Basic Statistical Mechanics
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Lecture – 32
Cluster Expansion and Mayer's Theory of Condensation Part-5

We have been discussing and deliberating on the ideal gas law where molecules do not interact. We have done monatomic gas which has given rise to an important expression of entropy of translational degrees of freedom which is Sackur-Tetrode equation. Then we did diatomic gas.

But to calculate the vibrational partition function, one needs to model the bond as harmonic oscillator. Then the solution from Schrödinger equations gives us the expression of the entropy and free energy and specific heat which turns out to be extremely important in context of the specific heat of solid and crystalline and amorphous solids and that is the way to think. Then we did polyatomic, but however all these ideal gas the molecules could be reach internal structure like in collateral molecules in water, methane and sulfur dioxide or methanol.

However, they are non-interacting that means the molecules are modeled as atom thing they can pass through each other, they do not see each other. Now in a high temperature and in low density the majority of the contribution to face things or to partition function come from non-interacting part. So this high temperature or low density gas works out quite well you know although they have this ideal gas is not a poor approximation yes it breaks down.

But as soon as you enter in dense liquids or dense gases, the molecules are non-interacting. It was very, very difficult you know people realize that very quickly and they were trying to get around it by this solid they get around by doing a bit by normal mode approximation like it was done by Einstein and Debye then in the quantum cases this Debye-Einstein statistics and Fermi did the studies, that was very useful by explaining superfluidity.

But that was also again we did not do to consider interaction we went to a representation and where we could do like you know in statistics it is just non-interacting particles in both statistics. I am suggesting it will be so important coming electron gas, but there is free electron gas. We did not have to take interaction into electron and data. It was like that till 1935or 1936.

But in 37 however a very significant development took place and that came from Joseph Mayer. Mayer then realized one very important thing that in order to understand the real gases and in order to affect gas liquid transition he was not thinking of liquid solid transition that was far from you know he was really just tried to do real gases, dense gases because you know from van der Waals equation of state.

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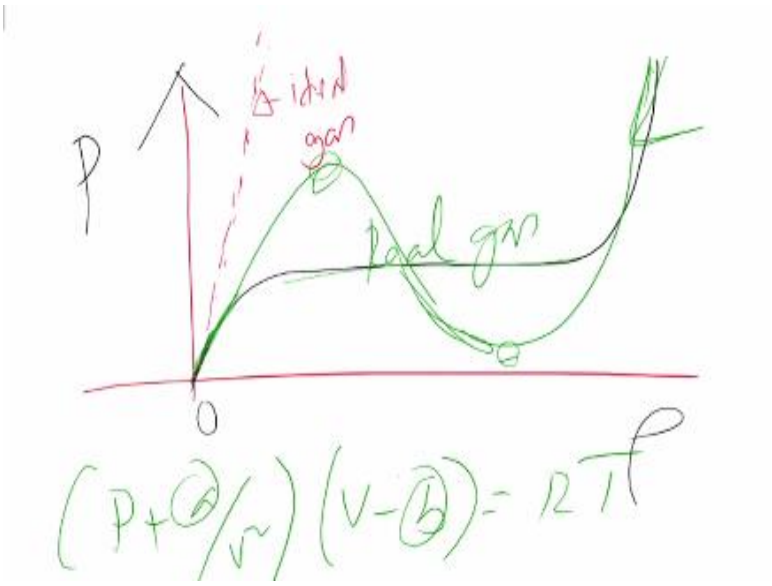

We know from van der Waals equation of state that if we can plot pressure against density then at very low density part $(\rho \to 0)$ it behaves like an ideal gas then it bends and then it undergoes a fresh transition with increasing density. So real gas bends from here then it bends like this and then it flats this is coexistence and this is the liquid.

However, Van Der Waals then tried to describe this behavior by a wonderful equation which is known as Van der Waals equation of state.

So Mayer was interested to describe this departure the departure from the ideal gas and Mayer just like van der Waals so before that Van Der Waals did that. Van Der Waals took an interaction and repulsion in molecule. So Mayer already knew that how to proceed he knew that we have to take the molecules even if the sphere they attract each other in intermediate distance very far of course they do not interact.

And strong repulsion arises when the molecules come very close to each other. The equation of state is as follows $\left(P+\frac{a}{V^2}\right)(V-b)=RT$.

In the van der Waals equation of state, where a talks of attraction b is the size of the molecules what is the size of the molecules that is nothing, but because they repel each other, the repulsion defines the size of the molecule diameter of the molecule.

So Mayer knew that Mayer knew that this is the way to go that I need to have attraction and at intermediate distance I need to have repulsion in very short distance when the molecule touch each and their interaction has to fall to zero when they move farther, but how to go about it. Van Der Waals did it chronologically remember he said okay the total amount of volume accessible to a molecule is total volume – the volume of individual molecule.

And then when a molecule going to hit the wall to different impression remember he was still following the Maxwell–Boltzmann kind of a kinetic theory picture of pressure the pressure because molecules interact molecules go and hit a wall and that molecule is pulled back because there are certain other molecules nearly to be attracted. So the ideal gas with a pressure P now that pressure gets decreased and volume get decreased.

So basically what he wanted to added okay I want a review affective pressure P and the affective volume P so that I get at it so still working PV equal to ideal gas law, but then he said okay the V actually is little reduced and the pressure that I nearly get that pressure would be if I want to get the ideal pressure then I had to add this terms to get the ideal. So I want to write PV = RT but P and V are different because of the interaction.

So then he got there that is the logic he gave to van der Waals equation of vector, but that will never work because we now need to we need a molecular description we are talking of microscopic, we are going to have a not this kind of hand waving argument which works reasonably well, but still hand waving. We want to have real molecules, real interaction potential that how do we go about it there is nothing there before Mayer did it. That is why Mayer contribution is so important and that is why he was spending a time on discussing Mayer’s theory.

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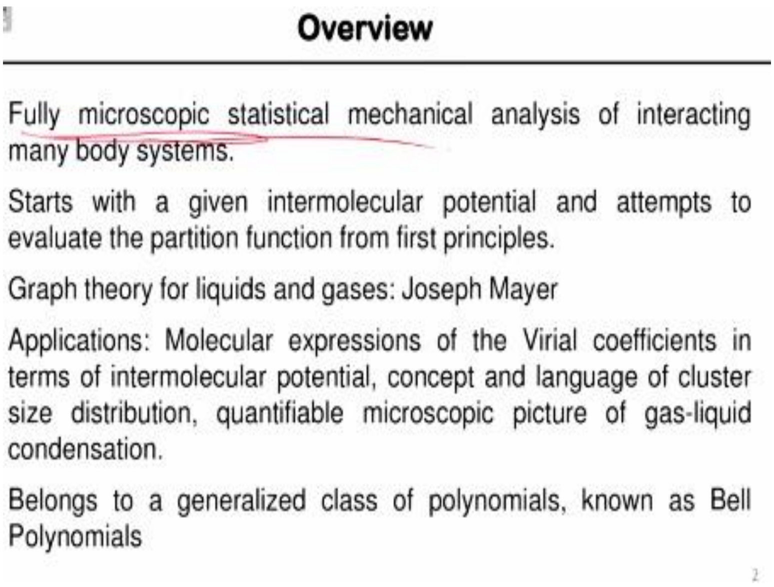

Overview

Fully microscopic statistical mechanical analysis of interacting many body systems.

Starts with a given intermolecular potential and attempts to evaluate the partition function from first principles.

Graph theory for liquids and gases: Joseph Mayer

Applications: Molecular expressions of the Virial coefficients in terms of intermolecular potential, concept and language of cluster size distribution, quantifiable microscopic picture of gas-liquid condensation.

Belongs to a generalized class of polynomials, known as Bell Polynomials

Okay we want a fully microscopic statistical mechanical analysis for interacting many body systems and what do we mean by interacting many body systems that again go down to a little bit now and let us see.

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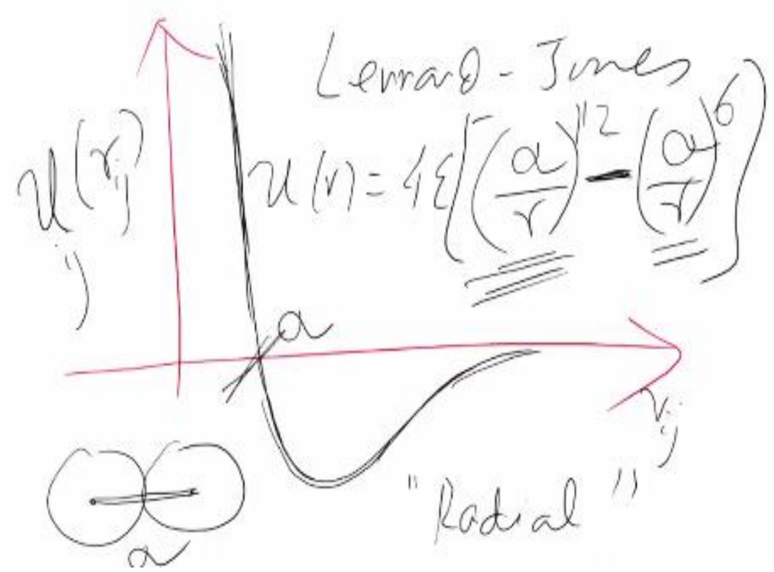

So I have a potential with the form $u(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$. In the interaction potential $\left(\frac{\sigma}{r}\right)^{6}$ denotes the attractive term and $\left(\frac{\sigma}{r}\right)^{12}$ is the repulsive term.

So this is 1 over 12 part and this is where the molecules kind of touch each other to reach the molecular diameter sigma and this is sigma then it presume the energy goes up when they separate a little then there is an attraction it is called London forces because of the induced dipole-induced interaction and I kind of go into that and then it goes like that. We will at one point of time talk of intermolecular forces.

But this is the kind of thing that I have one important thing to note that these are radial potential that it depends only on R there is no angle so they are just sphere simplest possible thing. So if we have this kind of interaction potential then you want to so to have start the intermolecular potential given intermolecular potential so I give the Mayer drawn a simple one.

Then we attempt to evaluate the partition function from first principle like sum over energy level interaction over $e^{-\beta H}$ that is the thing. So that was the thing that Joseph Mayer did and we are going to do that in the process introduced what to consider first graph theory of liquid and gases and the cluster expansion and he got a huge number of results that came out of this thing not only that, that made the beginning of classical statistical mechanics.

So it gave a designation of virial coefficients and it explained many of the things of van der Waals, language of cluster, size distribution of clusters which is so popular and microscopic picture of gas liquid condensation all these things came out and so this is interaction and we already done that.

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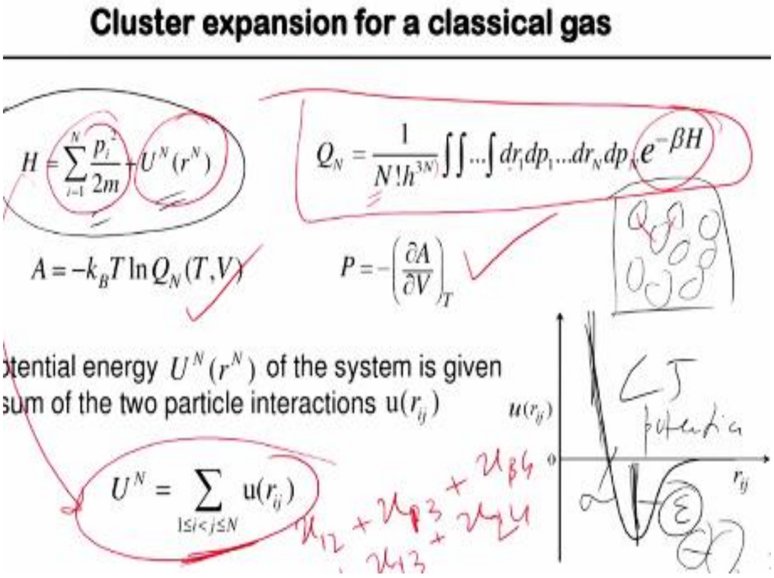

Cluster expansion for a classical gas

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

$$Q_N = \frac{1}{N!h^{3N}} \int\int \ldots \int dr_1 dp_1 \ldots dr_N dp_N\, e^{-\beta H}$$

$$A = -k_B T \ln Q_N(T,V)$$

$$P = -\left(\frac{\partial A}{\partial V}\right)_T$$

tential energy $U^N(r^N)$ of the system is given
sum of the two particle interactions $u(r_{ij})$

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

Now so let us start working now we have the N number of particles so in a system with volume V and have N number of sphere there not too low density and the spheres are interacting with that with that with the energy on potential and this is the molecular diameter

σ so two spheres are touching that it distance it goes little bit faster than drawn here and this is the depth of the maximum attraction potential and this is epsilon.

So that this is epsilon that epsilon this is epsilon. So we have this Hamiltonian kinetic energy + potential energy and we have to evaluate with that Hamiltonian we have to evaluate this partition function we have to evaluate this list and look at that I have these are vectors I have

$$Q = \frac{1}{N!}\frac{1}{h^{3N}}\int\int dq^N dp^N e^{-\beta H}$$

As we told in the very beginning that that this is a formidable thing of statistical mechanics to evaluate this integral this is the holy cradle of statistical mechanics to evaluate the partition function. If I have partition function I have everything I have free energy, entropy, I have specific heat, I have compressibility, but how do we get the partition function that is a problem. So whenever you try to do something so formidable as this one the idea is to divide and rule and divide and conquer and we will do that divide and conquer.

So then this is a partition function if I get the partition function I get the free energy and I get the pressure and the equation of state and the beta h this thing now this h is written this is the kinetic energy and this is the potential energy is sum over so we assume the potential energy pair with anything that very good approximation, but still a simplification goes wrong now and then, but perfectly okay with start with the sphere wise addictively.

That means total potential energy can be as a sum or I do not have to look at the notation here so that avoid double counting we have to say that the i runs in the range (1 to N-1) and j runs (i+1 to N). The terms will be written u_{12}+ u_{23} + u_{34} + u_{13} + u_{34} or u_{14} like that that means you have 13, 14 then 23, 24 like that so that I do not count it twice. So with this U_N now formidable because of the Lennard-Jones I said tau to calculate the partition function.

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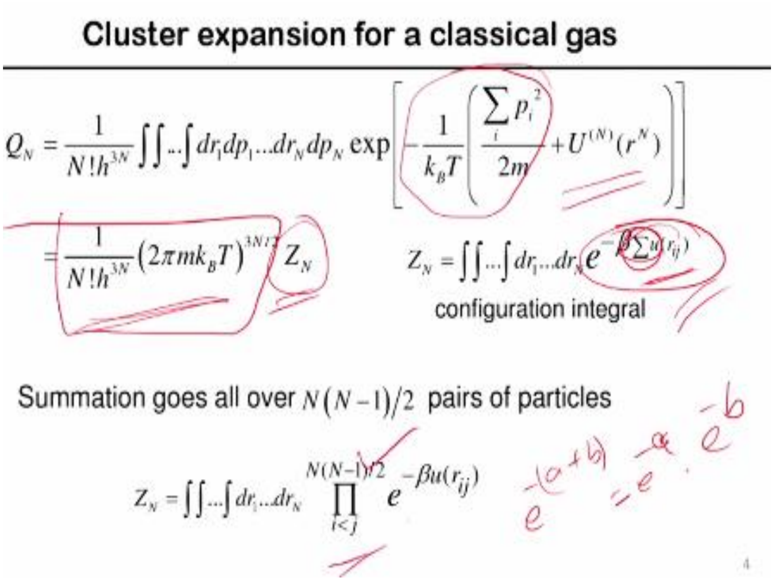

Cluster expansion for a classical gas

$$Q_N = \frac{1}{N!h^{3N}} \iint\cdots\int dr_1 dp_1 \ldots dr_N dp_N \exp\left[-\frac{1}{k_B T}\left(\frac{\sum_i p_i^2}{2m} + U^{(N)}(r^N)\right)\right]$$

$$= \frac{1}{N!h^{3N}}(2\pi m k_B T)^{3N/2} Z_N \qquad Z_N = \iint\cdots\int dr_1\ldots dr_N\, e^{-\beta\sum u(r_{ij})}$$

configuration integral

Summation goes all over $N(N-1)/2$ pairs of particles

$$Z_N = \iint\cdots\int dr_1\ldots dr_N \prod_{i<j}^{N(N-1)/2} e^{-\beta u(r_{ij})}$$

$$e^{-(a+b)} = e^{-a} \cdot e^{-b}$$

What do I do it now so I write down the partition function again putting the whole thing here. Now I immediately notice a classical partition function I can evaluate this part like I did in translational motion of gas.

And we know that part is gives separate actuator position and you can see the decomposition of beautifully since free energy is a log of that term they already start decomposing log this part the ideal gas part and the interacted part and this part is called the configuration integral is now contains all the non trivial contribution all the non trivial contribution of the affective interaction for the system.

This part makes gas to condense the liquid that cause liquid to go crystal this interaction part with let you and me to talk and work it out. So that is all in this configuration integral. So we are now going to find out how to evaluate that thing and we just rewrote that there are this sum like $e^{-\beta u_{ij}(r)}$. Now, we can write that quantity as a product because $e^{-(a+b)} = e^{-a}e^{-b}$.

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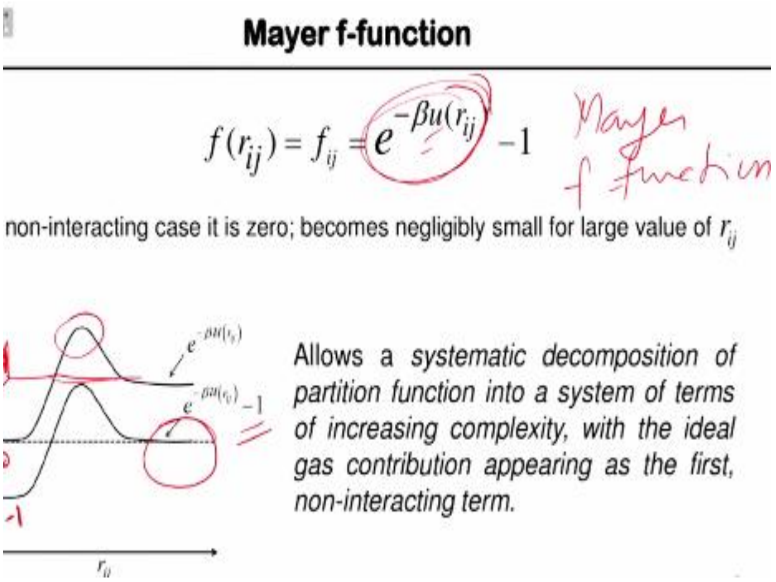

Mayer f-function

$$f(r_{ij}) = f_{ij} = e^{-\beta u(r_{ij})} - 1$$

Mayer f function

non-interacting case it is zero; becomes negligibly small for large value of r_{ij}

Allows a systematic decomposition of partition function into a system of terms of increasing complexity, with the ideal gas contribution appearing as the first, non-interacting term.

Now difficulty of doing this integration was people tried that this thing due to potential unfortunately goes to long distance goes to 0 and potential goes to 0, potential that goes to 1 and that is bad news for us because I have to integrate and something which is < 1 because $e^{-\beta u}$ can be < 1 in short distance greater than 1 in intermediate distance, but then tampers off to 1 because $e^{-\beta u}$ it is a very complex function.

So Mayer did brilliant thing at that point and he said okay this integrals that I am trying to do in configuration integral I am not convergent because they are getting lot of difficulties because if they long separation they are coming up with the contribution unit contribution 1 and that is not a good thing for me because I cannot do I want to separate it out so that I do not have to worry of the long separation part.

So introduce this function which is called Mayer f function which is f so this is called Mayer f function. He said okay let me write the following way $f_{ij}(r_{ij}) = e^{-\beta u(r_{ij})} - 1$. So that now r going to infinity r_{ij} going to separation between 2 molecules became very large, $e^{-\beta u}$ going to to 1 and then f_{ij} (r) going to 0 so this is embodied here.

So it is a $\beta u(r_{ij})$ which is causing the problem was going and this is actually it was this is 1 it was stopping at 1, but now I have taken it out 1 so it start negative it was before that it was starting when it was infinity you at short distance infinity it was starting from 0 and is intermediate distance when there attraction is becoming > 1 now I am taking out so it starts from – 1 and it can go above 1 also depending on this depth of the attraction, but now in long distance is going to 0 this is 0 line is going to 0.

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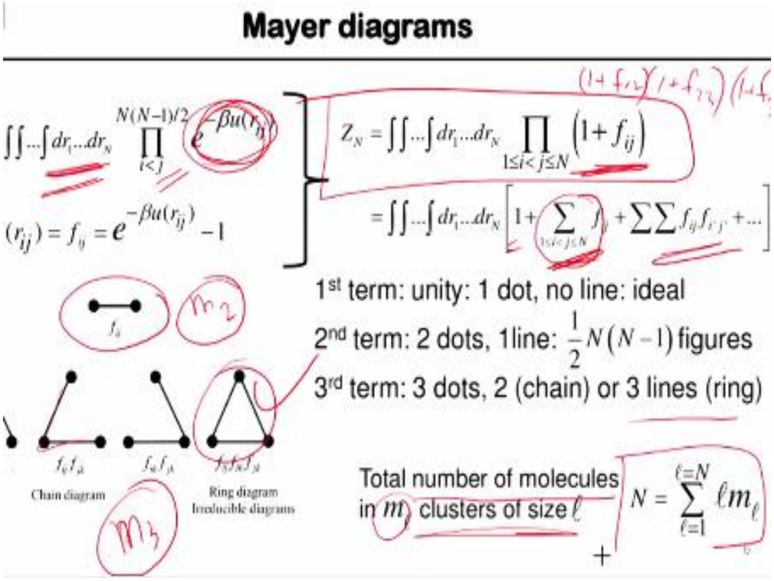

Mayer diagrams

$\int\int...\int dr_1...dr_N \prod_{i<j}^{N(N-1)/2} e^{-\beta u(r_{ij})}$

$(r_{ij}) = f_{ij} = e^{-\beta u(r_{ij})} - 1$

$(1+f_{12})(1+f_{13})(1+f$

$Z_N = \int\int...\int dr_1...dr_N \prod_{1\le i<j\le N} (1+f_{ij})$

$= \int\int...\int dr_1...dr_N \left[1 + \sum_{1\le i<j\le N} f_{ij} + \sum\sum f_{ij} f_{i'j'} + ...\right]$

1st term: unity: 1 dot, no line: ideal

2nd term: 2 dots, 1line: $\frac{1}{2}N(N-1)$ figures

3rd term: 3 dots, 2 (chain) or 3 lines (ring)

Total number of molecules in m clusters of size ℓ

$N = \sum_{\ell=1}^{\ell=N} \ell m_\ell$

So it is very good now I can try to do this integration then what Mayer did something really very, very interesting he said okay let me write the partition function now with a partition function is written as the product of now only position as

$$Z_N = \int dr_1....dr_N \left[1 + \sum_{1\le i<j\le N} f_{ij} + ...\right]$$

So my canonical partition function it becomes like that and then beauty is that I can decompose it now I can do that look I write it out like let us say 3 particles f_{12}, f_{23}, 3 particles system just let us consider that we have N = 3, 3 particles then I have first term is 1 second term is f_{12}, f_{23} then there are another set of particles they are binary term f_{12} f_{23}, f_{23}, f_{31}, but there is one term which is f_{12}, f_{13} all 3 are present.

So this is now done here is symbolically written you know 1 comes then these are the isolated terms which is 12 + 13 + 14 then these are the product terms. Now Mayer introduced these following to beginning of the graph theory and this is as far as I know the first application of graph theory of statistical mechanics. Is it okay first term which comes with a value 1 it is just 1 dot second term which is term are 2 dots and joined by line and line is a Mayer function then there are 3 dots and they are changed and there are 3 dots and I can calculate the total number of and then he said okay.

Let me now consider that total number of single particles as M1 this guy which is a cluster of size 2 total number of particles that m2 then total number of particles of then these things we call them m3 which includes this one. So now ml is the number of clusters of size l, but does not made any distinction where there is a simply connected doubly connected and then I can of course write.

And we are beginning to see something that kind of things we played the game in going micro canonical to canonical that kind of game we are going to play because these are constraint that will come in my partition function and I will do exactly like that I will try to write total number of ways I can distribute particles to this cluster and then you can imagine that I can have the constant and I will get it like Lagrangian undetermined multipliers and then we have done it before then what Mayer did okay we did something very smart.

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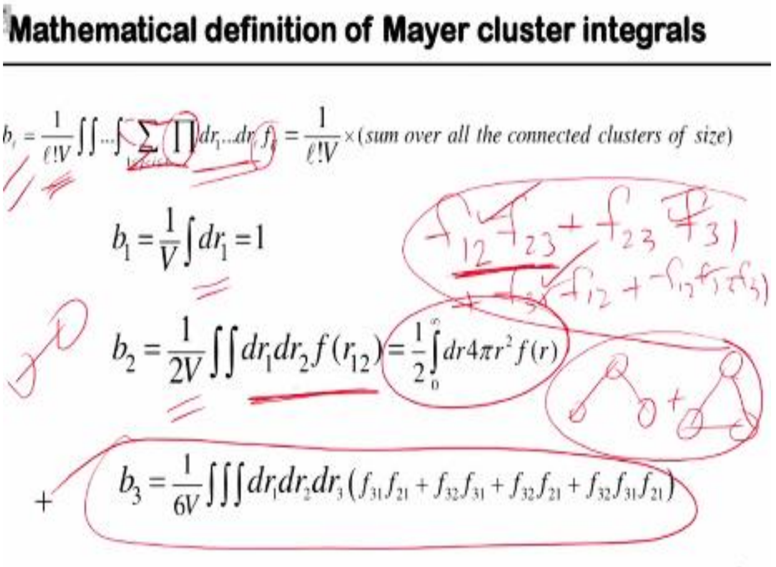

Mathematical definition of Mayer cluster integrals

$$b_\ell = \frac{1}{\ell! V}\int\int\ldots\int\sum\prod dr_1\ldots dr_\ell f_{ij} = \frac{1}{\ell! V}\times(\textit{sum over all the connected clusters of size})$$

$$b_1 = \frac{1}{V}\int dr_1 = 1$$

$$b_2 = \frac{1}{2V}\int\int dr_1 dr_2 f(r_{12}) = \frac{1}{2}\int_0^\infty dr 4\pi r^2 f(r)$$

$$b_3 = \frac{1}{6V}\int\int\int dr_1 dr_2 dr_3 (f_{31}f_{21} + f_{32}f_{31} + f_{32}f_{21} + f_{32}f_{31}f_{21})$$

He said well I have defined l number of ml at a number of clusters of size l. Now can I now give a way to cluster of size l he said okay I will do that because he now looked at the partition function he thought that they had nothing product and fij so now he said that I will now have all the integrals which are connected all the connected diagrams that state 3 particles f12, f23 + f b1 + f b1 + f12 + f22, fb1.

So these are all 3 particle clusters they are all connected they are chain diagram like this and these are chain diagram and venn diagram. So he said I put them all together and weight of this to the partition function I call it b_l the cluster integrals and then I define it as 1 over l! V the V is very important for reason I would say for mobilization and then I have integral over and b_1 and I have the product this is the product f_{12} that is the product.

Then this is sum and this is sum 1, 2, 3, 4 you just write it down and you will see it work out beautifully then b_l are sum of all this things. So for one single particle there is l! V and there is nothing inside dr I get 1 2 particles is ring I can do that and I say 1 over 2V and dr12 fr12 now I can change my coordinate system. I can go to particle 1 and say that this become already it is 1, 2 did becomes 1, 2.

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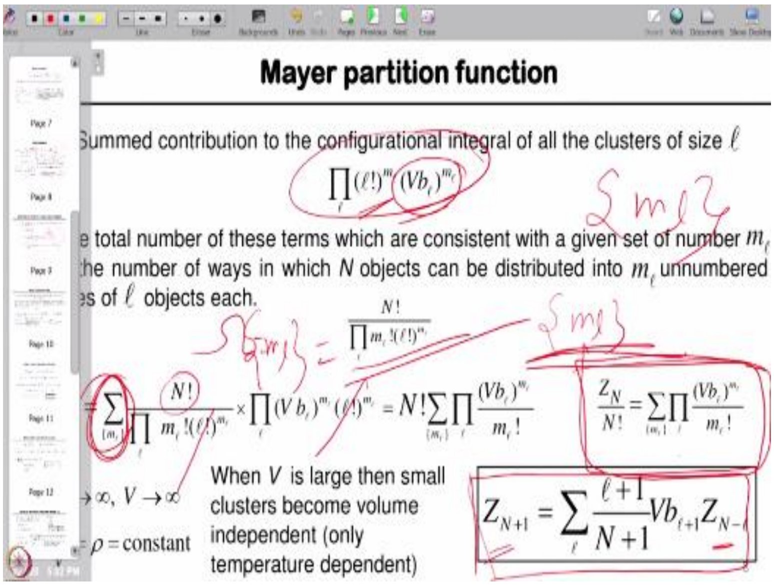

Mayer partition function

Summed contribution to the configurational integral of all the clusters of size ℓ

$$\prod_\ell (\ell!)^{m_\ell}(Vb_\ell)^{m_\ell}$$

$\{m_\ell\}$

e total number of these terms which are consistent with a given set of number m_ℓ
he number of ways in which N objects can be distributed into m_ℓ unnumbered
es of ℓ objects each.

$$\{m_\ell\} = \frac{N!}{\prod_\ell m_\ell!(\ell!)^{m_\ell}}$$

$\{m_\ell\}$

$$= \sum_{\{m_\ell\}} \frac{N!}{\prod_\ell m_\ell!(\ell!)^{m_\ell}} \times \prod_\ell (Vb_\ell)^{m_\ell}(\ell!)^{m_\ell} = N!\sum_{\{m_\ell\}}\prod_\ell \frac{(Vb_\ell)^{m_\ell}}{m_\ell!}$$

$$\boxed{\frac{Z_N}{N!} = \sum_{\{m_\ell\}}\prod_\ell \frac{(Vb_\ell)^{m_\ell}}{m_\ell!}}$$

$\to \infty,\ V \to \infty$

$= \rho = \text{constant}$

When V is large then small clusters become volume independent (only temperature dependent)

$$\boxed{Z_{N+1} = \sum_\ell \frac{\ell+1}{N+1} Vb_{\ell+1} Z_{N-}}$$

And then once you decompose like that the summed contribution to configuration integral because that is what we are trying to do the total configuration integral of cluster of size l so it is a graph theoretical decomposition that becomes this quantity. So there are ml clusters of size l and they come with a weight b_l and then Vb_l to the power ml where m_l is the number of clusters of size l and clusters of size l all of them put together.

And they bring together a size ml so that becomes that and this part is I have ml cluster each of them l so I can now in classical statistical mechanics I can rearrange them. So l factorial is the way I can distribute and there ml such cluster in my system at any time their ml are clusters of size l so they are factorial to the power ml so that becomes that. Now comes the important thing that how do I but these clusters can be many different size.

And they are fleeting they are not real clusters they are clusters which are mechanical clusters because they are connected by this bond f bond Mayer f bond. So since the arrangement is possible so out of total N number of particles how many ways I can count this cluster that is

N factorial by this just a combination where all of you have done in the school, multinomial. So now this is the way of one set of m_l.

And that one set of m_l I can do this is the number of ways Ω and then I need to make the product of partition function then the partition function is 1 over l factorial ml at these ml these ml cancels and N factorial remains here and then I get Vb_l to the power m_l at the sum over all possible combinations of this kind then I get this beautiful expression Vb_l is the exact and this is called Mayer partition function.

Now one can go do a lot with this thing we still have not done one thing so we learn that we have not calculated b_l we have not evaluated this things that what Mayer did, but in the process to introduce the cluster integrals there is recursive way you know the b_l then this actually nothing, but polynomial called dell polynomial and then that is described in my book then one can have a beautiful relation recursion relation between the energy which is allowed between Z_{n+1} and lower series.

So we can build up the configuration integral which is the total non trivial part of the partition function. So if I know this cluster integrals if I know this is called reducible cluster integrals then I can calculate the partition function.