Basic Statistical Mechanics
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Lecture – 30
Cluster Expansion and Mayer's Theory of Condensation Part-3

We derive PV = RT we derive the CV = 3 / 2 R all these things then we also did the diatomic in monatomic we did the entropy which is the Sackur Tetrode equation which is an extremely useful as I told you of when we did it we thought useful at all, but I told you that we are using it every day like in paper we are writing now on entropy of water, we use this entropy of Sackur Tetrode equation that expression we use.

Amazing that how that seemingly innocuous simple expression can be used in a very complex situations that is then we did harmonic oscillator and we got an expression for entropy of oscillation and that again goes over to entropy of the specific heat of solids for Einstein and Debye did, same expression. I am just trying to tell you the rich that you do one tiny little thing through statistical mechanics.

There is no other way you can do that this, Einstein or Debye, Einstein theory or specific heat comes through this partition function that is what Einstein did, he just calculated the specific heat through V to the power – ½ Hμ/ k_B T / 1 – e to the power –Hμ/ k_B T square, and you have a density of states g **Ω**, then you integrate that. Then we did entropy and specific heat and specific heat of, that was did by Einstein, entropy of the vibrational mode is also very important.

So when I calculate entropy of solid or free energy of solid, how do I do it? Theoretically, I calculate the enthalpy which I can do through computation simulations or I can some kind of Madelung constant, remember the summing over all the interactions they charged and computer simulation we can do that I take an FCC lattice and I calculate the interaction energy by adding up all the interactions.

But then I need the entropy, you would think that entropy of solid is very small not quite. Entropy of solid may be significant because of the low frequency oscillations and vibrations in many solids, then you again use your entropy from the harmonic oscillators. Your normal modes are your harmonic oscillators that is the first thing solid state physics you learn, like normal modes in a linear approximation.

These things go very well in linear response theory that is very, very important to understand. So free energy of solid if you want to calculate, we just published a paper very long paper 10 years' worth of work with my Japanese collaborators, Shinji Saito and I Ohmine and where we tried to get the super cool liquid and glass the free energy of the thing and specific heat and entropy and we use this exactly this expressions will derive here.

The entropy we remove the kinetic energy then we diagonalize if they disorder thing we get what is called quench normal modes and we then use those normal modes to calculate the entropy and the specific heat and that was came out I think earlier this year or end of last year or earlier this year long paper. Now many, many people are doing that so this specific heat and entropy of harmonic oscillator that you learn in here is used in practical applications in many, many cases.

Then comes the rigid rotator what they did in rigid rotator and we assume a rigid rotator because we assume that rotation and vibration are uncoupled which we know is not correct because in undergraduate physical chemistry when you do infrared spectroscopy, you get PQ all those branches, which are because of vibrations and rotation talk with each other, Coriolis coupling or centrifugal thing that he rotated very fast then the bond gets stretched or compressed.

The vibration and coupling is a wonderful stuff tells you lot of thing most importantly it tells you about the anharmonicity of vibration and that is a very, very important quantity for our understanding of bond breaking and the activation barrier. All these are very neatly and very successingly coupled and is a unified concept that we use one side spectroscopy and other side statistical mechanics have a side quantum chemistry and quantum mechanics.

Rigid rotator entropy and specific heat we do not have a simple analytical expression like unless we make low and high temperature assumptions when you do that we get expressions and then when you do the calculations you find a molecule like water the entropy from rotation about 30%, I showed you the table, but all these things that we did I am just summarizing and reminding you because they are very important things were non interacting limit.

I have a rigid rotator, I have a diatomic molecule, I have a monatomic molecule, but they are interacting within themselves, there are intramolecular forces, but there are no intermolecular force these molecules did not interact. However, you would not have water on your human body unless molecules interact with each other. You would not have a glass, you would not have a crystal everywhere molecules interact.

That is why I quoted Pauli I was fond of saying that I created condense matter in the repulsion were not there it would not have found. Crystal the hard spehe crystal this improved potential is the role our model of studying solid state or liquid solid transition. So now how do I go about doing interactions, I know the partition function I know the partition function is sum over e to the ei / k_BT.

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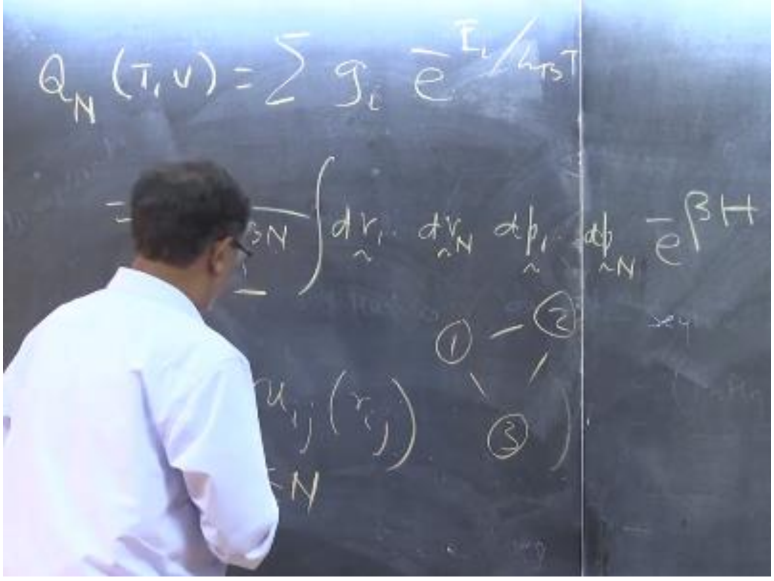

Today I will give a flowchart that is what I am talking so much and then we will do the calculations which are little formidable. So one will be in rigid rotator we found the degenerating factor remember 2 j + 1 that was in rigid rotator you have done in quantum mechanics, harmonic oscillator diatomic this gi = 1 particles in a box gi = 1 other way to do is classical indistinguishability Boltzmann put by hand.

And this is the one that we know after doing quantum. The best way to think about it to get this factor is to do the quantum and then come to classical from quantum which is an exact way of doing and you find that you have mastered that. This is other way that you can have a conceptual saying okay this is normalization of volume of a cell, but that kind of thing I do not particularly encourage.

I would rather say do the quantum and then come to classical and the Hamiltonian this is the total Hamiltonian kinetic energy and potential energy and this quantity is the many times we do not write all these thing we just write ij here and we put a prime here. That is the stat mech people standard notation you just do that then you do not have to write all this it is understood. So we are further assuming that interaction is a 2 body interaction means we are saying that if I have a 3 particles 1, 2, 3 then this interaction is sum of pairwise interaction.

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

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

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

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

$$Q_N = \frac{1}{N!h^{3N}} (2\pi m k_B T)^{3N/2} Z_N$$

There could be 3 particle interaction also which are important in some cases, but understanding much of condensed matter physics we do not need this 3 body interaction that is a fine tuning. We need sometimes, but like doing a liquid silicon we need the 3 body interaction, but much of the time that because when you are kind of they are metal or metalloid kind of things in 3 body or 4 body interaction play important role.

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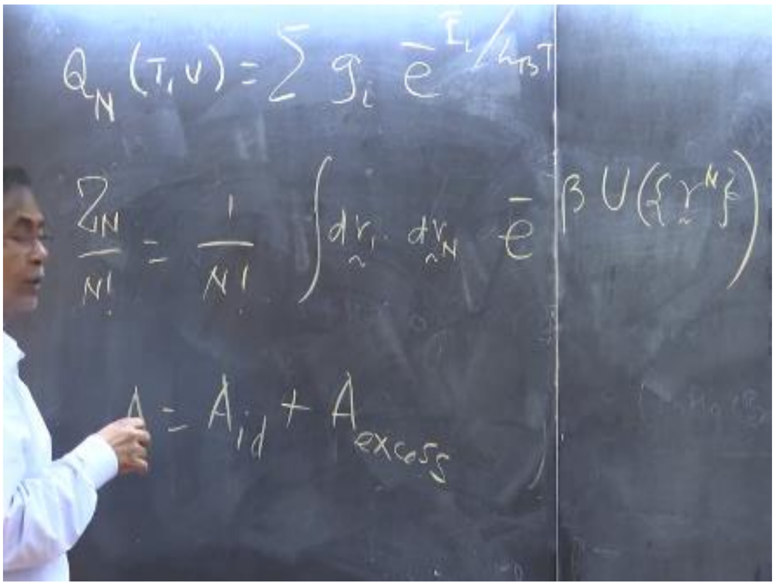

So now it is popular saying let the bull by the horn that means you have to do these complex things this integration where in a classical thing we can do the momentum integration because this is uncoupled it is a bunch of Gaussians I do not need to write that I will be cavalier about it because I know how to do it. So basically this is the thing I need to do so again if I need I will put them back I do not care about them.

So I will write Z_N / N ! I will not write the other thing 1 / N !. So this is the configuration integral I have taken out the momentum part you understand that I have integration over β h β h Hamiltonian has kinetic energy and potential energy they are uncoupled. The kinetic energy part π square / 2 M they are nothing but Gaussian not only that i and j are uncoupled x, y, z are also uncoupled.

So I can do the 3N integrals and then I get lambda to the power, lambda is de Brogli wave length 3 N / 2 that is a partition that I am not just writing because that is the part which give Sackur tetrode equation and PV = Nk $_B$T ideal gas, but right now I am not interested in that. Many times when you do the free energy we write free energy A = A ideal + A excess and A ideal because this is ideal part comes as a product here correct.

You understand that because e to the – β h is the exponential so that become product then I take the log free energy log of partition function and then the product comes out separately that I call ideal A ideal is the ideal gas free energy which we did and this is the excess part and this is the interesting part. This is a part we are now trying to do. So this part comes from the interaction summed particles and which is highly non trivial.

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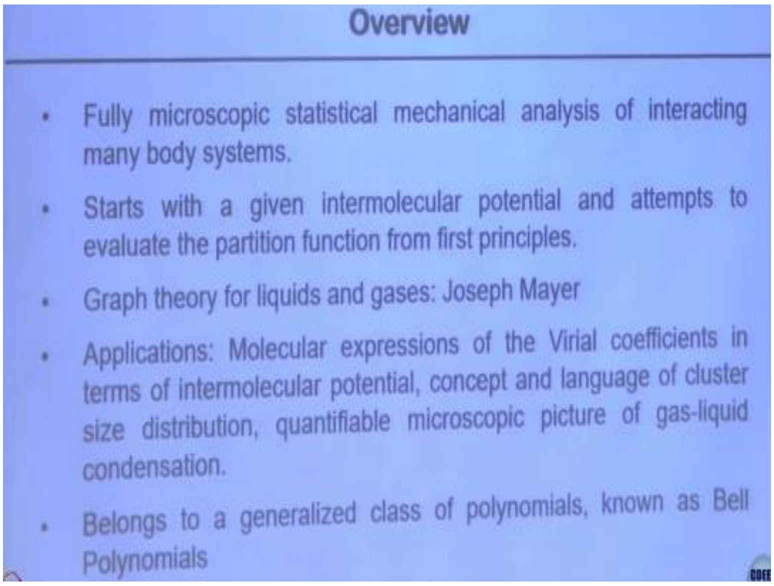

Overview

- 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

I will go back and forth I will use this a little bit then I will go back because I want to give a flowchart. I want to tell you how the thing is done so that you get the big picture and then doing the equations and filling this big picture, but going directly to the details does not help if you do not get the big picture because this is a big picture that will stay with you the understanding. The details will be remained in books which are always look up that is the way actually to do any interesting stuff.

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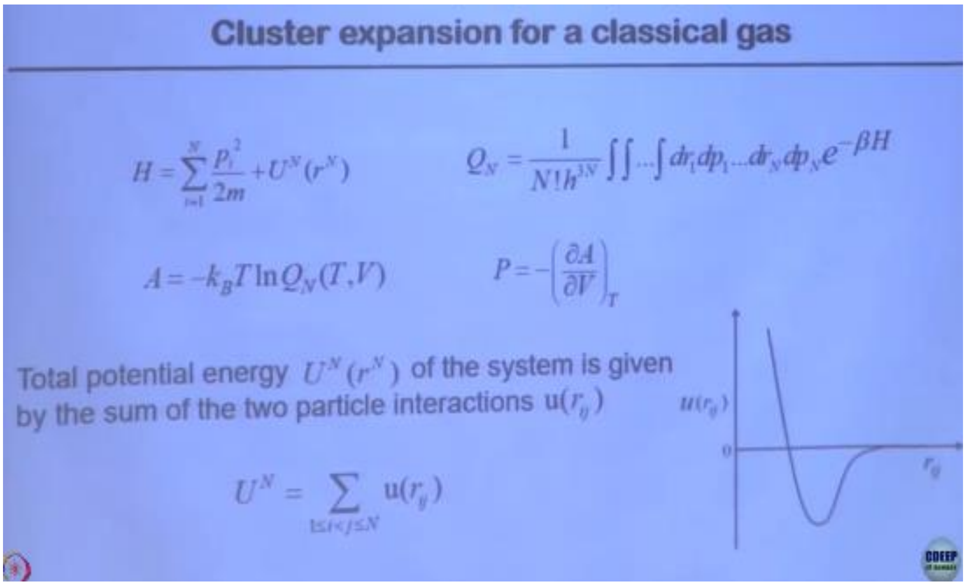

Cluster expansion for a classical gas

$$H=\sum_{i=1}^{N}\frac{p_i^2}{2m}+U^N(r^N) \qquad Q_N=\frac{1}{N!h^{3N}}\int\int\dots\int dr_1dp_1\dots dr_Ndp_Ne^{-\beta H}$$

$$A=-k_BT\ln Q_N(T,V) \qquad P=-\left(\frac{\partial A}{\partial V}\right)_T$$

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

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

So we did this here this, this and this interaction potential, we discussed at length and this is the pair wise interaction potential this is the total potential energy and as I just discussed here this is the quantity and I said I do not care about this part because this part is the ideal gas part. So when I take the log of that free energy I get and then I get everything from the

Helmoltz free energy. The reason you work in microcanonical ensemble is because I get entropy and pressure by taking derivatives.

It is far more complicated in getting in grand canonical partition function and doing of course is very difficult because you have no way to go unless you do particle in a box, but then in other systems with continuous potential you have no way to go when you go to microcanonical ensemble.

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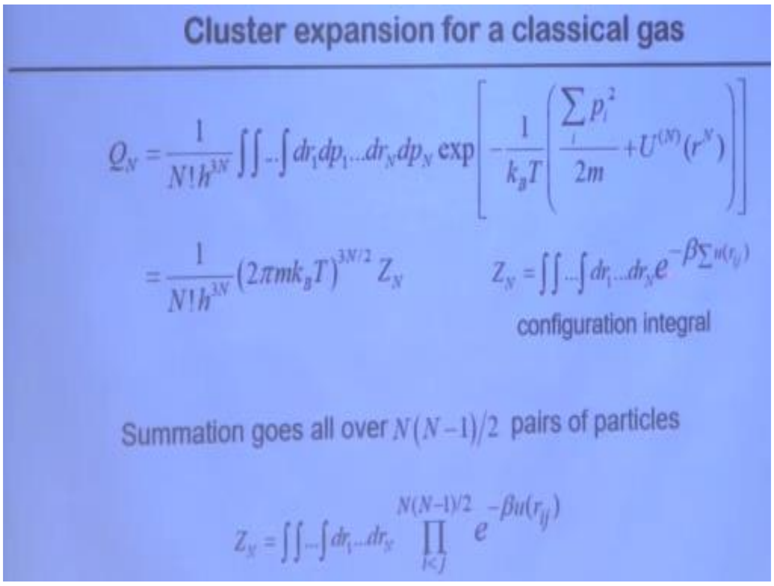

Cluster expansion for a classical gas

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

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

configuration integral

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

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

So this is the thing then so as I said before that this comes in a exponent u and u is the sum so I put that sum here then when I put this sum here this is like that then I realize that this quantity is nothing, but product the sum here this sum comes out as a product and then I looked at this integral and I had to do this integral in a very, very difficult way because two things these integral first is potential is fairly complex.

And to make it worse this potential goes to 0 when separation between 2 particles i and j becomes larger which indeed it should be it should go to 0, but that creates the problem is that I have to do this integral and if I do that integral then that integral goes to 1 you do not want that, you do not want to asymptotic part goes to 1 you want that asymptotic part goes to 0 and that is what Mayer did then it saturates unity that becomes hard. So partition function fails to converge also difficult to do then introduce Mayer f function.

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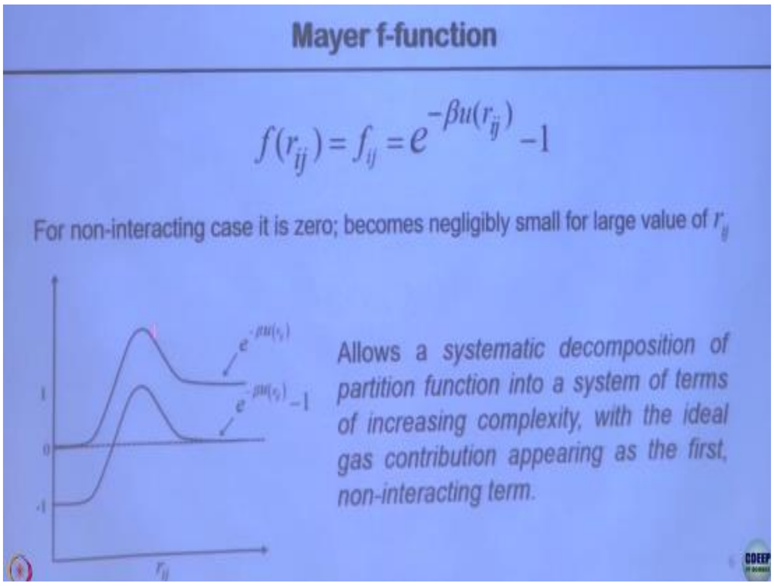

Mayer f-function

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

For 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.

So Mayer f function is the following function so the quantity that comes is e to the power – β ry this quantity that is the one way of dealing with that is the best and why it is the best because it is the simplest interaction potential is there. So there are 2 part of the interaction potential. One is this part which excludes particles volumes excludes certain regions of the configuration space to my particle because they are interacting and they are harsh impulsive at short distance.

Then, however other than that it has a entire volume to itself that part comes from here. So he then considered this he said okay let me introduce this function f and that then is like that his own sole idea was to make it go to 0 so now it goes to 0 alright and this is my we sometime we call it exponential bond because to a chemist, these are essentially bonds, they are interacting they are not chemical bonds, but you call some of them call them physical bonds, but this has become – 1 now.

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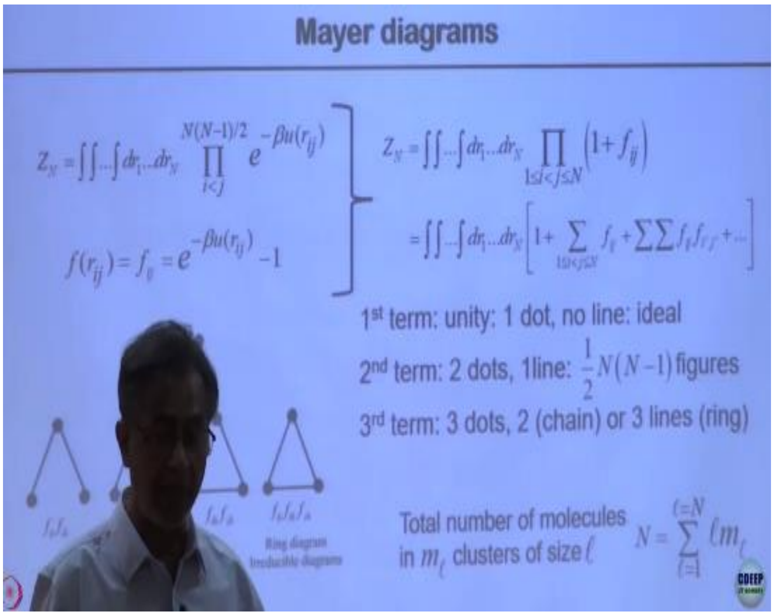

Mayer diagrams

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

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

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

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

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_ℓ clusters of size ℓ $N = \sum_{\ell=1}^{\ell=N} \ell m_\ell$

Now the advantage is that if I put this into there I will get this kind of terms. Now it has become I can decompose it into smaller parts that is important thing. Before I could not do anything and I can do something okay so then as we discussed the other day this is the decomposition I did with 3 particles then the first one is I put it here sum over one term is the first term is one.

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

Second term is a 2 particle term next term is a 3 particle term. So one part just dot more line when the second this is a bond fij is a bond that connects these 2 particles then this has 3 kind of then fourth like that. Total number of particle in the system is so ml now we say okay ml is the number total number of molecules in a cluster of size l. So cluster of size 2 how many total number of molecules 2 here 3.

So now however so instantaneously at a given position like in this room I have oxygen and nitrogen and say I have N number of them and let us consider only nitrogen so I have N number of nitrogen and now anytime they have mostly dispersed in the room, but now when they come together and they form clusters. They are cluster of diatoms, they are clusters of diatomic, there may be little bit more of that.

Much of the time I can describe this room by the function f_{12} at most they are diatomic, but you understand that whenever there 1 is coming under this interaction of the other through interaction potential I draw a bond, but these bonds are flickering bonds they are breaking and forming because as molecules come in together and going away and but the instantaneous state of nitrogen in this room is given by the ml.

And as we are talking and the N number of nitrogen molecule then m1 is 90% of that and then of the 10% another 90% are this one binary interaction and small number will be ternary interaction. So you immediately see if I want to describe the nitrogen in this room I do not need the ternary turn that much. I can see beginning to see an approximation at the low density that I can do with ideal gas plus a correction and that correction is the f_{12}.

Now I go to dense gas I go to nitrogen little bit denser and then to liquid then I need all the terms, but I have a systematic way to add them. This scheme will not work all the way, but this scheme will take us far and then a different theory takes home, but it is the beginning.

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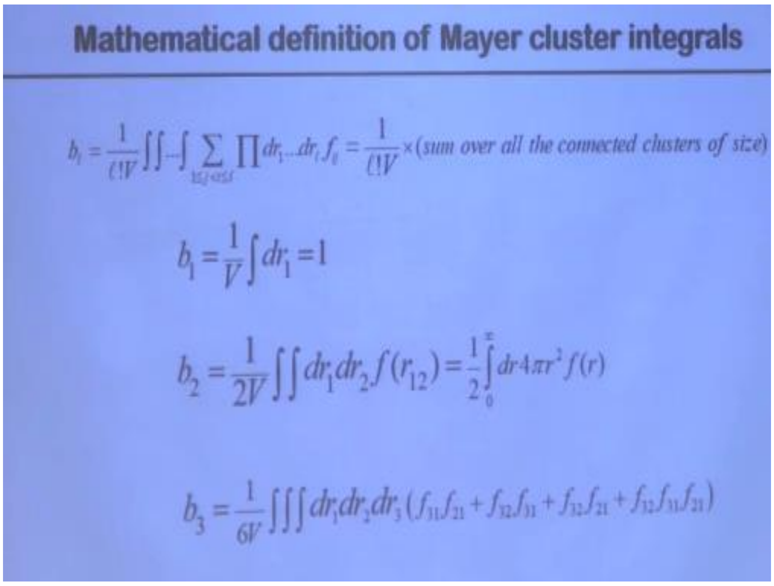

Mathematical definition of Mayer cluster integrals

$$b_l = \frac{1}{l!V}\iint\cdots\int \sum_{1\le j<i\le l} \prod dr_1 \ldots dr_l f_{ij} = \frac{1}{l!V} \times (\text{sum over all the connected clusters of size})$$

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

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

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

Now we define the cluster integrals called Mayer cluster integral which are in a given class is characterized by l. We are not making a distinction between this and this now we can then consider all these clusters now what are the clusters just in Feynman Path integral or anywhere these are nothing, but these general language of physics which started 1937 Mayer’s paper these are nothing but integrals.

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

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

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

So when you say graphs in physics they are integrals and then this is most powerful language in many body physics. In chemistry we use it in theory of liquid even these people the quantum chemist they do this T operator expansion all these different things essentially e to the power very similar thing goes on air. So there are certain universality and understanding all these things to understand 1 you basically know why 1 is doing this.

So this is then we can now calculate the okay but the dot first one is this quantity b1, b2 is this quantity and b3 I sum over everything. Remember these are my these 3 and last one the formidable one is this one. I can go on writing like that. So these are the Mayer introduced and this is the cluster integrals it is called reducible cluster integrals because this can be further reduced into this part and this part.

This is called irreducible we will handle and this is irreducible, but this can be explained in terms of this one. Now next what Mayer did okay as I told you that we are going to divide and conquer we have a full partition function we are reducing this total partition function into the cluster integrals then we reduce the cluster integral even further called irreducible cluster integrals.

Then you will see under certain approximation the irreducible cluster integrals are nothing but virial coefficients. Suddenly you see oh I can now have some limit, this is beautiful, it is rather complicated theory, though beautiful. We can connect it to experiments and you will see that this is really very, very nice. Now what we did we have to now find out that what is the decomposition.

Decomposition I want to express the partition function in terms of this reducible cluster integrals how do I do I know ml is the number of clusters of size l and when I say okay and this is my definition and remember that this is kind of a normalization factor put in here. L ! because the number of ways I can arrange 2 !s will come one is l ! and is ml !.

And as I was saying this is the kind of things looked into from the multinomial theories where you can arrange the particles in a box and you name the box 1, 2, 3, 4 like that and this is my l the number written on my box is l. So when I have 2 particle cluster I put it l = 2. I have a 3 particle cluster I put l = 3 now each of say l = 3 I have the 3 particle clusters and number of 3 particle cluster in my box label 3 is m3 and this is the way that one does exactly this problem is done in combinatorics.

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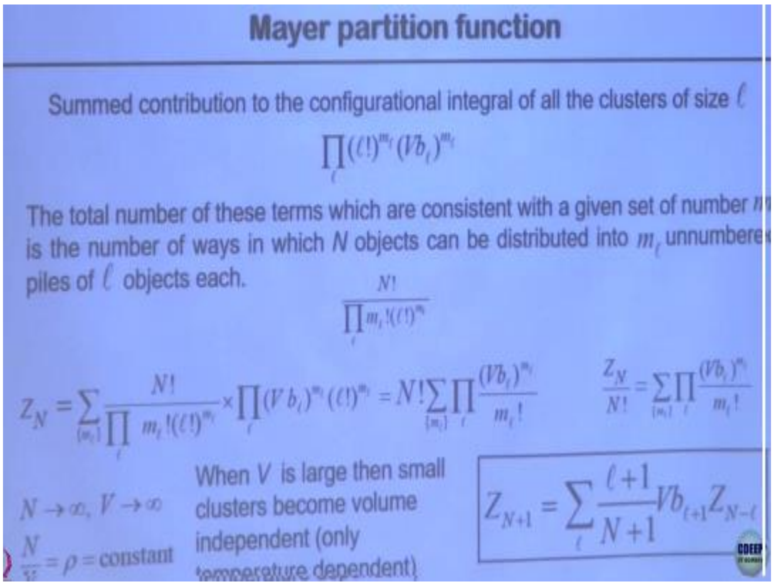

Mayer partition function

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

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

The total number of these terms which are consistent with a given set of number
is the number of ways in which N objects can be distributed into m_ℓ unnumbere
piles of ℓ objects each.

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

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

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

$\frac{N}{V}=\rho=\text{constant}$

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

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

When you do that this is what is the configuration integral of that this is just this thing because ml of them and this is the weight so this part is trivial right. Little less trivial is total number of ways we can combine them N of them into groups of l and this is distributed in unnumbered piles of objectives this is the quantity. So there are total partition function is a product of the 2 we will do the products they are certain cancellation l ! gets cancelled ml !s survive and vbl to the power ml.

And this is the beautiful expression is we call it is exact used also in quantum it is called Mayer-Ursell cluster expansion. So this is an expression of the partition function. It has certain advantage certain disadvantages but whatever it is it is exact. So this is called decomposition.

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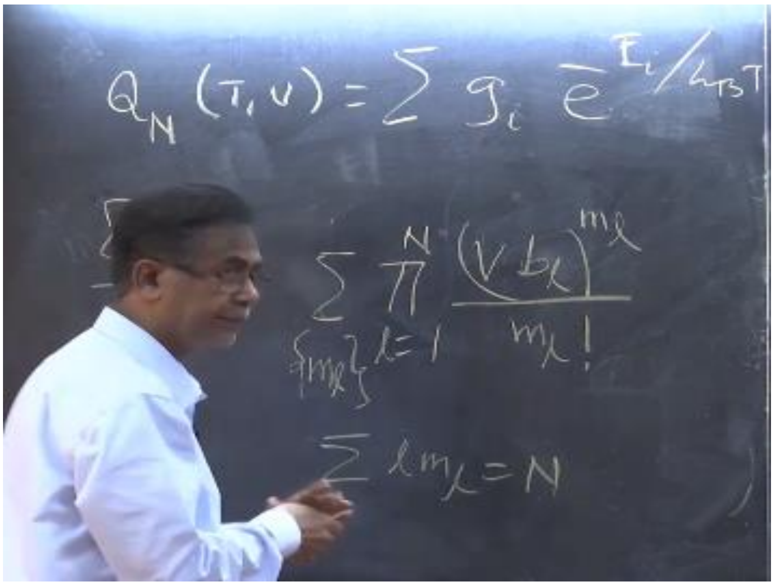

This is so beautiful let me write it down okay so this is the quantity I wrote down and the way to work with these exact partition function is to consider what you call thermodynamic limit we have to take N going to infinity V going to infinity such that N / V rho equal to constant that limit we will take. We will ignore this for the time being we will come back.

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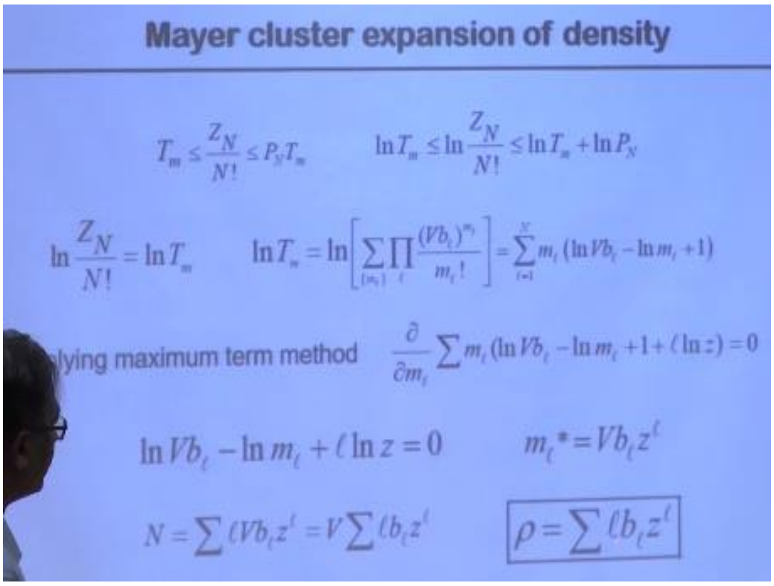

Mayer cluster expansion of density

$$T_m \le \frac{Z_N}{N!} \le P_N T_m \qquad \ln T_m \le \ln \frac{Z_N}{N!} \le \ln T_m + \ln P_N$$

$$\ln \frac{Z_N}{N!} = \ln T_m \qquad \ln T_m = \ln\left[\sum_{\{m_l\}} \prod_{l} \frac{(Vb_l)^{m_l}}{m_l!}\right] = \sum_{l=1}^{N} m_l (\ln Vb_l - \ln m_l + 1)$$

lying maximum term method $\frac{\partial}{\partial m_l} \sum m_l (\ln Vb_l - \ln m_l + 1 + l \ln z) = 0$

$$\ln Vb_l - \ln m_l + l \ln z = 0 \qquad m_l{}^* = Vb_l z^l$$

$$N = \sum l V b_l z^l = V \sum l b_l z^l \qquad \boxed{\rho = \sum l b_l z^l}$$

Now something very interesting how did Mayer go further and derive 2 very, very important thing which we call cluster expansions. One is the density in terms of lb and zl I will come back, but I just want to mention this two. We can derive it from grand canonical partition function also another thing is the pressure in terms of bl zl. I am giving you and then come back and so this things that we will derive now.

So look at the beauty density is l bl z where is the fugacity which is done just like β and canonical ensemble β become 1 over $k_B T$. How did β enter into the description in canonical partition function absolutely like Lagrange multipliers. Here also what is the constraint this is the constraint and that constraint enters through Lagrange multipliers now. B enters through which constraint energy exactly.

So temperature energy are conjugate quantities right so here what is the conjugate of number absolutely and then this is e to the power μ/ k so fugacity. It is just beautiful these things are. So I have an expansion I will derive in a minute density in terms of cluster integrals.

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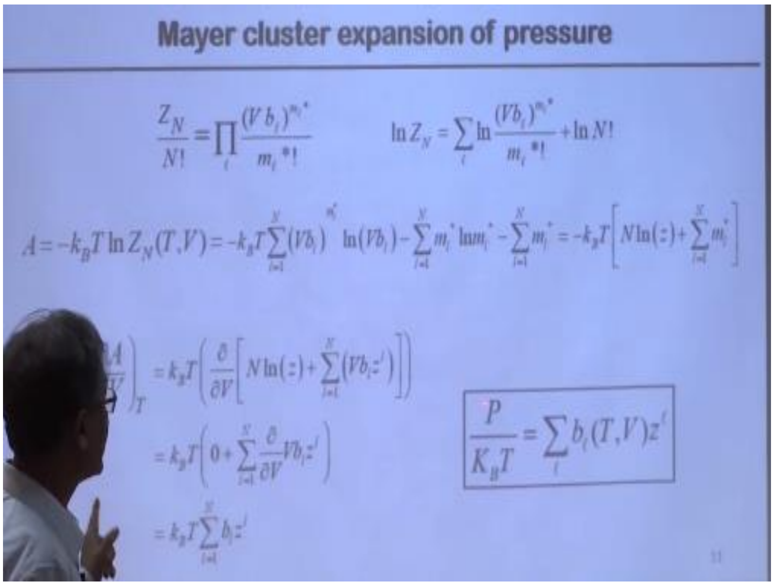

Mayer cluster expansion of pressure

$$\frac{Z_N}{N!} = \prod_l \frac{(V b_l)^{m_l^*}}{m_l^*!} \qquad \ln Z_N = \sum_l \ln \frac{(V b_l)^{m_l^*}}{m_l^*!} + \ln N!$$

$$A = -k_B T \ln Z_N(T,V) = -k_B T \sum_{l=1}^{N} (V b_l)^{m_l^*} \ln(V b_l) - \sum_{l=1}^{N} m_l^* \ln m_l^* - \sum_{l=1}^{N} m_l^* = -k_B T \left[N \ln(z) + \sum_{l=1}^{N} m_l^* \right]$$

$$\left(\frac{\partial A}{\partial V}\right)_T = k_B T \left(\frac{\partial}{\partial V} \left[N \ln(z) + \sum_{l=1}^{N} (V b_l z^l) \right] \right)$$

$$= k_B T \left(0 + \sum_{l=1}^{N} \frac{\partial}{\partial V} V b_l z^l \right)$$

$$= k_B T \sum_{l=1}^{N} b_l z^l$$

$$\boxed{\frac{P}{K_B T} = \sum_l b_l(T,V) z^l}$$

And now I have little bit more work I get now pressure another equation I will derive is this things. I have told you I will give you a flowchart. So I have an expansion these are called cluster expansion they can be derived also through a grand canonical partition function, but that does not have the physical picture it has in Mayer’s theory. Now I now give you 2 expansions one is density in terms of fugacity.

Then I give you another pressure is equation of state. Now if I give you 2 series and I tell you to eliminate this you have done in your class 11. Eliminate fugacity give me an expansion of pressure in terms of density. I give you everything I give you all the coefficients I have not told you how you are going to calculate them and I will tell you that, but I can eliminate like I have given 2 series.

One series is density in terms of fugacity another series pressure in terms of fugacity. Now I tell you eliminate fugacity give me a series of pressure in terms of density that is possible so long both the series are converging. When you do that you get the virial series that is the thing I kind of jumping and telling you. What is the flowchart now we have we start with the partition function we are getting a decomposition which is the cluster decomposition.

And exact partition function in terms so we formed earlier, when we go to cluster integrals then I get a partition function then I get 2 expansions which I eliminate and get the fugacity that allows me now to get the coefficients of cluster integrals and we will do that. The way one works out with this equation then is that we will do again the same game as we discussed we will take a maximum term method.

This is a principle of statistical mechanics it turns out that when you have see ml is the distribution of distributions please try to understand it distribution of distribution why as I said my nitrogen example there is any time ml the number of particles of number of cluster of size l that is the distribution. However, as this continuously changing there is a distribution of distribution.

Now however there is one distribution which maximizes the partition function and that is called maximum term method is a very already very well established method and probability of maximum term method. So we have to find the maximum that particular set of ml I call it ml star which maximizes the partition function and one can now show by mathematical analysis in the limit N going to infinity the maximum term method dominates.

So there is a distribution that is the reason a system is stable that is the reason we free energy is minimum it is all tied together. So now you can easily do a maximum term method there is a huge amount in Wikipedia and all these things in probability theory because it used in probability theory. Yeah exactly very good question excellent question we implement maximum term method through Lagrange multiplier.

Whenever we are doing maximizing or minimizing something subject to a constraint so the maximum term method is general method which we used even before, but like Lagrange multiplier is the weight we implement that. Whenever you are finding extrema of something with a constraint extrema means d/d alpha that quantity is 0, but you want to do it with a constraint if you do not have the constraint it will give you everything.

The constraint is done through like Lagrangian multiplier and that introduces undetermined coefficient which you apply to physics or experimental or our physical A and get what is undermined multiplier like we found out to thermodynamics β is $1/k_BT$. So this is what I have been talking of the flowchart that there is a grand scheme that is going on and we need to appreciate the grand scheme that how the whole thing is unfolding.