Basic Statistical Mechanics

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Lecture -54
Theory of Liquids Part - 4

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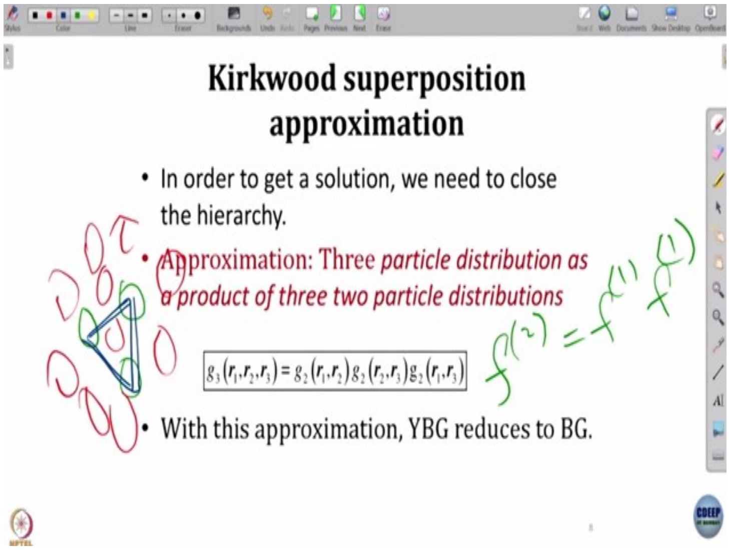

Kirkwood superposition approximation

- In order to get a solution, we need to close the hierarchy.
- Approximation: Three *particle distribution as a product of three two particle distributions*

$$\boxed{g_3(r_1,r_2,r_3) = g_2(r_1,r_2)g_2(r_2,r_3)g_2(r_1,r_3)}$$

- With this approximation, YBG reduces to BG.

So the assumption that was made by Boltzmann, many years ago was $f^{(2)}$ in full position and momentum I am not writing $f^{(1)}f^{(1)}$. That is what he was criticized. The story is that one owned it nobody knows that he committed suicide because of the huge criticism he faced because of that, because he introduced the concept of probability at in a time when everybody was very deterministic, very mechanical.

So more than 70 years later, John Gamble Kirkwood made this similar thing. He said okay I want to get ρ on g_2, well in homogeneous liquid ρ is not important, important is g_2 radial two particular distribution function that is what as we discussed yesterday. We get the static structure factor that is observed experimentally.

So g_2 is the essential quantity of liquid state, but I cannot get that because g_2 is connected to g_3. So we made this superposition approximation Kirkwood superposition actual or it should be called Kirkwood-Boltzmann superposition approximation that g_3 is now $g_2 g_2 g_2$, that means. If we consider three particles you know, of course, there are many others around here but even here.

But we want these three. We want these three $\vec{r}_1, \vec{r}_2$ and $\vec{r}_3$ what is now assumed is that this probability distribution of three particle correlation is a product of the two. So $g_3(\vec{r}_{1,}\vec{r}_2, \vec{r}_3)$ is now given by product of $g_2(\vec{r}_1, \vec{r}_2)$, $g_2(\vec{r}_2, \vec{r}_3)$ and $g_2(\vec{r}_3, \vec{r}_1)$ is called Kirkwood superposition approximation. When you make that and put it back into the;

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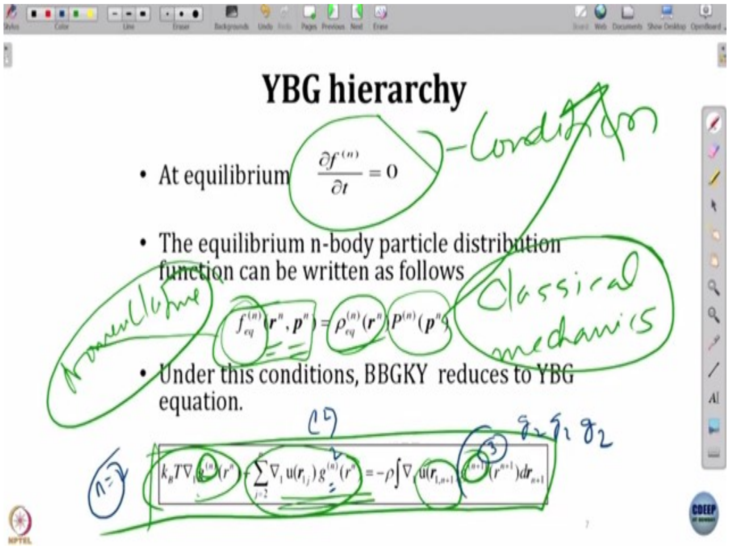

YBG hierarchy

- At equilibrium $\frac{\partial f^{(n)}}{\partial t} = 0$
- The equilibrium n-body particle distribution function can be written as follows

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

- Under this conditions, BBGKY reduces to YBG equation.

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

We get put it back into this equation, this equation, so now, if I am doing an equation of a $g^{(2)}$, n equal to 2, on right hand side n+1 is 3, $g^{(3)}(\vec{r}_1, \vec{r}_2, \vec{r}_3)$ now I will make $g^{(2)}(\vec{r}_1, \vec{r}_2) g^{(2)}(\vec{r}_2, \vec{r}_3) g^{(2)}(\vec{r}_3, \vec{r}_1)$, and of that now I can integrate over $\vec{r}_2$ and $\vec{r}_3$, I want these $g^{(2)}$ here I will make as $g^{(2)}(\vec{r}_1, \vec{r}_2)$ then, then I can take the $g^{(2)}(\vec{r}_1, \vec{r}_2)$ which is out of this integral, then I am left with the integration over $\vec{r}_3$ $\vec{r}_4$ $\vec{r}_5$ and all the n particles and $g^{(2)}(\vec{r}_2, \vec{r}_3)$ and $g^{(2)}(\vec{r}_3, \vec{r}_1)$ remains inside.

That means you get a simplification of the equations we are not going to go into details of that.

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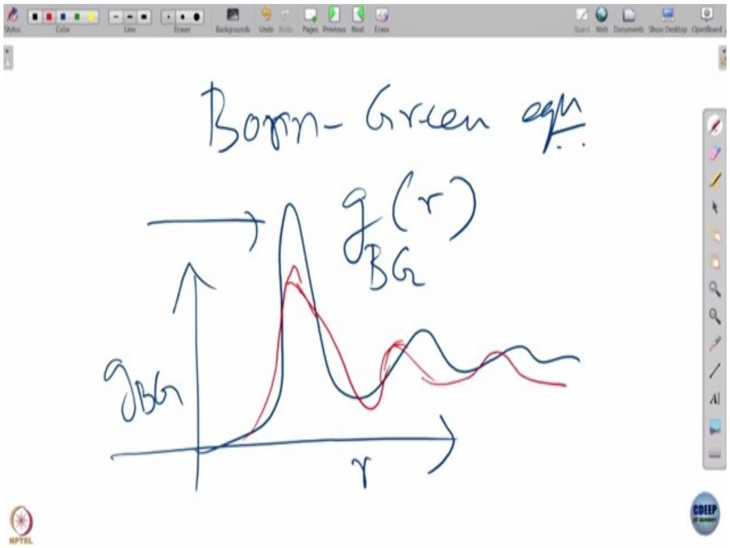

With that one kind approximation the equation to a simple Born-Green (BG) equation which is something which we, so what is the result that we get when you do that the I do not worry I do not have to Born-Green equation here you have to move to show the from Born-Green equation, which is much simpler equation, just as I described then you get the radial distribution function of the $g(r)$.

Born-Green equation and now you plot that against r. So, the real equation is something like that, then Born-Green equation falters on two counts, Born-Breen equation gets the peak but does not get the peak full and Born-Green equation does not get this maximum in right place. So, Born-Green equation falters.

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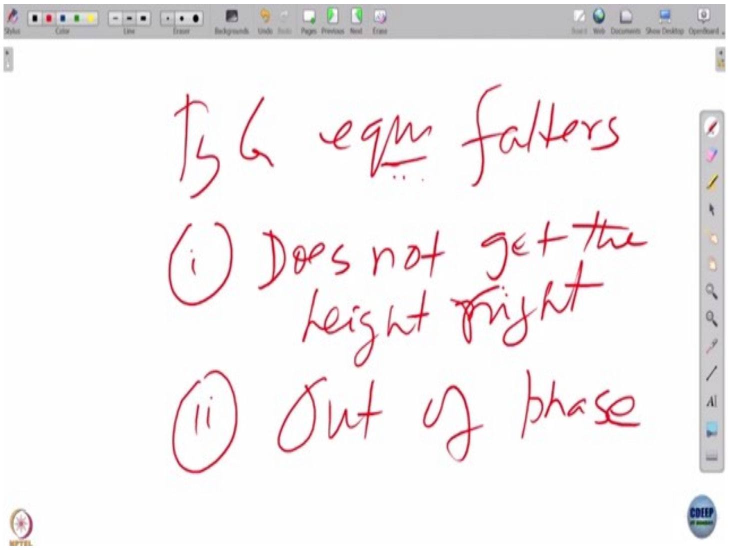

BG eqn falters

(i) Does not get the height right

(ii) Out of phase

So BG equations, falters, one does not get the height right of the first peak, out of phase and Born-Green equation. It will do too terribly a bad job but it was not good enough. There lot of attempts made to extend the BG equation. So, all the atoms get some good results and till 1990s people were working.

But then what happened being increasingly more and much better correction to Kirkwood superposition approximation brought in and improvements were shown but it did not work out that well that means it has become numerically very intensive and somehow and other equation has to be introduced because you know as I say $g^{(2)}$ in terms of $g^{(3)}$ and, $g^{(3)}$ in terms of $g^{(4)}$.

So whatever approximation will go at the level of $g^{(3)}$, turns out to be critical in determining $g^{(2)}$ and in addition to being the numerical, it did not quite, it was the progress, was not satisfactory and this was still those certain people working, these line of research that means from your Born-green equation which is exactly going to radial distribution function kind of as a road block.

This is something one should know that it did not work out that way then what happened? Then something very interesting happened because science always has the way to find its path.

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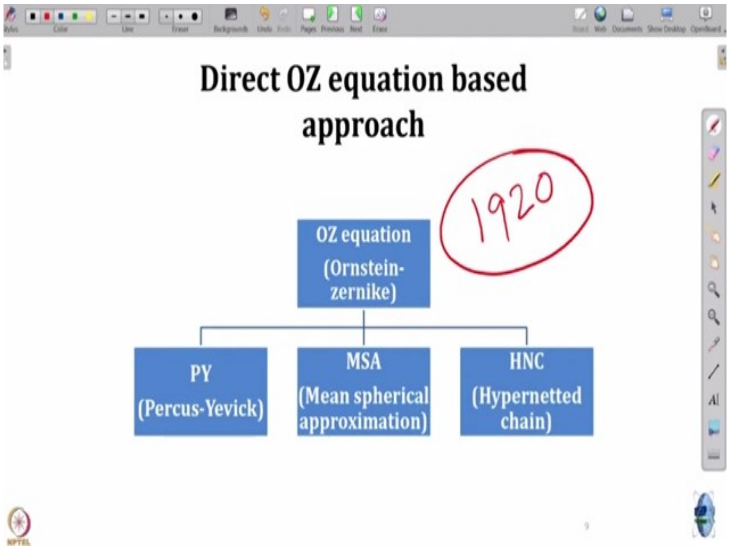

Direct OZ equation based approach

1920

OZ equation (Ornstein-zernike)

PY (Percus-Yevick)

MSA (Mean spherical approximation)

HNC (Hypernetted chain)

And so that, what happened is a different approach was taken, that approach goes back to 1920 when Ornstein-Zernike introduced a beautiful equation called Ornstein-Zernike equation to describe the critical phenomena. 1920 described critical phenomena, light scattering and the critical phenomena these it becomes opaque, you know, the critical opalescence that this is the huge fluctuations.

That can they could even that time it was very clear that there is because by that time Einstein's theory of diffusion and the fluctuation theory of Einstein was there, I said already $(\delta E)^2 = k_B T^2 C_V$. So, people understood that there are huge fluctuations are taking place and by that time Yevick equation was not even dreamed off, People had Lioville equation but people did not have Ornstein-Zernike equation.

Ornstein-Zernike equation are it took it to themselves, we realized something that is though it is a large-scale fluctuation taking place that giving the critical opalescence there is also short-range correlations. So radial distribution function or the two-particle correlation is diverging but short-range correlations need not diverge, I can build a long-range correlation just like we do in Ising model.

So long-range correlation can come out of short-range correlation, then how do I do that? What the Ornstein-Zernike equation does?

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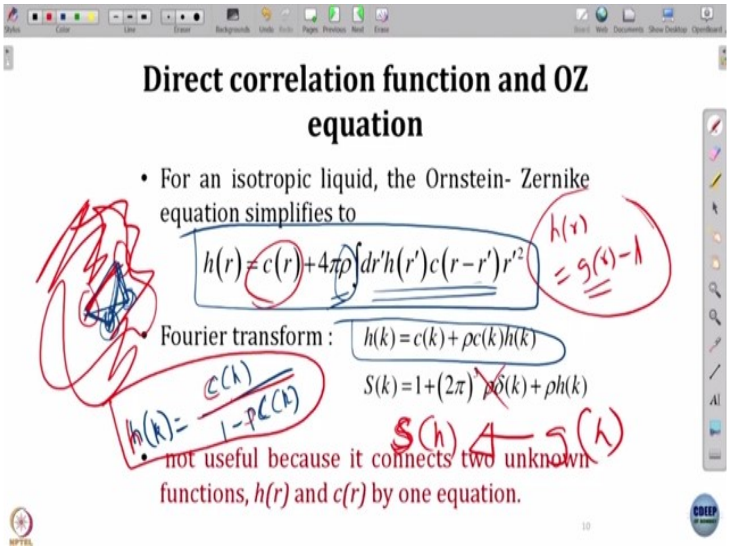

Direct correlation function and OZ equation

- For an isotropic liquid, the Ornstein- Zernike equation simplifies to

$$h(r)=c(r)+4\pi\rho\int dr' h(r')c(r-r')r'^2$$

$$h(r) = g(r)-1$$

- Fourier transform : $h(k)=c(k)+\rho c(k)h(k)$

$$S(k)=1+(2\pi)^3\cancel{\rho\delta(k)}+\rho h(k)$$

$$h(k)=\frac{c(k)}{1-\rho c(k)}$$

$$S(k) \leftrightarrow g(k)$$

- not useful because it connects two unknown functions, *h(r)* and *c(r)* by one equation.

They separate out; they said okay, two particle correlation which is called pair correlation; $h(r)$ is nothing but $g(r)-1$ and one thing that should tell that.

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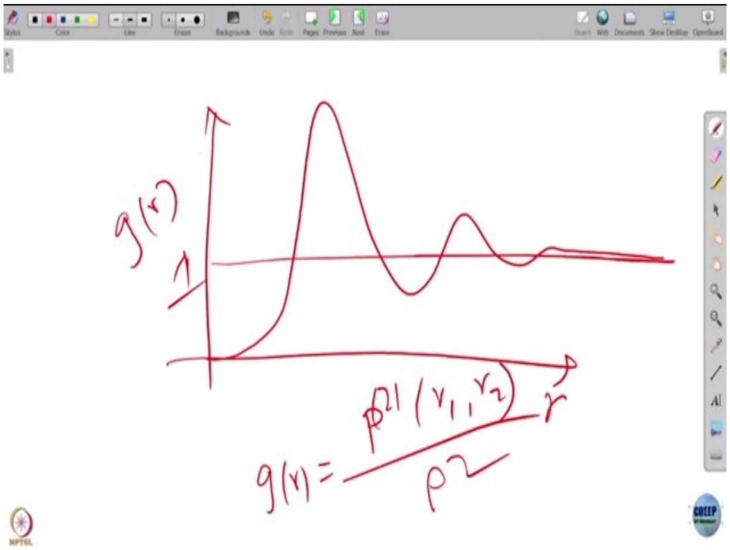

When I, the way we have defined $g(r)$ radial distribution function or two particle correlations. That goes to 1 because particles become uncorrelated and $g(r)$ is normalized $g(r) = \frac{P^{(2)}(\vec{r}_1, \vec{r}_2)}{\rho^2}$. So, when they become independent of each other $P^{(2)}$ become ρ^2, so $g(r)$ goes to 1. So, it makes sense then to take that out 1 and get the pair correlation function $h(r)$.

This is a non-trivial quantity because 1 is the trivial thing. So, it measures the correlation in addition to the product thing and what they said okay introduced a function called direct correlation function. So two particle correlation in front of all other liquid particles. Is there is a one thing, which is directed between them the direct correlation function and then there is something which is propagating through others.

So this correlation between these two is propagating between that because these molecules are interacting in addition to direct. There would be something which is propagating through the other particle like in hydrodynamics there is a term called advective, term which is very similar to that or many and other terms that we have. That there is a direct interaction between them and there is interaction propagating through the medium.

Then they said okay, if it, structure is very interesting if $h(r)$ equal to direct correlation plus other, particle is at r'. Then I have a direct correlation up to r' then guy and these have a direct interaction. Then similarly, there is a pair correlation then direct interaction that is the one summed up here. So, $\rho h(r)$ then gives the probability that you have a particle at that position.

$\rho c(r)$ You can also calculate but that there are no position dependent so that comes out. Now these a beautiful structure which can be Fourier transformed and then it is a convolution and Fourier transform of the convolution is the product of the Fourier transform of the two functions that is why the $h(k)$ becomes $c(k)+\rho c(k)h(k)$. This is very interesting, because now, I can get $h(k)$ from there in terms of $c(k)$.

So, $h(k)$ let me solve now $h(k)$ in terms of $c(k)$, is I bring this $h(k)$ here, so I get $1-\rho c(k)$, so $h(k)=\dfrac{c(k)}{1-\rho c(k)}$. So, my Fourier transformation function is given in terms of direct correlation function, that is very interesting that because I know the structure factor is given by $S(k)$ is given essential by $h(k)$. So, my structure factor is uniquely related to now, structure factor, so if I ignore the forward scattering this term is neglected then I have.

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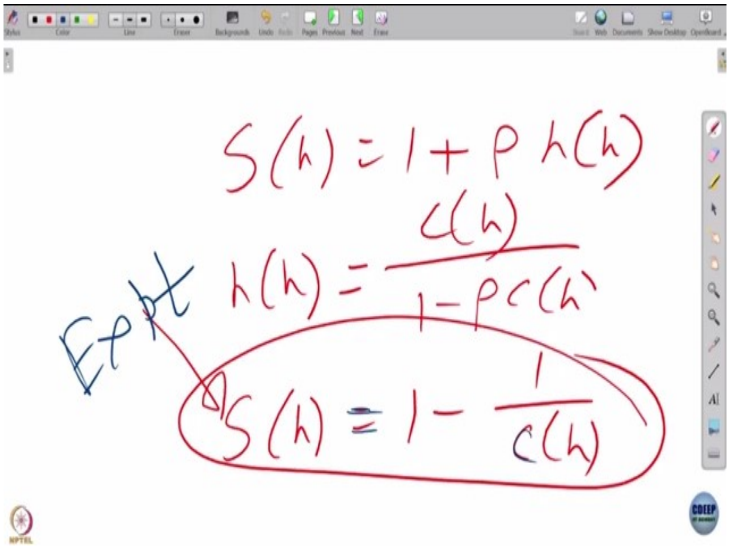

$$S(k) = 1 + \rho h(k)$$

$$h(k) = \frac{c(k)}{1-\rho c(k)}$$

$$S(k) = 1 - \frac{1}{c(k)}$$

$S(k)=1+\rho h(k)$ and I have $h(k)=\dfrac{c(k)}{1-\rho c(k)}$ and then I get $S(k)=1-\dfrac{1}{c(k)}$. So beauty is in their $S(k)$ is experimentally accessible. So I get directly the very important quantity is the direct correlation function. So this makes the direct correlation function of this approach so useful.

And then there are these beautiful one $g(r)$. Now, if I take the Fourier transform of this quantity

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then $S(k)$ almost meet us $g(r)$ and except these maximum is near $2\pi / \sigma$, nearest molecular distance and structure factor these are experimentally we get. These proves these beautiful thing, proves these nearest neighbour correlations and that is connected to $c(k)$ and $c(k)$ and $c(r)$ play a very important role in the statistical mechanics. But note the beautiful structure $S(k)$ and that this is very similar to what you get by $g(r)$.

They are not exactly the same because contribution here comes from other peaks also or second peak and third peak but these predominate this order at the $k = \frac{2\pi}{\sigma}$ measured in neutron scattering is a manifestation of the short-range order. So we started by saying liquid is the unique because of the short-range order that those short-range order are you are seeing here reflected in radial distribution function and in the static structure factor.

These are extremely important thing to the exchange I believe that $g(r)$ if not $S(k)$ should be taught even in the high school level because that what determines liquid not just the density you know. I can have pretty high density, liquid gas there is no never the critical do not forget about the critical temperature you know I can have.

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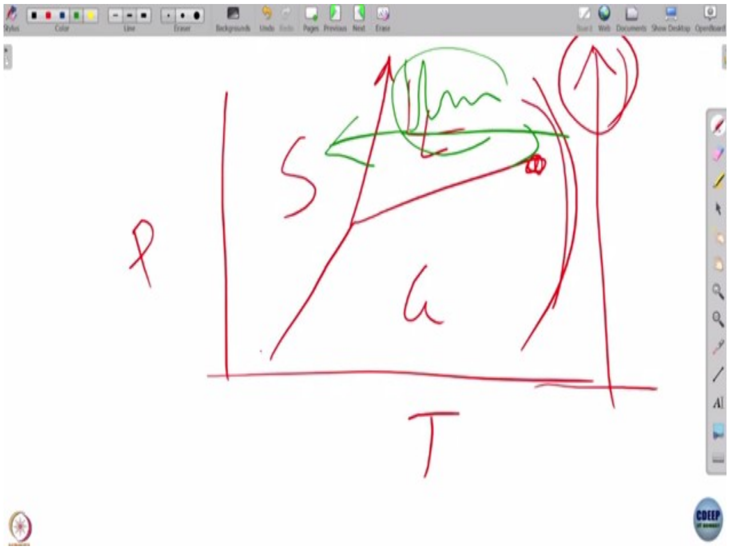

This is pressure temperature plane, so I am at the temperature here I can go to very high pressure, I can go to very high temperature, I can go to very high density, yes but there it is called supercritical this region is called supercritical liquid, so but you know what every carbon dioxide is a lot of work going on there but here you see the nearest correlation are there but much less, they are much sharper and much more structured liquid-gas here.

Actually, if $g(r)$ does not have that structure that liquid has here, if you do not have these structures, you would not have the liquid to solid transition. So liquid to solid transition of freezing is critically dependent on the local structure that is what I said that the local structure transcends long-range order. This is a beautiful thing so build up short correlation is essential for the establishment of long-range relation.

And the liquid is going to the crystalline or phase. So then there have been several approximations that have been mad. Now, if I go back to work Zernike equation then there is an equation is a beautiful equation as I said it is a lot of beautiful things many implications but one important thing is that each has one equation and two unknowns. Two unknowns are $h(r)$ and $c(r)$.

I already told you that I can get $c(r)$ from $h(k)$ but that already uses the Ornstein-Zernike equation. So the question of two, if I really need to develop a theory of liquid state then I have to get one more equation but we have an advantage now which we did not have been

YBG, that we know here $c(r)$ is a direct correlation. So we can make intelligent guesses at what should be the form of $c(r)$.

And that has been done to a great extent in handing the equations like Percus-Yevick equation, Hypernetted chain equation, Mean spherical approximations all these things came in and they are the one we will describe a little of that like one.

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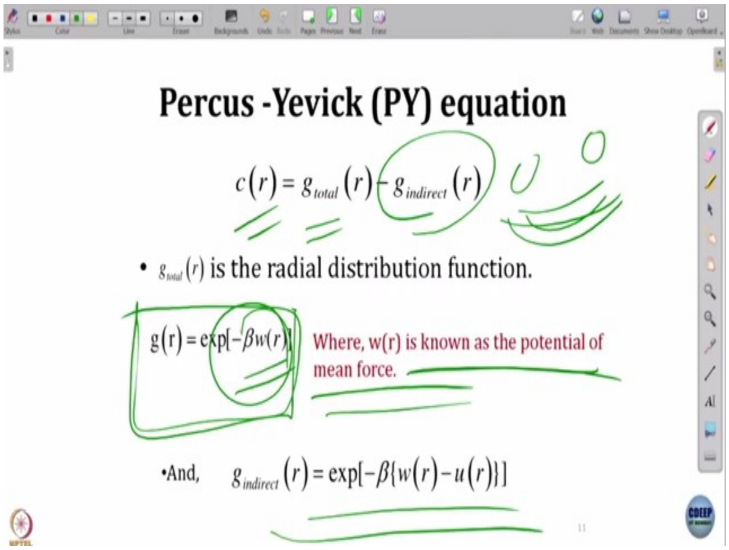

Percus -Yevick (PY) equation

$$c(r) = g_{total}(r) - g_{indirect}(r)$$

- $g_{total}(r)$ is the radial distribution function.

$g(r) = \exp[-\beta w(r)]$ Where, w(r) is known as the potential of mean force.

•And, $g_{indirect}(r) = \exp[-\beta\{w(r) - u(r)\}]$

So I now want one more relation between $c(r)$ and $g(r)$ and one popular one is given here by definition called potential of mean force that $g(r) = e^{-\beta w(r)}$, potential of mean force because if I, this definition if I take log of this $\ln g(r) = -\beta w(r)$ and $g(r)$ is kind of a potential because these two particles are separated by r. So, it makes sense to like $g(r) = -\beta w(r)$, and $w(r)$ is the potential of the mean force it makes sense.

Then one uses several different combinations of it makes sense because we have a total, you take the total for the indirect, so total take and then from the total I take out all that are propagating through here that is the indirect then, that of course leaves me with direct correlation function. That makes sense and then one uses several up uses this thing to define and indirect are then you have an equation between $c(r)$ and $g(r)$ the second equation that you are looking for.

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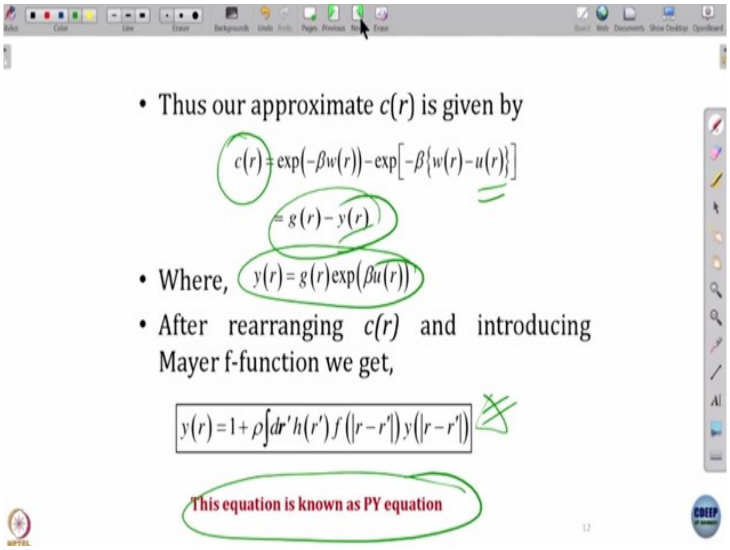

- Thus our approximate $c(r)$ is given by

$$c(r) = \exp(-\beta w(r)) - \exp[-\beta\{w(r) - u(r)\}]$$

$$= g(r) - y(r)$$

- Where, $y(r) = g(r)\exp(\beta u(r))$
- After rearranging *c(r)* and introducing Mayer f-function we get,

$$\boxed{y(r) = 1 + \rho\int d\mathbf{r}' h(r') f(|r - r'|) y(|r - r'|)}$$

This equation is known as PY equation

And that is worked out here approximations here is given by in terms of these potential of mean force and you are and essentially $c(r) = g(r) = y(r)$ is a very famous function, y function and very much like what does Mayer theory and the this $y(r) = g(r)e^{\beta u(r)}$ and that has been comes from these kind of definitions and $g(r)$ minus this $y(r)$ is a very important functions.

Then you get one more equation and this equation is when these equation is called Percus-Yevick equation and this we are not going through that the derivations in which are given in my book and we might come back to you and with me the derivation of this function this is a little bit more detail and please make a note that this I think we should have done that and then Percus-Yevick equation.

So this extra equation in addition to Ornstein-Zernike equation allows us to solve these for $g(r)$ and $c(r)$ together. These are approach is very successful is the Percus-Yevick equation.

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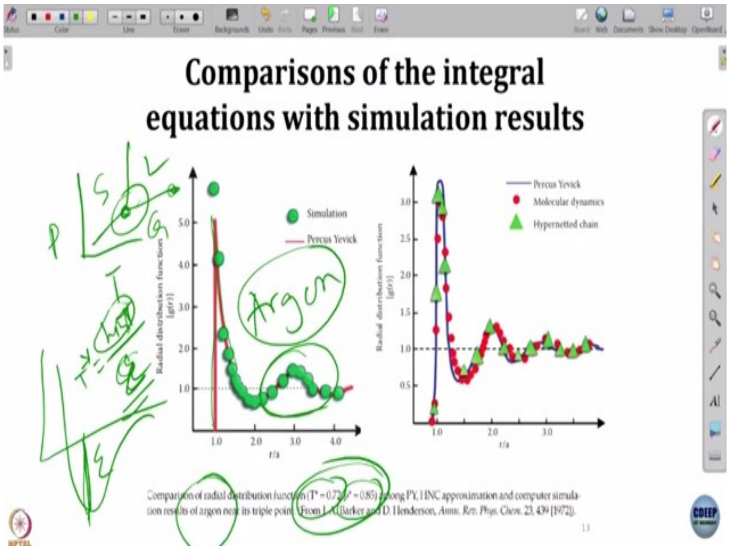

Comparisons of the integral equations with simulation results

Comparison of radial distribution function ($T^* = 0.72$, $\rho^* = 0.85$) among PY, HNC approximation and computer simulation results of argon near its triple point. From J. A. Barker and D. Henderson, *Annu. Rev. Phys. Chem.* 23, 439 [1972].

And here is the comparison of the integral equations with simulation results and here is far better than what BG equation. That is how it does it simulation and these are for Lennard-Jones systems of Argon and so this is for Argon near the triple point. So if we write pressure temperature then Argon has so much of the studies have been done near the triple point and here is the triple point where the $T^* = 0.72$ and $\rho^* = 0.85$.

As I was saying this is a typical density of the liquids and T^* one is a good number to remember as an $T^* = k_B T / \varepsilon$. So if Lennard-Jones potential is epsilon so T^* is a dimension is quantity which is $k_B T / \varepsilon$. Then in thermal energy divided by, so T^* is actually gives a measure of how high you are with respect to Lennard Jones well depth ε.

Now you see what Percus -Yevick equation peaks up quite a bit of the structure and it does very well here in getting the second peak that is what Born-Green approximation with Kirkwood approximation and failed to do, and then here one more thing Hypernetted Chain approximation which sometimes does better sometimes does worse but they are almost very close to each other. What becomes for this course we do not have to go into the details of the difference.

But they both do so basic then take home message is that theory of liquids have reached a quite a satisfactory stage, when it comes to these kind of spherical molecules like argon you know and also not too bad in molecules showing their dumbbell like nitrogen or oxygen these kind of molecules though forcefully sometimes pore is a problem but is reasonably okay. We can have a theory of liquid also of course we can get these simulations.

So all these beautiful work and that Percus-Yevick and Hypernetted Chain Spherical approximations turns to the Ornstein-Zernike equation, I have led us to a satisfactory understanding of the structure of liquids and the short-range order that is in liquid then what happens, that from 1970 or 1980 essentially, a huge number of simulations started coming.

The first argon simulation in a great way was done by Aneesur Rahman in 1964-1972 steering jar and Harmon. Harmon did the all the calculations of the water that was the pioneering simulations. In a series of paper, I think almost eight papers they simulated and deported the water with a stranger potential st2, potential which worked out quite well then much better what have been done.

So now simulations have become very powerful, so complex liquids like you know say, for example, I want to do methanol, I want ethanol, I want to sulfoxide, as we talked in the last two lectures. Since we need the radial distribution function from the further theoretical understanding of dynamical properties they are now obtained directly from simulations.

So the emphasis of theoretical research and theoretical effort has drifted and has moved away from these kinds of analytical work, analytical followed by numerical work. That is Percus-Yevick and Hypernetted chain. It has moved from there it has moved to the domain of simulations and then one gets the radial distribution function or three particle correlations directly from solutions.

The issue then become the issue of the force field in order to get simulation to agree with the experiment we need very good force field. How do molecules interact with each other? That explains the present emphasis of all grant proposals theory, research work is development of forces. Because computers have reached a stage where if you give me the force field, I can calculate the radial distribution function, I can calculate the three particle correlation, I can calculate the diffusion equation velocity correlation function.

The problem remains you know when I want to do long term behaviour then simulations can or cannot give you, but you basic very interesting features come with solution cannot explain just numbers do not suffice. You need to have a theory, you need to have equations. So that is what the theory of liquids it stops here, one thing I have not given the derivation is the derivation of the Percus -Yevick equation, that is given in my book.

And we might take a class one to come to that just a 15- 20 minutes class to make the derivation which I do not have with me right now, and well we I would need to need to talk a little bit about $y(r)$ function and other things and with that we stop the discussion on theory of liquids and we leave you with this beautiful picture of $g(r)$ and r, and this defines actual liquid in our mind this these two pictures that are giving you with slides define the picture okay then bye for now.