Basic Statistical Mechanics
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Lecture – 31
Cluster Expansion and Mayer's Theory of Condensation Part 4

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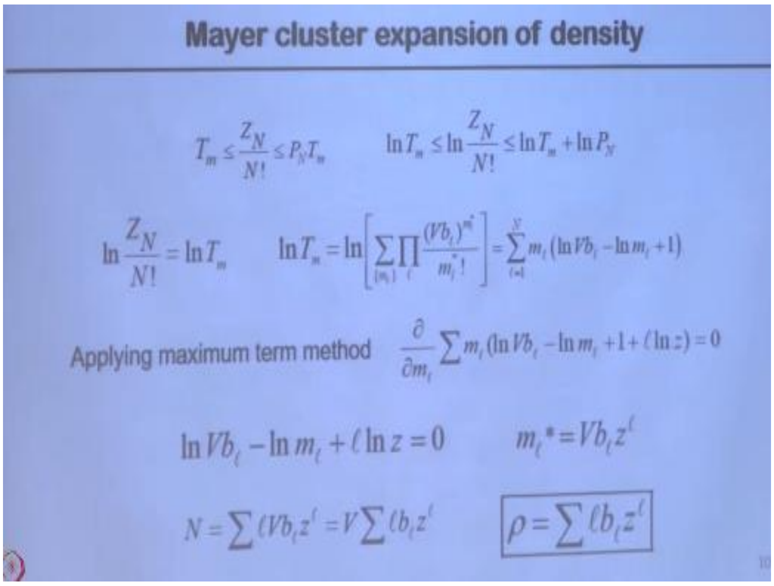

Mayer cluster expansion of density

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

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

Applying maximum term method $\frac{\partial}{\partial m_\ell}\sum m_\ell(\ln Vb_\ell - \ln m_\ell + 1 + \ell\ln z) = 0$

$$\ln Vb_\ell - \ln m_\ell + \ell\ln z = 0 \qquad m_\ell^* = Vb_\ell z^\ell$$

$$N = \sum \ell Vb_\ell z^\ell = V\sum \ell b_\ell z^\ell \qquad \boxed{\rho = \sum \ell b_\ell z^\ell}$$

So now let's do the maximum term method. Maximum term method is bounded and a very vigorous method that means you know there is this quantity P and which is very small one can show that maximum term method and the reminder goes to zero. So now I want to replace the partition function by logarithmic term.

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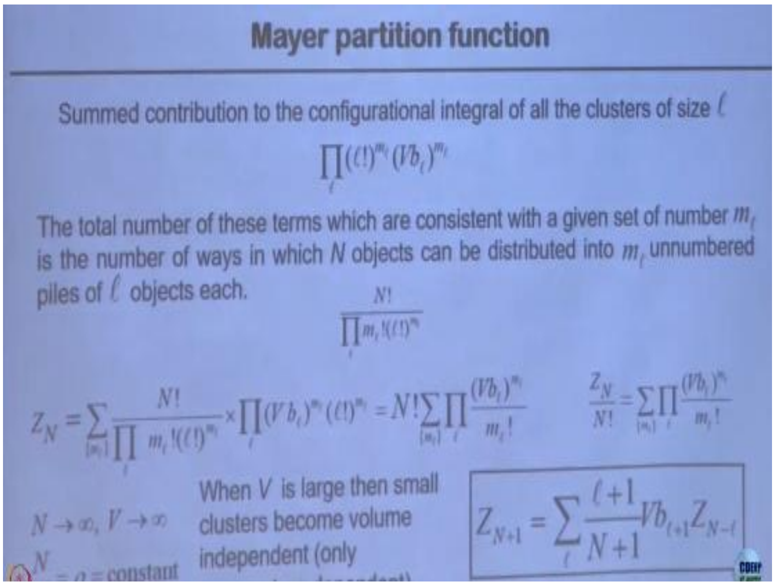

Mayer partition function

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 m_ℓ is the number of ways in which N objects can be distributed into m_ℓ unnumbered piles of ℓ objects each.

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

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

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

N $= \rho =$ constant

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

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

So what I am going to do now I am going to take that m_l^* so I am not going to do the sum now I am going to replace that by $1/m_l^*$ which maximizes these things. So I do not have the sum anymore. So this is the quantity I have to maximize. So, now we do that using maximum term method.

Because we are just maximizing m_l^* so now I take the log of that. Now, I take the log of that with the constraint that m_l^* = N. Applying a maximum term method with the constraint provides the extra N. This comes from there everywhere it should have been m_l^* actually. So now you understand the details and you also understand the great picture.

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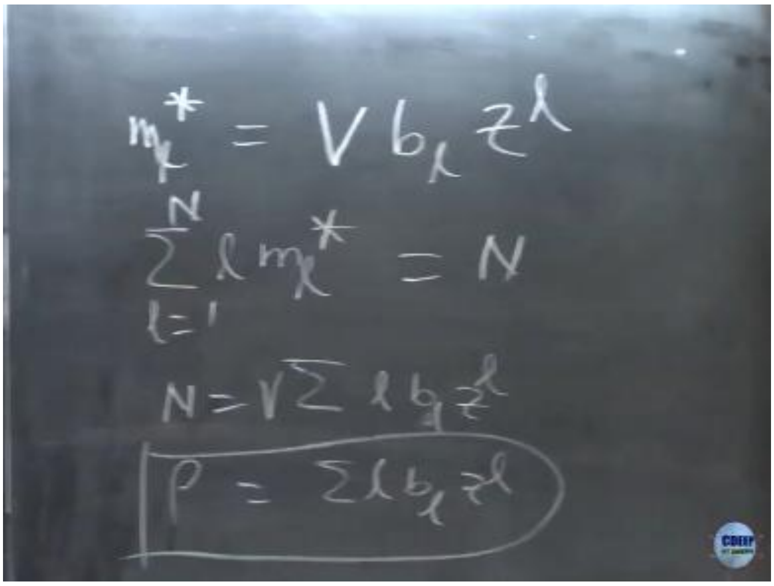

$$m_\ell^* = V b_\ell z^\ell$$

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

$$N = V \sum \ell b_\ell z^\ell$$

$$\boxed{\rho = \sum \ell b_\ell z^\ell}$$

So Now we have

$$\sum_l l m_l^* = N$$

$$N = V \sum l b_l z^l$$

$$\rho = \sum l b_l z^l$$

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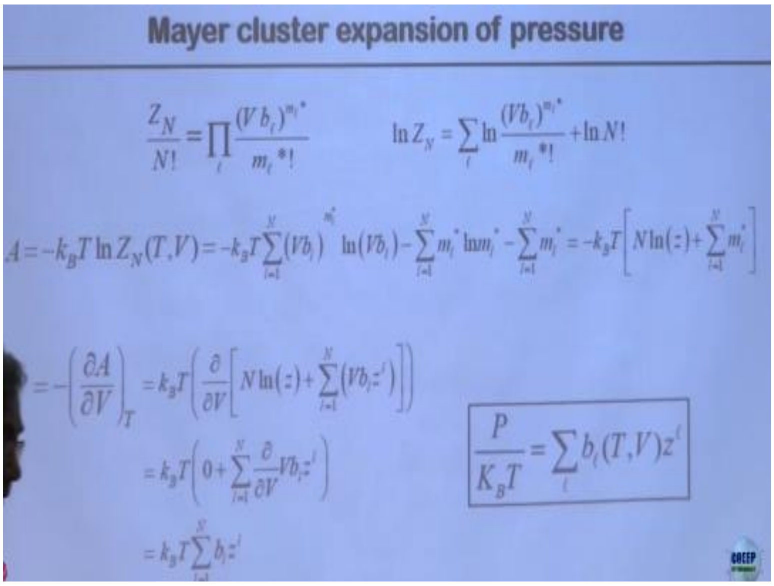

Mayer cluster expansion of pressure

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

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

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

$$=k_BT\left(0+\sum_{l=1}^{N}\frac{\partial}{\partial V}Vb_lz^l\right)$$

$$=k_BT\sum_{l=1}^{N}b_lz^l$$

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

Then I can now calculate the free energy. Free energy in terms of m_l^* I know that m_l^* is the quantity here right I know m_l^*. Now partition function does not have the sum this is correct then I can calculate the free energy by m_l^* coming out the ln of that Vb_l.

Then right now if you go into the very detail of the equations you will get lost. This you can check it up and it will take me one probably half an hour more to do that so I do not want to do that and it is probably since these are details of keeping at that level of probably these are not detail you can read to the detail it will take you 10 minutes to do it, but you can do it. So that goes inside and I cannot do that.

There are these 2 terms here. ln z will go to 0 when we employ d/dV, but I have this term left Vbl term left. Then I get pressure.

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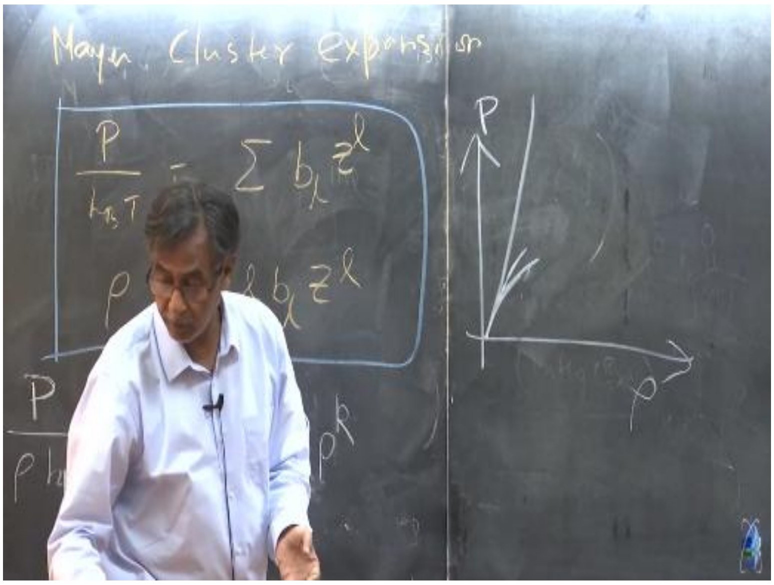

So when you call a Mayer Cluster Expansion you know this is the thing basically matter of a choice and these are exact one can do probably somewhat simpler way through the grand canonical ensemble, but there are some results, but you would not get from there. So these now as I was saying the game plan now is to eliminate fugacity from this expansions. Both are exact.

Elimination of fugacity from here gives you another infinite series that infinite series we are following and this is a virial series that is one of the things taught in your high school also. The pressure is expanded in terms of density. The second virial coefficient which we will show is exactly given by f_2 term of Mayer Cluster Expansion. f_2 term is an integral over intermolecular potential.

So now from historically from b_2 the interaction potential the first force field was derived from B2 because it was done after Mayer did. One finds that second virial I can get this second virial coefficient how I plot pressure versus density and this is the ideal gas, but as interactions become important I see this starch deviating. So I know experimentally this quantity and the fast part of deviating is very temperature dependent.

Like high temperature it is like this, low temperature it is like that. So from there a fitting, I get the temperature dependence once again virial coefficient and I will now show you the second virial coefficient is the integral over first elusive cluster integral or b_2 second virial coefficient. So I am going little bit back and forth to give you the understanding of what is going on. This will not meet immediately, but very important.

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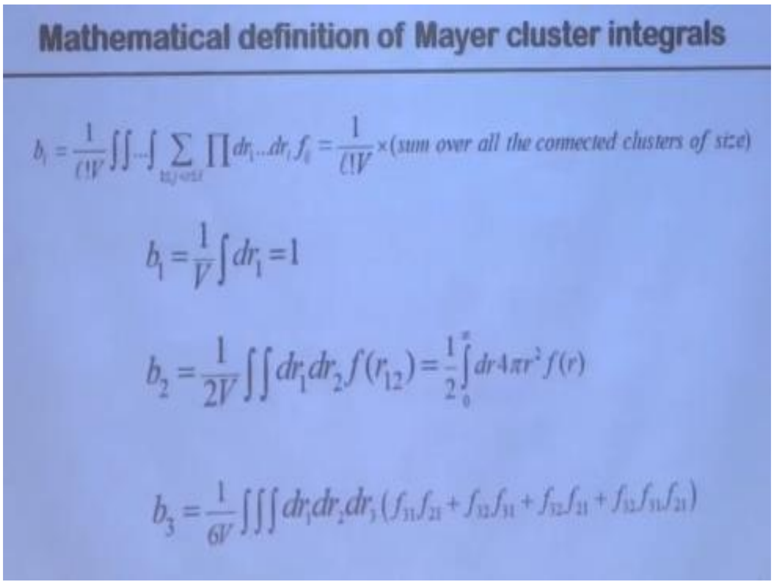

Mathematical definition of Mayer cluster integrals

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

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

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

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

So what Mayer did then this bs that you have done are called reducible cluster integrals this side with a definition given here these are integral.

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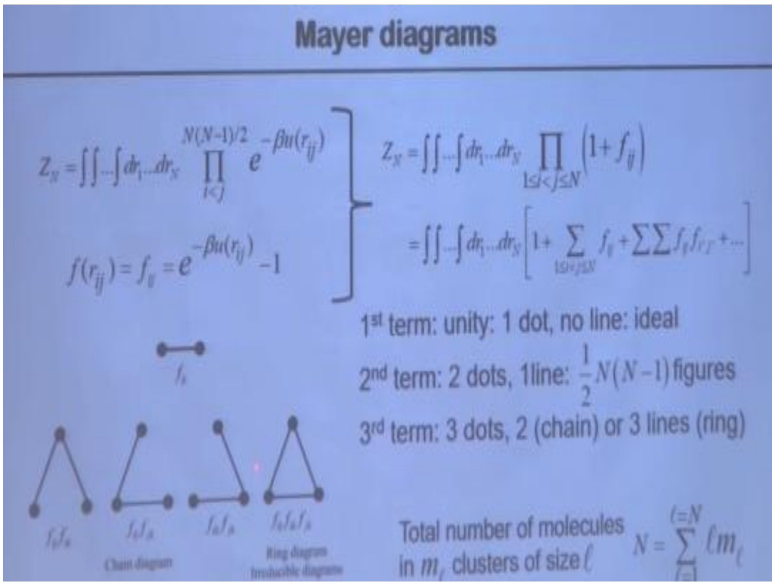

Mayer diagrams

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

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

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

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

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 $\quad N = \sum_{l=1}^{l=N} l m_l$

However, as we know that this cannot be reduced any further, but this can be reduced. So now we think is it possible for me to express bl following the same logic that I can now say okay I have a cluster the weight I have given as bl that weight now that particles now I can now define these quantity as 1 it is constructed of 2 bonds if of them are same bond, but this is a different thing. So can I further decompose these group of clusters into these quantity and this quantity given that this is irreducible.

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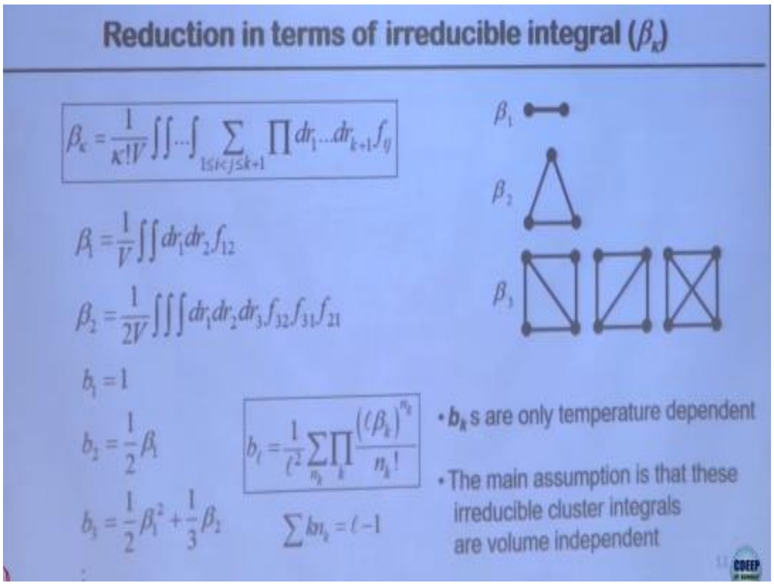

Reduction in terms of irreducible integral (β_κ)

$$\boxed{\beta_\kappa = \frac{1}{\kappa! V}\int\int\cdots\int \sum_{1\le i<j\le k+1}\prod dr_1\ldots dr_{k+1} f_{ij}}$$

$$\beta_1 = \frac{1}{V}\int\int dr_1 dr_2 f_{12}$$

$$\beta_2 = \frac{1}{2V}\int\int\int dr_1 dr_2 dr_3 f_{32} f_{31} f_{21}$$

$$b_1 = 1$$

$$b_2 = \frac{1}{2}\beta_1$$

$$b_3 = \frac{1}{2}\beta_1^2 + \frac{1}{3}\beta_2$$

$$\boxed{b_l = \frac{1}{l^2}\sum_{n_k}\prod_k \frac{(l\beta_k)^{n_k}}{n_k!}}$$

$$\sum k n_k = l - 1$$

- **b_k** s are only temperature dependent
- The main assumption is that these irreducible cluster integrals are volume independent

And that was the next thing that Mayer did reduction in terms of irreducible cluster integral. Now he said okay let me define these at the fundamental quantities this as this I cannot reduce any further this and these are the quantity this actually should have one more because it should have the one without a bond that somehow is not given here.

We can do the exactly same thing that I now want to distribute in my m_l or n_l how many of them are this kind and how many of that kind. So we do the exactly same analysis we did before and you get slightly different expression, but you can show that it goes over further decomposition and this however has an approximation in the process of going these approximation that you have to assume that these are volume independent.

Only then this reduction can be done and that turned out to be very important limitation in this theory which made the theory more questionable at high density. So I will not spend too much time on this if I want to do it I will do it later, but right now I am going to do something else that this is the irreducible cluster integrals. So now my aim is to show these quantities the second virial coefficient these quantities the third virial coefficient and sum of all these things and the fourth virial coefficient.

And as I told you these are important historically and also for forceful development even today. So basic idea is that this is the thing and then there is a reduction there is a distinction you should know beta 1 is 2 particle.

So β_1 is first of the irreducible integral that gives on to b_2. So b_3 is 3 particle clusters so this has 2 of this, but there is one stand out which is β_2. So when I think of b_3 that is how it was done. The way I always do or you can always do you can always I never do it this way I always write down 2 particle then I do the 3 particle then I go to 4 particle then I see the pattern that is how Mayer did it.

That does not come from the air that come from these definitions. So there is a 3 of them I think 3! they have all the same value so 3! cancel the 3 I think you are left with 2 that work it out, but as per I remember 1 over 3! into 3 and then you left with 2 and here however nothing is there so 3 comes in because 3 of them are not there and that is why you get a 3!.

Stockmayer did the theory of Sol-gel transition where the polymers get together and form gel. there is a difficult Combinatorics of this kind and that was also done by Goeppert Mayer and Stockmayer wrote the paper and acknowledged to the contribution of Goeppert Mayer in that theory and in Chicago when they came even then Goeppert Mayer did not have any office.

So now let me go back and forth little bit. Now so these are the integrals the same as with a factor of 2 same as the second of reducible cluster integral the first of irreducible integral there is this difference of one between them, but this is the integral you have to remember. So is f_{12} and remember f_{12} is Mayer f function.

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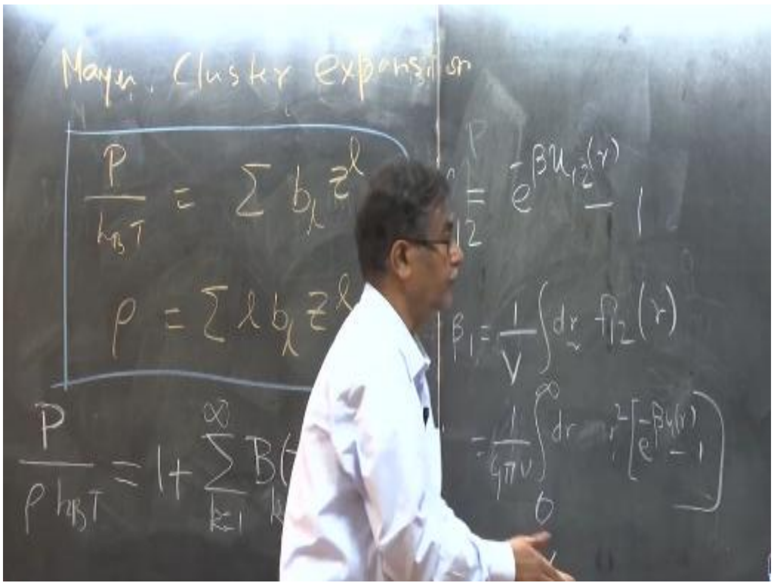

So f_{12} is these quantity is $e^{-\beta U(r)} - 1$.

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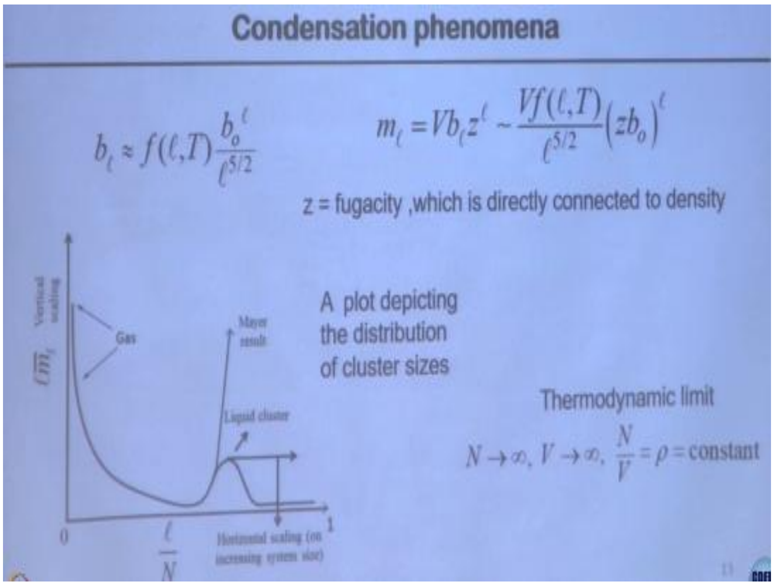

Condensation phenomena

$b_\ell \approx f(\ell,T)\frac{b_0^\ell}{\ell^{5/2}}$

$m_\ell = Vb_\ell z^\ell \sim \frac{Vf(\ell,T)}{\ell^{5/2}}(zb_0)^\ell$

z = fugacity ,which is directly connected to density

A plot depicting
the distribution
of cluster sizes

Thermodynamic limit

$N \to \infty,\ V \to \infty,\ \frac{N}{V} = \rho = \text{constant}$

Now I will show you how that happens and we will stop after that. Before that one tiny little bit that one can go and calculate the average number of these clusters by using there is what turned out is very powerful that these exact partition function is nothing, but a class of polynomials called Bell polynomials a very powerful polynomials used a famous mathematician Bell that has been used in many ways particularly in study of zero of polynomials.

That polynomials allow to write a recursion relation it is just bit of good luck. Now if I can write this then if you can give me the z_1 and then give me next one I can get higher level partition function so I can construct physical recursion relation the input of course are the b_l +

1. So if I have that I can construct this partition function. If I can construct the partition function, I can calculate what is the average number of clusters in the polynomial.

By using these as the weight so this is the weight of your one particular distribution right. If I have the partition function when I calculate that weight I am not going into the greater details of that, but then you can now say okay lm_l is the number of clusters lml is number of particles in size of cluster l m_l is the number of clusters of size l each of them have l. So lm_l is the number of particles in cluster of size l.

Now we plot it against l / N, N is total number of particle l is the size of the cluster then you find when you have high temperature then this goes to zero, but in lower the temperature you find a second pics appears that second pics is the liquid. So a second big cluster appears with l / N close to 1, slightly less than 1, maybe at 0.8. So as you hit the coexistence this big signals the appearance of a macroscopic cluster in the system.

So liquid is envisaged in Mayer’s theory as a macroscopic cluster. So when you cool down like nitrogen we have I cool it down and make the density large then the particles come close to each other they all start interacting. I call a system a liquid when all the particles are interacting or one of them impacting many others, but if one is interacting it is a 10 it is a good number actually means correct almost correct number.

Then the neighbors of that my 10 neighbors they are interacting with another 10 then another 10. So liquid means when the particles are all talking with each other or molecules are talking that means in this description they are part of the same cluster. They are talking with each other means they are connected by a bond this is not a chemical bond the bonds are breaking and forming, but they are interacting.

So liquid is that not each particles does need not interact with everybody. So this is again I repeat ml is number of particles in cluster of size l lml is number of clusters of size l lml is number of particles in that cluster and then this is N equal to small one or so 1 / N equal to very small that are the gas the small clusters. When they are large these goes close to when l is close to N that means a gigantic microscopic clusters this is close to 1 maybe 0.8 or so.

So low temperature this peak appears high temperature there is no peaks. This is a low temperature high temperature I should have just like this so that should have been there and it is not there. So this is a nice physical picture that comes as I told you ideal gas does not form liquid. Liquid forms because of interactions and that interactions lowest level is the second or third virial coefficients that is not perfect theory by any means. These theory take you all essentially picture and how interactions are taken into account, but that is the universal scheme all other theory flew from that.

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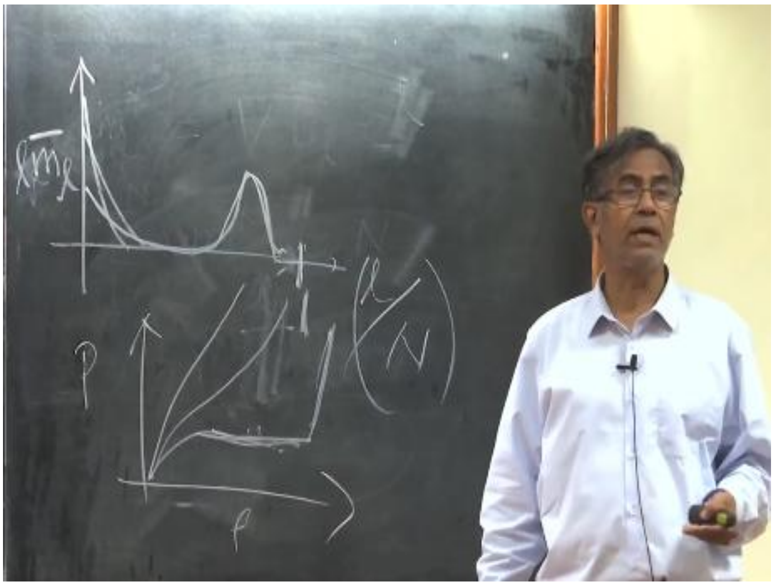

So if I take now l ml and then l / N and as she asked in the high temperature gas phase this is just like this and lower the temperature increase the density it becomes like that then finally that appears this is 1. So this is the pure gas no liquid, large clusters are appearing then at the coexistence you have lots of gas and then also one gigantic cluster. So if I plot this thing as pressure versus density then this is like that which is here.

Then it becomes more like that which is this one and then it becomes. So this one is this one gas and liquid are together this is the coexistence. So you have one gigantic cluster which is the liquid is amazing when your liquid is in a equilibrium with a vapor phase just like in glass of water clearly one the liquid you have this and look at the number of particles interacting with each other.

But your liquid your gas is just cluster of two or three there is a huge separation and one is stabilized by entropy which is your gas, one is largely stabilized by your enthalpy which is this phase and this nearly took huge amount of time what people to describe this phase transition huge amount of I always consider phase transition is where almost all our concepts came including high energy physics.

Because that is where came the order parameter that is where came the interactions of own atoms and molecules. So phase transition is one everybody should study the free energy diagram and all this things similar chemical kinetics is deeply although independently it was developed in the beginning.

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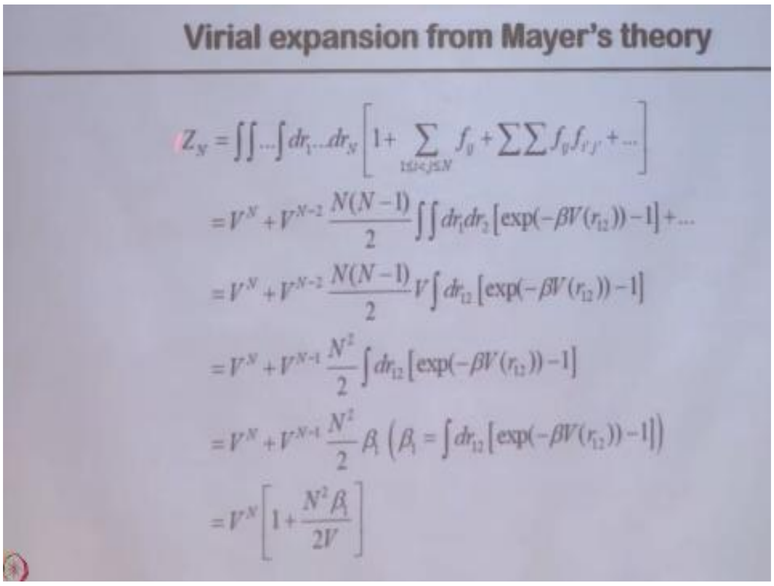

Virial expansion from Mayer's theory

$$\begin{aligned}Z_N &= \int\int\ldots\int dr_1 \ldots dr_N \left[1 + \sum_{1\le i<j\le N} f_{ij} + \sum\sum f_{ij} f_{i'j'} + \ldots\right] \\ &= V^N + V^{N-2}\frac{N(N-1)}{2}\int\int dr_1 dr_2 \left[\exp(-\beta V(r_{12})) - 1\right] + \ldots \\ &= V^N + V^{N-2}\frac{N(N-1)}{2} V\int dr_{12}\left[\exp(-\beta V(r_{12})) - 1\right] \\ &= V^N + V^{N-1}\frac{N^2}{2}\int dr_{12}\left[\exp(-\beta V(r_{12})) - 1\right] \\ &= V^N + V^{N-1}\frac{N^2}{2}\beta_1 \left(\beta_1 = \int dr_{12}\left[\exp(-\beta V(r_{12})) - 1\right]\right) \\ &= V^N\left[1 + \frac{N^2\beta_1}{2V}\right]\end{aligned}$$

Now one little bit because I do not know when you limit first one little bit the virial expansion of Mayer’s theory. So then I go to the partition function and I say okay I expand this there is expansion and I start putting my ways together. I take only the this term then we know N into N– 1 two of them. I do rest of the integrals V to the power N – 2 there are only 2 I cannot do which two are kept here they are vector integrals.

So I am interested in this part I am interested in this part or this part. I am not doing this one, but I am doing a tiny little part to make it simple full derivation can be done that will be little complex so I am not doing it.

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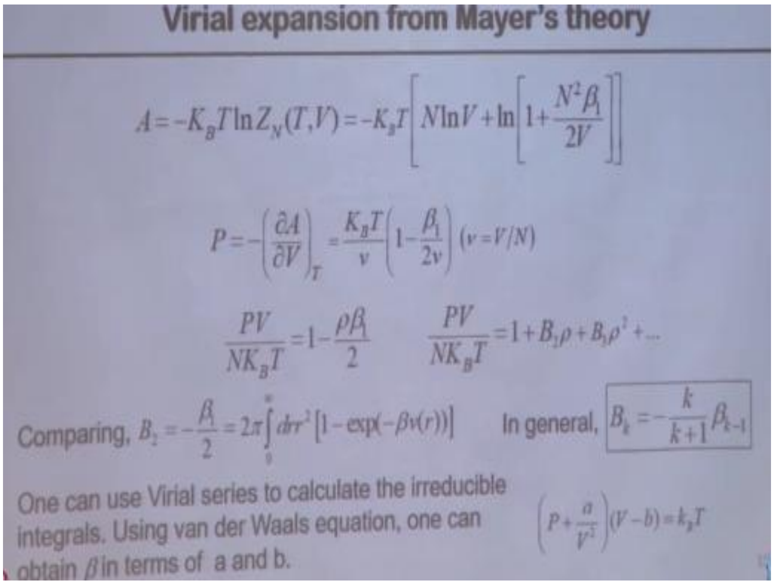

Virial expansion from Mayer's theory

$$A=-K_BT\ln Z_N(T,V)=-K_BT\left[N\ln V+\ln\left[1+\frac{N^2\beta_1}{2V}\right]\right]$$

$$P=-\left(\frac{\partial A}{\partial V}\right)_T=\frac{K_BT}{v}\left(1-\frac{\beta_1}{2v}\right)\ (v=V/N)$$

$$\frac{PV}{NK_BT}=1-\frac{\rho\beta_1}{2} \qquad \frac{PV}{NK_BT}=1+B_2\rho+B_3\rho^2+\ldots$$

Comparing, $B_2=-\frac{\beta_1}{2}=2\pi\int_0^\infty dr\,r^2\left[1-\exp(-\beta v(r))\right]$ In general, $\boxed{B_k=-\frac{k}{k+1}\beta_{k-1}}$

One can use Virial series to calculate the irreducible integrals. Using van der Waals equation, one can obtain β in terms of a and b.

$$\left(P+\frac{a}{V^2}\right)(V-b)=k_BT$$

So now I am going to do that put that back in my partition function this zn I put it back in my free energy this definition then I log this is the large volume N NV and then I take this derivative and then this becomes 1 / V that becomes 1 here and that derivative gives do this is suddenly developed, but at the end of the day this is V / N so PV / N cavity you get exactly from here you get exactly this term.

So this is the first of an expansion so PV / N cavity is this virial series. So now I identify b_2 as second virial coefficient.

There is a beautiful expression second virial coefficient which describes these bending here is in terms of Mayer cluster integral and this is the general expression one can derive and a little bit I can go to van der Waals equation I can find out my virial coefficients this is a homework problem you always did you expand it pressure in terms of density and equate this things you get this again virial coefficient third virial coefficient go back find out the betas.

Find out your Mayer Cluster integral which can be done by use a very similar recursion relation. So you can construct whole statistical mechanics that lies under van der Waals and that has been done. So we stop here today.

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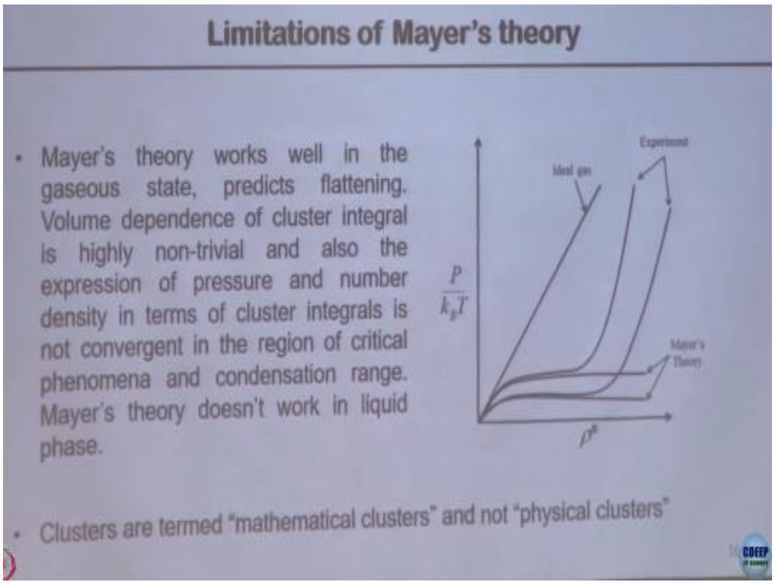

Limitations of Mayer's theory

- Mayer's theory works well in the gaseous state, predicts flattening. Volume dependence of cluster integral is highly non-trivial and also the expression of pressure and number density in terms of cluster integrals is not convergent in the region of critical phenomena and condensation range. Mayer's theory doesn't work in liquid phase.

- Clusters are termed "mathematical clusters" and not "physical clusters"

There are some limitations one of the major limitation is that when one goes to that level it is the only temperature dependent doing this integrals the way we find only when volume dependence of those integrals are neglected and that is the so this is the it does not describe because it diverges there and it does not describe the liquid state. So Mayer theory does not work in the liquid, but it describes how liquid forms, it describes how similar it develops.

And it describes how similarities are there. So what we will do now after this we will do Landau theory the theory of resistance and I am hurrying a little bit any questions you quickly ask. That is a virial series. No say for example when you go to liquids then something fundamentally different appears here for that you need infinite number of them and that part where it is based out.

But it require as I said yes it reproduces this complete flattening it reproduces this part, but then it does not because for that people have done little better and corrected this theory, but people are quite happy with this part that it starting from an interaction potential to see how a temperature dependent behavior emerging was really quite satisfying and the concept of clusters we then turn to percolation this is the way after that percolation theory was done solider transition done.

So this played as a catalyst of development of hell lot of things that is why historically in statistical mechanics these things should not be ignored Mayer's theory. People do not teach it because it is too complex as you have seen and so next we will do on phase transition I will explain little bit more. Okay I think we will stop here today. Thank you.