Neutron Scattering for Condensed Matter Studies
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Week 11: Lecture 28B

Keywords: Stochastic dynamics, Doppler shift, QENS, Self-correlation function, MARX-Mode detector

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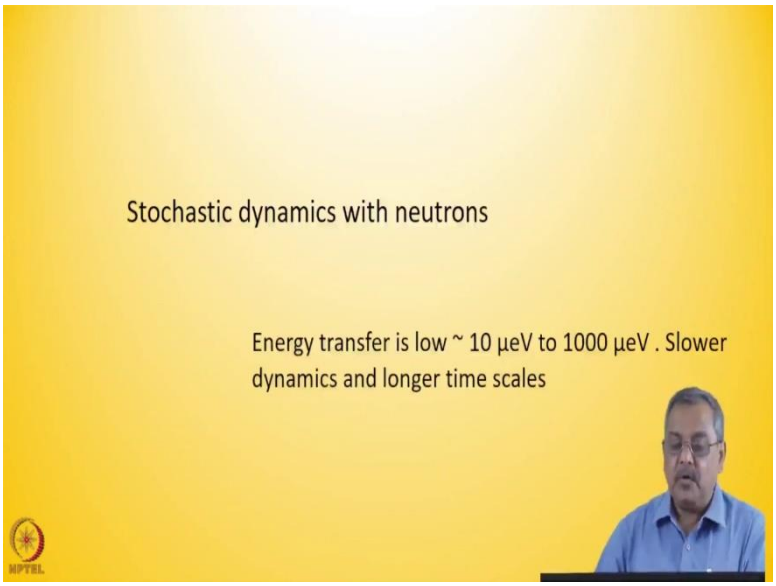

I will continue with inelastic neutron scattering for stochastic dynamics in materials with neutrons. What do I mean by stochastic dynamics?

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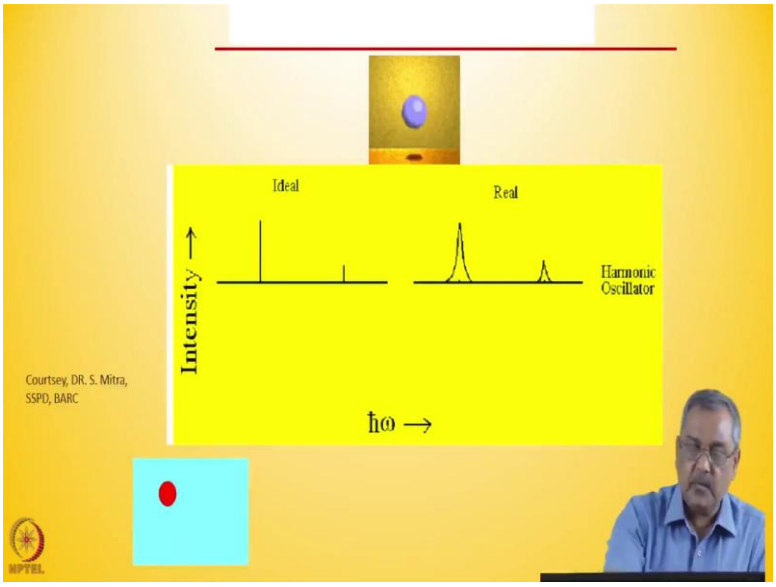

Here, this is a ball bouncing from the ground. This is a periodic motion. Whereas, let us consider this is a hydrogen atom (in H_2O), which is diffusing, let us say in water. This motion is stochastic. We know that it is like Brownian motion and that is the difference between a periodic motion (bouncing ball) and a stochastic motion (H_2O molecule in water).

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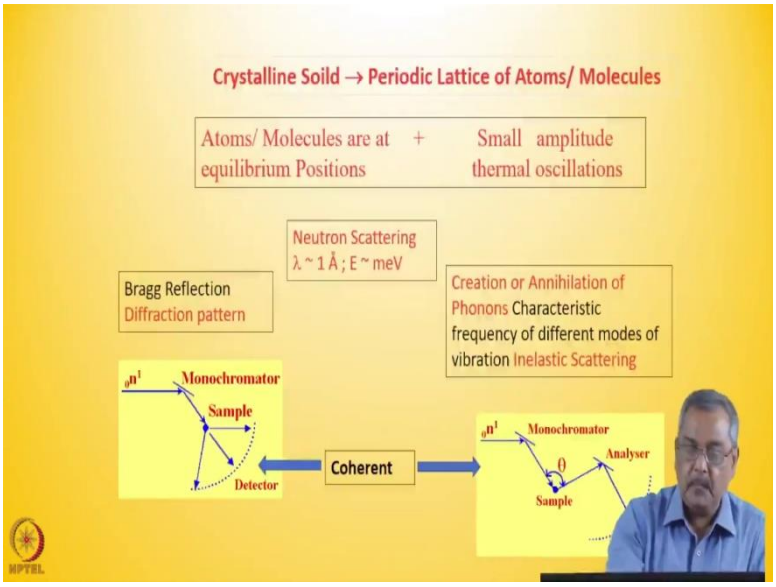

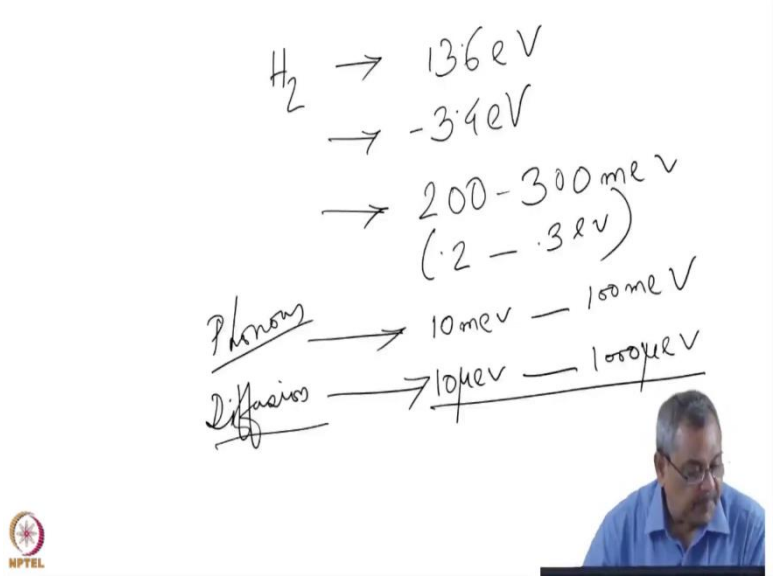

For this I need to give you an idea about the energy scale. Let us do an energy hierarchy, high to low. We know, a hydrogen atom has ionization energy is of ~13.6 eV. The first excitation energy is around -3.4 eV. Vibrational modes of hydrogen will be around 200 to 300 meV or 0.2 to 0.3 eV. These will have a strong overlap with the phonon energies. Phonons will have typical energies around 10 meV to 100 meV. Most of the instruments in the world will go at best up to 100 meV. So, there is some overlap (with vibrational modes) , but of still lower

energy. Then I will go diffusion. This is a stochastic motion which I am going to discuss in this part.

Here, we may be talking about energy transfer of 10 μeV to about 1000 μeV. This is the range of energy transfers that we need to go ahead with if we want to talk about or understand diffusion in solids (or liquids). With this let me go ahead and introduce you to diffusion.

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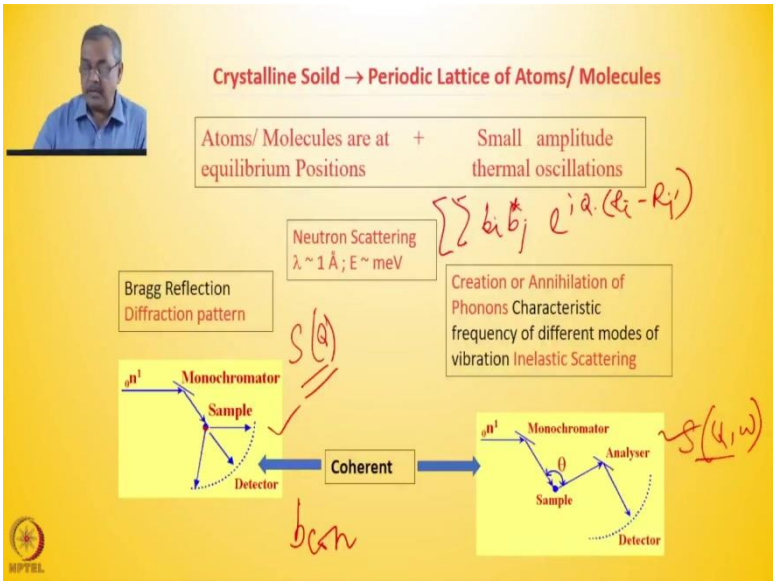

So far what we have discussed is this, please see the sketches. I had talked about diffraction where we had a neutron beam hitting a monochromator, coming to a sample and then we had a detector/detectors surrounding the sample. This was, as we talked about, S(Q) and here we were just bothered about in which angle the neutrons have gone and no energy analysis was done.

In case of phonons, we had a monochromator and the sample, but we also did energy analysis, following the scattering. So, in diffraction we had measured $S(Q)$ while here (for phonons) it was $S(Q, \omega)$. But in both these cases, they were coherent processes. In case of diffraction, if you remember, we used the expression $b_i b_{j'}^* e^{-iQ.(R_i - R_{j'})}$ when we talked about the scattered intensity. And in case of phonons also we were talking about coherent motion of atoms and molecules in a crystalline solid. So, both of these were coherent, and we use b_{coh} to understand these structures or dynamic. So, we will use samples with large values of b_{coh}. Except for the fact that for density of state measurements, I can use a sample with a large b^2 value because there was an incoherent approximation to coherent structure.

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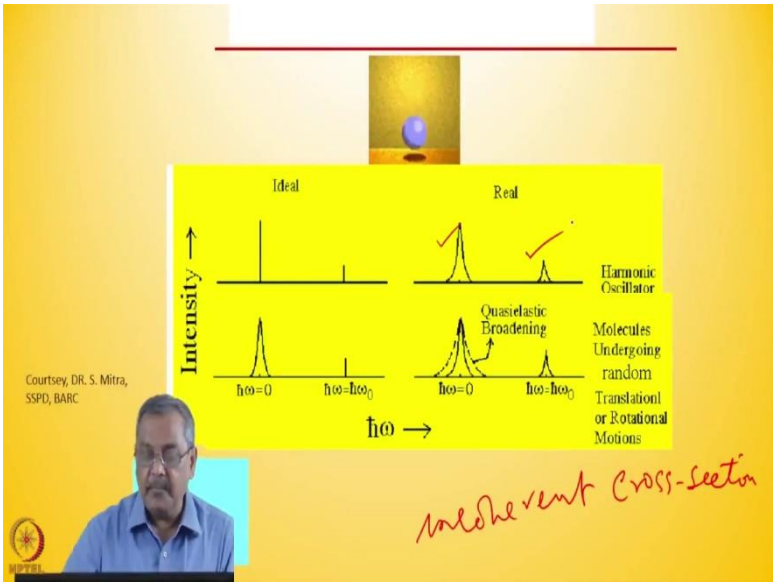

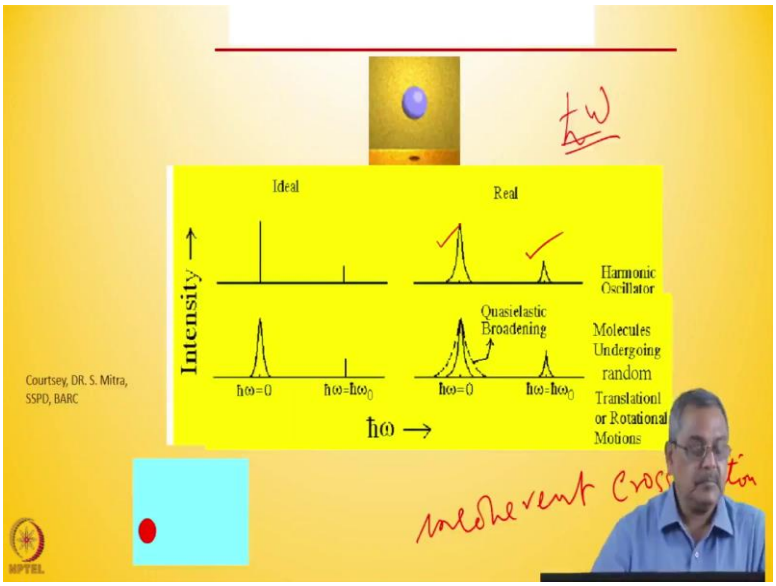

Now we will go ahead and discuss stochastic motions. Here, we will be talking about incoherent cross-section and we will be talking about self-correlation of an atom with itself in time. When we talked about vibrational energies, as I showed you 200 to 300 meV, then there will be a peak, which you can see in Raman scattering or even a neutron scattering at an ω value corresponding to the energy of that particular vibrational mode periodic motion.

For a harmonic oscillator, this is the ideal case and this is a resolution plotted.

In case of stochastic motion, it is the Doppler shift.

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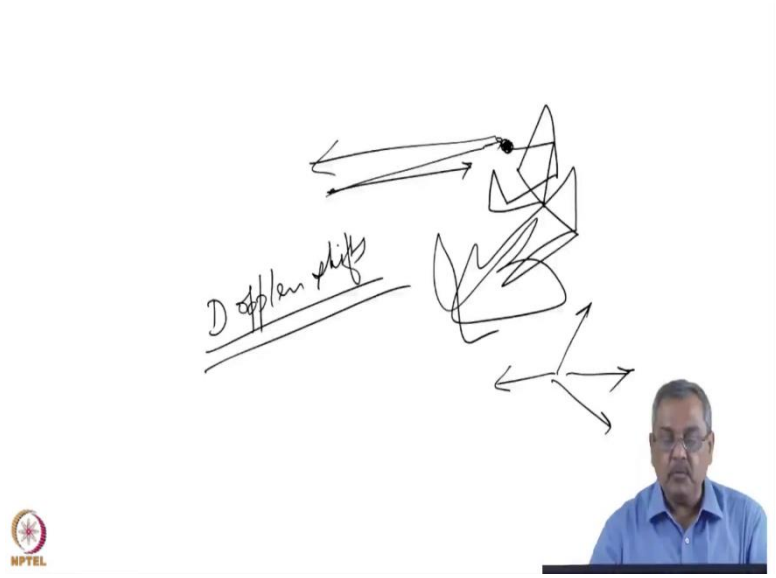

The way which I have to explain is that a neutron comes and hit an atom is undergoing a random motion in a liquid or in a solid. This neutron hits it and goes back and this may be moving towards the neutron or away from the neutron or in some other direction and this Doppler shifts the neutron energy. And neutron energy gets a broadening.

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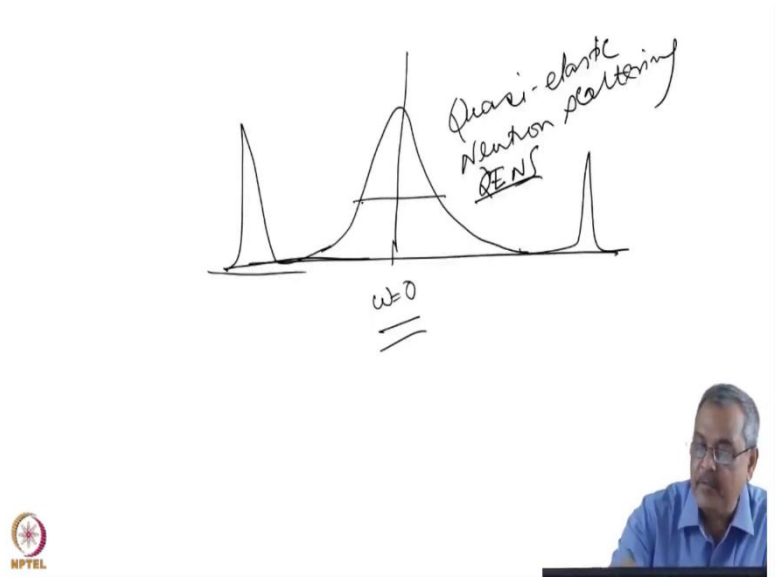

Now, the data will look somewhat like this. If I consider $\omega = 0$ as a new energy transfer, now, this will get broadened. The inelastic will come somewhere far away from the $\omega = 0$ line. That is why it is called quasi-elastic neutron scattering, or QENS. Here, what I am looking at is the broadening of the elastic peak due to motion of the molecules that Doppler shifts the atom and this width gives me information about the diffusion in the medium. By medium I mean it can be liquid or it can be a solid.

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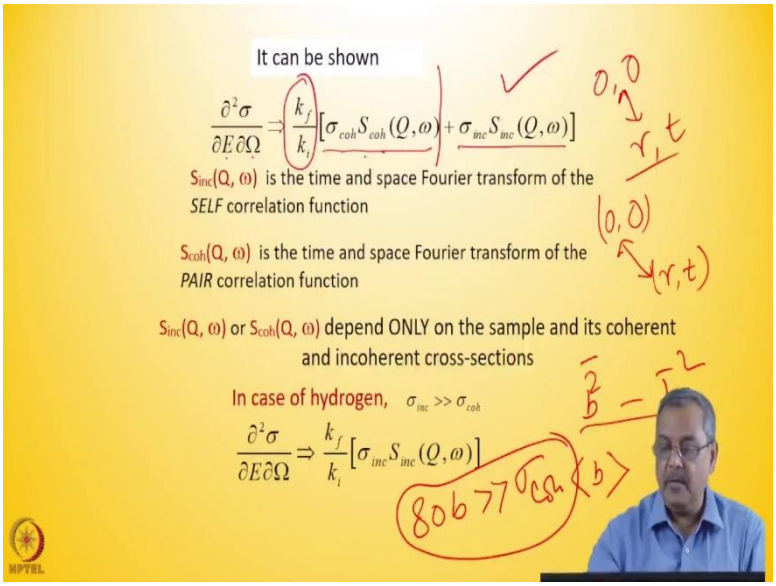

Now, let us first look at the double differential scattering cross section $\frac{d^2\sigma}{dEd\omega}$, giving scattered neutrons per unit solid angle per unit energy interval. In this relation, $\frac{k_f}{k_i}$ term is used for normalizing the flux by the ratio, number of neutrons coming in by number of neutrons going out. The number of neutrons going out is proportional to the velocity at the final energy energy E_f. And there is a number of neutrons coming in with an energy E_i and the velocity given by proportional to k_i.

In the scattering cross-section, we have two parts; one is coherent part another one is the incoherent part. This part (coherent) gives me pair co-relations. Whether structure or dynamics, it talks about two particles; one particle at one point at a time and another particle at another point at another time. It is a particle at time $t = 0$ at the origin (arbitrary), another particle at position r at time t.

Now, when we talk about incoherent part then it is only about self-correlation of a particle, that means, if the particle is at origin $t = 0$, it tells about the probability of the same particle at a position r at time t. And there are the different particles when we talk about coherent. That is why, in structural work at temperature T equal to 0, the position of one particle in a crystalline lattice tells you the position of all other particles. In case of phonons, the position and velocity of a particle at one position tells me the position and velocity of all other particles, they are related through phonons.

S_{inc} and S_{coh}, depend only on the sample and its coherent and incoherent cross-sections as I discussed earlier. that incoherent cross-section is $\sigma_{inc} = 4\pi(\overline{b^2} - \bar{b}^2)$ and the coherent scattering cross-section is related to average value of b. $\sigma_{coh} = 4\pi\bar{b}^2$. This is the average part, it comes here, and the incoherent part comes here.

In case of hydrogen σ_{inc} is nearly 80 barns is much greater than its σ_{coh} or scattering cross-section of many other elements Hence, when we talk about self-correlation functions and try to do an experiment, unlike all other experiments which we discussed so far, were actually pair correlation function-based, hydrogen is desirable atom as this has got a very large cross-section.

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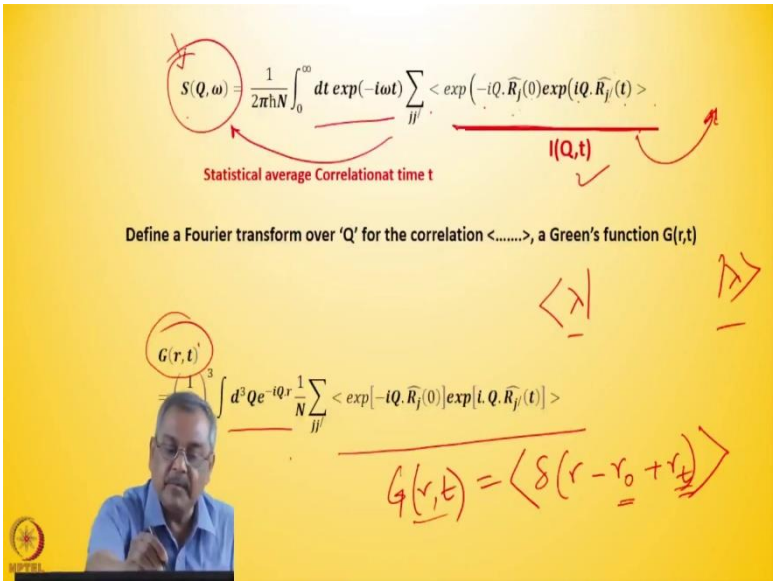

I discussed this part earlier, when I introduced the scattering law. If you remember that in the intermediate scattering function, I had a statistical average between the initial state of energy λ. What I calculated was actually, correlation function for the particle j at $t = 0$ and the particle j' at time t. This is the correlation function in intermediate space given by $I(Q, t)$.

Now, Fourier transform of $I(Q, t)$ over time takes me to the scattering law $S(Q,\omega)$. This is what I measure in a neutron scattering experiment. And the other way around, if I take a Fourier transform of $I(Q,t)$ over momentum *'Q'*, I go to $G(r,t)$ which is in real space (and time). So, if I go from here using a time integral, I go to $S(Q,\omega)$ which we measure. If I take a Fourier transform over Q as I wrote here, I go to the correlation function in the real space and time.

Now, $G(r,t)$ is, if I considered the same particle classically, it means $\langle\delta(r - r_0 - r(t))\rangle$, average over all the atoms and molecules in the system. This tells me that given a particle at

origin at time $t = 0$ what is its probability being at r at time t, this is $G(r,t)$ which we will get if you can get it from a $S(Q,\omega)$.

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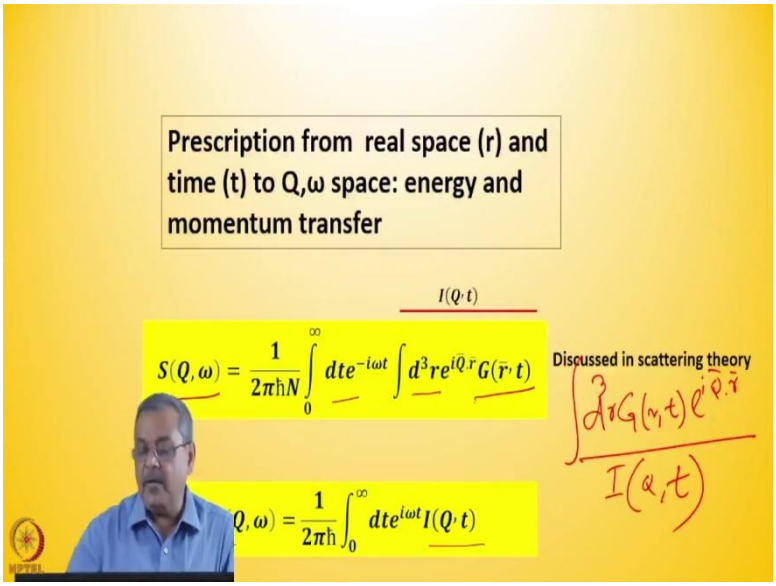

Now, this is what I mentioned specifically, that double Fourier transform of $G(r,t)$ over time gives and space gives me $S(Q,\omega)$ and single Fourier transform of $G(r,t)$ over space gives me I(Q,t) whose Fourier transform over time takes me to $S(Q,\omega)$. This was just to remind you.

So, if I know by some model what is the expression/form of $G(r,t)$, I can estimate what will be the analytical form of $S(Q,\omega)$ or $S(Q,\omega)$ I can model into $G(r,t)$, and get information about the system, specifically about the diffusion constant.

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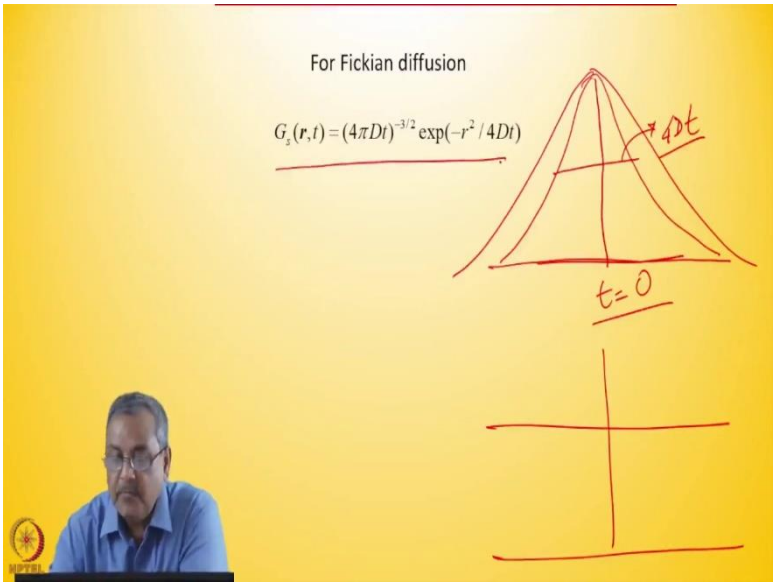

For Fickian diffusion this solution is known, G_s means the self-correlation function. This is easy to explain; suppose a particle is at origin at time $t = 0$, this function is a delta function. Now, as time goes the particle diffuses and there is a Gaussian distribution regarding location of the particle with time. The width of the Gaussian function is $4Dt$ at time 't' with respect to the particle at origin (arbitrary) at $t = 0$. That means, as time increases this Gaussian becomes broader and broader and ultimately at t equal to infinity this distribution becomes flat, i.e. the particle may be anywhere. So, this is the relationship that is valid for Fickian diffusion.

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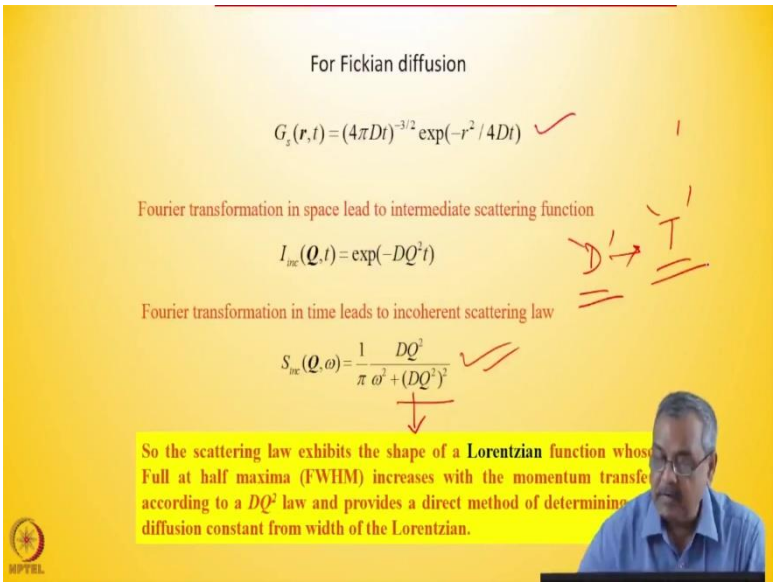

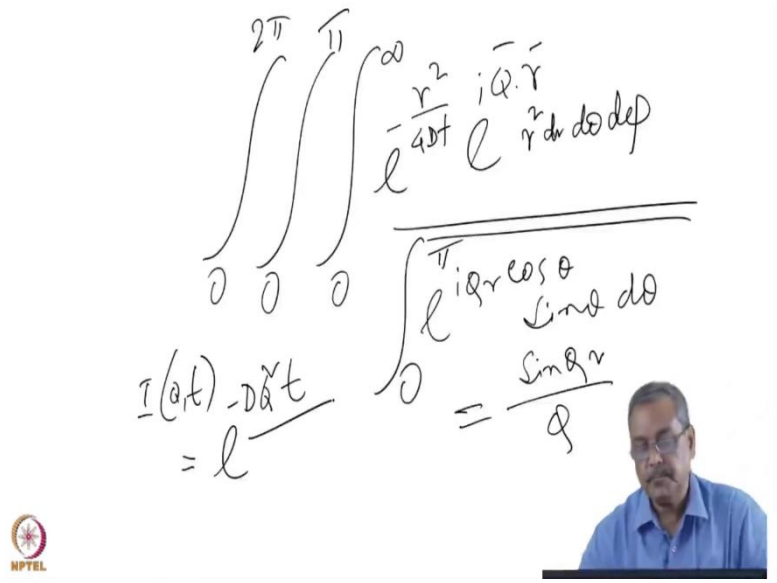

Now, let me come to the Fourier transform of the Gaussian because I need $I(Q, t)$ and $S(Q,\omega)$. Please note that for the term $\exp(-r^2/4Dt)$ in the expression of $G(r,t)$. I can do a Fourier transform over space,

$$\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} e^{-r^2/4Dt} e^{iQ.r} r^2 dr d\theta d\varphi .$$

I leave this integration to you. You can write $Q.r$ as $Qr\cos\theta$ and then the integration over theta can be written as $\int_0^{\pi} e^{iQr\cos\theta}\sin\theta\, d\theta$ which is equal to $\frac{\sin Qr}{Q}$. I leave it to you to show. Then you have to do a integration over r^2dr. And ultimately the intermediate scattering function will be $\sim e^{-DQ^2t}$.

Now, you need one more Fourier transform and you get $S_{inc}(Q,\omega)$, which is a Lorentzian. So, the scattering law for the self-correlation function starting from here shows a Lorentzian whose full width at half maxima is dictated by DQ^2. Now, if I can do this experiment, that means, measure $S_{inc}(Q,\omega)$, at various Q values, then you can see that the width of the Lorentzian will vary with DQ^2 and from there I can try to get information on the diffusion constant *'D'* interestingly. The width of this Lorentzian is typically tens of micro electron volts to hundreds of micro electron volts. So, this is a very low energy transfer experiment in which if we measure the Lorentzian, actually it is a Lorentzian convoluted with a Gaussian resolution function known as Pseudo-Voigt function from which we have to find out the value of DQ^2 and further plotting DQ^2 at various values of Q will give me the diffusion constant in the system. If the

temperature of the experiment is *T*, then we obtain at the temperature *T* what is the value of the diffusion constant.

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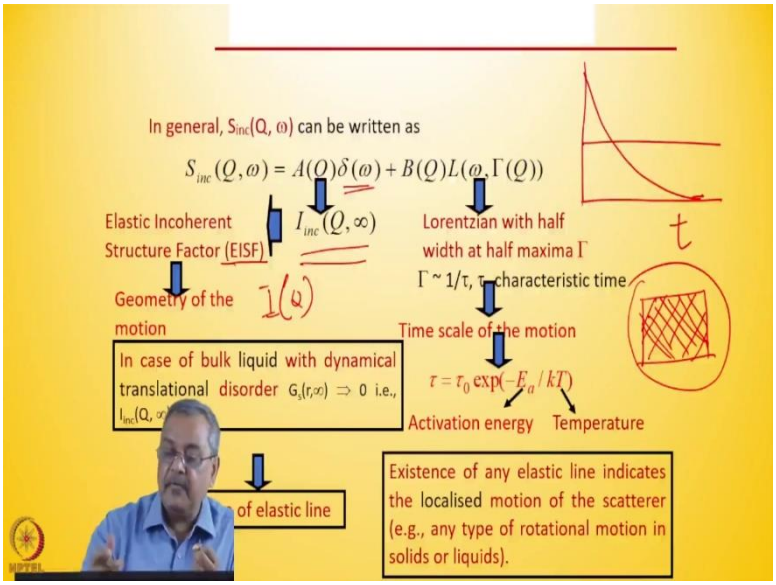

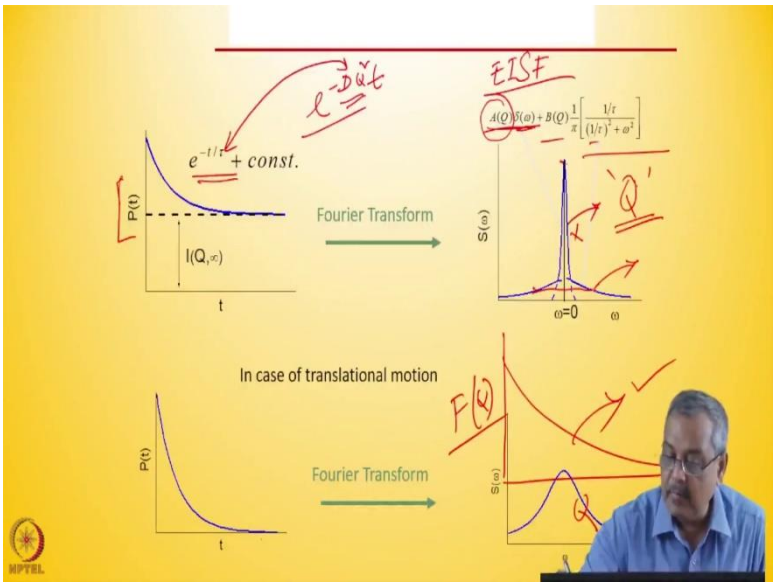

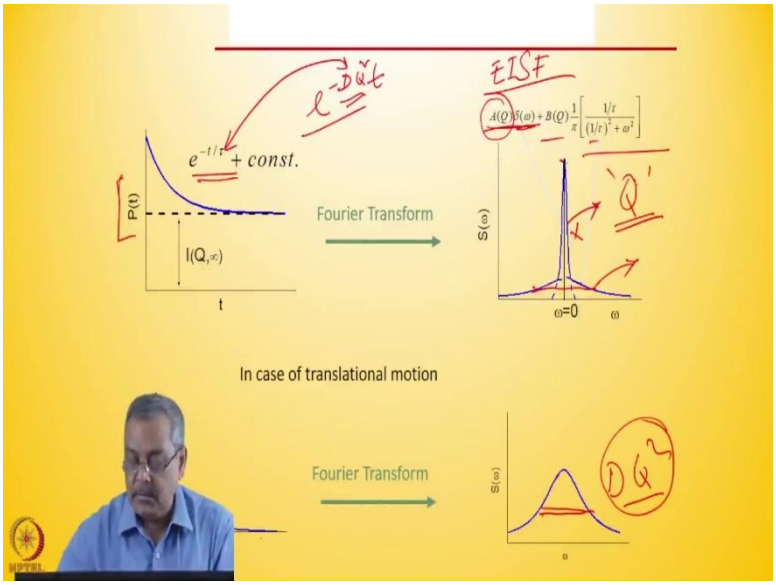

Now, there are two issues. One is that S_{inc}, of course, it has got a part that is Lorentzian as I wrote here because of the time correlation or diffusion. But there is another part where if I have a position correlation that is going to 0, another kind of correlation. Suppose an atom, say a hydrogen atom, is inside a box of finite size, then if I consider at time t equal to infinity, this particle due to stochastic motion will get uniformly distributed inside this box.

And so, now, the $I(Q,t)$ at $t = \infty$does not go to 0, but goes to a finite value. This finite value is because the particle is in a box or in a cage of finite size. If I say, I do not know the dimension of the cage, but studying this distribution $I(Q,\infty)$ we can estimate the dimensions of the cage. We can see that since the particle is distributed inside the cage, the correlation function does not go to 0 and then I can write it as $I_{inc}(Q,\infty)$, Because at time $t = \infty$ it gets distributed in the box uniformly, It gives an additional factor in the scattering law called elastic incoherent structure factor (EISF).

So far whatever we discussed, that elastic factor is always coherent, structure factor is always due to coherent scattering. A single particle, at $t = \infty$, it gets distributed inside a box, then this is like a form factor of an atom. We will be observing in terms of intensity, as a delta function at $\omega = 0$, as a function of Q, which is known as elastic incoherent structure factor.

This plus we have a Lorentzian with half width at half maxima~ DQ^2. The temporal relationship is~ $e^{-t/\tau} + constant$. So, one is that the probability of the same particle as $t = \infty$ which has a uniform value depending on the cage size and there is also a time dependent $e^{-t/\tau}$ part.

Now, the time dependent part is $e^{-t/\tau}$; earlier also I wrote e^{-DQ^2t}. So $\tau = 1/DQ^2$, the timescale of motion and the diffusion constant are related and then I have an $A(Q)$ term which is elastic incoherent structure factor (EISF), , because though this is incoherent scattering self-correlation but the particle, if it is in a cage then it has got a structure factor centered at zero energy transfer and a Lorentzian for the dynamics, with a pre-factor. Of course, as I wrote here, there will also be an instrumental resolution factor as well. So, this is the resolution factor, this is the Lorentzian, and this is the elastic incoherent structure factor. And the Fourier transform of this one will give me a Lorentzian whose width will give me $1/\tau$ or DQ^2, both are correlated. And also, one elastic factor for the diffusing particle in a cage. The elastic factor should have ideally been a delta function, but, because of resolution, it is broadened. This experiment has a particular Q value since it is done at a certain angle, at a certain momentum vector transfer. The intensity of this elastic peak, because we know, when we did form factor, it goes like a form factor and falls as a function of Q. The intensity of this delta function EISF peak will depend on the Q value.

If I can estimate this fall through EISF vs Q plot, then I can talk about the dimension (and geometry) cage in which the particle is moving. So, interestingly, I can find out the diffusion constant from the width of the Lorentzian centered at $\omega = 0$, but also, from the intensity of the EISF peak, which is elastic incoherent structure factor, and its Q dependence will give me the geometry of the cage. I will come back to it once again.

If I consider that the particle diffuses to infinity, for example consider a water molecule in a glass of water. I can consider the dimension of the glass in our length scales as infinity. So, the water molecules can go anywhere and then my probability of finding the particle in some volume with time *t* goes to 0, because it has gone to infinity. And then in that case, we will not have a delta function elastic peak. So, this part (EISF) will not be there. We will get only the Lorentzian of width $1/\tau$ or DQ^2. And measurement at various angles or at various Q values will give me the width of the peak. And from there, we can find out the diffusion constant for the diffusing system.

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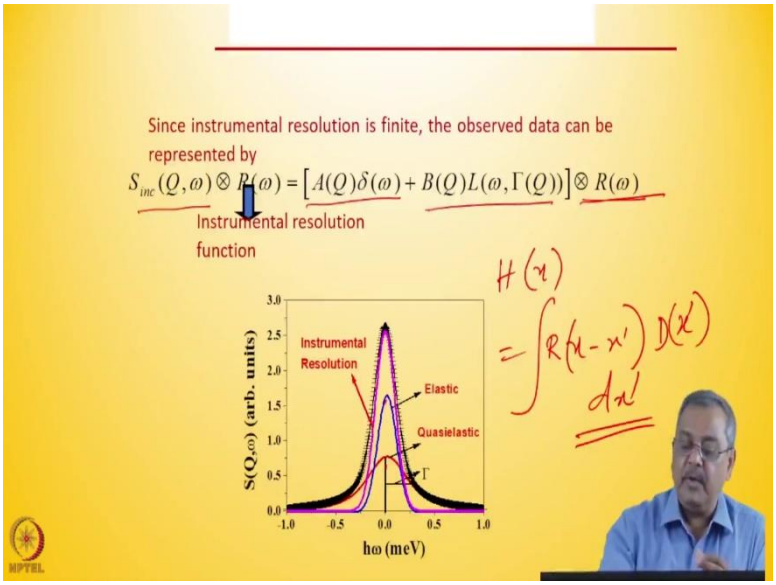

Now, the instrument resolution broadened $S_{inc}(Q, \omega)$ has got an elastic part (if particle is in a finite cage) and has got a Lorentzian part at $\omega = 0$ also broadened by the resolution. That means the convolution of the resolution function R with data D is given by,

$$H(x) = \int R(x - x')D(x')\, dx'.$$

So, every point of the data set is broadened by the resolution function and it will look like this plot. From this we have to deconvolute the resolution and then get the true width, from which we get the DQ^2 value.

This is the elastic part, and this is the quasi-elastic part, as shown. If it is a finite geometry of the cage or confinement for the diffusing particle, then we will have an elastic part as I showed you, elastic incoherent structure factor (EISF).

Please look at the top sketch. This is elastic incoherent structure factor. This is because the same particle as we go to t infinity, gets distributed over a volume. If it is a box then it is a finite volume or if it is an unbound movement then it can go to infinity. When it is a bound movement, then we get an elastic term.

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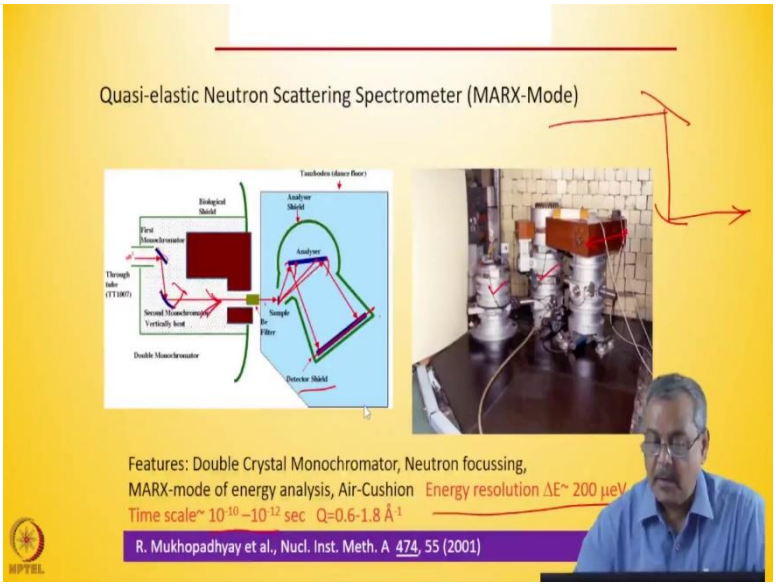

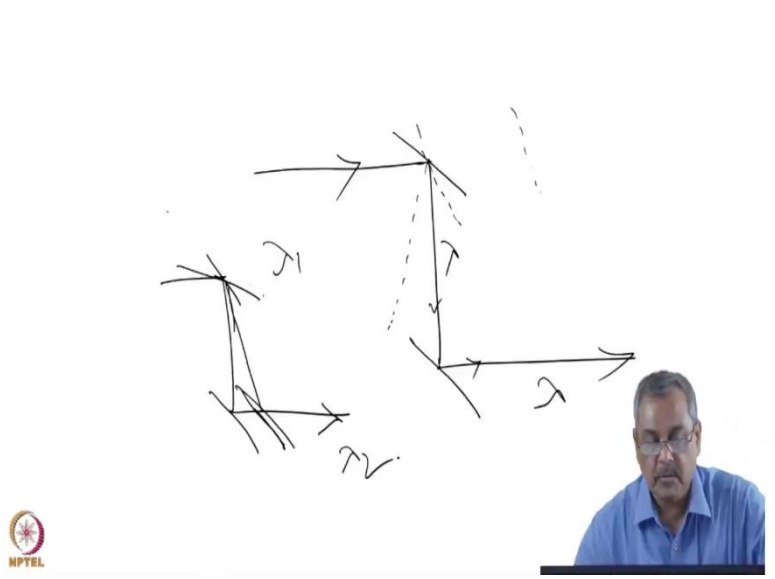

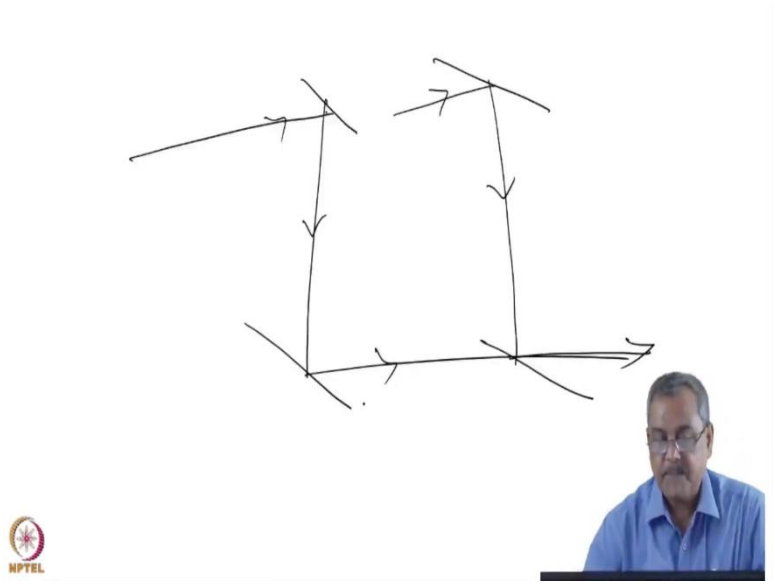

Now, I will explain to you with respect to the instrument that we can use at Dhruva, how the quasi-elastic scattering is done. This is a quasi-elastic neutron scattering spectrometer (MARX-Mode) at Dhruva. First, we have a double crystal monochromator for choosing the incident wavelength. This geometry is very interesting because we have two monochromators parallel to each other and one is a focusing monochromator vertical bend.

First, let me just draw two plane monochromators. This (1st plane monochromator) gives me a λ and this (2nd plane monochromator, parallel to first one) gives me the same λ after Bragg reflection. Now, if I change this angle (incident angle for 1st monochromator) to choose a different λ, then the reflected beam will go in some other direction. So, what we do actually is: translate and rotate the second monochromator back and forth, so that the emerging beam moves in the same direction though with a different wavelength.

So, by keeping the 1st monochromator fixed and only changing it's the incident angle, then the reflected angle () also changes and I can move the (2nd monochromator to catch the reflected beam. And both of the monochromators are rotated and the second one is translated to keep the outgoing beam direction same for two wavelengths. I hope I have been able to make you understand the geometry and working of the double monochromator system.

Now, if I rotate the first monochromator and the second monochromator and move them, then I can keep this outgoing direction fixed, but I can change the wavelength of the neutron going out. After that the sample is put. Here you cannot see the monochromators, you can only see the sample position and the analyzer. The analyzer is an extended crystal and you can see from here the angle neutrons make on the analyzer are different.

And because the angles are different, the neutrons of different energies will be reflected by different parts of the analyzer. So, that means, the detector, which is a one-dimensional detector here, captures scattered neutrons of different energy at two different ends. And ultimately, I get the distribution of energy, reflected from the sample in one scan of the detector or maybe I can extend the energy range of the scan by rotating the detector around the analyzer.

So, that is why you can see the analyzer arm is there and this is a one-dimensional detector arm and the detector can rotate around the analyzer to change the energy range. So, in one setting we get a certain energy range. And for this setting, the average Q value is given. I can have an energy resolution of 200 μeV and the typical Q range is 0.6 to 1.8 $Å^{-1}$ and timescales are 0.1 nsec to picosecond on this instrument at DHRUVA.

So, the energy resolution is around 200 μeV and I can study diffusion or stochastic motions using this spectrometer. Let me explain once again, the neutron comes on this monochromator and this is reflected by two monochromators and by rotating and shifting the monochromator on a rail I can keep the direction of the outgoing beam fixed.

Additionally, the second monochromator is not flat but it is vertically focused. Vertically focused means the beam is being focused on to the horizontal plane. So, that does not make my angle resolution poorer, but it gives me some gain in intensity. So, it is a vertically focused monochromator and it is in Bragg reflection geometry in parallel with the first monochromator. Now, if I change the incident angle, then I have to change the angle for the second monochromator here and I also have to translate it and then outgoing direction remains same in this setup. This is the double crystal monochromator at Dhruva.

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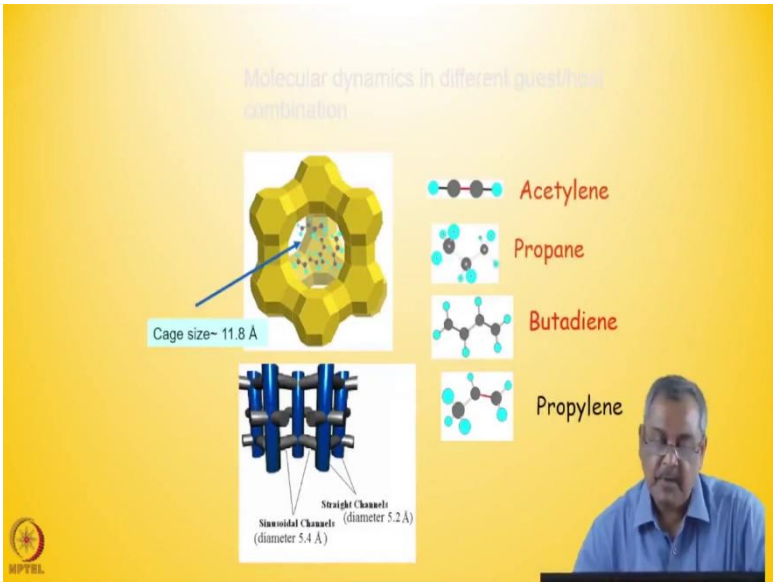

I will discuss some of the results obtained on this instrument. I will discuss movement of various organic molecules inside a zeolite cage. It is of deep technological interest to understand how these particles move in such cage materials.

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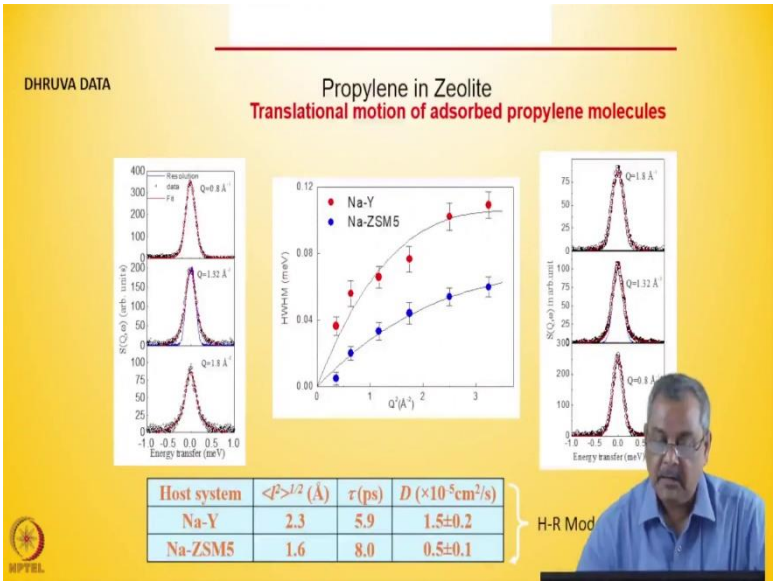

I will discuss these experimental results later.

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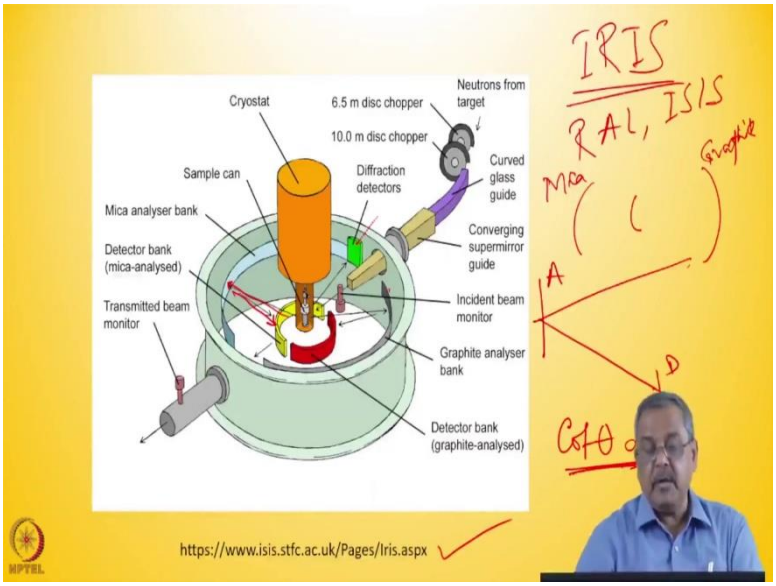

I will also show you in the same go, the IRIS spectrometer at RAL, Rutherford Appleton Laboratory, ISIS, which is a spallation neutron source. I will show you the main parts of the instrument. Of course, there is a cryostat for the sample. The neutron comes here; the sample table is at the center and there are two sets or banks of analyzers. One is a graphite analyzer bank, another one is a silica analyzer bank on a circle surrounding the sample. The detector bank, also on a circle surrounding the sample, but at a lower diameter compared to the two analyzer banks. The analyzer banks are mica and graphite, so, they give two different energy ranges for the scattered neutrons here and interestingly the detector is at a lower radius, working in back-scattered geometry.

So, here if you consider scattering vertical plane, this is the analyzer and this is the detector in back-scattering geometry. So, the neutron first goes to the analyzer and reflected back to the detector. So, this is almost backscattering geometry. And in the backscattering geometry, we know that the Bragg peak gets the best resolution because resolution vs angle goes as $\cot\theta\, d\theta$.

So, when you go to large angle, that is theta almost equal to 180°, then this gives me the best resolution in terms of energy or $\frac{\Delta d}{d}$ or in energy because in this case $\frac{\Delta d}{d}$ ultimately will translate into energy of the outgoing beam.

In the MARX-Mode detector at Dhruva, they have one position sensitive detector that can rotate around a graphite analyzer. At IRIS, they have detector banks, a large number of detectors most probably more than 50 and the details of it is available at this site.

And I will discuss results from both of these instruments for comparison. And, in the IRIS instrument, they also have kept a diffraction detector at the backscattering geometry. So, this can also give one long *d* (lattice parameter) structural information about the sample. Whereas, at the same time you can do quasi-elastic neutron scattering using this instrument. I showed you two instruments at different sources and I will discuss some results in the next lecture.