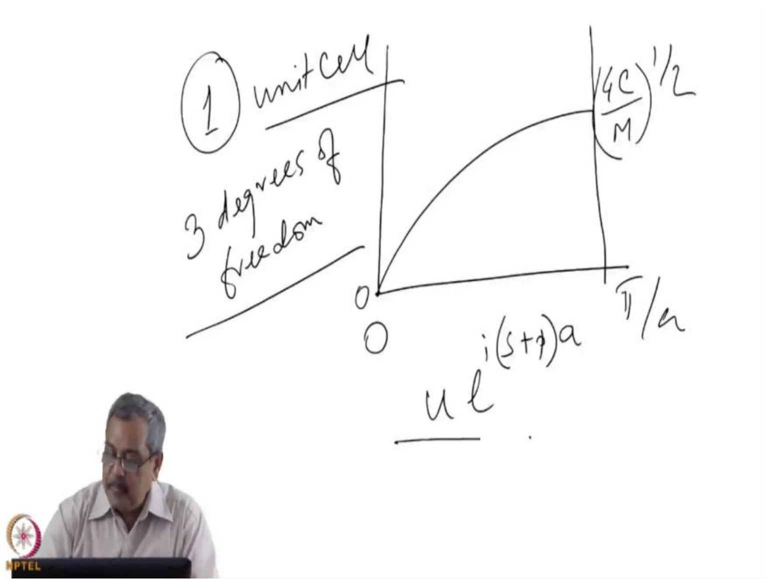

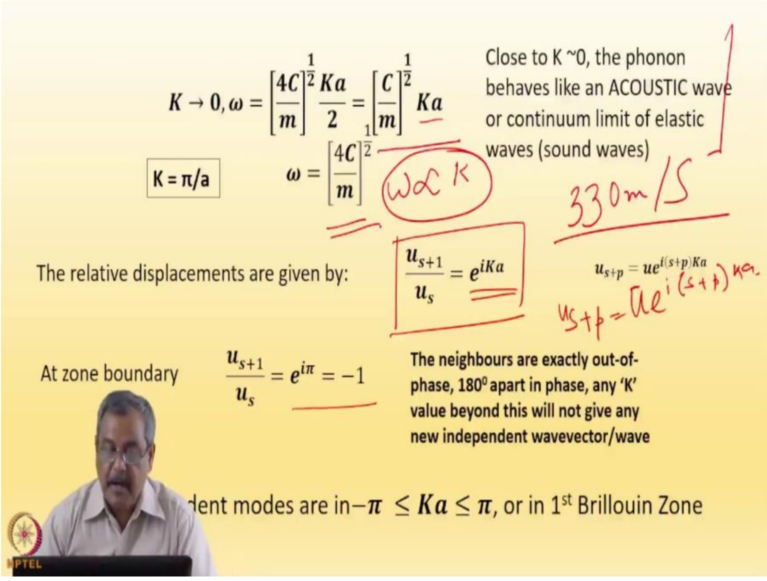

That means, for a monatomic case, this is the phonon dispersion curve. In this curve, at zone boundary that is at $K = \pi/a$, we have $\omega = \left[\frac{4C}{m}\right]^{1/2}$ and at $K = 0$ we have $\omega = 0$. For the simple case it is a sinusoidal curve. There is 1 atom in the unit cell, so, there are 3 degrees of freedom and I have shown you the dispersion relation for one.

Now, basically, when you have particles or planes of particles, this wave which I wrote as $e^{i(s+p)Ka}$, this displacement can be longitudinal or transverse. First let me point out one by one: we have phonons only in the first Brillouin zone, we need to do a measurement where the phonon wavevector (q) goes from 0 to π/a and maybe also on the negative side of the origin .

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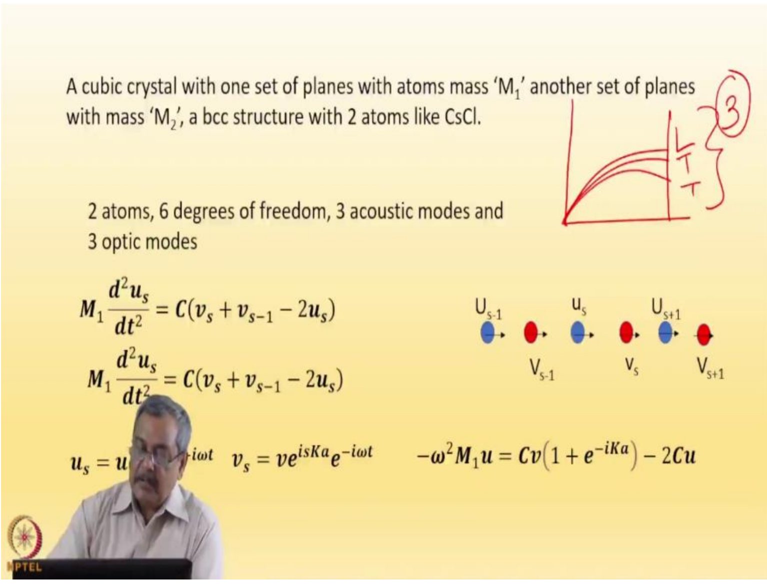

Second, if I have a monatomic crystal that is one atom per unit cell, then I have 3 degrees of freedom and among them we can have one longitudinal and two transverse modes. But all three of these are called acoustic waves.

Now, suppose there two atoms per unit cell. As an example, let us consider CsCl crystal.

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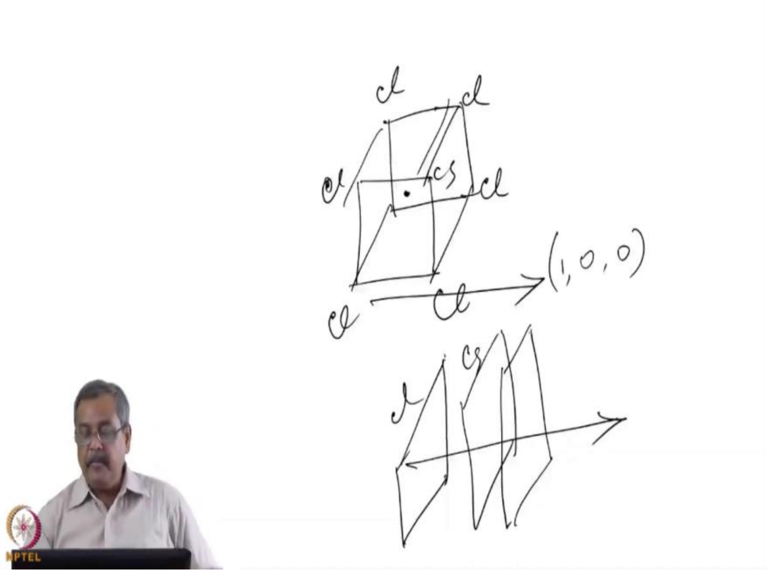

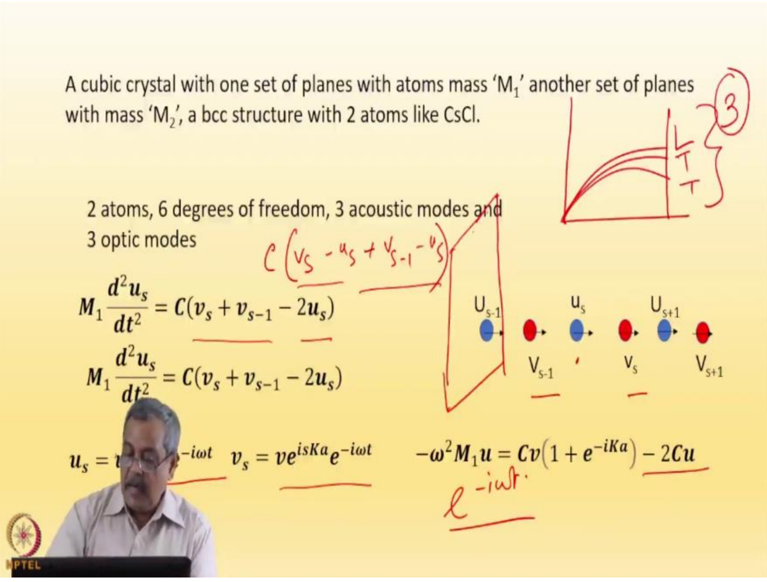

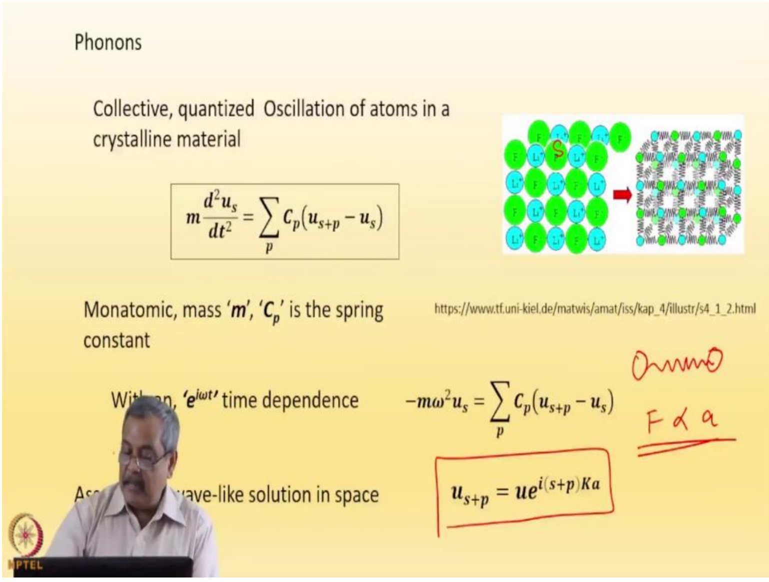

CsCl has a bcc structure where one set of atoms, say Cl, are at the eight corners of unit cell and one, Cs, is at the body center. Now, that means, if I consider a propagation vector in (100) direction in reciprocal space then in real space this will have planes like this; I will have planes of chlorines followed by planes of cesium, then again planes of chlorine and so on. This is how if I go in (100) direction. I will have planes of atoms which now I am showing as a chain (in the plane of the paper).

Now there are two movements. In general, there are two atoms of different mass, but they are also part of a traveling wave like solution. This concept was brought in I think by Egerton, but this is the basic concept of phonons. These are the frequency pattern, or the displacement pattern is a wave, and actually, when there are a number of atoms in a unit cell, we can find out what are the number of waves that are possible, which you can consider as independent of each other. That means, we can break down all the frequencies and all the displacement in terms of eigenvalues and eigenvectors.

Now, we are considering only nearest neighbor interaction. When we have nearest neighbor interaction, then motion of equation of motion for atom with mass M_1 is given by,

$$M_1\frac{d^2u_s}{dt^2} = C(v_s + v_{s+1} - 2u_s)$$

Here, $(v_s + v_{s+1} - 2u_s)$ is sum of two terms and is equivalent to $(v_s - u_s + v_{s+1} - u_s)$. Similar to monoatomic case, now we take two solutions for two atoms as, $u_s = ue^{isKa}e^{-i\omega t}$and $v_s =$

$ve^{isKa}e^{-i\omega t}$ we will consider solutions for u_s and v_s again. Earlier I had chosen a traveling solution like this. Substituting these in equation of motion, we have

$$-M_1\omega^2 u = Cv\left(1 - e^{-iKa}\right) - 2Cu$$

$$(2C - M_1\omega^2)u - C\left(1 - e^{-iKa}\right)v = 0$$

Similarly, for the second atom also it will be

$$-M_2\omega^2 v = Cu\left(1 - e^{-iKa}\right) - 2Cv$$

$$(2C - M_2\omega^2)v - C\left(1 - e^{-iKa}\right)u = 0$$

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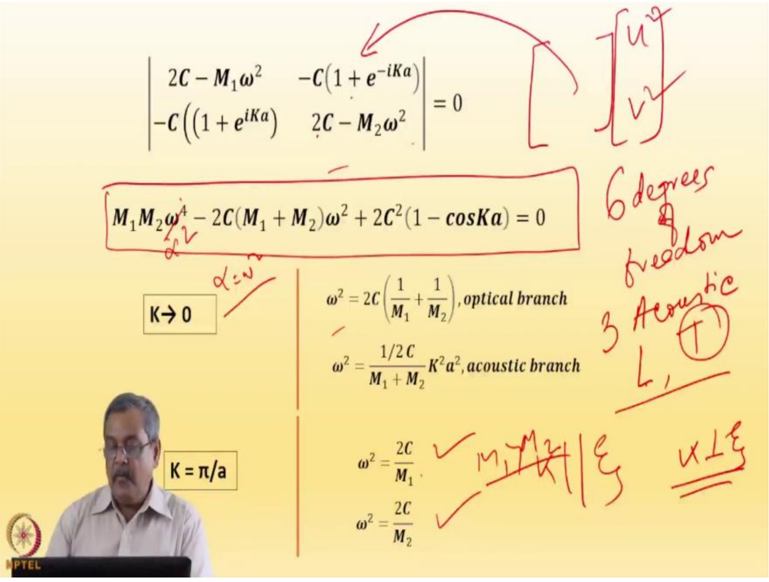

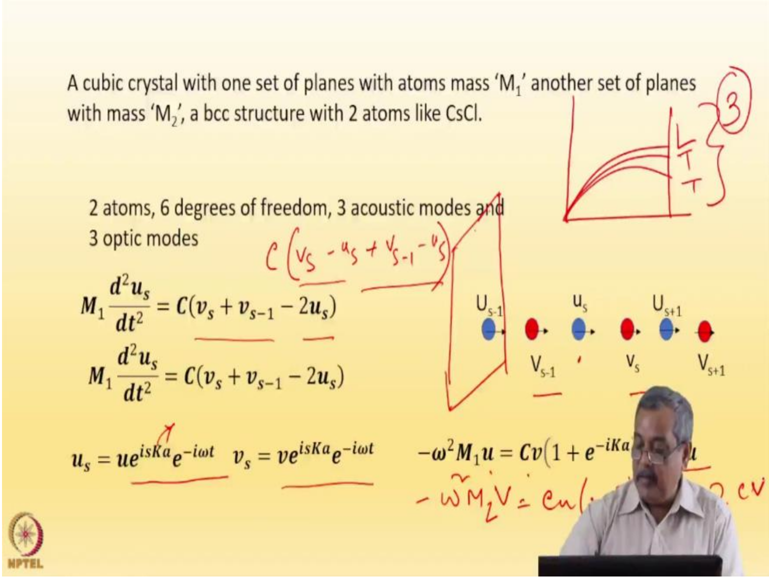

Now, I have got two equations in u and v and I can write down the coefficient to form a determinant and for real solution this determinant should be 0. Which results in,

$$M_1 M_2 \omega^2 - 2C(M_1 + M_2)\omega^2 + 2C^2(1 - \cos Ka) = 0$$

This is the equation we obtain for the motion of the two particles. Interestingly now, I have got 6 degrees of freedom (for two atoms in the unit cell). I know that out of these, 3 will be acoustic, because there is one longitudinal and two transverse wave solutions. Longitudinal means the particle displacement and the wave propagation direction are parallel and in case of transverse wave propagation and the particle displacements are perpendicular to each other and that can happen in two planes.

For this equation, I have got two solutions. For the case when K goes to 0,

$$\omega^2 = 2C\left(\frac{1}{M_1} + \frac{1}{M_2}\right) \; and \; \omega^2 = \frac{\frac{1}{2}C}{M_1 + M_2}$$

And when $K = \pi/a$, we have

$$\omega^2 = \frac{2C}{M_1} \; and \; \omega^2 = \frac{2C}{M_2}$$

So, these will be the solutions, when I have two atoms per unit cell.

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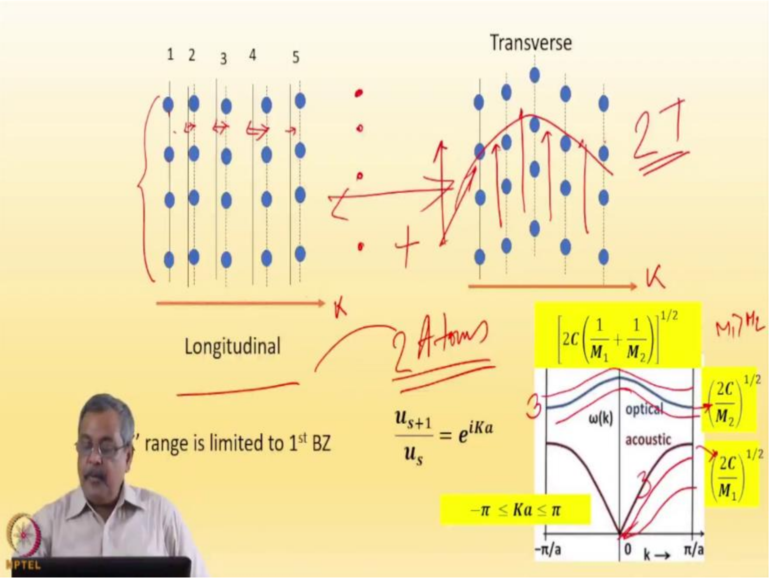

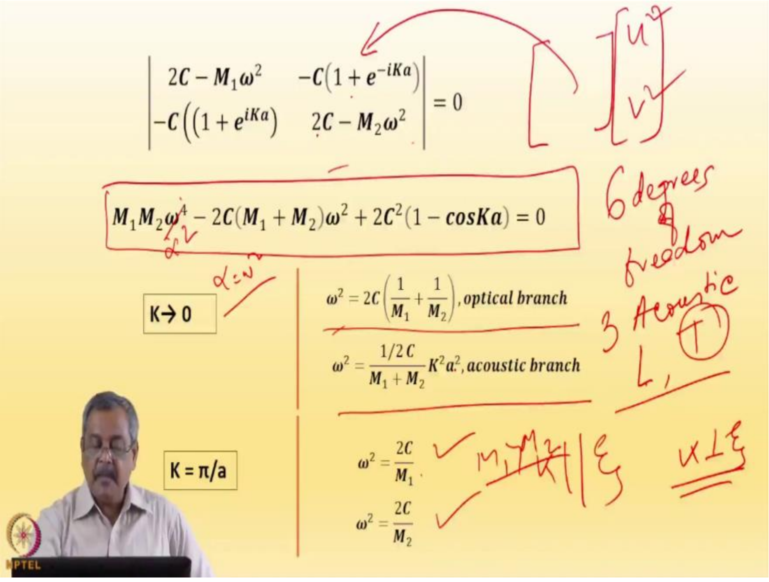

Now, how does the displacements look like? When I say longitudinal waves, please note that the direction the wave is propagating shown in figure. And I showed the displacement of this plane of atoms. You can see that the second plane of atom is displaced this much, the third plane maybe displaced a little more, the fourth plane little more, then again it keeps reducing, and finally when it comes to a plane completing the wave, I get back to the plane, which I have assumed as central plane. So, that is a longitudinal wave. Here the displacements follow a sine curve. Whereas in case of transverse waves shown in right side of figure, the second plane is displaced transverse to the propagation (K) direction. So, you can see that planes are displaced upward (here), successively a little more then a little less and ultimately it comes down to the displacement of the central plane. That means, the sinusoidal wave I can draw like this.

In case of transverse waves, I have two directions perpendicular to the direction of propagation, hence, there are two transverse waves. In case of only one atom, these two modes together longitudinal and transverse acoustic waves make up for the total degrees of freedom which is three.

When we have two atoms, then also the number of acoustic waves will be three. Along with that, there will be optical waves. You can see that at $K = \pi/a$, if we have $M_1 > M_2$ then among the two solutions at the boundary $\frac{2C}{M_2} > \frac{2C}{M_1}$ and solution for the optical branch will be $\frac{2C}{M_2}$ at the boundary. But at $K = 0$, you know that the solution for the optical branch is, $\omega^2 = 2C\left(\frac{1}{M_1} + \frac{1}{M_2}\right)$, a constant value for a system, and for acoustic branch $\omega^2 \propto K^2$ or $\omega \propto K$ barring a constant factor.

Now, we have worked three optical branches and three acoustic branches for 2 atoms. I hope I was able to make you understand the displacement patterns in case of monatomic and diatomic lattice and this can be further generalized for any kind of lattice.

Now, this I call acoustic because I said earlier that for these branches ω goes to 0 as K goes to 0 and as K goes to 0 the medium behaves like a continuum. So, what about the optical waves?

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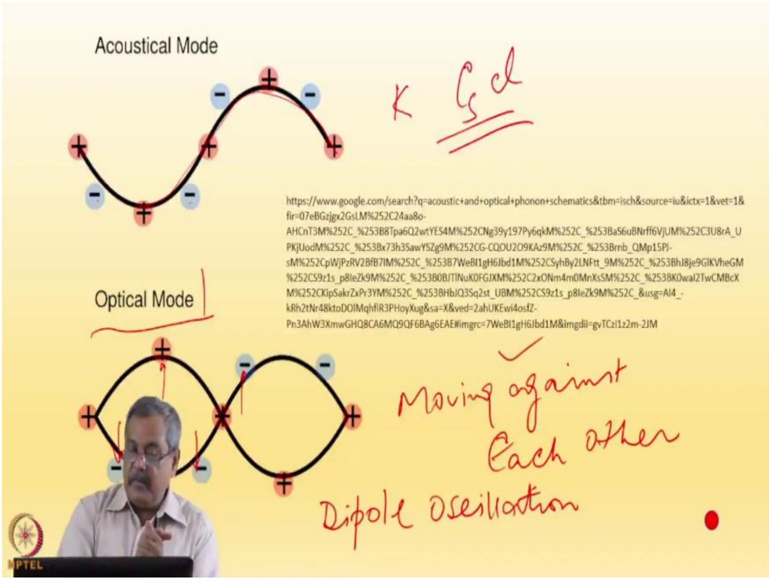

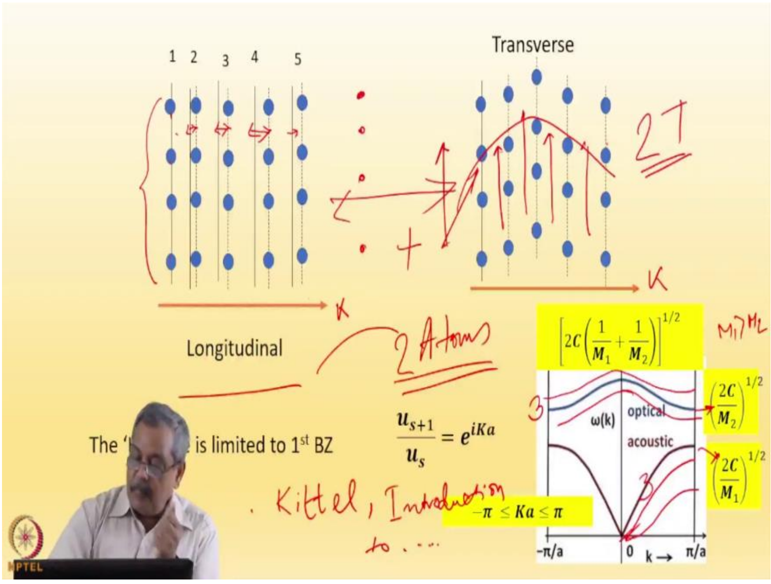

Here I show you the displacement model of the acoustic mode and the optical mode borrowed from here. Please see that in the acoustic mode, the atoms move in the same direction, and the amplitude of their oscillation varies as per the wave vector *K*, which is the wavelength of this oscillation. But they all are falling on the same wave pattern. So, when this is one atom going down, the other one is also going down when it is going up, all of the atoms go up (with varying amplitude) and this is a displacement pattern.

In case of optic mode, please note that even if the wavelength is kept same, the nearest atoms are moving in opposite direction. So, the atoms are moving against each other.

This part of my description I have borrowed from the book by Kittel, Introduction to Solid State Physics.

I have talked to you about acoustic modes and optical modes. When atoms are moving against each other, if the center of mass is fixed and if there are ions as I showed you in CsCl, when ions are moving against each other it looks like a dipole oscillation. This dipole oscillation is able to couple with the electric field of an electromagnetic wave and can absorb or emit electromagnetic waves. That is why these are called the optical modes when the atoms are moving against each other with the center of mass fixed.

Acoustic mode, goes to sound wave in the low K continuum limit. And optical mode are capable of absorbing or releasing electromagnetic radiation because in case of ionic solids, they will be like oscillating dipoles.

With this I will stop. In the next part, I will go into more generalized description of phonons and then we will talk about various measurements.