Keywords: Liquid and Amorphous systems, Structure factor, Reverse Monte Carlo, Random numbers, Pair Correlation Function, Hot Neutron Source, Fourier Inverse

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As I already said that *G(r)* and *S(Q)* are Fourier transform of each other, which tells us that we need to go to larger *Q* values if I do a direct Fourier transform if we want to see small *r* structure. Smaller '*r*' demands larger *Q* scans . And in case of liquid and amorphous systems, typically, we can think of going to 15 to 20 Å^{-1}. More importantly, I also need smaller 'λ' or high-energy neutrons for obtaing larger 'Q' values at the same scattering angle '*θ*'.

Let me again mention to you that I earlier discussed with you something called a hot neutron source.

Number of neutrons *vs* energy curve from a reactor source is a Maxwellian at room temperature with 25 to 30 meV peak and lesser number of neutrons at smaller as well as at larger energy. A cold neutron source shifts the Maxwellian peak to lower energy, resulting in gain in neutrons at lower energies, so that we can use low energy neutrons. Later, I will discuss with you the usage of cold neutrons in experimental facilities.

Similarly, for high-energy neutrons, we can think of shifting the spectrum to the higher energy side by using something called a hot neutron source. But at the moment there are not too many

hot neutron sources available. At ILL Grenoble there is a hot neutron source where a graphite block at around 1500 to 1600 °C is maintained inside the reactor core.Thermal neutrons from these regions enter the hot sourc and the spectrum gets shifted to higher energy. Liquid and amorphous instrument should be using neutrons of higher energy.

Hot neutrons are preferable for liquid and amorphous diffractometers. This is one difference in experimental facility which studies diffraction from liquid and amorphous material. In case of spallation neutron sources, interestingly, we get lot more number of hot neutrons inherently, because in case of spallation neutron sources, once the proton beam hits a target, it generates neutrons with very high energy. It can go up to 100 MeV and these neutrons are brought down to thermal energies using moderators, surrounding the target material. But if we use less moderated neutrons then they are inherently hot (higher energy). So, in case of spallation neutron source, inherently, we have access to more number of hot neutrons and liquid and amorphous experiments can be desirably done better at spallation neutron source.

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5 PSDs. 148⁰ largest angle ✓   15 Å⁻¹
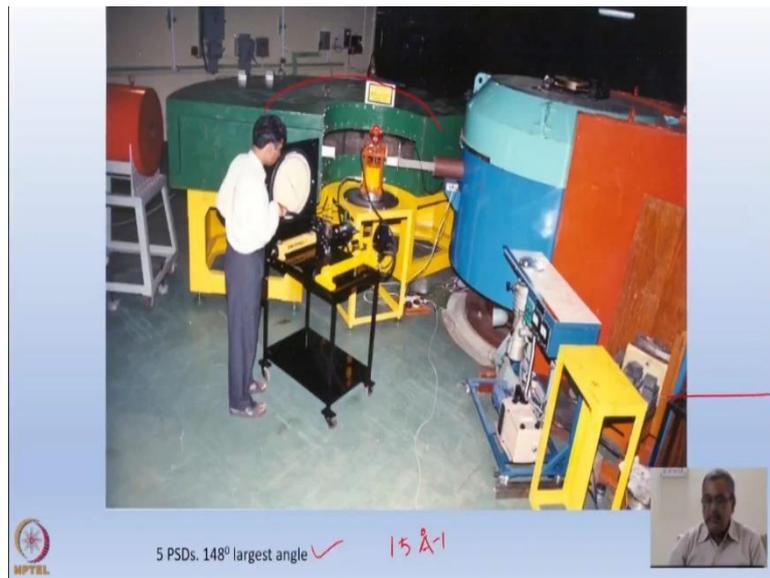
With that I will come to the experimental setup what we have in Dhruva. Experiment setup for this in Dhruva looks very similar to the instrument that we use for diffraction from powder materials for crystallography. This is the detector bank surrounding the sample here. But we have five position sensitive detector and the largest angle we use is around 148°. We can also go to smaller 'λ'. we can set the monochromater for smaller 'λ'. So, at the same angles we can go to higher Q values. 148° is the largest angle and the available Q value is approximately 15 Å⁻¹.

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5 PSDs. 148⁰ largest angle ✓   15 Å⁻¹
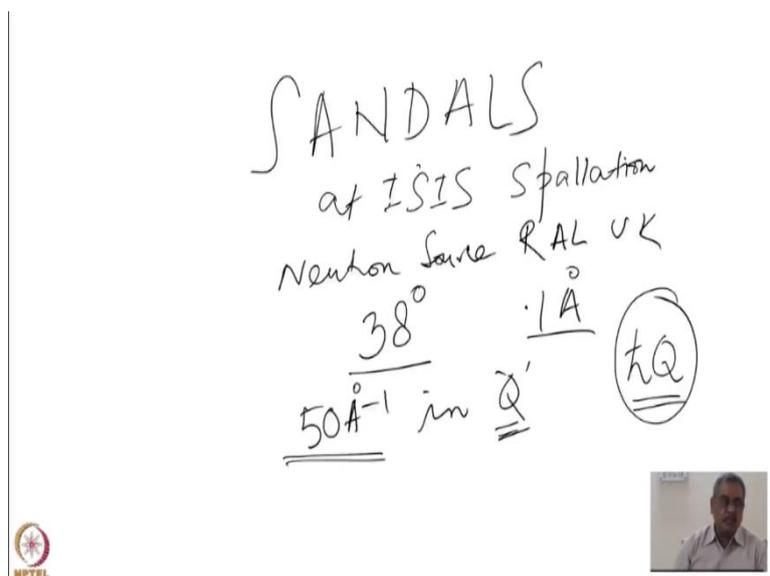
I must compare this with the SANDALS spectrometer at ISIS spallation neutron source, Rutherford Appleton Laboratory, UK. At SANDALS, the angle used in the instrument is not too large. The largest angle is 38°. But because we have access to very small wavelength neutrons even up to 0.1 Å, so it is possible to go up to 50 Å^{-1} in Q values. I must mention here one thing: when I say Q, actually, it always represents $\hbar Q$, the momentum transfer. I am measuring intensity in momentum space. It is usually shown in scattering as a function of *'Q'*. But always we talk about '*Q'* as if this is the momentum transfer which is slightly erroneous because the momentum transfer is given by $\hbar Q$. In all the experiments we will be discussing about Q as momentum transfer. So far, I have talked to you about Q and later also I will be talking to you about Q only when I talk about diffraction experiment.

We can go up to 50 Å^{-1} in Q in SANDALS and I will try to give some results from there also. Coming back to the experiments that has been done in Dhruva, I will just go ahead.

Before I start again, in case of crystalline material, $Q = G$, for a diffraction peak, as I mentioned to you earlier. And this expression gives me the structure factor, $S(hkl) = \sum_j \bar{b}_j e^{-2\pi i(x_j h + y_j k + z_j l)}$. This is from crystallographic symmetry. But in case of liquid and amorphous material, the structure factor can be written like this.

$$S(Q) = 1 + \frac{1}{\langle \bar{b}_j \rangle^2} \sum_{ij} (c_i c_j)^2 \bar{b}_i \bar{b}_j \left[S_{ij}(Q) - \delta_{ij} \right]$$

It is starting from the same source but this gets modified to this. I will avoid the derivation here but, in this expression, $S_{ij}(Q)$ is partial structure factor for components i and j, and δ_{ij} takes care of the incoherent part. but b average, $\langle b \rangle$, for example in a multi-component system is given by $\sum c_i \bar{b}_i$ where c_i is concentration of the ith component with coherent scattering length $\bar{b}_i$. The $S(Q)$ is the total structure factor and we also have partial structure factors, $S_{ij}(Q)$.

To understand this, we will be discussing $S(Q)$ for vitreous silica and Germanium Selenium glasses, two solid amorphous materials. In these caseswe have got several average distances. Partial structure factor means there can be Si-Si distance, Si-O distance and O-O distance in case of SiO_2. All of these together will give us the partial structure factors and the sum of them will give us the total structure factor that we measure in an experiment. These structures can be stimulated and tested against the experimental result. Similarly, in case of germanium selenium glasses, I have Ge-Ge distance and also Ge-Se distance. Both of these comprise the partial structure factor and the sum of them is the total structure factor.

Often, we write about radial particle distribution N(r). The Fourier transform of S(Q) will give g(r) and with this, $N(r) = 4\pi r^2 \rho g(r)$. $N(r)$ gives me the probability of particle numbers between r and $r + dr$ distancewhere ρ is the average particle density.

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Ge_xSe_{1-x} glass

In the Monte Carlo (MC) method used, a trial g(r) and its analytically known S(Q) are taken. The g(r) is then modified randomly at any randomly chosen r. For every change in g(r), its S(Q) is modified at every point analytically

$$\chi^2 = \sum_i \frac{\left|S_i^{exp} - S_i^{MC}\right|^2}{\sigma_i^2}$$

Percus Yerick hard sphere

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We minimize χ^2 by modifying the model through MC and accepting the move with probability $e^{-\frac{\Delta\chi^2}{T}}$ where 'T' is a fictitious temperature

Let me just show you a result and how we did the data analysis. In this case the data analysis was done by us using a model known as Monte Carlo g(r). I will briefly tell you what it is. The discrete points are the diffraction data from Ge_xSe_{1-x} glass and you can see various values of x that were used to prepare the glasses. In this graph, solid lines are the fits obtained by us. And there is excellent fit. We did not do direct Fourier transform because you can see that our results stopped at approximately 15 $Å^{-1}$. So, direct Fourier transform is certainly not a good idea with this darta set. We assumed was a Percus Yerick hard sphere pair distribution. What it is? I will just briefly explain to you.

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In case of Percus Yerick hard sphere, we locate a number of hard spheres in a certain volume. In this case, there will be selenium and germanium atom sizes and then we pack them in a certain volume. But if the hard spheres intercept, then the interatomic potential is infinity when they overlap, because two hard spheres cannot penetrate each other. And if they do not penetrate then V(r) is zero.

So, V(r) is infinity for r less than equal to r_0 (size of an atom) and otherwise zero. With this assumption, this Percus Yerick hard sphere model will create a linear one-dimensional g(r) for our sample in real space. This g(r) is our input to start with a given configuration. And we generate the configuration using an interatomic potential described above

That means we just put the hard spheres, if they intercept each other, we immediately say this configuration is not possible, put it somewhere else and at some other point. After creating the configuration allowing it to equilibrate and then we find out g(r), one-dimensional g(r) for the configuraion. Now, once we have created the g(r), we can always use Monte Carlo method to modify it.. Here we have a Monte Carlo result for the structure factor in Q and we also have the experimental results to compare.

We try to minimize the difference between the experimental result and the Monte Carlo $S(Q)$. One $S(Q)$ is the experimental data and the other $S(Q)$ is from model which has come from g(r) that we started with.. And we have to minimize the difference between these two.

$$\chi^2 = \sum_j \frac{\left[S_i^{exp} - S_i^{MC}\right]^2}{\sigma_i^2}$$

That is what we did with this data. So, σ_i^2 is the experimental error bar which is square root of neutron counts (N) at every point in $'Q'$. Every time we change the g(r), the S_i^{MC}, the Monte Carlo structure factor, changes and then there is a change associated with χ^2 which you call $\Delta\chi^2$.

We accept the change with the probability $e^{-\frac{\Delta\chi^2}{T}}$. I will explain to you a little bit in details because this Monte Carlo technique has been heavily used for Ising model. This technique is very similar here and I would like to tell you how it is done here, taking the help of Ising model Monte Carlo (MC).
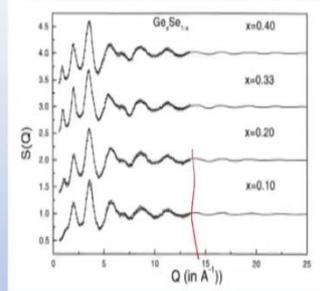
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Ge$_x$Se$_{1-x}$ glass

In the Monte Carlo (MC) method used, a trial g(r) and its analytically known S(Q) are taken. The g(r) is then modified randomly at any randomly chosen r. For every change in g(r), its S(Q) is modified at every point analytically

$$\chi^2 = \sum_i \frac{|S_i^{exp} - S_i^{MC}|^2}{\sigma_i^2}$$ Percus Yevick hard sphere

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We minimize χ^2 by modifying the model through MC and accepting the move with probability $e^{\frac{\Delta\chi^2}{T}}$ where 'T' is a fictitious temperature

Consider a spin half 2D-lattice for Ising spin model. When I flip a spin, we know that the interaction energy is $\sum J_{ij} S_i.S_j$, in this case let us assume nearest neighbor interaction. Then for one atom there are four atoms as nearest neighbor. If I flip this, there is an change in energy ΔE from this expression. So, in one-step I randomly flip one spin. This is same as what I am doing for the liquid and anomorphous system when I randomly shift one sphere. Now, when I randomly flip a spin, there is an energy difference of ΔE. This I will be comparing with $\Delta\chi^2$, a virtual energy, in case of the structural MC.

Now, if the change in energy ΔE is less than 0 then we accept the new spin configuration because the flip is reducing energy. If it is increasing the energy, do I reject it? No, I accept it

with a probability $e^{-\frac{\Delta E}{kT}}$. This is a Boltzmann factor. That is how a Monte Carlo simulation of Ising spin model done.

That means, it accepts even if the energy is increased with a probability $e^{-\frac{\Delta E}{kT}}$. How does it do? We know that if ΔE equals to infinity then the exponential probability becomes zero. That means we cannot flip. But if this is a finite number then the probability will also be finite., Because at any stage, I do not know whether the nearest neighbor was already flipped or not, or if all of them are already flipped then the change in energy (increase or decrease) will be 4 times some basic unit. If two of them are already flipped it will be two times of the basic unit etc. So, what do we do actually? In the computers today, there are facilities to generate random numbersbetween 0 and 1. Now, this one, $e^{-\frac{\Delta E}{kT}}$, if I scale it between 0 and 1 after I have got the positive change in energy, if the generated random number is smaller, I accept the move, even if the system energy has increased. I always accept the move, if $\Delta E < 0$.
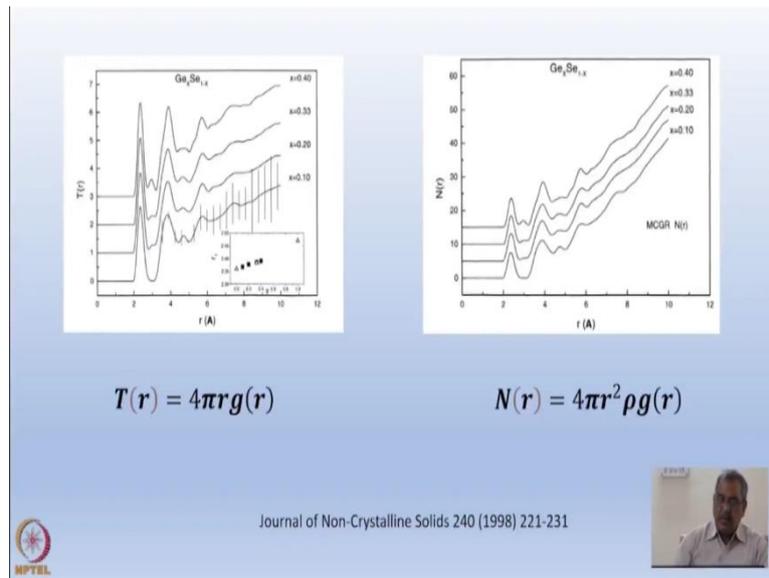
So, I choose a random number and compare this with $e^{-\frac{\Delta E}{kT}}$. If the random number is to $\leq$ $e^{-\frac{\Delta E}{kT}}$ $(positive\ \Delta E)$, it means the move is allowed .. In the present case, no energy is involved but a structure and a corresponding match between experimental and the model is involved and $\Delta\chi^2$is the indicator of mismatch, is involved instead of , ΔE

Now, I compare the $\Delta\chi^2$ with the energy change in case of spin glass, associated with spin-flip, what I showed you here, ΔE. Then I accept the move with the probability of $e^{-\frac{\Delta\chi^2}{T}}$. for an increase of mismatch in a parameter space of the cumulative error.. T is a fictitious temperature, which I can fix What will happen actually, if I use a very large T?

You can see with $e^{-\frac{\Delta\chi^2}{T}}$, it will be exponential of a very small number,almost equal to 0. The exponential term will be close to 1. So, all the moves will be accepted with a high probability. Reason being, when you have a high temperature for a medium then the dynamics takes over. And the energy increase is accepted because there is lots of energy in the medium to randomize the material. And if T = 0 then no moves for energy increase will be accepted because the exponential term be zero. My random number space is 0 to 1. You can see that if T is large, this goes to almost 1 and almost all the moves are taken. I can start with a large T and keep coming down in (virtual) temperature with simulation.

There are various other techniques which I do not want to discuss here but this is how we generated the model, changed the model Monte Carlo *S(Q)*, compared with the experimental data and finally accept the S(Q) which gives us minimum error. This is what is shown here. And this is a comparison between experimentally obtained *S(Q)* and the model *S(Q)*.

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$$T(r) = 4\pi r g(r) \qquad\qquad N(r) = 4\pi r^2 \rho g(r)$$

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From that model we can get various parameters of the amorphous system, in case of germenium selenium glass. This is the evaluated T(r) distribution function. This work was published in Journal of Non-crystalline Solids. The data and the figures are taken from this publication.

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Reverse Monte Carlo
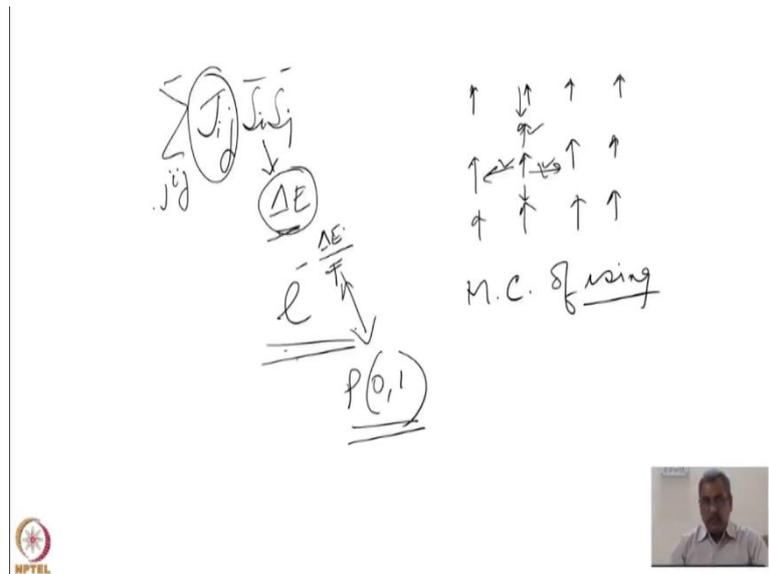-----R. L. Mcgreevy

One starts with a 3-dimensional arrangement of atoms and molecules.

In normal MC energy is minimized by randomly changing the atomic arrangement. An interatomic potential is required.

In Reverse MC one reduces

$$\chi^2 = \sum_i \frac{\left[S_i^{exp} - S_i^{MC}\right]^2}{\sigma_i^2}$$
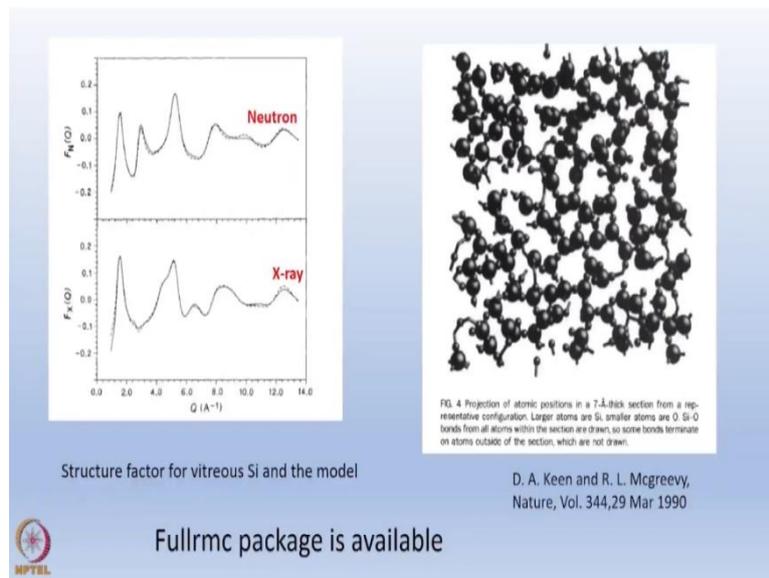
Structure factor for vitreous Si

Presently, the most used technique for liquid and amorphous systems is a reverse Monte Carlo by R. L. Mcgreevy. We had used a one-dimensional g(r) to simulate S(Q) in case of germanium selenium glass. But the reverse Monte Carlo takes a three-dimensional arrangement of atoms and molecules. This is much closer to reality.

In a normal Monte Carlo simulation, as I showed you in Ising model, one tries to minimize the energy and higher energy configurations can also be accepted. In general, we are trying to find out the minimum, in energy space. In that case, for normal Monte Carlo, we need to define an interaction energy.
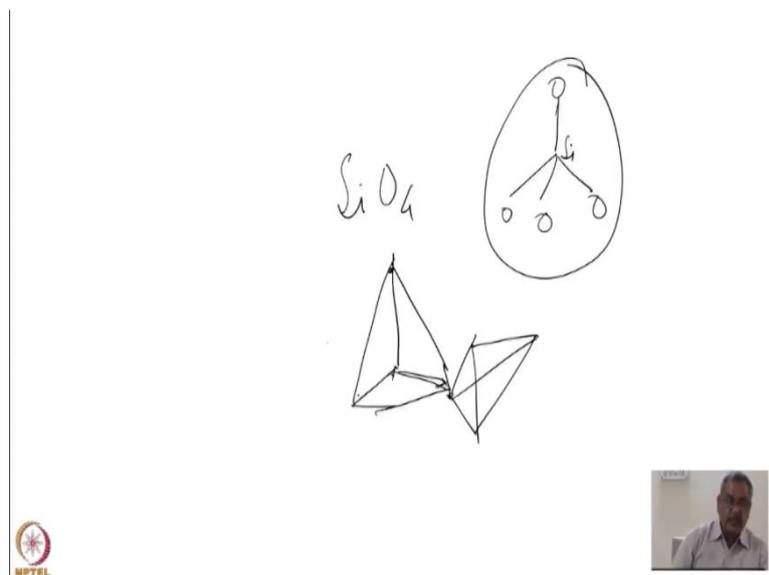
Here also when you are talking about arrangement of atoms and molecules, I need to identify some equivalent of energy if I want to do a simulation: a physical simulation. But what we do actually? I play with the arrangement of the atoms in three-dimension and create the corresponding structure factor, then using Monte Carlo, compare it with experimental structure factor and try to minimize their difference. I will show the result for vitreous silicon.
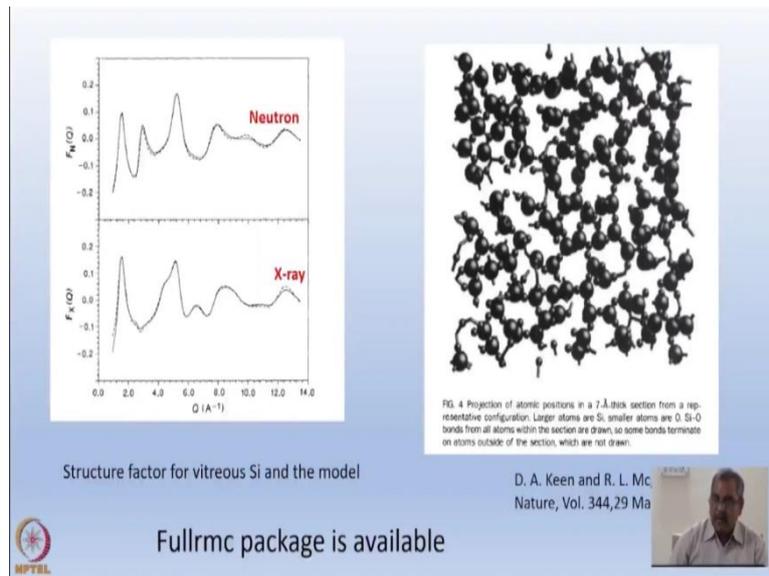
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Structure factor for vitreous Si and the model

D. A. Keen and R. L. Mcgreevy,
Nature, Vol. 344,29 Mar 1990

Fullrmc package is available

This was a paper by McGreevy. You see this is the neutron structure factors, simulated as well as experimental data are plotted together. And this is the atomic arrangement in the right panel. This is for SiO_4 which forms tetrahedra.

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Structure factor for vitreous Si and the model

FIG. 4 Projection of atomic positions in a 7-Å thick section from a representative configuration. Larger atoms are Si, smaller atoms are O. Si-O bonds from all atoms within the section are drawn, so some bonds terminate on atoms outside of the section, which are not drawn.

D. A. Keen and R. L. Mc.
Nature, Vol. 344,29 Ma

Fullrmc package is available

We talk about SiO_4 units which forms a tetrahedra. This is the tetrahedra. Now, we can play with the orientation of this tetrahedra and length of the bonds and then try to generate the experimental values.

This arrangement is projection of atomic positions in a 7 Å thick section from a representative configuration. Here, large atoms are silicon, small atoms are oxygen, silicon oxygen bonds from all atoms within the section, are drawn. Some bonds terminate for atoms outside the section which are not drawn. Basically, he played with the silicon oxygen tetrahedra orientations which is a basic unit for vitrous silicon. Most interestingly, this is a corner shearing tetrahedra. That means if I consider another tetrahedra with these corners, , with respect to one tetrahedra, the other tetrahedra can share corner with it and they can orient with respect to one another. Some bonds will get elongated but they can also orient. So, the tetrahedra remains in tact because these bonds are strong. The silicon oxygen tetrahedra remains more or less undisturbed but the orientation changes, while these are corner sharing tetrahedra and not edge sharing.

At the moment, Fullrmc package is available online. Anybody can use it and it is an important simulation package, if you are interested to do neutron or x-ray studies of liquid and amorphous material. This is the best possible package which you can use to do the reverse Monte Carlo simulation and get a good fit to the experimental results.

(Refer Slide Time: 27:23)

H-bonded simple alcohols: 2- Propanol
Cyclic chain clusters through H-bonding using neutron diffraction

- Pre peak is observed in ND data
- Explained on the basis of hexamer association of molecules
- Open Chain clusters like tetramer or other models ruled out

H(Q) is the total structure factor

$$H(Q) = H_d(Q) + H$$

I earlier talked about molecular clusters. These are work done in Dhruva, in our group. The reference that I missed here, will provide later. This was done by PSR Krishna and his group regarding structure of propanol liquid. I will provide you the reference in the next lecture. Here, total structure factor which has been measured, is a sum of two parts. One is that there are propanol molecules in H bonded simple alcohols. Two distinct parts mean that the structural correlation between two molecules and this is the structure inside the molecule: the intramolecular structure and intermolecular structure. And here through reverse Monte Carlo stimulation, one found that there are clusters of molecules here!

This indicated that in the liquid where we assume that molecules are able to move freely, actually, there are molecular clusters. But I must mention, this clusters must be having some time scale. So, these clusters are forming and breaking and again forming and breaking. But the thing is that, at any instant of time, these clusters,exist in this alcohol and that is the finding of this work on liquid and amorphous material.

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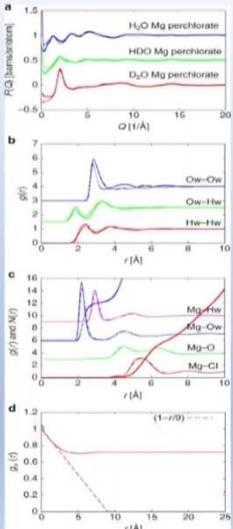

As I told you that up to 50 Å^{-1} is possible at SANDALS, I just attempt to show one result from SANDALS.

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This is a *Nature* paper I will provide the reference. I missed it and my apologies for that. I will provide the reference in the next lecture. The most interesting finding in this experiment, in this solution of magnesium perchlorate, they observe from the partial structure factors that there is a drastic effect on water structure. They get a water structure which is commensurate with the higher pressure on water . Because we know that water has got a structure like this.

Every H_2O in the solution has this structure and there is also hydrogen bonding between two water?

There is signature in the structure that the water is under higher pressure in this solution. This is a result from the SANDALS and you can see that the data are taken up to very high Q values. I will like to stop today the lecture on liquid and amorphous systems. A brief introduction to single crystal will be done in the next part.