Introduction to Molecular Thermodynamics
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Lecture – 39
Classical Statistical Mechanics (Contd.)

Welcome in today's lecture we are going to talk about the application of classical statistical mechanics to understand the structure of simple liquids. So, the, we will start by identifying the key elements in describing the liquid structure. Of course, very name suggests that we are not really used to having a concept of liquid structure. When we draw the molecular structure of any sample we think about the solids for example, where we have a regular periodic array of atoms or molecules arranged such that; it does not matter which length scale you are looking at you are going to be having a periodic repetition of the same structural motif, but in the liquids such structural motif is not expected to be there.

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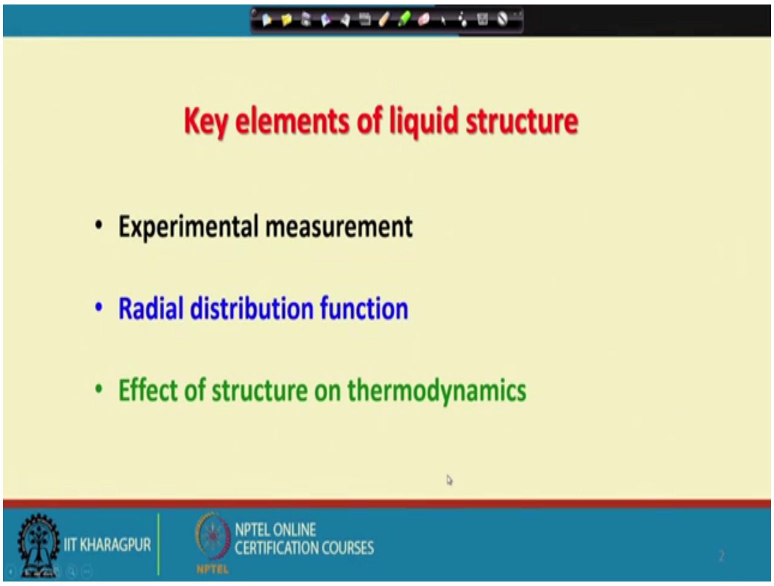

Key elements of liquid structure

- Experimental measurement
- Radial distribution function
- Effect of structure on thermodynamics

And therefore, I shall start by looking at the experimental determination of what I mean by liquid structure, what kind of signature does the underlying liquid structure is obtained when experimentally the structure is measured. And then I am going to talk about the central idea the key concept in liquid structure; that is given in terms of radial distribution function. And finally, I am going to use the radial distribution function to show you that the structure of the liquid indeed has effect on the thermodynamic properties.

So, let us start by discussing the determination of liquid structure by X ray scattering. So, as you may have encountered in your under studies on solid state chemistry that, X ray scattering is usually used in the case of determination of structure in the case of solids, but the same principle can be used in the determination of structure of liquids as well. So, what is the basic set up?

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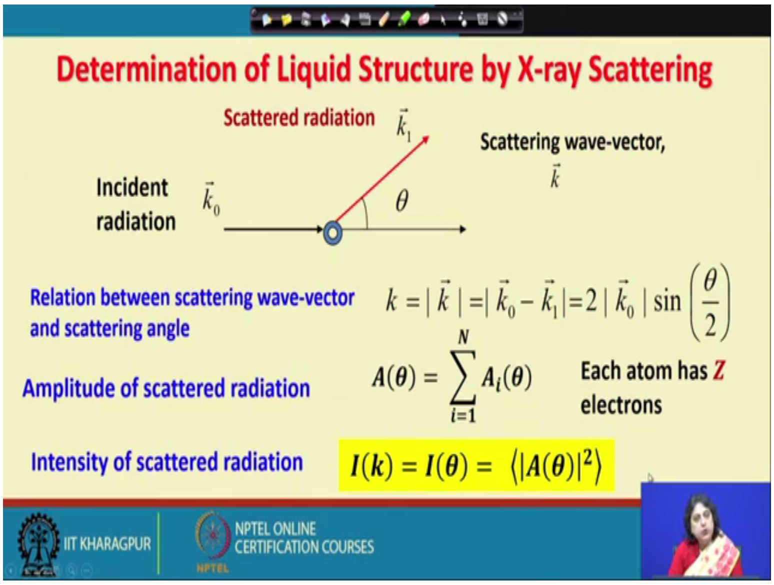

Determination of Liquid Structure by X-ray Scattering

Scattered radiation $\vec{k}_1$

Scattering wave-vector, $\vec{k}$

Incident radiation $\vec{k}_0$

θ

Relation between scattering wave-vector and scattering angle $k = |\vec{k}| = |\vec{k}_0 - \vec{k}_1| = 2|\vec{k}_0| \sin\left(\frac{\theta}{2}\right)$

Amplitude of scattered radiation $A(\theta) = \sum_{i=1}^{N} A_i(\theta)$ Each atom has Z electrons

Intensity of scattered radiation $I(k) = I(\theta) = \langle |A(\theta)|^2 \rangle$

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The basic setup is as follows, you are going to use an incident radiation which in this case is X ray and let us say that the incident radiation propagates in this direction characterized by the wave vector k naught. And when this radiation impinges on the sample then the X ray would interact with all the electrons present in the system and it would be scattered. Some of the radiation will proceed in the original direction of the incident radiation, but some of it will be scattered in different directions.

Now, if I want to know in which direction the radiation has been scattered, I will be use the concept of what is known as a scattering wave vector, which is given by this difference vector between k naught and k 1. Now obviously, the scattering wave vector depends on the scattering angle theta. So, basically if I go back and try to understand the relationship between the scattering wave vector and the scattering angle, I find that due to the interaction of the incident radiation in the with the electrons of the sample. There is a phase difference between the scattered wave vector and the and the incident wave vector, and this is given in terms of the scattering wave vector which is related to this angle theta. And this relationship is given by k is dependent on k naught modulus of k naught into sin of theta by 2. So basically, then the task is you go on collecting using a moveable collector the scattered intensity at different values of theta. So, you move it in the pathway of the scattered radiation and as a function of theta or as or equivalently as a function of k, you find out what the scattered intensity of scattered radiation is.

Now, if I look back and try to understand the source of this scattering I understand that the amplitude of scattered radiation will depend on theta and at every theta there will be contributions coming from all the atoms present in the system. So, if I have capital N atoms present in the system and if the sample is such that these atoms the scattering pattern is not really dependent on and the scattering of the ith atom of the is independent of the scattering from jth atom, then I can very easily write down that the total amplitude of scattering at angle theta that will depend on all the amplitudes collected from scattering originating from the ith atom and sum them over all the N atoms, but I should also remember that each atom has Z electrons, where Z is the atomic number of the atom.

And therefore, the amplitude of scattered irradiation at an angle theta it actually is obtaining contribution from all the Z electrons associated with each atom and I have N such atoms. As a result, the total intensity of scattered radiation is going to be an average over all these contributions. So, I can say that if I measure the intensity act different theta I am equivalently talking about measuring the intensity at different wave vectors and that can be related to the amplitude of the square of the amplitude of the scattered radiation at that particular angle.

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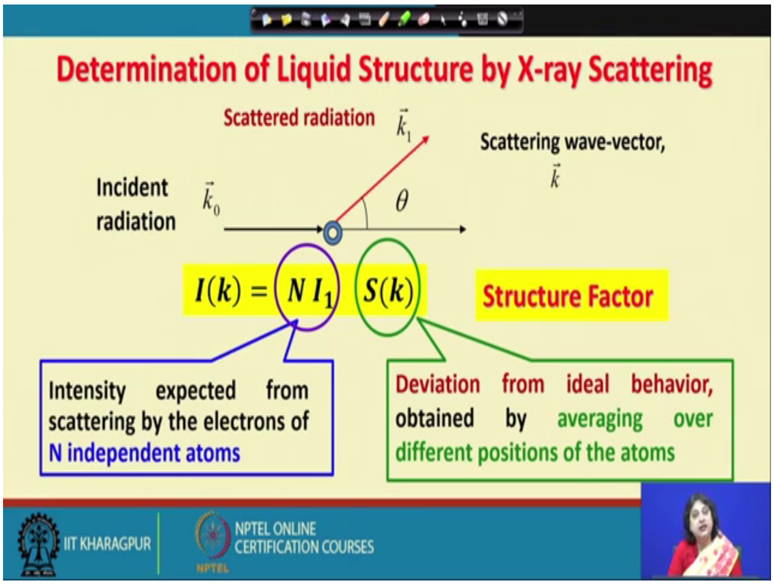

Determination of Liquid Structure by X-ray Scattering

$$I(k) = N\, I_1\, S(k)$$

Structure Factor

Intensity expected from scattering by the electrons of N independent atoms

Deviation from ideal behavior, obtained by averaging over different positions of the atoms

Now, how do I interpret this intensity I of k? In order to do that we talk about relating in this this intensity at k, in terms of 2 factors the first factor as shown here is N I 1 and the second factor is S of k. I am not going to discuss how I derive this because that would require you to understand the classical and quantum theories of scattering. So, those who are interested later on you can read this up, but for the purpose of today's lecture I am going to use this result from scattering theory and try to explain to you what we get as the outcome of my experimental measurement of liquid structure.

Now, let us look at N I 1. If I have N atoms in my scattering sample then N I 1 is the intensity expected from scattering by the electrons of capital N independent atoms. So, in this case I 1 is the intensity of scattering obtained from 1 atom and if I have a total of N such independent atoms. Then I will be having this total contribution coming from these N independent atoms as N I 1. Now the second factor that I have is the S of k. So, this is a factor which depends on k and this is known as the structure factor. So, what does the structure factor tell us? It tells us that in the scattering pattern there is a deviation from the ideal behavior where all the N atoms are independent of each other.

The position of the ith atom does not depend on position of jth atom in the ideal case, but in reality, there will be correlated to each other between the positions of different atoms. So, S of k tells us about the deviation from ideal behavior and this is obtained by averaging over different positions of the atoms. And please remember that the X rays are being scattered by all the Z electrons associated with each atom present in the sample and therefore, this S of k contains an averaging over contributions from all electrons originating from different atoms which whose positions are correlated with each other.

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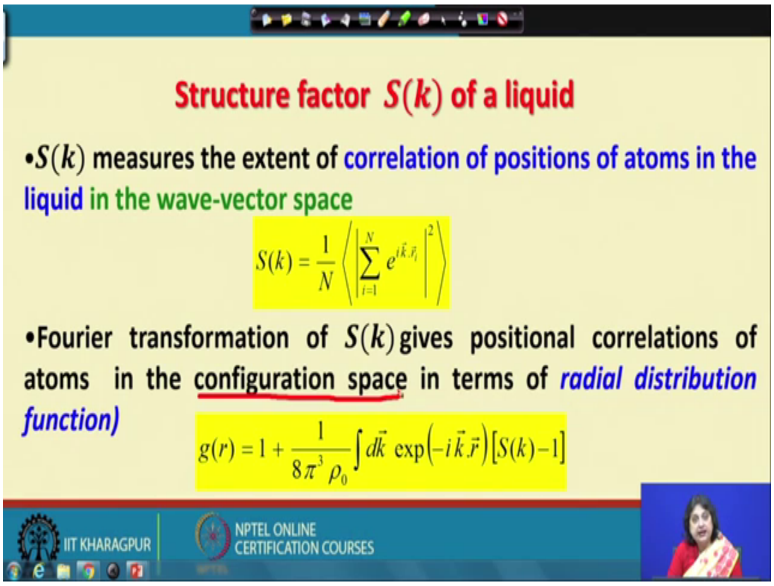

Structure factor $S(k)$ of a liquid

- $S(k)$ measures the extent of correlation of positions of atoms in the liquid in the wave-vector space

$$S(k)=\frac{1}{N}\left\langle\left|\sum_{i=1}^{N}e^{i\vec{k}.\vec{r}_i}\right|^2\right\rangle$$

- Fourier transformation of $S(k)$ gives positional correlations of atoms in the configuration space in terms of *radial distribution function)*

$$g(r)=1+\frac{1}{8\pi^3\rho_0}\int d\vec{k}\,\exp\left(-i\vec{k}.\vec{r}\right)\left[S(k)-1\right]$$

And therefore, I would say that the structure factor of the liquid tells us the extent of correlation in positions of the atoms, but since I am measuring the S that is a structure factor in the wave vector space that is S of k therefore, the extent of positional correlation is measured in the scattering experiment in the wave vector space. And if I look at the exact expression for S of k this can be derived as you can see that here the S of k depends on the positions of the different atoms present on the system. And this is a Fourier transform of those functions of those positions.

Now, if I want to visualize where in the 3-dimensional space the different atoms are located, what we have to do is; we will have to carry out a Fourier transformation of S of k and if I do that that gives me what is known as the radial distribution function. So, the radial distribution function is defined formally as the Fourier transformation of S of k so, that the information that we had in the wave vector space is now, converted into a position correlation of the atoms in the wave vector space; which means that if I Fourier transform S of k. I get how the positions of the different atoms present in the system are described in relation to each other in the 3-dimensional Cartesian coordinate space for example, where each atom is described in terms of it is Cartesian coordinate x y and z.

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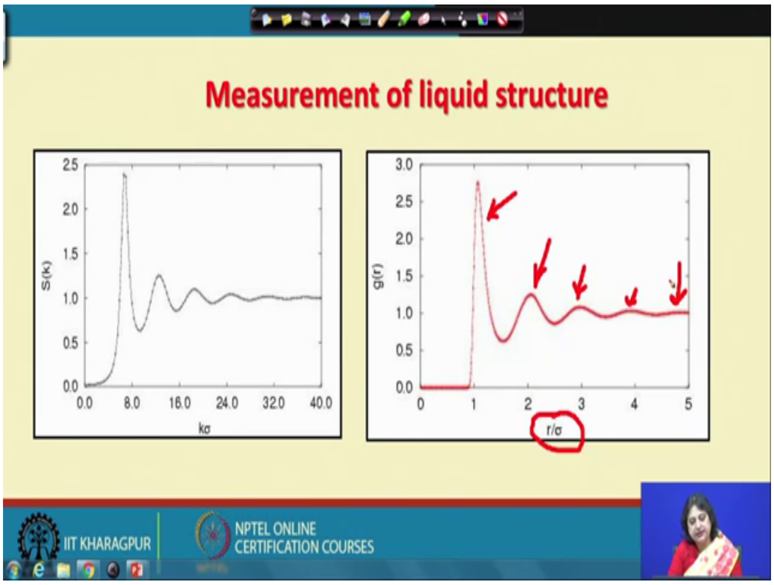

Measurement of liquid structure

And therefore, to summarize the experimental observation in the measurement of liquid structure this is what we measure, we measure S of k as a function of k from the scattering experiments. And as you see that there are signatures of correlation in the wave vector space as given by the appearance of these peaks and different values of k in S of k.

Now, if I Fourier transform this response in that case what I get is g of R. So, g of R tells me that this is the deviation from an ideal gas like behavior in the structure of the liquid and therefore, here the peaks that I see here at r approximately equal to sigma or r approximately equal to 2 sigma or 3 sigma etcetera. These are the positive deviations from the ideal gas behavior saying that; if I have 2 molecule 2 atoms at roughly at a distance of one point 1 or 1.2 sigma then their positions are highly correlated. And as you see that these correlations become weaker and weaker as given by the height of the peaks as we go for higher pair distances and then it goes to 1 when they are separated by a very large distance which is the scenario of an ideal gas.

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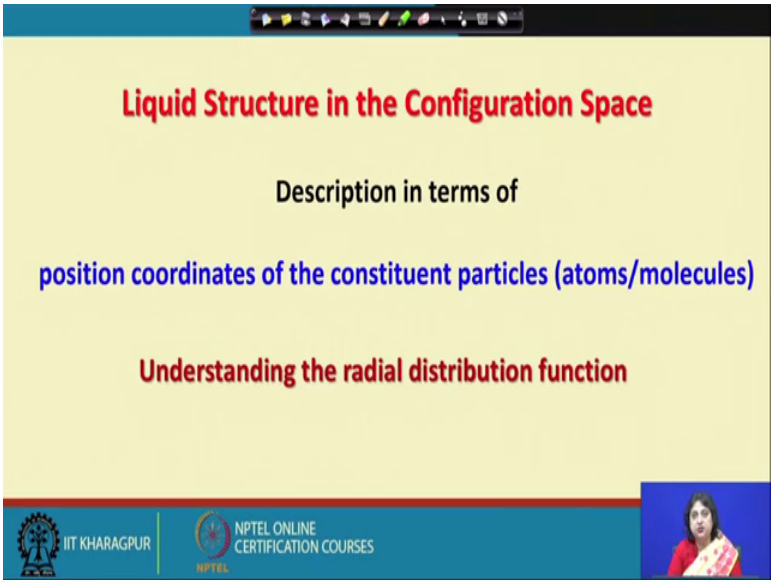

Liquid Structure in the Configuration Space

Description in terms of

position coordinates of the constituent particles (atoms/molecules)

Understanding the radial distribution function

So, in the next part of this lecture what I am going to do is I am going to talk about the quantitative description of the liquid structure in the configuration space, where I explicitly discuss this correlation in the position coordinates of the constituent particles of my sample liquid sample and with that I would like to introduce the concept of the radial distribution function, which I showed to you in the previous slide as g of R. So, g of R is a quantity that we can get from the experimental data, but the question that I am asking now is, what is the kind of picture that we have associated with a microscopic state of the liquid this is something like this

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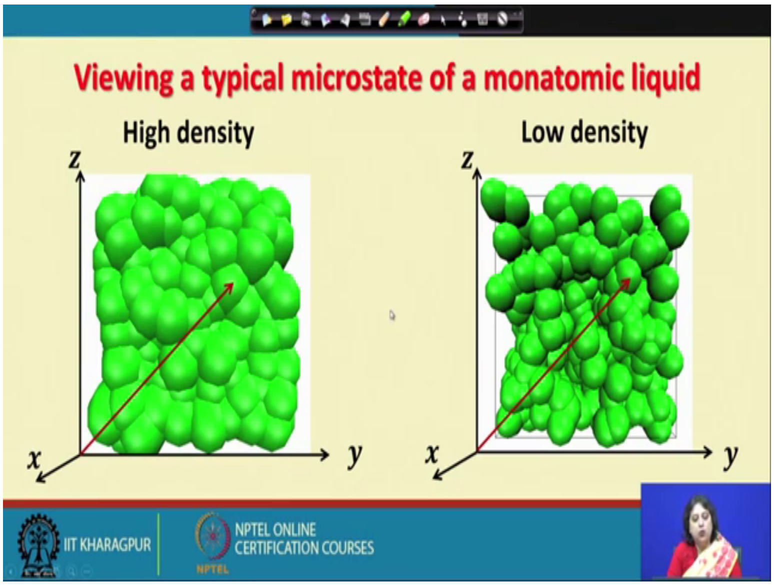

Viewing a typical microstate of a monatomic liquid

So, here I am showing you a typical microscopic snapshot of a liquid sample at a very high density. As you see that here each of these particles these their Vander Waal surfaces as shown in this picture and they are really touching each other ok. They are very closely packed, soft spheres which are packed into the given volume V at a given temperature and a total number of particles is fixed.

If I had a low-density sample, you will see that there are lots of void spaces and although some of them are touching each other. There are void spaces where no atoms are there which are very close to each other. Now if I want to have a quantitative description of microstates like this what I will do is, I will set up the laboratory fixed frame of reference of coordinates like the xyz coordinates.

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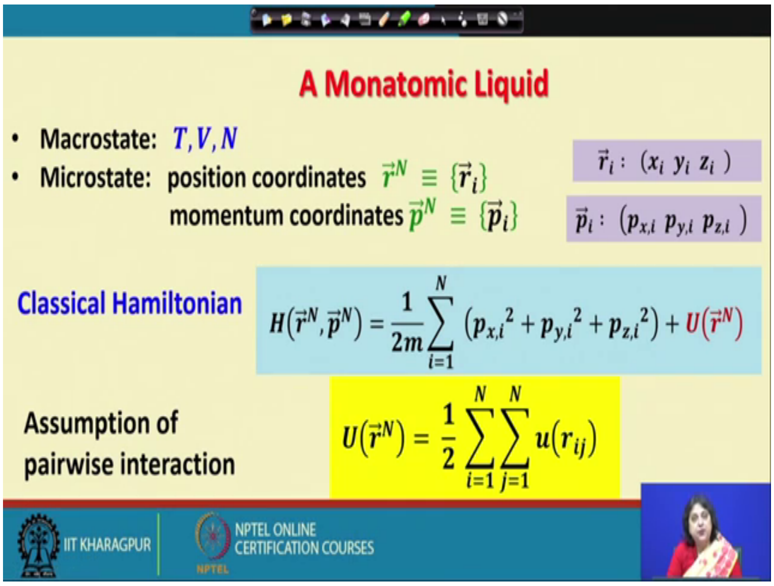

A Monatomic Liquid

- Macrostate: T,V,N
- Microstate: position coordinates $\vec{r}^N \equiv \{\vec{r}_i\}$
  momentum coordinates $\vec{p}^N \equiv \{\vec{p}_i\}$

$\vec{r}_i : (x_i\ y_i\ z_i)$

$\vec{p}_i : (p_{x,i}\ p_{y,i}\ p_{z,i})$

Classical Hamiltonian

$$H(\vec{r}^N,\vec{p}^N) = \frac{1}{2m}\sum_{i=1}^{N}\left(p_{x,i}^2 + p_{y,i}^2 + p_{z,i}^2\right) + U(\vec{r}^N)$$

Assumption of pairwise interaction

$$U(\vec{r}^N) = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} u(r_{ij})$$

And for each atom I will associate with it a 3-dimensional vector giving it is xyz coordinates. Now then using the standard description of classical mechanics I will associate to a system having capital N particles in the canonical ensemble 3 N position coordinates and 3 and momentum coordinates and I will write down the classical Hamiltonian in terms of these position and momentum coordinates, but a interesting point is a liquid is a an interacting system; therefore, I will have a non 0 contribution of the potential energy which depends on the configuration or the position coordinates of all the N atoms present in the system.

Now once we have this then we can say that if I assume that the potential energy arises from pair wise interaction, then I can write that the total potential energy is the sum of all type of pair interactions that are present between every possible distinct pairs present in the sample.

Now, let us try and have a pictorial understanding of what I mean by the potential energy being represented as pair wise interaction.

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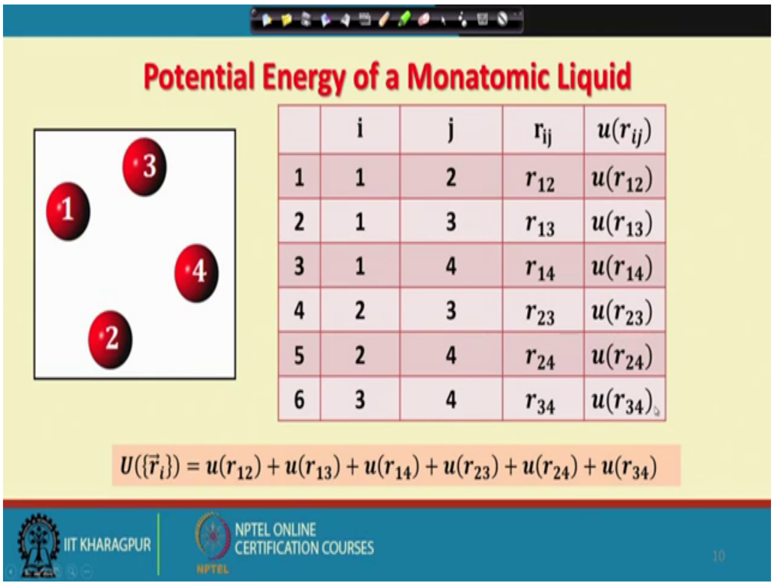

Potential Energy of a Monatomic Liquid

	i	j	r_{ij}	$u(r_{ij})$
1	1	2	r_{12}	$u(r_{12})$
2	1	3	r_{13}	$u(r_{13})$
3	1	4	r_{14}	$u(r_{14})$
4	2	3	r_{23}	$u(r_{23})$
5	2	4	r_{24}	$u(r_{24})$
6	3	4	r_{34}	$u(r_{34})$

$$U(\{\vec{r}_i\}) = u(r_{12}) + u(r_{13}) + u(r_{14}) + u(r_{23}) + u(r_{24}) + u(r_{34})$$

So, let us say that here I have a snapshot of my liquid sample, where these red balls are the atoms of the liquid sample and they are labeled as 1 2 3 4 for our convenience; of course, if you take a liquid sample like liquid argon all these atoms are going to be indistinguishable, but for our purpose of understanding I have labeled them as 1 2 3 4 and then I can actually write down all possible pairs i and j. And you can see very easily that there will be 6 such pairs and, in this case, if for every pair I can find out for example, the distance between the 2 atoms which I call rij. So, if I consider 1 and 2. I am measuring r 1 2 and the interaction in an energy potential energy between 1 and 2 is given by u of r 1 2. And I can repeat this for all the 6 pairs possible and then I can write down the total potential energy as a sum of these 6 paired interactions.

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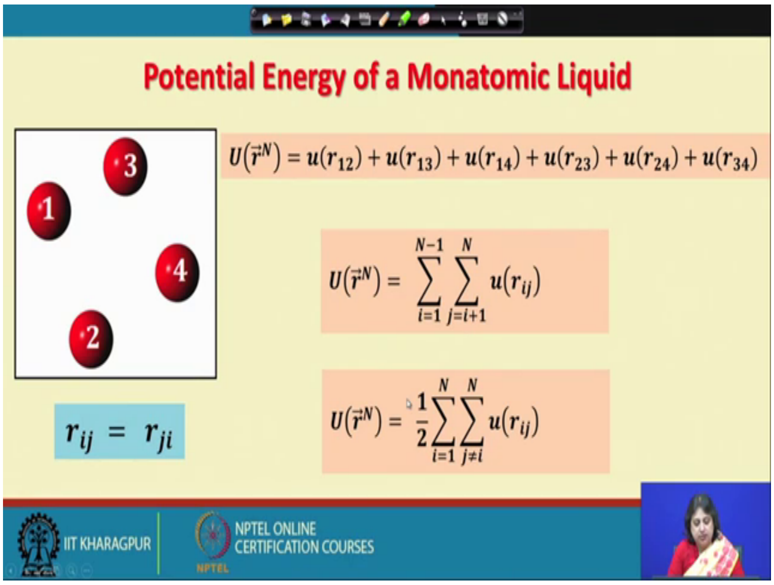

Potential Energy of a Monatomic Liquid

$U(\vec{r}^N) = u(r_{12}) + u(r_{13}) + u(r_{14}) + u(r_{23}) + u(r_{24}) + u(r_{34})$

$$U(\vec{r}^N) = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} u(r_{ij})$$

$r_{ij} = r_{ji}$

$$U(\vec{r}^N) = \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i}^{N} u(r_{ij})$$

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And when I write down this kind of expression I can use a condensed notation, I can say that I am summing over all u of r ij by summing over I going from 1 2 N minus 1 and j going from i plus 1 to N. So, that is exactly if you put n equal to 4 here you will retrieve this expression, but noting that rj I is equal to r ij it is also convenient to write that u r N is a double summation like this, where I is not equal to j, but each of i and j will run from 1 to N. So, I am double counting 1 2 and 2 1. So, I will divide the sum by half in order to avoid over counting.

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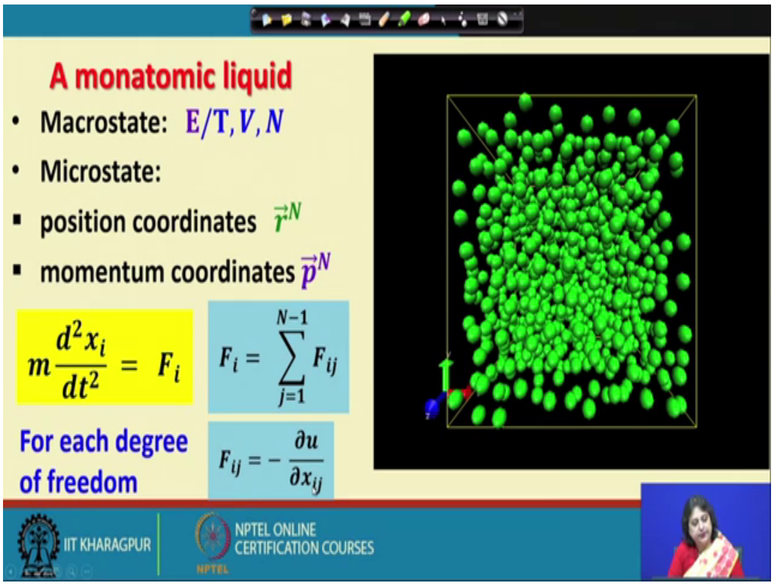

A monatomic liquid

- Macrostate: E/T, V, N
- Microstate:
- position coordinates $\vec{r}^N$
- momentum coordinates $\vec{p}^N$

$$m\frac{d^2x_i}{dt^2} = F_i \qquad F_i = \sum_{j=1}^{N-1} F_{ij}$$

For each degree of freedom

$$F_{ij} = -\frac{\partial u}{\partial x_{ij}}$$

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Now, with this idea in mind then what happens is one can think of the different microstates of the system by solving for example, the equation of motion which is given here. And I find that for every degree of freedom there is an equation of motion say the degree of freedom is x i and this is going to depend on f i where f i is the force acting on the ith a degree of freedom or the ith particle here because of all other n minus 1particles present in the system. Now what is f ij? F ij that is the force on the ith particle because of the presence of some other particle j in the medium is related to the derivative of the pair interaction u with respect to their separation ok.

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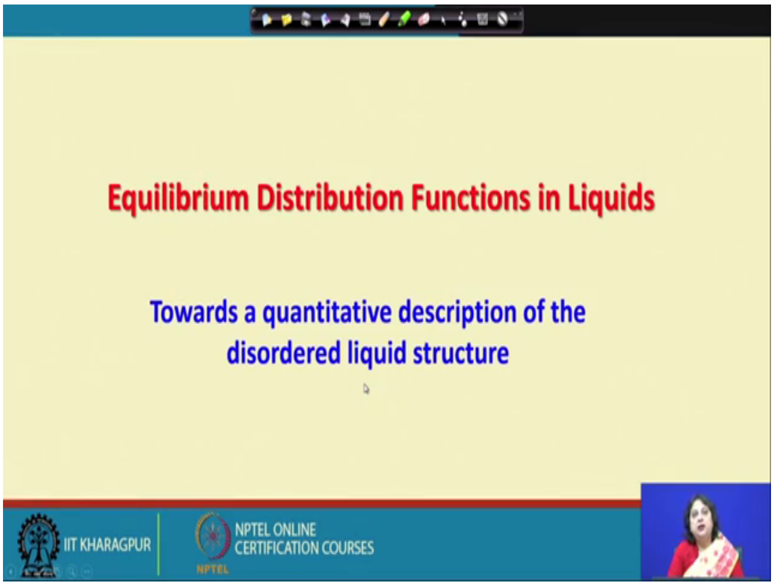

Equilibrium Distribution Functions in Liquids

Towards a quantitative description of the disordered liquid structure

So, basically then in the configuration space we are trying to develop a quantitative description of the disordered liquid structure, and this is done in terms of an equilibrium distribution function in liquids knowing that I have at hand under a given condition of T V N a very large number of microstates.

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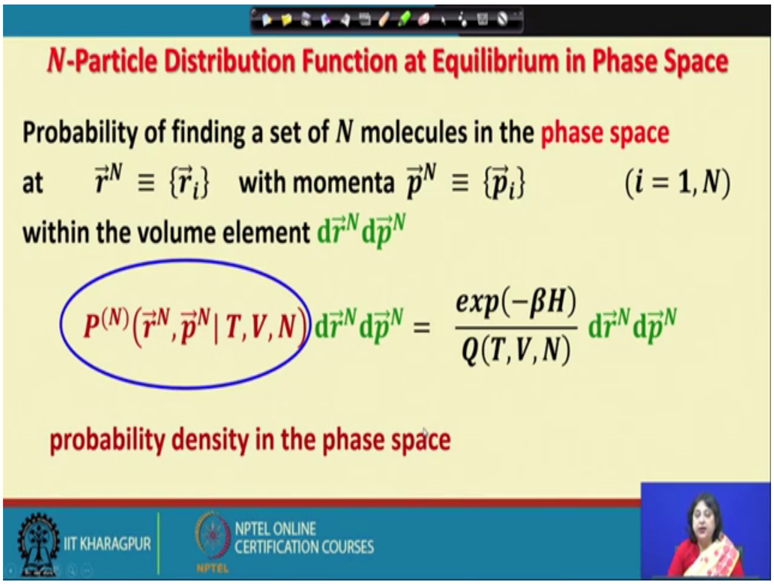

N-Particle Distribution Function at Equilibrium in Phase Space

Probability of finding a set of N molecules in the phase space

at $\vec{r}^N \equiv \{\vec{r}_i\}$ with momenta $\vec{p}^N \equiv \{\vec{p}_i\}$ $(i = 1, N)$

within the volume element $d\vec{r}^N d\vec{p}^N$

$$\boxed{P^{(N)}(\vec{r}^N, \vec{p}^N \,|\, T, V, N)}\, d\vec{r}^N d\vec{p}^N = \frac{exp(-\beta H)}{Q(T,V,N)}\, d\vec{r}^N d\vec{p}^N$$

probability density in the phase space

Now at equilibrium we know that the probability of finding a set of N molecules in the phase space within volume element which is given in terms of d r N d P N. That can be very easily written down in terms of the e to the power of minus beta h, that is a full Hamiltonian of the system and divided by the canonical partition function. So, in this case what I have done is I have indicated by this P capital N, the probability density in the phase space or the probability associated with unit volume in the phase space of observing a state point characterized by certain values of r N and certain values of P N.

So, when we talk about the n particle distribution function at equilibrium in the configuration space.

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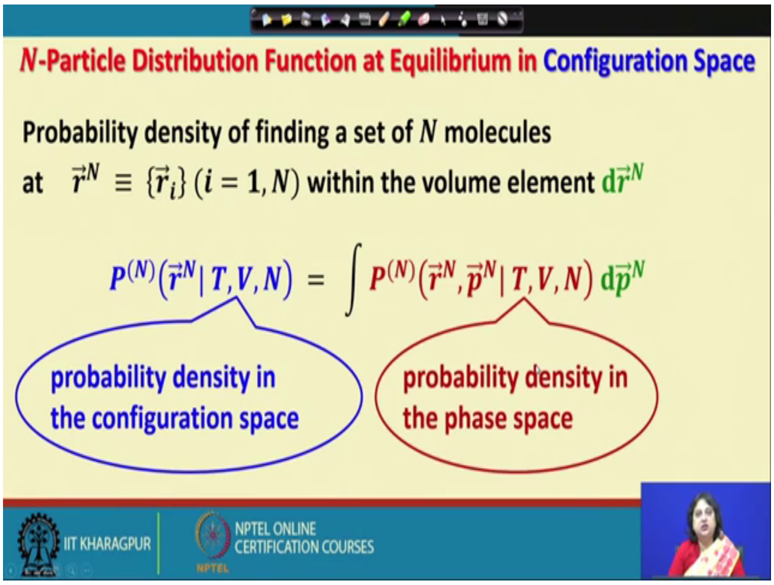

N-Particle Distribution Function at Equilibrium in Configuration Space

Probability density of finding a set of N molecules at $\vec{r}^N \equiv \{\vec{r}_i\}$ $(i = 1, N)$ within the volume element $d\vec{r}^N$

$$P^{(N)}(\vec{r}^N | T,V,N) = \int P^{(N)}(\vec{r}^N,\vec{p}^N | T,V,N)\, d\vec{p}^N$$

probability density in the configuration space

probability density in the phase space

Then we are asking the question what is the probability density of finding a set of capital N molecules at a given configuration, which is characterized by a set of coordinates like r 1 r 2 r 3 etcetera and I am looking at some volume element infinitesimal volume element in the configuration space. And this can be obtained from the full phase space n particle distribution function by integrating over the all the possible values of momenta of the N particles. So, in this representation then what I would say is I have expressed the probability density in the configuration space in terms of the probability.

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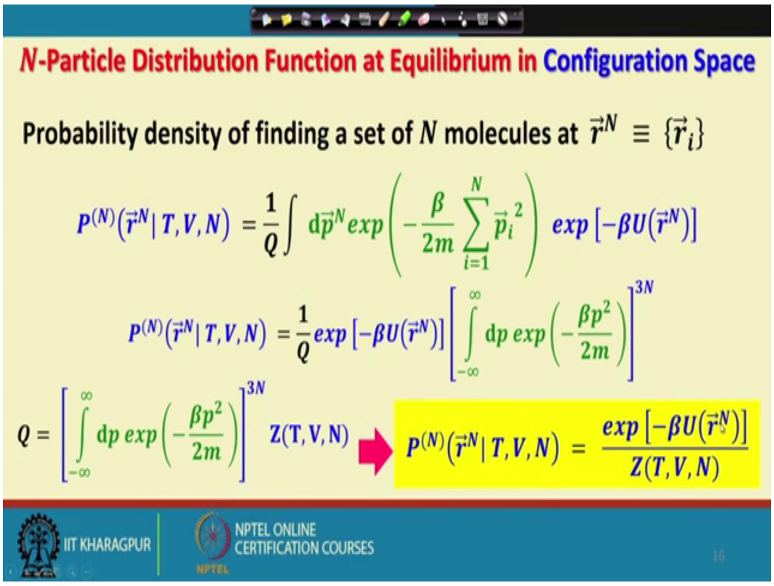

N-Particle Distribution Function at Equilibrium in Configuration Space

Probability density of finding a set of N molecules at $\vec{r}^N \equiv \{\vec{r}_i\}$

$$P^{(N)}(\vec{r}^N | T,V,N) = \frac{1}{Q}\int d\vec{p}^N exp\left(-\frac{\beta}{2m}\sum_{i=1}^{N}\vec{p}_i^{\,2}\right) exp\left[-\beta U(\vec{r}^N)\right]$$

$$P^{(N)}(\vec{r}^N | T,V,N) = \frac{1}{Q} exp\left[-\beta U(\vec{r}^N)\right]\left[\int_{-\infty}^{\infty} dp\; exp\left(-\frac{\beta p^2}{2m}\right)\right]^{3N}$$

$$Q = \left[\int_{-\infty}^{\infty} dp\; exp\left(-\frac{\beta p^2}{2m}\right)\right]^{3N} Z(T,V,N) \Rightarrow \boxed{P^{(N)}(\vec{r}^N | T,V,N) = \frac{exp\left[-\beta U(\vec{r}^N)\right]}{Z(T,V,N)}}$$

Density in the phase space and then what I can further say that this probability density in the configuration space can be explicitly written up using the expression of the probability density in the phase space. And I understand that in that case I will be integrating over all possible momentum values of this contribution coming from the Hamiltonian ok.

Now if that happens I can very easily show that this is going to be nothing but the configuration dependent part unchanged, but this integration part separately coming out, but if I use the definition of capital Q, we have already discussed this I can simply have it separated into the integration over the momentum part and then the configuration integral. So, if I combine all these results what I find is that, the equilibrium in particle distribution function is dependent on e to the power of minus beta u divided by the configuration integral.

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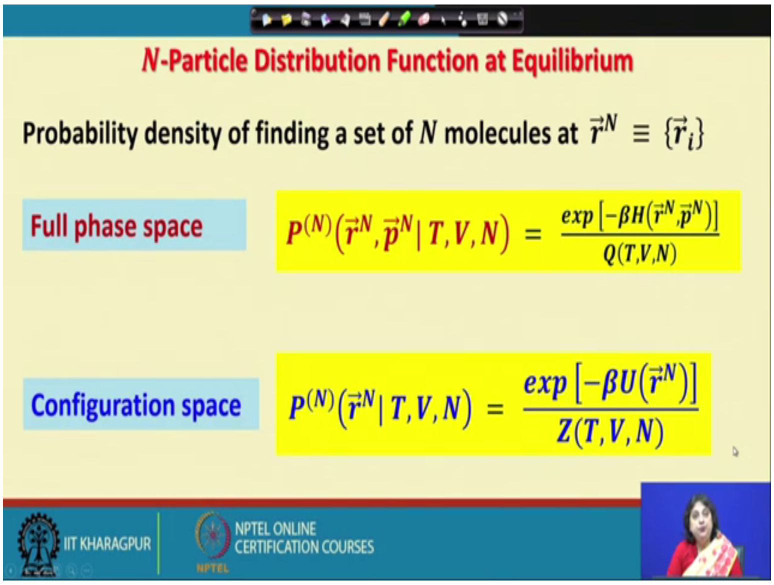

N-Particle Distribution Function at Equilibrium

Probability density of finding a set of N molecules at $\vec{r}^N \equiv \{\vec{r}_i\}$

Full phase space $P^{(N)}\left(\vec{r}^N, \vec{p}^N \mid T, V, N\right) = \dfrac{\exp\left[-\beta H\left(\vec{r}^N, \vec{p}^N\right)\right]}{Q(T,V,N)}$

Configuration space $P^{(N)}\left(\vec{r}^N \mid T, V, N\right) = \dfrac{\exp\left[-\beta U\left(\vec{r}^N\right)\right]}{Z(T,V,N)}$

And therefore, if I compared in the full phase space the equilibrium probability density of finding a set of N molecules at a given configuration is dependent on the total Hamiltonian and it is divided by normalized by the canonical partition function.

On the other hand, in the configuration space, the associated probability density is dependent only on the potential energy and it is normalized by the configuration integral. And now you understand the relevance of the name configuration integral. Now what is the outcome?

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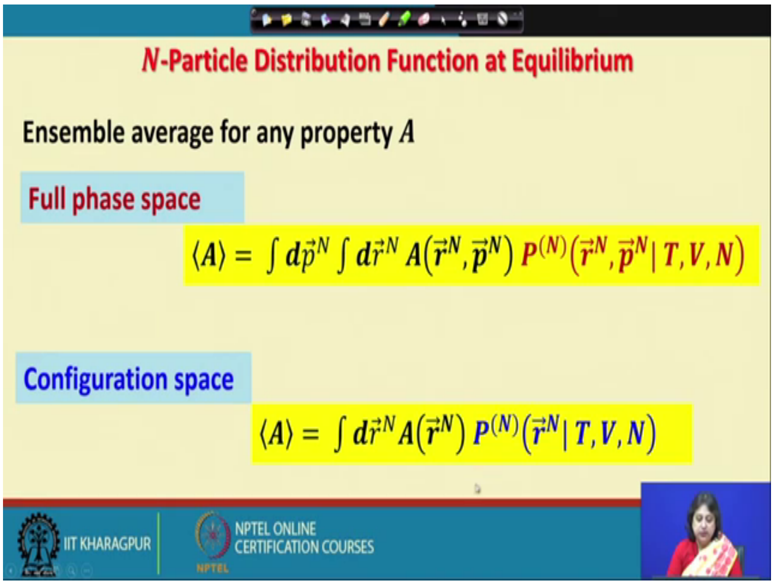

N-Particle Distribution Function at Equilibrium

Ensemble average for any property A

Full phase space

$$\langle A\rangle = \int d\vec{p}^{N} \int d\vec{r}^{N}\, A(\vec{r}^{N},\vec{p}^{N})\, P^{(N)}(\vec{r}^{N},\vec{p}^{N} \mid T,V,N)$$

Configuration space

$$\langle A\rangle = \int d\vec{r}^{N} A(\vec{r}^{N})\, P^{(N)}(\vec{r}^{N} \mid T,V,N)$$

The outcome of this definition is if I want to calculate some ensemble average for any property A if I am using the full phase space in that case I will be using the full phase space probability density, but in the configuration space what I will be using is the configuration space probability density.

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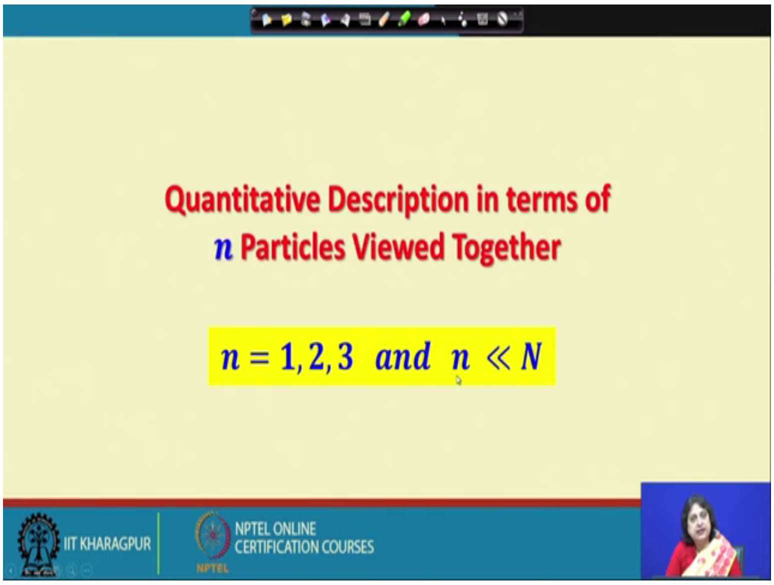

Quantitative Description in terms of *n* Particles Viewed Together

$$n = 1,2,3 \quad and \quad n \ll N$$

Now using this idea, we are now going to talk about a small n part number of particles viewed together to obtain a quantitative description of the liquid structure.

Now, what is small n? Small n is going to be a number like 1 2 or 3, which means that for a real sample this small n is much much less than the total number of particles present.

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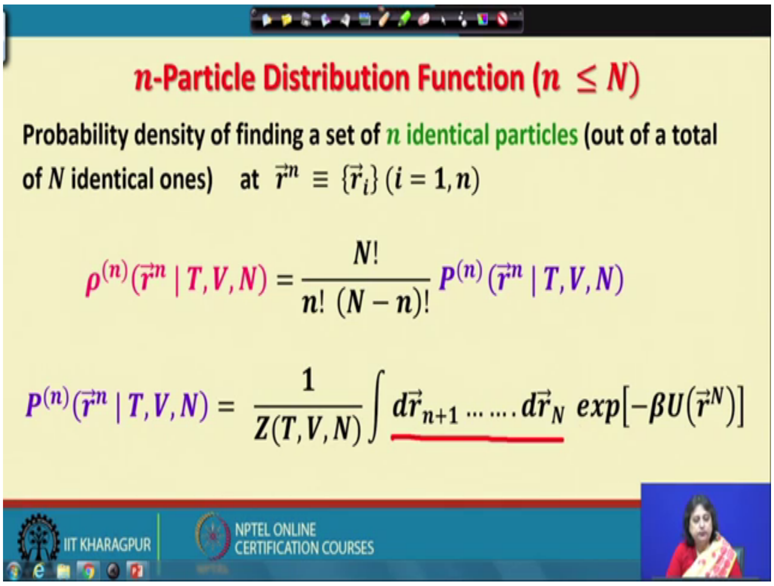

n-Particle Distribution Function ($n \le N$)

Probability density of finding a set of n identical particles (out of a total of N identical ones) at $\vec{r}^n \equiv \{\vec{r}_i\}\ (i = 1, n)$

$$\rho^{(n)}(\vec{r}^n \mid T,V,N) = \frac{N!}{n!\ (N-n)!} P^{(n)}(\vec{r}^n \mid T,V,N)$$

$$P^{(n)}(\vec{r}^n \mid T,V,N) = \frac{1}{Z(T,V,N)} \int \underline{d\vec{r}_{n+1} \ldots\ldots d\vec{r}_N}\ exp\left[-\beta U(\vec{r}^N)\right]$$

So, how do I define this n particle distribution function this is the probability density of finding a set of n identical particles out of a total of capital N identical ones at some given positions ok. And this by definition is related to this equilibrium configuration space probability density multiplied by the number of ways in which you can choose small n particles up from an set of capital N. So, let me remind you that we have already said that this P N is nothing but d r n plus 1 to d r N then e to the power of minus beta U and r N by Z T V N.

So, this is the probability of observing once you have a set of small n particles chosen out of a collection of capital N, then this is the probability of observing those n particles at a given position in configuration space irrespective of where the other capital N minus small n particles are located. So, this is taken care of by integrating over the position of all other particles that are not being considered.

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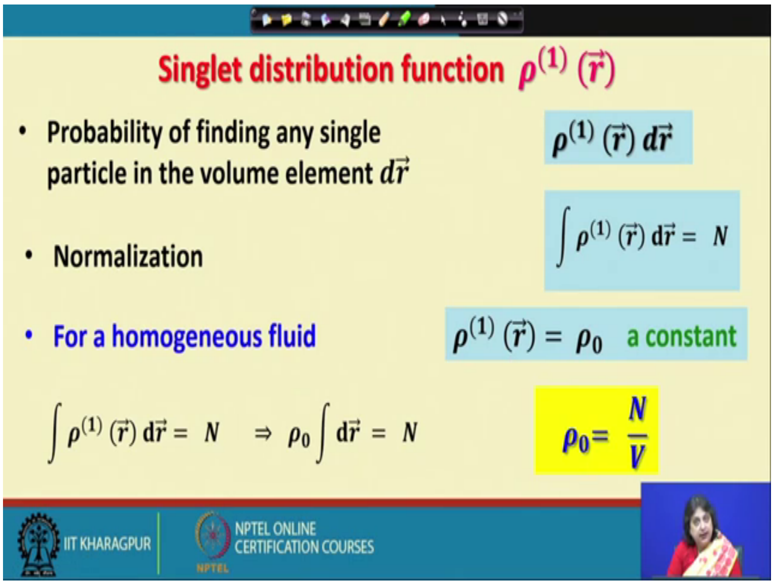

Singlet distribution function $\rho^{(1)}(\vec{r})$

- Probability of finding any single particle in the volume element $d\vec{r}$ — $\rho^{(1)}(\vec{r})\, d\vec{r}$
- Normalization — $\int \rho^{(1)}(\vec{r})\, d\vec{r} = N$
- For a homogeneous fluid — $\rho^{(1)}(\vec{r}) = \rho_0$ a constant

$$\int \rho^{(1)}(\vec{r})\, d\vec{r} = N \quad \Rightarrow \rho_0 \int d\vec{r} = N \qquad \rho_0 = \frac{N}{V}$$

So, this brings us to the concept of ok. Let us think about small n equal to 1. So that is supposed to be the easiest case. So, what is the probability of finding a single particle in the small volume element in the configuration space, this is given by rho 1 r dr, but this is a probability distribution function therefore, I would require that if I normalize it I am talking about finding single particles in small small volume elements if I integrate over the entire space; I must be getting the total number of particles back. Now for a homogeneous fluid it does not matter which small volume element I am looking at; this number should always be the same because it is homogeneous it does not depend on which portion of the sample I am looking at rather this is going to be a constant.

Now, if I look at the normalization constant then I find that this means that this constant is nothing but the total number of particles divided by V, which is the average number density of the system ok. So, for a homogeneous fluid I find that the rho 1 r which is the singular distribution function is nothing but the number density of the liquid.

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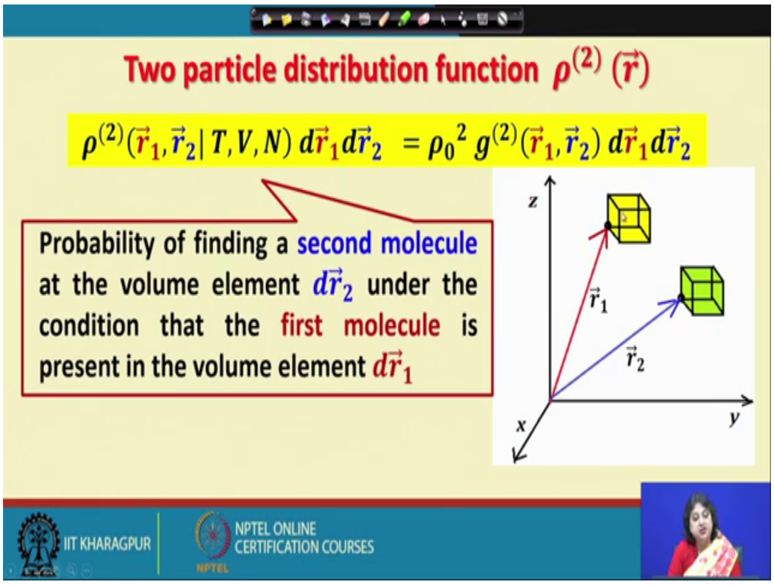

Two particle distribution function $\rho^{(2)}(\vec{r})$

$$\rho^{(2)}(\vec{r}_1,\vec{r}_2|T,V,N)\,d\vec{r}_1 d\vec{r}_2 = \rho_0^2\, g^{(2)}(\vec{r}_1,\vec{r}_2)\,d\vec{r}_1 d\vec{r}_2$$

Probability of finding a second molecule at the volume element $d\vec{r}_2$ under the condition that the first molecule is present in the volume element $d\vec{r}_1$

Now, if we think about the 2-particle distribution function, here I am talking about the probability density of finding 2 particles simultaneously at the positions r 1 and r 2 obeying the same conditions of temperature volume and number of particles. So, this is the kind of picture that I have in mind. And this by definition is given by rho naught square into g 2 multiplied by the associated volume element in the configuration space. Now here I understand that this is the probability of finding a second molecule 2 within this volume element that is shown in green here under the condition that there is a first molecule present in the volume element the r 1.

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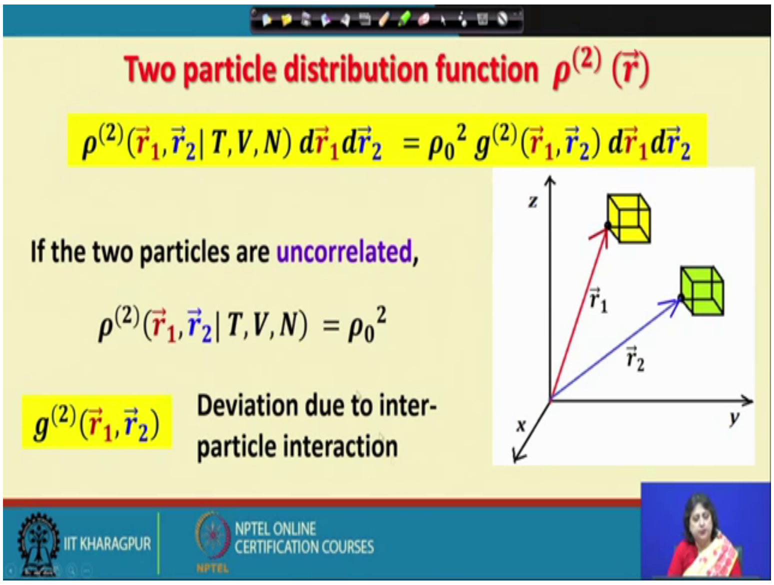

Two particle distribution function $\rho^{(2)}(\vec{r})$

$$\rho^{(2)}(\vec{r}_1,\vec{r}_2|T,V,N)\,d\vec{r}_1 d\vec{r}_2 = \rho_0^2\, g^{(2)}(\vec{r}_1,\vec{r}_2)\,d\vec{r}_1 d\vec{r}_2$$

If the two particles are uncorrelated,

$$\rho^{(2)}(\vec{r}_1,\vec{r}_2|T,V,N) = \rho_0^2$$

$g^{(2)}(\vec{r}_1,\vec{r}_2)$ Deviation due to inter-particle interaction

And now when I use this definition then I understand that I already have this particle 1 fixed at this position somewhere within this volume element. And I am asking if the position of a second particle is correlated to it is position. Now if these 2 particles are uncorrelated they will behave as single particles, and their probabilities are going to be given by the individual singlet probability distribution, which in the case of a homogeneous system is nothing but rho naught square.

And then I would identify from this definition what exactly g 2 means. G 2 is actually is telling me that this would be the deviation in the observed probability distribution of rho 2 due to the inter particle interaction between my particle 1 and particle 2.

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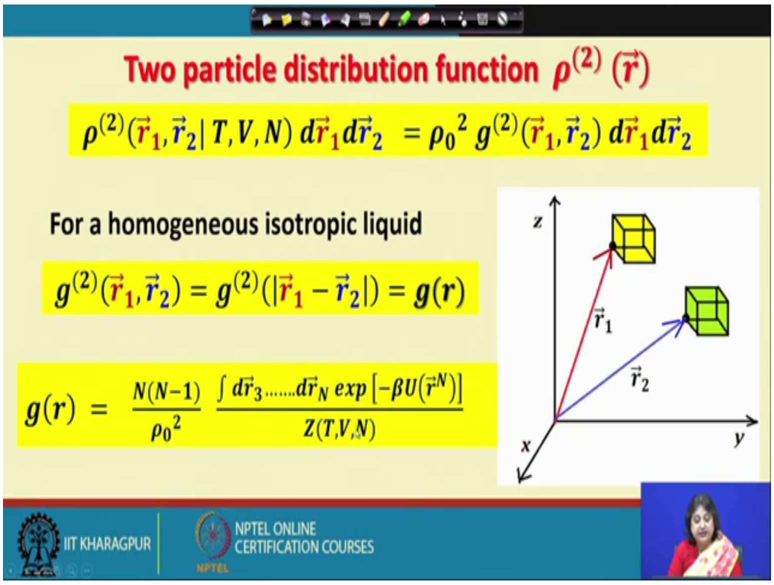

Two particle distribution function $\rho^{(2)}(\vec{r})$

$$\rho^{(2)}(\vec{r}_1,\vec{r}_2|T,V,N)\,d\vec{r}_1 d\vec{r}_2 = \rho_0^2\, g^{(2)}(\vec{r}_1,\vec{r}_2)\,d\vec{r}_1 d\vec{r}_2$$

For a homogeneous isotropic liquid

$$g^{(2)}(\vec{r}_1,\vec{r}_2) = g^{(2)}(|\vec{r}_1-\vec{r}_2|) = g(r)$$

$$g(r) = \frac{N(N-1)}{\rho_0^2}\,\frac{\int d\vec{r}_3 \ldots\ldots d\vec{r}_N \exp\left[-\beta U(\vec{r}^N)\right]}{Z(T,V,N)}$$

Now, when I do this then for a homogeneous isotropic liquid it does not matter what exactly the values of r 1 r 2s are rather it depends only on the difference between the 2 position vectors and rather the magnitude of the inter particle separation and then I can use this expression to define formally what g of R or the radial distribution function is. G of R says that this is the deviation from ideal be gas behavior when you have chosen to any 2 particles from an assembly of capital N particles and then average over all possible positions of the other capital N minus 2 particles using the probability of each of these position other microstates weighed by the corresponding probability density.

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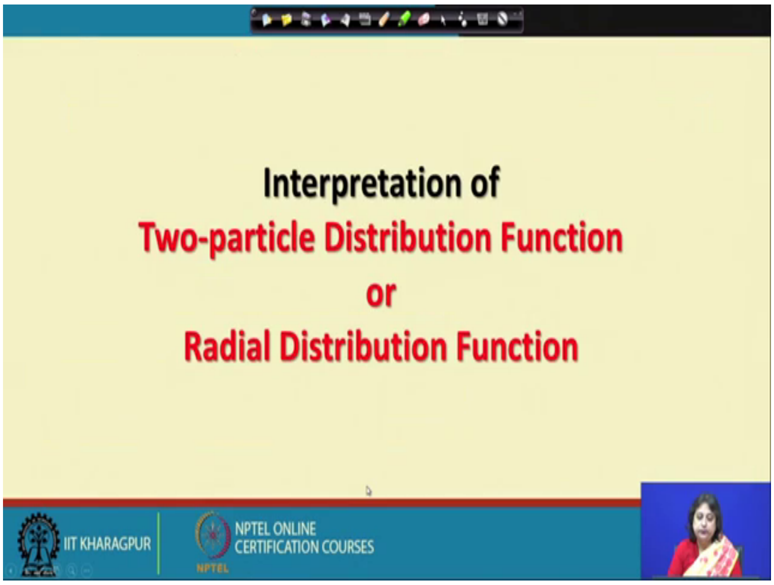

Interpretation of
Two-particle Distribution Function
or
Radial Distribution Function

So, if I now try to interpret what this radial distribution function is.

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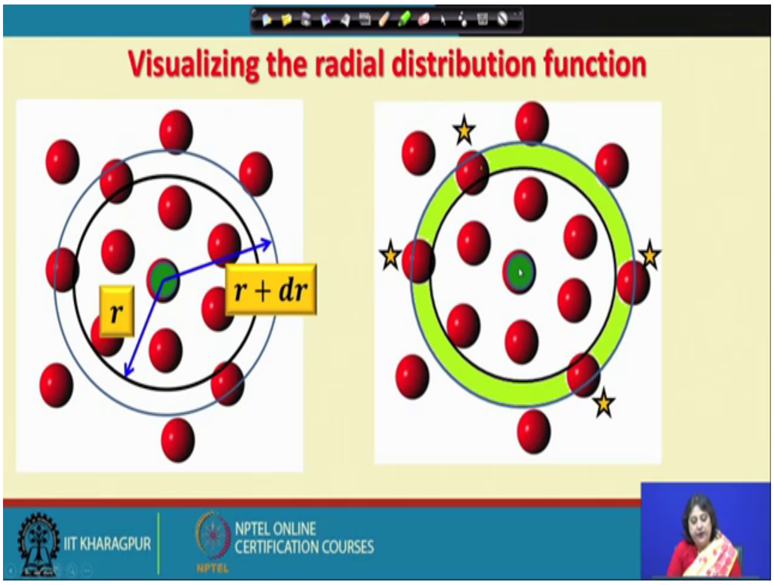

Visualizing the radial distribution function

Let us say that I this is a typical snapshot of my liquid sample. So, I have a monatomic liquid comprised of these red balls representing each of the atoms in the medium. So, what I do is let me tag this particular atom and then set up a circle in the 3 dimension it would be a sphere of radius r. Then I also set up another sphere of radius r plus d r having this original attacked particle and the center ok. So now, I what I have is I have a thin spherical shell of width d r. And I what I will do is with the tact particle at the center

I am going to count the number of particles that have their center within this spherical zone. So, in this picture I have 4 atoms that are present within this spherical zone and when I have this tact particle at the origin

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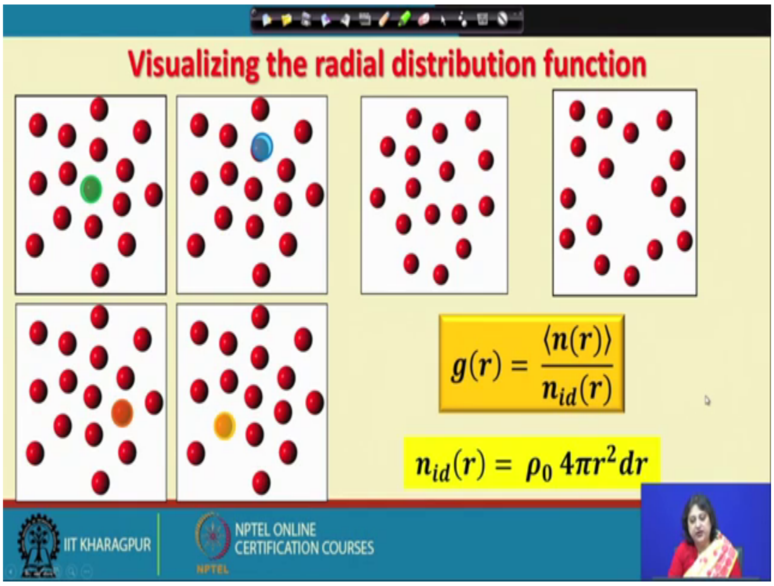

Visualizing the radial distribution function

$$g(r) = \frac{\langle n(r) \rangle}{n_{id}(r)}$$

$$n_{id}(r) = \rho_0 \, 4\pi r^2 dr$$

Now, when I take other structures I do not confine myself to considering a single structure, but I look at I tagged all other particles present in the same structure and calculate this number in our present within this spherical shell of thickness d r between the sphere of our radius r and sphere of r plus d r. And I also average over all other possible microscopic states that can be accessed either by molecular dynamics simulation or by Monte Carlo simulation, and then I estimate g of R as the average number that have got the where an r is the number of atoms who had their center within that spherical shell of thickness d r.

And this has been averaged over all atoms in a given microscopic state and then averaged over all possible microscopic states under a given condition of T V and (Refer Time: 32:13), since g of R is a deviation from ideality I would take a ratio of in our average with n ideal r. And n ideal r is nothing but the singlet probability distribution multiplied the by the volume of the spherical shell.

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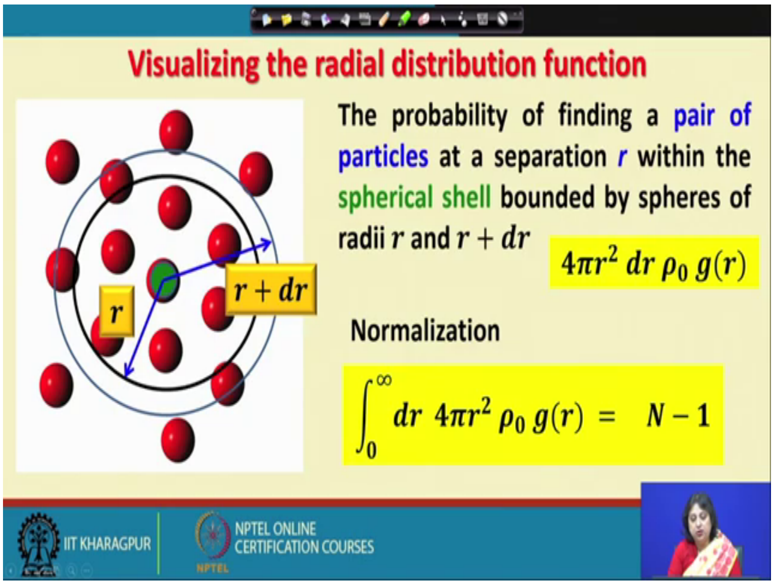

Visualizing the radial distribution function

The probability of finding a pair of particles at a separation r within the spherical shell bounded by spheres of radii r and $r + dr$

$$4\pi r^2\, dr\, \rho_0\, g(r)$$

Normalization

$$\int_0^{\infty} dr\; 4\pi r^2 \rho_0\, g(r) = N - 1$$

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So now what we say is well once we know the definition of gr then what is the probability of finding a pair of particles at a separation r, within this spherical shell bounded by these 2 spheres this must be given by 4 pi r square rho naught into g of R in a system where the particles are interacting. Now once again I am talking about a distribution function a probability distribution function, which should be normalized and if I integrate over all possible values of r; then I must retrieve N minus 1, why N minus 1? That is because I was counting the number of particles keeping one particle already at the origin therefore, I must be retrieving N minus 1 when I do the normalization.

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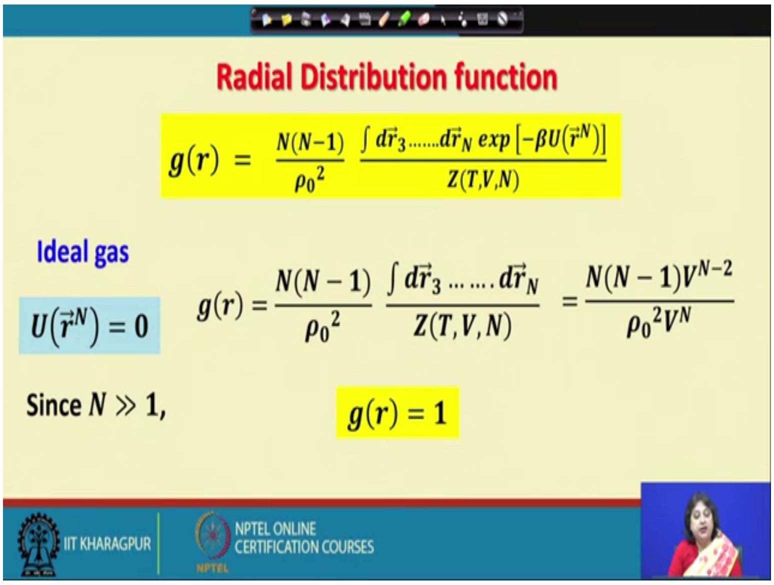

Radial Distribution function

$$g(r) = \frac{N(N-1)}{\rho_0^{\,2}} \frac{\int d\vec{r}_3 \ldots\ldots d\vec{r}_N \exp\left[-\beta U(\vec{r}^N)\right]}{Z(T,V,N)}$$

Ideal gas

$U(\vec{r}^N) = 0$

$$g(r) = \frac{N(N-1)}{\rho_0^{\,2}} \frac{\int d\vec{r}_3 \ldots\ldots d\vec{r}_N}{Z(T,V,N)} = \frac{N(N-1)V^{N-2}}{\rho_0^{\,2} V^N}$$

Since $N \gg 1$,

$$g(r) = 1$$

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So, for an ideal gas; obviously, if I put the potential energy equal to 0 I should be able to retrieve the fact that g of R is equal to 1.

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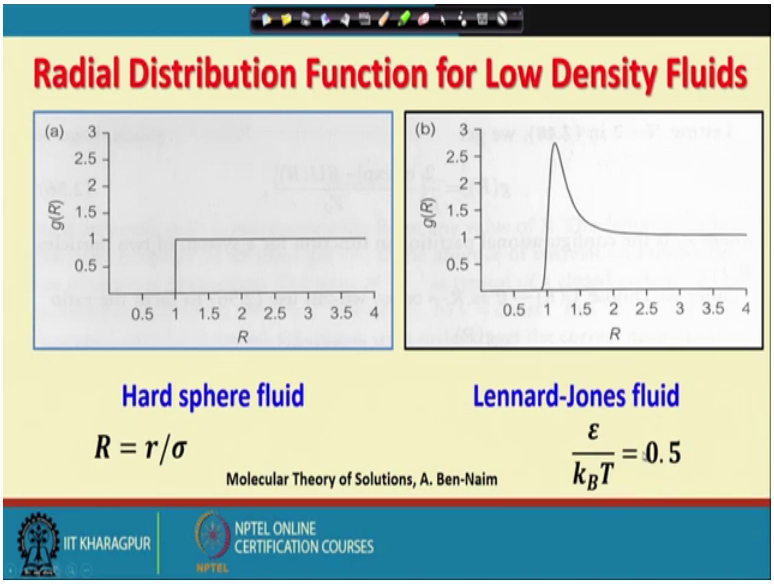

Radial Distribution Function for Low Density Fluids

Hard sphere fluid

$R = r/\sigma$

Lennard-Jones fluid

$\frac{\varepsilon}{k_B T} = 0.5$

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But if I look at the low-density fluids like a hard sphere fluid or a Lennard Jones fluid, I see that in the case of g of R initially it is 0 because 2 hard sphere fluids cannot cross into each others zone because here r is less than sigma, but beyond that this is equal to 1 because it behaves like an ideal gas.

Now, in the case of a Lennard Jones fluid you see the behavior because of the presence of the attractive component is giving rise to a peak; it says because of the short range attraction present in the Lennard Jones fluid therefore, in the range where the inter particle separation is of the order of 1 to 1.5 sigma, sigma is the hard sphere diameter then they will be held close together and therefore, there will be a high positional correlation as given by this peak in g of R.

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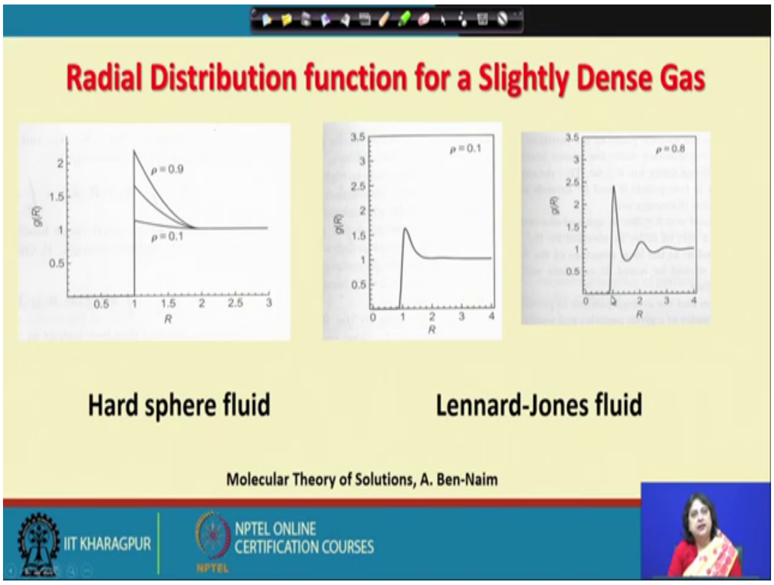

Radial Distribution function for a Slightly Dense Gas

Hard sphere fluid

Lennard-Jones fluid

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So, as you see that if you go on increasing the density then this structure goes on increasing; and starts showing signatures of not only a set of atoms in the first in the at the distance r about sigma, but nearly about 2 sigmas and so on and so forth. And a lower value of the peak height means that the atoms at r equal to small r equal to two sigma is less correlated than those atoms present at r equal to sigma.

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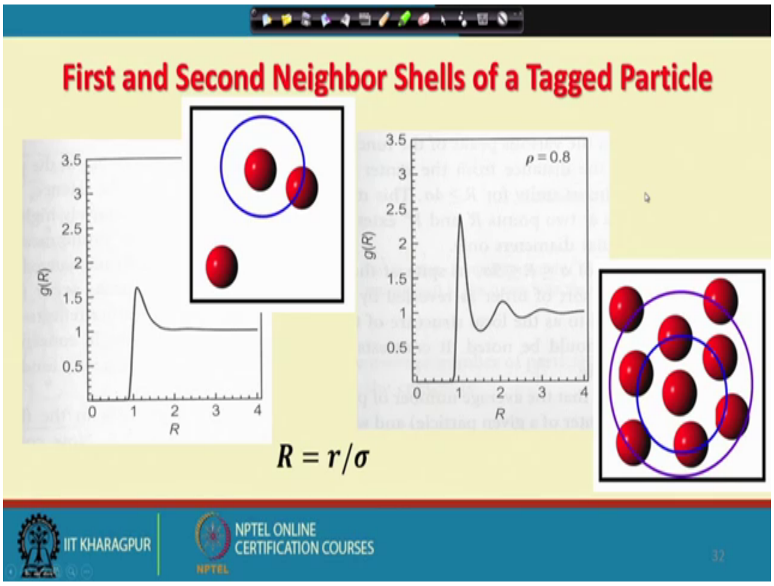

First and Second Neighbor Shells of a Tagged Particle

$R = r/\sigma$

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So, basically then we can think of a first and second near neighbor shell of attacked particle. So, this is where I have a very low-density system and when I look at the thin spherical shell around it I find that maybe there will be 1 particle in on an average within this spherical whose center will fall within this spherical shell. So, that is the presence of this particle on an average is indicated by this small peak in g of R.

But if I look at a highly dense system, then as you see that for my tanked particle which is this one because of a higher density there will be more number of particles present in the system within this spherical shell. And this is given by the higher height the greater height of the first peak that I see at a distance of the inter particle separation small are nearly about sigma. And then if I look at the second spherical shell still I will be able to find more and more particles because it is a dense system and finally, at very large distances the correlation goes to one which is the ideal gas limit.

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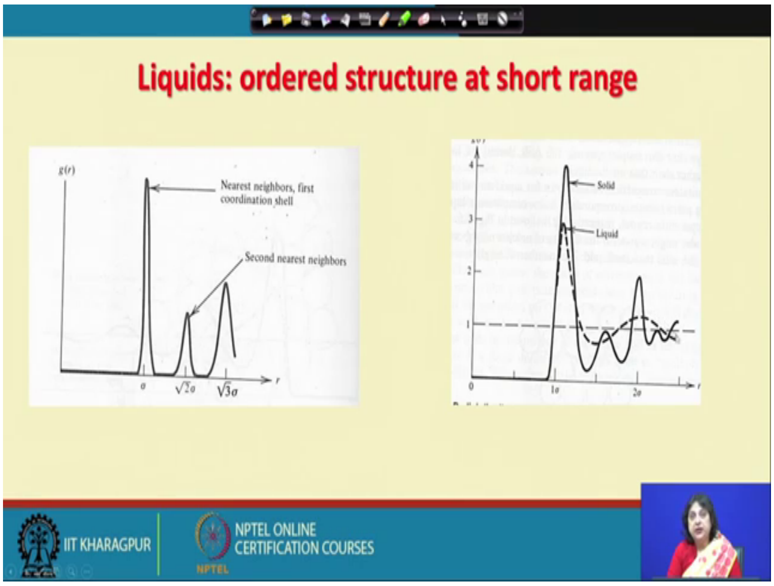

Liquids: ordered structure at short range

And the use of ideal distribution function is to interpret the structure of liquid in comparison to the solid state. This is a typical g of R for the solid-state structure, as you see all the peaks here they are very sharp and they have great heights that is because in the case of solids these atoms cannot move from their mean equilibrium position very much and you always have a certain number of atoms from a given distance, but in the liquids the atoms have translational motion. And therefore, not only the peaks become wider because of the translational degree of freedom they are less correlated and less structured than the solid therefore, liquids are ordered structures at short range, but it is not ordered like solid at the long range.

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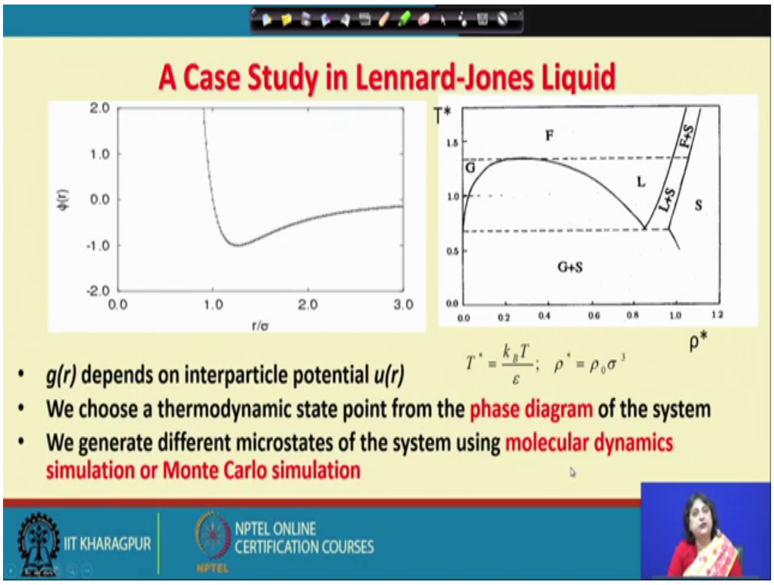

A Case Study in Lennard-Jones Liquid

$T^* = \frac{k_B T}{\varepsilon}$; $\rho^* = \rho_0 \sigma^3$

- *g(r)* depends on interparticle potential *u(r)*
- We choose a thermodynamic state point from the phase diagram of the system
- We generate different microstates of the system using molecular dynamics simulation or Monte Carlo simulation

And if you just go ahead and look at different types of liquids.

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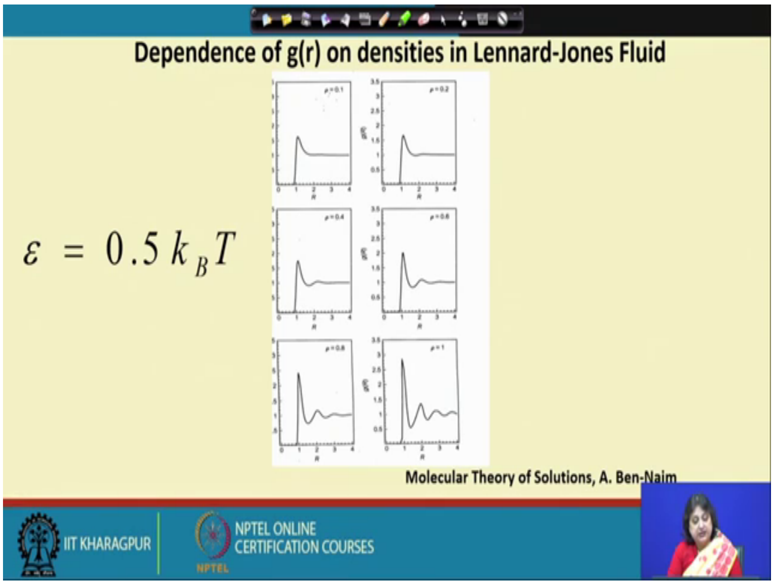

Dependence of g(r) on densities in Lennard-Jones Fluid

$$\varepsilon = 0.5\, k_B T$$

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In the case for example, the Lennard Jones liquid you can see that the appearance of the structure depends on the density that is which thermodynamic state that you are in.

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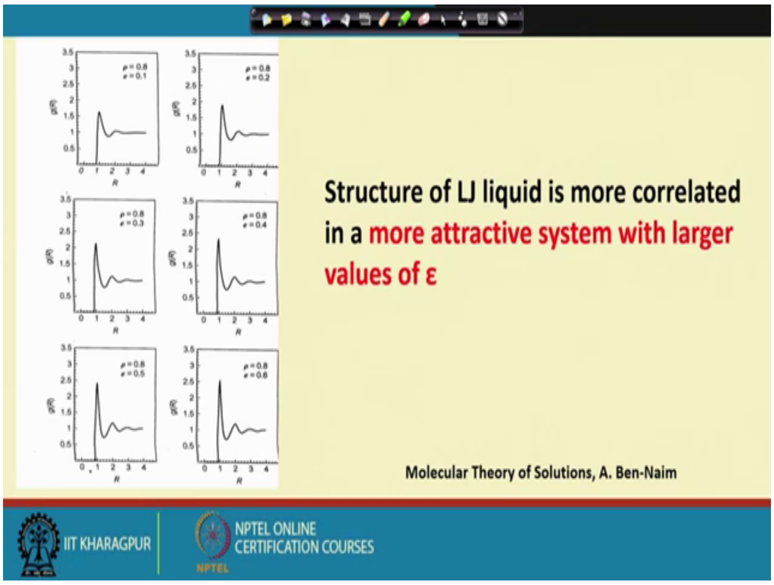

Structure of LJ liquid is more correlated in a more attractive system with larger values of ε

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Or it will depend on the how attractive the system is for a given density. For example, if you have at a given density a low attraction the structure is less and, but you have a higher attraction, you see that the positional correlation between the particles in the first and the second neighbor shells are much, much greater.

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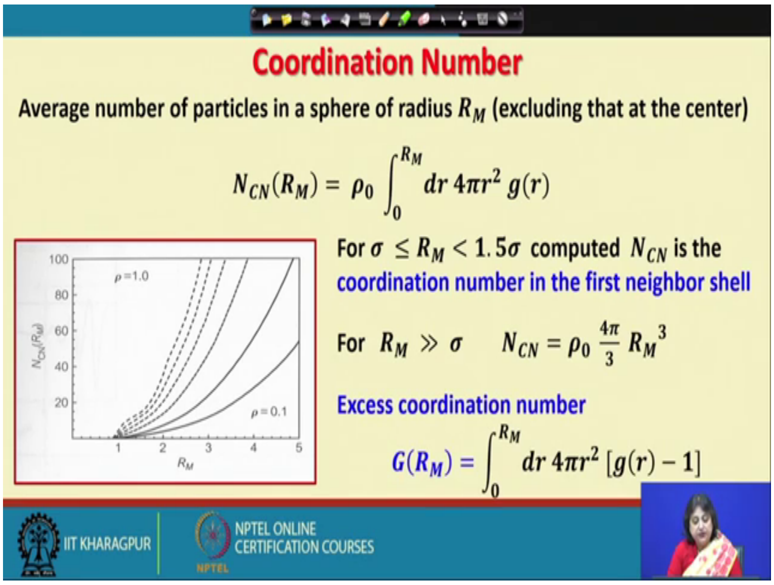

Coordination Number

Average number of particles in a sphere of radius R_M (excluding that at the center)

$$N_{CN}(R_M) = \rho_0 \int_0^{R_M} dr\, 4\pi r^2\, g(r)$$

For $\sigma \leq R_M < 1.5\sigma$ computed N_{CN} is the coordination number in the first neighbor shell

For $R_M \gg \sigma$ $\quad N_{CN} = \rho_0 \frac{4\pi}{3} {R_M}^3$

Excess coordination number

$$G(R_M) = \int_0^{R_M} dr\, 4\pi r^2\, [g(r) - 1]$$

And finally, I can also find out the coordination number from the g of R.

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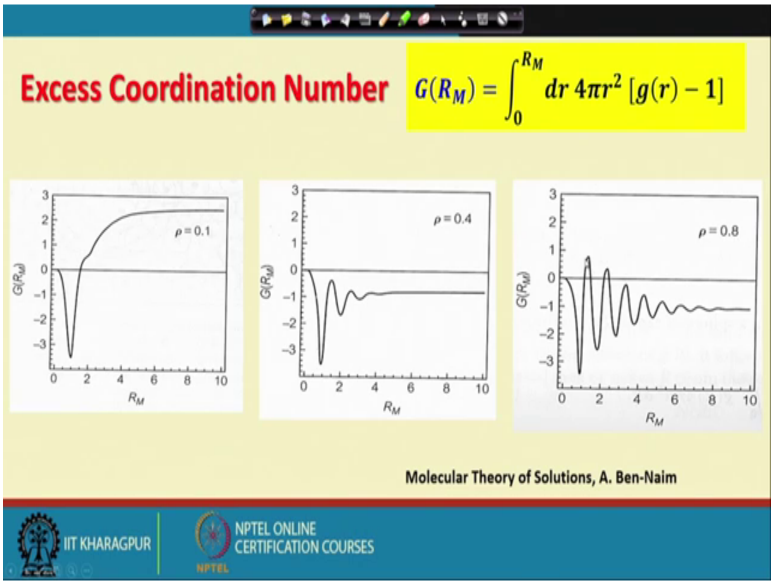

Excess Coordination Number

$$G(R_M) = \int_0^{R_M} dr\, 4\pi r^2 \left[g(r) - 1\right]$$

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And from the concept of g of r, one can very easily find out whether you have a buildup of neighboring particles around a center, a central particle or a buildup lowering of number of particles on an average around attacked particle. So, here as you see that these peaks positive peaks are appearing at certain distances, but it is negative it is because that each molecule is a hard sphere like at short range and therefore, these negative peaks are associated with the excluded volume associated with each neighbor in every neighboring shell.

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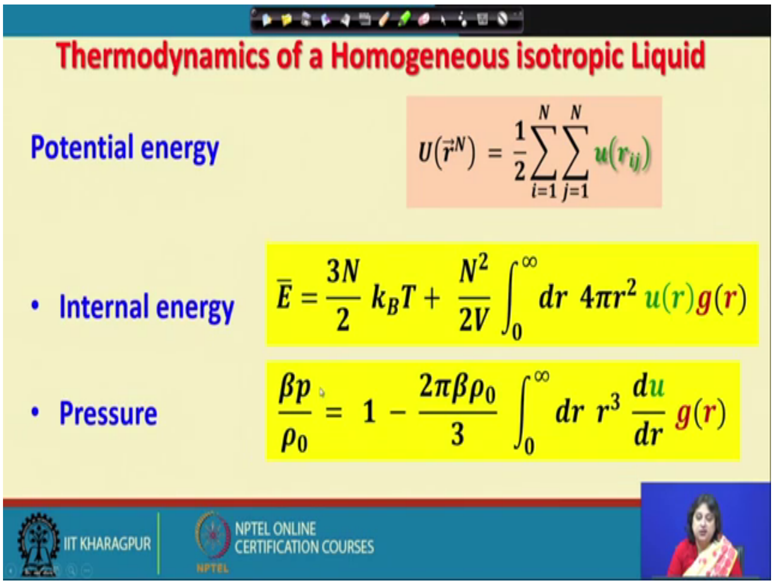

Thermodynamics of a Homogeneous isotropic Liquid

Potential energy

$$U(\vec{r}^N) = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} u(r_{ij})$$

- **Internal energy**

$$\bar{E} = \frac{3N}{2} k_B T + \frac{N^2}{2V}\int_0^{\infty} dr\; 4\pi r^2\, u(r) g(r)$$

- **Pressure**

$$\frac{\beta p}{\rho_0} = 1 - \frac{2\pi\beta\rho_0}{3}\int_0^{\infty} dr\; r^3 \frac{du}{dr}\, g(r)$$

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And finally, if I know the potential energy of a system I can express the internal energy and the pressure in terms of g of r. I am not asking you to work this out rather I am trying to demonstrate here that the knowledge of the radial distribution function and the pair interaction, gives you a handle to explain how the underlying structure and interaction can dictate the thermodynamic properties of a liquid.

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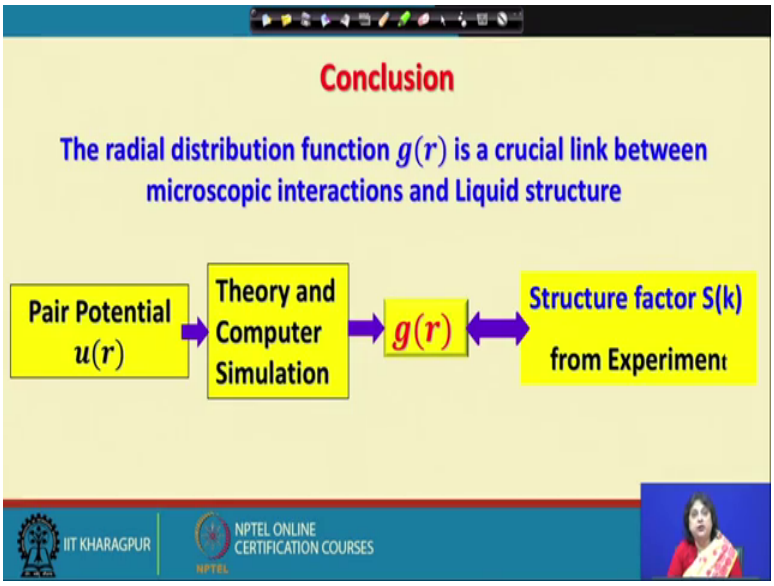

Conclusion

The radial distribution function $g(r)$ is a crucial link between microscopic interactions and Liquid structure

Pair Potential $u(r)$ → Theory and Computer Simulation → $g(r)$ ↔ Structure factor S(k) from Experiment

So, in conclusion what I would say is I have a radial distribution function as a crucial link between the microscopic interactions and the liquid structure. So, whatever we do we end up with getting the g of R; g of r can be determined from experiments through the Fourier transformation of the structure factor, and you can also have a model of the pair potential which you can use in theoretical or computational simulation studies to find g of r. And therefore, once you do that even for a disordered liquid phase you can find out what the structure is.

Thank you.