Basic Statistical Mechanics
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Lecture – 29
Cluster Expansion and Mayer's Theory of Condensation (Part 2)

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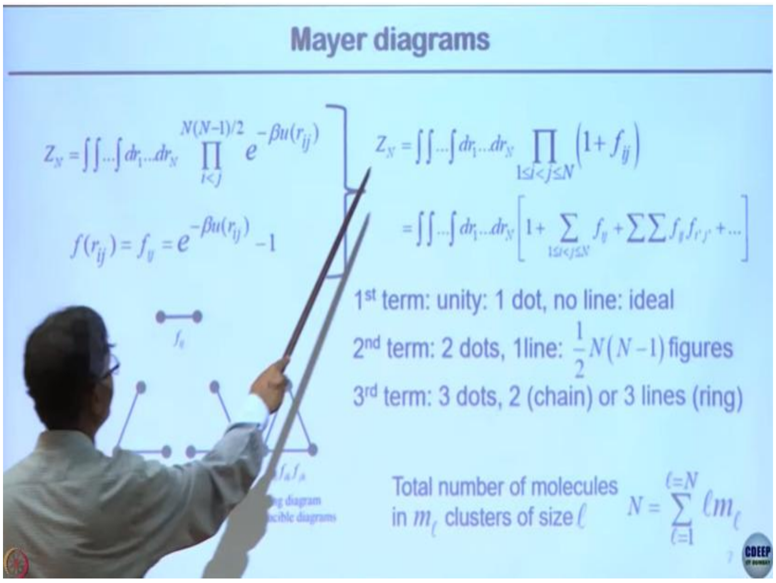

Now these are the two things so partition function now is 1 + f_{ij} and what is a product. So now I can do the product the first product all of them are 1. So I write 1 + c this is a binary so 1 + f_{12} + f_{13} + f_{14} +.. then multiplying 1 + f_{23} + f_{24} +… that 1 + f_{34}+.., 1 + f_{45} +.. like that.

But this is the one of the simplest at this level okay if I do that then every product has a 1 in front of it. So, one of them will become 1 right then all of them so I multiply the next one will be binary term okay. Let us do the simple one to see that it is the way it is working.

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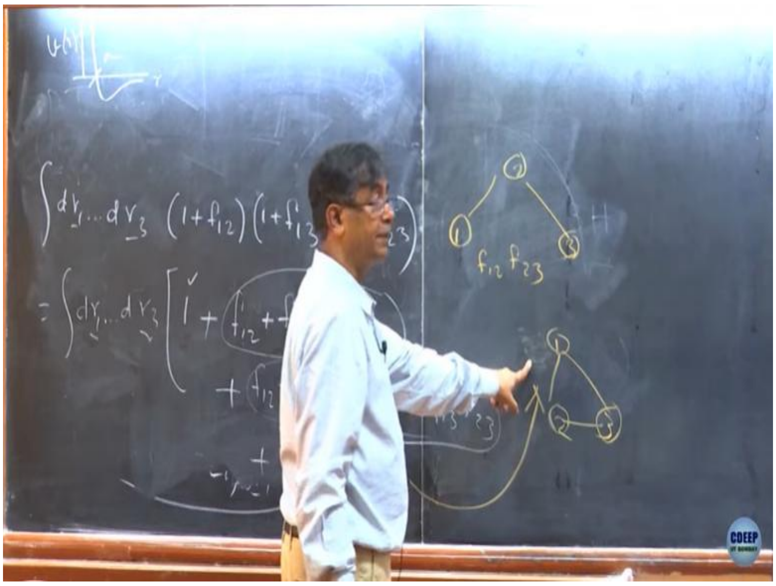

So let us see I have 3 particles dr_3 okay then I have is that okay. Now if I do that first term is 1 next term is f_{12} + f_{13} + f_{23} okay then next term is binary f_{12} f_{13} + $f_{13}f_{23}$ then I have one term f_{12} f_{23},f_{13}. So, I have this term then bunch of one particle term then there are 3 particle terms but the 3 particle terms of two kinds.

So, this is a kind of the 0th particle term this is the one which is the ideal gas. So, if I do not have any interaction then Mayer already told us the f terms will be 0 that is why he removed it so then if I do then only keep this term then I the ideal gas so the partition function is just the ideal gas.

Next term then in the is this binary interaction term two particle term and this becomes your secondary coefficient we will see that and these the 3 particle term has of two kinds one we call chain diagram because this is 1, 2. So this is this kind of term f_{12} okay this f_{12} this is f_{23} the one I have done here is this thing this is f_{12}, f_{23}, right. So, all the combinations of 3 particles but chain diagrams we are not but everything is doubly connected.

So, this one if I draw the graph I will find 1, 2, 3 because 12, 23, 13, or 31 this is a different beast these are called ring diagrams in the language of physics and chemistry. Now these are the chain so let us see what did Mayer do with all these beautiful stuffs. So, this is called decomposition of a partition function this is universal this is the one which is used in everywhere in your physics and chemistry in many body.

When you talk of many body physics this is what is done if you take (()) (04:58) or any many body physics books this is the first thing that anybody do there it is called Mayer cluster expansion okay. So now there is a graph theoretical representation the first term is unity ideal gas term 1 dot no line an ideal gas. Second term 2 dots and a line and the black dots also have a meaning and I will come to that black and white is man that is a graph theoretical language that is used and they are such figures or graphs.

Then third term is these 3 dots are 2 lines and 3 lines so 1 is a chain diagram which has two lines and 3 lines. So then the line is a bond line can be considered bond because this is the interaction between them and the bond is a kind of mathematical bond because the f is has the characteristics you have to remove the hard sphere part to make it chemical bond if you do that it is called a physical cluster which has also been developed but we are not going to go into that.

Now as I was saying the dots means in statistical mechanics or that it has been to be integrated over however if you have an external field which can I can add an external potential like in homogeneous system like you want to take an external electric field which is position dependent or you want to take a surface effect as a wall which has an interaction potential at certain specific location then that has to be included in your description then you need to have an extra term.
Okay now what I have to do now in order to evaluate the partition function I have to sum over all these diagrams right. All these diagrams need to be summed over how do I do that it is a formidable. So, we have made some progress we have now beginning to see that how I am getting ideal gas I am beginning to a decomposition thing are simpler but I have not solved the problem.

All the difficulties are now hidden in these terms I have a graph theoretical representation of interaction between particles which is neat and clean. But I have to make further progress next thing what Mayer did was he said okay he realized that this is a dot is a kind of a 0 particle. These are 2 particles these are 3 particles then I can go on have that the next one if I of course I have 4 particles in the many body system.

Then I have the diagrams which are connecting 4 particles now then what he said okay all these which are 3 particles he called bunch them together then there are 4 he bunched them together knowing very well that there is a difference between them. One realizes that this one is essentially product of this one okay and I would be able to evaluate them if I know how to integrate this quantity.

But that at this point not necessary because I need to bunch them together again a number of particles in a cluster. So, let me call them a cluster this is where cluster expansion comes in and I bunch these together knowing well there is a difference. But I call them together.

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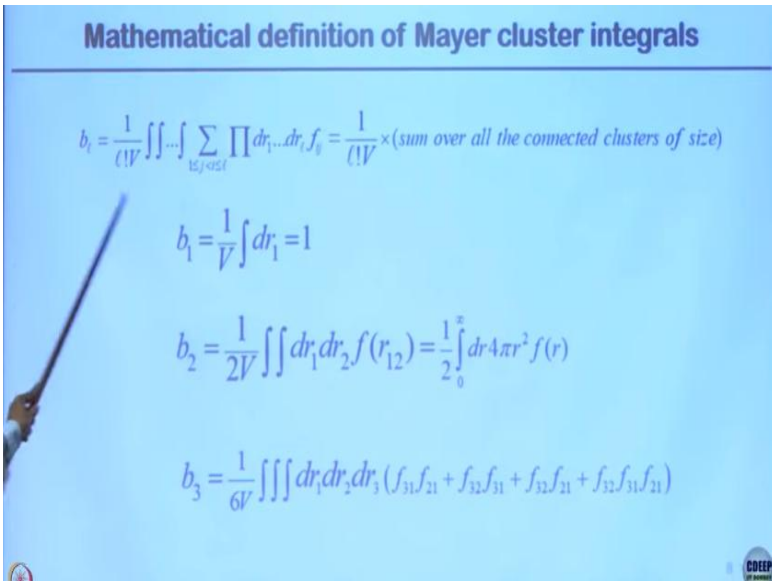

So, this is what now called the cluster integrals so all the l particles are brought together they might be doubling they are all connected they might be doubly connected that is okay it includes all of them they can be even more than doubly connected. Because if I have 4 particles then not only it can be ring it can be line in between.

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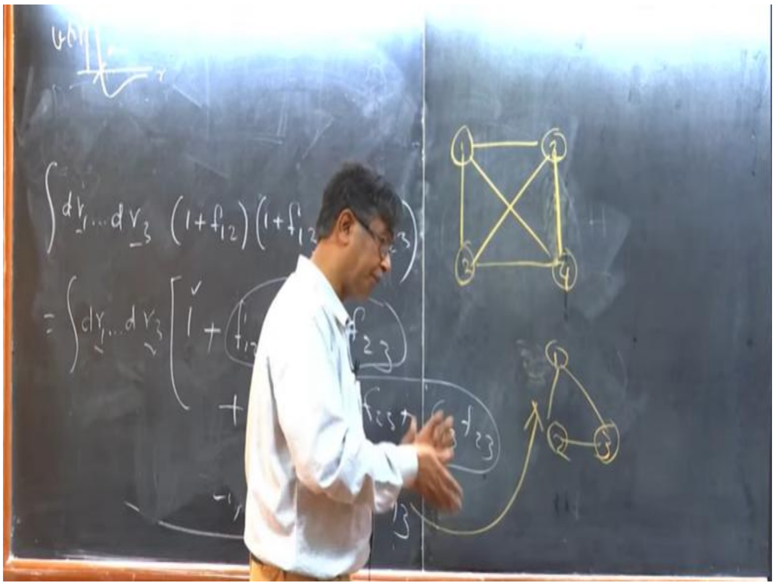

Okay so I can have so 4 particle cluster consists of all versions of that then this then these okay it turns out that if we do not have any of them then it is same as it can be replaced in terms of the integral of f_{12} ring 1 also can be done with certain difficulty but this one becomes very difficult you have to remember this particular thing is an integration on 4 particles.

So, there are 4 particles into 3 each particle has 3 coordinates. So this is a 12 dimensional integral I can select origin as 1 but still I have 9 dimensional (()) (10:53) and this was the difficulty that one could do but you some people were extremely brave they did evaluate up to 5, 6 for hard sphere one can do when they up to 9 or 10 and that gave rise to beautiful theories (()) (11:16) and all these things which you might not have time to go through but there is amazing exciting things happened in 1960 and 1970.

Because it had to wait little bit till that because of computers to come into existence and these are played a extremely important role when it was put on the lattice and critical phenomena that was called the high temperature expansion or series expansion done by Sengers and Green and many other people okay. So, the reducible cluster integral of size l is this best I put all the graphs together okay.

I have put a normalization here you will see that is very useful I have put a V here and this is this particular thing has a volume V now when I do that then for b_1 then I get 1 and I do b_2 then it is this quantity dr_1 dr_2. I put there is a definition right now and it will be handy definition. So I have put certain normalization here knowing what will happen. So there is a definition which will be absorbed nothing to worry about that.

So I now calculate b_2, b_2 now this diagram so that diagram as I look at the diagram I immediately know I have to integrate about this I have to integrate over that and I have f_1 and that is the advantage of a graph or that that is the whole thing of Feynman's graph theoretical technique was that they could write down the graphs. And then from the graph so you do not go do the algebra instead you write down the graphs and then translate the graph into an integration okay.

Similarly, we are doing so this becomes that so now I see $dr_1 dr_2$ why it has put in you can now understand I can change my coordinate to 1 so then it becomes 12 and this is 12. So I can integrate over my origin you know there is nothing so long there is an external field
You are beginning to see certain things that you know radial distribution function kind of nature character is coming out b_3 which is a lot of fun you have now this 3 dimensional integral f_{31}, f_{21}, f_{12}, f_{32} all these things together I do not know where f_{12} has disappear here but it has to have f_{12}, f_{23} everything.

Now comes a lot of fun this is really beautiful term now we have to say that if I go back to partition function then I have to make two things how can I group them together into one term and then I can calculate how many of them are there.

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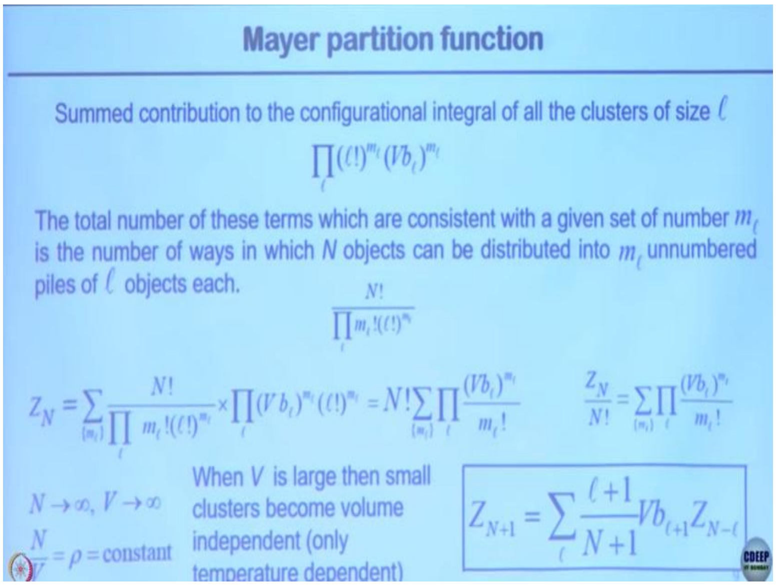

So, two steps and this is a little difficult but please try to think. So, some contribution of the configuration integral all the clusters of size l look at that sum over all the connected things. So now this is the quantity I want this is still very formal I am grouping them together I am not evaluating them please do not get it wrong. I am just grouping them together I am developing a language semantics to be used that is how a big problem is done.

A big problem is divided into bits and pieces divide and conquer I am dividing it now. The conquer part will come later okay so that division I have now introduced cluster integral it is called Mayer's reducible cluster integral and that now so what I need in the partition function is this part. That part is then bl l factorial V okay and all the particles there that I know how to do so then the sum contribution to configuration trigger the thing that I have written here.

All 3 particles are here that would be then all the factorial to the power m_l because m_l is the number of clusters of size l and all of them come with this same weight Vb_l by definition so Vb_l to the m_l. This you can just to work out one of them you will find this is exactly includes everything. Now comes the important part that so this is the total contribution so if I have m_l number and will have constraint on m_l.

If I have m_l number of cluster of size l it is then I am now is going to do a permutation-combination. I am going to say how many ways I can distribute or I can put essentially marbles into boxes and the boxes are my cluster of size l. So I have N number of particles I have to put them in boxes so in a it is a very famous combinatorics I think in one of the very popular problem in IIT-JEE in multinomial distributions actually very typical those who have done IIT this is one popular every 2, 3 years this comes even then is very difficult to do.
And then you find how many ways I can distribute that, that quantity is this quantity multinomial okay all right you have to do little bit yourself but it is not difficult just do it with a 3 particle you will be able to do if you like there is a lot of this particular part is lot of fun. Then I want to get the partition function so this is the weight of total weight come to the partition function contribution to the partition function all l number of clusters.

Those all, l like here all 3 all 2 and they how many of them will be given by this the total configuration of my system. So, what I have done now let us see that I have instant configuration and instant configuration I have $m_1 = 20$, $m_2 =15$ and $m_3 = 5$ then it will change because my cluster distribution will change I have to include all the cluster distributions. But each distribution this 20, 15 or so 5 they will come with a weight that weight is given here the total number of ways I can get that and this is the weight to the partition.

So that particular cluster size distribution contributes this much in terms of integrals to the partition function and these matches the number of ways I can form that cluster size distribution. So I have to now multiply these two and when I multiply these two then this b1 factorial l factorial get cancelled and I get this beautiful expression called Mayer's this is called Mayer's partition function

$$\frac{Z_N}{N!} = \sum_{\{m_l\}} \prod_l \frac{(Vb_l)^{m_l}}{m_l!}$$

So let me write this now right even now we have just on the way to do the things we have not solved the problem but we are on our way to solve it.

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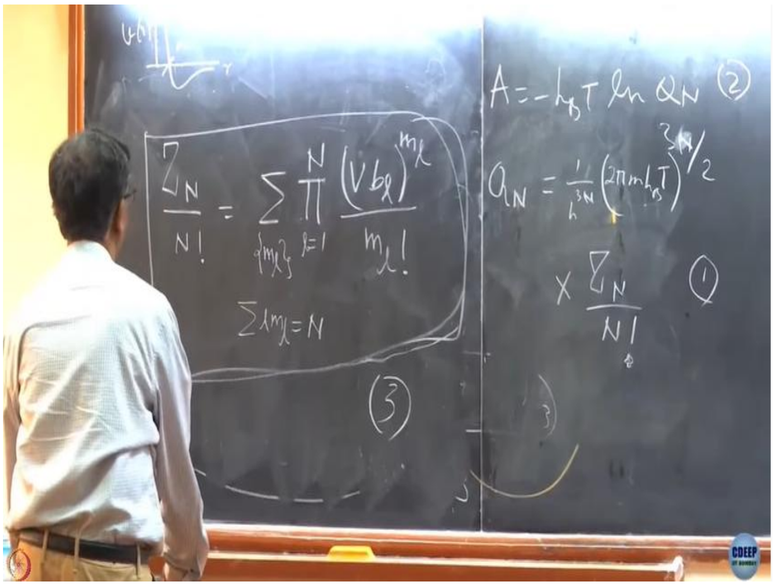

So Mayer partition function is the configurational part this is exact why it is exact because this is nothing but bunch of definitions okay but now from there one can start playing some very interesting games. So, ignore that last part here with not important at this point that means I am saying this part is not important at this point. So this is the one that we need to evaluate.

So once we know Z_N remember if I know Z_N then I know the canonical partition function and canonical partition function

$$Q(N,V,T) = \left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3N}{2}} Z_N$$

this is the canonical full canonical partition function and free energy is $F = -k_B T \ln Q$. So, this is the equation number 1 this is could be equation number 2 and this is the equation number 3 and this is called this one that you are saying is a fast expression of the cluster expansion and or the cluster decomposition and then one goes on doing the A.

So, in this decomposition of the partition function into smaller or simpler terms b_l is very strongly dependent on temperature because b_l is the integration over Mayer's factor it is also dependent on the volume because you know your total range of you are integrating of the total volume. So, when b clusters appear, they fill the surface or they fill the volume and this can be done many different ways one way may or did it will do otherwise through a exact recursion relations that one can solve this problem again bit by pieces. So, next part of the puzzle is to get the cluster integrals.

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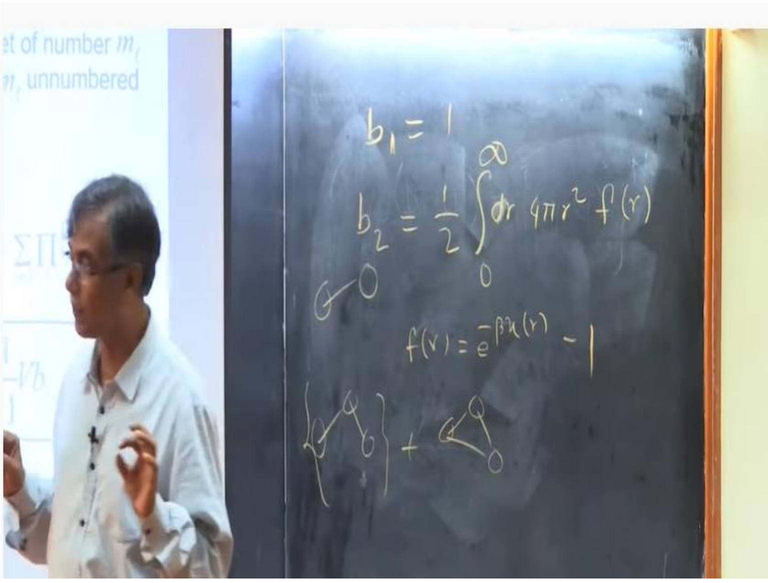

So, in cluster integrals we know $b_1 = 1$. Now I want to do b_2 and we so I can calculate b_2 now and $b_2 = \frac{1}{2}\int dr 4\pi r^2 f(r)$ so see that is what I see even in the two particles there we have to have a quadrature but I can trivially put and for a hard sphere I can evaluate it exactly. This one that becomes your secondary coefficient exactly that is one of the great achievements then when you go to b_3, b_3 has all these 3 particles.

So, this is a two-particle cluster that means this b_2 is this quantity. Now b_3 will be this bunch of bunches of this plus now if you choose to neglect these ring diagrams your problem is solved. All you need is f_{12} and that already shows gas liquid transition the condensation appearance of infinite cluster. So, the way theory always works you have to work very hard up to certain amount of term.

Then there are certain you are beginning to get your rewards and you begin to see how things happen how interactions make things different from ideal gas? How interactions even two particle interactions formation of trees because f_{12} like that kind of open diagrams are the trees how the trees come and they influence the thermodynamic properties of the system. What I am saying what you can do this is this is follow 1 to 23 that decomposes when you do the integration you connect you choose here then it will be this integral.

And this integral no the product of the two up to all the chain diagrams that you can do just trivial or is like a convolution is one it is no problem and that is why ring diagram suddenly becomes so much more even at that level it becomes so much more complicated up to chain diagram things are easy and this is a very common thing in all over many bodies. Ring diagrams we can still do there are certain ways to make certain progress it is when you have lines inside the ring.

So, this one now had become 9 dimensional I can reduce it to 3 and 6 dimensions but I have to do it numerically. But we can still make a lot of progress that we will continue to do. But I will change give you the slides and you please familiarize yourself little bit because what we will do from now from will show some very important class of relations cluster expression just does not mean this it also means expansion of density in terms of fugacity which is very important part of physical chemistry.

You can have an expansion of density in terms $\rho = \sum l b_l z^l$ that is exact that you can also do from grand canonical partition function and that expression or the pressure in terms of b_l Z_l the fugacity and elimination of these two cluster expansion gives you viral series. So, now for the first time you really begin to see and first time you see that why viral coefficients are used to extract the force field.

Remember the fast force field in this world was extracted from the real coefficient there was (()) (29:08) fast force field the basic ingredient is the molecular size then is the depth epsilon. So, the remember Van Der Waals made a mistake he got a size 8 times in the molecular size okay but what Van Der Waals did was actually building a kind of things attraction by hand and a kind of a priory which did not work out well.

So Mayer for the first time gave expression exact expression of viral coefficient then we study the temperature dependence viral coefficient which is very easy from the equation of state experimentally fitted to that gave you the Lennard-Jones potential 1940s that was the beginning of the our force field culture okay. Even now this is essentially one of the part of the things that one uses okay anything else we will stop here now.