Keywords: Mesoscopic Length Scale, SANS, SAXS, Cold Neutron Source

In today's lecture, I will be introducing you to scattering for mesoscopic world.

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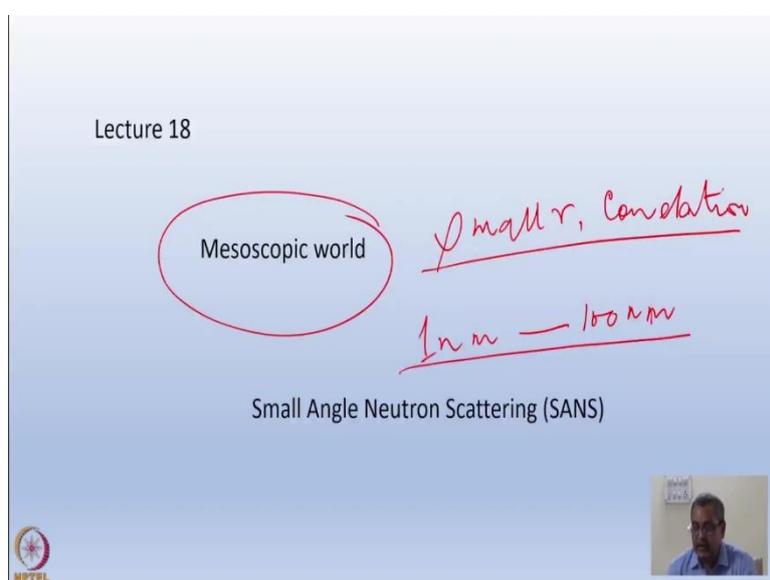
In the microscopic world of the crystallographic samples and also of liquid and amorphous samples with small 'r' (~Å) correlations at Å length scale., In brief, I was probing, either through Bragg diffraction or through liquid and amorphous diffractions at large 'Q' ranges (10-50 Å^{-1}) . Now, I am moving on to a world where I play with the resolution and I try to see things which are typically in 10 Å to 1000 Å length scale. This is the mesoscopic world. There is lot of interest to understand structure at this length scales. Mostly people talk about inhomogeneities. Here I will deal with specific examples, studied using small angle neutron scattering.

When I say small angle neutron scattering possibly, I am a little wrong because it is actually small Q neutron scattering. In the popular parlance, small angle neutron scattering (SANS) is accepted as a term and SANS is a very well-known technique. And today, any major neutron source will have not one, but several of these SANS instruments. But before I start the subject

of SANS, I have a responsibility to tell you briefly about single crystal neutron diffraction and also to provide some references.

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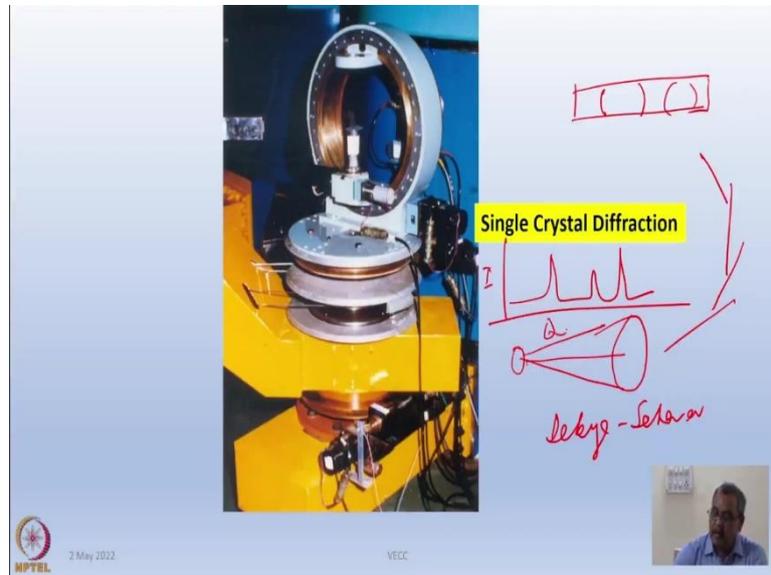
There are small differences between the experimental set up for single crystal diffraction and powder diffraction. This is how the sample table looks like in case of single crystal neutron diffraction. As I showed you earlier, in case of a powder crystal, from the sample, at a certain diffraction angle, you have a Debye Scherrer cone and my detector, I showed with photographs of Debye camera, for simple x-ray diffraction, cuts a piece of this cone of Bragg intensity and from there I can get the d-spacing. Even in case of position sensitive detector-based neutron instruments that I showed you, I take a horizontal plane in which I have these detectors. In case of liquid and amorphous samples, I cover a larger angle while in case of crystallographic samples, I cover slightly lesser angle in a horizontal plane and get peaks in this detector plane. It is intensity versus Q data in a horizontal detector geometry.
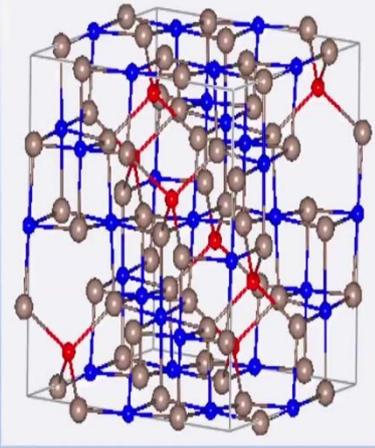
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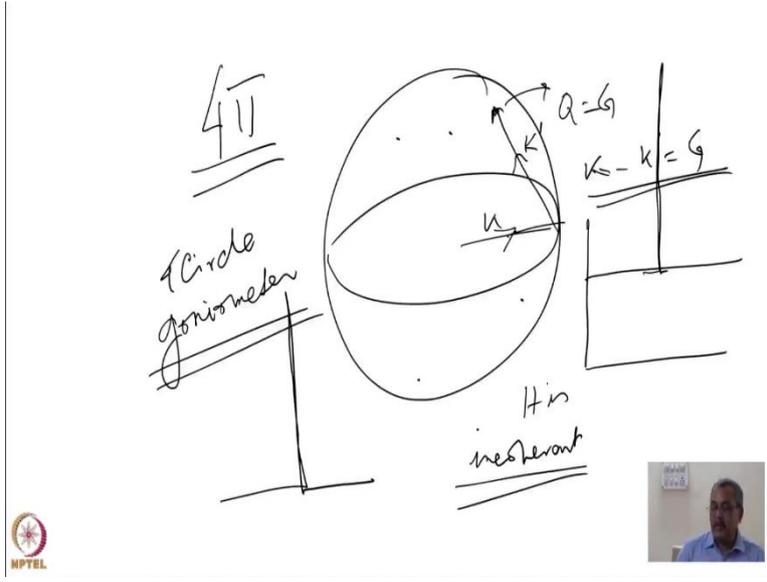
Single Crystal Diffraction

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Hydrogen bonding in Single crystal

Here, because it is a single crystal, I do not have a Debye Scherrer cone, but what I have is an Ewald sphere and whenever my scattering vector touches the Ewald sphere, I mean the sphere touches a lattice point there is a reflection because it satisfies $\bar{Q} = \bar{K} - \bar{K}' = \bar{G}$ in three-dimensional world (anywhere in 4π solid angle) , and there will be reflected beam in that direction.

That means, my sample will send the reflected beam to entire 4π solid angle and not in a plane because the sample is a single crystal. So, we have a goniometer which is known as a four-circle goniometer on the sample table. Without giving too much of details, the role of the goniometer is to bring the diffracted beam to the horizontal detector plane of the table, by rotation of the sample around two axes.

We know that by rotating it through Eulerian angles, I can bring the reflected beam from anywhere in 4π direction down to the horizontal plane on which the detector is rotating. The is four circle goniometer's role is to bring the reflection down to the plane of the detector, because the detector is heavy and it is not possible to cover all 4π angle or move it along the horizontal axis in a vertical direction. This is the trick we play by using a 4-circle goniometer.

In this case, as I told you earlier that we can study single crystals, but more importantly, in case of neutron, we can study hydrogenous single crystals, which is very important as hydrogen has a large scattering cross section. You may question that I told you earlier hydrogen is an incoherent scatterer, how will it give coherent Bragg peaks? It should only give an incoherent background, because hydrogen has a small coherent scattering cross-section. But in this case, because it is a single crystal, the reflected beam is extremely narrow and very sharp, almost a realization of true delta function because it is so narrow and sharp. I do not have to care about the background under the delta function peak because I have very large intensity in the beam at a diffraction peak.

And that is why unlike powder diffraction, I can easily use hydrogenous single crystals and hydrogen bonding is one of the most popular topics in single crystal neutron diffraction of hydrogenous samples. Also, because the reflected beam is extremely narrow, so, to capture the beam on the detector, I do not go very far, I bring the detector closer. When I come close, I intentionally compromise on $\Delta\theta$. Because it is such a narrow beam, I need to capture it on a detector and I add a large $\Delta\theta$ for the detector to make the convoluted intensity wider. I cannot use too many examples, but I just show you a single structure obtained at DHRUVA. , This is

the kind of structures we can obtain with single crystal neutron diffraction. But most importantly, we can solve a structure ab initio. Structure determination is different from what we did for powders, where we did Rietveld refinement. In case of Rietveld refinement, we start with a model structure and keep on refining it so that my experimental results match with the model. Here, we do not have to go for any model, we can find out the hydrogen bonding and the entire structure of the single crystal from ab initio data fitting. This is a major difference between single crystal and powder diffraction. I will stop discussion on single crystal diffraction here.

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Moreover, last time, I discussed with you the results from amorphous and liquid samples. So, I will not get into details of the discussion again. But in the last lecture, I missed some references, which I have provided here. And this is the data from SANDALS in ISIS spallation neutron source at Rutherford Appleton Laboratory UK.

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This is the data from Dhruva, where this is the *H(Q)* the total structure factor which helped us to find molecular clusters in liquid alcohol sample. So, not only we have the amorphous structure, but we also have these molecular clusters in the liquid. This is possibly a unique result of this experiment and I have provided the promised reference for it. Now, let me dive into small angle electron scattering or SANS.
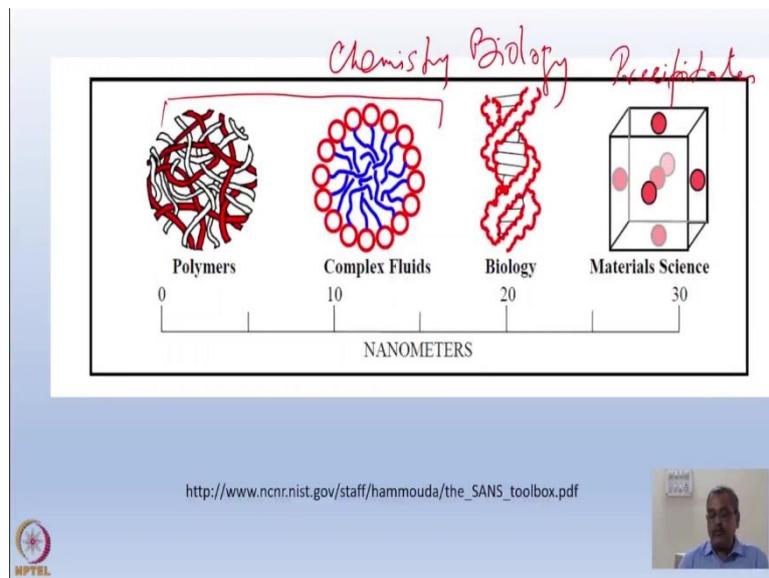
As I told you earlier that the mesoscopic world is studied using SANS. So, here are just some examples I have taken from several references. You can use polymers, complex fluid etc. This structure shows something called a micelle obtained from surfactant molecules, where the molecule has got a head group which is hydrophilic here and a tail which is hydrophobic. And when you put these surfactant molecules, in a solvent, they form this kind of structure known as micelle. You can study and get information about these kinds of structures using SANS techniques. This technique is extremely useful for biological samples at larger length scale and also in studies in material science involving precipitates.

So, metallurgists, biologist, chemists and physicist all communities are interested in SANS for mesoscopic structure and they find this technique very useful. I am going to talk to you about this technique today.

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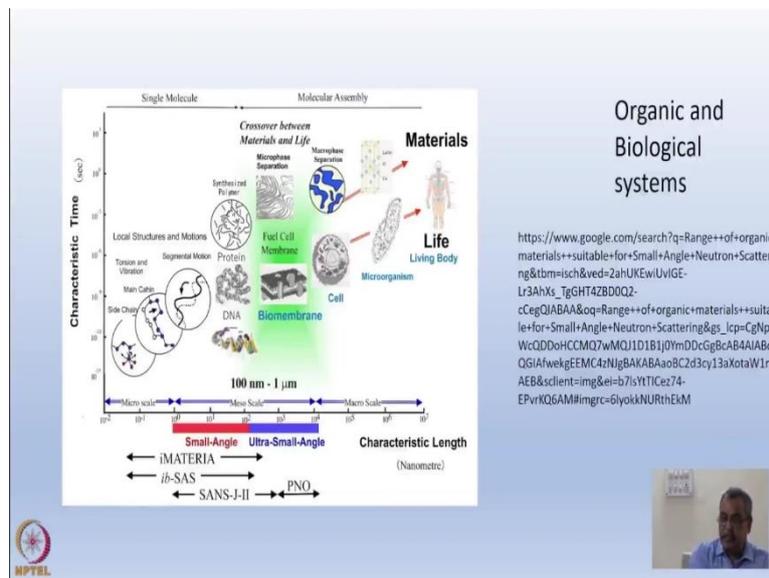
This slide is from a Japanese website for biological samples. They have mentioned various objects like bio membranes to microorganisms that you can study with small angle neutron scattering or SANS. Now onwards I use the word SANS, but remember that what I am talking is actually a small 'Q's scattering.

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We are using it to study mesoscopic size for example, inhomogeneities in a media: please remember the word inhomogeneity. What I mean is that when you have some kind of a matrix: it can be a liquid or it can be a solid and you have an inhomogeneity in it which have got different scattering length density (SLD) with respect to the matrix. , Please note the term SLD.

I have forgotten about the microscopic structure of the medium and I am talking in terms of density and not in terms of atomic positions, which I did till now, in powder crsytallites, in liquids and amorphous systems and in single crystals. I was talking about atomic positions and trying to solve the structure. Now, I am talking about scattering length density or SLD.

Why scattering length density?

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FT on space/momentum

$I(Q) \xleftrightarrow{F.T} G(r)$

'Q' and 'r' are the Fourier Transform of each other and are canonical conjugates
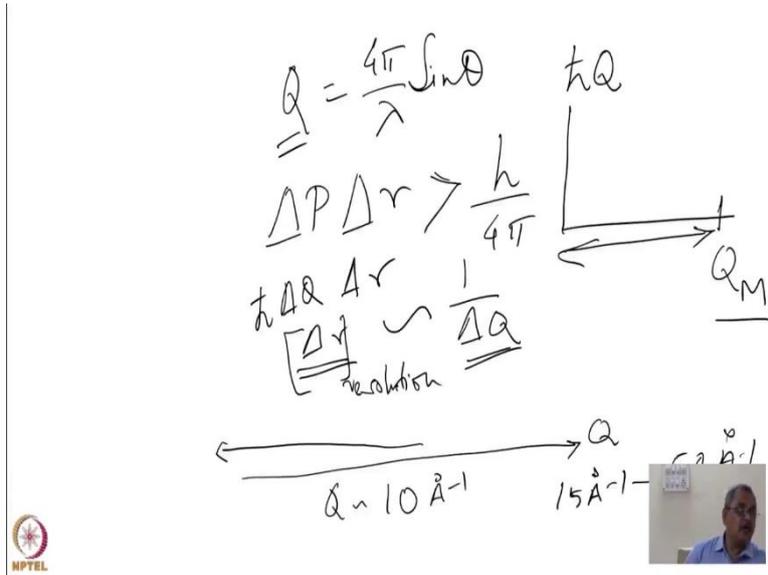
In a scattering experiment the inherent spatial resolution, depends on the maximum wavevector transfer or 'Q_{max}'

$$\Delta r \sim \frac{1}{Q_{max}}$$

$$Q = \frac{4\pi}{\lambda} \sin \theta$$

If one wants to bring the resolution to mesoscopic length scale, one needs to go for smaller 'Q_{max}'

Let me just go back to what I taught you in lecture 3 or 4. The real space correlation function is '*G(r)*' which is a Fourier transform of '*I(Q)*' that you measure and when I talked about model fitting using reverse Monte Carlo my target was to go from here ('*Q*' space) to the real space ('*r*'). But what does quantum mechanics tell us? I will use the uncertainty principle here. We are talking about wavevector transfer in an experiment, a $Q = \frac{4\pi \sin \theta}{\lambda}$. This is a wave vector transfer and momentum transfer is $\hbar Q$.

Now, we know from uncertainty principle that $\Delta p . \Delta r \geq \frac{h}{4\pi}$. Δp is nothing but $\hbar \Delta Q$ and with this $\Delta r \sim \frac{1}{\Delta Q}$. So, your inherent resolution in an experiment is dictated by quantum mechanics or rather by uncertainty principle. I will call it the resolution in real space and it depends on $\frac{1}{\Delta Q}$. Now, what is the ΔQ? Is it the Q resolution of my experiment? No, you are doing a Fourier transform over the entire Q values that you have used in the experiment, so it is the range of wavelength transfer in an experiment

ΔQ is Q_{max} because this is the range over which you do your Fourier transform. So, when we talk about Q_{max}, then please see that so far, I have been talking about smaller and smaller separation between structural units and the structure that I wanted to resolve were in atomic length scale, that is structural atom (molecular) positions. And because spatial resolution Δr and ΔQ are inversely proportional to each other, we talked about larger and larger values of Q_{max} If you remember, when I talked about crystal diffraction from powder samples, I went to $Q_{max} \sim 10$ Å^{-1}. I would have loved to go further, but fact is that here we do a refinement, so, 10 to 12 Å^{-1} was good enough to refine a structure. When we have a very crude model and not a

specific model in case of liquid and amorphous systems then I went up to $Q_{max} \sim 15$ Å^{-1} in Dhruva or if I talk about Rutherford Appleton laboratory as spallation neutron source, I talked about experiments up to 50 Å^{-1}.

I went to such large Q_{max} value because I might attempt direct Fourier inversion and large Q is required. Now, I have gone in the other direction and want to do experiments at low values of Q. It is possible to achieve this either by going to low angles or by going to long wavelengths and that is why this is called small angle neutron scattering. Q_{max} dictates what is the spatial resolution in the experiment.

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Now, let me discuss various diffraction techniques under the definition of small angle scattering. We have small angle neutron scattering (SANS), small angle X-ray scattering (SAXS). We have light scattering. The range of wavelength for light will be 3000 Å to 7000 Å . X-rays, you know often use Cu-kα, which is 1.54 Å. I have written typically 1 Å and I can go for softer x-rays. For small angle neutron scattering the typical wavelengths used are ~ 5 Å. Every technique has its plus and minus properties. For example, in light scattering because λ is very, very large compared to x-rays and neutrons, so, 1/λ or Q is very, very small. Actually 1000 Å will give me 0.001 Å^{-1}as a typical number. In case of light scattering this is a plus point because when it is such a small Q, I can see very large objects. Smaller the Q, larger the object I am studying. Larger the Q, smaller the length scale that I am probing. So, I can see very large objects, but here the most important thing is light demands transparency. You cannot do light scattering unless your medium is transparent..

But if you take say 1.54 Å Cu-kα radiation that you will have a penetration depth of typically say 10's of micron. If you go to softer x-ray, say 100 Å,which is possible in our RRCAT Indore facility, they will have even lesser penetration depth. Then, in case of small angle neutron scattering, you can go to longer wavelength and penetration is not a problem. So, you can use a solution/sample of typically fractions of a millimeter to millimeter thickness in which neutrons will easily penetrate.One will decide the thickness of the sample to the extent we can see single scattering, because multiple scattering is a nuisance for data analysis in scattering experiments. And we typically use neutrons of wavelength around 5 Å.

Here I must mention to you that when I want to use long wavelength neutrons, a fact I discussed with you earlier is the general issue of intensity of neutrons as a function of energy at a reactor or spallation neutron source. As energy of neutrons goes up, λgoes down,, λ goes inversely with energy.I have a Maxwellian energy distribution, which is shown here. If I want to go to longer wavelength, then it is better if I can modify the spectrum using a cold neutron source to improve neutron intensity at the onset. Cold neutron source is a cryogenic moderator (liquid hydrogen, liquid deuterium etc.) kept inside the reactor that re-thermalizes this flux to lower energies. The area under the curve, remains more or less same, maybe slightly less, but you see an increase in the number of neutrons with longer wavelength and for small angle neutron scattering, we need longer wavelength neutron.

I talked to you earlier about diffraction from liquid and amorphous systems when I needed to go to very large Q values. I went to very short $\lambda$and a spallation neutron source is an ideal place

to do such experiments because there neutrons are inherently produced with very high energy. Similarly, for cold neutrons reactors have slight advantage.