Neutron Scattering for Condensed Matter Studies
Professor Saibal Basu
Department of Physics
Homi Bhabha National Institute
Week 7; Lecture 18C

Keywords:Guinier Law, Porod's Law, Fractal dimension, Scattering Length Density (SLD), Contrast Variation

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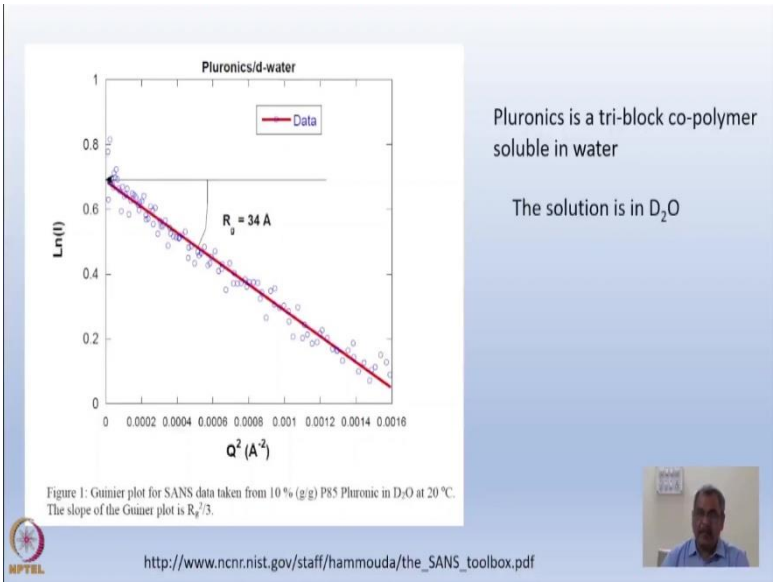

In the last module, I talked to you about Guinier approximation and showed you how we can get hydrodynamic radius or radius of gyration of a mesoscopic object, with example of the Pluronics.

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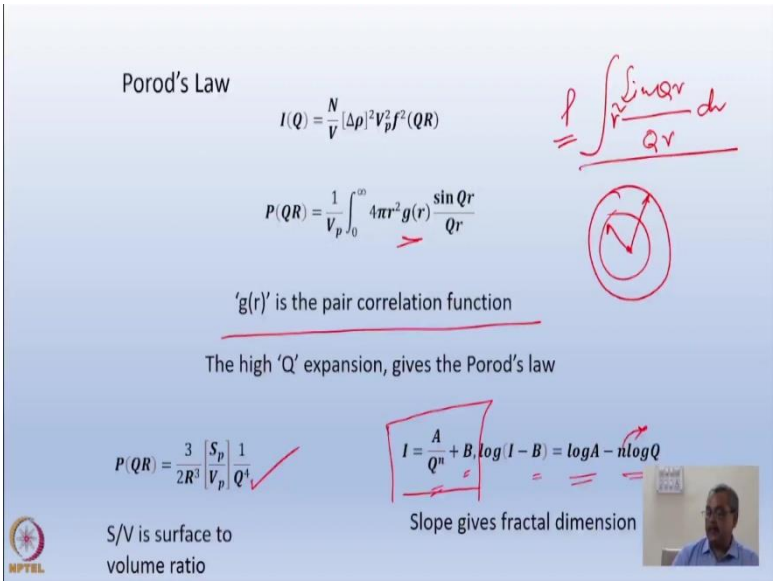

Next is Porod's law. Here I can write down the P(QR), or f^2(QR) in this expression, in terms of a pair correlation function. g(r) is the pair correlation function. If you remember earlier I had done this exercise for the form factor. If you remember $\int_0^R r^2 \frac{sinQr}{Qr} dr$. I took a constant density ρ outside the integral. I talk in terms of pair correlation function, that means given a sphere with particle density ρ if there is a particle with here, what is the probability of getting another particle at another place, which is at a distance 'r' from here. That is given by g(r) and in common knowledge this is called the pair correlation function.

Now the high Q expansion gives the Porod's law and the Porod's law for smooth surfaces goes as $P(QR) = \frac{3}{2R^3}\left[\frac{S_p}{V_p}\right]\frac{1}{Q^4}$, where $\frac{S_p}{V_p}$ is a surface to volume ratio for a scattering object (mesoscopic here). And here, if I plot log of *'P(QR)'*, you can see A is a constant plus background that is the intensity here. Because pair correlation function, gives me the intensity *'P(QR)'*. So, I equate intensity to a background plus A/Q^n and then if I do a log plot of it, that means log of intensity minus the background, I get log(A) - n log(Q), this *n* gives you the *'fractal'* dimension of the surface of the object under study.

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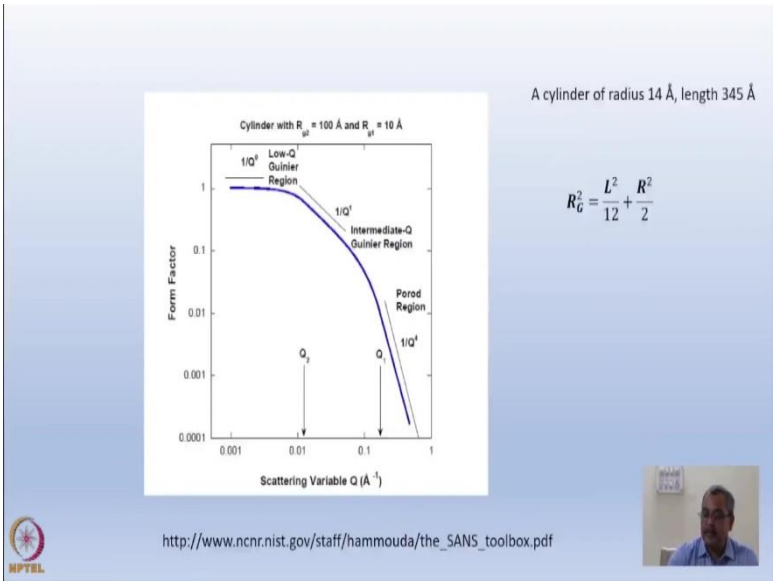

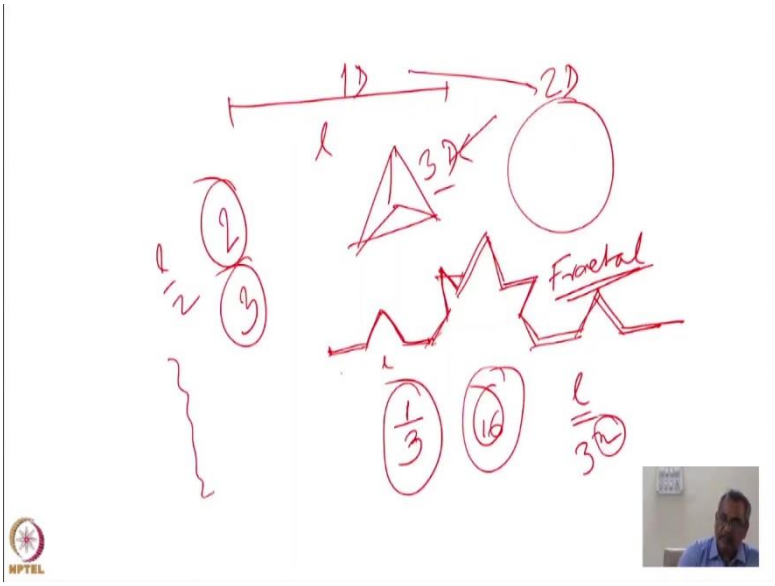

When I say dimension of a surface, most of the objects that you usually see are defined by integral dimensions, for example, a straight line (1D), a circle (2D), or a pyramid (3D). But the fact is that there are objects, which have dimensions between these integral values. Let me explain this with one simple example. Suppose, I have got a scale of length *l* with which I measure this object. So please see, this is *l, l, l, l or 4l*. So, if I measure it with a scale or with a ruler which has got *l* as minimum count, I get the length 4*l*. But now, on this object , let me try to put something else.

Let me put such breaks at half a distance, t as shown in the figure. Now, you see in this object, if I measure with a ruler which has *l* as minimum count, I still have 4*l* length. if I reduce the minimum measuring length to *l*/3, then I measure 16 units now. Let us have an object which is one dimensional like a straight line. If the line has a length *l 'l'* and if I have a measuring

ruler or measuring rod, which can measure *l*/2, the measurement will linearly scale. It will go to 2 units. If I make it one third, it will go to 3 units. But for this object when I made the minimum length one third, you measure 16 units! This is a fractal object.

Fractal objects do not go linearly or with any integral power of 3 (this example). It is a non-integral power of 3, when you reduce the scale to one third. I can say it is 3^n and it is not 3^2 or 3^3, but this is some non-integral number. This *n* is a *fractal* dimension. The concept comes the way things are embedded in space. One example is possibly, if you take a tree and its leavesand if you try to measure the dimension of the surface of the tree or let us say, the length of the coastline of India,

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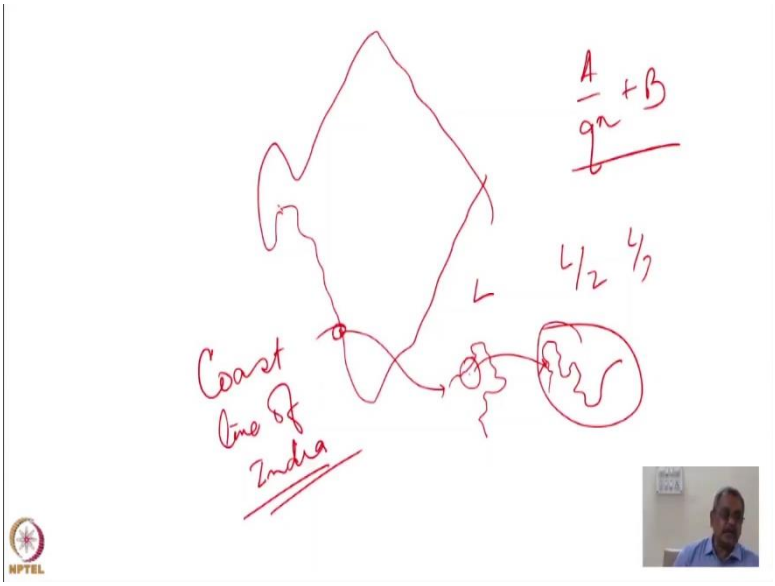

This is how the coastline looks like. If I looked here, and I measured with a length scale *l*, I will get some length for this coastline. But if I magnify this coastline here, it is actually somewhat like this. And if from *l*, if I go to *l*/2 as minimum measuring unit, or *l*/3, the length I measure is not 3*l* or 2*l*, but longer. Or again if I take a part of this and furtherexpand it, this is not a straight line, it will be something like this.. So, as you go to smaller and smaller length scales, the length of the coastline of India changes but not linearly with the unit, because it is a fractal line.

Now, this fractal dimension, we can measure using SANS, because I have Porod's law, which is $\frac{A}{Q^n} + B$, where 'n' is the fractal dimension of the surface of the object under study. And in our experiments, we can find out whether the object that I am trying to see has a smooth surfaceor it has a fractal surface.

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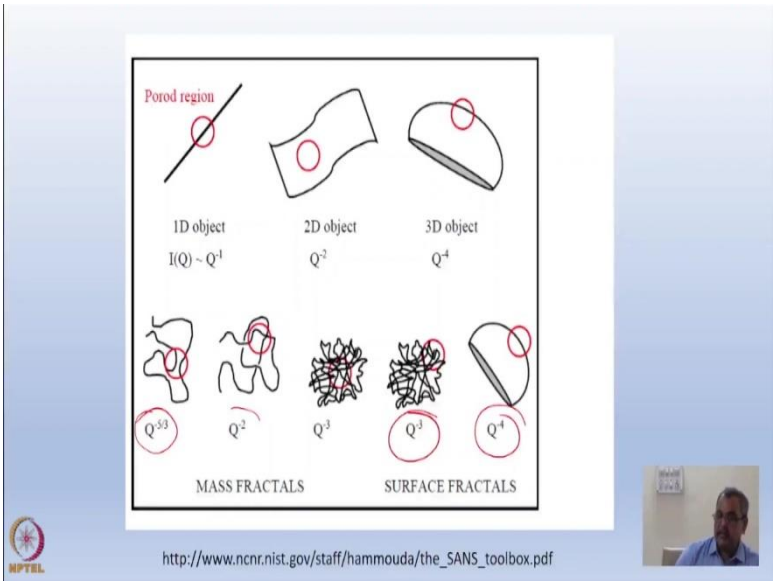

I have just taken examples of some fractal surfaces from this NIST toolbox. These are one-dimensional, two-dimensional and three-dimensional objects. And the Porod's law will give you Q^{-1}, Q^{-2}, Q^{-3} while fitting SANS data at larger 'Q' values from the slop of the *log(I)* plot . But when you go to mass fractals, or surface fractals, you find this Porod's law changes. And from here, we can always find out the fractal dimension of the object that you are studying using SANS experiment. I will give you examples later.

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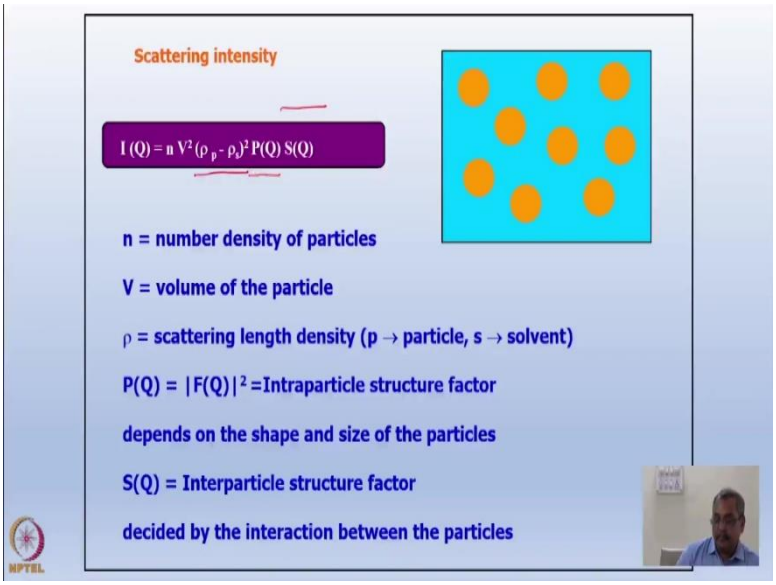

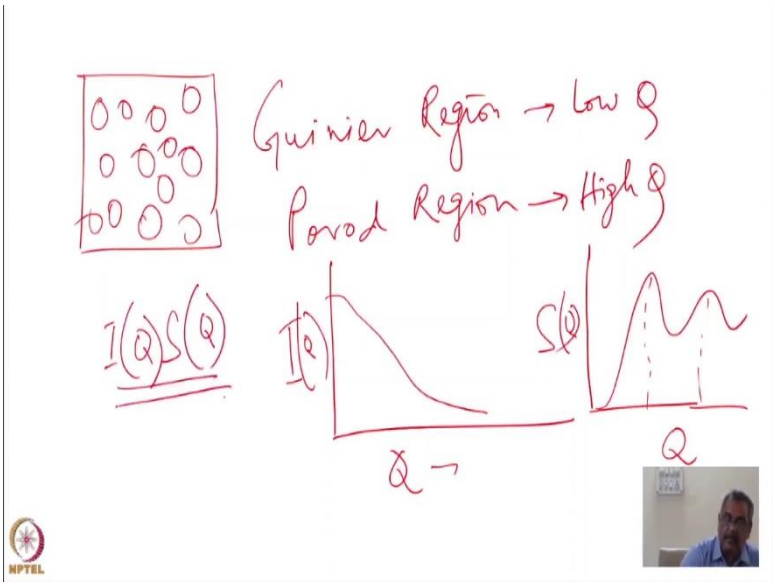

I have introduced you to Guinier region which is low *'Q'* region and Porod region which gives me surface to volume ratio at high *'Q'* [within *'Q'* limits of SANS]. So, with this, let me get on to something called the contrast factor. As I told you earlier that the intensity has got several factors in it as shown in the expression $I(Q) = nV^2(\rho_p - \rho_s)^2 P(Q)S(Q)$. n is number density of particles with 'V' volume of the particle. We have got a contrast factor$(\rho_p - \rho_s)$, between the solvent and the particle,. Then you have the form factor *'P(Q)'* for the particle and you have something called a structure factor *'S(Q)'*. What is the structure factor? I will borrow the concept from liquid and amorphous system that I taught you.

If you have a very dilute system, then one particle's location is not correlated with the location of another particle. And what you measure in this experiment is just as I described you so far,

the form factor for a particle *'P(Q'*. But now, if I keep increasing the density of particles, then location of particles become correlated, because one, the particles cannot penetrate into each other and then as I argued earlier for liquid and amorphous system, there is short range correlation and a structure factor *'S(Q)'* will like this. That means you have peaks at specific *'Q'* values.

But these peaks are not well-defined peaks, as you find in Bragg diffraction. It basically signifies the correlation shells around a central particle, and its average over the entire ensemble of mesoscopic objects. So, now we have *'P(Q)'* multiplied by *'S(Q)'* that gives me the intensity *'I(Q)'*.

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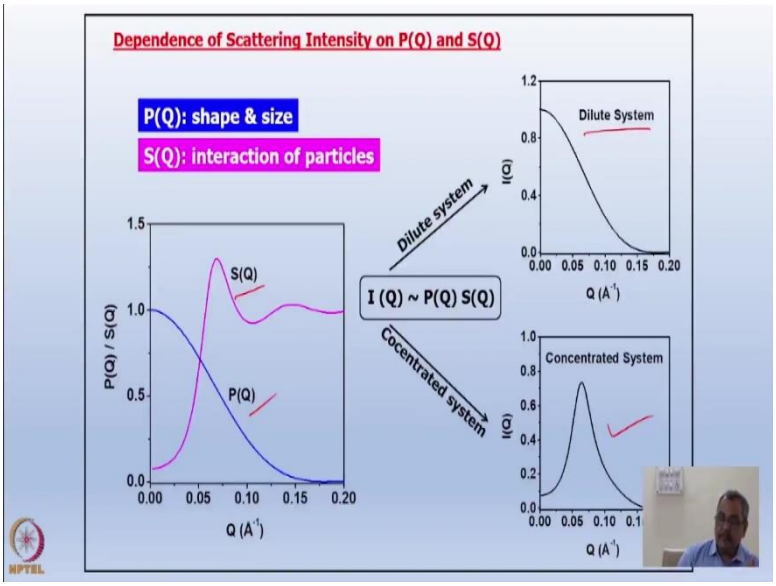

Basically, this slide integrated the whole thing. If you have a dilute system, you have got a form factor *'P(Q)'* here. When you have a concentrated system, you have got a peak in *'S(Q)'* and what you have in intensity *'I(Q)'* is a multiplication of *'P(Q)'* and *'S(Q)'*: both of them acting together. Multiplication of the two is something what you are going to measure when you do a small angle neutron scattering. Please note that, I am borrowing concepts from microscopic world and applying to mesoscopic world.

When I talked about microscopic world, I talked about atoms or ions surrounded by atoms or ions. Here, I am talking about larger particles like the micelles originating from the surfactant particles, pores in a solid rock or it can be precipitated in a matrix of metallurgical alloys. Here the particles are large (~nm), but the concepts are very similar:you have got a structure factor,

which tells you the nearest neighbor distances and you have got a form factor which talks about the object's geometry and my experiments measure both of them.

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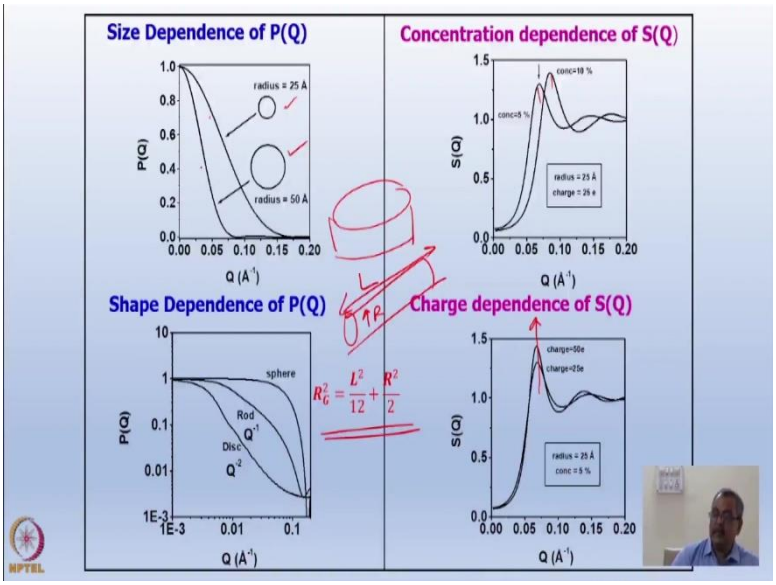

First there is a size dependence. Suppose I take the simplest example of a spherical object, so my '*P(Q)'* will fall faster if I take a dilute system of larger radius particle. The intensity will fall faster in *'Q'* compared to a smaller radius particleand from the log of intensity plot I can get the radius of gyration of these particles.

Now, comes the shape dependence. Many times, the organic assembly that I talked about, they need not be spherical always. They can be rod-like, or they can be like a disk and for all these you can find out the average hydrodynamic radius or radius of gyration which is given by R_G^2. For a rod I have written here the expression for radius of gyration, R_G, where R is the radius and L is the length of the rod. The nature of fall of intensity vs *'Q'* is different for different geometry in small angle neutron scattering.

So, SANS helps you to figure out the not only the size of the particle, but also the shape of the particle. Similarly, if the objects are in a solution (mostly this is true for a solution), when you increase the concentration of such particles, *'S(Q)'* will change. For example, when the concentration is increased from 5% to 10% for a particle of radius 25 Å and the charge of a 25e e you can see the peak position in *'S(Q)'* changes.

Similarly, when the charge increases, but the radius remains same, it is exactly similar to what I discussed earlier the in case of sodium chloride molten liquid. It was an ionic liquid where the ionic interaction stabilizes the distances. Here also same thing happens with charge. If there

is charge, then most likely the positively charged core would like to repel and maintain a certain distance with respect to nearest positive ion.

As we increase the charge on the object (e..g. micelle) this distance becomes better define and *'S(Q)'* peak goes up with charge, because higher charge means more columbic repulsion and they define the nearest shell more accurately with less fluctuation. So, this is the size dependence and concentration dependence of the data in case of small angle neutron scattering for various particles.But I repeat again these are not microscopic particles. I am harping again and again that these are mesoscopic sized particles and not ions or atoms.

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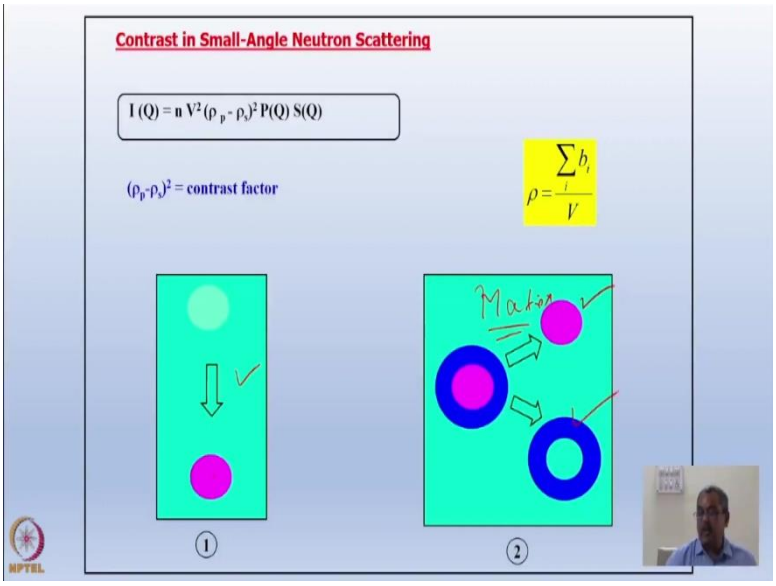

Manipulating contrast factor is a very interesting part of this talk and it is related to SANS technique. I wrote intensity depends on contrast! Now, this is where we can do a very interesting manipulation. Please see this diagram with a particle and the solvent with their respective scattering length densities: ρ_P and ρ_S, P and S corresponding to 'Particle' and 'Solvent' respectively. I can play with ρ_P and ρ_S, which are the scattering length densities for the particle and the solvent. ρ is sum over scattering length density of a particle divided by its volume.

Using various contrast, you can actually make different parts of a particle visible for SANS experiment. An example, the particle is invisible here, you can play with the matrix scattering length density and you can make the particle visible: How? I will tell you shortly. This is a very important technique used by organic chemists and biologists, for SANS.

Let us say you have a particle which has a core and shell structure, as I show here. I can play with the matrix. I can manipulate the contrast of this particular matrix (mostly H_2O +D_2O in various ratio) and when I match the core with the matrix, you see the shell or if I match the shell with the matrix, you will see the core in SANS experiment. So, using SANS in two different experiments, I can find out the core structure or I can find out the shell structure. How?

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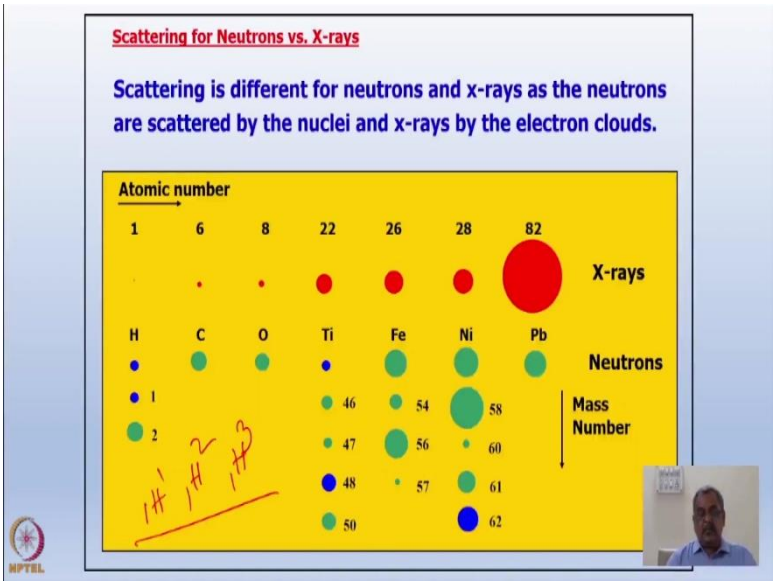

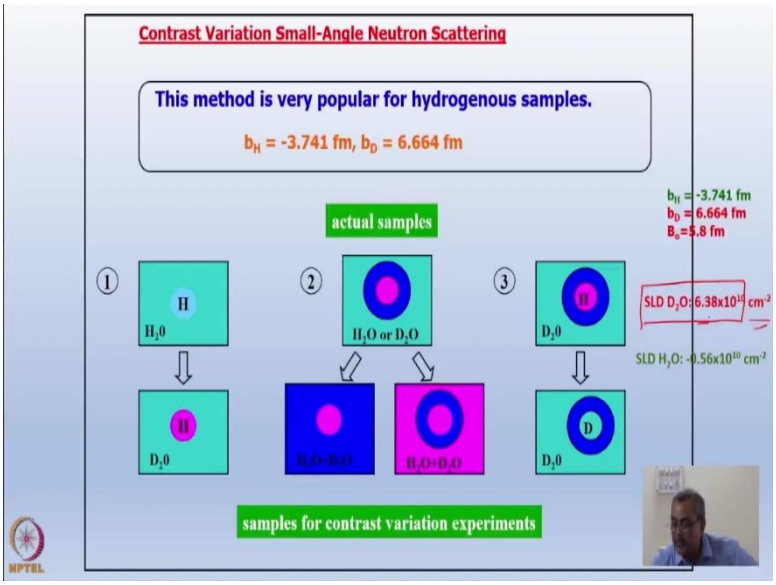

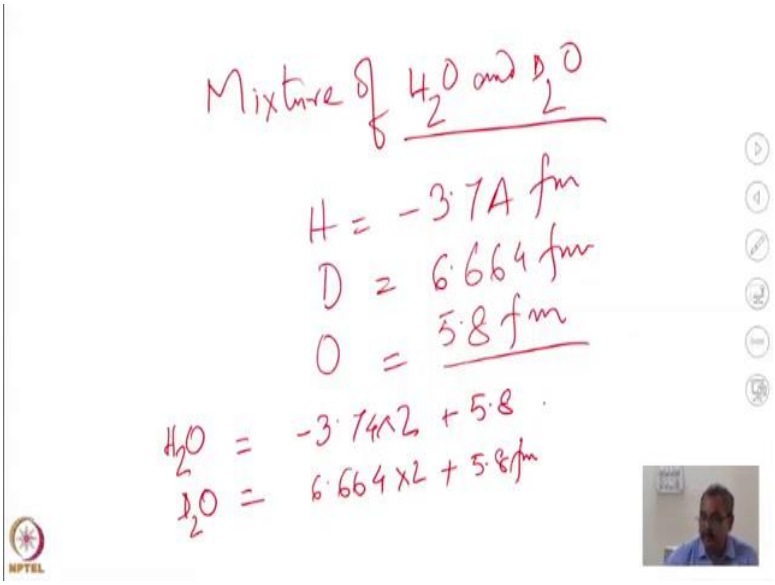

Scattering length is different for neutrons for different isotopes of an element. Hydrogen has three isotopes and they have different coherent scattering lengths for neutrons and that gives us a very interesting technique in our hand, which is contrast matching of a mixture of H_2O and D_2O. Let me just work it out for you.

This is for example, I have indicated hydrogen has a negative scattering length. why negative I will explain later, but now accept the fact that hydrogen has a negative scattering length of -3.74 fm. Deuterium has a scattering length of 6.664 fm and oxygen has 5.8 fm. H_2O has got to 2H and 1 O, so, [-3.74 x 2 + 5.8] fm is its scattering length. D_2O has [6.664 x 2 + 5.8] fm molecular scattering length. Let us work out their scattetring length densities.

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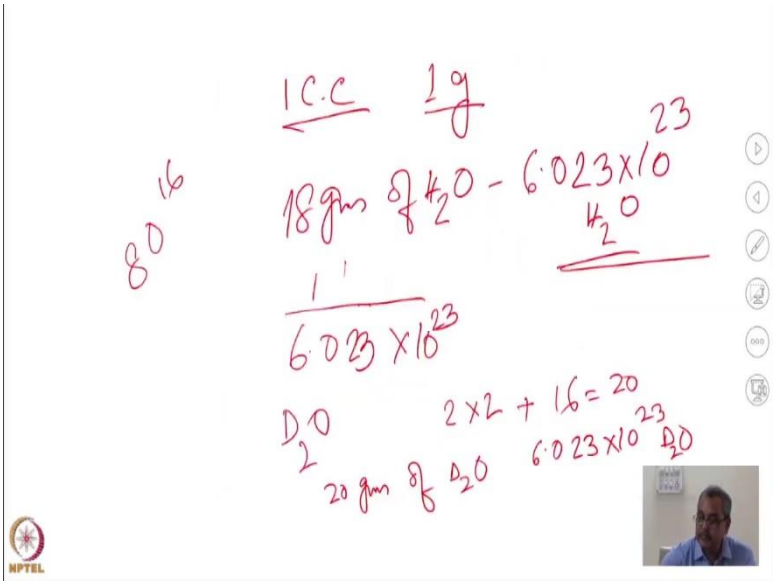

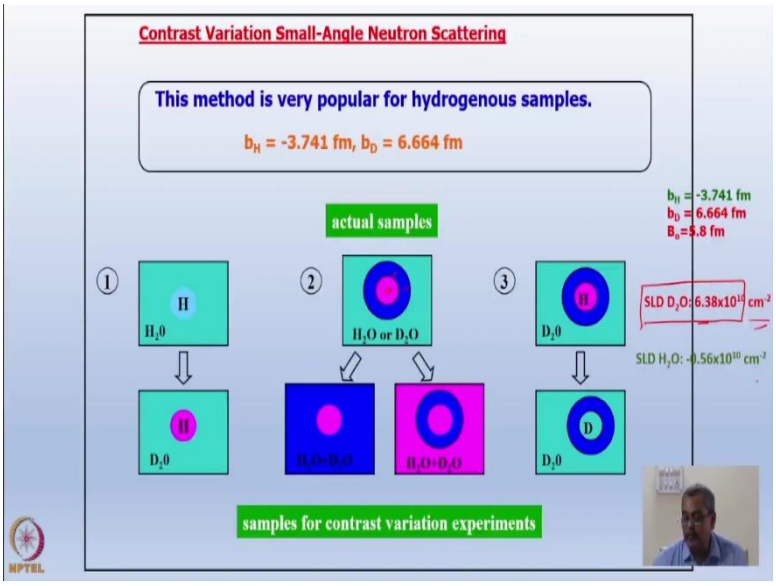

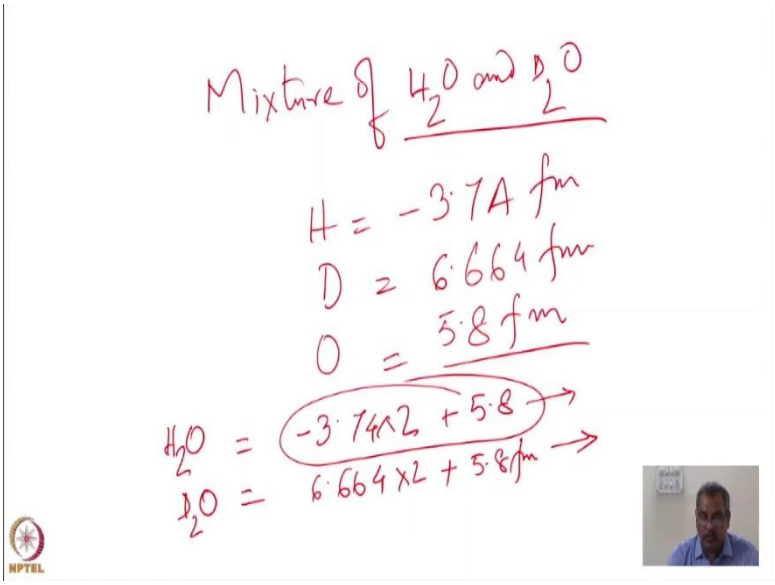

We know that $1cm^3$ water weighs 1 gram and we also know that 18 grams of H_2O will have 6.023×10^{23} [Avogadro's No.] H_2O molecules. I have worked out here these two values so for each molecule. Now 18 grams of H_2O has got 6.023×10^{23} H_2O molecules. That gives me the scattering length density for H_2O. Similarly, for D_2O, 20 grams of D_2O have 6.023×10^{23} molecules. We evaluate 1/20 of this, that is the number of molecules per $1cm^3$, multiply it with the scattering length that I evaluated for H_2O and D_2O and what you get is a very interesting thing.

In this simple calculation, you will find that the scattering length density of D_2O is 6.38×10^{10} cm^{-2}, which is a positive number. And the scattering length density of H_2O is -0.56×10^{10} cm^{-2}, a negative number. When I mix D_2O and H_2O then I can even make the scattering length density of the mixture as zero, by choosing proper ratio of the two. But most importantly, if I know the chemical formula of the core, and the shell, in our examples, whatever experiments you are doing, I can make a solution to match the SLD with either core or shell. It is with presumption that I am putting these large objects in a solution of D_2O and H_2O. Between H_2O and D_2O, the chemistry remains same.

When I put them in a solution, I can match the scattering length density of the solution either with the shell or with the core. And in the process, I can sort of eliminate different parts of the object in my experiment and I make samples with varying contrast of my choice. For example, if the sample is only hydrogen based, I put it in pure D_2O. If it is hydrogeneous, but with different scattering length densities of various parts, I can play with the mixture and tune the contrast. For example, if I put 1 cm^3 of water plus 1 cm^3 of D_2O,

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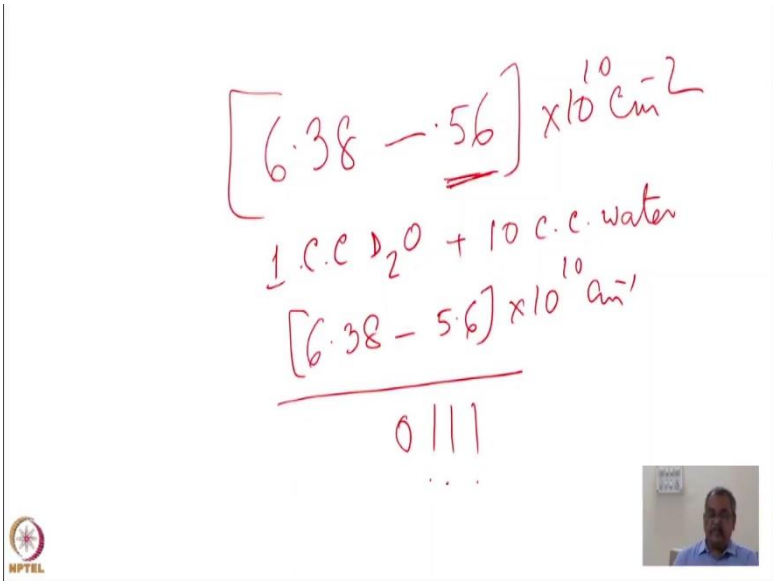

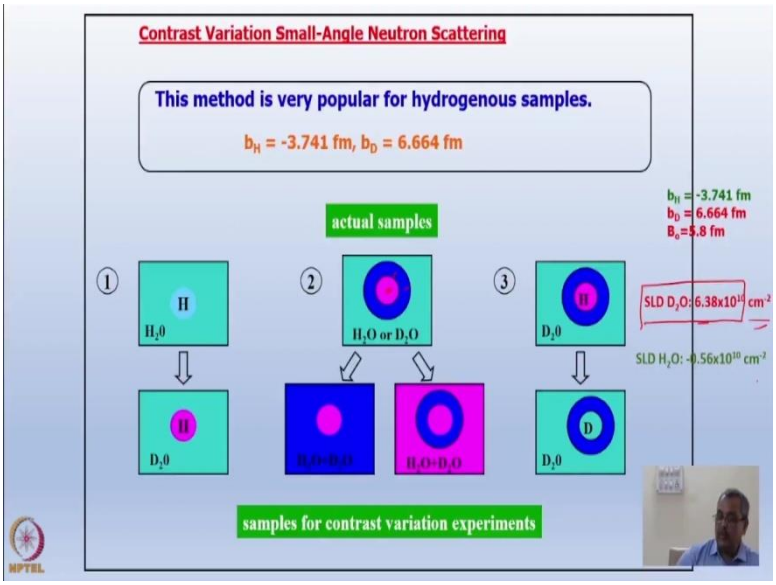

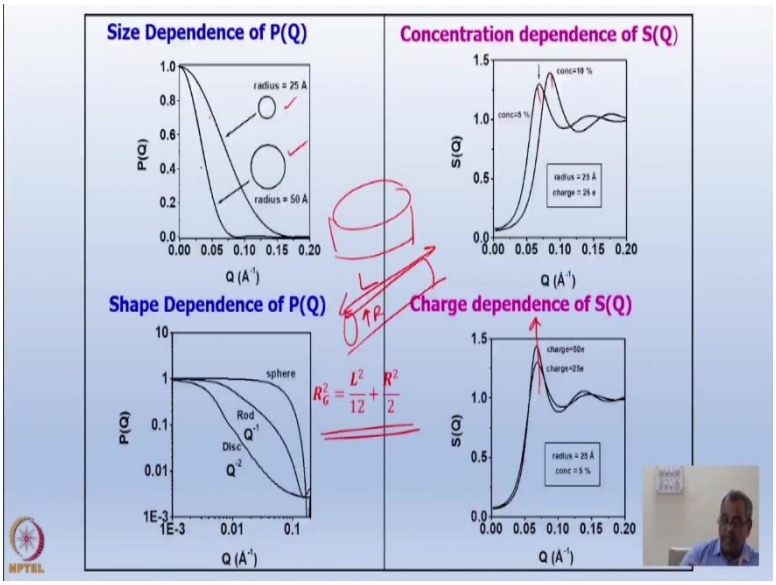

you can see the SLD becomes (6.38 -0.56) x 10^{10} cm^{-2}. So, you can see if I put 1 cm^3 of D_2O with 10 cm^3 of water then it will be (6.38 -5.6) x 10^{10} cm^{-2}. If I increase water slightly more, may be 11 cm^3 or 12 cm^3, I can make this SLD equal to 0.

So, I can make a matrix with zero SLD, but that is not the done always. What is done basically, in this kind of core shell structure, to match various parts of the object and the solution's SLD. Then you can find out the geometry of the object because you can find out the size , and shape of various parts, from the experiment. You can find different parts of the volume by eliminating various parts of the object through tailored SLD. It is an extremely strong technique available only with neutrons because H_2O and D_2O has got a huge contrast between them.