Neutron Scattering for Condensed Matter Studies

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Week 12: Lecture 30A

Keywords: Stochastic Motion - Instruments and Experiments, QENS, Spin-echo Spectrometer, Velocity selector

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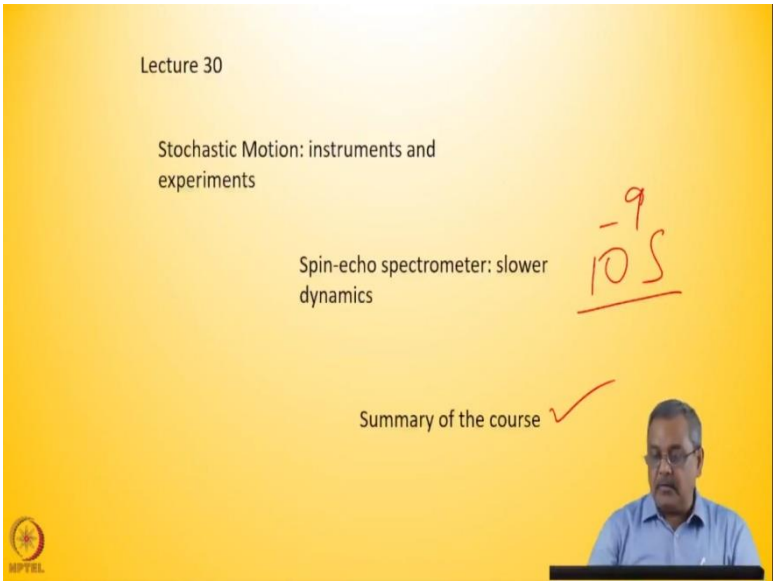

We are in the last stage of Inelastic Neutron Scattering. I was just discussing Stochastic Motion: possible instruments and the kind of experiments that have been done. Earlier I was talking about quasi–Elastic Neutron Scattering. I will give a few more examples in that field. Then I will explain to youa spectrometer known as spin-echo spectrometer which can be used for understanding slow dynamics, possibly the slowest dynamics with longest time scale of 10^{-9} sec in nanosecond range.

And in the second part of the talk, I will summarize whatever I taught so far in this course. Because it is important to tell you exactly how to go about your experiments and what analysis we have been doing regarding various neutron scattering technique.

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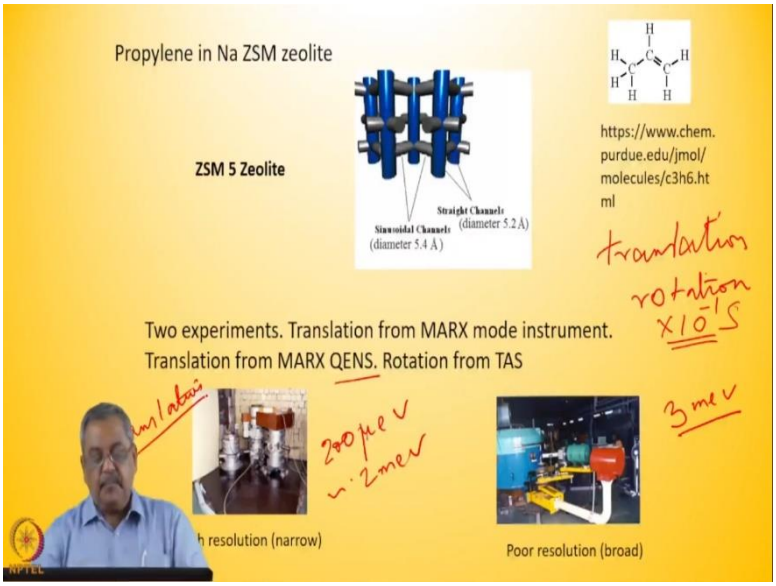

Now, coming back to stochastic motions using quasi-elastic neutron scattering; if you remember last time I discussed the dynamics of propylene molecule in Na ZSM zeolite which has got this kind of channels in it. And as I mentioned to you earlier also that often you have competing time scales which are quite different from each other present in the same system simultaneously.

In this system, there are translation of the molecules and their rotations in ZSM zeolite cages. The rotational motions are much faster, with almost a factor of 10 smaller time scale i.e 10^{-1} smaller time scale compared to translation. Translation is slower. The experiment was done in two different instruments with two different time resolutions. One is the MARX mode quasi-elastic neutron scattering instrument at Dhruva. Here, the resolution is around 200 μeV or aound 0.2 meV. The other instrument was Triple Axis Spectrometer (TAS) at Dhruva and here the resolution was around 3 meV. So, the resolution here is narrower by a factor of approximately 10. The translation which is slower of the two, was observed or the diffusion constant was determined using the instrument known as MARX QENS.

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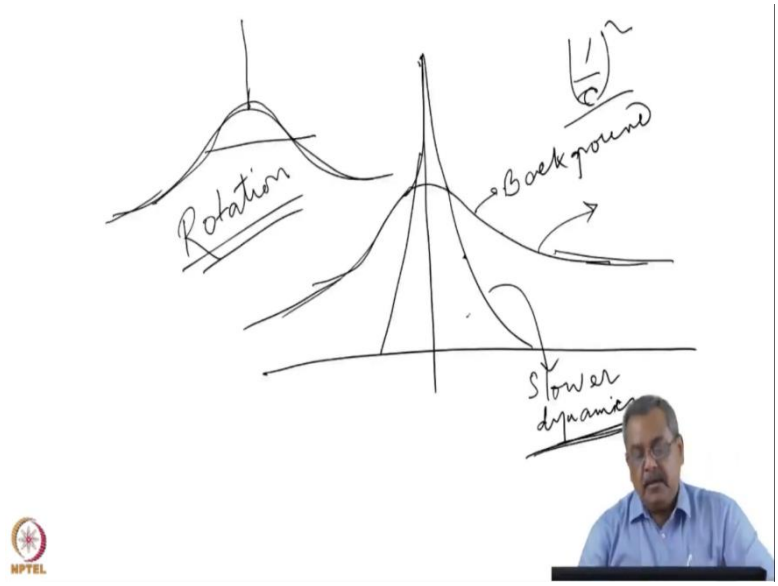

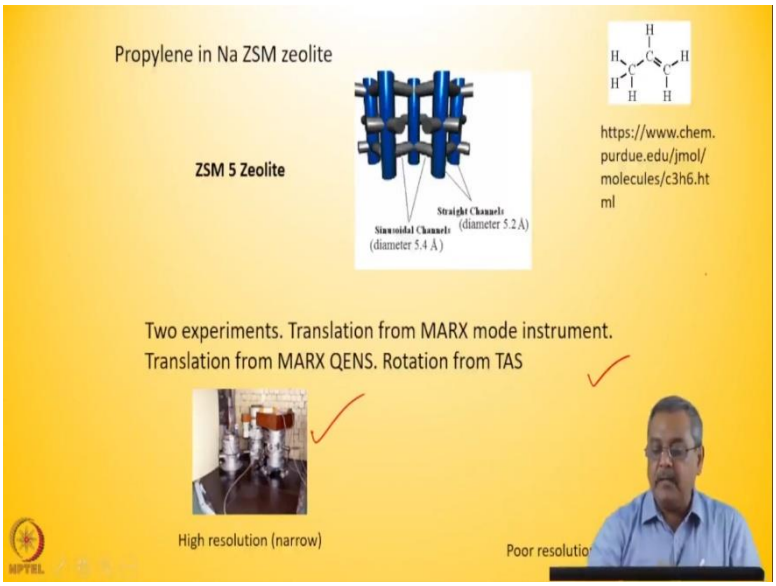

When I talk about two different time scales as I mentioned earlier that it is possible that both of the motions are quasi-elastic, but one is a narrower component and the other one is a broader component. The narrower component is associated with slower dynamics. Slower dynamics makes the associated time scale longer and so you see it as a narrower (in energy) component because, if you remember that the Lorentzian has a $\sim \left(\frac{1}{\tau}\right)^2$ width where τ is the time scale associated with the dynamics.

So, for translation, since, it is slower the Lorentzian is narrower. And here in this case, because the rotation is much faster, so it is broader part, it may be taken as a background for the

experiment in which I measure the slower translational dynamics. The quasi-elastic broadening represents the translational dynamics of the organic molecule.

On the other hand, when I go to an instrument which has got a poorer (or broader) resolution that is 3 meV in TAS, compared to 0.2 meV in case of the slower dynamics, in that case this part (QENS broadening due to translation) will become delta function. And I can measure the width of the elastic line over here that in the present case will involve rotation of the molecule.

What I wanted to emphasize or bring home is that to measure various time scales, we need instruments with different resolutions. And I discussed this with respect to two instruments, triple axis (TAS) and QENS instrument in Dhruva. But I will use an example where one will use other advanced instruments.

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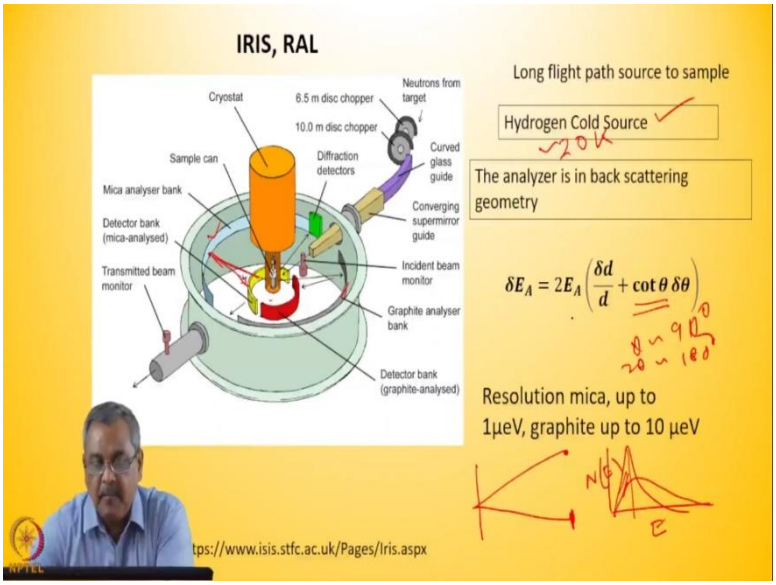

For example, this is the IRIS quasi-elastic neutron scattering instruments at ISIS spallation neutron source in Rutherford Appleton laboratory, UK. This works on time-of-flight principle. There is a long flight path from the source to the sample. After the sample, interestingly, you will find that there are mica analyzers and graphite analyzers. The scattered beam goes to the mica analyzer and comes back to the detector.

This is almost a 180° reflection. The scattering angle θ is around 90° and we know $\cot\theta$ gives the best resolution when θ is around 90° or 2θ is close to 180°. So, both the analyzers are at back scattering geometry. The analyzers are curved on a circle and the detector bank is at a smaller radius.

This is a vertical scattering geometry. The sample is here, at the centre. The reflected beam comes back vertically (scattering in a vertical plane) to the detector. The displacement of the scattered beam, between the sample and the detector bank is in a vertical plane. So, the detector is here and the analyzer is there the sample is over here. The beam goes to the analyzer and then comes back to the detector in a near 180^0 scattering.

It is not only that there is a horizontal angle, which is measured on the detector bank which determines the Q value, but there is also a vertical displacement of the beam between the analyzer and the detector. The scattered neutron is vertically displaced from the analyzer which sends it back to the detector.

In this kind of advanced sources, because we need low energy neutrons, it is perating on a hydrogen cold source. There is a nearly 20 K hydrogen cold source which shifts the spectrum of neutron energy, as I explained to you earlier that the thermal spectrum is shifted in energy. With a cold source and one has better intensity of long wavelength neutrons and you get more number of desirable neutrons over here.

The geometry is such that we have better resolution because the analyzer is in a back scattering geometry. You have higher intensity of long wavelength or low energy or cold neutrons. So, this is a high flux time of flight instrument which is there in a spallation neutron source. I will quickly present some result.

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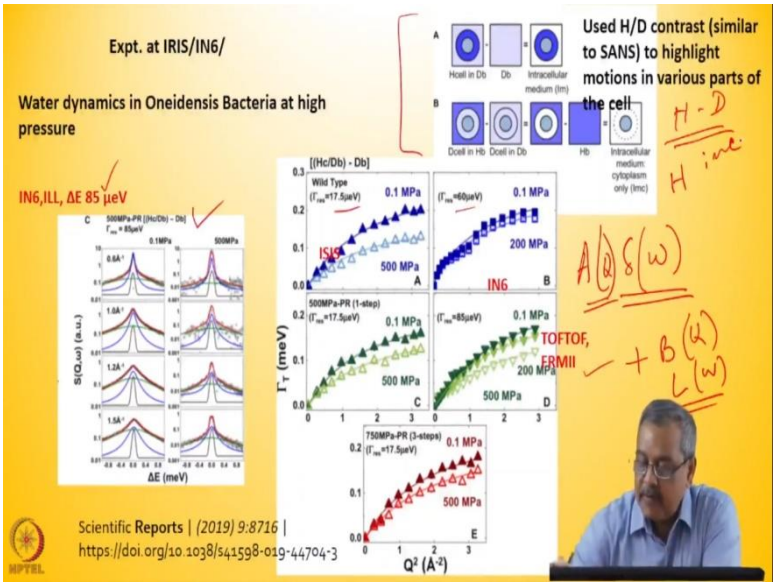

Interestingly, this result comes from experiment at three places/sources. It has quasi-elastic neutron scattering data which was done at IN6, ILL, Grenoble with an energy resolution of 85 μeV. It has also been done at ISIS, RAL where the half width at half maxima of the beam was around 17.5 μeV a factor of 5 down from ILL.

It was done at IN6 in Grenoble where the resolution was around 60 μeV and also it was done at TOFTOF at FRM II with a similar 85 μeV resolution. This is the quasi-elastic scattering where the experimental data has been fitted with a quasi-elastic part and an elastic part.

Because we know that if it is a diffusion over infinite length then there is a only a $\delta(\omega)$ term and there is no EISF term, because the hydrogen that we are discussing is diffusing to infinity. If it is a finite geometric diffusion then always, we have a $\delta(\omega)$ with a Q dependent form factor like term, which tells us the geometry of the cage in which the particle is diffusing plus we have also the Lorentzian in energy which gives you the quasi-elastic broadening and getting back to the diffusion constant that we can find.

In this case the elastic peak is shown and also the quasi-elastic fitted peak and then the full width at half maxima values are plotted vs. momentum transfer *'Q'*. But the highlight of this is for one sample in which attempt had been to find out the dynamics of water in Oneidensis bacteria, experiments were done at three different sources with three different resolutions.

In addition, the experimentalist used a hydrogen deuterium contrast. In case of quasi-elastic neutron scattering, we know that hydrogen has largest incoherent scattering cross section which is nearly 80 barns and hydrogeneous sample is used.

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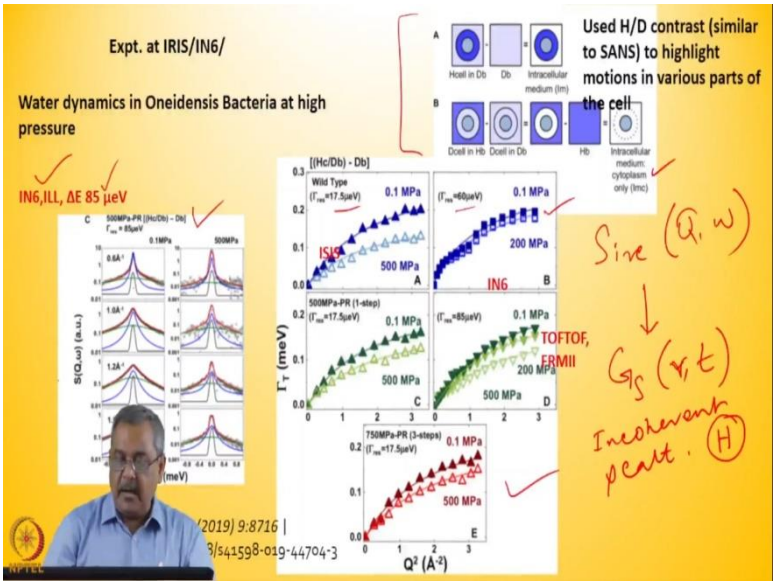

So, if we replace hydrogen with deuterium in parts of the bacterial cell then we can highlight the diffusion of hydrogen in some parts, because for $S_{inc}(Q, \omega)$ it is the self correlation and for measurement of this we need something which has got large incoherent scattering, in this case hydrogen.

Similar to small angle neutrons scattering or SANS, here also the experimentalists had used contrast by selectively deuterating a part of the bacteria. And this data is basically for everything which is inside the bacterial cell. But most importantly, this experiment was done to look at the dynamics of hydrogens or water in the cytoplasm of the cell.

Such kind of very slow dynamics in biological systems, I mentioned to you earlier, can be studied using quasi-elastic neutron scattering at various sources. I had given examples earlier from our experience at Dhruva and this example is a combination of three experiments: one at IRIS which is at Rutherford Appleton Laboratory, and IN6 quasi-elastic neutron spectrometer at ILL Grenoble with broader resolution, which will measure the broader part of the translational spectrum and also at TOFTOF FRM II and this result is a combination of data. Data is about full width at half maxima of the quasielastic peak. But the data refer to different kind of motions. The narrower resolution or the better resolution data will hide the slower motion and the faster motions will be described by full width at half maxima of the quasi-elastic peak.

This is what I wanted to show you regarding quasi-elastic neutron scattering from various samples. This was an example taken from biology which is quite common these days as people come to understand dynamics of various molecules. Possibly, quasi-elastic neutron scattering

is the only tool that can give you such slow dynamics in biological systems and its role is immensely important to understand structure also. I showed you earlier the structure at mesoscopic length scale using SANS and in this case dynamics inside a cell, the cytoplasmic dynamics was studied.

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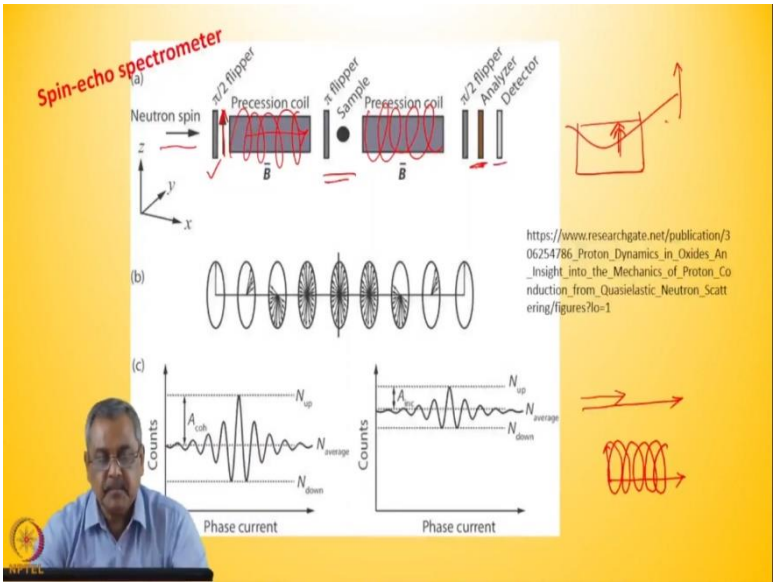

I want to bring you to another spectrometer, which is a very interesting spectrometer known as spin-echo spectrometer. How do we measure inelastic neutron scattering using a spin echo spectrometer? Here, first we polarize a neutron beam possibly by reflecting from a polarizing neutron supermirror and then we have a $\frac{\pi}{2}$ flipper.

Because this is reflected from super mirror having polarization in this direction. The reflected beam has the polarization direction which is parallel to the polarization in the supermirror plane. That means if I have the beam coming, it has got a polarization which is along the given polarization direction in the mirror.

There is a $\frac{\pi}{2}$ flipper here. Flippers I have discussed with you earlier. They are basically combination of magnetic fields to change polarization direction of a neutron beam. So, this $\frac{\pi}{2}$ flipper flips it by 90°. I have got a coil through which the neutron passes. The field is in this direction (along the beam direction). So, if the field is in this direction (along the beam direction) and the neutron spin is normal to it then as the neutron travels through the coil, it preceses around the field, which is called larmar precession. All of you are aware that a magnetic field forces a spin to precess, if it is normal to it.

After that I have got a π flipper. π flipper flips the polarization of the neutron by angle π and then there is a precession coil in which the neutron precesses in the opposite direction. And after that again there is a $\frac{\pi}{2}$ flipper and energy analyzer followed by the detector. So, what the spin-echo instrument does?

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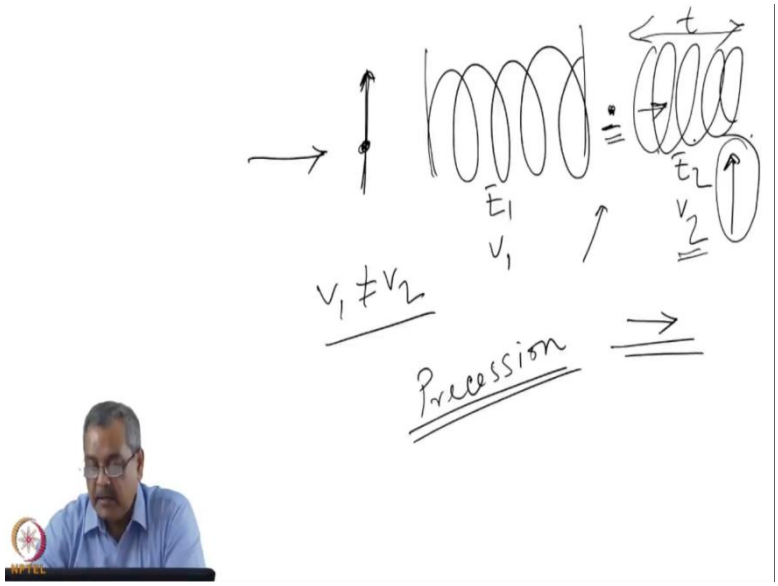

Basically, what it does is this.

First if there is a neutron with a single spin and it preceses, reaches the sample, gets scattered by the sample and then if I force it to precesses it in the opposite direction then if there is no energy exchange, the neutron spin will come out with the same spin over here.

Now, let us consider the case that there is an energy exchange between this neutron and the sample. If this is E_1 (incident energy) and this is E_2 (scattred neutron energy), the corresponding velocities are v_1 and i v_2 and $v_1 \neq v_2$ in case of energy exchange. These two parts, the coil before the sample and the coil after the sample, they are identical. That means in case of no energy exchange, there is an echo condition, it comes out (after second coil) with the same polarization. But in the case, if there is an energy exchange then the time spent in this coil (second coil) is different because the velocity is different. If it is a slower velocity, the neutron will spend longer time, if it is a higher velocity or higher energy then it will spend shorter time in the second coil. And this precession angle will not be same after the sample. It will come out with a polarization direction which is different from from the spin echo condition and this change can tag the energy transfer.

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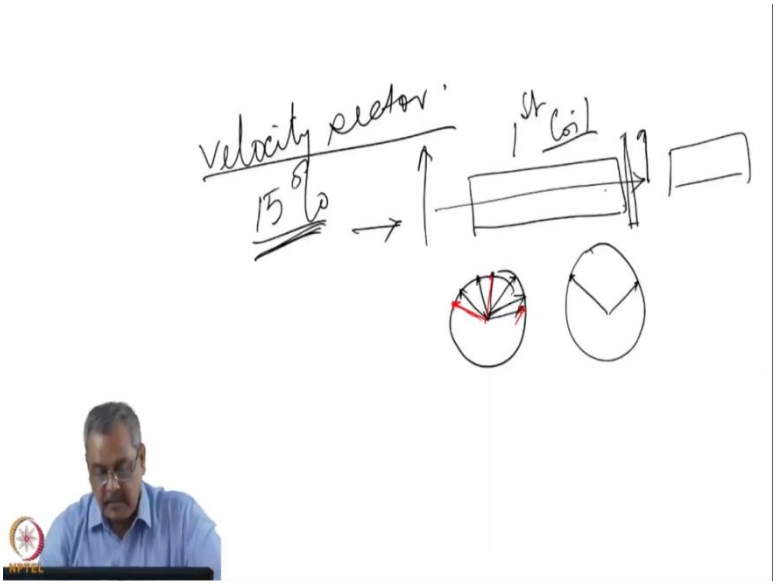

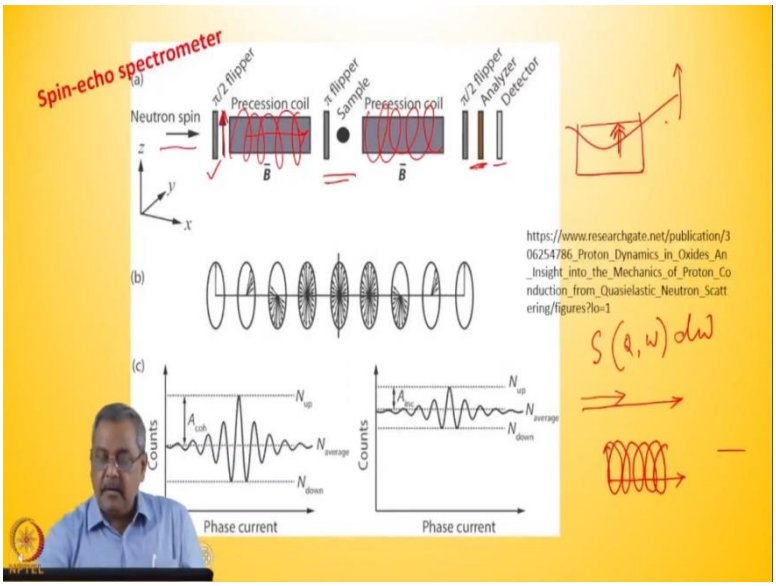

Now, what is done in reality? First one uses a velocity selector. Velocity selector is a monochromater which can give a broad energy spectrum; hence, have poorer energy resolution, typically around 15%. We have got a neutron beam which is passing through the first coil. I will show the neutron's passage as a block diagram. So, there is a neutron coming in this direction then it has been flipped by the $\frac{\pi}{2}$ flipper, and now, it is going through the first coil before the sample. Since, there is a velocity spread, so now, if I consider looking at the neutron from this direction, now the neutron spin will fan out. It will fan out because neutrons of different velocity will undergo different precession. These precessions can be as large as 20000, 10000 precessions inside this length of the coil. Now, it has fanned out. There is a π flipper in my schematic, so, it flips the neutron spin by π. So, here, for a distribution of the incident energy it has fanned out.

Let me just change the color a little bit in the sketch. The faster neutron possibly is here and the slower neutron possibly is here because of fanning out. The faster neutron has this angle and the slower neutron has this angle on an average. This is the angle of precession. Now, when I flip it by π then they interchange. This faster neutron by π flipping will go there, if you consider this as fastest. And the slower will go in the other direction, Once I have flipped it. If I took it through the second coil, say, without any energy exchange, I should have gone back to the same velocity distribution. But now, for inelastic scattering, this distribution of polarization angles will be different.

What one monitors is ccounts versus phase current because we keep changing the phase current. So, this is the counts N_{up} and N_{down} neutron. You can see depending on the intensity and precession, you have got an oscillatory input, N_{average} is basically this dotted line and this two shows N averages up and down. This is for the incoming and this is for the outgoing.

If I can measure this distribution in a detector using an analyzer then I can find out what is the intensity of these neutrons vs energy. And ultimately, I can translate it into $S(Q, \omega)d\omega$.

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This is a spin-echo instrument at NIST. These are the arms, the first arm and the second arm and this angle dictates what is the Q value of this instrument in an experiment.

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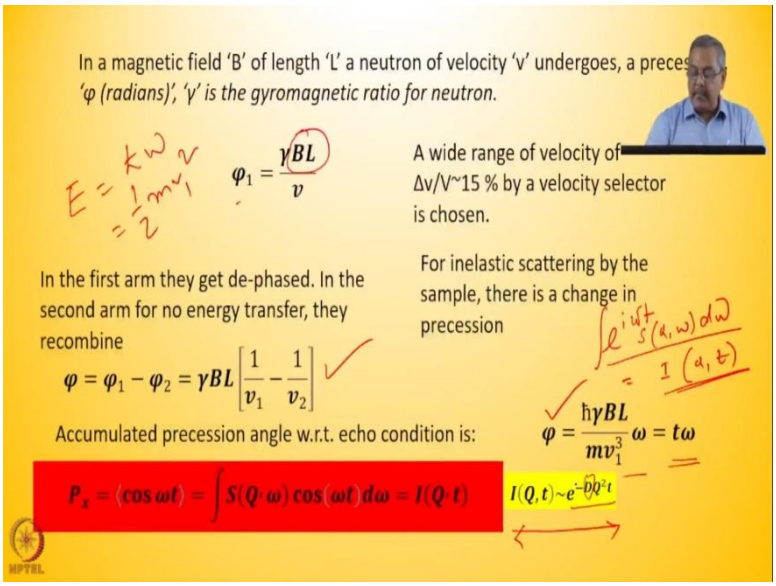

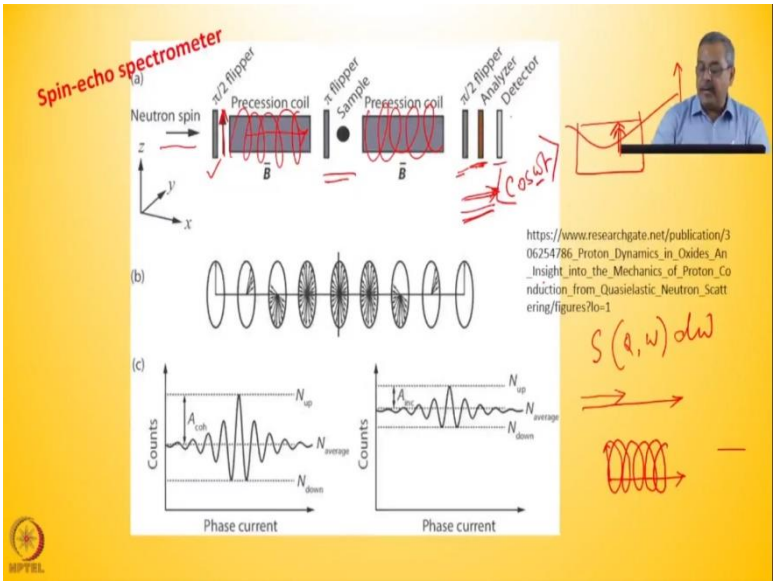

Now, let me just quickly tell you the algebra of this process. φ_1 is the precession angle. If the velocity is v then L/v is a time it precesses and γ is gyromagnetic ratio for a neutron. Then $\frac{\gamma BL}{v} = \gamma Bt$ is a precession that a neutron undergoes for spending time t in the field path, in the field B of length L.

, This velocity has a wide distribution and now, if the outgoing velocity is v_2 then two neutrons get de-phased with respect to each other because of different precession angle. The de-phasing I can write down as, $\gamma BL\left[\frac{1}{v_1} - \frac{1}{v_1}\right]$. For this φ phase difference. They are exactly same in resonance. I can write in terms of energy exchange $\hbar\omega$. So, I multiply that the numerator by $\hbar\omega$ and the denominator by $\frac{1}{2}mv_1^2$ which is the energy of the neutron. So, $E = \hbar\omega$ inelastic condition $= \frac{1}{2}mv_1^2$., I get this expression. The phase φ due to precession in radians is given by this expression. This is nothing but ωt.

After the instrument we have got a $\frac{\pi}{2}$ flipper. That flipper flips it to the direction in which the neutron spin came in. After you have got an analyzer, it analyzes the spin of the outgoing neutron and this spin precession, after the analyzer, depends on $\cos\omega t$.

Because $'\omega'$ is the energy exchange and 't' is the time it has precessed in the field, average value of $< \cos\omega t >$ over all the velocities is measured in the detector. Because analyzer does not do it spin by spin but it integrates over all the ω after $\frac{\pi}{2}$ flipper and then sends it to the detector.

That means what I measure is an average value of $\cos \omega t$, $\langle \cos \omega t \rangle$. And that average value of $\cos \omega t$ is nothing but $\int cos\omega t\, S(Q,\omega) d\omega$ is the probability of scattering with an energy transfer $< \omega >$ with the momentum transfer Q. ωt is the precession angle in the two arms and the de-phasing caused by that. And we integrate over all the energies.

But now, we know that $\int e^{i\omega t} S(Q,\omega) d\omega = I(Q,t)$. And if I do integration of $\int I(Q,t) dt\, dt$ we get $S(Q,\omega)$. The real part of that expression expression $\int e^{i\omega t}\, S(Q,\omega) d\omega$ the gives me $I(Q,t)$. So, the takeaway is that in case of spin echo what I am measuring is not $S(Q,\omega)$, but because this integration is done by the instrument, what I measure is $I(Q,t)$, the intermediate scattering law and for a Fickian diffusion, we know it is given by $e^{-DQ^2 t}$. So, I can directly fit the exponential function and measure the D values from the intermediate scattering law.

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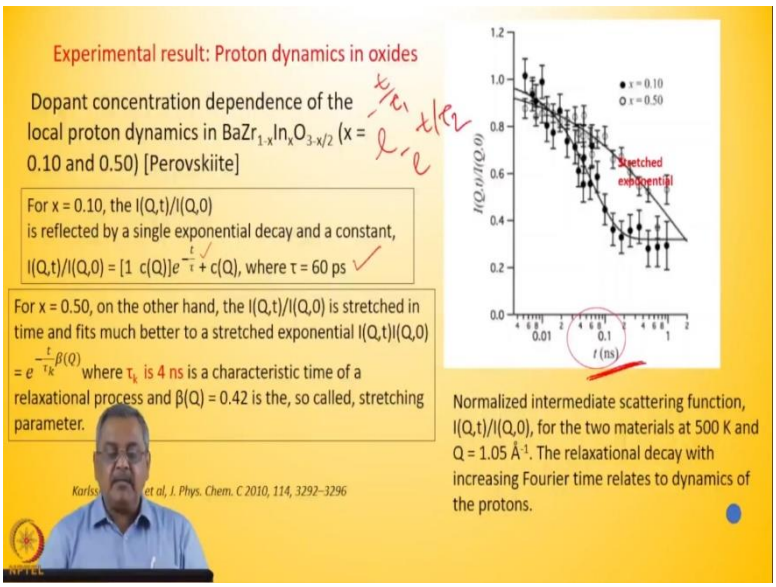

This is a result obtained from a spin echo measurement.

This is about proton dynamics in oxide materials. The sample is barium-zirconium-indium-oxide, $BaZr_{1-x}In_xO_{3-x/2}$, in which we have varied this x value, content of indium between 0.1 and 0.5. It is a Perovskiite structure. In the experimental result, which is normalized to $I(Q,0)$, one can see this fall. This is the intermediate scattering function that I am measuring directly in the experiment.

In this case, for x = 0.1, in $BaZr_{0.9}In_{0.1}O_{2.95}$, we have an exponential fall for the measured $I(Q,t)$. This was fitted with an exponential fall and a constant. Where this time constant or the residence time of a protonwas given by 60 picoseconds.

But when we go to x = 0.5, the intermediate scattering law becomes a stretched exponential and the authors mentioned that in this case the stressed exponential comes in because there are many exponential functions or there are many time scales associated with the residence time of the protons and all of them added together gives us a stretched exponential for the intermediate scattering law $I(Q,t)$.

This is a typical result from a spin-echo instrument. I would like to point out to you the time scale is in nanosecond. So, possibly this is the slowest dynamics that one can see in a neutron scattering experiment using spin-echo. Spin-echo instruments are available in several major reactor sources like ILL, Grenoble and at NCNR reactor, NIST, USA.

If you compare this with respect to let us say phonon dynamics which are actually in the range of 10^{-14}-10^{-15} second, it is a much slower dynamics, even slower than bulk diffusion that we discussed earlier. So, we can use the spin-echo instrument for observing such slow dynamics. With this, my discussions on inelastic neutron scattering ends. In the next part, I will quickly summarize what we did in the course till now.