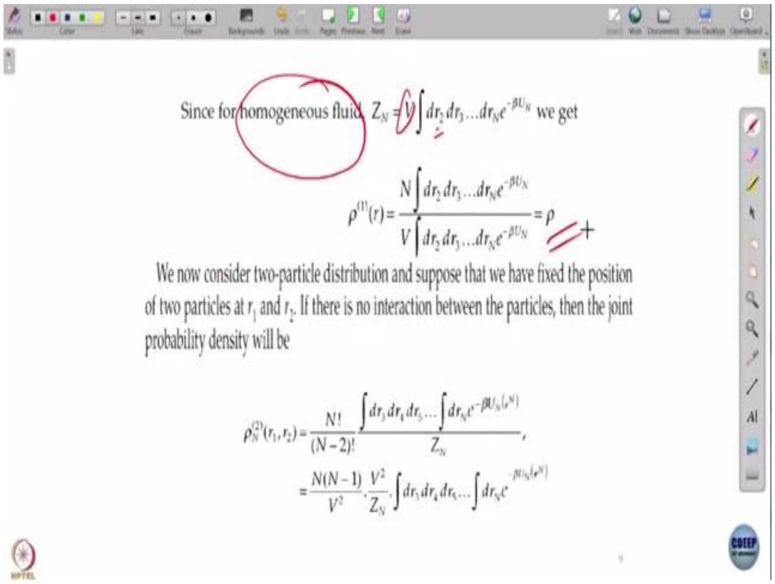
Basic Statistical Mechanics
Prof. Biman Bagchi
Department of Chemistry
Indian Institute of Technology, Bombay
Indian Institute of Science, Bangalore

Lecture - 52
Theory of Liquids Part- 2

(Refer Slide Time: 00:16)



Since for homogeneous fluid $Z_N = V\int dr_2 dr_3 \ldots dr_N e^{-\beta U_N}$ we get

$$\rho^{(1)}(r) = \frac{N\int dr_2 dr_3 \ldots dr_N e^{-\beta U_N}}{V\int dr_2 dr_3 \ldots dr_N e^{-\beta U_N}} = \rho$$

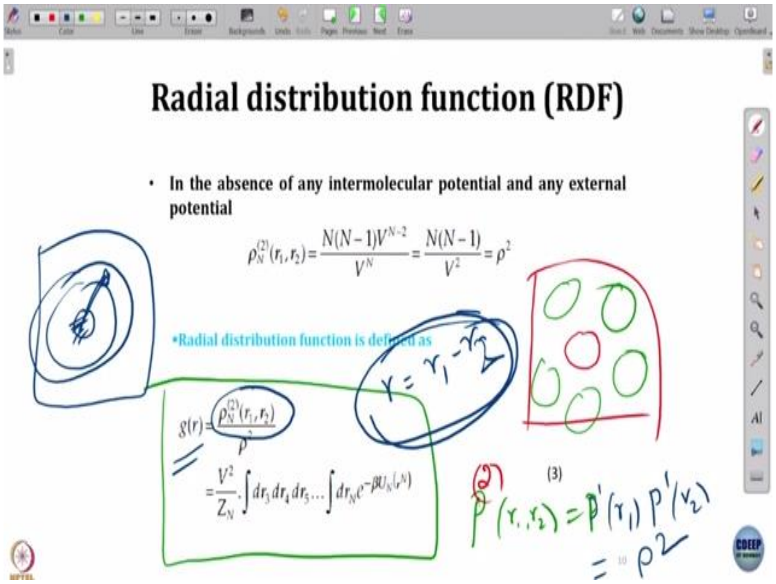
We now consider two-particle distribution and suppose that we have fixed the position of two particles at r_1 and r_2. If there is no interaction between the particles, then the joint probability density will be

$$\rho_N^{(2)}(r_1, r_2) = \frac{N!}{(N-2)!}\frac{\int dr_3 dr_4 dr_5 \ldots \int dr_N e^{-\beta U_N(r^N)}}{Z_N},$$

$$= \frac{N(N-1)}{V^2}\cdot\frac{V^2}{Z_N}\cdot\int dr_3 dr_4 dr_5 \ldots \int dr_N e^{-\beta U_N(r^N)}$$

Now, I go to the most important quantity that important quantity is;

(Refer Slide Time: 00:24)



Radial distribution function (RDF)

- In the absence of any intermolecular potential and any external potential

$$\rho_N^{(2)}(r_1, r_2) = \frac{N(N-1)V^{N-2}}{V^N} = \frac{N(N-1)}{V^2} = \rho^2$$

- Radial distribution function is defined as

$$g(r) = \frac{\rho_N^{(2)}(r_1, r_2)}{\rho^2}$$

$$= \frac{V^2}{Z_N}\cdot\int dr_3 dr_4 dr_5 \ldots \int dr_N e^{-\beta U_N(r^N)} \quad (3)$$

$r = r_1 - r_2$

$\rho^{(2)}(r_1, r_2) = \rho^1(r_1)\,\rho^1(r_2)$

$= \rho^2$

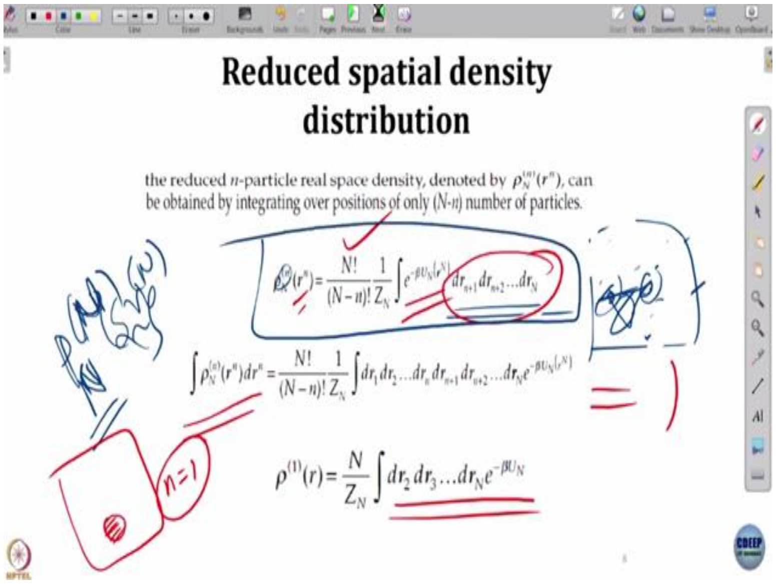
The two particle distribution function which is defined here, so now I want to know that what is the probability if I have one molecule here another molecule here in other words, I also want to know later in homogeneous system, how many molecules are there? I have been discussing. So, now I go by the following important definitions the radial distribution function is joint probability of having r1 and r2, one at r1 another r2 and that is divided by ρ^2.

Because, if this probability is independent of each other $P^{(N)}$ is independent of each other then P^N(r1 ,r2) will be it is P2 then r1, r2 then I will have P1 r1, P1 r2 and that I just showed in a motion is the same so that becomes I just showed in homogenous system these is nothing but density so then P r1 r2 if there is no correlation, then it will be the Rho square so it makes sense now you define quantity where the joint void distribution which is P N r1 r2 is divided by ρ^2 .

Because in the limit in the original no correlation, and also in the limit when r1, r2 are widely separated then r1 and r2 widely separated In these notation r is r1- r2. So as you showed it, please make these corrections in a second addition, we will fix all these things. So the radial distribution function, now we have this g(r) is the radial distribution function again I motivated that it is in a it is number of molecules in a shell at a distance r.

This gives g(r) and it is a very pivotal quantity in theory of liquids. Now, go back. So we showed this is rho r, now we want to do two-particle distribution just type motivated in there that then will be in the from;

(Refer Slide Time: 03:02)



Reduced spatial density distribution

the reduced n-particle real space density, denoted by $\rho_N^{(n)}(r^n)$, can be obtained by integrating over positions of only (N-n) number of particles.

$$\rho_N^{(n)}(r^n) = \frac{N!}{(N-n)!}\frac{1}{Z_N}\int e^{-\beta U_N(r^N)} dr_{n+1} dr_{n+2} \dots dr_N$$

$$\int \rho_N^{(n)}(r^n) dr^n = \frac{N!}{(N-n)!}\frac{1}{Z_N}\int dr_1 dr_2 \dots dr_n dr_{n+1} dr_{n+2} \dots dr_N e^{-\beta U_N(r^N)}$$

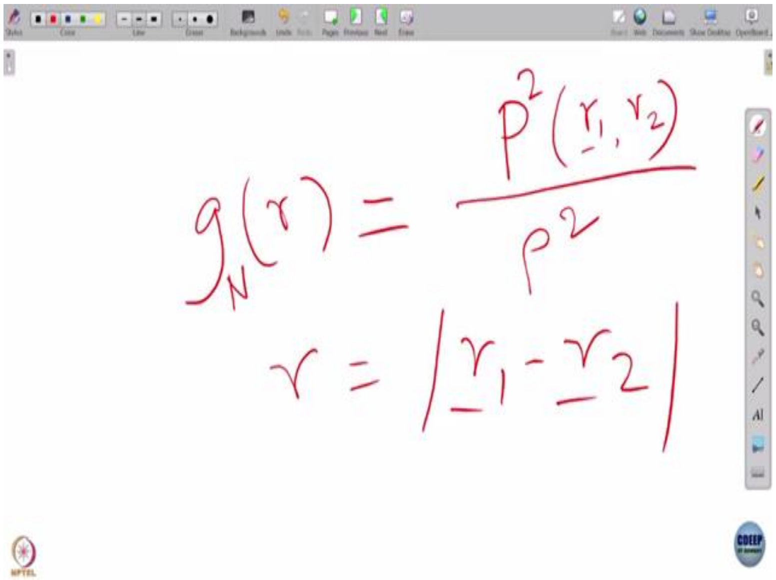
$$\rho^{(1)}(r) = \frac{N}{Z_N}\int dr_2 dr_3 \dots dr_N e^{-\beta U_N}$$

N-particle distribution which is defined here $\frac{N!}{(N-n)!}$ of this quantity then I get two-particle $P^{(2)}$ r1, r2 a little bit. I am comfortable with both r1 and r2 because in at the end of the day, you know,in homogeneous liquid it is only the distance between them. It is both r1 r2 not needed it is I can select my coordinate of 1 and then I can only call consider r2 as a distance r. So basically it is a distance is scalar that becomes which is far simpler quantity.

The r1, r2 if I keep it as a vector then it is 6 dimensional. But what really matters is homogeneous liquid is one dimension. So which the tremendous implementation and something people should be aware of. So just from the last one I get this thing I integrate over r3 r4 r5 that to rn, and then the configuration integral Mayer's configuration integral. And $\frac{N!}{(N-2)!}$, now that of course I can now divide.

I can start seeing how ρ^2 will come out I can then this quantity will be ρ^2 N going to infinity these quantity will be ρ^2 and then if they are not interacting then Z_N is V^n and then this V^2 will another V to the power N-2 will come here, so I take back these conditions that. So these are very clever limit by multiplying and divided by this square okay. So the motivation of g(r) is now clear motivation of g(r) is that is where is clear and so.

(Refer Slide Time: 04:52)

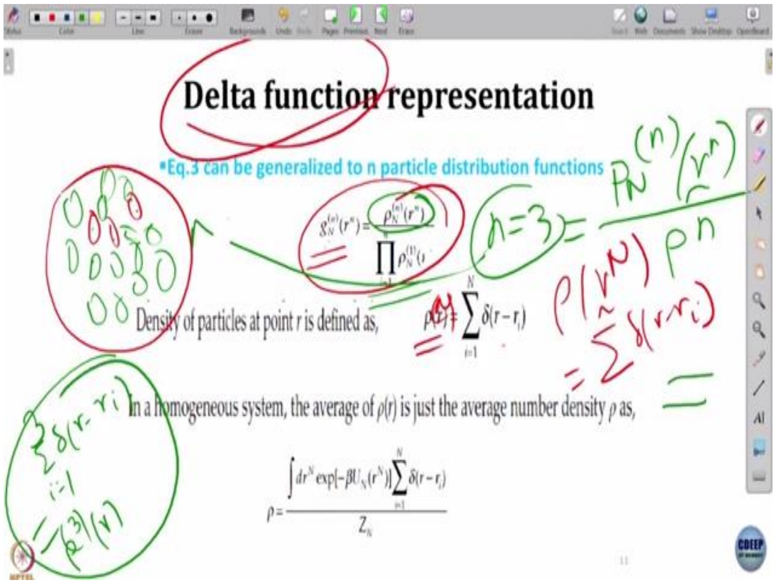


$$g_N(r) = \frac{P^2(\underline{r}_1, \underline{r}_2)}{\rho^2}$$

$$r = |\underline{r}_1 - \underline{r}_2|$$

In n-particle $g_N(r) = \frac{P^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2)}{\rho^2}$ but r1, r2 what we need actually is a |r1 – r2|. So, this is the radial distribution function, which is the probability of getting that, they are two particle separation r that is the central quantity of our discussion here, okay?

(Refer Slide Time: 05:27)



Delta function representation

- Eq.3 can be generalized to n particle distribution functions

$$g_N^{(n)}(r^n) = \frac{\rho_N^{(n)}(r^n)}{\prod \rho_N^{(1)}(r_i)}$$

Density of particles at point r is defined as, $\rho(r) = \sum_{i=1}^{N} \delta(r - r_i)$

In a homogeneous system, the average of $\rho(r)$ is just the average number density ρ as,

$$\rho = \frac{\int dr^N \exp[-\beta U_N(r^N)] \sum_{i=1}^{N} \delta(r - r_i)}{Z_N}$$

So now go generalized to n particle distribution many times we need three particle distribution g3. So from the discussions, I have done this is g N and then density then ρ_r. I give a this delta function is kind of a simple but straight forward thing that we now want to be talking of N-particle, this is not quite correct r N equal to so I that means that n is missing these $\delta(r - r_i)$.

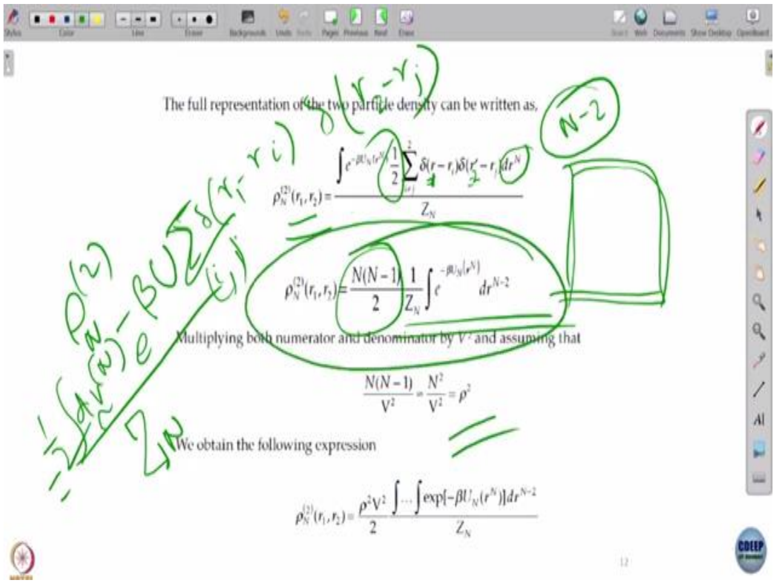
So they N-particles and this is a complete distribution of N particles, that means what is saying that is essentially P(N) but the delta function representation, but the quantity is that I can go to g n and particle so they are what one is saying that I have N particles in a N particle system I have tagged small n particles and I want to know what is the probability of this in a huge system, there are many, many molecules which are not which are going to integrate over.

But I have so the green last rate at the total N, so what my small n is 3 so I want this three particle positions and the r1, r2 and r3 and that what is the probability of having three particles are having r1, r2, and r3 when n=3, there I have that description and I define at as the three particles the probability distribution the normalized by ρ^3 this is done for homogeneous system that I give otherwise.

I will just make it $\frac{P_N^{(n)}\left(r^n\right)}{\rho^n}$ that would be this quantity. As I said delta function means you can say okay I can write this thing now as $\sum_{i=1}^{3}\delta\left(\boldsymbol{r}-\boldsymbol{r}_i\right)$, so i have the position of this three, and that is then will be $\rho^{(3)}$(r). So this is the definition of delta function represent that as an advantage we will see later.

So homogeneous system this averaging that we are talking this comes out like that is not very important okay.

(Refer Slide Time: 08:05)



The full representation of the two particle density can be written as,

$$\rho_N^{(2)}(r_1,r_2)=\frac{\int e^{-\beta U_N(r^N)}\frac{1}{2}\sum_{i\neq j}^{2}\delta(r-r_i)\delta(r'-r_j)\,dr^N}{Z_N}$$

$$\rho_N^{(2)}(r_1,r_2)=\frac{N(N-1)}{2}\frac{1}{Z_N}\int e^{-\beta U_N(r^N)}\,dr^{N-2}$$

Multiplying both numerator and denominator by V^2 and assuming that

$$\frac{N(N-1)}{V^2}\approx\frac{N^2}{V^2}=\rho^2$$

We obtain the following expression

$$\rho_N^{(2)}(r_1,r_2)=\frac{\rho^2V^2}{2}\frac{\int\cdots\int \exp[-\beta U_N(r^N)]\,dr^{N-2}}{Z_N}$$

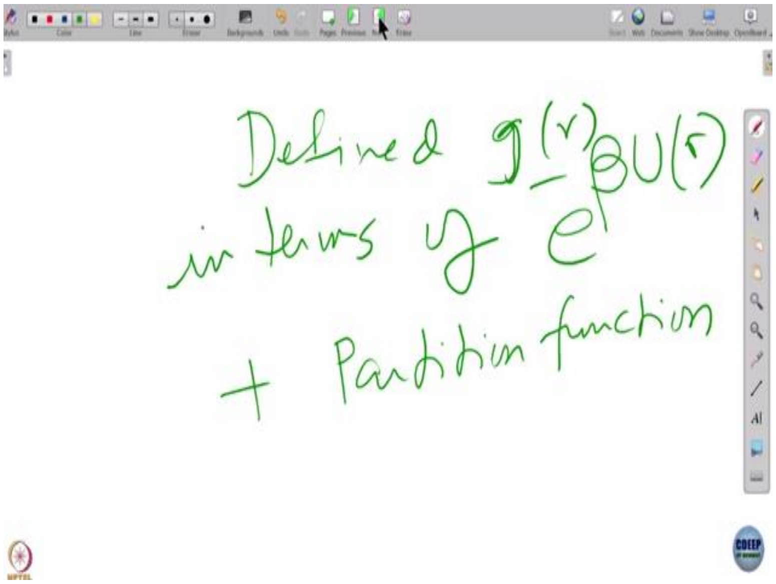
So now however in a two particle distribution it becomes kind of interesting because then I can now write your two particles r1 and r2, then I can write okay one particle at I have to sum over this is this in just constant particles there is same or not constant identical particles then I can say my ρ(r) at r1 and r2 is just integrate over all the other molecules n number of integration the r ^{n}.

$$\rho_N^{(2)}\left(\boldsymbol{r}_1,\boldsymbol{r}_2\right)=\frac{\int e^{-\beta U_N(\boldsymbol{r}^N)}\,\frac{1}{2}\sum_{i\neq j}^{2}\delta\left(\boldsymbol{r}-\boldsymbol{r}_i\right)\delta\left(\boldsymbol{r}'-\boldsymbol{r}_j\right)d\boldsymbol{r}^N}{Z_N}$$

But before all our definitions we are making this integration to N-2, but now because of delta function representation I can put it in and say, one particular r and another particle is r′ actually if I have to look at that then that should be r1 and r′ is r2, this becomes the then delta r1- r i delta r2 - r j, I sum over all i and j and if I make them double sum then I have to take over counting I have avoid that I have to take half, which is half.

This is a ρ(r1, r2) so if I can do that now, the number of ways I can pick it up is $\frac{N(N-1)}{2}$ verticals, then this is the same thing. As that we have done in the last page also and same thing again repeated here. So nothing new is repeated here.

(Refer Slide Time: 09:58)

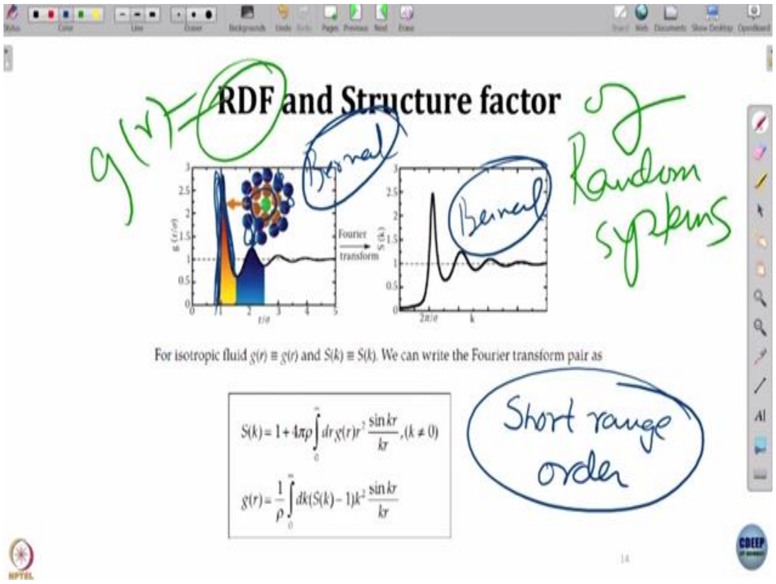


Defined $g(r)$ in terms of $e^{-\beta U(r)}$

+ Partition function

So we have now developed a definition of g (r). So we define g(r) In terms of $e^{-\beta U(r)}$, so starting from n partition function. Starting from partition function we get this quantity and a definition of g(r) we have not evaluated here yet, but we have structure, next what happens?

(Refer Slide Time: 10:46)



RDF and Structure factor

$g(r)$ of Random systems

Bernal

For isotropic fluid $g(\mathbf{r}) \equiv g(r)$ and $S(\mathbf{k}) \equiv S(k)$. We can write the Fourier transform pair as

$$S(k) = 1 + 4\pi\rho \int_0^\infty dr\, g(r) r^2 \frac{\sin kr}{kr}, (k \neq 0)$$

$$g(r) = \frac{1}{\rho} \int_0^\infty dk (S(k) - 1) k^2 \frac{\sin kr}{kr}$$

Short range order

So now we take a little bit back and say okay what do know about gr? Before evaluate gr which is difficult but has been done with great accuracy in many large numbers of systems, but there is two ways one can get it directly one is radial one is the computer simulation and neutron scattering and also as I told you these days the x-rays in the random system so what we are doing is essentially a random system, so actually a random system and liquid one of them.

But of course the what I am doing is also for glasses that goes for very much glasses and which is more materials, surface things like, you know mobiles this surface of the mobile great need for the structure of the liquid crystals, you must all those things exactly follows these terminology that is why the terminology though we are doing the context of liquids, these are terminology and the nomenclature that goes into perfect soul **of** physics and chemistry.

So the radial distribution function RDF radial distribution same as g r, is RDF so how do they look? Now we have plotting here radial distribution function of say around this blue one, this is little bit silly drawing that because there are too much of a structure really do not known too much of a structure but what it regards this shown that this is the center one the red ones are the first layer and the blue ones are the second layer and I do one I should draw something more maybe okay.

So now you see, near the first layer this one there is a very sharp peak almost reminds you of the crystal. Because liquid has a considerable amount of short range order all the liquids, water short range order it is of the kind of thing we discussed in Ising model same short range order, molecules are placed quite like a crystal in the first layer, so this is the radial distribution function structure there is a sharp first peak.

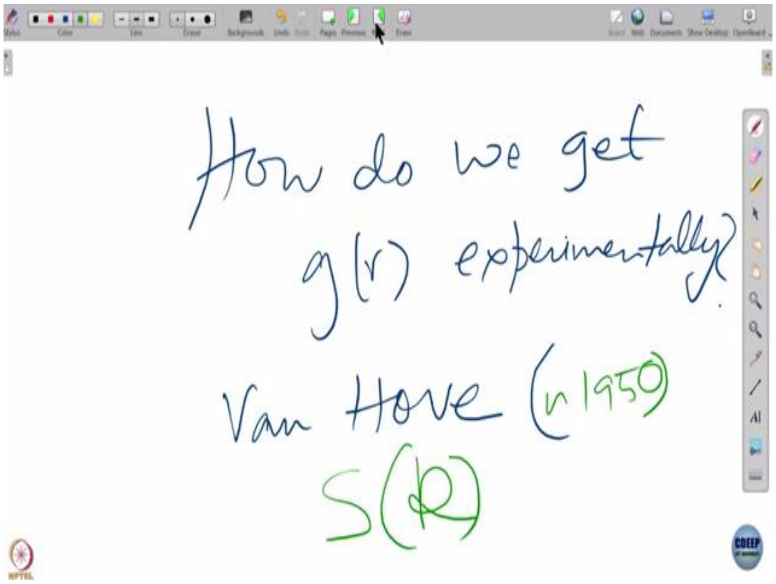
But the first structure in the first layer is due to the extended volume interaction because the molecules are packed together they are touching the surface then comes the second layer because the the first layer is structured second layer is also structured, that structure is like you are packing people see in a bus like in places like Kolkata or Mumbai bus will be crowded. So if you are in a centre of a crowded bus then the people around you will be finite number.

And there will be you will find 4 or 5 people around you then if it is a big bus then another 4, 5 or 10, around the second layer, so the hard sphere interaction that you cannot penetrate two molecules cannot penetrate that it has a volume and size that dictates this arrangement. That is what I mean that is the hard sphere part of the interaction repulsive part of the interaction that determines the structure of liquid.

This is very, very important the structure of a liquid is determined by these repulsive hard sphere interaction dynamics also it will get extended by that but phase transition and many properties is a competition to the repulsive part of the interaction and the attractive part of the interaction is to together drive the properties of a liquid and the so this is what now g r, if I now do this calculation like just it is exactly what Bernal did, he is genius.

So if you do that then this is the Bernal kind of g(r) that we get, radial distribution function in your homogenous system of that gives you how many molecules are placed at what distance now the important thing to know the structure factor where you get the g r?

(Refer Slide Time: 14:41)



How do we get $g(r)$ experimentally?

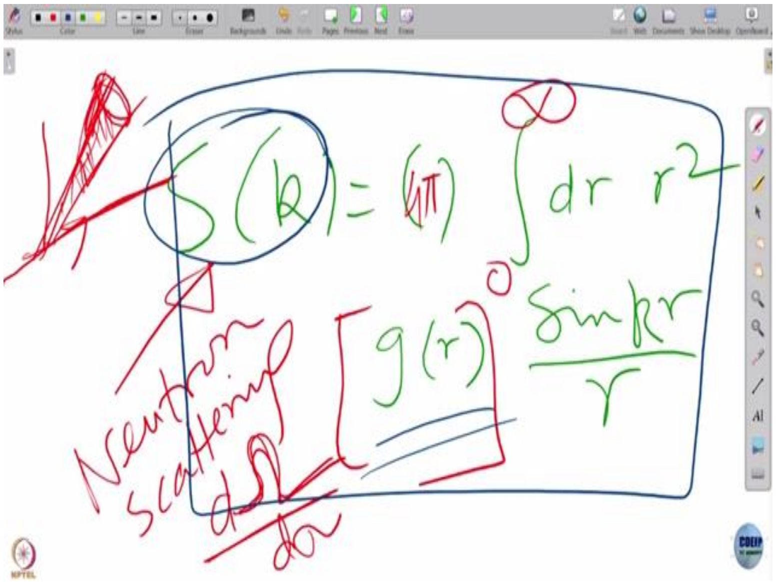
Van Hove ($\sim$1950)

$S(k)$

So how do you get g(r)? Experimentally, so long I have been talking of partition function. Experimentally does not care about your partition function, it can you want to measure and indeed we can directly measure this was shown first time and done on the first time Van Hove a great physicist around 1950, it is I think 47 to 50 around at that time after second world war when it comes scattering it comes.

He could get the scattering cross section from liquid and that he will structure factor came and that from then these are the equations will briefly derive but will not go very detail into that that the structure factor is which is measured from neutral scattering cross section is exactly given by radial distribution function, so S(k) is essentially given by;

(Refer Slide Time: 15:53)

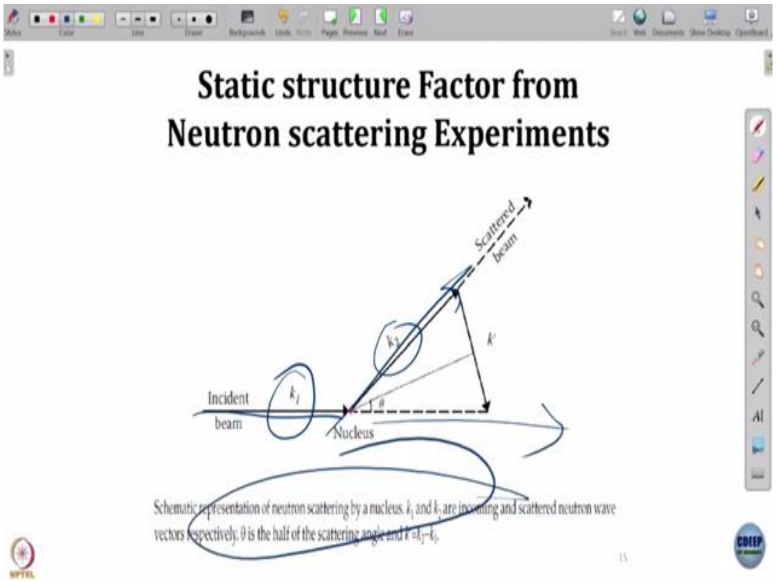


$$S(k) = 4\pi\int_0^\infty dr\, g(r) r^2 \frac{\sin kr}{kr}$$

Certain pre factor, this is the equation work, it go like, so it is essentially Fourier transformation of so this is my g(r) this is Fourier transform other factor like 4 π are here and so this is the one that I get from neutron scattering. So from differential cross section, we describe d by σ, this is this total scattering cross sectional differential, because what is the amount that goes into if incoming beam coming then gets as scattered then what goes into an angle located at σ?

That is this cross section is connected to total number because exchange of momentum exchange of momentum is k is the difference of momentum between incoming and outgoing and that is because of the positions the length scale and that will show the derivation but this is as I told you which is what? Is equation we as a golden equation, so static structure factor is k by neutron scattering is gives you radial distribution function. I think upto to an extent that is the most important take home message of this lecture.

(Refer Slide Time: 17:35)

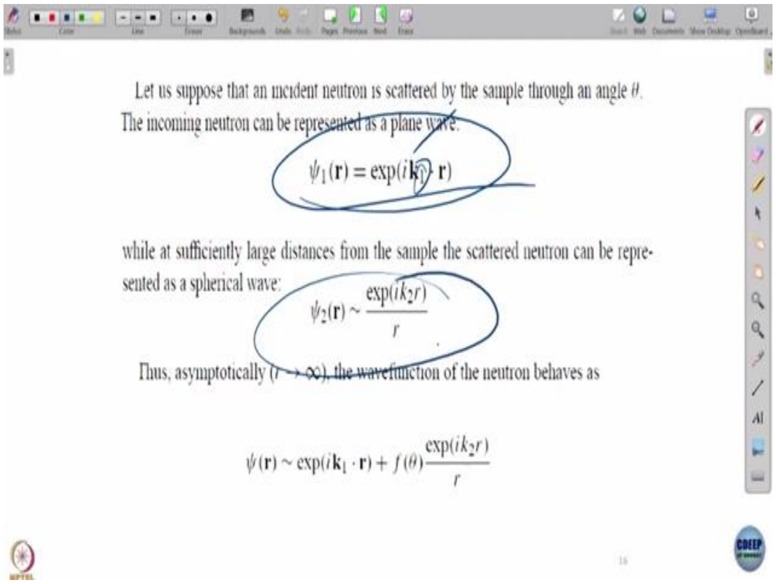


Static structure Factor from Neutron scattering Experiments

Schematic representation of neutron scattering by a nucleus. k_1 and k_2 are incoming and scattered neutron wave vectors respectively. θ is the half of the scattering angle and $k = k_2 - k_1$.

So, now this is now going to do now should that starting with the geometry that incident beam comes in gets scattered. So the ki is instead beam k 2 is this scatter is going to forward scattering then representation of neutron scattering. If we can do that;

(Refer Slide Time: 17:49)



Let us suppose that an incident neutron is scattered by the sample through an angle θ. The incoming neutron can be represented as a plane wave:

$$\psi_1(\mathbf{r}) = \exp(i\mathbf{k}_1 \cdot \mathbf{r})$$

while at sufficiently large distances from the sample the scattered neutron can be represented as a spherical wave:

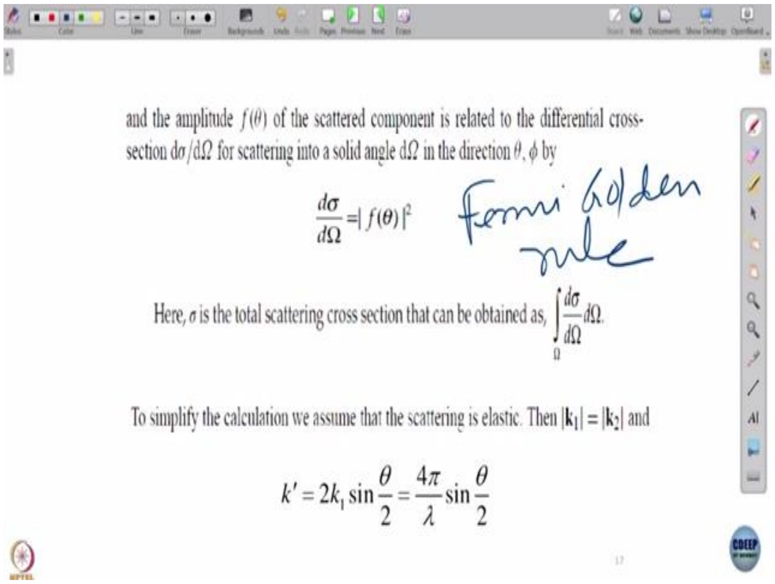
$$\psi_2(\mathbf{r}) \sim \frac{\exp(ik_2 r)}{r}$$

Thus, asymptotically ($r \to \infty$), the wavefunction of the neutron behaves as

$$\psi(\mathbf{r}) \sim \exp(i\mathbf{k}_1 \cdot \mathbf{r}) + f(\theta)\frac{\exp(ik_2 r)}{r}$$

Then plane wave becoming neutron is a plane wave around k i going out it is also a plane wave k2 then one can write the wave function last total wave function that is going out is linear combination of the two, but most important part is that

(Refer Slide Time: 18:13)



and the amplitude $f(\theta)$ of the scattered component is related to the differential cross-section $d\sigma/d\Omega$ for scattering into a solid angle $d\Omega$ in the direction θ, ϕ by

$$\frac{d\sigma}{d\Omega} = |f(\theta)|^2$$

Fermi Golden rule

Here, σ is the total scattering cross section that can be obtained as, $\int_\Omega \frac{d\sigma}{d\Omega} d\Omega$.

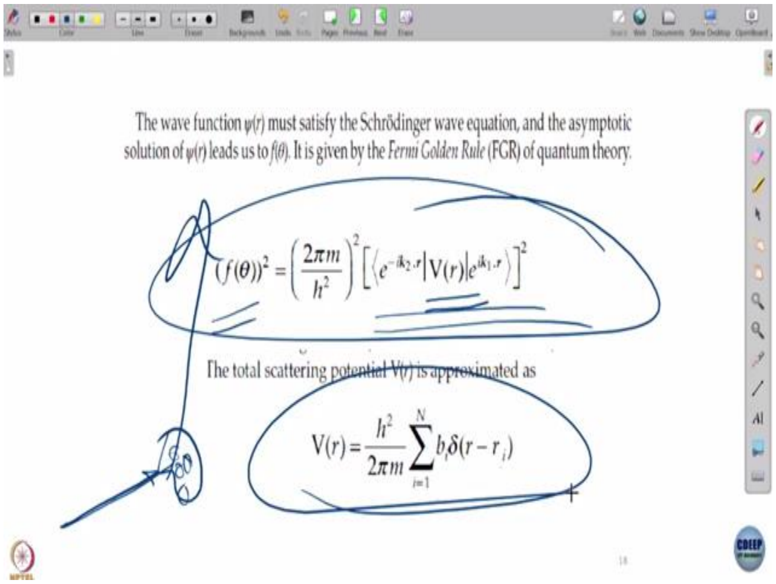
To simplify the calculation we assume that the scattering is elastic. Then $|\mathbf{k}_1| = |\mathbf{k}_2|$ and

$$k' = 2k_1 \sin\frac{\theta}{2} = \frac{4\pi}{\lambda}\sin\frac{\theta}{2}$$

17

That is comes from Fermi golden rule. So scattering cross section, square of the interaction between them and once you do that.

(Refer Slide Time: 18:24)



The wave function $\psi(r)$ must satisfy the Schrödinger wave equation, and the asymptotic solution of $\psi(r)$ leads us to $f(\theta)$. It is given by the *Fermi Golden Rule* (FGR) of quantum theory.

$$(f(\theta))^2 = \left(\frac{2\pi m}{h^2}\right)^2 \left[\left\langle e^{-i\mathbf{k}_2 \cdot \mathbf{r}} | \mathrm{V}(r) | e^{i\mathbf{k}_1 \cdot \mathbf{r}} \right\rangle\right]^2$$

The total scattering potential V(r) is approximated as

$$\mathrm{V}(r) = \frac{h^2}{2\pi m}\sum_{i=1}^{N} b_i \delta(r - r_i)$$

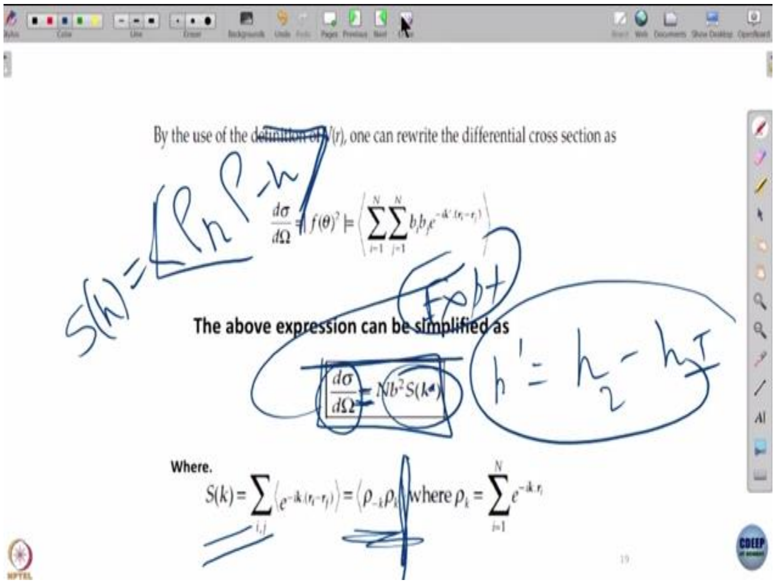
18

This is the Fermi golden rule,

$$\left(f(\theta)\right)^2 = \left(\frac{2\pi m}{h^2}\right)^2 \left[\left\langle e^{-i\mathbf{k}_2 \cdot \mathbf{r}} \,|\, \mathrm{V}(r) \,|\, e^{i\mathbf{k}_1 \cdot \mathbf{r}} \right\rangle\right]^2$$

this is square of the interaction between so the particle coming and here is my sample the neutron interact with my molecules here and gets scattered off and that case is giving by this scattering here which is nothing but interaction of the neutron at a particles at position r_i an incoming neutron and that is r- r_i, sum of the rate of function the kind of thing we told before. So this one now can be transformed into by

(Refer Slide Time: 18:59)



By the use of the definition of V(r), one can rewrite the differential cross section as

$$\frac{d\sigma}{d\Omega} = |f(\theta)|^2 = \left\langle \sum_{i=1}^{N}\sum_{j=1}^{N} b_i b_j e^{-ik'\cdot(r_i - r_j)} \right\rangle$$

The above expression can be simplified as

$$\frac{d\sigma}{d\Omega} = Nb^2 S(k)$$

Where.

$$S(k) = \sum_{i,j} \left\langle e^{-ik\cdot(r_i - r_j)} \right\rangle = \langle \rho_{-k}\rho_k \rangle \text{ where } \rho_k = \sum_{i=1}^{N} e^{-ik\cdot r_i}$$

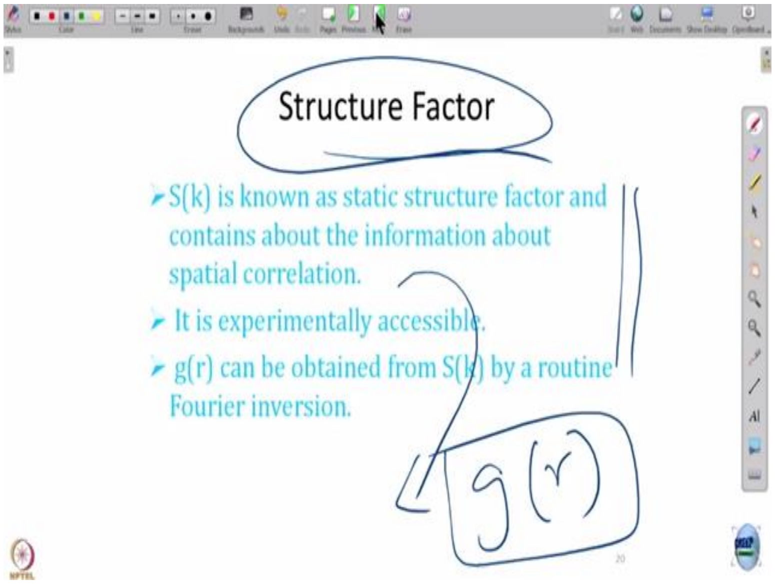
Fairly simple, algebra and using the delta function representations one can show that the scattering cross section is connected to this k prime is written as k_i, $k_2 - k_i$, that we just will do later. This is the structure factor and one can also show that the structure factor is k is same as rho k rho - k,

$$S(\boldsymbol{k}) = \langle \rho_k \rho_{-k} \rangle$$

that is done in the book and that is the same as this quantity and for static structure factor which is measured by forget about this k by this.

This is experimental quantity, this is the experiment and this relation is the theory and this S k is nothing but the radial distribution functions as we yeah this is the equation. So you know, S k from neutron scattering and then we can invert this Fourier transform again to get g r and S k is getting from neutral scattering by the following; fairly trivial manipulation that this is measure experimentally that directly gives S(k) once you know the parameter V.

(Refer Slide Time: 20:22)

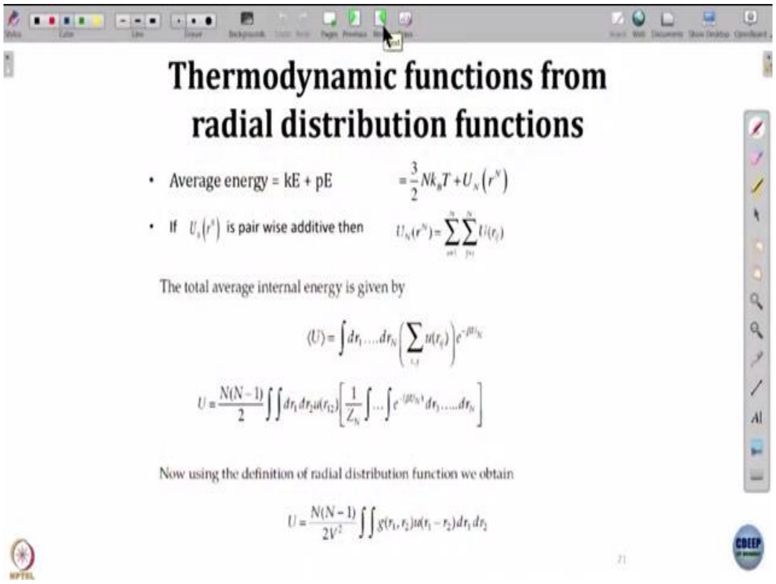


Structure Factor

- S(k) is known as static structure factor and contains about the information about spatial correlation.
- It is experimentally accessible.
- g(r) can be obtained from S(k) by a routine Fourier inversion.

Thus we are done now, it is known as the static structure factor and this gives the correlation and we just show that this gives us the g r most important quantity, not just in liquids but in glasses, in materials and everywhere else, that is what the huge number of people are measuring the neutron scattering, Okay? We are done.

(Refer Slide Time: 20:46)



Thermodynamic functions from radial distribution functions

- Average energy = kE + pE $= \frac{3}{2} N k_B T + U_N(r^N)$
- If $U_N(r^N)$ is pair wise additive then $U_N(r^N) = \sum_{i=1}^{N} \sum_{j>i}^{N} U(r_{ij})$

The total average internal energy is given by

$$\langle U \rangle = \int dr_1 \ldots dr_N \left(\sum_{i,j} u(r_{ij}) \right) e^{-\beta U_N}$$

$$U = \frac{N(N-1)}{2} \int\int dr_1 dr_2 u(r_{12}) \left[\frac{1}{Z_N} \int \ldots \int e^{-(\beta U_N)} dr_3 \ldots dr_N \right]$$

Now using the definition of radial distribution function we obtain

$$U = \frac{N(N-1)}{2V^2} \int\int g(r_1, r_2) u(r_1 - r_2) dr_1 dr_2$$

So the thermodynamic, one can get the thermodynamic functions for radial function and we will continue that in the next class, little bit of this radial distribution functions and that is today I will stop and take up from here and then we will go tomorrow to, a very related thing which is theory of polymers.