Basic Statistical Mechanics

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Lecture - 51

Theory of Liquids Part 1

Welcome back to our continuing exploration of statistical mechanics. We have been starting interacting systems, the systems that allow us to explain the natural phenomena and though we actually model the different natural phenomena by certain approximations and certain pictures and things which;

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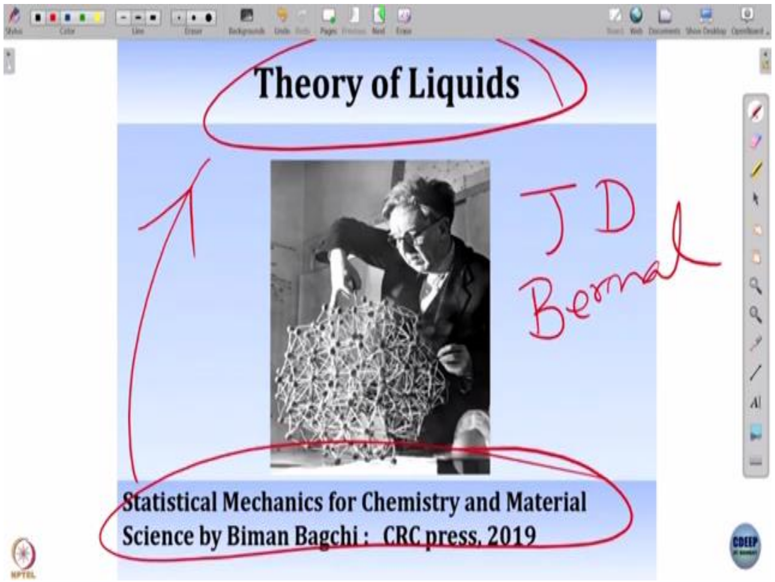

Theory of Liquids

J D Bernal

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Then goes into theory of**,** become matured into a theory over the many decades and years. So in the theory we just were doing osmotic pressure we are doing binary mixture and which is a phonology that came from the experimental observation that you need to put a pressure to steam the, stop the flow of solvent a pure solvent to the solution and that of course is a consequence of interaction between solute and solvent.

But we did not have any experimental estimation of the magnitude of this interaction. And osmotic pressure allows us, the magnitude of the osmotic pressure allows us to do that but how we did not know. So that was the theory of McMillan and Meyer who developed a detail theory which is the extension of Meyer’s theory of real gases and phase transition in terms of Meyer’s cluster expansion that we have done in great detail.

And that is why the Meyer's theory played a very important role because it allowed us to think in terms of interaction in terms. They decomposed into two particle, three particle, four particle interactions. Then McMillan Meyer took that to theory of solutions and then they explained that okay this could be the expression of osmotic pressure. In the process they derived the osmotic pressure of the ideal gas law.

Then it exactly become osmotic pressure equal to RT just Pi becomes CRT and C is the concentration of the solute or a RT X solute mole fraction of the solute, which is just the ideal gas law. So that, so the MacMillan and Meyer could derive the ideal gas law just like you derive the ideal gas law from elementary statistical mechanics. They what they did was what Meyer did they derive the virial series**,**

But in the process they introduced an effective interaction. Now that immediately give me the idea that then I can, if I could really play around with that play with that I will be able to get an estimate of the effective interaction very sort after quantity between two solid molecules; From osmotic pressure the way Lennard-Jones build its potential from second virial coefficient but when you try to do that in the Lennard-Jones way.

The second virial coefficient used what Meyer gave, there is B2 is the integration over the Meyer a function Fr which is exponential minus Ur by KBT - 1. So that is the effective interaction. So WAAR and that I can also explain in terms you know and experimental another verification of that is the radial distribution function; How two molecules A and A are connected to each other, which we get from neutron scattering.

We can estimate on molecules are arranging we test with each other, that is one another way, another tool to get into the intermolecular correlations how molecules are arranged in respect to each other. So that the radial distribution function how A in a binary mixture A molecules are placed around A molecules B molecules are placed on B and A molecules are placed around B.

These are the radial distribution function for partial radial distribution function in pure case we call it just radial distribution function gr.

But they are dependent on intermolecular interactions; they are dependent on this effective interaction of MacMillan and Meyer or which Flory parameters as we discussed, but how do you go about it? I told you and we will show there experimentally we get an estimate of that directly through structure factor which was first time became available after Second World War through neutron scattering;

When neutron beams become available. These days complex system we also get two x-rays, solids we always got two x-rays but presently development allows random systems also to be x-ray because a trace have become now very intense from synchrotron. So these are more recent developments in the last 10-15 years that high-intensity x-ray and getting structure of random or liquids from x-ray but before we did only two Neutrons.

So now we need several theories, we need to understand how do I discuss radial distribution function which I tell you gives you a; or arrangement of the molecules one, all the molecules around one tact molecule, one specified molecule, one chosen molecule and then the neutral scattering. So this is the; what will be the topic of today's lecture and I will be able to do it again, it has been done in a quite great detail in this book.

And we probably will not be a great justification of this beautiful subject of theory of liquids; But it is done you know much more in this book. However we will be able to take you through the basic understanding, the basic physics, basic chronology, the basic aspects of the field to give you an intuitive feeling and also certain amount of workings of the theory. Now this picture here is an interesting picture which we obtained from one of J.D. Bernal’s co-worker.

He was a wonderful person professor J.D. Bernal and he was the first to really map this obtained structure of polymers proteins many of the things from x-ray. He is called the father of you know could be considered one of the father of the biological crystallography. So this person J.D. Bernal is doing here is he built a structure of liquid water and he then playing around it and seeing how does this many of these things work with, but what is famous for these J.D. Bernal is this following experiment;

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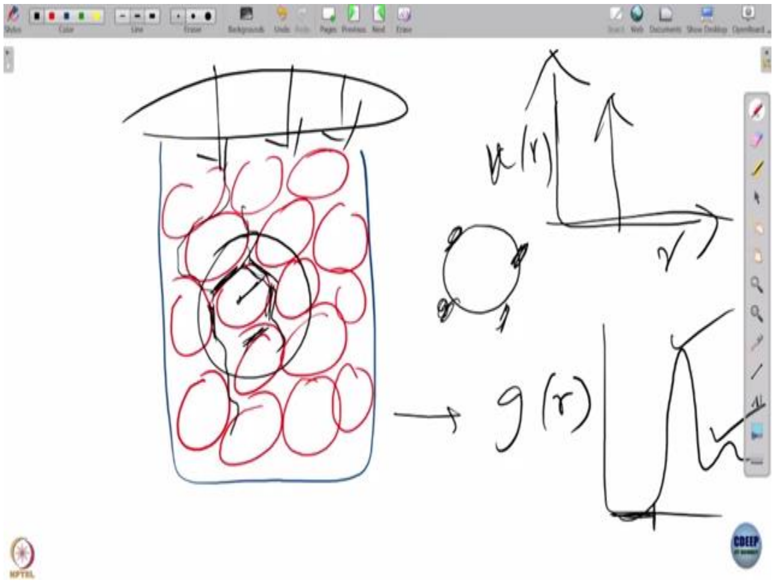

And this has the first thing of theory of nickels. He took a big jar and then he put lot of marbles, spherical marbles and he jam packed them. Then he did something really interesting, then he put, he poured some sticky paint like ink or many sticky and that goes inside these all particles throughout. But then he could take out and see around a sphere where are the other molecules, because that is where this ink has not gone through.

So he will find on the surface of molecule there are patches like that from that he would find out what is the arrangement of molecules around that marble. From that he calculate, he found a radial distribution function and when long, long later in computer simulation hard sphere potential, radial distribution function was indeed calculated by computer simulation is very difficult to do these things analytically.

Now we have some methods, analytical methods it have found that the radial distribution function the number of molecules around his gr; He found is nothing of course there could be nothing inside here, 0. Then there is sudden these arrangement goes like that and like that, first peak, second peak. Bernal got it almost exactly correct. So that was one beauty of fist experiments of J.D. Bernal.

So J.D. Bernal is the father rightly called the father of the theory of liquid structure, he is the one who experimentally measured by this very smart simple experiment the radial distribution function around hot spheres. Let go around.

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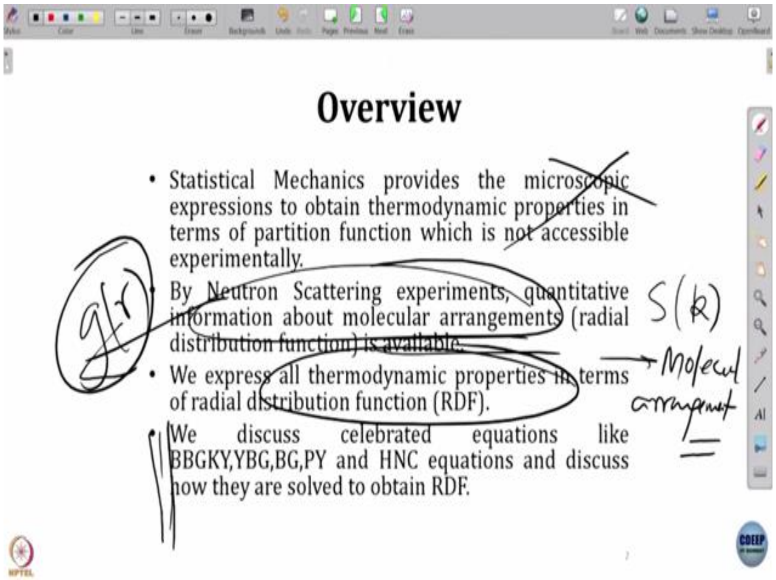

Overview

- Statistical Mechanics provides the microscopic expressions to obtain thermodynamic properties in terms of partition function which is not accessible experimentally.
- By Neutron Scattering experiments, quantitative information about molecular arrangements (radial distribution function) is available.
- We express all thermodynamic properties in terms of radial distribution function (RDF).
- We discuss celebrated equations like BBGKY,YBG,BG,PY and HNC equations and discuss how they are solved to obtain RDF.

g(r)

S(k)

→ Molecul arrangment

Now the statistical mechanics at that time it was still at infancy because we had started having some equations, J.D. Bernal did that in 1935 and our beginning of the theory of liquid started in 1930s or 1940s when the Jacques Yvon in France, Kirkwood in United States, Born**,** Max Born in Germany they started putting a theory of liquids together by using the methods of statistical mechanics.

It probably not surprising; that all of these things followed the pioneering cohort of Fowler and Guggenheim in 19 late 20’s and early 30’s. And then the pioneering work of Joseph Meyer in 1937. So this work of Fowler, Guggenheim and Mayer opened really a floodgate and people started seeing how to do a theory of liquids in terms of the interaction potential. So basic aim is I give you an interaction potential and you give me a structure of liquids.

And what do you mean by structure of liquids? We mean the radial distribution function. We mean that water the probability of having one molecule and another molecule and that will go directly into the radial distribution function, we go back and forth in these things because sometimes the structure of a book the way it is developed does not do a good justice to the neither the historical development nor the driving force inherent in any field.

So, microscopic thermodynamic properties partition all these things the statistical mechanics that we have all done with many times. Now Neutron scattering experiment gives you molecular arrangement, this is what I am saying. So Neutron scattering gives you a cross section called S(k), the structure factor that is comes from that gives you molecular arrangement and molecular arrangement is nothing but g(r).

So Neutron structures give me g(r) radial distribution function that I am going to talk about now. Then all the thermodynamic properties can be in terms of g(r) and there are lots of equations that have been derived which are of some importance for theory of liquids but on a course of this kind we might not spend too much time on that. Because you know it is this lecture should be viewed as a stepping stone or an intermediate between a book of physical chemistry like Atkins, Castel and Moore last on; from that book the contents into the real world of research and statistical mechanics and computer simulation. So this is kind of connect these many things. So in, you should take this course in that spirit that we are going to give you an understanding and a motivation of what we do.

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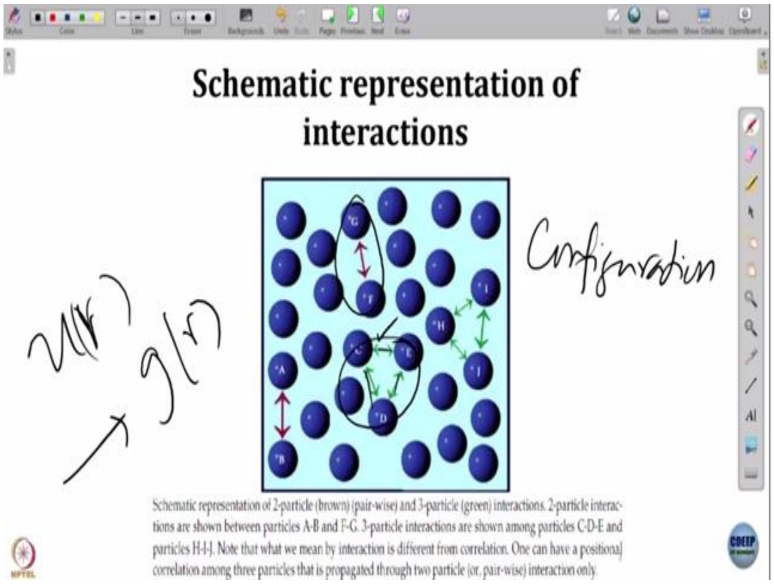

Schematic representation of interactions

Schematic representation of 2-particle (brown) (pair-wise) and 3-particle (green) interactions. 2-particle interactions are shown between particles A-B and F-G. 3-particle interactions are shown among particles C-D-E and particles H-I-J. Note that what we mean by interaction is different from correlation. One can have a positional correlation among three particles that is propagated through two particle (or, pair-wise) interaction only.

So now this is again schematic representation, this one interactions we are talking that here you can see two particles interacting, then three particles interacting but by three particle interaction I do not mean a three body interaction potential, I just mean that three particles are there so the interaction potential is could be present a pair of selective, some of these interaction these interaction and these interaction.

So now any given microscopic configuration of a given at a given time a snapshot of a liquid is a very primitive and approximate because everything is spheres one component atomic all these things but, if that captures such huge amount of phenology and huge amount of microscopic phenomena that it is really is the kind of a the model, the benchmark model of statistical mechanics that we play our theories and gain our understanding and then explain complex system.

So, basic idea is that if I can understand and describe this system I can describe complex systems, very simple. So, these kinds of interactions now at present I know how to consider this interaction in terms of Lennard-Jones potential. I have a basic idea of how these structures are though I do not have the microscopic information. Now I want to know that if I give you the density, temperature, pressure and the interaction potential can you give me;

If I give you u(r) can you give me g(r)? if I give you interaction potential can you give me the radial distribution function that is the whole question and how to get that, that is the aim of this and this lecture. Let then go ahead.

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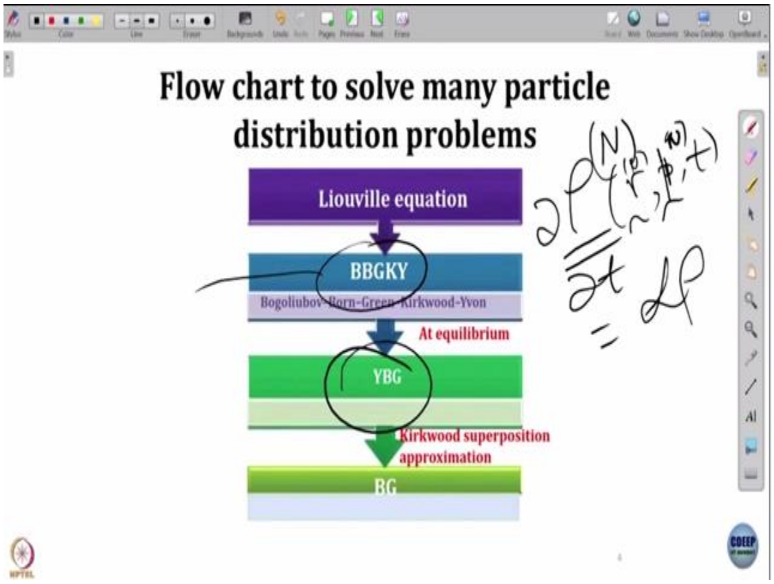

Flow chart to solve many particle distribution problems

Liouville equation

BBGKY

Bogoliubov-Born-Green-Kirkwood-Yvon

At equilibrium

YBG

Kirkwood superposition approximation

BG

$$\frac{\partial \rho^{(N)}(\underline{r}^{(N)}, \underline{p}^{(N)}, t)}{\partial t} = \mathcal{L}\rho$$

So the basic flow chart again, I am very much fond of flow chart but unfortunately for you this flow chart will not be too much of a useful, but still let us go through it that we start everything which I have not told you this equation is called Liouville equation and that is Liouville of N-particle that means you have N-particle hold in particle distribution in position and time. This is what Boltzmann tried to do.

These are N-particles, an equation of motion of that is a Liouville equation by the Liouville operator. We have not taught told you about that. That can be reduced essentially into an equation called BBGKY equation which goes to equilibrium Yvon-Born-Green equation.

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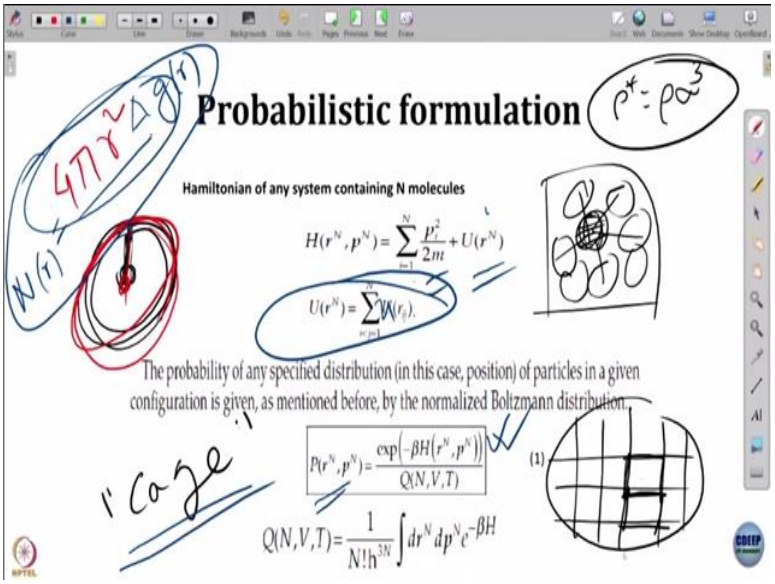

Probabilistic formulation

$\rho^* = \rho a^3$

Hamiltonian of any system containing N molecules

$$H(r^N, p^N) = \sum_{i=1}^{N} \frac{p_i^2}{2m} + U(r^N)$$

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

The probability of any specified distribution (in this case, position) of particles in a given configuration is given, as mentioned before, by the normalized Boltzmann distribution.

$$P(r^N, p^N) = \frac{\exp(-\beta H(r^N, p^N))}{Q(N,V,T)} \quad (1)$$

$$Q(N,V,T) = \frac{1}{N! h^{3N}} \int dr^N dp^N e^{-\beta H}$$

$4\pi r^2 \Delta g(r)$

$N(r)$

'Cage'

Now what we want to do that the radial, how do we talk of radial distribution functions? So radial distribution functions as I said that I have these kind of molecules and I tag one molecule and now I want to tell the liquid is homogeneous, there is no heterogeneity anywhere. When we say homogeneous what do you mean, we mean that if I follow a local I make a cubic grid, I make a grid.

This is something what called spending a little time that I have this big thing and I make it into small grids and now a grid is such that it has 10, 12 molecules, that is kind of size. That means it is a two molecular diameter here, two molecular diameter here and two molecular diameter in a cube and that has 10, 12 but maybe 20 molecules. If I am, the system a grid like that then now I can mentally just like we constructed ensemble and Ergodic hypotheses all the step, we can look into it with I say I have a microscope and I counting number of atoms and molecules into that grid. When I say homogeneous I say that these grids over a time averaging long time has the same number of molecules of a grid of the same size, that is what homogeneous means that they are the same. So there is no heterogeneity that means no permanent long term one region has more density than the other region.

So we are talking of homogeneous system. Now in such a homogeneous system I now want to describe what is the probability of? I want to describe the structure and as I repeatedly saying the way of getting the structure is how many molecules are there at certain distance r. So I have a molecule here then I say okay, I give you a distance r and I can now give a small shell around that, my picture similar to grid.

And what is the probability or how many molecules will be in that grid? If I know how many molecules in the grid at a distance center that is distance r, I construct a shell then I will be knowing about the molecular arrangement about my center molecule. I know how many molecules are there and that really tells me many things that will tell me what is the cage around my center molecule.

These called caging or case structure in a liquid because of high density, as we discuss the density of liquid remember by introducing quantity $\rho^* = \rho\sigma^3$ and σis molecular diameter and that is very large is about 0.8 typically, where crystal is one so liquid is a very dense system. But it is random but I need to know how many molecules are around my and at what distance they are?

If I know that then I will be able to calculate quantities like diffusion, I will be able to calculate quantities like viscosity and many other properties and that will come very handy when I want to do chemical reactions because how two reactants come close together, where are they placed that will give me an idea of the rate of the chemical reaction or they will get me about the solvation structure;

How one dye molecule is solvated? How a reactant is solvated in water? Is very important to know that in order to know the many properties. So what we are beginning to do is to beginning to take a short at those kind of things. Coming back again continuing with my picture here, this picture of how many molecules are there in a shell? These I now say number of molecules in a shell if this volume, the volume is 4π if at a distance r then volume of that shell is $4\pi r^2$ and width is Δr of my shell or Δ.

This is the volume of the shell. So now if I say probability of finding a molecule at r is this quantity g(r) whom I call radial distribution function, then that gives me number of molecule at a distance N. So these are wonderful relation that number of molecules at in a shell at a distance r total number is volume of the shell which is $4\pi r^2\Delta$, delta is the width of the cell, $4\pi r^2\Delta$ and g(r).

Then g(r) gives you the probability of finding a molecule at a distance r and gr is the radial distribution function which is the central quantity of theory of liquids. So now how do you go about it? How do you go about calculating the cage? We do what we have done before we are taught to do, we write down a Hamiltonian, this is the momentum term and the total amount of potential energy and total potential, this should be small u again $u(r_i$.

The probabilities in this case is the, so I want now the probability what are the locations, what is the probability where are the molecules distributed with what momentum complete distribution complete equilibrium distribution of all the N-particles. I do not know what I will do it with but let me think about it that will be Pr^N, PN and that is trivial but I know it is e to the minus beta H, so I give you one particular configuration that;

My molecules first molecule is in r1, second molecule in r2, third molecule is in r3, fourth molecule in r4, fifth molecule is in r5 all like that n molecules in n positions, I give you that so I give you locations of each molecules. You can exchange then classical systems nothing much nothing changes here but given the positions I can now calculate the interaction potential, this quantity.

Now I have the also momentum position or the momentum, momentum gives me kinetic energy. So this is what actually Liouville equation does is the time dependence of things. I am suddenly bringing Liouville equation because we had one slide on this Liouville equation. We will talk of Liouville equation slightly not much because it is a more complex and the level which probably we are not going to take this course to.

So this is my Boltzmann distribution in a general sense with all the N molecules and this is the partition function.

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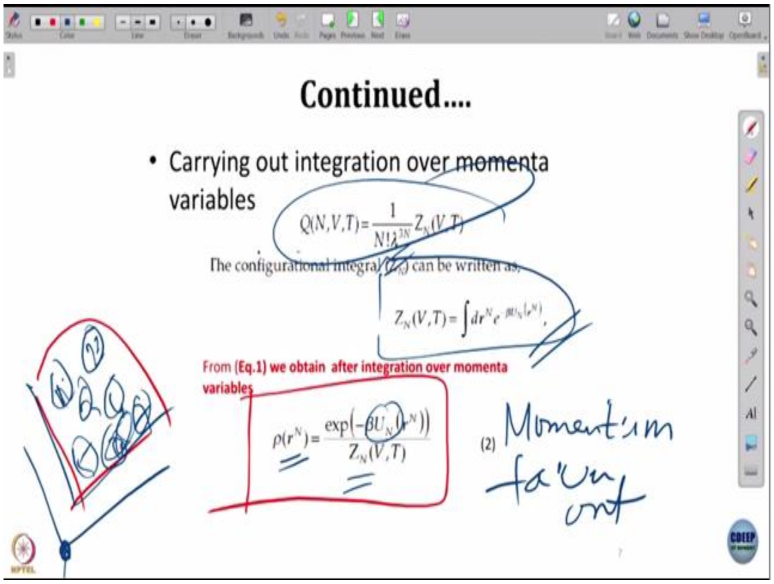

Continued....

- Carrying out integration over momenta variables

$$Q(N,V,T)=\frac{1}{N!\lambda^{3N}}Z_N(V,T)$$

The configurational integral (Z_N) can be written as,

$$Z_N(V,T)=\int dr^N e^{-\beta U_N(r^N)},$$

From (Eq.1) we obtain after integration over momenta variables

$$\rho(r^N)=\frac{\exp(-\beta U_N(r^N))}{Z_N(V,T)} \quad (2)$$

Now let me see if I do things correctly here the part then I go to configuration integral that we have done in Meyer's theory then this is the configuration integral with βU, this is just kinetic energy term is taken out and kinetic energy term goes into this de Broglie you have been. So now I can be little bit more I have removed the I have factored out, momentum taken out, because of classical system I can take momentum taken out, then I have this equation, is same thing.

I am just saying probability of molecules at given positions 1,2,3,4,5,6,7 molecules say I give their positions with respect to coordinate system which can be corner of the box or any external different systems, I know all the positions and if I know the position of each particle I know the interaction energy and then these the configuration integral.

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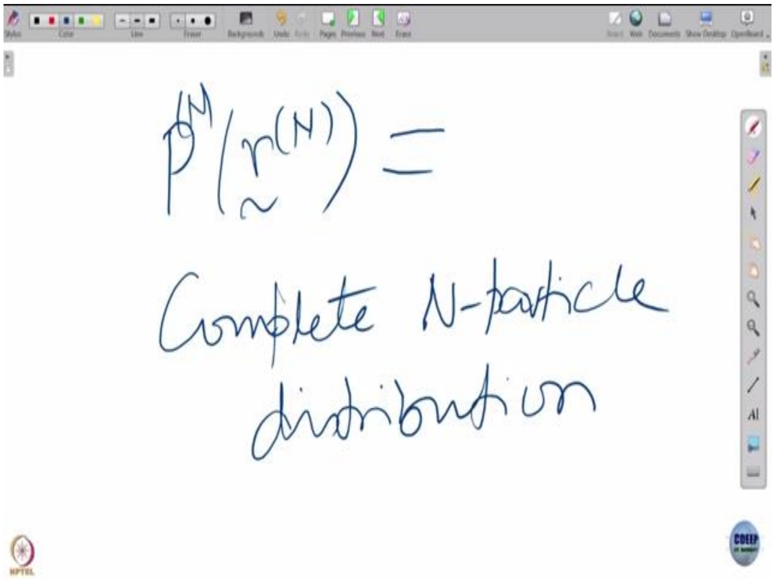

$P^{(N)}(\underset{\sim}{r}^{(N)}) =$

Complete N-particle distribution

So this is the complete $P^{(N)}(r^{N})$, PN put wherever you want is the complete N-particle distribution, is a complete distribution, this is all the information that we need. But it is very difficult to get, it is a hugely difficult quantity to get and now we are going to simplify the things because we most of the time experiments and theory and all our applications we did not need, we do not need the full N-particle distribution, I do not need to knew where each particle is there.

I need to know much reduced description, I need to know how many molecules around one molecule, that is the radial distribution function not the complete distribution. Well complete distribution is very good quantity, very noble quantity but we do not need that in our theory and applications and equations that you derive that quantity does not come. Of course if I know that then I know gr but we need g(r) we do not need the full thing.

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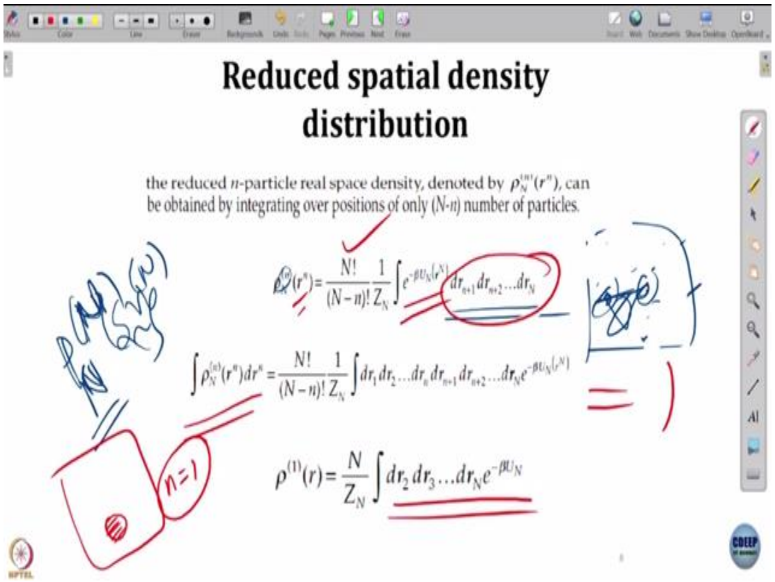

Reduced spatial density distribution

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.

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

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

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

So now this is defined in the following way just as you would expect that the; that this is the full distribution function. So in order to get a reduced distribution on a lower dimension, distribution of fewer particles what I need to do I need to do integrate out I need to, I do not need you, so I need all the other, so I need smaller number, so instead of P($_N$)N position of N-particles all the N-particles of all the molecules of N-particle system.

One is the number of particles in the system other is this order of the distribution function, I do not need that. So but however I do I am continuing with classical mechanics that means I am saying okay. In this huge number of particles there I want these this and these 1 2 3 where are they? I am not yet, I am now still specifying then and there. So then I would integrate out all the other ones.

I will integrate out that, I will integrate out that, I will integrate out that. So what I will do? I will just erase these guys; I will integrate them out or I will kill them out in our earlier in Mayer theory thing. So these are the things I am integrate out all others, I am integrate out all others, I am integrate out. But I have to keep the Boltzmann factor and then I say okay, how many ways I can get these my reduced number of particles out of N-particles the how many ways I can pick them up.

Then that is $\frac{N!}{(N-n)!}$. Note that small n factorial not denominator because we still have the distinguishable particles in their locations which these locations are given by these rn. We have not yet met that assumption that their positions can be in depth. I am not doing that yet. Then I of course if I integrate over all of them then I should get equal to 1. That 1 is missing here but I think the probably is there in the textbook.

Now so now I want to now go to the reduced description, I want to know that I have only one here, if I am only one particle I want to know in this case let us consider inhomogeneous system, there is a gravitational field, external field. So I want to know what is the probability of one molecule here? Then what I do as I said, I integrate over everything else so I integrate over all other from 2, 2n and from here I have $\frac{N!}{(N-n)!}$ because I now have small n = 1.

So I have n factorial in my own factorial that is n by N Zn but I have integrate out everything else, d2, d3, dr2 all these things have been done. What do I get next? You can of course guess what you get next?

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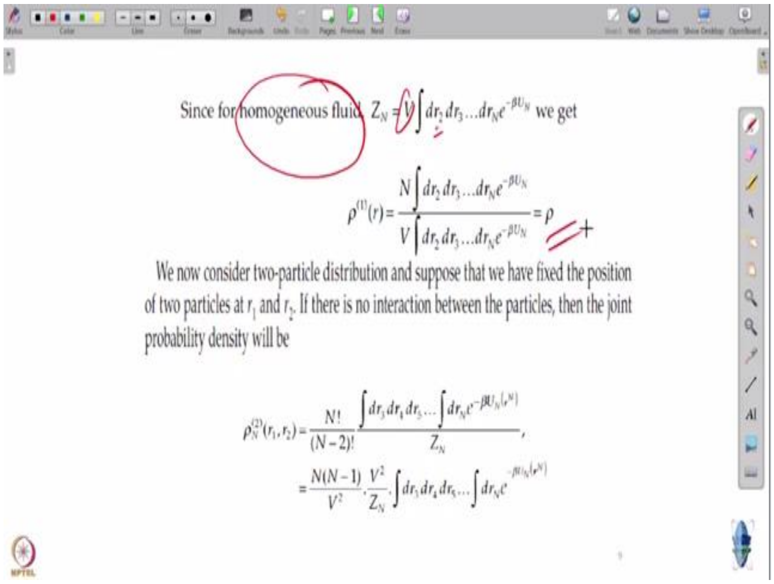

Since for homogeneous fluid $Z_N = V\int dr_2 dr_3 \ldots dr_N e^{-\beta U_N}$ we get

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

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

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

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

So when you do that what if homogeneous liquid I can anyway integrate over because I can choose one molecule as the central molecule and everything else I can integrate over. Then I integrate over the last one, so these dr2, dr3 with respect to the central tagged molecule. Then the last I integrate over the tagged molecule that give me a volume V. If I do that they are the same, then in your homogeneous liquid I get density, single particle density is the number density. This is a trivial exercise but important exercise that shows that I am formulating it correctly.