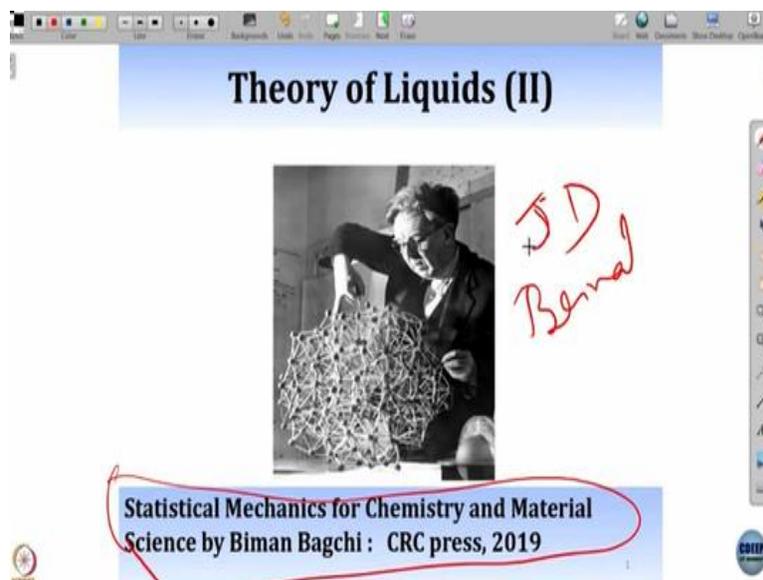


**Basic Statistical Mechanics**  
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**Lecture - 53**  
**Theory of Liquids Part- 3**

Welcome back, and good morning or good afternoon depending on where you are and what time you are listening to the lecture. We were doing, continuing from the last lecture on the theory of liquids, which is a big subject. There are books written on this chapter and it has been an intense area of research for a last more than a half century, aided very much by computer simulations. I will give a name of the few books along the way where you can take a look into it for more details. In addition to this book that we have the statistical mechanics of the Liquids.

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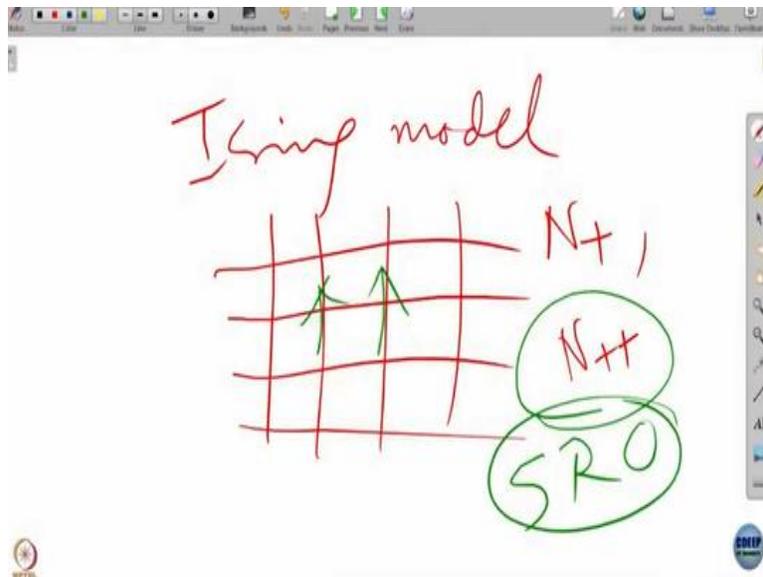
That we have here, there are several other books. In this book what we have been trying to do and I am telling repeatedly the whole idea is to get the kind of a statistical mechanical starting point or statistical mechanical view of physical chemistry and also materials chemistry. So as I repeatedly tell that in undergraduate physical chemistry you pick up a book say, Castellan or Atkins using huge number of chapters.

You will have liquids, you have phase rule, will have phase equilibrium, you will have chemical potential, you will have kinetic theory of gases, you will have binary mixtures, the polymer, huge electrolytes chapter after the chapter. And much of them, the chapters have given you graphs, certain results and certain equations like Debye-Huckel-Onsagar equations, so derivation is done like a rudimentary way.

Things like solvation are described in terms of pictures, liquids I have told you that is the density between the gas and the solid. But as they do not give good job even into other describing the properties of liquids which are so important for chemical industry and for biology. So the theory of liquids that have been developed in last 50 years we discussed the theory based on statistical mechanical theories.

And aided heavily by computer simulation, nothing would have been possible in computer simulations, did not play the important role that it played which will talk about more in detail. As I said here last lecture that all it started with J D Bernal at Cambridge, the famous crystallographer, J D Bernal got into his aims to really find out the local structure, short range structure of liquids and this is what we already meant by structural and go back to Ising model again;

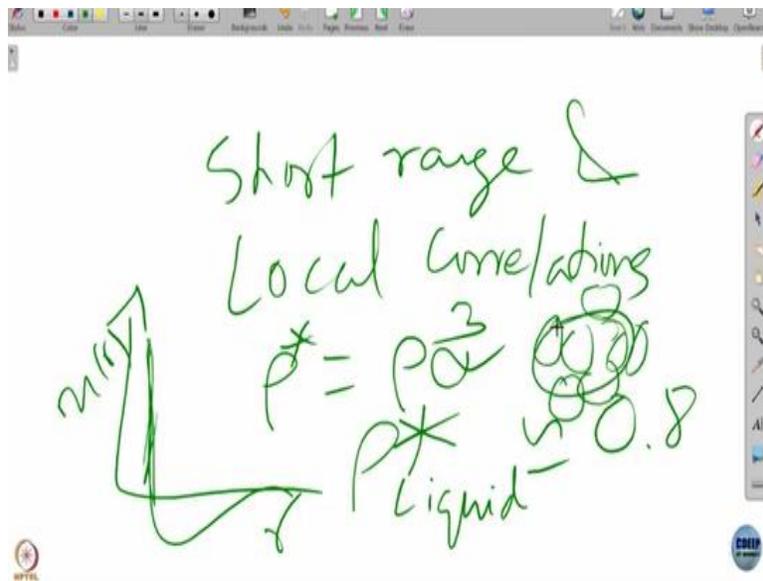
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The famous our starting point Ising model, we introduced in the spins up and down and we introduced quantities, the two important quantities  $N_+$  which we call long range order, but there is one short range order  $N_{++}$ . What  $N_{++}$  does? If the spin is up here and the spin up there,  $N_{++}$  tells me the number of such pairs. Now when the two up spins are next to each other that gives you a short range correlation that is why it is called short range order.

We use short range correlation. In many places this short range or local correlations are very, very important.

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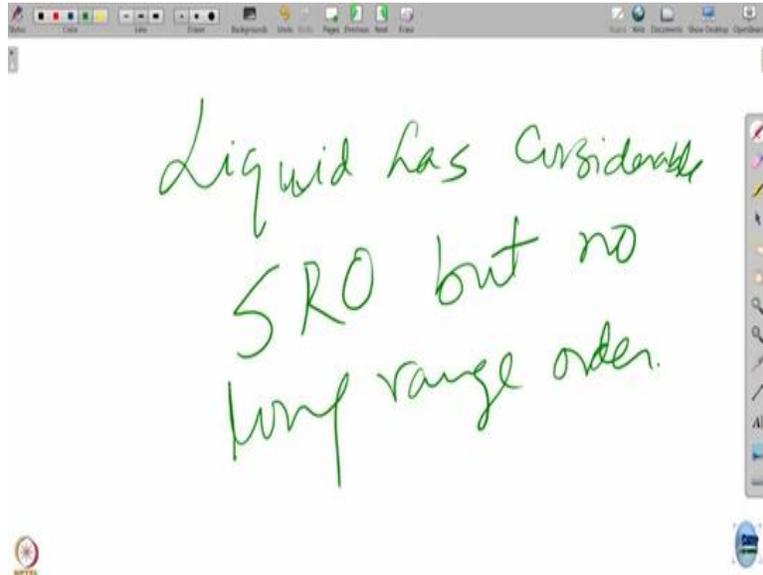


So short range and local correlations, so the more quantity way of telling of the liquid in addition to saying that the density is between gas and the solid and I already described everything should be in terms of  $\rho \sigma^3$  is molecular diameter then  $\rho_{\text{liquid}}$ ,  $\rho^*_{\text{liquid}}$  is typically 0.8 is a wonderful number, semi quantity. It is not fully quantitative, but it is far better than saying density of liquid is between gas and solid.

Density of gas is about 0.1 in this unit dimensionless  $\rho^*$ , density of solid 1, liquid is sitting next; much of a liquid is sitting next to the solid. So as a result of the cross proximity and the hard sphere can be possible interaction we already talked about, the potential that we repeatedly using that because of these parts that determine structure of the liquids in the interaction potential.

As the part of this, we have molecules touching each other, as a molecule touching each other they have a lot of short range order, that is exactly like the  $N_{++}$  in short range local correlation.

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So my new definition of liquid would be liquid has considerable short range order but no long range order. But solid has both short range order and long range order. In ferromagnetic system or lattice, most of the spins are aligned and they are very large degree of short range order, ofcourse no long range order, non-zero magnification. So you need to now think of liquid as something which is rather unique. We do not face this thing in the solid state physics.

The presence and the importance of short range order, that is not in system in solids, solids attracts long range order that is enough. The gas on rather than neither short range order nor long range order, so liquid then the new definition of liquid should be that it has a short range order and that is like in Ising model  $N_{++}$ .

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**Reduced spatial density distribution function**

- The reduced n-particle real space density, can be obtained by integrating over positions of only (N-n) number of particles.

*n particles in an N particle system*

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

*How will we get probability distribution functions?*

Now we can go back doing next of all things, so how do we talk of this short range order and the liquids? I try to tell you that liquid is very unique because of its short range correlations that in the liquid state that is what defines a liquid. But we do not have average density does not tell me of that then we did a new language to develop this short range order and that language comes in terms of distribution function.

Which has been described in detail in our book, whole chapter is on the distribution function. So what we actually want that, at the simplest level that if want my molecule here in the liquid then what is the probability of finding another molecular distance  $r$ ? That tells the primary importance which gives you locally at the nearest neighbor level how molecules are packed? That is the quantity that picked up by neutron scattering in static structure factor.

And how the local caging that means the central molecule of the high density gases the very important quantity of liquid the density is large like the  $\rho^*$ . Even the water which we call low density liquid because of the open framework structure even that has  $\rho^*$  is 0.72. And methanol have  $\rho^*$  is about 0.88 or something like that goes to 0.9 and acetonitrile it goes to again 0.89.

So you see molecules are densely packed, or every liquid attains the environmental conditions of pressure and asymptotic temperature it is densely, so this is very important to realize that. As it is densely packed then what is happening, we call each molecule is caged by its nearest neighbor.

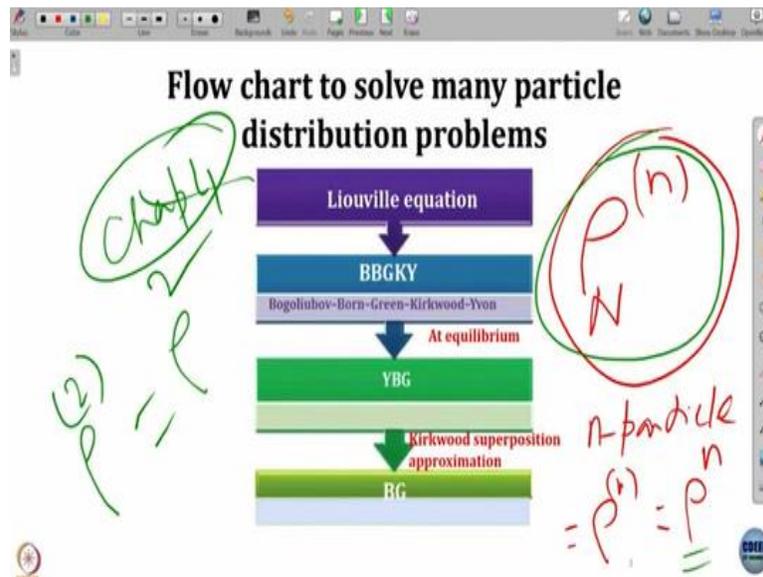
And the strength of this caging determines to a great extent dynamics and static properties of the liquid, like specific heat, all these things are determined partly by this property.

Then how do we describe it? We start in a grand way we said, okay, I want to have not just two particles having distance, I want to have many particles, what are these? So this particle is that in position  $r_1$ , then it is  $r_2, r_3, r_4$ , I want to have  $N$  particle distribution. So that is not defined by very simple by one is the partition function configuration integral of Mayer, number is picking it up, then I integrate it out all the ones which are not my  $N$ .

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

So this is a  $n$  particle distribution function volume, in a  $N$  particle distribution. So  $N$  is the total number of particles in the system and  $n$  is the number of particles, among all we are looking at the correlations. So this is the picture then that we have very ambitious and trying to look into many body correlations and this turns out to be extremely important in this order any these languages, just the Standard language of all many body systems, that is glasses, liquids, liquid crystals, everywhere, this is the language that is used.

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So there is a flow chart which is given in the book and how to go about to getting this  $\rho_N$ , this quantity that we just discussed that  $n$  particle correlation. I want to know that how  $N$  selected

particles are correlated? That means if they are not correlated, of course this probability of  $N$  particles will become  $\rho$  becomes  $\rho^n$  as we discussed in the last lecture, are independent.

These are joint probability distribution these  $\rho_n$  that I am talking here, this thing is a joint probability distribution and if they are not correlated at all, that is the gas phase then I will say, what is the probability of one particle at one position and the second particle have another position that we just have  $\rho^2$ , where we equate the relation. But in crystal, not at all if I know one particle position, I know the other particle position uniquely.

In the liquid that is in between but there are certain correlations had one particle here the probability of having another particle in a position can be more it can be less. How do I talk about that? That is what radial distribution function comes in and we written but let us go back in the very beginning how it all started, it started with the grand equation of statistical mechanics as that is Liouville equation.

We will talk a little bit about it but we will not be do full job on the Liouville equation, that could be a lecture by itself and we are working on a series of time dependent statistical mechanics, a book can probably a course and there will work little bit more in Liouville equation. The derivation of this equation is given in chapter 4 of my stat-mech book, so you can look it up there, there is not a bad job done there.

But usually as one of my students was telling today, that is very most of the stat- mech books; this is not a good job has been done but that it actually the good job has done in a beautiful book by Tolman, Richard Tolman in statistical mechanics that is an ancient book that is a beautiful book. So we start in this flow chart everything starts in Liouville equation, then you go to BBGKY equation, Bogoliubov-Born-Green-Kirkwood- Yvon, 5 big names.

Born, Max Born, Bogoliubov very famous scientist and very famous stat- mech guy and then he is involved in many, many things including superconductivity, he wrote a beautiful book on statistical mechanics, which I used to have one hard copy, then Green, the father figure in stat-

mech, then Kirkwood and Yvon. These are time dependent equations, we will just discuss slightly on them.

And then they made into a time independent equation for equilibrium, at equilibrium that become Yvon, Born and Green. Then certain approximation is done to get the Born-Green equations that we discussed little bit.

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The slide shows the derivation of the BBGKY equation from the Liouville equation. It includes the following content:

- Title:** BBGKY equation from Liouville Equation
- Liouville equation:**  $\frac{\partial f^{(N)}}{\partial t} + \{f^{(N)}, H\} = 0$
- Where:**  $\{f^{(N)}, H\} = \sum_{i=1}^N \left( \frac{\partial H}{\partial p_i} \frac{\partial f^{(N)}}{\partial q_i} - \frac{\partial H}{\partial q_i} \frac{\partial f^{(N)}}{\partial p_i} \right)$
- Alternative form:**  $= \sum_{i=1}^N \left( \frac{p_i}{m} \frac{\partial f^{(N)}}{\partial q_i} - \sum_{j=1}^N \nabla_j u_{ij}(r_{ij}) \cdot \frac{\partial f^{(N)}}{\partial p_i} \right)$
- Handwritten notes:**
  - Green circles around  $f^{(N)}$  and  $H$ .
  - Red circles around the Poisson bracket and the derivative terms in the expansion.
  - Green text: "N body distribution position + time dep."
  - Red text: "VV" in a circle.
- Caption:** We can derive BBGKY equation starting from Liouville equation.

So the Liouville equation as I said the grand equation it work or full N body distribution, N body full every particle in the system. Not at all in n body distribution, it is both position and time dependent, it is dependent.

$$\frac{\partial f^{(N)}}{\partial t} + \{f^{(N)}, H\} = 0$$

It is same as the Hamilton equations of classical mechanics, essentially same as Newton's equation but you know the difficulty of Newton's equation in theoretical work that it is comes in terms of momentum and positions of the particles.

That is great to computer simulations many of things but when you want to try to analytical work in the kind of distribution functions. You have to put in the terms of delta functions and have to go to probabilistic distribution, that equate the Newton's equation of motion as such is not used, it is transformed into a probabilistic equation, we will do that thing in very routine in time dependent statistical mechanics.

We write an equation which is stochastic equation and then we transform into probabilistic equation and that is a very common game we play, that this game went back to long ago and the person who did first that is Liouville and he derived this beautiful equation,

$$f^{(N)}(t) = f(r^{(N)}, p^{(N)}, t)$$

so  $f^{(N)}$  that I have defined that  $f^{(N)}$  depends on, it is depends actually on if  $f$  as position of  $N$  particles, momentum of  $N$  particles at a time  $t$ .

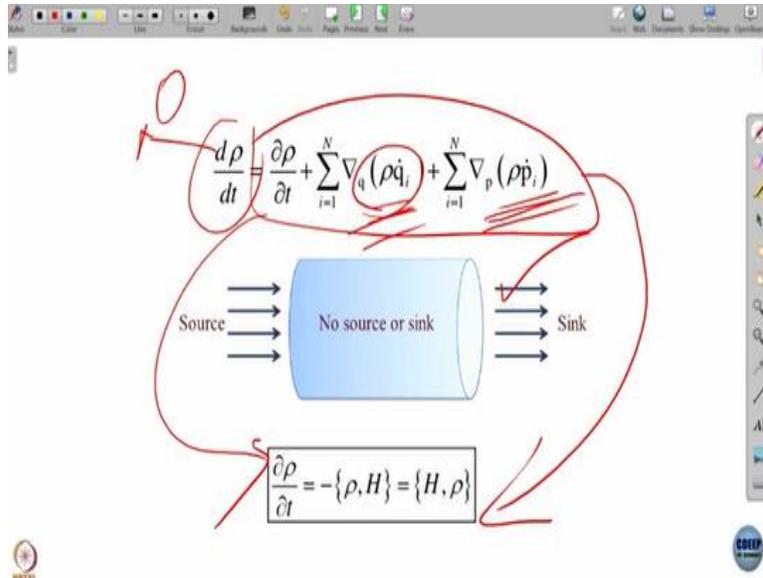
So  $f^{(N)}$   $t$  which is in a shortcut version actually depends on positions and momentum, positions and momentum for all the  $N$  particles, very important all the  $N$  particles and this is a commutator which comes from Hamilton's equations, one can be give a very simple derivation will discuss the derivation in the next page. But this is a commutator of Poisson-Bracket in quantum mechanics that becomes commutator because Liouville equation is a quantum coefficient.

$$\{f^{(N)}, H\} = \sum_{i=1}^N \left( \frac{\partial H}{\partial p_i} \cdot \frac{\partial f^{(N)}}{\partial q_i} - \frac{\partial H}{\partial q_i} \cdot \frac{\partial f^{(N)}}{\partial p_i} \right)$$

But in classical mechanics, this is the Poisson-Bracket with the Hamiltonian as this and you can easily see this  $H$  is just squares are just dots that  $dH/dp_i$  and  $dH/dq_i$ , this is we know in Hamiltonian's equations. But  $dx/dp_i$  on the other hand we know that this is nothing but kinetic energy term of the Hamiltonian momentum, it is a momentum here and this is the potential energy part of the Hamiltonian that needs to be force term.

So, this should be the force acting on a particle  $i$  and that would be then come from interaction  $\nabla V$  term and this part remains the same, this part remains the same, this part remains the same.

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One can again go back and let me find out the idea in one line derivation of Liouville equation is that, let us see that in a cylinder, what is the change, total change of the density? You may remember this is phase space density in the very first and second class that we talked about. Phase space density means in my  $6N$  dimensional phase space, a point, I can now talk in the  $6N$  dimensional phase space what are the number of particles in a small volume element in a phase space?

Now that allowed me divide that number of particles, number of points in the phase space, that is number of microscopy states of the system in this small volume element, that gives a density of the phase space and that time derivative, total time derivative I am trying to get. However in that small volume element in phase space, particles cannot be created destroyed, so they can just move through like I have shown in this picture, they can moving through, so there is no sink or there is no source term.

Then when I write that, the molecules moving through then density and the velocity, then dense the way they get is the density into velocity streaming out velocity of the momentum, which is the derivative of the force term and that is now this is the phase space density has to be conserved these goes to zero and what is left here is stated is nothing but and this can be shown that these terms are nothing from Hamiltonian's equations comes from these things.

So this is a one line derivation, did little bit better job on this but we are not going to spend more time, but this is Liouville equation. So Liouville equation is fine.

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**BBGKY hierarchy**

$$\frac{\partial f^{(n)}}{\partial t} + \sum_{i=1}^n \frac{\mathbf{p}_i}{m} \cdot \frac{\partial f^{(n)}}{\partial \mathbf{q}_i} - \sum_{\substack{i,j=1 \\ j>i}}^n \nabla_{\mathbf{q}_i} u_{ij} \cdot \frac{\partial f^{(n)}}{\partial \mathbf{p}_i} = \sum_{i=1}^n \int \dots \int \nabla_{\mathbf{q}_{i,n+1}} \cdot \frac{\partial f^{(n+1)}}{\partial \mathbf{p}_i} d\mathbf{q}_{n+1} d\mathbf{p}_{n+1}$$

- BBGKY equation is an exact relation between the  $n$ -particle and the  $n+1$ -particle reduced probability density function.
- It is not closed.
- Cannot be used without approximations.

We love that equation but Liouville equation was used in many purposes but it was brought to theory of liquids by this five distinguished scientists

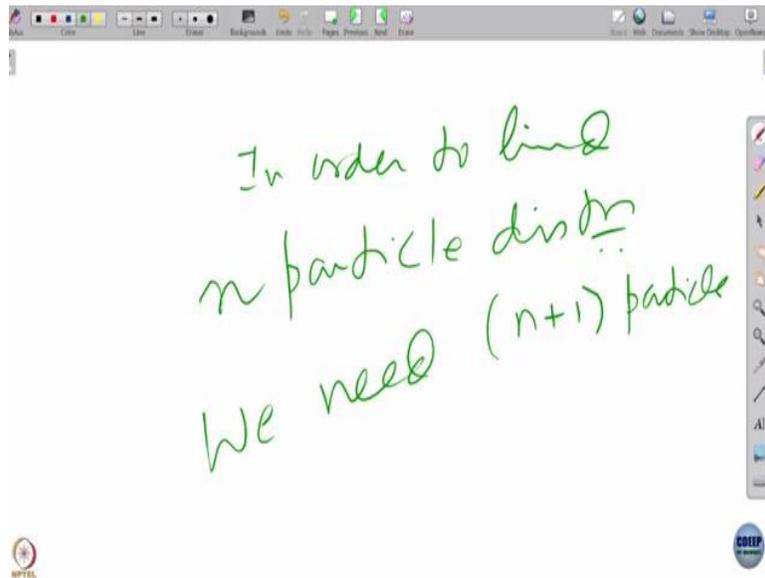
$$\frac{\partial f^{(n)}}{\partial t} + \sum_{i=1}^n \frac{\mathbf{p}_i}{m} \cdot \frac{\partial f^{(n)}}{\partial \mathbf{q}_i} - \sum_{\substack{i,j=1 \\ j>i}}^n \nabla_{\mathbf{q}_i} u_{ij} \cdot \frac{\partial f^{(n)}}{\partial \mathbf{p}_i} = \sum_{i=1}^n \int \dots \int \nabla_{\mathbf{q}_{i,n+1}} \cdot \frac{\partial f^{(n+1)}}{\partial \mathbf{p}_i} d\mathbf{q}_{n+1} d\mathbf{p}_{n+1}$$

and they showed that the force that is there which is this term, now I can try to get that force, it decompose the force such that I have  $n$ - particle distribution function, so I have to say four particle distribution function then I have the other particles which are here.

I want to have this four particular distribution function, then I can separate the part to the acting from the force themselves internally and between themselves and the one that with outside, that is what is done here. That is, within that sum is upto  $n$ , then the other one is from  $n$  to  $N$  all other particles, when you decompose that then you can say, in order to defined  $f_n$  have to integrate over  $d\mathbf{r}_{n+1}$ ,  $d\mathbf{r}_N$ .  $f^{(n)}$ , that integral over  $n+1$  to  $n$ , those extra coordinates in order to get my reduced description. That is done here, so from BBGKY equation is one step process but the important thing to note in BBGKY, that in order to get  $n$  I am connected to other distributions. That means I cannot eliminate this, so my  $n$  particle distribution gets connected to higher order distribution function. This is called hierarchy.

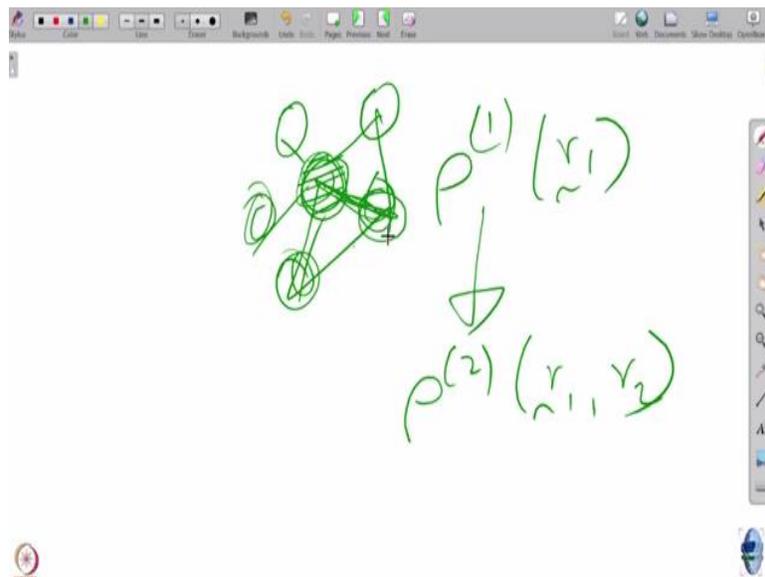
So BBGKY equation is an exact relation between the  $n$  particle and the  $n + 1$  particle reduced probability density function. So when you integrate that, these other ones, then here you can show by separating out it goes to  $n + 1$ , so we are landed up in a trouble that;

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In order to find  $n$  particle distribution we need  $n + 1$ . This you can understand easily;

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If you want to find in a system where there is an external field to create inhomogeneity and I want to find, what is the probability that 1 at  $r$  1? Then I need to know, the force coming from all other particles and I can integrate out and I can show this is connected with two particles

distribution function because the force are coming from all this particles. So when I integrate out in order to do one particle distribution, I need to know two particles distribution.

Then in order to two particle distribution, I need three particle distribution, like that, so this is called hierarchy. We have been a slightly going at a fast pace and the basic idea is to give you the flavor of this subject and the books are there, particularly my own book and you can look into that.

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**YBG hierarchy**

- At equilibrium  $\frac{\partial f^{(n)}}{\partial t} = 0$  — Condition
- The equilibrium n-body particle distribution function can be written as follows  
 $f_{eq}^{(n)}(r^n, p^n) = \rho_{eq}^{(n)}(r^n) p^{(n)}(p^n)$  — Classical mechanics
- Under this conditions, BBGKY reduces to YBG equation. — Hypothesis

$$k_B T \nabla \cdot \left( \frac{\partial f^{(n)}}{\partial r} \right) + \sum_{j=2}^n \nabla_{r_j} \cdot u(r_j) g^{(n)}(r^n) = -\rho \int \nabla_{r_{n+1}} \cdot u(r_{n+1}) f^{(n+1)}(r^{n+1}) dr_{n+1}$$

So what we do now? What is the next step? Dynamical approach of dynamics through BBGKY hierarchy is extremely difficult and has not been much done, very early attempt to do these kind of things was the Boltzmann's famous kinetic equation approach, Boltzmann tried to do this actually,  $f_1, r_1, P_1, T$  and he found that just that he found here, through a binary collision is connected to  $f_2, r_1, P_1, r_2, P_2, T$ . So the first BBGKY hierarchy was attempted in a little bit form by great Boltzmann himself.

And he landed up that he could not do it and so he made the approximation of what is molecular chaos so sort out in German, thy he was heavily criticized for this is, very sad story. However we are doing here in equilibrium statistical mechanics, we are at this structure of liquids not the dynamics. So we now at equilibrium, the time dependent of the distribution, the solution we are looking at is a time invariant.

That means there is a class of solution which does not depend on time. We are not interested how distribution functions are changing with time, and that is done by putting that equal to 0.

$$\frac{\partial f^{(n)}}{\partial t} = 0$$

$$f_{eq}^{(n)}(\mathbf{r}^n, \mathbf{p}^n) = \rho_{eq}^{(n)}(\mathbf{r}^n) P^{(n)}(\mathbf{p}^n)$$

When you do that, then one can go to make certain change of variables and one is done here equilibrium of n is talk in terms of equilibrium, classical mechanics that position and momentum separates out, so momentum goes out and we have left with the equilibrium of the n particle distribution.

So this is nothing but a definition or a nomenclature, this is the condition of equilibrium, when you combine these two, go back to which we get another formidable equation,

$$k_B T \nabla_1 g^{(n)}(\mathbf{r}^n) + \sum_{j=2}^n \nabla_1 u(\mathbf{r}_{1j}) g^{(n)}(\mathbf{r}^n) = -\rho \int \nabla_1 u(\mathbf{r}_{1,n+1}) g^{(n+1)}(\mathbf{r}^{n+1}) d\mathbf{r}_{n+1}$$

that now derivative with respect to first particles  $g^{(n)}$ , that gives you we now separated in just like BBGKY hierarchy we separated out one particle with the others. So if derivative with respect to one is now with respect to all other particles.

So the force coming from this is one particle 1 from others. Now just like BBGKY hierarchy I separate it out that one particle thing from the higher particles, so when I do that, I find that nth one gets connected to n +1. It really makes sense to write down on this 1, that means  $g_1 \rho_1$  then what you will find that  $K_B T$ .

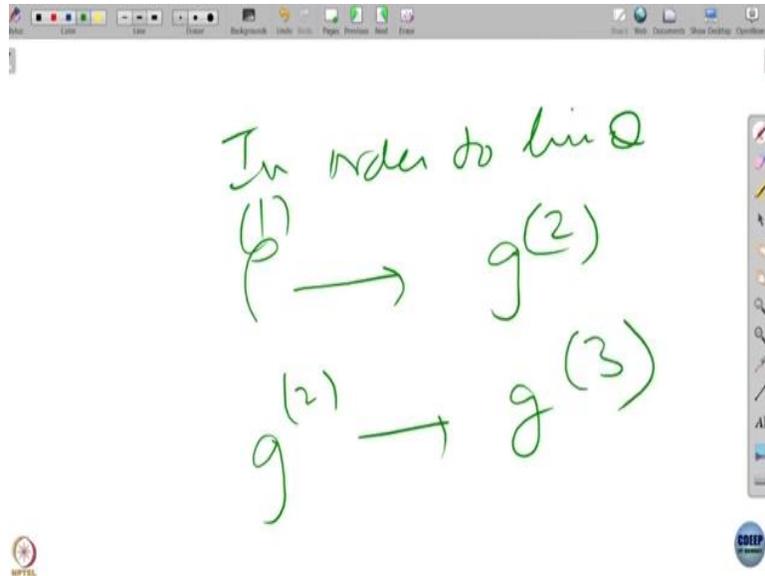
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$$k_B T \nabla_1 \rho_1(r) = \frac{\rho_1(r)}{Z} \int dr_2 \dots dr_n \nabla u_1 g_2(r)$$

Let me try to do that, that  $k_B T \nabla_1 \rho_1(r) +$  this term,  $g = 2$  to  $n$ . So, I have now, plus  $\nabla_1$  of  $g_1$ ,  $g_1$  is nothing but  $\rho_1$ , so this is  $\rho_1$ . Then what I find that on the right hand side, I have now  $\nabla_1 u_1$ ,  $u$  is the intermolecular interaction of the total potential energy of the first particle. So then I get terms which is  $dr_2 \dots dr_n$  and then I have  $g_2$  here and then  $\nabla$  in a potential acting on the 1 particle, this comes from all other particles.

So I have 1 that particle here and I am looking at that distribution of probability of that particle here, but I need in order to get that I will see this earlier equation showed that I will have  $g_2$ . So this is in a nutshell, this equation for  $g_1$  and  $g_1$  is  $\rho_1$ . So  $\rho_1$  depends on  $g_2$ ,  $g_2$  is the radial distributional function. So this is the equation I have left out certain details, but you understand that is way this is going to go.

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So we are in a loop because so in order to find  $\rho$ , I need  $g^{(2)}$ , you have to find  $g^{(2)}$ , I need  $g^{(3)}$ , very similar to what Boltzmann found many years ago is better to get that perspective does not he told much of the time that is something exactly what Boltzmann made, he made an assumption, which is very similar to we are going to right now.