Neutron Scattering for Condensed Matter Studies
Professor Saibal Basu
Department of Physics
Homi Bhabha National Institute
Week 7: Lecture 20 B

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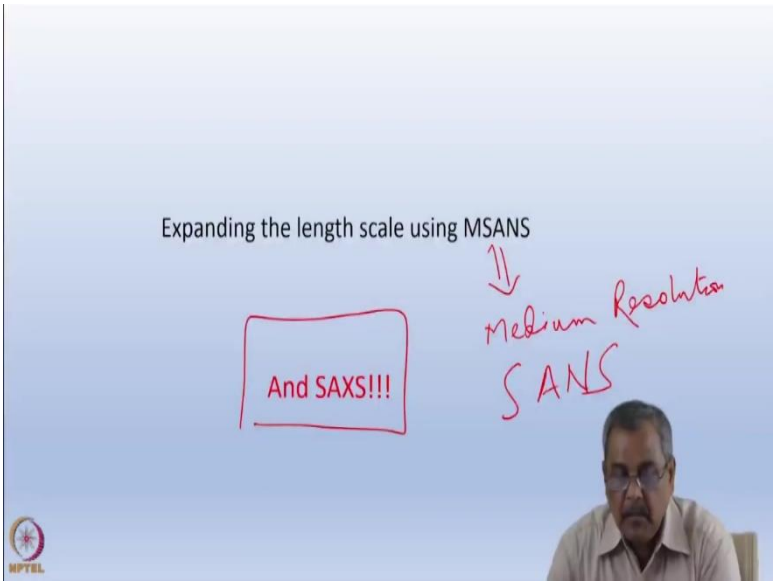

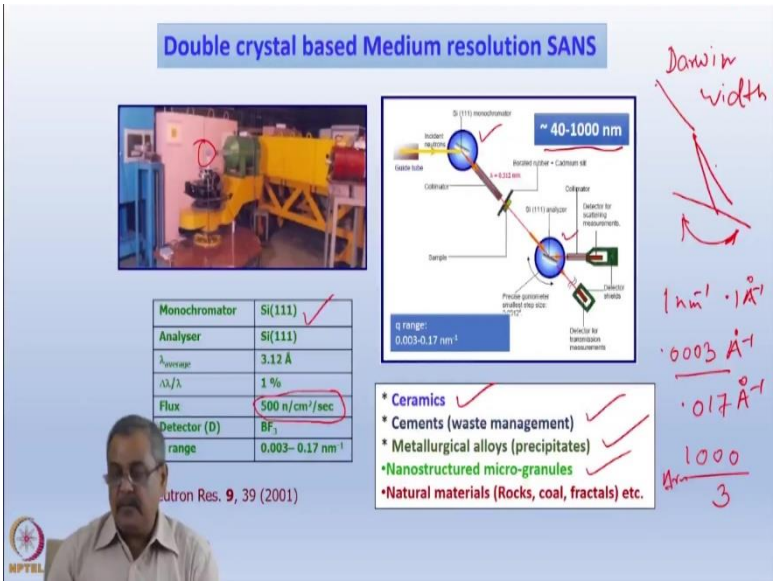

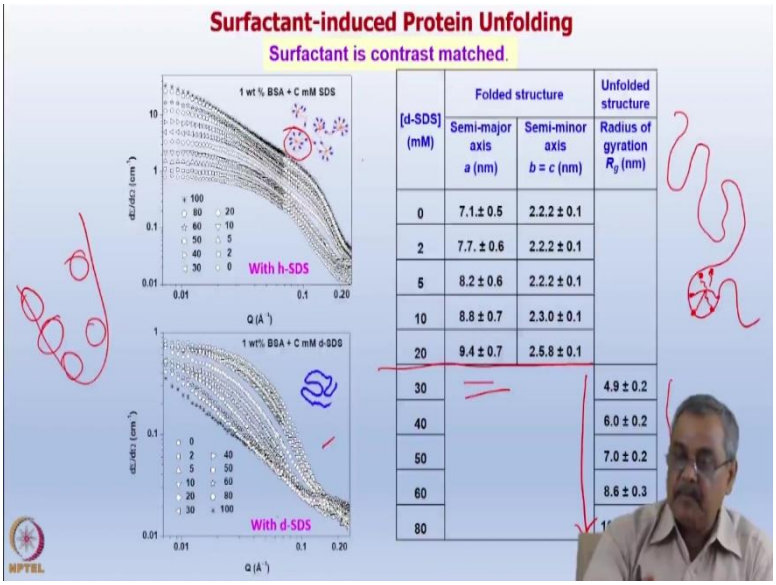

Now, I will move on to medium-resolution SANS (MSANS) and small angle x-ray scattering together, as I promised. Let me remind you that I talked to you about double crystal based medium resolution SANS in Dhruva. You can see a photograph of that on the guide tube. The monochromator is Si(111), one which is inside the guide you cannot see and the second monochromator is on the rotation stage. You can see that this instrument is on the guide and we have a monochromatic wavelength of 0.312 nm which is 3.12 Å. We have the second monochromator which is shown here, a silicon single crystal disk and this the one we rock. By rocking the second monochromator, I copy the rocking curve of the first silicon monochromator if there is no sample in between.

Remember that there is some inherent broadening with the neutron beam, which is not the just the Darwin width because it is a perfect single crystal. When I put the sample between the two monochromators, then that causes a broadening of the beam from the first monochromator and when I rock the second crystal then I copy this broadening onto my detector and in this way, I can go to a lower Q value because the incident beam is very, very narrow. And I can talk about probing length scales in the range of 40 nm to 1000 nm.

For this instrument, $\Delta\lambda/\lambda$ is vary at good i.e. 1%, and the flux is low. You must accept it because it is a single crystal diffraction of the beam which is coming from the first crystal, a polychromatic beam and I get only 500 neutrons/cm^2/sec. The detector is a BF_3 detector and in end-on geometry. The q range is low. It is 0.003 to 0.17 nm^{-1}. If I translate it into Å, 1 nm^{-1} is 0.1 Å^{-1} because 1 nm is equal to 10 Å. That means this goes to 0.0003 Å^{-1} to 0.017 Å^{-1}.

Really speaking, this is actually covering a different q range compared to what I showed you earlier that was 0.01 to 0.2 $Å^{-1}$ Where I showed an example of surfactant induced protein unfolding. I am in a different range of q and different range of problems also. This instrument has been used for studying ceramics, cements, pores in cements, metallurgical alloys and micro granules.

I will take an example from the micro granules. This being in a lower q range, it can see larger inhomogeneity sizes. So, if I consider ~ 1/0.003, spatial resolution for Q~0.003 $Å^{-1}$, it becomes 1000 divided by 3 or ~330 Å which is a Δr resolution as per uncertainty principle and as you can see that you can see very large objects using this machine.

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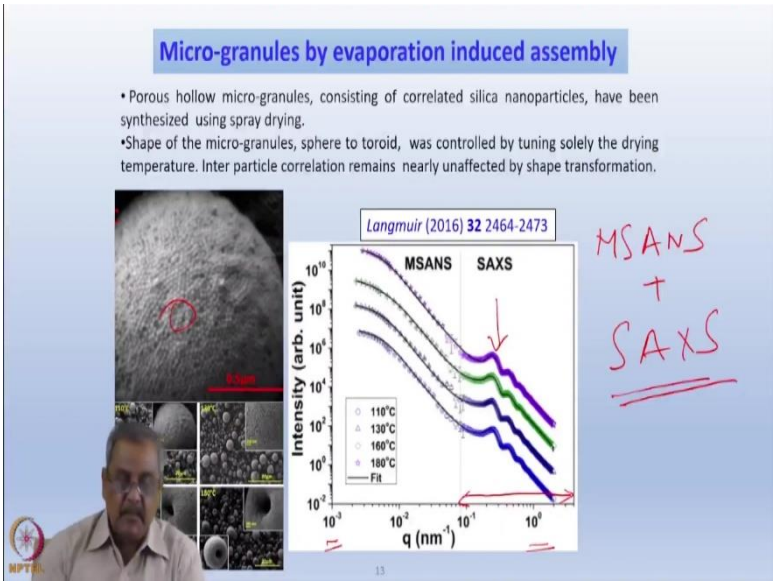

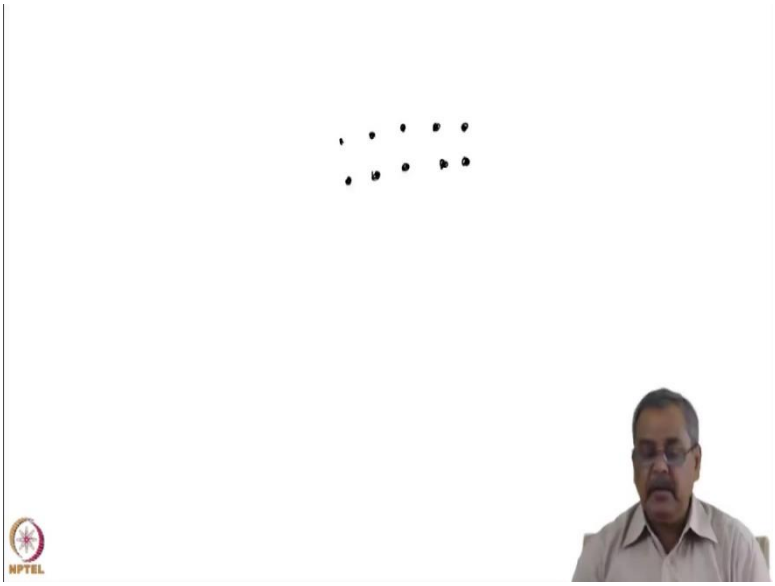

I will choose one example on silicon micro granules. We have purchased silicon nanoparticles, the nanoparticles are smaller in size, you put them in solution, throw it in a spray dryer and let the water evaporate because spray dryer has heating and then what you get is structures like this. You can see the nanoparticles here, and you can see the whole structure which is spherical. But depending on the temperature at which you dry up the granules this assembly of these nanoparticles can have different structures.

First, I show you, what I promised you that how you can stitch together small angle neutron scattering and small angle X-ray scattering data. You can see here, this part of the data, the larger *Q* side was taken using exactly the same sample structure but by doing smaller X ray scattering. And the principle and the design of instruments are very, very similar. You have a large flight path, you have a collimated to collimate down the beam and you have a detector. So, this data (SANS) and this data (SAXS), are stitched together and you can see that we have covered a very large *Q* range, 10^{-3} nm^{-1} that means 10^{-4} $Å^{-1}$ to 1 $Å^{-1}$. And basically, in the overlap region, we match both the data from the sample. I mean, we basically scale the x-ray data and also scale the error functions, so, and then we get a continuous curve.

This is the matching of MSANS here with SAXS. This is used at other places also, where you can even do in situ SANS and SAXS. I will use an example in my later part. So, this is the stitching of SANS data and SAXS data to cover a large *q* range and you can see the fits give me the basically the dimension and the structure of the assembly of nanoparticles.

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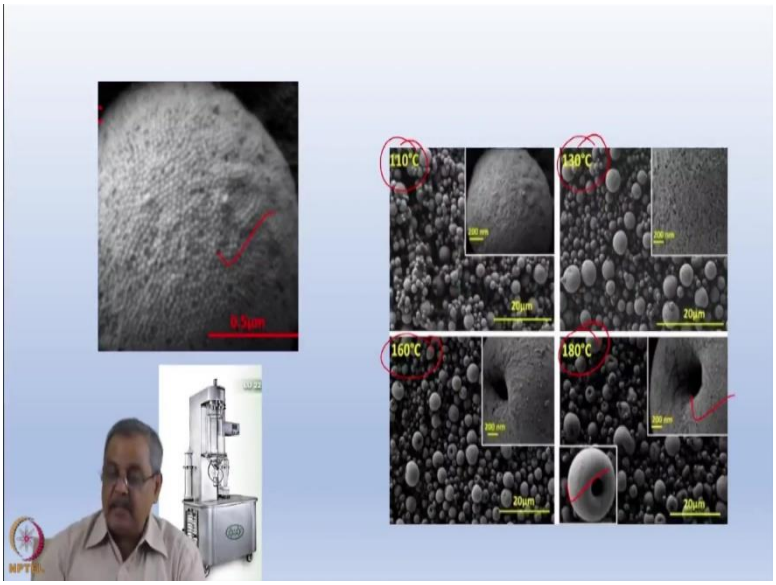

This is a commercial spray dryer which is available with us, which gives assemblies with very large length scale, typically ~ 0.5 μm or 5000 Å. But you can see depending on the drying temperature you get different structures from spherical to toroidal. You will get even more interesting structures. I will come to it shortly. So, depending on the heating, you can play with the assembly of nanoparticles and that makes it a very interesting method.

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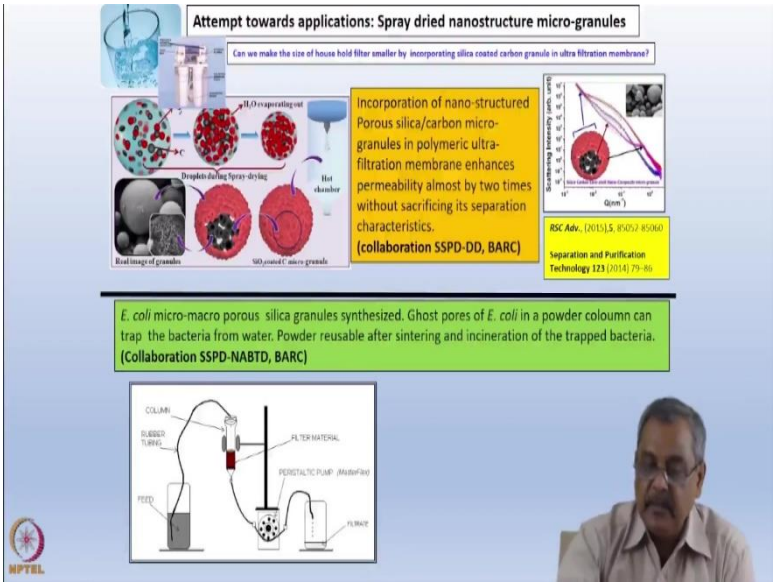

Here, while we are drying the nanoparticle in the spray dryer, we added E coli bacteria which you know causes stomach upset to the solution. So, what happens is, when these structures form, they also accommodate the E coli in their structures.

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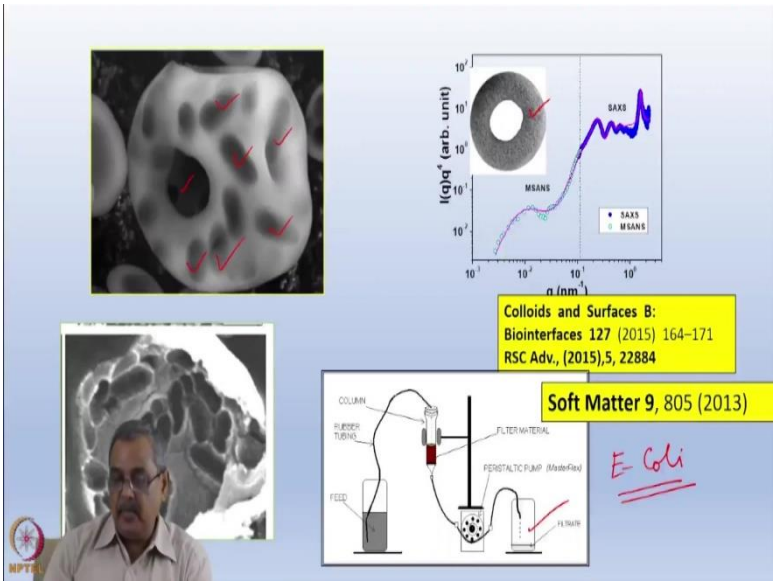

You can see this is the structures fromed on drying and then if I burn out the E coli, then we have these gaps which can accommodate E Coli. I have given the reference here where an attempt was made to arrest E-coli. When we were drying the silicone particles, we added E coli bacteria to it and then we burned out the E coli bacteria by heating to create the recesses. And you please see this I(q) vs q^4 with stitched MSANS data and SAXS data. This rise comes because you we multiplied *I(Q)* it by q^4 to see the Porod region and the surface area of this structure.

When we do it then there are gaps in the structure which can accommodate E coli and then when try to use it as a water filter, interestingly, it could filter out E coli bacteria. I consolidate by saying we started with micellar structure, went into protein unfolding in biology to large structures with nanoparticles. This is almost like a you can choose we can use assembly of such nano structure. You can actually set-up, of a water filter that are used in every home. Here, this water filter can actually remove E coli bacteria from water this setup was made and tested.

With this example, I come to an end of the discussion on q range that can be used in Dhruva, the kinds of studies that have been undertaken on these instruments. You can see that small angle neutron scattering is important for basic science as well as in applied fields from the examples in micelle, protein unfolding and removal of E coli bacteria.

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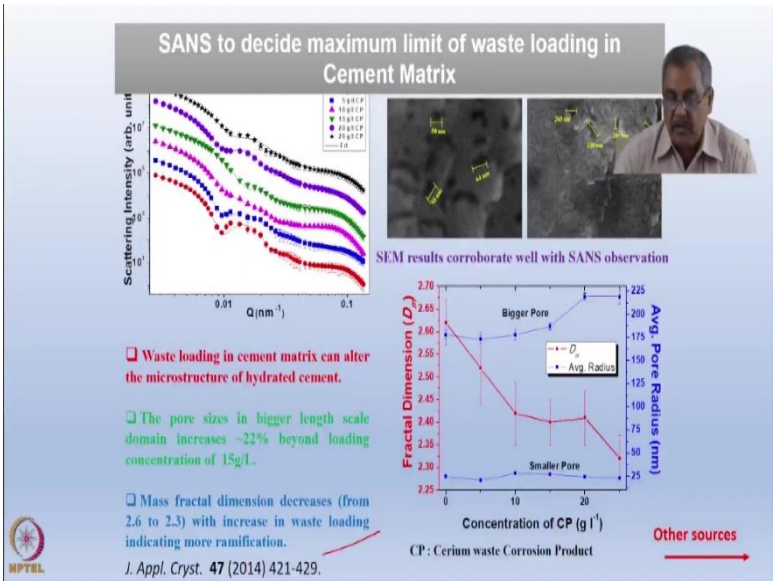

Now, the same SANS machine has also been used to understand nuclear waste loading in cement matrix. Waste loading is an important thing in nuclear technology. When we run reactors, we create lots of nuclear waste, which needs to be first immobilized and then stored.

They are immobilized in glasses. They can also be immobilized in cement because cement has lots of pores. Those pore sizes were studied using MSANS. We could see that the fractal dimensions decrease, when you start loading cement with nuclear waste and studied how the fractal dimension changes. This is another application of SANS to understand the importance of utilizing cement for immobilizing nuclear waste.

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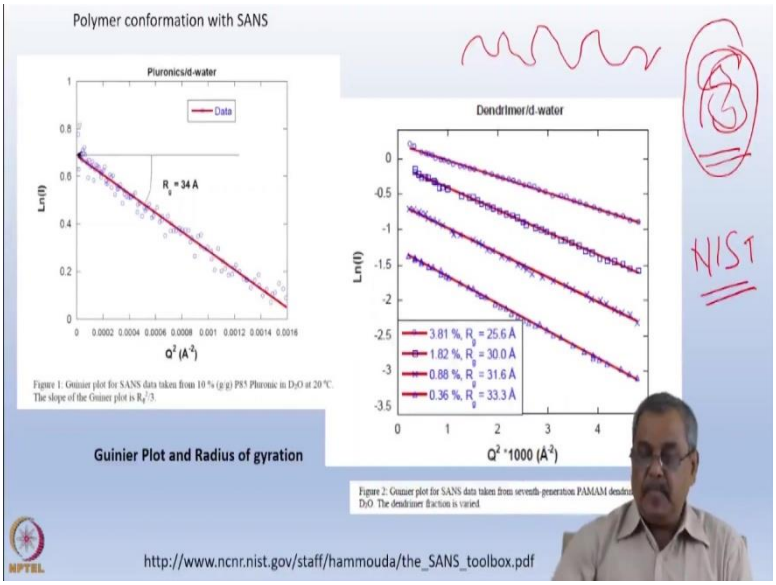

With this I come to some other examples from other sources. Actually, these are earlier examples. These work on various polymers were undertaken at NIST in USA. One observation is that you can see the polymers are basically linear chains and in solutions they tend to fold up and the radius of gyration from the Guinier region of SANS can be found out. This is pluronics polymer in deuterated water. This gives an R_g of 34 Å, which means that it folds up in water with a structure which has got a radius of gyration of 34 Å.

Similarly, dendrimer is another multi branch polymer also studied there and you can see that the log plot is a straight line, because the slopes are different the radius of gyration differs based on the concentration of the dendrimer in deuterated water. This is another example of finding out radius of gyration of polymers using small angle neutron scattering. This work was done at NIST in the USA, in Gaithersburg.

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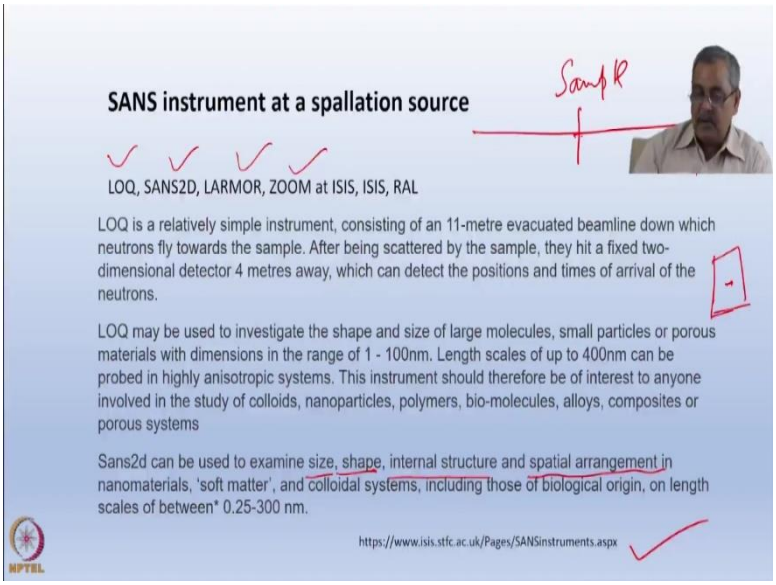

I will just quickly mention the SANS instruments at various major sources. I have taken example of the SANS instruments that are available at ISIS Spallation neutron source in Rutherford Appleton Laboratory. There are a number of small angle machines because of the high demand. One of the most used is LOQ, SANS2D, LARMOR and ZOOM. All of these are small angle neutron scattering machines and the structure of the machines are similar to what you find in a reactor. Only thing is that here we use time of flight techniques to determine the λ and the q values, otherwise the rest of the structures remain same.

LOQ is a relatively simple instrument. So, depending on the collimation and intensity of neutron that you can retain, you try to make the flight path long because you need good collimation. So, there is a long flight path before the sample. And after the sample, you have a long flight because the farther you take your detector. If I put a two-dimensional detector small q scattered data will be well separated from the direct beam if you can go farther. You have to have a large flight path before the sample to collimate the beam and you have to have a large flight path after the sample to get the small q data. There is an 11 m evacuated beam line down with the neutrons flight path towards the sample and then they have got the two-dimensional detector fixed 4 m away. You can play with the distance of the detector depending on how much resolution you would want. LOQ can investigate sizes from 1 nm to 100 nm. Length inhomogeneities up to 400 nm size can be probed in highly anisotropic system.

I have just given information what is on their site for SANS2D. Basically, size, shape, internal structure and spatial arrangement determination is important for understanding such soft

matter. Many times, we have fitted prolate spheroid, you must have noticed. We have also found out the fractal dimension of these objects. Those are the internal structures and also determined the spatial arrangement in nanomaterial soft matter.

All the things I discussed so far is soft matter. Soft matter means they are viscoelastic they have very small shear stress to change their shapes and they can be bent easily. That is the definition of soft material. I told you earlier that studies of them are very important today for science as well as for applications.

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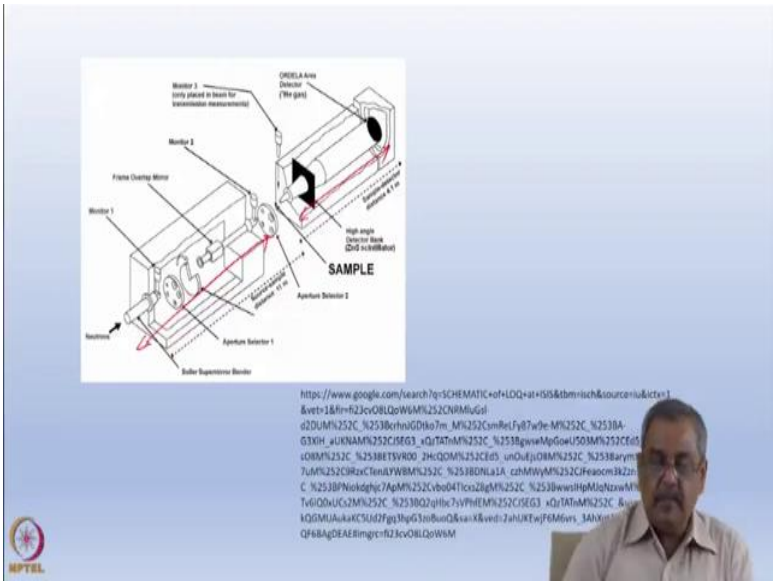

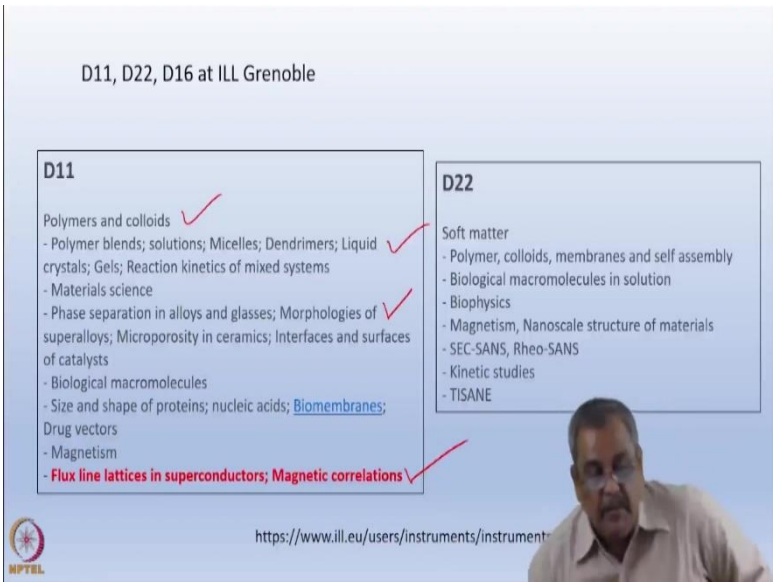

This is just a schematic of the LOQ instrument. You can see that there is large flight path before the sample and there is a large flight path after the sample. First one dictates the collimation of the beam and the second on dictates resolution with collimation on the detector.

Similarly, if I talk about the high flux research reactor at ILL, Grenoble, there are D11, D22 and D16 instruments and more beamlines. I just chose these as they are the small angle neutron machines at ILL and you can see that polymers and colloids were studied on these instruments. I gave you examples on polymers, polymer blends, Micelles, dendrimers. I showed you the dendrimers with rigid spatial base Gemini surfactants. I also mention phase separations in alloys and glasses, though I did not show an example of that. Super alloys, biological macromolecule have also been studied. I will now give you an example of flux line lattice in superconductors. It is a extremely interesting study in fundamental science, and I will explain this to you. And similar range of studies that you can carry out on D22.

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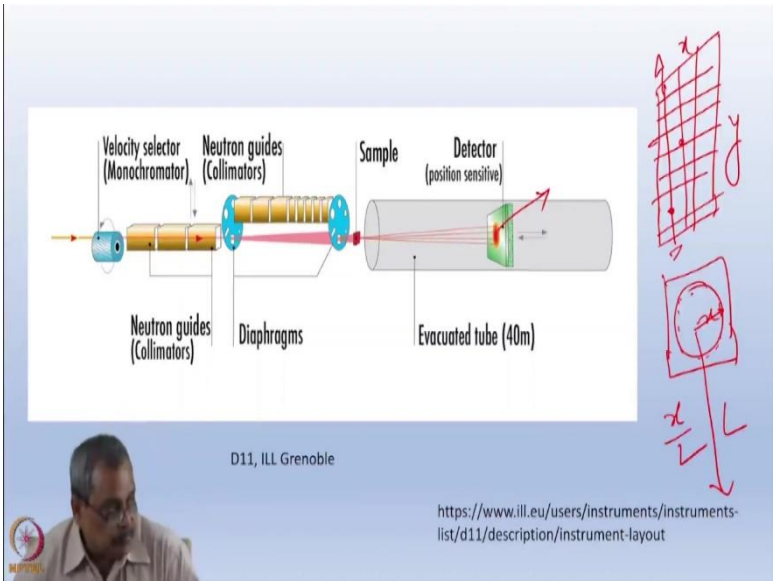

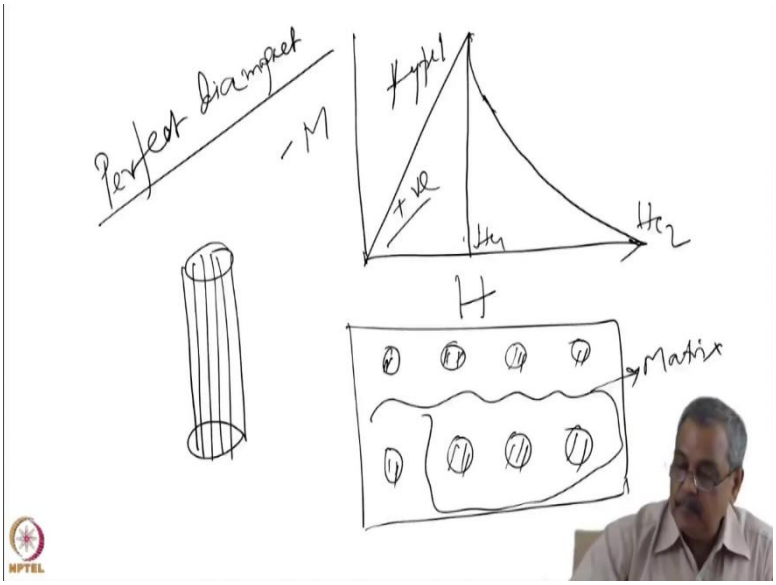

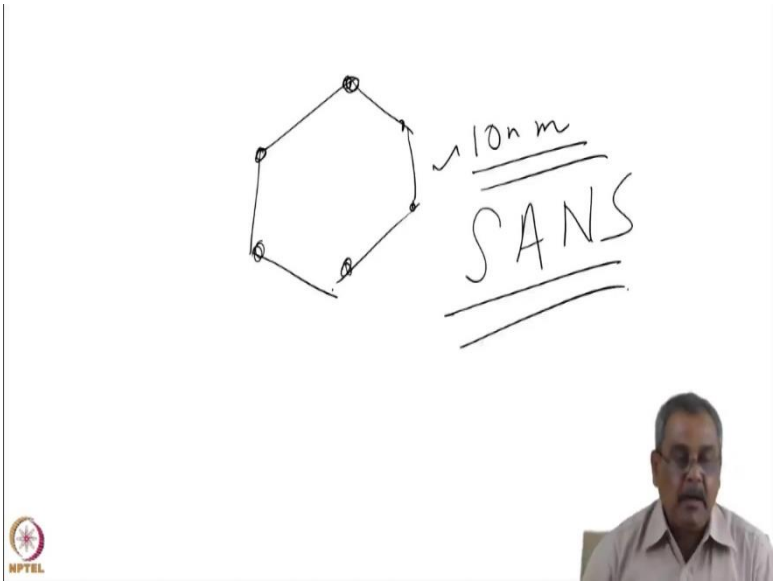

I will talk about flux line lattice where the arrangement in beamline is very similar to earlier examples. you can see the large flight path. I keep showing you the schematics, because small angle machines have a general criteria of a large flight path before the sample to collimate the beam anda large flight path after the sample to dictate good resolution for small angle machines.

I must mention here that these detectors are two-dimensional position sensitive detectors. I discussed with you earlier about one-dimensional position sensitive detectors. The position is sensed on a wire where the neutron beam hits. The signal depends on the charge collected at two ends of the wire. Now, in two dimensional detectors, you have got a X-Y lattice cross of these wires. I am telling you in a very simplistic way. Now, if the neutron hits here, I can find out on the *x* axis and *y* coordinates, where the neutron has been detected and assign the intensity to that particular pixel and ultimately you will get a structured figure like this. So, if it is a two-dimensional detector, you might get a circular cone of intensity on this, which is the small angel intensity. Because of the sample to detector distance *'L'*, if this is *'x'* than *x*/*L* will be the angle with a small angle scattering intensity.

Now, let me may introduce you to superconducting flux lattices. I have jumped the subject, so, I have the responsibility of telling you what is a superconductor and what is a *d*-wave superconductor? The thing is that you must have been taught in your master's degree that in superconductor, you have Cooper pairs and Cooper pairs form between two electrons at the macroscopic length scale. If I plot magnetic moment in the sample (M) versus applied field (H) in a type-I super conductor up to some *'H'* the system resists entry of the field in the superconductor. so, it is '-*M*'in the plot. Beyond a certain field the field enters the superconductor and then the superconductivity is destroyed. But in a type-II super conductor,

at some field it starts penetrating the medium in form of flux line bundles. So that there is a field called H_{C1} where the field starts penetrating the medium and at the field H_{C2} the field completes the penetration and the superconductor becomes normal. However, in type-I, it suddenly goes normal and the super conductivity disappears. Superconductor is known as a perfect diamagnet and does not allow entry of magnetic fields.

In type 1 it suddenly allows the magnetic field entry and becomes normal, while in type 2 superconductor there are vortices that means magnetic flux lines are in form of vortices and if we take a superconductor cross section there are these vortices. It was shown by Abrikosov that the surface energy of these vortices is positive in type-I superconductor so they don't form here, but in type 2 this surface energy is negative and helps to reduce free energy by having vortices. So, these are magnetic flux lattices embedded in the basic matrix. That means these will be superconducting parts and the vortices are non-superconducting part Now, the question comes that if there are vortices, I may allow them to form a lattice now with each vortex repelling one another. When two particles are repelling each other then these vortices should form a hexagonal lattice. Now, the length scale of this hexagonal lattice is large, unlike crystallographic structure the length scale is large: of the order of 10s of nm. That means, even if I see a Bragg peak from this lattice, it should be at a low q and that is where the SANS becomes very important. Now, I will give you a very interesting example.

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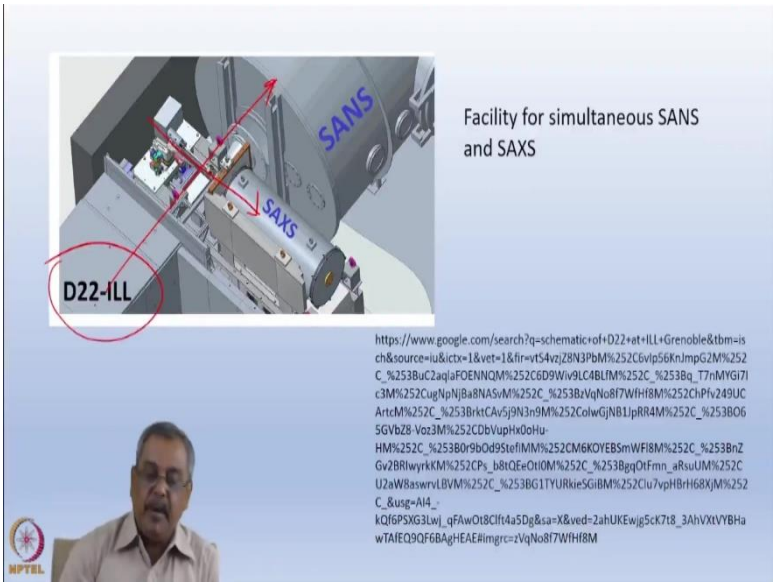

Actually, in case of D22 at ILL you have the facility of doing small angle neutron scattering and small angle X-ray scattering simultaneously on the sample. So, you can do SANS in this direction. And on the same sample, you have got a small angle X-ray machine which detects

SAXS data in this direction. So, you have crossed the sample with neutron beam and small angle X ray beam and you can do in situ studies and later you can also stich the data. This is what I was talking about. In our system we had to take out the sample from MSANS and collect the SAXS data separately. Here you can do it at the same time in D22. Now, I will go back to Vortex Lattice.

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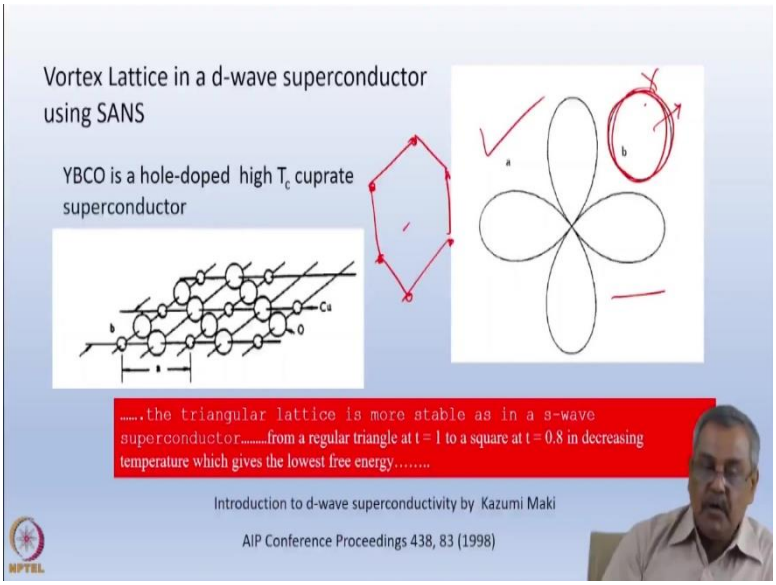

Study of vortex lattice in a *d*-wave superconductor using SANS is my target. I talked to you about type 2 superconductor in which there are vortices. Now, in conventional superconductors, the coupling happens between the electrons of up spin and down spin and then they were called *s* wave superconductors. The *s* wave superconductor had an order parameter which is spherical in momentum space and for a spherical *s* wave superconductor the vortex lattice as I told you, should be a hexagonal structure.

Now comes new high T_c superconductors like, yttrium barium copper oxide (YBCO), which is a *d* wave superconductor. The *d* wave superconductor means basically you can see that this is a *d* wave order parameter., The copper oxygen planes in YBCO are where holes are doped.

And basically, it is a *d* wave superconductor and without getting into the argument how *d* wave superconductors are justified, there are some interesting observations in the *d* wave superconductor. One is that under high field this hexagonal lattice which you find in *s* wave superconductors also form initially at low filed for *d* wave superconductors. It will form a hexagonal lattice with the vortices that is embedded in the matrix. But as we increase the field the hexagonal lattice should distort to a square lattice!

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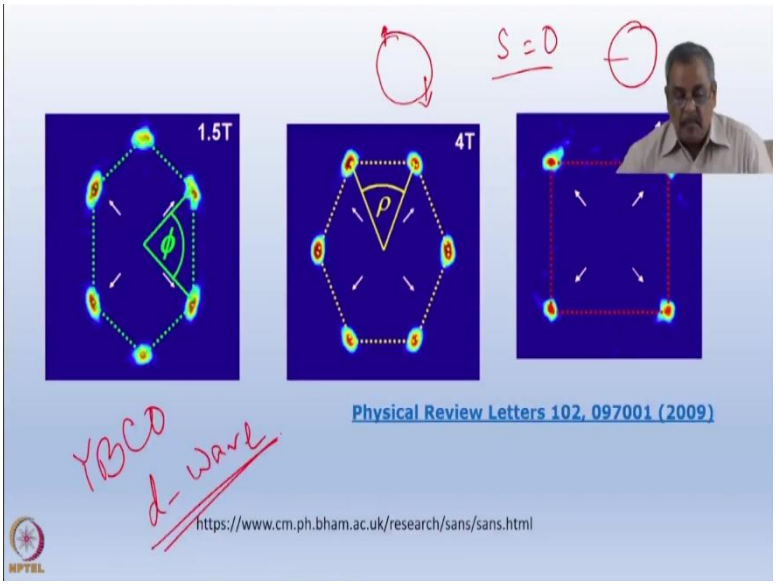

Now let us see the experimental results is done on a small angle instrument. You can see this is the low field data at four Tesla and as you go to nearly 11 T (high field), you get the square lattice in the diffracted beam. So, this experiment is a huge justification for accepting that YBCO is a *d* wave superconductor.

Actually, these are the new justifications for accepting that the superconducting order parameter need not be just s-wave and this square lattice is an observation of high field vortex lattice. This is a large picture from a YBCO which is an excellent result. You can see that so, far we have been discussing applications in chemistry biology and engineering. This is the deep physics observation, where it justifies the fact that YBCO is *d* wave superconductor.

I will come back to superconductors later when we talk about thin films. But with this example, I draw curtain on examples in SANS experiments. And now, we will move forward to another mesoscopic techniques like neutron reflectometry. Thank You.