Neutron Scattering for Condensed Matter Studies

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Week 10: Lecture 26B

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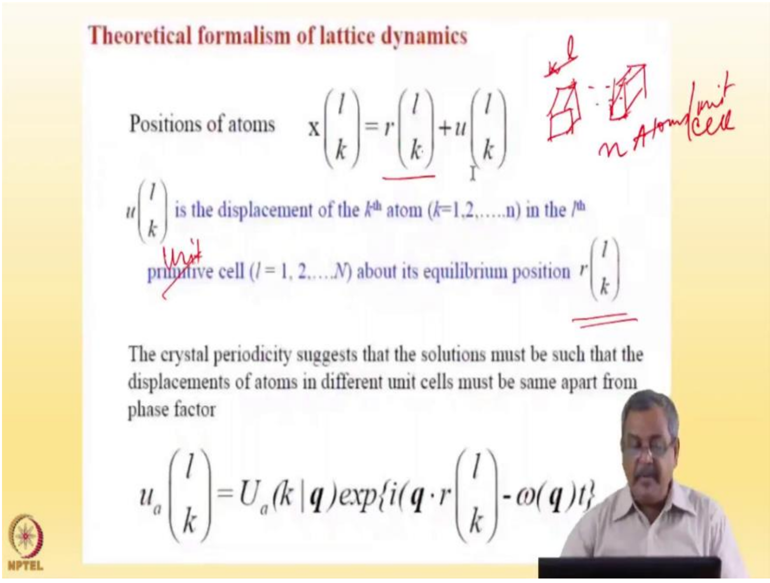

Here I come to some generalized descriptions of formalism in lattice dynamics. The reason being that regarding phonon experiments, which I will get on to after a little while, it is important for such experiments to carry out calculations or simulations before we take up the experiment. Reason being that in an inelastic neutron scattering experiment for the phonon, neutron intensities are much smaller than the Bragg peak intensity (in a diffraction experiment). These are low intensity experiments, possibly two orders of magnitude lower, compared to typical diffraction experiments. That is why to have a successful experiment, it is necessary that we carry out the lattice dynamical calculations for the sample beforehand (and plan the experiments). Especially if it is a single crystal sample, it is easy to tackle the experiment theoretically. But the fact remains that it is not so easy to get single crystals. For a single crystal sample, it is easy to handle computationally and we need to carry out detailed lattice dynamical calculations regarding the phonon dispersion curves. Then only we take up the experiment. That is a general trend. Unlike, let us say an x-ray diffraction experiment, where one will make a sample by chemical route or by some other route and first thing he does is to put it an x-ray diffraction instrument.

Here before we take up lattice dynamics experiments on an instrument it is important that we understand the phonons and how they behave in the single crystal sample. With this introduction I will start and first let me just write down something known as dynamical matrix.

First about positions of atoms. Here the protocol is that I am writing x (a displacement) when I say the k^{th} atom in the l^{th} unit cell. That means there are unit cells after unit cells in the solid and I mark one among them (l^{th}). I am talking about the k^{th} atom in the l^{th} unit cell if there are n atoms per unit cell.

So, then the k^{th} atom in the l^{th} unit cell is given by its equilibrium position $r\binom{l}{k}$ plus a displacement $u\binom{l}{k}$ about this equilibrium position, so that position of this atom is,

$$x\binom{l}{k} = r\binom{l}{k} + u\binom{l}{k}.$$

Earlier you saw that I took solutions which are wave like. Here also we do the same, only the notation is slightly different.

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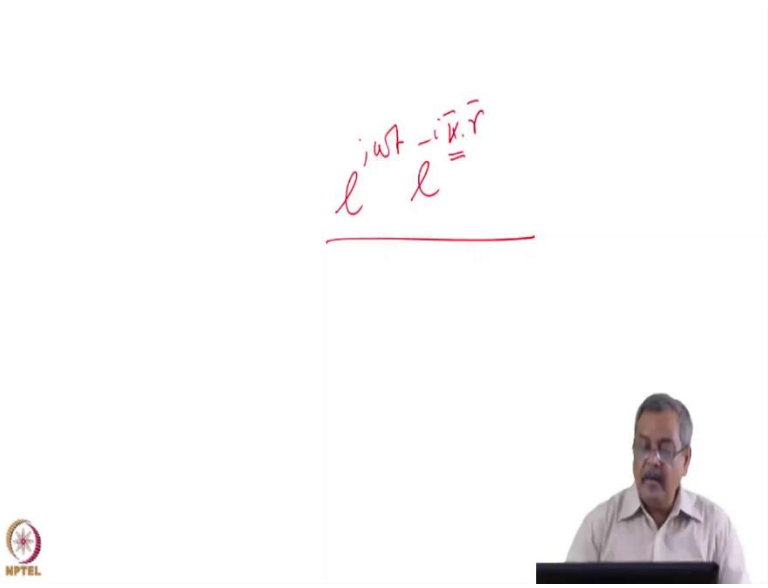

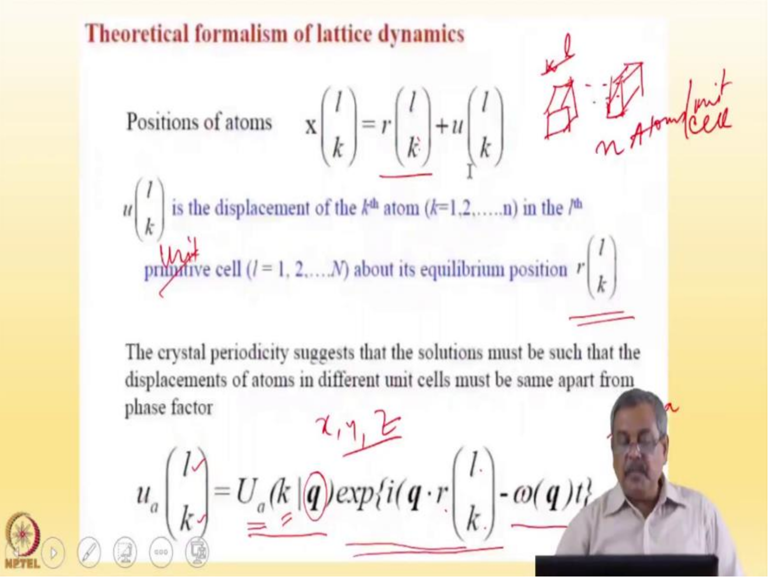

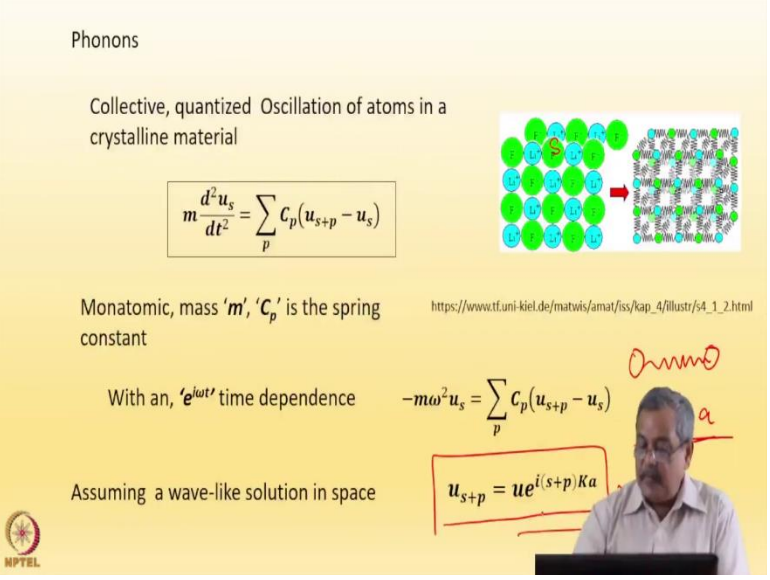

We know that a travelling a solution is given by $e^{i\omega t}$ in time and $e^{-i\boldsymbol{K}.\boldsymbol{r}}$in space where K gives the wavelength of the spatial variation and ω gives the temporal variation. This is a travelling wave solution. With this much understanding, let us move forward.

Solution for k^{th} atom in the l^{th} unit cell is given by,

$$u_\alpha \binom{l}{k} = U_\alpha(k|\boldsymbol{q}) \exp\{i(\boldsymbol{q}.r\binom{l}{k} - \omega(\boldsymbol{q})t)\}$$

where the α represents the x, y, z components, r is equilibrium position of k^{th} atom in the l^{th} cell. $U_\alpha(k|\boldsymbol{q})$ is, say x component of the k^{th} atom for the phonon of wavevector $\boldsymbol{q}$. This is for total displacement, denoted by u_x or u_y or u_z for the k^{th} atom in the l^{th} cell. This is coming from the phonon of wavelength q. Earlier I wrote a solution: $u_{s+p} = ue^{i(s+p)Ka}$for the displacement, which is the travelling wave solution with a pre-factor. Here I have written the same in a slightly more generalized platform. I have chosen phonons with a wavevector $\boldsymbol{q}$ and this is the k^{th} atom in the l^{th} unit cell. Its displacement can be in a direction (x, y or z) given by α.

Then this is given by a travelling wave solution, which has equilibrium spatial wavevector part given by $\boldsymbol{q}.r\binom{l}{k}$ and the temporal variation given by $\omega(\boldsymbol{q})t$ exponential in time. So, this is the displacement vector.

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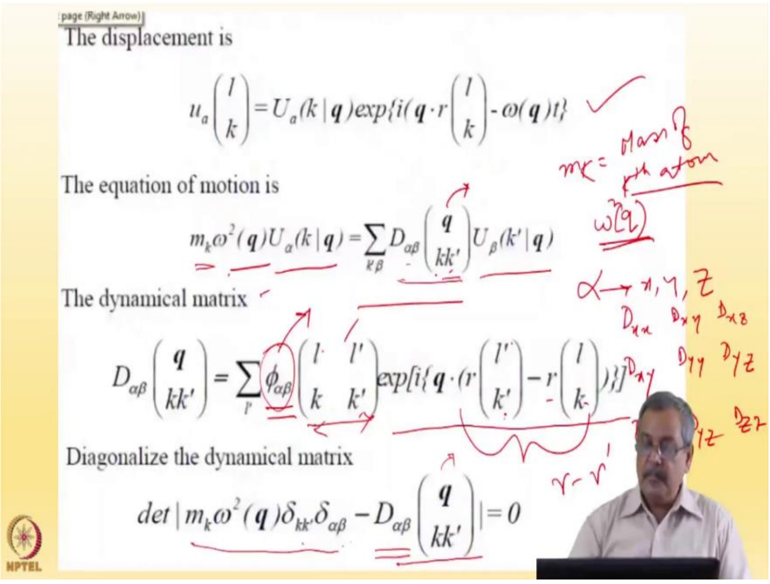

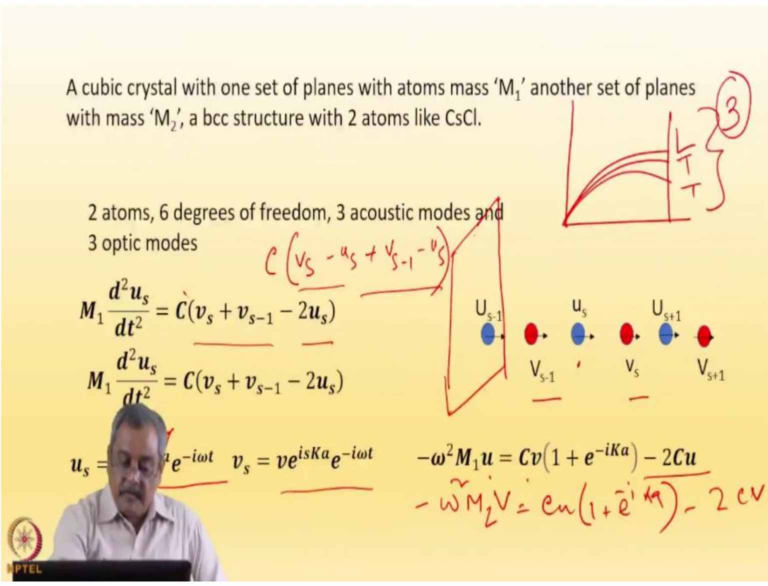

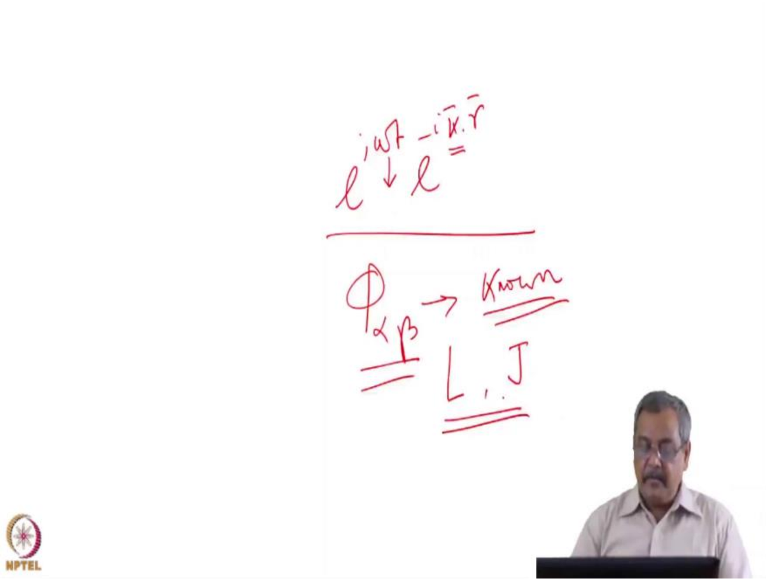

Now, in this formalism also, I will go for the travelling wave solution for the equation of motion. For example, here I have written the equation of motion,

$$m_k \omega^2(\boldsymbol{q}) U_\alpha(k|\boldsymbol{q}) = \sum_{k'\beta} D_{\alpha\beta}\binom{\boldsymbol{q}}{kk'} U_\beta(k'|\boldsymbol{q})$$

where m_k is the mass of k^{th} atom. Earlier I just wrote ω^2 but here I have written $\omega^2(\boldsymbol{q})$. ω as a function of $\boldsymbol{q}$ means depending on the phonon wave vector ω will be different. Earlier, the displacement vector was written as u, while here it is written as $U_\alpha(k|\boldsymbol{q})$ where $\alpha \rightarrow x, y, z$ are components of the displacement. This is summed over matrix $D_{\alpha\beta}$.That means, the matrix can be $\begin{pmatrix} D_{xx} & D_{xy} & D_{xz} \\ D_{yx,} & D_{yy} & D_{yz} \\ D_{zx} & D_{zy} & D_{zz} \end{pmatrix}$. This is the dynamical matrix between k^{th} atom and the k' atoms for a phonon wave number vector q and then we have $U_\beta(k'|\boldsymbol{q})$ component. That means, the α component. Or if I say α is the x-component of displacement, and the corresponding dynamical matrix element $D_{\alpha\beta}$ if β is y then it will be D_{xy} which also depends on the phonon wave vector and the interaction between k and k' atoms.

The dynamical matrix does dictate the force. Because if you remember in the earlier simpler expression, I used the force constant, *C*. Now, the same I have replaced with a more generalized and mathematically more compact expression. So, this is the force constant. Force constant is denoted by $\phi_{\alpha\beta}$.Basically the direction pairs are *xy*, *xx*, *yz*. So, $\alpha\beta$ will dictate the force between k^{th} atom in the l^{th} cell and the k' atom in the l' cell and their respective *x*,*y*,*z* components. These are two atoms which are interacting and the interactions are direction dependent. Further, there is an exponential term in the relation for the dynamical matrix, $\exp\left[i\left\{\boldsymbol{q}.\left(r\binom{l'}{k'}-r\binom{l}{k}\right)\right\}\right]$ which is having the equilibrium position of two interacting atoms. The term $r\binom{l'}{k'}-r\binom{l}{k}$ actually represents the distance. If you remember, I can write it as $r'-r$, I am showing the indicators because this is the distance between the k' atom in the l' cell and the between k^{th} atom in the l^{th} cell., I may write it down as a determinant of coefficients.

So, this is the dynamical matrix which basically defines the force between two atoms at two different unit cells with a travelling wave like solution for the phonon. The displacements are connected through the force constants and are represented by a determinant which is the determinant of the coefficients.

$$\left|m_k\omega^2(\boldsymbol{q})\delta_{kk'}\delta_{\alpha\beta}-D_{\alpha\beta}\binom{\boldsymbol{q}}{kk'}\right|=0$$

Hence $D_{\alpha\beta}\binom{\boldsymbol{q}}{kk'}$ represents that for the phonon number vector is $\boldsymbol{q}$ and we are talking about interaction between k and k' atoms given by $D_{\alpha\beta}$ in terms of the force constant. $\delta_{kk'}\delta_{\alpha\beta}$ in determinant means the diagonal terms will have these terms equal to 1 and non-diagonal terms will be 0.

Now, the solutions. We are trying to solve this equation and actually we have to know the force constants $\phi_{\alpha\beta}$. If we have to do a phonon calculation then the force constants should be known. We can use various models for the force constant. (As an example), we can use Lennard-Jones potential which is known to all of you. If these are ionic solids, then there will be ionic potential which we have to use. We need to know the force constant between the atoms when we try to solve the dynamical matrix and find out the eigenvalues $[\omega_j]$ and eigenvectors $[\xi_j]$ for the frequency and the displacement vectors.

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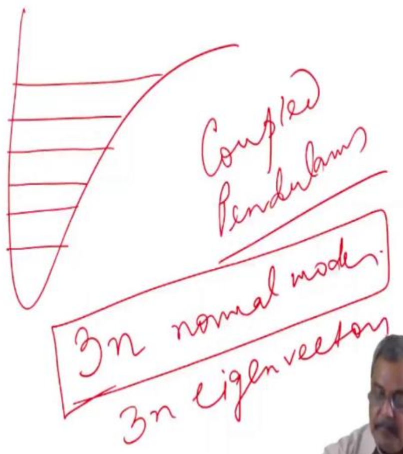
Solutions of the equation is possible if the force constants [ϕ] are known. The solution gives eigenvalues $[\omega_j]$ and the eigenvectors/displacements $[\xi_j]$

Dynamical matrix is Hermitian, so solutions or ω_j^2 are real, but for stable solution ω_j should be real. For imaginary ω_j the oscillation can't be sustained

$\omega_j^2 < 0$, -ve

For 'n' atoms in the unit cell there are 3n eigenvalues and eigenvectors. After diagonalizing the dynamical matrix, we get the eigenvalues and eigenvectors

In general → $\begin{bmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ \vdots \end{bmatrix}$



The displacement is

$$u_\alpha\begin{pmatrix} l \\ k \end{pmatrix} = U_\alpha(k\,|\,\boldsymbol{q})\exp\{i(\boldsymbol{q}\cdot r\begin{pmatrix} l \\ k \end{pmatrix} - \omega(\boldsymbol{q})t\}$$

The equation of motion is

$$m_k\omega^2(\boldsymbol{q})U_\alpha(k\,|\,\boldsymbol{q}) = \sum_{k'\beta} D_{\alpha\beta}\begin{pmatrix} \boldsymbol{q} \\ kk' \end{pmatrix} U_\beta(k'\,|\,\boldsymbol{q})$$

m_k = Mass of kth atom

The dynamical matrix

$$D_{\alpha\beta}\begin{pmatrix} \boldsymbol{q} \\ kk' \end{pmatrix} = \sum_{l'} \phi_{\alpha\beta}\begin{pmatrix} l & l' \\ k & k' \end{pmatrix} \exp[i\{\boldsymbol{q}\cdot(r\begin{pmatrix} l' \\ k' \end{pmatrix} - r\begin{pmatrix} l \\ k \end{pmatrix})\}]$$

Diagonalize the dynamical matrix

$$\det|\,m_k\omega^2(\boldsymbol{q})\delta_{kk'}\delta_{\alpha\beta} - D_{\alpha\beta}\begin{pmatrix} \boldsymbol{q} \\ kk' \end{pmatrix}| = 0$$

Now, when I say ω_j is an eigenvalue that means, it is basically the energy associated with a particular phonon and for that phonon ξ_j will give the displacement vector. Dynamical matrix is a Hermitian matrix. We know this because the forces are real. Hence, dynamical matrix is Hermitian, so, its solutions in terms of ω^2 should be real. So, ω_j^2 are real but real does not mean positive, if $\omega_j^2 < 0$ then ω_j will be imaginary and as we have the term $e^{-i\omega t}$, such a phonon decays with time., For imaginary ω_j, the oscillations cannot be sustained.

Hence, the phonons that are quantized oscillation of the atoms in a crystalline solid should have ω_j greater than 0, while the imaginary ω_j will decay and will not be able to sustain in the system.

Now, for *n* atoms in the unit cell we know that there are 3*n* degrees of freedom and hence there will be 3*n* eigenvalues and 3*n* eigenvectors. After diagonalizing the matrix, we get the eigenvalues and eigenvectors. So, what I am trying to do? Basically, since, there are 3*n* atoms in the unit cell, I am trying to find out 3*n* number of independent harmonic oscillators. We are familiar with the harmonic oscillators which has got solutions like this (drawn). So, here my attempt is under the assumption that these are coupled oscillators. I will request you to look into coupled harmonic oscillators or coupled pendulums. On internet several videos are available and you can see how the couple pendulums oscillate in space and time. Here I have got 3*n* normal modes. So, my attempt is just like classical mechanics that we try to divide the oscillations in terms of independent oscillations. And that is why we have got 3*n* normal modes and we also have 3*n* displacement patterns in terms of 3*n* eigenvectors. I will give an example.

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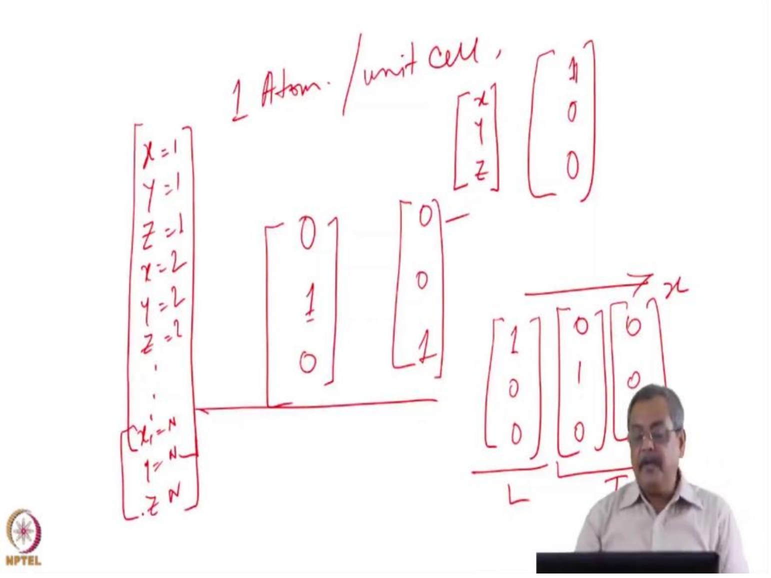

The first example that I showed you was just 1 atom per unit cell, then I have three modes. That means I have got x, y, z components of movement, $\begin{bmatrix} x \\ y \\ z \end{bmatrix}$. Now, if it is a longitudinal acoustic phonon, then this eigenvector will be $\begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}$ if I consider its propagation is in the x direction then other displacements will be 0 and this x displacement will be 1; there can be some constant term before or after, but eigenvector is $\begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}$.

Similarly, for the transverse phonon, if I consider the plane is a yz plane, so, for 1 transverse mode, the displacement is in the y direction and eigenvector will be $\begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix}$ while for the other transverse mode the displacement in the z direction and eigenvector will be $\begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$. So, for acoustic phonons with one atom per unit cell I have got these three displacement eigenvectors.

For n number of atoms then I have a long column vector, which has x, y, z components for first atom, then for second atom and so on till the n^{th} atom in the unit cell. I have a long column matrix. As an example, if there are two atoms.

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$$\begin{bmatrix}1\\0\\0\\1\\0\\0\end{bmatrix} \quad \begin{bmatrix} \\ \\ \\ \end{bmatrix}$$

$$\begin{bmatrix}0\\1\\0\\0\\1\\0\end{bmatrix}$$

$[\omega_j] \quad [\xi_j] \rightarrow$

Solutions of the equation is possible if the force constants [ϕ] are known. The solution gives eigenvalues $[\omega_j]$ and the eigenvectors/displacements $[\xi_j]$ $e^{-i\omega t}$ $e^{-\omega t}$

Dynamical matrix is Hermitian, so solutions or ω_j^2 are real, but for stable solution ω_j should be real. For imaginary ω_j the oscillation can't be sustained

$\omega_j^2 < 0$, -ve

In general → $\begin{bmatrix}x_1\\y_1\\z_1\\x_2\\y_2\end{bmatrix}$

For 'n' atoms in the unit cell there are 3n eigenvalues and eigenvectors. After diagonalizing the dynamical matrix, we get the eigenvalues and eigenvectors

Then for the longitudinal acoustic mode it will look like this 1, 0, 0 first atom, 1, 0, 0 for the second atom, $\begin{bmatrix}1\\0\\0\\1\\0\\0\end{bmatrix}$. Similarly, for the two atoms transverse acoustic mode will be like $\begin{bmatrix}0\\1\\0\\0\\1\\0\end{bmatrix}$ or $\begin{bmatrix}0\\0\\1\\0\\0\\1\end{bmatrix}$. In general, it is like this.

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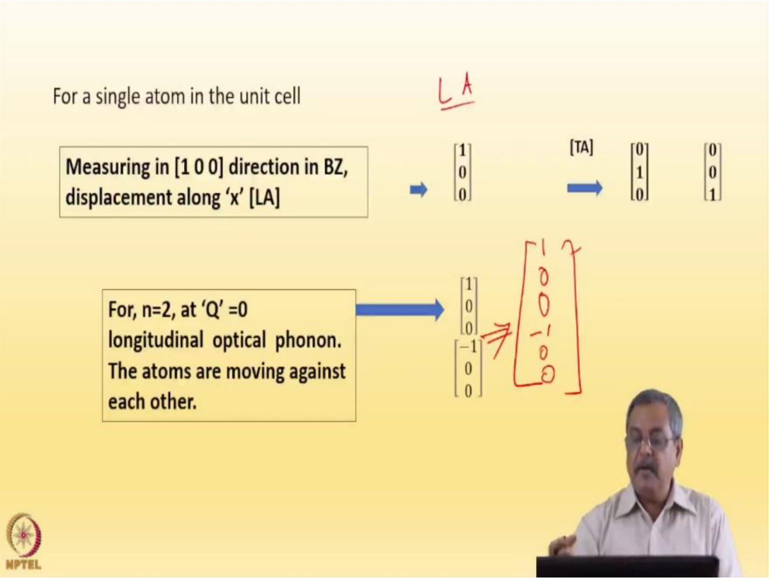

Now, let us consider a longitudinal optical phonon at $q = 0$. In case of optical phonon, the atoms do not move in the same direction but they move opposite to each other. For example, if one atom is moving in x-direction then second atom will be moving in -x-direction and in this case, longitudinal phonon will be $\begin{bmatrix}1\\0\\0\\-1\\0\\0\end{bmatrix}$. This is the displacement vector. T

This gives you a sense that for a given number of atoms in unit cell how to write down the eigenvectors. The eigenvalues are $\omega_j^2(\boldsymbol{q})$ that means, the j^{th} branch for the q value of the momentum vector in the Brillouin zone.

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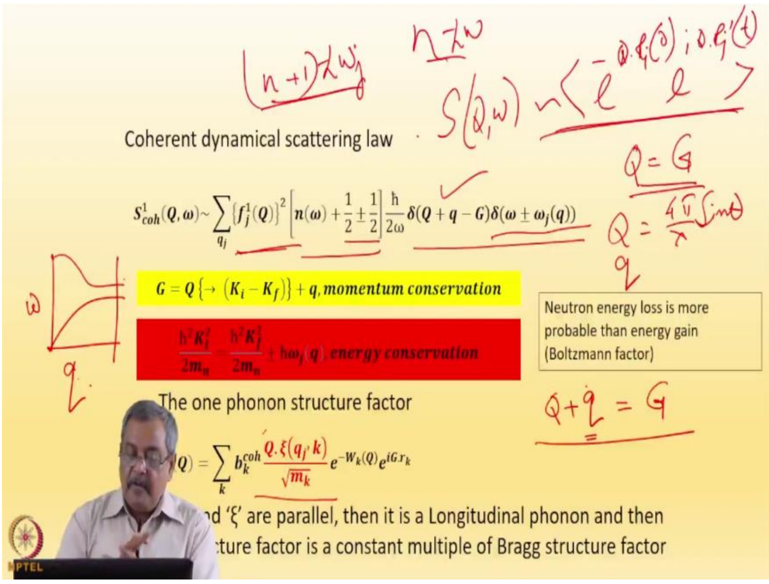

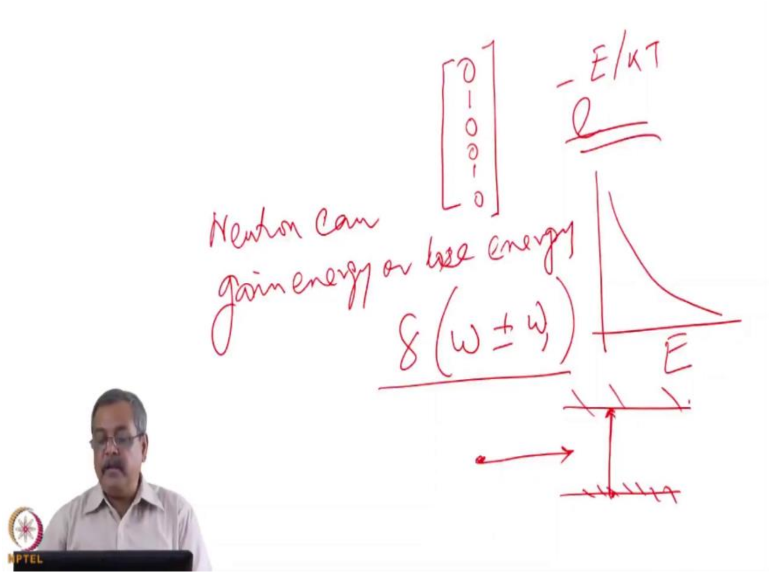

Now, instead of deriving the entire scattering law let me just give the expression for it to you and then explain the terms in it,

$$S^1_{coh}(Q,\omega) \sim \sum_{q_j} \{f^1_j(Q)\}^2 \left[n(\omega) + \frac{1}{2} \pm \frac{1}{2}\right] \frac{\hbar}{2\omega} \delta(Q + q - G)\delta(\omega \pm \omega_j(q))$$

If you remember, earlier, we had talked about scattering law, in which apart from other terms we had an ensemble average term $\langle e^{-iQR_j(0)} e^{iQR_j{'}(t)} \rangle$ which is the space-time correlation function that gives me the scattering law which also includes a phonon structure factor $\{f^1_j(Q)\}^2$, number of phonons, $\left[n(\omega) + \frac{1}{2} \pm \frac{1}{2}\right]$ and two delta functions. In an earlier delta function, if you remember when we did diffraction, because there was no energy transfer, we said the Q should be equal to G a reciprocal lattice vector. This leads to Bragg's law of diffraction. Now, we not only have a Q which is a momentum transfer, but we also associate it with a phonon wave vector (q) and all of them have associated momentums with them. That tells me that in this case, the momentum transfer (Q) which depends on the angle at which you are measuring the neutron intensity and the phonon wave vector (q), these two together should be equal to some reciprocal wave vector (G) and this is the conservation law for total momentum, $G = Q + q$.

Similarly, the conservation law for energy in this case is, $\frac{\hbar^2 K_i^2}{2m_n} = \frac{\hbar^2 K_f^2}{2m_n} \pm \hbar\omega_j(q)$; the neutron in the process of scattering can either gain energy or lose energy. That is why we have the term $\delta(\omega \pm \omega_j(q)$ where $\omega_j(q)$ is the phonon energy.

Interestingly, when the neutron loses energy then it excites one phonon, and when neutron gains energy then one phonon is deexcited and it gives energy to the neutrons. That means, there are two ways of energy transfer between the neutron and the sample phonons. But because of the Boltzmann factor, $e^{-E/kT}$ at any temperature T the lower energy levels are more populated than the higher energy levels. So, the population in lower levels is much higher compared to upper energy level and interacting neutron has a higher chance of exciting it from lower to higher level and lose energy to phonon.

So, this gives a momentum conservation law and the energy conservation law together with a one phonon structure factor weighed by the number of phonons. We know that if there is a gain in the number of phonons then it is $[n+1]\hbar\omega_j$ in the number of phonons of normal mode ω_j with temporal frequency ω_j and when there is reduction in the number of phonons, then the term is $n\hbar\omega_j$. So, this summation this takes care of the loss and gain in the energy together with the structure factor.

Now, let me explain to the structure factor in case of phonon measurements. I have written it down here. Please note that apart from this prefactor part in red, $\frac{Q.\xi(q_j k)}{\sqrt{m_k}}$, this is exactly the same as structure factor that we derived for a finite temperature diffraction experiment.

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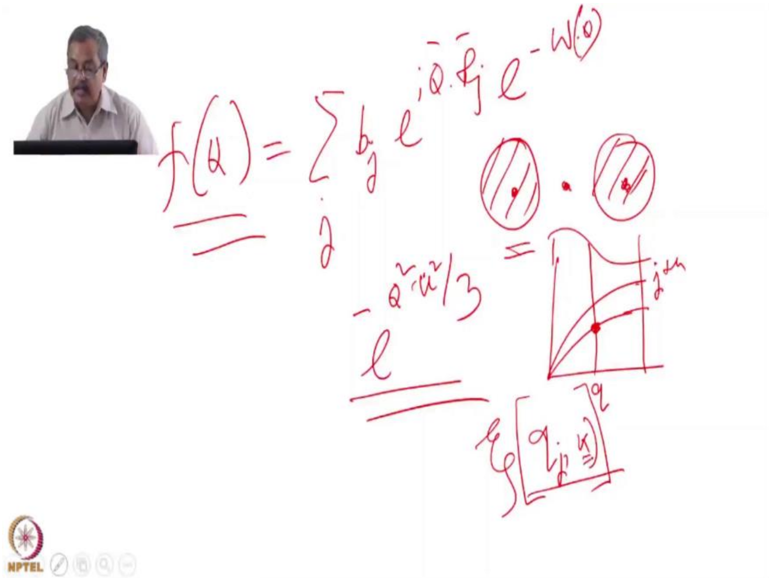

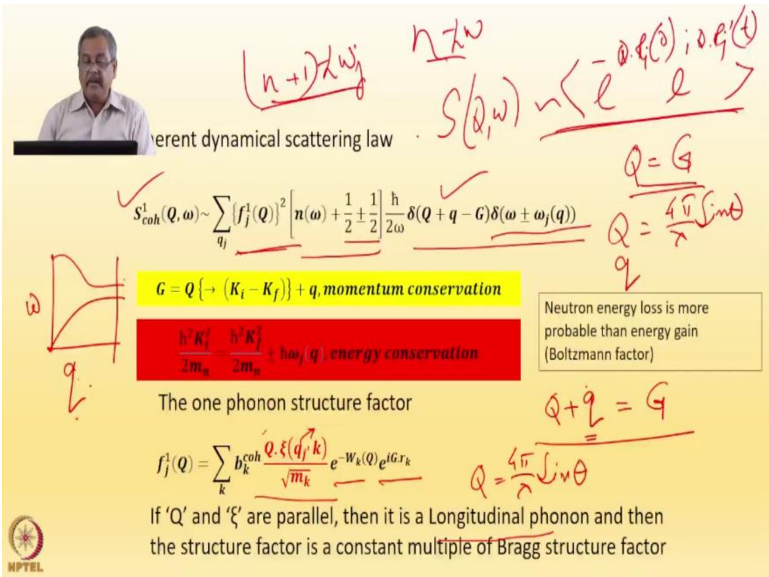

Let me just recall that expression of structure factor for a lattice at 0 K. It was $f(Q) = \sum_j b_j e^{-iQ.R_j}$. For a finite temperature we argued that as atoms starts vibrating around the mean position so they effectively become larger and we get a Debye-Waller like factor and the relation for structure factor at finite temperature is, $f(Q) = \sum_j b_j e^{-iQ.R_j} e^{-W(0)}$. Actually, the Debye–Waller factor was $e^{-Q^2u^2/3}$.

Now, let us look at the expression here. Apart from this phonon displacement term $\frac{Q.\xi(q_j k)}{\sqrt{m_k}}$, where ξ is the eigenvector for the j^{th} phonon with wave vector q_j, and this is the k^{th} atom with mass m_k. So, displacement vector for the k^{th} atom for the phonon vector q_j; it must be confusing what I mean is there are phonons, so, this is the q value possible for the j^{th} phonon which I have written as q_j and this phonon has a displacement pattern for all the atoms. So, this is a phonon wavevector q_j for the k^{th} atom in the unit cell that gives me the ξ displacement vector for the j^{th} phonon and the corresponding displacement for the k^{th} atom. So, this is what the phonon displacement vector and then we have this term exactly what he had for the 0 K structure factor. This is a Debye–Waller factor as I discussed earlier.

Now, this is the one phonon structure because there is also possibility, though small, that you can have two phonons getting excited by neutron or three or multi phonons, but we will restrict ourselves to one phonon excitation which has the largest probability.

Now, let us consider that case of a longitudinal phonon. Longitudinal phonon means, the phonon wave vector transfer Q and ξ are parallel. When the displacement vector and the momentum vector or the propagation direction are parallel then these are longitudinal phonon. In that case, $Q.\xi$ is some constant and then, apart from some constant, the expression for the one phonon structure factor exactly same as the Bragg structure factor. That means, wherever I have got a large value of the Bragg peak for the longitudinal phonon, I should also have a good coherent dynamical scattering or scattering from the phonon.

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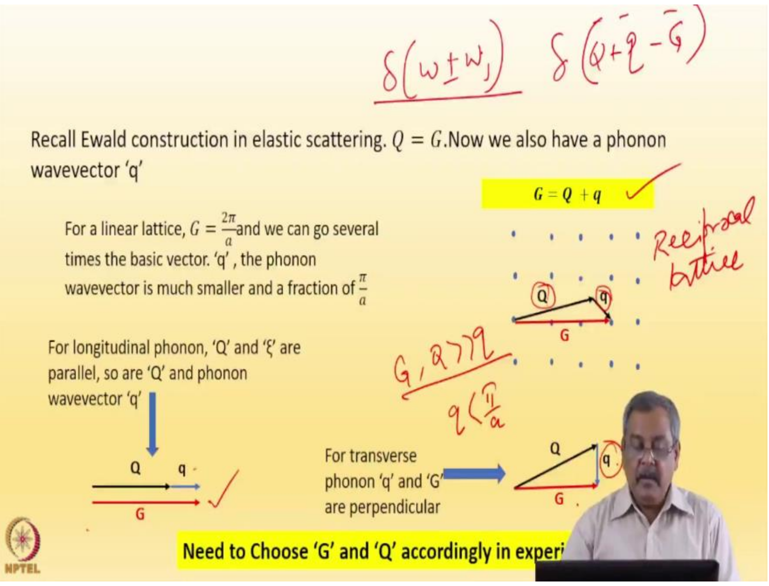

I had written down two conservation laws corresponding to two delta functions, $\delta(\omega \pm \omega_j(q))$ and $\delta(Q + q - G)$, here the momentum conservation demands that reciprocal lattice vector, $G = Q + q$ where Q is momentum transfer and q is phonon wavevector.

Now, let me look at the reciprocal lattice shown here. Here I need not restrict myself to first Brillouin zone. The phonon wave vector needs to be restricted by first Brillouin zone, but G can go over several Brillouin zones and that is why I showed the G here it is 1, 2, 3 apart, but this G in general should be equal to $Q + q$. This is a vectorial representation, this (Q) is the momentum transfer $\frac{4\pi \sin\theta}{\lambda}$ and this is a q vector for the phonon within the first Brillouin zone. So, G and Q can be much larger than the q which is less than $\frac{\pi}{a}$ in its length.

Now, let me just show you two cases.

One is that longitudinal phonon where G and Q are parallel and so are Q and q and this is how the vector equation looks like $\boldsymbol{G} = \boldsymbol{Q} + \boldsymbol{q}$.

If it is a transverse phonon, then this phonon wave vector q is perpendicular to the G vector or the reciprocal lattice vector. And then I show the vector diagram where $\boldsymbol{G} = \boldsymbol{Q} + \boldsymbol{q}$, but now the $\boldsymbol{q}$ and $\boldsymbol{G}$ are perpendicular to each other. That means for our experiments, if I am using a single crystal, the orientation of the sample and the values of $\boldsymbol{Q}$ and $\boldsymbol{G}$ has to be chosen in a manner, when I am either measuring a longitudinal phonon or an optical phonon. We have to choose the G and Q accordingly for a single crystal sample.

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I will just stop here and get into experiments later.

This is the triple axis spectrometer at Dhruva. I will try to give examples in inelastic neutron scattering from some other sources also. Typically, the triple axis spectrometer is like this, this is the huge monochromator drum (for arresting harmful radiation escaping from the reactor core) at the center of which there is a monochromator.

This photo I have shown you earlier also and you have seen that the monochromator drum contains a monochromator at the center of it. Here is the sample. So, this is the second axis. This is the first axis and then around the sample, you have got an analyzer, which rotates along with the detector in a $\theta - 2\theta$ mode. So, these are the three axes.

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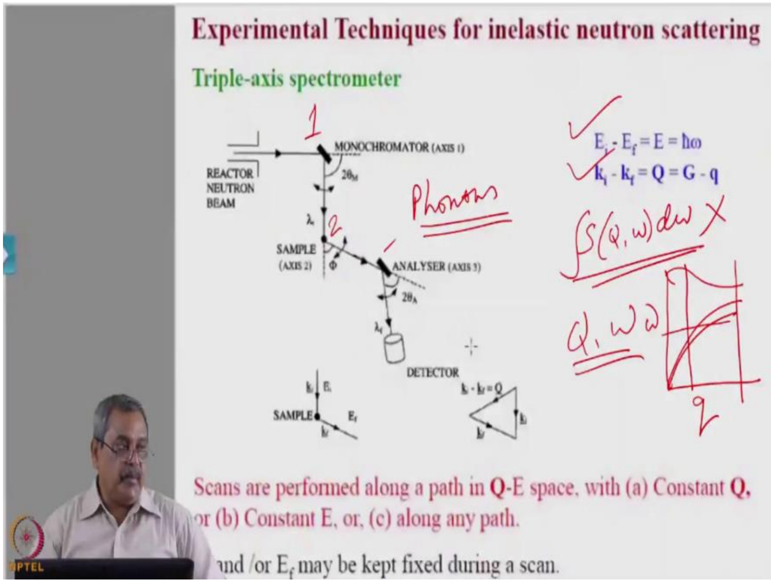

This is how the diagram looks like. You can see that in the triple axis spectrometer, we have as first axis a monochromator, second axis is the sample axis because you need to orient the sample and the third axis is an analyzer for energy analysis of the scattered beam. In earlier experiments on structure, we did not have this, because we were doing diffraction, we were integrating $S(Q,\omega)$ over ω and we only had a detector for diffraction data.

Now, we cannot do this. We have to do the energy analysis of the scattered neutrons. We need to have conservation of energy and conservation of momentum in this experiment. So, scans are performed in a certain path in the Q, E- or Q, ω - space i.e in the energy transfer space.

If these are phonon dispersion relations either I can do a scan with a constant value of Q and by varying energy transfer or I can do a scan on constant ω in the space by varying Q. Mostly E_i and E_f may be kept fixed and we can keep varying the Q by going to different angles or we can manipulate in a way where Q is kept fixed, and we go to different final energies. Usually, incident energy is kept fixed and the final energy can be varied by changing the analyzer angle. Both the scans are possible which we will discuss on the next day. But this is the basic arrangement of a triple axis spectrometer.

This is the most used spectrometer for phonons. There are other spectrometers which I will come to, like filter detectors spectrometer and quasi-elastic neutron scattering spectrometer where you look for stochastic motion or molecular vibrations. But, triple axis spectrometer is generally most favored for phonon measurements. With this I stop today.