Neutron Scattering for Condensed Matter Studies

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Week 12: Lecture 29A

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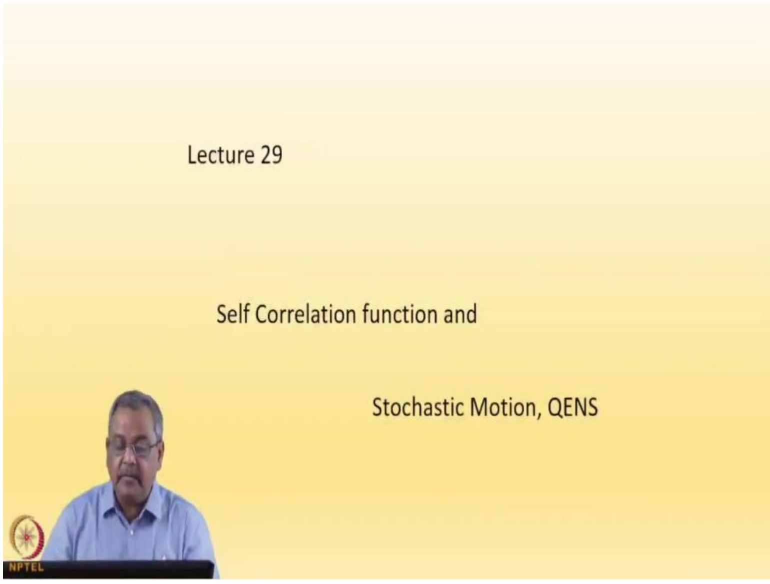

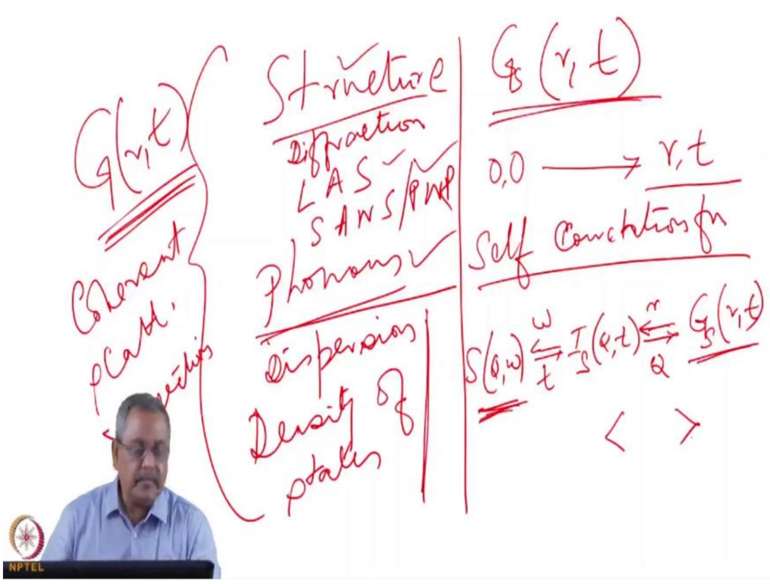

We will continue with our discussion on self-correlation function and stochastic motion. If you remember that I have continuously mentioned to you that for stochastic motion, we are studying self-correlation function.

I need to mention that in studies related to structures and phonons, like crystalline diffraction, short range correlation in liquid and amorphous systems, SANS for mesoscopic systems, Polarized neutron reflectometry, phonon dispersion relation then density of states; for all these studies coherent scattering cross sections are used. Because, for structure at any length scale that is short length scales in liquid and amorphous materials, crystallographic structure, or in mesoscopic structure, we are talking about how one particular atom or molecule or a scattering unit is positioned with respect to another one. So, we are talking about $G(r, t)$, when they are distinct particles. That is also true for phonons, because these are collective oscillation of atoms. So, there is coherence in their motion. And knowing the motion of one particle, we can always derive the position and motion of other particles. When density of states are simply an integration of over q, the phonon vector and it is also a coherent phenomenon. So, for all these (structure and dynamics) we use $G(r, t)$, and we use coherent scattering cross section. In these experiments, the incoherent scattering cross section is a nuisance, it is a background.

But, when we talk about self-correlation function, $G_s(r, t)$, in stochastic motion experiments, it is for the same particle which is at origin at time $t = 0$its location at a time 't' at a place 'r'; we find using probability, if it is a stochastic motion like diffusion. This is a self-correlation function. While we are discussing about self-correlation function, we are aware that we have $I(Q,t)$ which is a Fourier transform of $G_s(r, t)$ over r. If I come from r to Q in this direction or Q to r in the opposite direction it is $G(r, t)$ and then once more a Fourier transform over ω and 't' we go to $S(Q,\omega)$, the experimentally measured data.

In an experiment, we measure $S(Q,\omega)$ and we try to find out what is the $G(r, t)$? In the present case that I am discussing stochastic motion this $G(r, t)$ is specifically a self-correlation function$G_s(r, t)$. This is to the self-correlation function and what we get is the scattering law for the dynamics of a single particle, averaged over all the particles. So, we take an ensemble average and this is what we are looking for.

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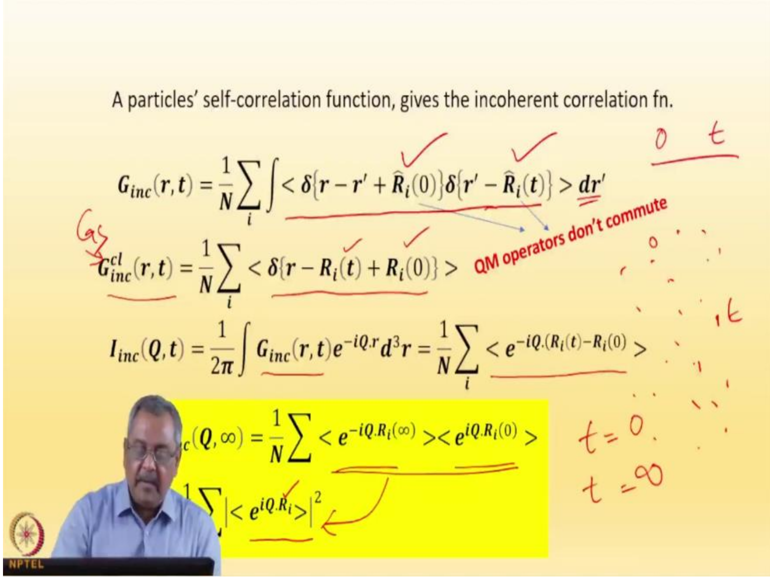

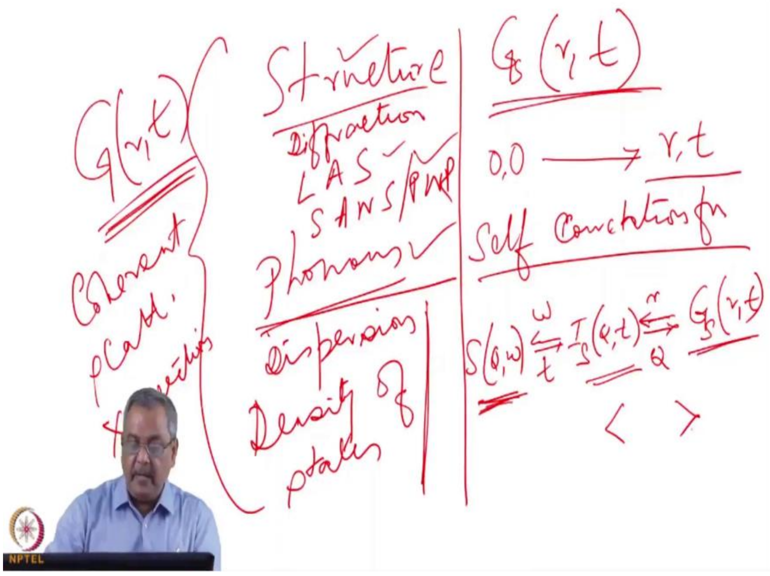

In quantum mechanical terms, I can write the pair correlation function in this manner. Please see. Here, I have written down the position vectors in terms of operators. These are operators in quantum mechanics and that is why I have taken extra pain in writing that have two delta functions where $\delta\{r - r' + \hat{R}_i(0)\}$ and $\delta\{r' - \hat{R}_i(t)\}$ are the position of the same particle at time 0 and time t.

But because in general these operators do not commute, I have taken care to write them as the average of two delta functions and then the integration is over space for dr'. If I convert it to a classical expression, it becomes simpler to understand, it is basically $\delta\{r - R_i(t) + R_i(0)\}$.

So, it is a position vector at time = 0 and at some later time *'t'* for the distance represented by a delta function $\delta\{r - R_i(t) + R_i(0)\}$.. I think I should also mention, this is G_s self-correlation function and the incoherent intermediate scattering function which I wrote just now for you. The incoherent function, this is nothing but a Fourier transform over d^3r of this G_{inc}.

$$I_{inc}(Q,t) = \frac{\pi}{2}\int G_{inc}(r,t)e^{-iQ.r}\,d^3r$$

This is nothing but once they put this delta function in this as G_{inc}, you can see it is,

$$I_{inc}(Q,t) = \frac{1}{N}\sum \langle e^{-iQ.(R_i(t)-R_i(0))}\rangle\langle e^{iQ.R_i(0)}\rangle$$

sum over all the particles and also average over the ensemble.

So, if I have number of particles in the system, at least formulism wise, I should add up particle by particle, its position at 0 time and its position at time *t*.I also do an ensemble averaging for the function $e^{-iQ.(R_i(t)-R_i(0))}$.

Now, when we talk about $t = 0$ and $t = \infty$, basically, when this averaging is done, $R_i(t) - R_i(0)$, interestingly, then there is no correlation between these positions, means the position at the time $t = \infty$, is no way correlated with the position at time $t = 0$.

And then this averaging, I can do it separately. So, I have broken it up,

$$I_{inc}(Q,\infty) = \frac{1}{N}\sum \langle e^{-iQ.(R_i(\infty))}\rangle\langle e^{iQ.R_i(0)}\rangle$$

into minus exp $[-iQ.(R_i(\infty)]$ and I have ensemble average of that, and also ensemble average of the other part exp $[iQ.R_i(0)]$. Please note that I started from this pair correlation function in real space and its Fourier transform gives me this. And here, there is an averaging over ensemble average of these two variables. But here, I am considering these two positions as classical variables and not as operators. I can do the averaging independently and this is nothing but average value of $e^{-iQ.(R_i(\infty))}$ at infinite time and $e^{iQ.R_i(0)}$ at zeroth time. The particle position can be anywhere at zeroth time, and the particle position can also be anywhere after infinite time has elapsed and they are not correlated. That is why the averaging is done independently and this is nothing but, position of the i^{th} particle's ensemble average and mod of the and squared, this comes up as a mod of its square. So, basically, what I am looking for is the position of a particle in space.

Now, if this particle is diffusing over entire space, then any position can be chosen or if it is chosen in this infinite size dimensional space or if it is a finite dimensional space, then I need to find out the average position of a particle R_i at any time t or at t equal to 0 (any arbitrary time origin) and mod square of $< e^{iQ.R_i} >$.

So, basically, I need to find out R_i, of a particle or what is the probability of its position vector? R_i is a position vector and then basically the ensemble average of that.

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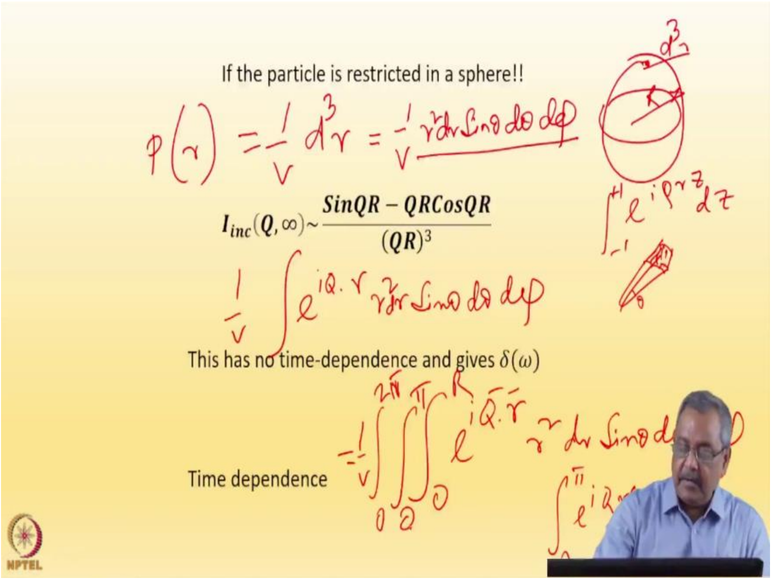

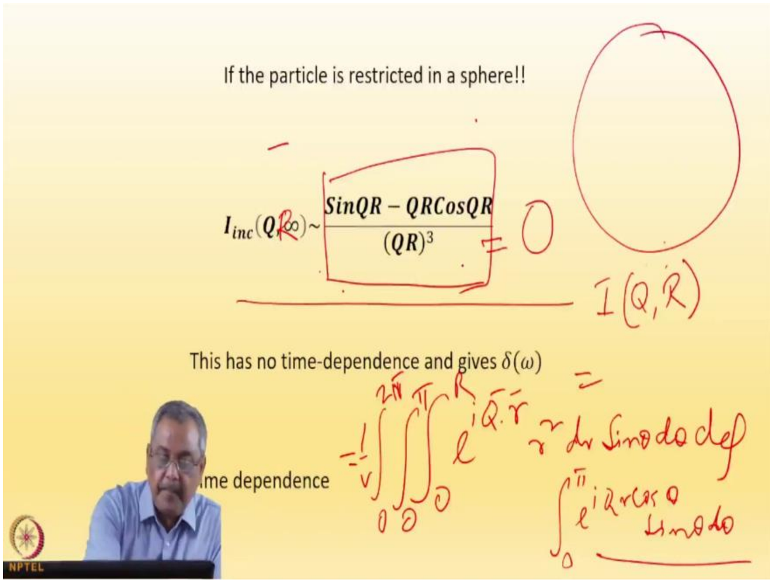

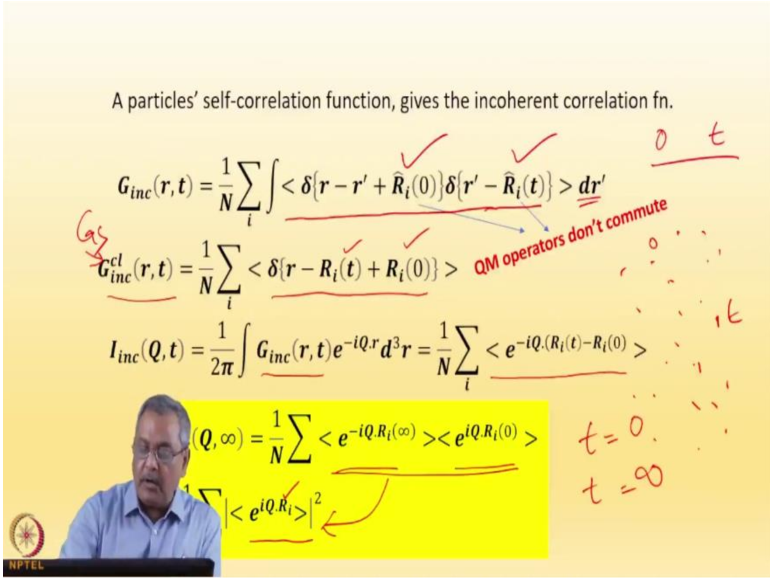

Now, let us take a simple case. If it is a particle is restricted in a sphere, what is the probability of finding it in a small volume d^3r, it is nothing but $1/V$ into this fundamental volume d^3r. That is a probability that the particle is in a volume d^3r. This is equal to $\frac{1}{V}r^2dr\sin\theta\, d\theta d\varphi$ in spherical coordinates and that is nothing but a small volume which is between r and r + dr, θ and $\theta + d\theta$, φ and $\varphi + d\varphi$. This is a small elemental volume. This is a fundamental volume in spherical polar coordinates.

If I take $\frac{1}{V}$ out this has to be so $e^{iQ.r}$ so, then with the probability element we have, $\frac{1}{V}\int e^{iQ.r}r^2dr\sin\theta\, d\theta d\varphi$. Here, I integrate over the entire sphere of radius say R, so in this integration, r goes from 0 to R, θ goes from 0 to π and φ goes from 0 to 2π. This covers the sphere and for all the probabilities in, all the small elemental volumes, which have been taken all over the sphere. This integral we have done many times; I will just give you hints that $iQ.r$ is $iQr\cos\theta$. In this case integration is simplified as,

$$\frac{1}{V}\int_0^{2\pi}\int_0^{\pi}\int_0^{R} e^{iQr\cos\theta}r^2dr\sin\theta\, d\theta d\varphi$$

Where by substituting $r\cos\theta = z$, we have limits z from -1 to +1. And then next integration of 0 to R for the result of this integration multiplied by r^2dr. This we have done also when we calculated the form factor for a sphere, it is the same integral and then $I_{inc}(Q,R)$ will have a form like this.

So, for a finite sphere the form is like this. But if I talk about I_{inc} when this sphere going to infinity that means, the particle is diffusing in an infinite medium, then you can say the expression goes to 0. So, there is no time dependence for this I_{inc}. That means $I_{inc}(Q,R)$ the elastic line (EISF) $=\frac{\sin QR - QR\cos QR}{QR^3}$ for a finite sphere of radius 'R'.

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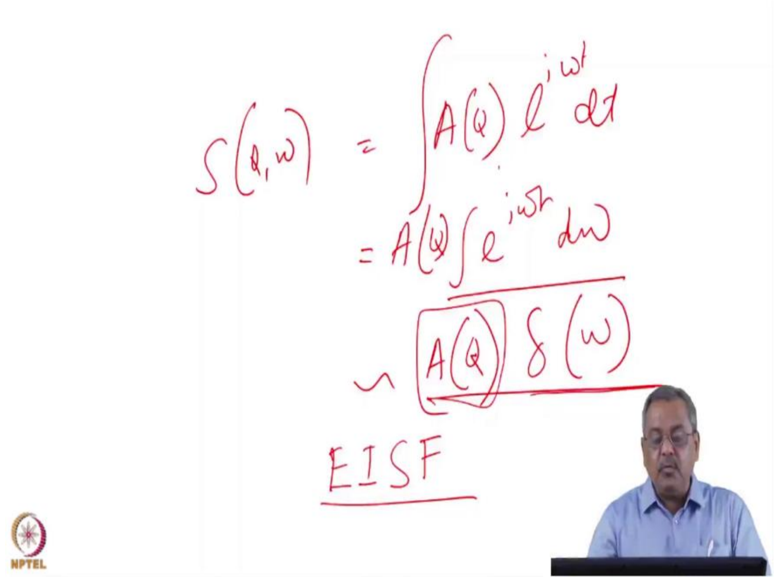

We have an intermediate scattering function, $A(Q)$, which does not have a time dependence. So, if I do a time Fourier transform of it to go to $S(Q,\omega)$, this has no time dependence and it is just $A(Q)\int e^{i\omega t}d\omega$. So, now this becomes a delta function in energy and can be written as, $\sim A(Q)\delta(\omega)$. This is, barring a few constant values, has a Q dependent part, $A(Q)$, and a $\delta(\omega)$. That means, in my scattered intensity, I have a pure delta function with a Q dependence in my experimental data, known as elastic incoherent structure factor. I have mentioned it earlier also that this is because of the diffusion of the particle in a finite size cage.

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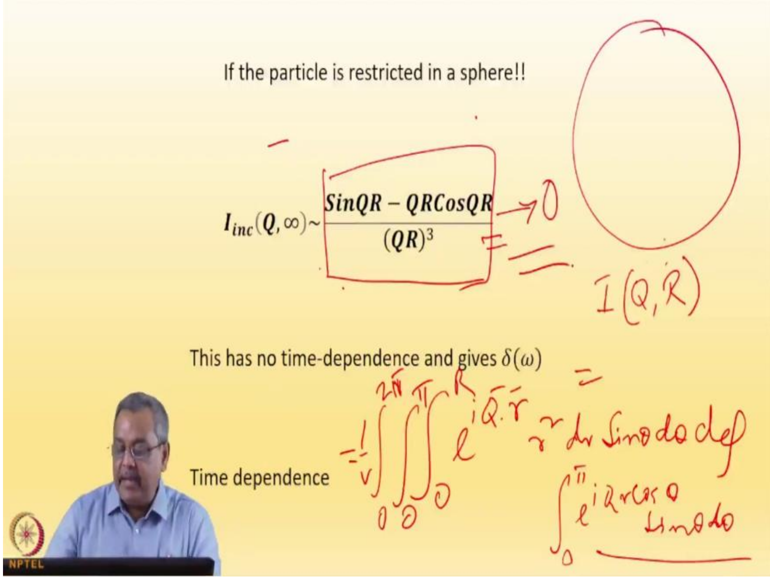

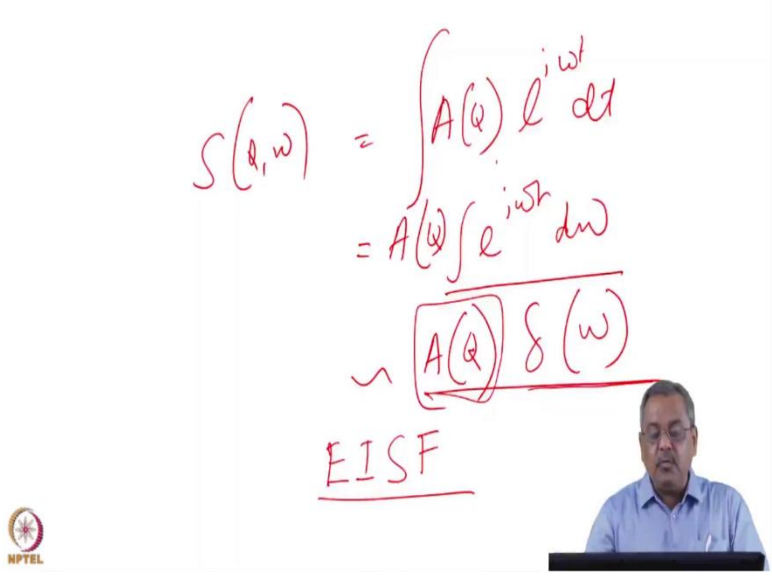

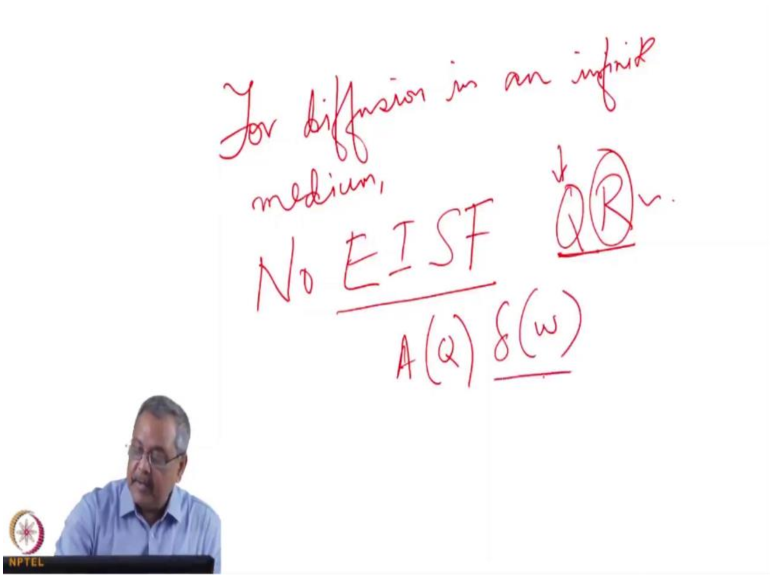

Now, if I go to a sphere which is of infinite radius then this $I_{inc}(Q, \infty)$ goes to 0. Then the $A(Q)$ which I wrote as a pre-factor of $\delta(\omega)$is 0. For diffusion in an infinite medium no EISF i.e. no elastic part. But, if the medium in which the particle is diffusing, is finite, there is an EISF. actually, the R depends on Q and if Q is large then R has a small and when it is a finite size, then depending on the angle or the Q value that I can probe the finite size is quantified. But in general, in an infinite medium, there is no elastic incoherent structure factor, but in a finite medium, we have a *A(Q)*. When I say $\delta(\omega)$ what I mean is this.

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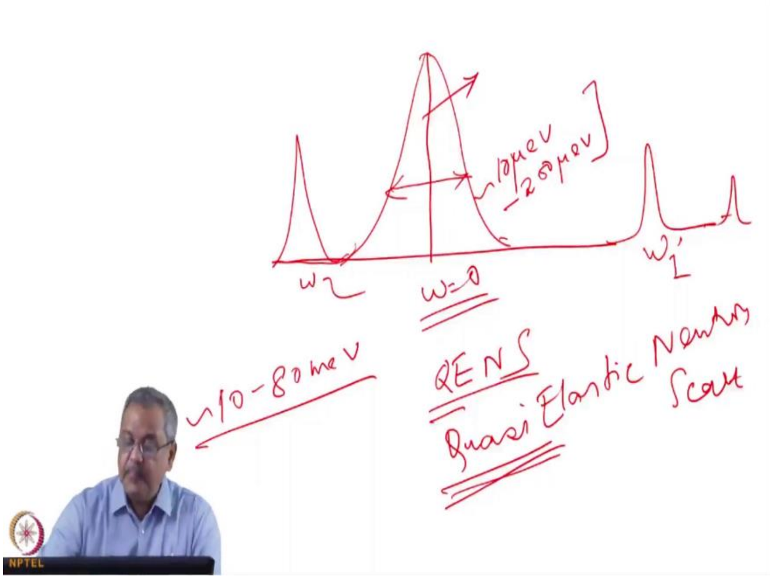

First, we consider that there is an energy transfer in the medium due to the interaction between the neutron and the diffusing particles. So, $\delta(\omega)$ is there that means, this delta function is at $\omega = 0$. There is no energy transfer. What we are discussing now is quasi elastic neutron scattering. This is because, this elastic line gets broadened due to energy transfer. That is why it is called quasi elastic neutron scattering. It is almost elastic. This is basically as I mentioned to you earlier, is a broadening of this elastic line due to doppler shifting of the neutron by the diffusing particles.

The inelastic intensities are far away from the ω equal to 0 part. They can be ω_1, ω_2 etc as shown. These may be phonons and other inelastic lines. We know that the phonons we talked about, have energy transfer of the order of 10 to 80 meV. But, the incoherent scattering coming from self-diffusion of a particle just broadens out the elastic peak and we measure this broadening.

This broadening can be studied with 10 to 200 μeV resolution, depending on how tight energy resolution that one can have. Since this is broadening of the elastic line, that is why it is called quasi elastic neutron scattering.

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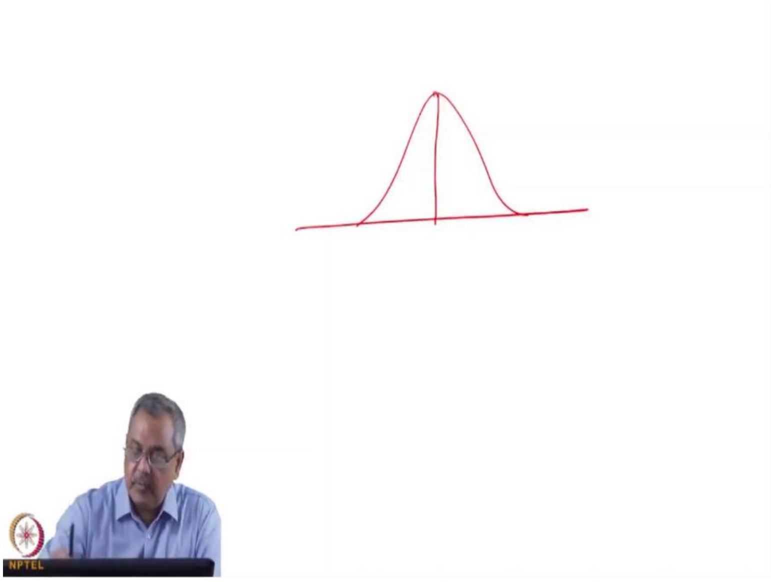

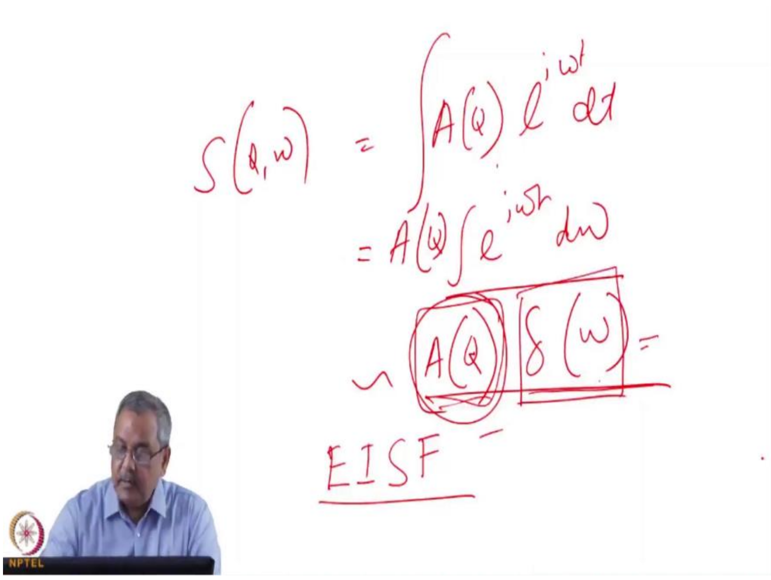

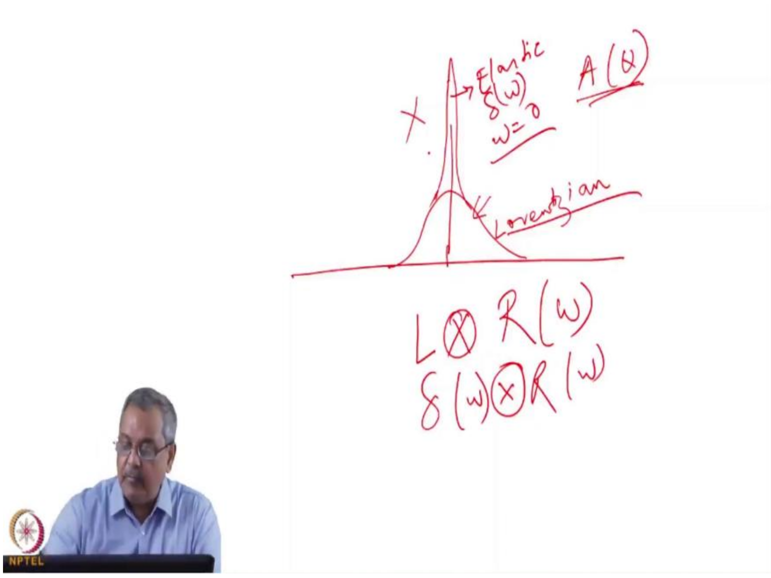

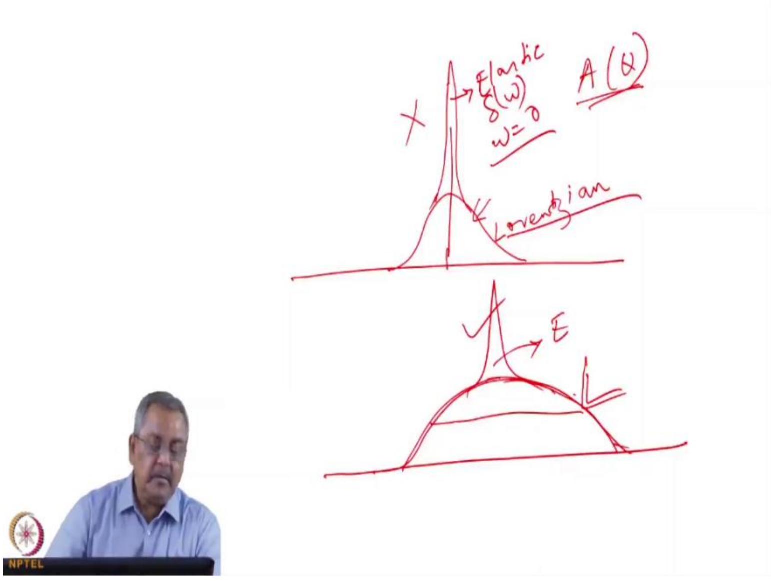

There is broadening of the elastic line due to diffusion. But, as I discussed with you just now, that there is also a pre factor $A(Q)$ a term which is purely elastic. We not only have a broadening of the elastic line, but we also have a purely elastic term coming from the finite geometry of the cage in which the particle is diffusing.

Let me now draw it a little differently. The time correlation in the systems gives me a Lorentzian and $A(Q)$ gives me an elastic term riding over this Lorentzian. Why it is Lorentzian I will come to just now. I have mentioned it earlier again, now I will show you how it comes.

I have got a Lorentzian plus an elastic line $\delta(\omega)$ or $\omega = 0$ line if it is a particle, which is diffusing in a finite medium. If it is diffusing in an infinite medium, I do have the Lorentzian, but I do not have the overriding elastic line at $\omega = 0$ line.

This Lorentzian is convoluted with the instrumental resolution and this elastic line $\delta(\omega)$, is also convoluted with the instrumental resolution, and that is why the delta function gets broadened. So, now what we have, is as follows. In my experiment, I have an elastic line (EISF) and I have an inelastic Lorentzian. And this EISF comes when the particle is diffusing in a finite medium.

I will use examples to show you what sort of finite mediums we are talking about. But this Lorentzian comes from the diffusion of the particle in that medium and it actually indicates the dynamics of the motion in terms of diffusion constant. Most importantly, that we can get diffusion constant and cage geometry simultaneously from these QENS experiments.