Basic Statistical Mechanics
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Lecture - 33
Cluster Expansion and Mayer's Theory of Condensation (Part 6)

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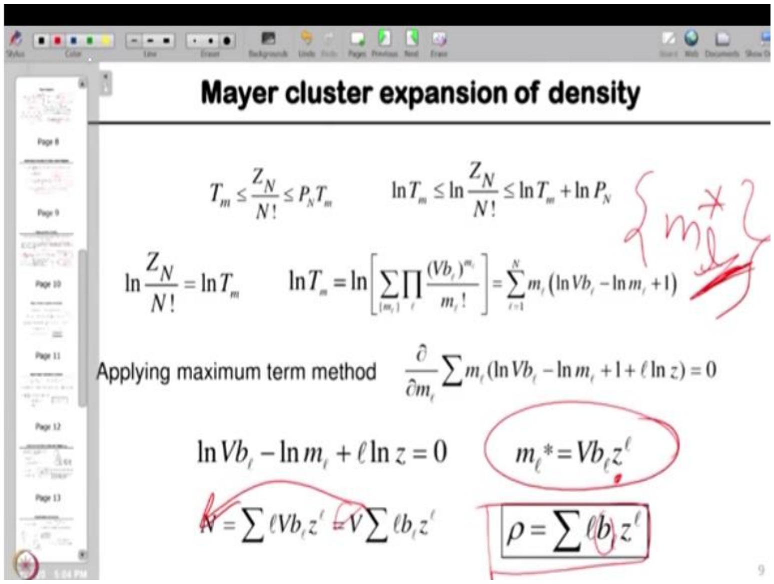

Mayer cluster expansion of density

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

$$\{m_\ell^*\}$$

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

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

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

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

Mayer went on to show that how this analysis that he did the maximum term method. He picked up that that particular cluster and the analysis is fully given here that maximized the partition function. This is the same as the Lagrangian multiplier, but before that he showed that maximum term method is the one that works.

That is sufficient in the limit of infinite size of the system, N going to infinity, total number of particles going to infinity, volume going to infinity such that N/V, the ratio of number of particles of volume densities fixed. In that limit that maximum term, the distribution m_l* this distribution that maximizes that is enough. Everything else is redundant. That beautiful analysis of maximum term method combined with Lagrangian multiplier.

And he could show that m and Z here, which tells the weight of a cluster that is the undetermined in the Lagrangian multiplier, undetermined coefficient. Z is the undetermined coefficient. We show later that Z is nothing but fugacity, but if it is there, then lm_l*= N and then we get n over there V and we get a beautiful thing, which is called Mayer cluster expansion. The density is lVb_lZ^l. So now we have a beautiful relation in terms of the cluster integrals bilateral.

And cluster integrals are nothing but those integrals that contain intermolecular interactions. So because of the cluster integrals, we have now the connection, we are building that; we made the connection with intermolecular interactions and the way.

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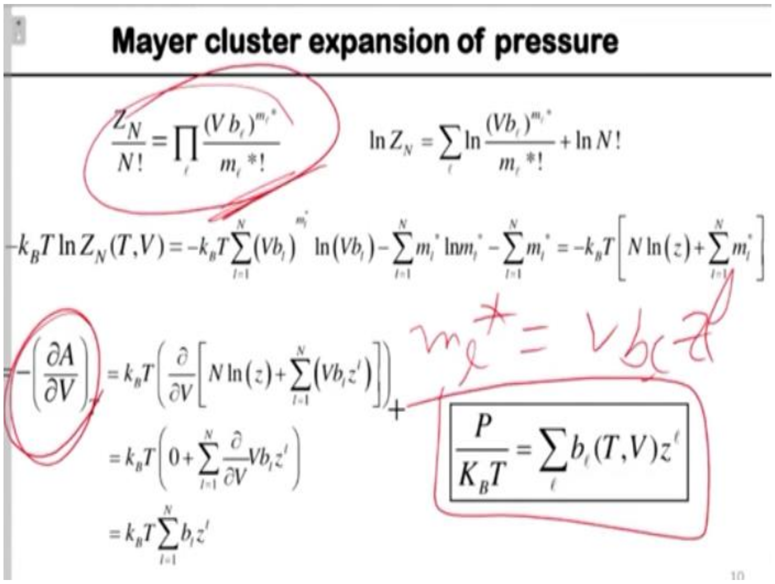

Mayer cluster expansion of pressure

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

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

$$m_l^* = V b_l z^l$$

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

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

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

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

So this is a beautiful stuff, then he went on and go back. So these now write the partition function about one particular distribution. So we are talking of distribution of distribution, because m_l gives the number of clusters of size l and but we have picked up one particular such distribution, we call it m*. For example, that can be in a 100 particle system m_1 can be 58, m_2 can be 32, m_3 can be 12, something like that and they must add up.

So m_1 is 58 that means there are 51 monomers, then I say okay there are 12 dimers, then 2 into 12, 24 particles in that. So 58 + 24 is now 82. Then I have 6 dimers, so that is 18. So I will have now 100 or I say I have that is the distribution I have that maximizes. Now when n is not 100, but billions of billions, then a distribution I pick up like that is one that is representative of the system, then I can go and calculate the partition function.

Once I know the partition function, I get the free energy and then from this partition, I get the free energy and from the free energy I can get the pressure, which is dA/dV here and then I can show by using these relation $m_l{*}Vb_lZ^l$ I get this thing. So now this is another such cluster expansion, which is Mayer's theory.

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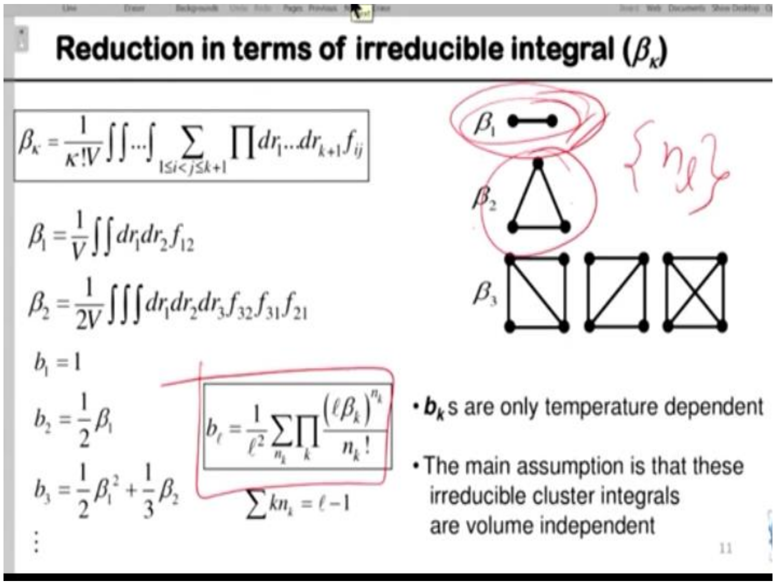

Reduction in terms of irreducible integral (β_κ)

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

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

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

$$b_1 = 1$$

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

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

$$\vdots$$

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

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

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

And then further development is done in terms of irreducible cluster integrals because those are V_l contains both chain and ring. So you have to break down into rings and chain separately and evaluate them separately that has been done for fairly complex number of systems, very large number of things and so this is called reduction in terms of irreducible cluster integrals and the definitions one can do like β_1 is these quantities β_1. Then this is called β_2.

Now you can see if I have only chains and rings, then β_1 and β_2 is enough and if I have only changed in my system no rings, like in diluted lighter gases, then β_1 is enough. What turned out now β_1 is the second variable coefficient, this become the third variable coefficient. That is the beauty of Mayer's theorem. Now we play the same game how many of these β_1 in the system, I call that n_l and then how many ways I can distribute into the n_l.

The same ω and then I made the product of the 2 and I get exactly like Mayer partition function another expression, which is the story goes that Joseph Mayer could do the earlier these derivations, he could do this thing. He could do, he was stuck. He could not go to reducible cluster integral and the further development was done by his wife Maria Goeppert Mayer who entered to get a Nobel prize, for the nuclear shell theory.

So Maria Goeppert Mayer whom Mayer met in Gottingen and married and brought her to Columbia University was instrumental in many, many such, such calculations of combinatories and difficult things.

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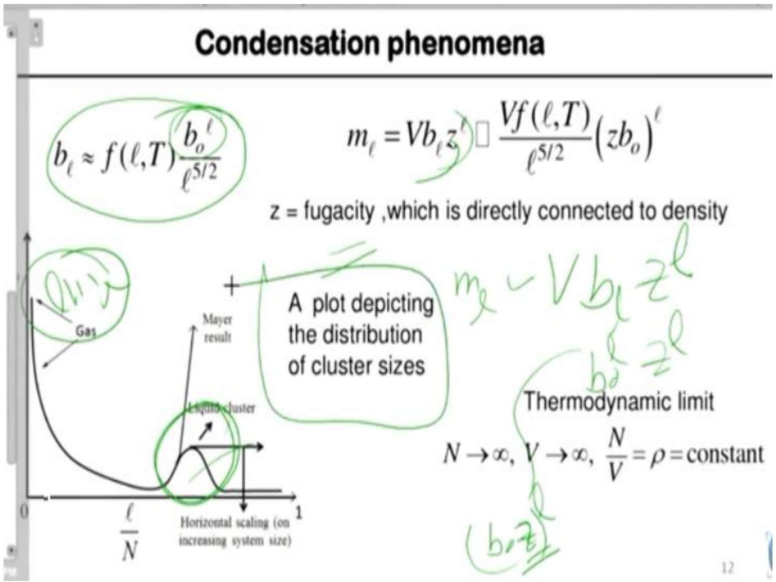

Condensation phenomena

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

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

z = fugacity ,which is directly connected to density

A plot depicting the distribution of cluster sizes

Thermodynamic limit

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

So when that Z^1 goes on and one can go on to describe the theory of condensation in a beautiful way that means one could use these things and one could now show to get the maximum term method and one can show from the maximum term method that these 2 things that one does that maximum term method gives these ml star, what we already showed is Vb_lZ^l and Z is the fugacity and b_l one can show is this quantity.

It has exponential scaling, then one goes to ml and since ml goes as bl to the power Zl and since bilateral, sorry ml is Vb_lZ^l and V goes as V naught to the power lZ_l. So you combine and get V naught to the power Zl and when fugacity changes such that Z becomes greater than V naught inverse, then you suddenly have very large clusters appearing. The system which is shown here as a distribution of lm_l is a versus l, lml is the number of clusters of size l and l is number of particles in the cluster as ml.

lm_l is number of particles in this size of cluster l and that then has this beautiful Mayer's picture is that a big large cluster appears in the system and that is the gas-liquid transition. So this is the coexistence. This would become the liquid. So Mayer did not quite get there, but he got the picture right. His formulation was rather extended to many, many great creations and so there is a beautiful scaling also that depicted. This is the plot depicting the distribution of cluster sizes.

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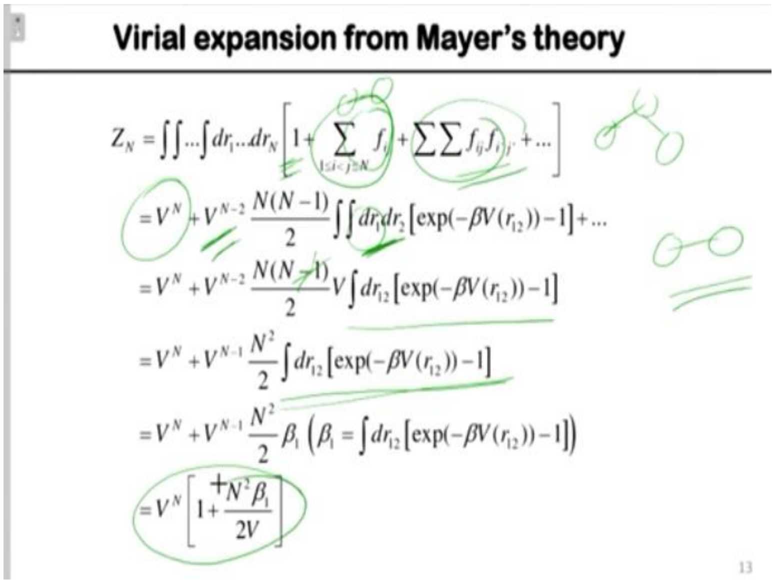

Virial expansion from Mayer's theory

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

$$= V^N + V^{N-2}\frac{N(N-1)}{2}\int\int dr_1 dr_2 \left[\exp(-\beta V(r_{12})) - 1\right] + \ldots$$

$$= V^N + V^{N-2}\frac{N(N-1)}{2} V\int dr_{12}\left[\exp(-\beta V(r_{12})) - 1\right]$$

$$= V^N + V^{N-1}\frac{N^2}{2}\int dr_{12}\left[\exp(-\beta V(r_{12})) - 1\right]$$

$$= V^N + V^{N-1}\frac{N^2}{2}\beta_1 \left(\beta_1 = \int dr_{12}\left[\exp(-\beta V(r_{12})) - 1\right]\right)$$

$$= V^N\left[1 + \frac{N^2\beta_1}{2V}\right]$$

Then what one does, the next thing was a wonderful thing that is a virial expansion of Mayer's theory. So Mayer then went on to show that in a low density or large volume, he can work his theory around and show that the free energy at the partition function and the free energy and pressure has an expansion in density, which essentially comes from these 2 things, one is pressure is b_lZ to the power l and density is Vb_lZ^l. So these are two series.

This is series 1 and this is series 2. Now I can eliminate the fugacity from series 1 and 2 and I can get a series of pressure in terms of density and that exactly is virial series. That was what was done by Mayer and is described here. So we will go now, write down the partition function just like this. This is all the binary. This is the ternary. So these are all the binary chain. These things 2 bonds and just keep these 2 terms nothing else, because this low density or large volume limit.

Then I can do so to this one, this is just ideal gas V^N. Then there are how many ways I can have the n number of particles get into that dimer; that is N to N – 2 by this and V^{N-2} come out, because the 2 integrals are here. It is V^{N-2} and then I have other one will be 3 particles N to N – 1, N – 2 by 6 and V^{N-3}. I am not taking that into account.

So now I can if I take that this quantity, then I can change again origin to 1 and these becomes 1, 2, this becomes 1, 2. Then this becomes that thing and one I integrate I get V, so then I get these kind of things and n is very large. So these can be neglected I get $N^2 / 2V^{N-1}$, then $V^{n-1} n^2 / 2$ and this integral. Now I define this integral as beta 1 and then I get $N^2\beta_1 / V$ as this term.

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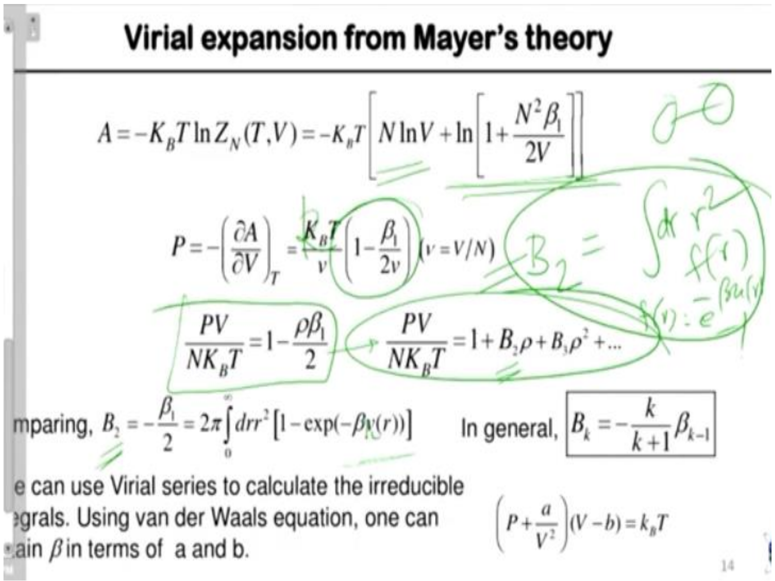

Virial expansion from Mayer's theory

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

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

$$B_2 = \int dr\, r^2 f(r)$$

$$f(r) = e^{-\beta u(r)}$$

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

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

e can use Virial series to calculate the irreducible
egrals. Using van der Waals equation, one can
ain β in terms of a and b.

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

Then I go and calculate the free energy from in this lower case, Boltzmann's constant, then I work it out, then this is the ideal gas term, then this is the term that is coming from retaining only the chain diagram the dimer and then when I do that, I found that this is all lower case. This is the correction that comes to pressure the $\beta_1/2V$ and this v is V/N and then you get, this is the correction that comes out, that means pressure PV / Nk_BT becomes $[1-(\rho\beta_1/2)]$ and this we now compare this with the virial series, you get 1 + B_2 that you will find all these calculations are done here and this will be passed on to you. So one gets the first term of the virial series and that is a beautiful things that you get now molecular expression. The important thing is a molecular expression of the virial series and that is in terms of these series.

So I now have second virial coefficient in terms of $\int_0^\infty drr^2 f(r)$. So this is the second virial coefficient and f(r) is $f(r) = e^{-\beta u(r)} - 1$. So these now tells a way to do the second virial coefficient. Now this has played a very, very important role in this particular derivation of second virial coefficient with exceedingly important role and this is the following.

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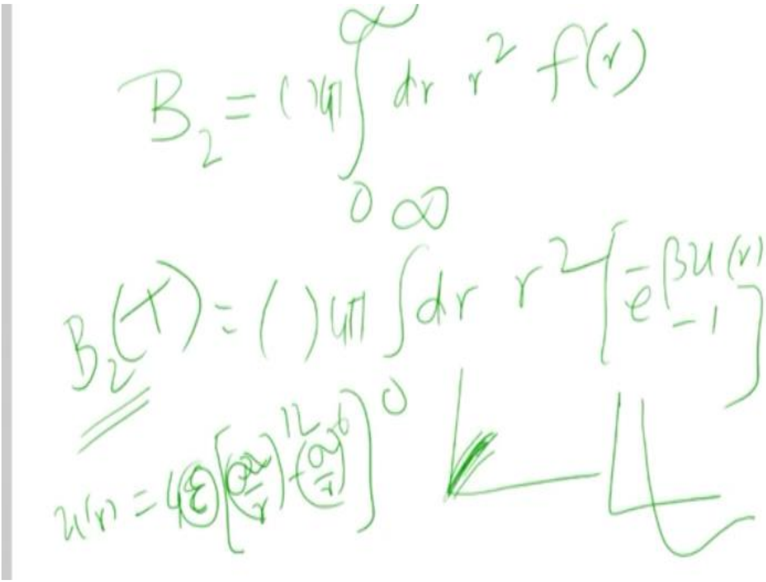

So now I have a second virial coefficient, which is given in terms LP factor. I am not too interested in that $\int_0^\infty drr^2 f(r)$ and then I have, okay of course 4 pi and other things are there and density. Now u(r), so before this we did not have, we had forms like the Lennard-Jones interaction potential, but he did not know how to get them. Quantum calculations, they are far off and very difficult, but now suddenly I have a beautiful expression of the second virial coefficient.

So I go to equation, I get this part which will be quite nicely given by the second virial coefficient. Now I do the temperature dependence of this guy. So I get now second virial coefficient temperature dependence. So now I fit it. So by knowing the temperature dependence of second virial coefficient experimentally and knowing Mayer’s expression of the second virial coefficient in terms of interaction potential, I could now get my, so this was the first time.

So these values of epsilon and values of sigma in the interaction potential, they came out first times were calculated by using Mayer’s expression of the second virial coefficient. So Mayer expression of second and third virial coefficient and fourth virial coefficient played a very, very important role. People started doing a molecular microscopic theory of condensation. They get the virial coefficient. Now they see the virial coefficients which were introduced phenomenologically.

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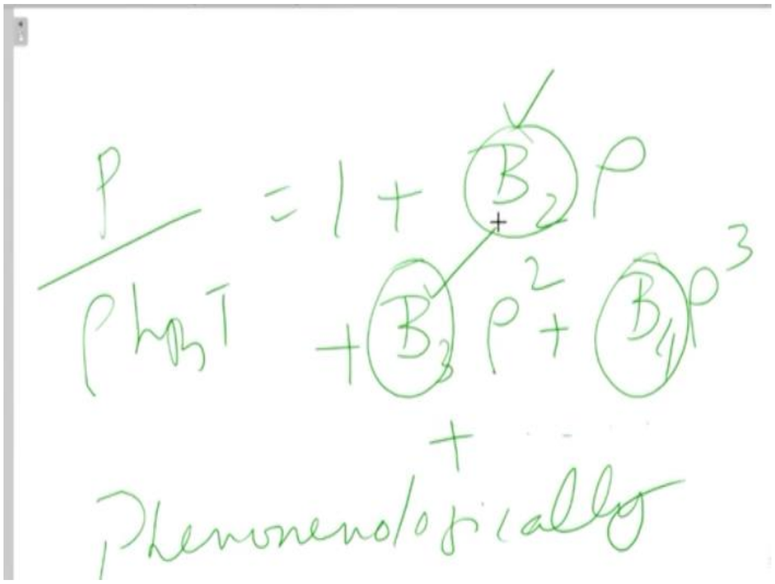

The virial coefficient was introduced because this was written down $\frac{P}{\rho k_B T} = 1 + B_2\rho + B_3\rho^2 + B_4\rho^3 + \ldots$. So these are just virial coefficients, second virial coefficient, third virial coefficient, fourth. They are phenomenological. This was virial phenomenologically from the experimentally determined equation of state, but now we are told as what is B_2 in terms of interaction potential.

Mayer told us what is B_3 in terms of interaction potential. Now I can go back use Mayer's expression and the experimental values of second virial coefficient temperature dependence. I can get the interaction potential. So this was the huge significance of this approach, the cluster expansion, the Mayer A function, the cluster integrals BL and in the usual contestant beta 1 which you can work out. They are all done here, was to get the interaction potential.

So then we talked all these days the force fields, all the glory of things to computer simulations. We derived very complex systems, but the fast things came out. So the real coefficient is more than 100 years old. Even at the time of Mayer, it was 40-50 years old, but one did not know that it is coming from interaction coefficient. One can expand Van der Waals equation of state and get the virial series, but one found out that does not work.

That means that is why actually A and B was determined, but that did not work well, because they are phenomenological. They are not robust, but Mayer's theory gives us a robust way to look into the interaction potential and evaluate and that played extremely important role in our development. So even today the values of the force field that we call for argon, the sigma and epsilon comes from these kind of things. The epsilon is 119 K that comes from these analyses and so there are certain limitations of Mayer's theory.

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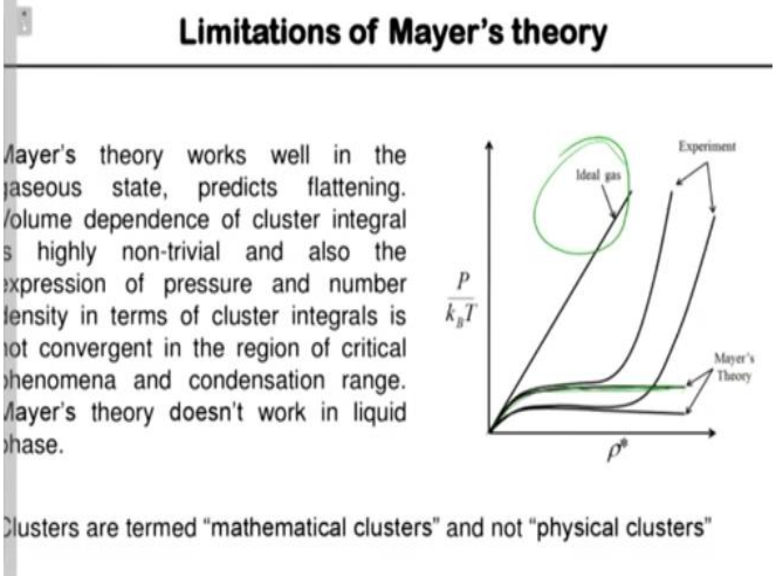

Limitations of Mayer's theory

ayer's theory works well in the aseous state, predicts flattening. olume dependence of cluster integral s highly non-trivial and also the xpression of pressure and number ensity in terms of cluster integrals is ot convergent in the region of critical henomena and condensation range. ayer's theory doesn't work in liquid hase.

lusters are termed "mathematical clusters" and not "physical clusters"

That this is the ideal gas and this is the Mayer's. Unfortunately, if you do Mayer's theory, you know it kind of gives the condensation, but then it remains flat and there are many, many reasons for that and we are not going to go into that in this detail. You can get that in the book.

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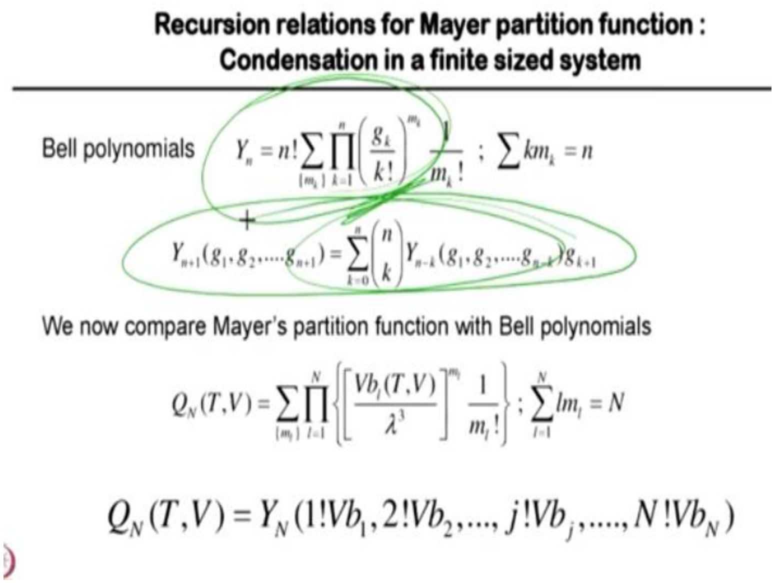

Recursion relations for Mayer partition function : Condensation in a finite sized system

Bell polynomials $Y_n = n!\sum_{\{m_k\}}\prod_{k=1}^{n}\left(\frac{g_k}{k!}\right)^{m_k}\frac{1}{m_k!}$; $\sum k m_k = n$

$$Y_{n+1}(g_1, g_2, \ldots g_{n+1}) = \sum_{k=0}^{n}\binom{n}{k} Y_{n-k}(g_1, g_2, \ldots g_{n-k}) g_{k+1}$$

We now compare Mayer's partition function with Bell polynomials

$$Q_N(T,V) = \sum_{\{m_l\}}\prod_{l=1}^{N}\left\{\left[\frac{Vb_l(T,V)}{\lambda^3}\right]^{m_l}\frac{1}{m_l!}\right\} ; \sum_{l=1}^{N} l m_l = N$$

$$Q_N(T,V) = Y_N(1!Vb_1, 2!Vb_2, \ldots, j!Vb_j, \ldots, N!Vb_N)$$

Then there are many studies beautiful, beautiful studies that have been done. So we are talking of this finite to the Bell polynomials. The Bell polynomials are a class of generalized polynomials, very powerful polynomials which exactly has the same formula, which nobody knew, Mayer did not know. We did not know for many years, but the advantage is that if that is so, then they have a beautiful recursion relations which we can use now and this is the recursion relation, Bell polynomial recursion relation, which now can be used to evaluate Mayer partition function.

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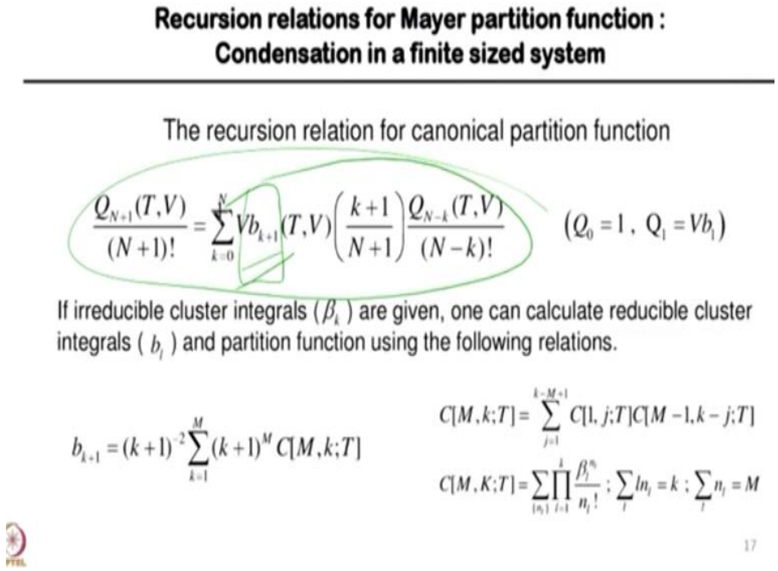

Recursion relations for Mayer partition function : Condensation in a finite sized system

The recursion relation for canonical partition function

$$\frac{Q_{N+1}(T,V)}{(N+1)!} = \sum_{k=0}^{N} Vb_{k+1}(T,V)\left(\frac{k+1}{N+1}\right)\frac{Q_{N-k}(T,V)}{(N-k)!} \qquad (Q_0 = 1,\ Q_1 = Vb_1)$$

If irreducible cluster integrals (β_k) are given, one can calculate reducible cluster integrals (b_l) and partition function using the following relations.

$$b_{k+1} = (k+1)^{-2}\sum_{k=1}^{M}(k+1)^{M} C[M,k;T]$$

$$C[M,k;T] = \sum_{j=1}^{k-M+1} C[1,j;T]C[M-1,k-j;T]$$

$$C[M,K;T] = \sum_{\{n_l\}}\prod_{l=1}^{k}\frac{\beta_l^{n_l}}{n_l!} ; \sum_l l n_l = k ; \sum_l n_l = M$$

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And that is a beautiful stuff and you get this beautiful relation of Mayer body. So if we can have some reasonable cluster integrals, then we can do a good job, but the difference is that these problem remain. We made considerable progress, but we did not solve the problem, because the reducible clustered integrals are not available. Even today, they are not available. Irreversible cluster integrals have been evaluated by great pain and it works out somewhat better for many techniques and they are for hard sphere kind of a system when there is no attraction.

It works out within the while, there is a very large number of irreversible cluster integrals. Virial coefficient has been evaluated up to 11 and that means beta F. Irreversible cluster integrals of beta 10 has been done by Grab theoretical methods, a method that Mayer initiated but for Lennard-Jones it has been done only up to some 6 or 7 irreversible cluster integrals, that is not enough, because when it goes to liquid phase, then all the particles become connected. So there is kind of gel that forms and the Mayer's theory breaks down, but you know but we should be happy with what we got and there are some things that are done.

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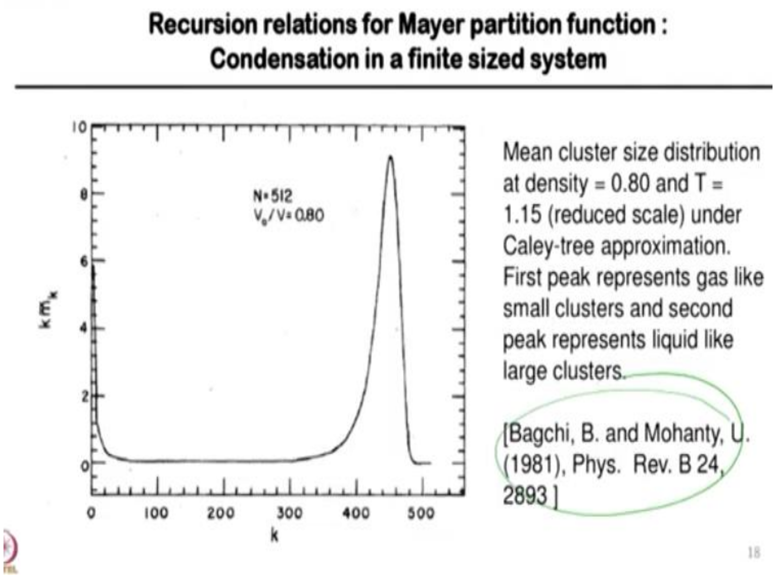

Recursion relations for Mayer partition function : Condensation in a finite sized system

Mean cluster size distribution at density = 0.80 and T = 1.15 (reduced scale) under Caley-tree approximation. First peak represents gas like small clusters and second peak represents liquid like large clusters.

[Bagchi, B. and Mohanty, U. (1981), Phys. Rev. B 24, 2893]

So we will stop here today and there are some old articles that we wrote long, long time ago and is described in the book that the applications of Mayer partition function to the real systems and so we stop here now.