Neutron Scattering for Condensed Matter Studies
Professor Saibal Basu
Department of Physics
Homi Bhabha National Institute
Week 6: Lecture 17 A

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Till. Now, I have been discussing with you diffraction from crystalline solids. Now, I will move on to diffraction from liquid and amorphous systems. Very briefly, I will also mention the special features of single crystal diffraction in this lecture.

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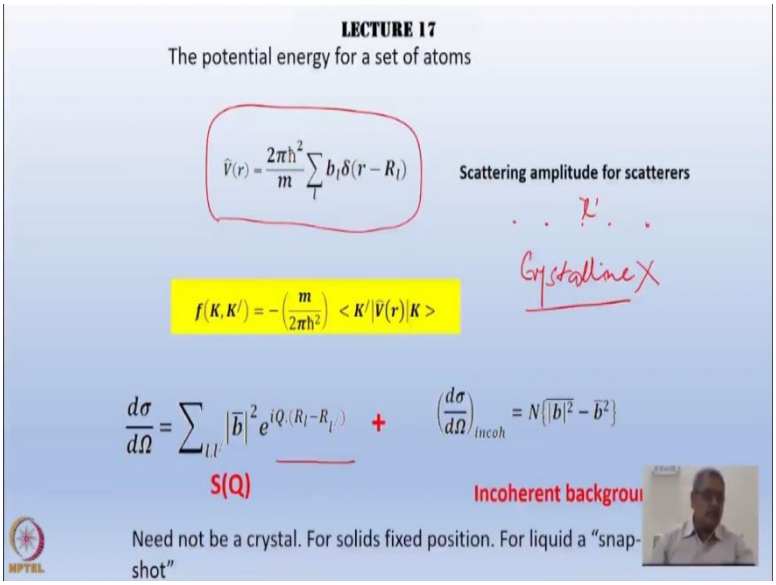

When we talked about crystalline solids, before that in the general formalism of neuton diffraction, I introduced you to the potential energy as seen by a neutron,

$$V(r) = \frac{2\pi\,\hbar^2}{m}\sum_l b_l\,\delta(r - R_l)$$

This is a scattering amplitude for an arrangement of scatters. Scatterers are at points 'l' and total scatting potential is the sum of the delta functions. In this expression, I have not mentioned anywhere that this is crystalline. This is just a general arrangement of scatterers. I also showed

you that under Born approximation the scattering amplitude of going from K to K' wave vector is basically given by, $f(K,K') = -\left(\frac{m}{2\pi\hbar^2}\right)\langle K|\hat{V}(r)|K'\rangle$.

Then I wrote the scattering intensity per unit solid angle $\left(\frac{d\sigma}{d\Omega}\right)$ which has a coherent part where the coherent scattering amplitude is multiplied by the structure factor and a coexisting incoherent background which is coming from the fluctuation of scattering amplitude around a mean value. This is a recollection of what we did. But in these expressions, nowhere I have assumed that the material is crystalline but these are solids and the atoms are fixed at some points. Now, another question comes when I am talking about liquids and amorphous systems. Then for liquids, the atoms and molecules are moving around.

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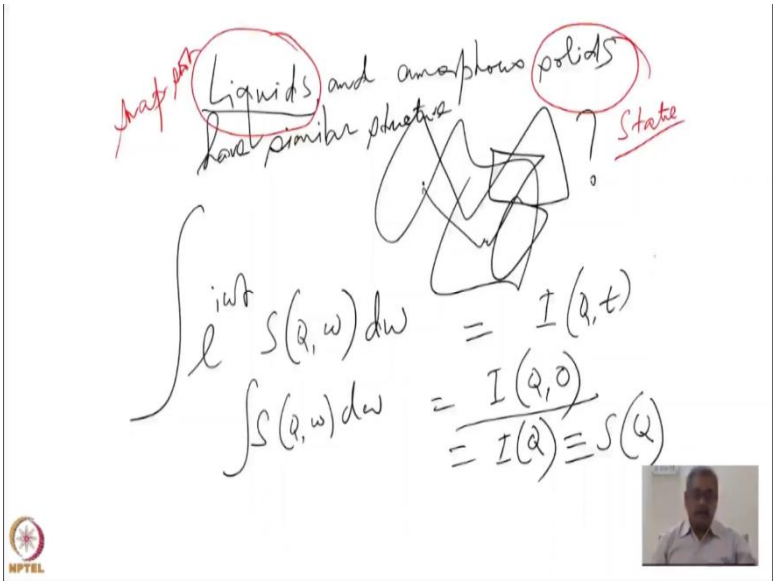

For a liquid, the atoms and molecules are continuously diffusing inside the liquid then structure-wise what will it show in an experiment?

If you remember if one integrates $e^{-i\omega t}S(Q,\omega)$ over $d\omega$, it results in $I(Q,t)$. In this integration if t = 0 then it is equivalent to $\int S(Q,\omega)\ d\omega = I(Q,0)$. For most of our structure works I can call it $I(Q)$ or $S(Q)$ what I will be measuring in a scattering experiment. There t = 0, but there is no defined origin of time. Basically, the experiment is done over a finite time and I keep adding snapshots over snapshots over snapshot and I get a time averaged picture which is same as what we get from static particles at their sites.

Liquids and amorphous solids have similar structure. In case of liquids, it is a snapshot and in case of solids it is a static picture. Otherwise, I will show you that structurally they are similar.

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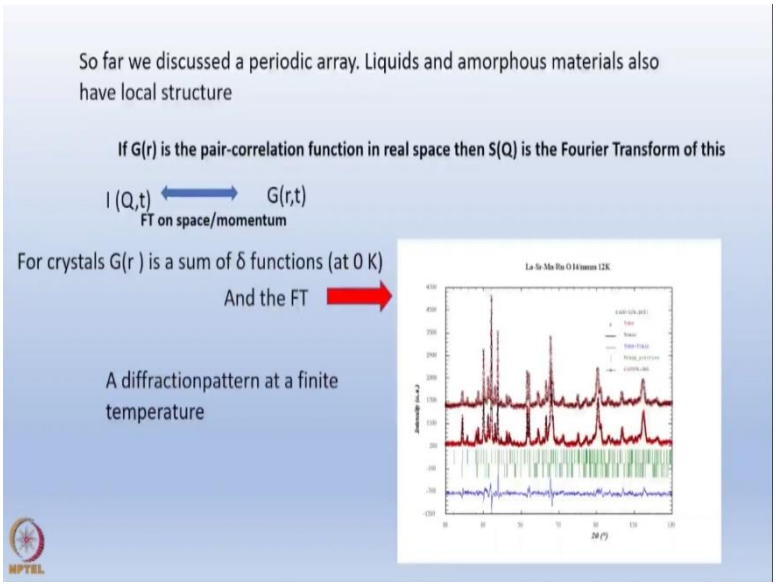

So far, we discussed the periodic array having long-range order. Does it mean that liquids and amorphous solids, do not have any structure at all because they are disordered materials in our common parlance. It is not true. All of these have local structure. I will give an example.

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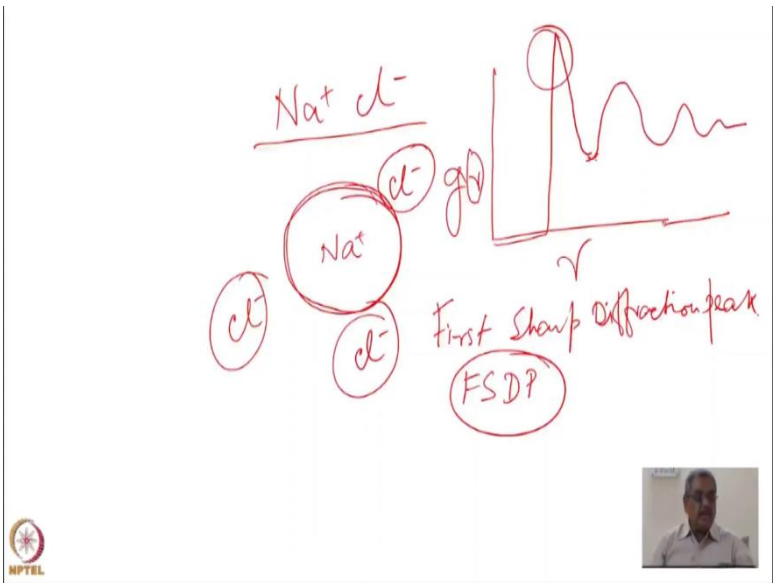

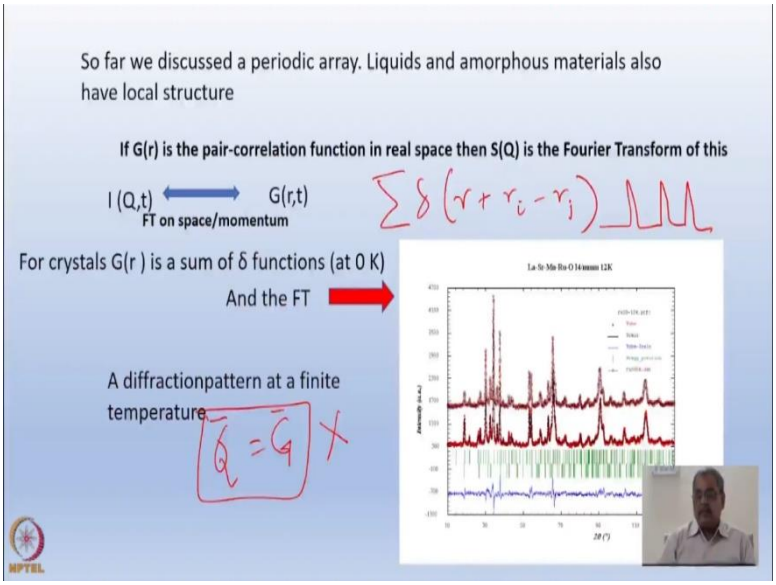

Let us consider a case of sodium chloride. It is very simple to explain with respect to a molten sodium chloride salt. If I take molten sodium chloride salt then a central sodium atom, it will like to be surrounded by chlorine because of its ionic potential. If I calculate the structure factor for this molten salt or g(r) in the real space and time then up to some distance from the origin, g(r) or pair correlation function is zero because nothing can come closer than that distance to the central atom or core. It can be a hard sphere. Here, it is an ionic core. But after that the chlorine occupants will have a sharp peak and then the peak will fall. After that most probably the chlorine number will go down and there will be more sodium atoms surrounding the core.There will be a second range of correlation and g(r) oscillates and finally go to the density of the liquid.

So, you have to have local structure here and we talk about first sharp diffraction peaks in amorphous solids and liquids known as FSDP. So, always these amorphous and liquid disordered materials, do have local structure and this is of great interest in many cases. Because we would like to know the molecular and atomic arrangement in such liquids and I will elaborate it with a few examples.

In case of periodic lattice, we do have a sum of delta functions, if I take out temperature effect. So, my correlation function is a sum of delta functions which are atoms sitting at locations. And its Fourier transform gives an intensity pattern that I will obtain, if I do a diffraction experiment with a periodic lattice. I have just picked up a random diffraction pattern, one on Lanthanum- Strontium-Magnesium data obtained in a diffraction machine at Dhruva.

Here, because of periodicity, we also have lots of selection rules. For example, when I do the diffraction from a periodic lattice, I told you that a scattering vector Q has to be equal to G, one of the reciprocal lattice vectors. In case of liquid and amorphous structures, we do not have a reciprocal lattice. Hence, this kind of selection rules are not applicable to liquid and amorphous materials. Because of this $Q = G$, I discussed with you before I went to diffraction problems that there is something called Ewald construction where the scattering vector hits the Ewald sphere every time the there is a reciprocal lattice point on the Ewald sphere. If there is a reciprocal lattice point, cutting the Ewald sphere, you will have a diffracted beam in that direction.

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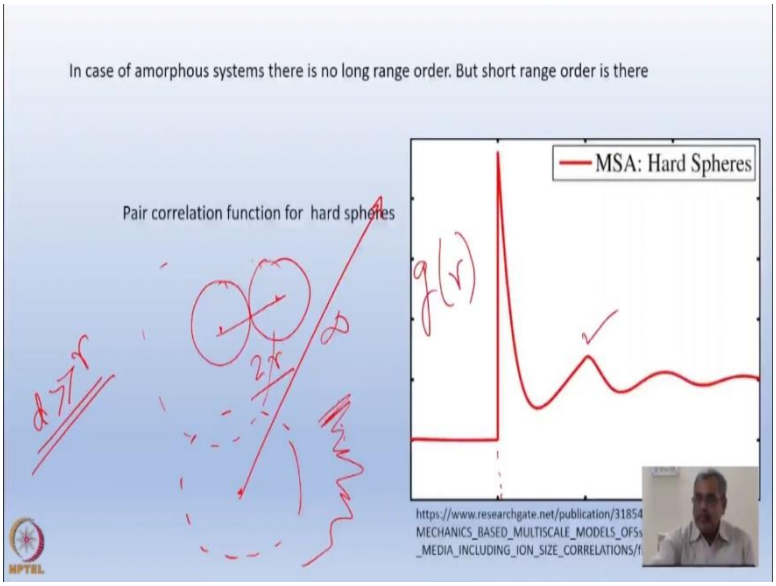

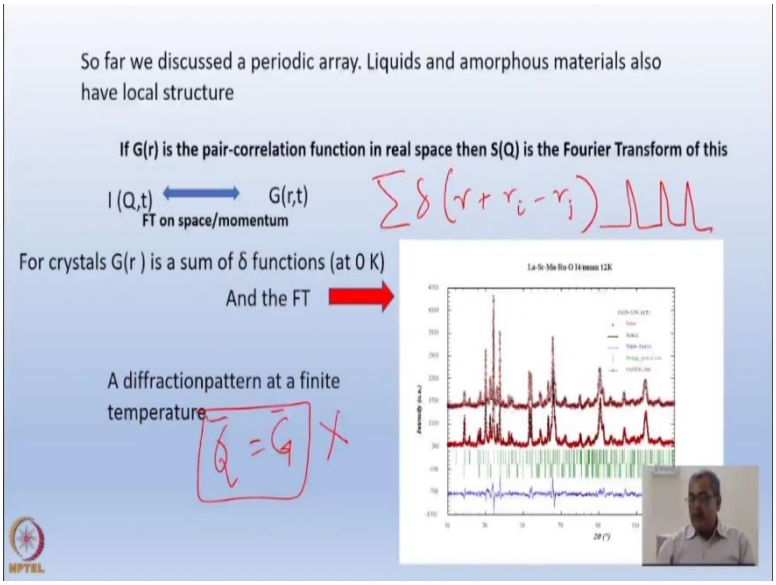

We do not have this kind of sharp peaks in case of liquid and amorphous systems but what we have is something like this. It is a simulated pattern for an arrangement of hard spheres. Hard spheres means that the spheres can at best touch each other and if their radius is r then the minimum distance between the centers can be $2r$ and no distance can be below that. But then in this arrangement, because the spheres are touching each other, you will have arrangement of other hard spheres around the central hard sphere and then I will have a sharp peak in pair correlation function g(r). I must mention it here for you to be cautious. When I say center, the center is also not fixed for a system. Any atom can be taken as a center and then this local arrangement appears. When I talk about this distribution, it is an average over a whole arrangement of spheres and any sphere can be the center of our coordinate system and then you have this distribution. After that you have the second shell. You can see, what happens actually the second shell around the central atom. The central one can be anywhere and the distribution is averaged over various statistical ensembles: ensemble of the hard spheres. This average shows a very sharp first peak in the g(r). Then there is a second peak. If I have a center here, the first one is pretty well defined but the second shell is diffused, third one is even more diffused. When you go very far away, at a distance much much larger than the radius of the sphere then you get a constant g(r). Because then the correlation function goes to the average density of the liquid (or amorphous solid). So, this is what I get when I talk about a crystalline solid and this is what I get when I talk about an amorphous solid or liquid. This is what we will be trying to understand and measure in our experiments using liquid and amorphous systems.

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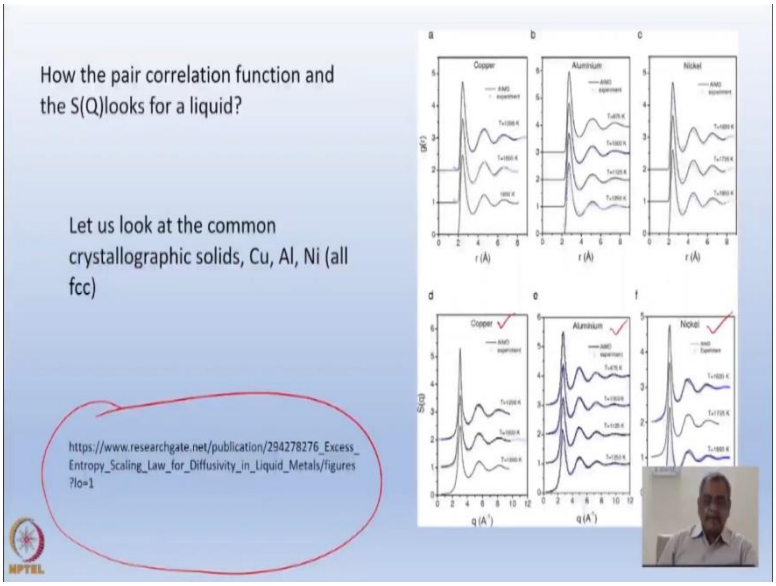

How does the pair condition function look in liquid or amorphous state? I have chosen some results from common metals that you are aware of, copper, aluminium and nickel. In solid form, all of them form fcc lattice. Iron forms bcc. This is how it looks if you measure the S(Q) of these materials in liquid form. You can simulate the same data using a random arrangement of spheres. Here the experimental data and the fitted curves are shown for copper, aluminium and nickel. So, you can see that when the metals are melted, still they retain the local structure and their g(r) evaluated from the fit of this data are given on the top panel. So, hard spheres are a good point to start with in case of liquid and amorphous system simulation.

In case of crystallographic structure, if you remember, we talked about 32 point groups, 14 Bravais lattices and 230 crystal space groups. We can input the crystal structure as one of those space groups and also, we can define the magnetic structures in terms of the propagation vector. In case of liquid and amorphous systems also, either we have to resort to direct Fourier transform or try a model-fitting.

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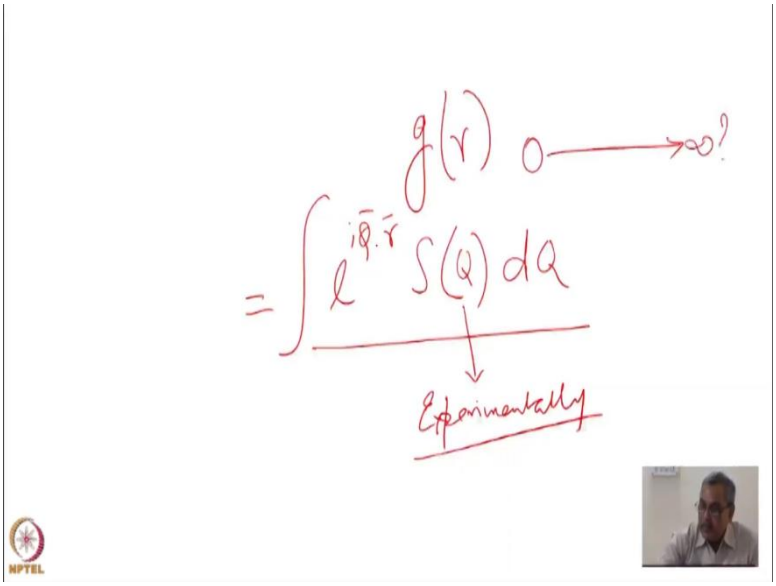

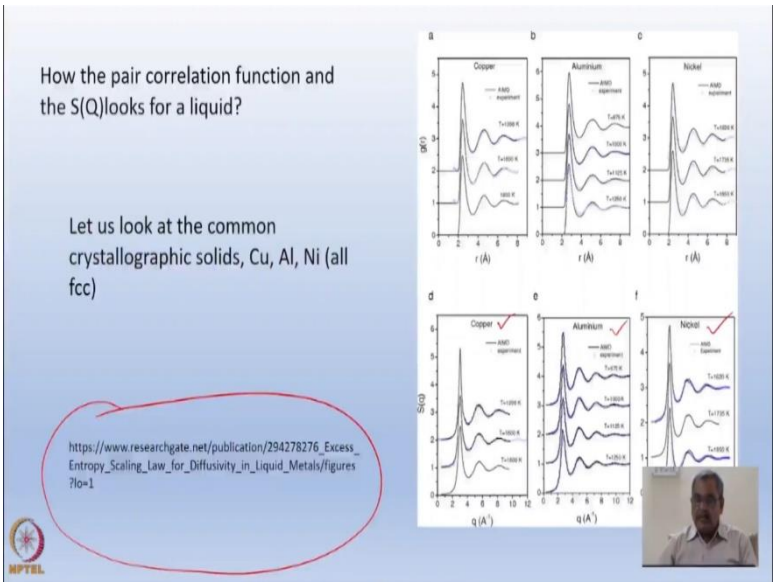

We are aware that g(r) is a reverse Fourier transform from S(Q). This is what we can measure experimentally and we can directly Fourier transform it to get pair correlation function g(r). But when we say we can directly Fourier transform, it means the range of my experimental Q has to be 0 to infinity.

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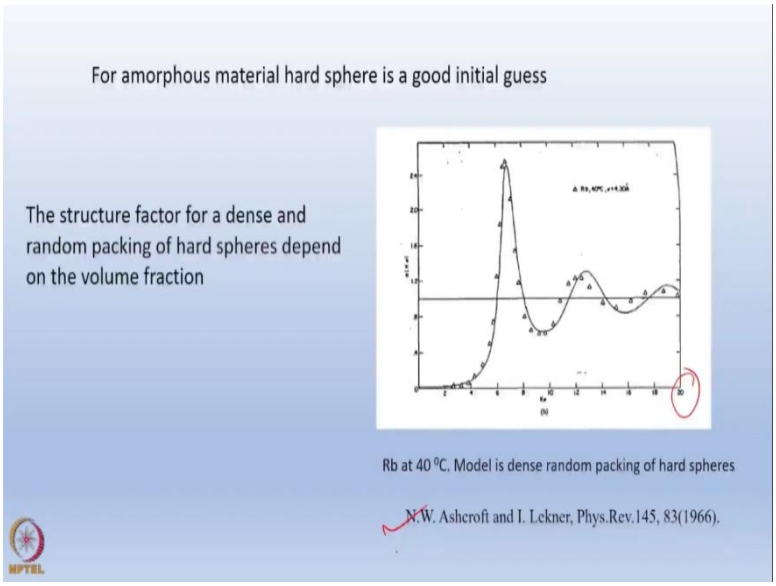

This is an example. Here, rubidium is at 40 °C and you can see the structure factor. These triangles are the experimental points and the continuous curve is modelled from a random dense packing of hard spheres and they match reasonably well, the experimental data over the entire Q range. Reason for using a model is that I told you, I need to Fourier transform over a very large range of Q: which is often not possible.

For example, you see this experiment. We could go to 20 $Å^{-1}$ in the experimental setup. So, that infinity gets curtailed to 20 $Å^{-1}$ and when you have a sharp drop (no data beyond 20 $Å^{-1}$), if you put $S(Q) = 0$ then that sharp drop in Q space will give rise to artificial oscillations in $g(r)$ when we do a Fourier transform. Here the authors have followed the other option: . They have simulated a dense packing of hard spheres, calculated the g(r), played with the g(r) and matched it with the experimental value. So, similar to what we did in case of crystallographic material, here also, we usually start from a model and then go ahead and create the S(Q) and check it with respect to the experimental S(Q). I will come to this in more details in the later parts.

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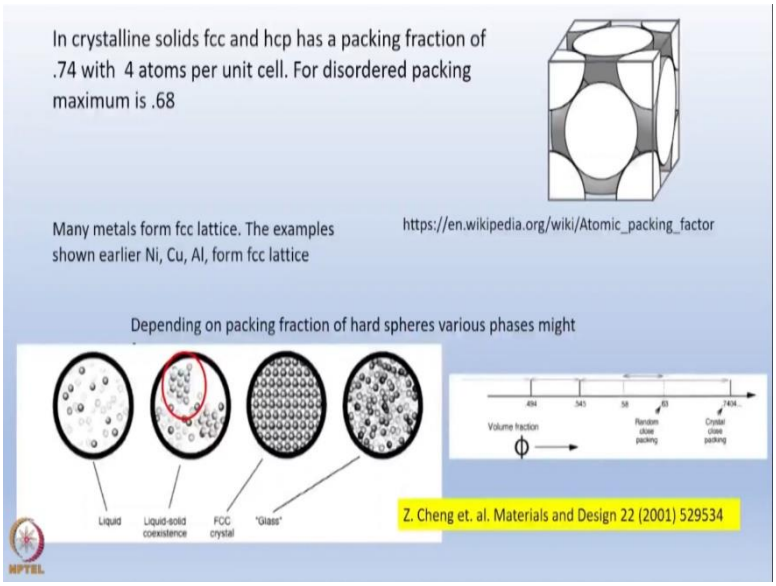

In crystalline solids, we know fcc and hcp have packing fraction of 0.74, highest packing fraction..

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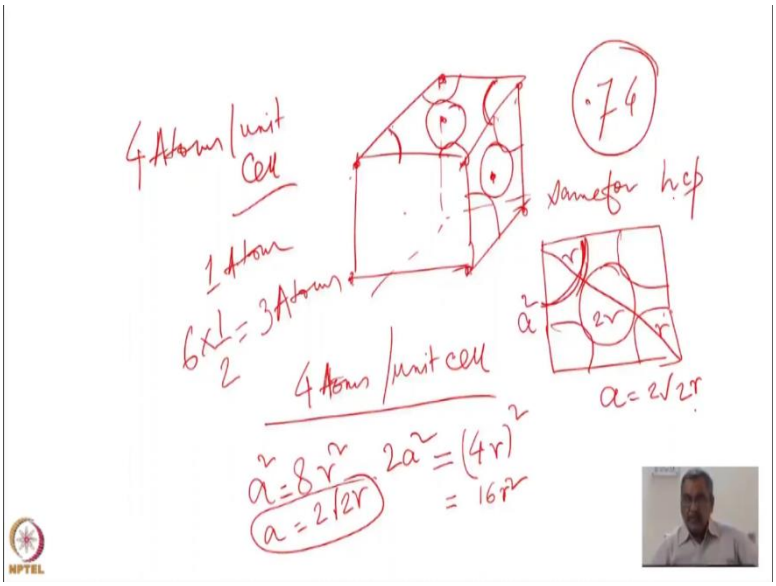

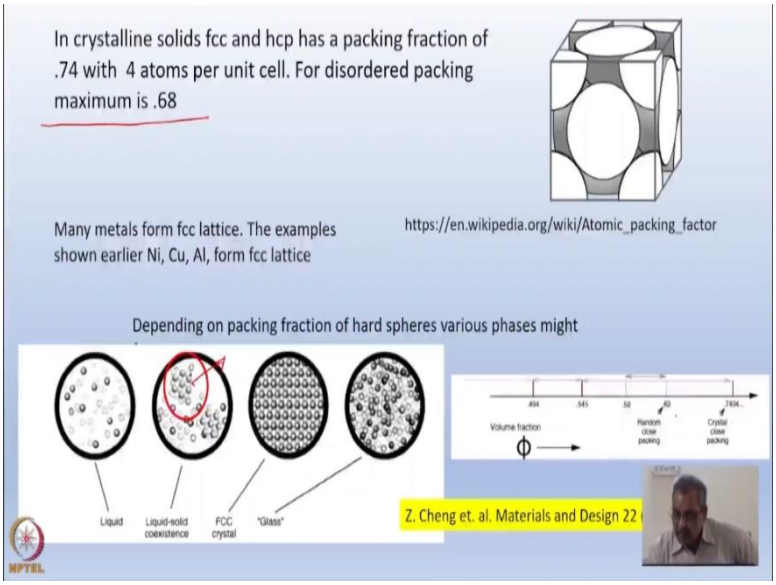

Let me just remind you than an fcc is a face centered crystal which, as I mentioned, includes nickel, copper and aluminum. Here, you have got one atom at every corner, and also one at the center of every face. Actually, this drawing does not indicate the fact that you can consider the atom as a sphere. So, at the center there is a large sphere, then there is a sphere here. There are four atoms per unit cell because we have eight atoms at corners and each is shared by eight unit cell. So, each one contributes one eighth per unit cell. So, from the corners, we get one atom and there are six faces and in the six faces we have got one atom at the center of each face. I am now drawing the atoms as spheres such that they touch each other. Then we have got six atoms on six faces, each atom is shared by two neighboring unit cells sharing the face. So, it comes to three atoms from face centers and in total there are four atoms per unit cell. Now, I can show you from this diagram taken from Wikipedia, the packing fraction in the cell. This is how they they are packed. When you have four atoms per unit cell then calculation of the packing fraction is done like this. If I look at a face then we have a central atom touched by 4 corner atoms. So, here in this fcc packing, each atom is touching the neighboring atom.. Assuming *a* as the side of unit cell and r is the radius of each sphere(or atom), it comes out to be $r = \frac{a}{2\sqrt{2}}$. So, under the geometrical configuration that the atomic spheres are touching each other the packing fraction comes out to be, $4 \times \frac{4\pi r^3}{3} \times \frac{1}{a^3} = 0.74.$

Packing fraction is same for hcp (hexagonal closed packed) structure. But when you do random packing of spheres, in case of amorphous materials, we get some very interesting outputs. One is that the maximum packing you can get up to 0.68 depending on the packing fraction of the number of atoms that you have got in a certain volume. You can get various phases of the

material. This is a very interesting problem which is basically packing of hard spheres. There have been cases where people are talking about packing of cylindrical materials or packing of flat biscuit like objects.

Chaikin is one experimentalist who has done a lot of this work. This is taken from one of his work. Here, you can see that it goes from liquid to a glassy phase, depending on the density of the hard spheres. In between you also can see fcc crystal structure. Interestingly, at certain densities between liquid and glass, there is a liquid/solid coexistence and that means there are solid like clusters of molecules. But in between you have got gaps between such clusters. So, there is a liquid solid coexisting phase and here they have given a line where the depending on the volume fraction, we can see that starting from 0.494 packing fraction. You get random close packing and crystal close packing. Random close packing gives me somewhere around 0.6364 packing fraction.

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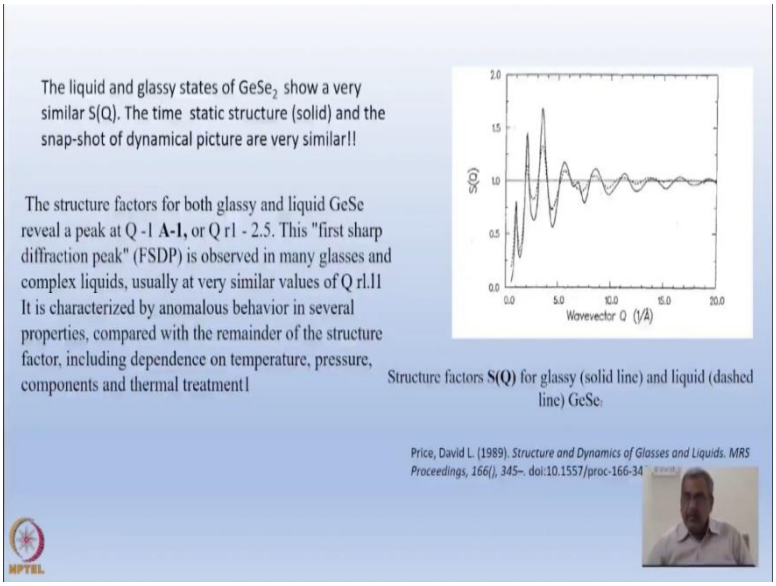

Now, regarding the liquid and solid glassy state of Germanium, as I told you earlier, the snapshot picture of the liquid is very very similar to the amorphous structure in a solid. This is an experimental data for $GeSe_2$ glass. You can see that S(Q) is very very similar for the liquid and glassy states except that the liquid peaks, the dashed line, are slightly less intense. But the structure is very similar. If I talk about shells around the central atom, they are very similar and also there are pre peaks. The peak at around 1 $Å^{-1}$ is the first sharp diffraction peak. This is also observed in many glassy and complex liquids and are almost at similar values of Q around 1 $Å^{-1}$. This is is a characteristic of anomalous behavior..

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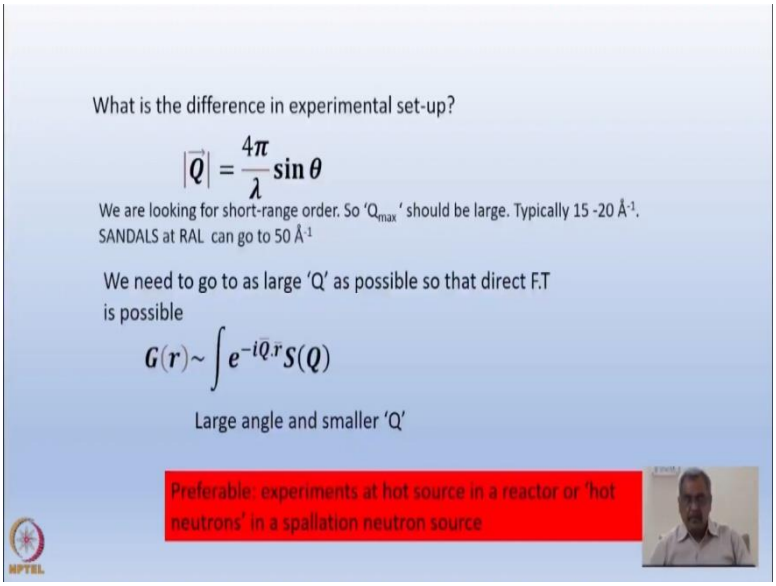

Now, what is the difference in the experimental setup between crystal diffraction and liquid and amorphous diffraction? This is a very important issue.

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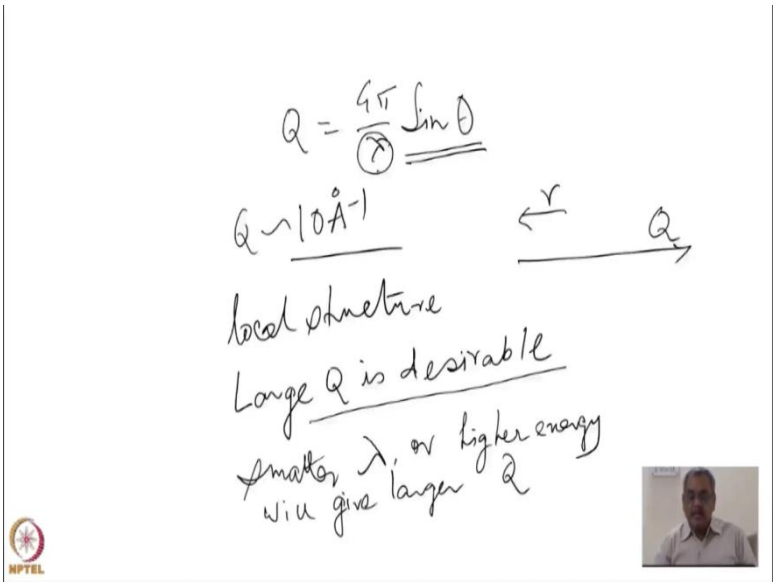

What I want to pose here is how a crystal diffractometer will be different from a liquid and amorphous diffractometer. Let us just start with the most basic quantity that we are aware of and measure in a diffraction experiment. That is $Q = \frac{4\pi \sin\theta}{\lambda}$. Invoking quantum mechanics, we know that if we are going to see smaller and smaller distance 'r' in real space, I need to go to larger and larger Q values in momentum space.

So, typically, in our crystal diffractometers the *Q* values were ~ 10 $Å^{-1}$. But now, I am looking for local structure in a liquid/amorphous solid so I need to go to larger *Q*. But how do I go to large *Q*?

Also, if I want to do a direct Fourier transform from '*Q'* space to '*r'* space, I need to go to large '*Q'* value. Now, how do I go to large *Q* values? One method is by increasing the scattering angle *'θ'*. So, my angular range has to increase. Another possibility is that if I can go to smaller *'λ'* values, as you can see from this expression.

At the same *'θ'*, a smaller *'λ'* or higher energy neutron , will give larger '*Q'*. r I need to go to larger angle which I can do by using more detectors covering larger angles, In addition I can also use, for the same angles, another value of shorter 'λ' which will allow larger Q values.