# Basic Statistical Mechanics
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## Lecture – 28
## Cluster Expansion and Mayer's Theory of Condensation (Part 1)

Today, what we will start on is an important area of statistical mechanics, important both for physics and chemistry and as I keep telling you that these are fairly regularly taught in most places in the world, at least in serious places. Now why these things are important is the following:till now we have done ideal gases and ideal gas the particles do not interact though they have many interesting properties and particularly useful expressions like entropy specific heat that we use later.

However, a system under is interesting because they interact with each other they undergo phase transition an ideal gas does not go undergo phase transition, you plot P against 1/V you know it just never shows any bend.

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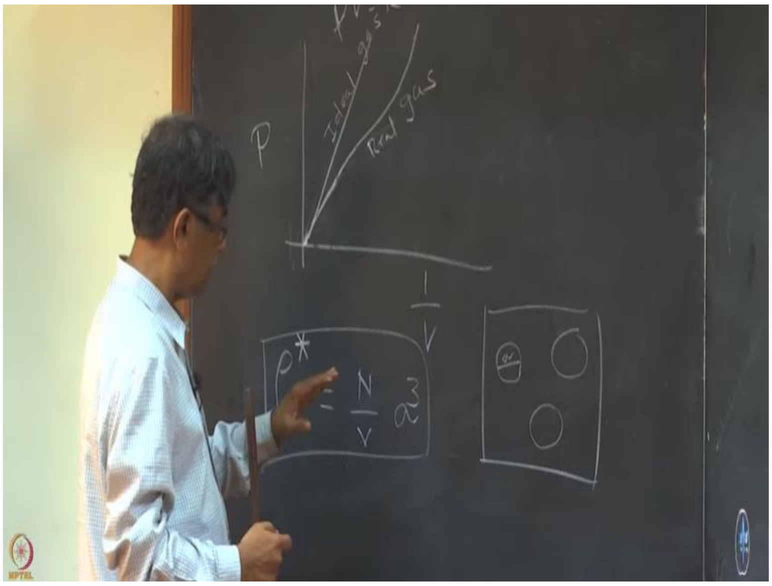

Like if I plot P against 1/V then remember it is a straight line and this is the that is how it goes okay that s where universal gas constant was found out. In real world however when you high temperature, it is something like that but when you go to low temperature then it undergoes a phase transition and this is gas, this is liquid and then it goes undergoes one more phase transition, is the crystalline state.

So, these breaks and this is the coexistence are because the phase of the system goes discontinuously from gas to liquid to crystal. An ideal gas which does not interact does not show the phase transitions, it just goes on linearly. When people started looking into that then what the first thing that you find that was noted by Van der Waals that if this is the ideal gas which was known for long time, then a dense gas when density of gas I little bit quantify what is the density because it is very important.

Then it starts deviating from the a then it goes like that but it starts deviating from the ideal gas behavior. So, this is the ideal gas which is PV = RT. This is real gas, at lower temperature it undergoes phase transition but you do not need to talk about it right. We will talk about it at length but right now let us see that we are just not that low temperature we are intermediate temperature, but we start seeing the departure from the ideal gas behavior as I said this was observed by Van der Waals and many other people.

So, the people then tried to explain this it was clear very early that this is because of interactions between atoms and molecules. Now in order to talk of interactions I need to talk about separation (length scale) between two things and the way we talk is introduce a dimensionless quantity $\rho^* = \frac{N}{V}\sigma^3$ where N is number of particles in a volume V and $\sigma$ is the molecular diameter.

so N sigma cube is kind of a fraction of the volume occupied by molecules. So this gives you a measure that if these kind of molecules and if this is sigma then pi/6 sigma cube would be the volume each one occupies then you get a measure of that. So in the $\rho^*$ is very significant by making it dimensionless we get some very important what is called the convergence for example.

The r $\rho^*$ is typically in the liquid is between 0.8 or 0.85 to 0.95; gas is between about 0.1 or so. So, in between these gas and liquid there is a huge coexistence which really takes you from 0.1 to 0.6 or so these are very important numbers. Why it is important because you know I tell you some numbers like water $\rho^*$ is 0.76 then acetonitrile, think as for remember something like 0.85, methanol little bit more dense it is about 0.9.

So, when you in number density if you look at them number density this part varies quite dramatically from one liquid to another liquid even of the order of one order of magnitude. But however, when you do the $\rho^*$ there is a universality that appears, the universality is that this is that we have a suddenly a dimensionless quantity to characterize a liquid okay.

Now I have a number, I can put ok this is the density rho star where I have a liquid this is where it is I do not have to talk of those numbers like $10^{22}$ or a density of water $10^{23}$ per cc, those kind of big numbers are really does not make many sense to a scientist. A scientist must make them understandable something we can grasp we can kind of think.

And this $\rho^*$ also at the same time is the kind of a fraction is proportional to the fraction of the total volume occupied by the molecules or atoms if I consider them as hard spheres. They are not hard spheres but there is a big repulsive potential and because of the rough potential you have size and that is why Pauli was fond of saying that that he created the solid state or condensed matter physics because of Pauli exclusion principle and all the you have the in a hard repulsive part of the potential and solid exists because of that hard repulsive part of the potential.

Pauli was known for making many interesting jokes okay. So, this is an important thing that the number density now. As I just said in the ideal gas which we derived last two three lectures that we have these expressions, they are very nice expressions, but they are not they cannot explain phase transitions. Phase transitions exist as Pauli also said called condensed matter because particles interact you and me, we exist because we interact.

For some people it does not bother that whether you exist or not or you know or why you exist but for some crazy people it is important to know why you exist. So, these teaching in India which is a very “What” based; I remember our school questions were always what is this famous for? what is the capital of Hawaii or whatever? what is the capital of Madagascar? so what are the important goods made in Nigeria?

It is all about “what” and you go very far by just doing “what”. We do not say “why” and why these things happen? why you get this particular fruit in that Mediterranean? then come even deeper level is “how”; how it happens? You know Feynman, you must be joking Mr.

Feynman, there is very interesting chapter you should read Richard Feynman’s father was a salesperson he wanted to make his son a scientist.

So, whenever he had time, he was at home he would make scientific toys and then he would take his son into the park, their little track mountainous region he would go and he would teach them he would teach them this the bird that is the this is what that is bird and then I think Feynman was always a show off right. So, he showed up little bit and then whole locality every father and mother started taking their children out for trekking.

And then they all knew names of every bird or everything and they now in turn asked Feynman hey do you know the name of that word and by the time Feynman forgot it. Then Feynman s father told him a very important thing which Feynman said was important all his life that the name is not important. It is important that what it looks like it is important this kind of bird does this kind of things and you find in this area.

So, you know many of our education system is this “what” based we do not even go to “why” and then of course “how” is little far. So, coming back we are now going to ask a few questions why a phase transition takes place and how do we explain that?

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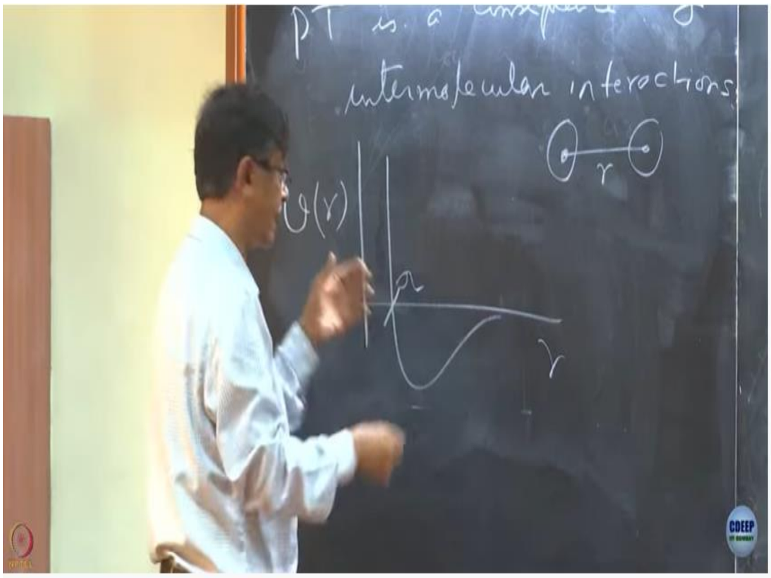

So, this is a long and very, just like chemical reaction dynamics which has got probably one of the most celebrated theories and most celebrated Nobel laureates coming from Rudy Marcus, Polanyi, Ahmed Zewail and many others more recently essentially the paper of 1976 which gave Levitt and Karplus the Nobel prize was also essentially doing enzyme kinetics.

Now in physics and also part in physical chemistry it is equally respected and celebrated is the phase transition and the condensed matter.

So, because that is how materials form and now that is how we understand how something forms then of course thermodynamic properties are important like compressibility as we discussed and other resistivity then of course electronic properties which somehow people are more focused on, but you have to make the material first before you start electronic properties.

So basically, why and how the phase transition occurs? Gas to liquid and liquid to solid. So, this is the question that will be asking today and next few lectures. Now as I just told you how to go about it, I told you that ideal gas does not have a phase transition because there is no interaction between them. So, phase transition is a consequence of intermolecular interaction, actually everything is interesting is in intermolecular interactions.

So, let us first define what is what I mean by intermolecular interaction, the simplest one or one of the simplest one is intermolecular interaction V(r), r is the separation between two molecules I have the simplest thing in mind. There are two molecules and the r is the separation from center to center we are against r and I have this is the one short term part of that this I call molecular diameter sigma $(\sigma)$.

This is harshly repulsive; remember Pauli’s comment this is because of electronic overlap of the electrons electron density. This is an attractive part. Hard sphere itself is a very interesting system and in any statistical mechanics huge amount of study goes on just to study the hard sphere part where that hard sphere part is not really realistic like this is the this potential called Lennard-Jones potential explains properties of noble gas very well.

That is what the first kind of things that people developed. So, these V(r) is written as these are the things, I will be using this called Lennard Jones 6-12 potential.

$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

This repulsive part that is very short range and diverging and this is the attractive part this is the part which is given by this minus sign here.

So, this is the one of the simplest interaction potentials. Okay now with phase transition due to interactions and if this is a kind of interaction potential I am having and that is what I was mentioning to you, even at a two body potential I cannot solve Newton’s equation I can reduce it to a quadrature and three body I cannot solve at all that is why we need to go to statistical concepts. Now keep a little bit of that upstairs but then I am going to do the rest of the how do you go about doing statistical mechanics.

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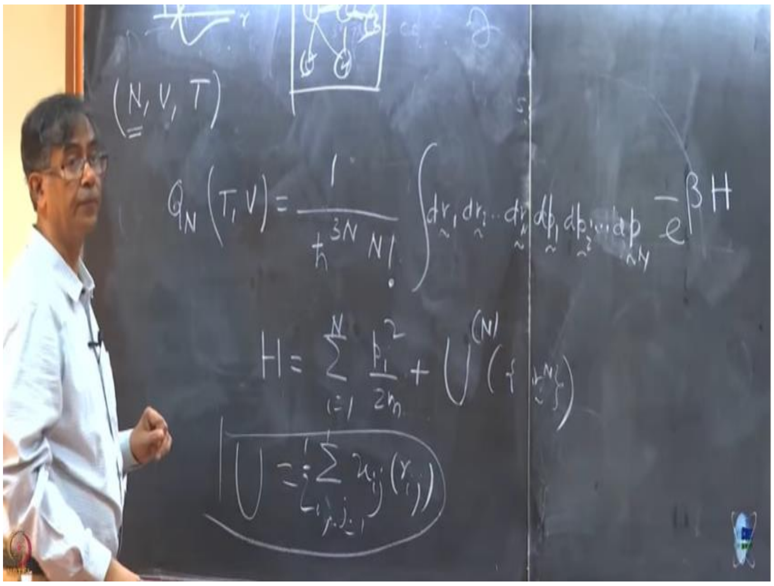

So, I keep V(r) , let me just keep this one that is enough okay. So, we cannot do now. How do I start about it? I want to consider N number of molecules and volume V at temperature T that is I want to work in canonical ensemble and now I want to calculate the partition function of this quantity. So statistical mechanics tells me if I want to calculate free energy, I want to calculate the equation of state pressure versus density, I have to work in one of the ensembles.

Micro chemical ensemble, in this case is incredibly difficult, that because the constraint of constant energy does not lead me to any easy, it is not amenable. So canonical ensemble we can make some progress, grand canonical also we can make progress. But this is the one historically as I told you before you work and canonical particle means I have a system with a total number of particles N which are interacting among themselves with this potential and I put them in a volume V and at temperature T.

Now if I decrease the volume or decrease temperature these system from gaseous state would go to liquid then to solid and how do I describe this sequence of phase transitions? How do I decide that at what temperature or density a gas, water for example we know at 100 degree centigrade and atmospheric pressure goes from steam to liquid water and then 0 degree centigrade goes to ice, what determines it?

What determines this temperature 100 degree centigrade or 0 degree? What determines water goes into hexagonal open structure? What determines iron goes to FCC? And what determines sodium goes to be BCC? What determines when you form nanoparticles what are the size of the nanoparticles? So, these are the questions and you can understand this when you start asking why and how life does not remain that simple anymore.

It is probably much easier to mix A and B or some sample together in a solution put in a bomb I know one of my colleagues puts in a bomb I know actually some kind of glass jar and they increase the temperature and they get nano material and they get a paper which is not a bad way to live actually. Because here you have to think and hard but I told you always that the famous story one guy was a trying very hard to climb Mount Everest.

And then one of his colleagues was lazy and he said why do you want to climb this one you know you can be easily like me lying on bed why do you want to climb that that his great answer was that no it is there it is just there so I have to climb. Now I now start this climbing. So you know we have already introduced the notation I am always a bit worried, think 3N then I have to integrate remember I have to integrate over all the positions then I have to integrate all the momentum if you have any problem you please let me know.

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

Because I have this constraint here is the Hamiltonian right and Hamiltonian is sum over they are I assume all of them same mass i = 1 to n then I have interaction potential U, N particle interaction potential that depends on r this is a notation I told you which means is depend on N particles and U interaction potential.

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

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

This notation or you can put i, j both from 1 to N. If you do that you have to put half to avoid double count. So basically, this is my system main 1, 2, 3. 4, 5 and so I am having interaction between 1 and 2, 2 and 3, 1 and 3, 1 and 4 this all these interactions so this U is sum of all the interactions. Okay the kinetic energy, and potential energy.

Now we immediately note one thing that in a classical statistical mechanic, quantum is difficult, but in classical statistical mechanics this integration of the momentum is a trivial part because these are nothing but gaussian integral which we did before and it does not overlap with position at all. So, I can do the integral part (momentum part) and then write rest as another function which then would involve integration over the interaction potential. Kkay this is the game. So, basically this is let us little bit summarize.

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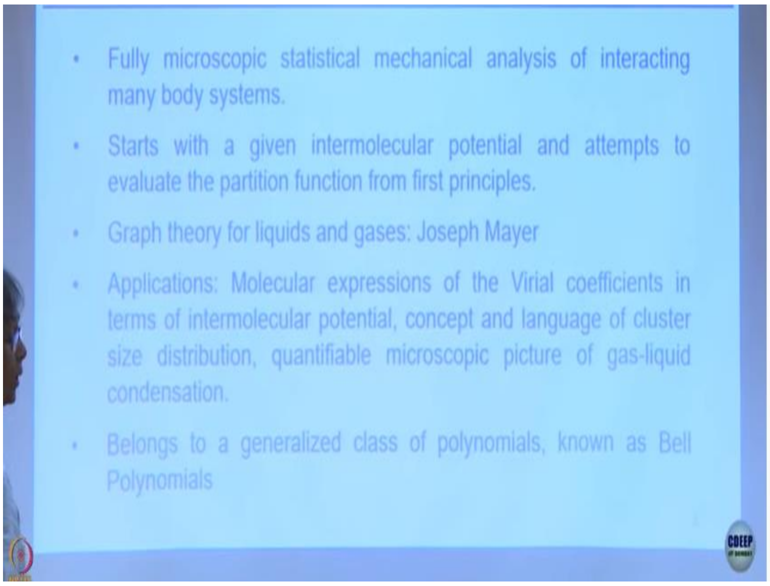

- Fully microscopic statistical mechanical analysis of interacting many body systems.
- Starts with a given intermolecular potential and attempts to evaluate the partition function from first principles.
- Graph theory for liquids and gases: Joseph Mayer
- Applications: Molecular expressions of the Virial 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

Fully micro analysis of interacting many body systems that we are trying to do starts with a given intermolecular potential, in our case we are assuming Lennard-Jones does not matter you can do anything you want what we are going to develop is a graph theory of liquids and gases this was introduced by Joseph Mayer and then it went into quantum.

Actually, many of the quantum things that people do many kind of many cluster expansion, coupled cluster and all the kind of things, it was basically started in Stat. Mech. even before all the Feynman graphs and all these things, it happened it happened 1937 that Joseph Mayer formulated the theory that we are going to describe is a very pretty theory very nice and beautiful theory and has tremendous insight into it.

We will derive expression of the partition function; we will derive the molecular expression for Virial coefficients in terms of intermolecular potential, we will go towards the radial distribution function and microscopic nature of gas-liquid condensation. It has been attempted by many people to go to liquid to solid that does not work so why but it gave rise this theory gave rise to the most successful theories of liquids that we know today that are in in all the textbooks.

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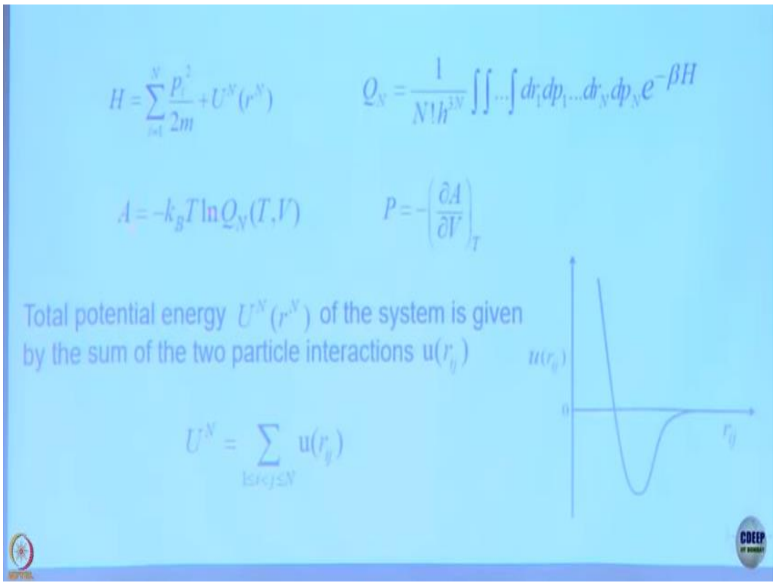

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + U^N(r^N) \qquad Q_N = \frac{1}{N!h^{3N}} \int\int \ldots \int dr_1 dp_1 \ldots dr_N dp_N e^{-\beta H}$$

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

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 this is the partition function and what if we can evaluate that partition function I can get the free energy and if I can get the free energy I can get the pressure, as a pressure as function of volume and that was the that is called the equation of state and that should show the phase transitions in the presence of interactions. And then this Hamiltonian which is to be integrated over with the Boltzmann factor is given by kinetic energy plus total potential energy and total potential energy is here.

And this another notation that we use where you already put that I showed you here 1-2, 1-3, 1- 4 then 2-3, 2- 4 you do not have 2-1 because you have this constraint that j has to be greater than i. So, the one that comes later has to be bigger than that is a way to arrange this kind of arranging we do in theoretical research repeatedly everywhere.

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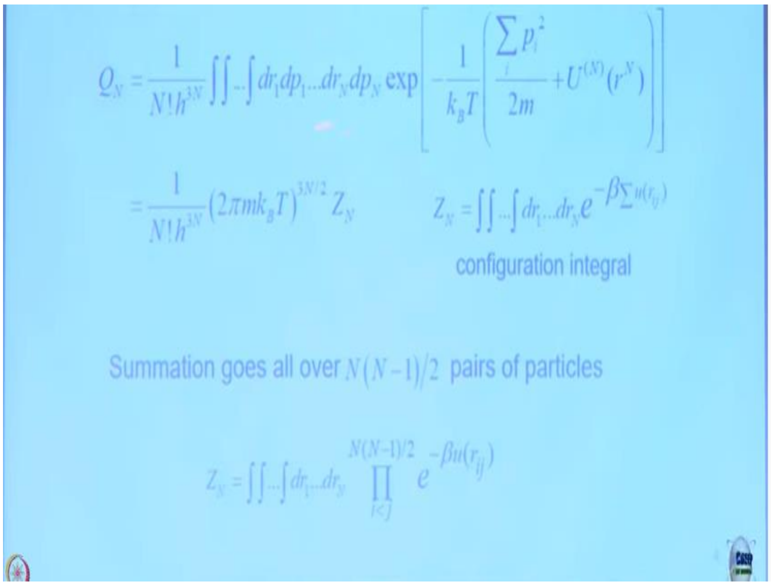

$$Q_N = \frac{1}{N!h^{3N}} \int\int ...\int dr_1 dp_1 ... dr_N dp_N \exp\left[ -\frac{1}{k_B T}\left( \frac{\sum_i p_i^2}{2m} + U^{(N)}(r^N) \right)\right]$$

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

configuration integral

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

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

Okay now so this is what I have been telling that we now do that, the full thing in full glory and this integration is that I can now carry out that we did in monatomic gas, ideal monatomic gas this is exactly. So, in ideal monatomic gas this part is 0 because molecules do not interact with each other, then I only have this integral to do and that is what it comes here and that is what de Broglie wavelength by taking h, check me on that.

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

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

where

$$Z_N = \int\int ...\int dr_1 ... dr_N e^{-\beta\sum u(r_{ij})}$$

So, 1/ factorial lambda to the power 3n but main important thing that that set aside main important than the effect of interactions is take in the $Z_N$ we are following in Mayer's 1937 notation this is called the configuration integral as from here is configuration integral. Some things in our signs are get less credit and as I was telling you that in the folklore and the in terms of the huge contributions another person, we hardly talk about is Willard Gibbs who single-handedly do it so much.

Similarly, the one person Mendeley, we consider to be we do not celebrate enough another person who did his enormous amount contribution is Joseph Mayer okay. So now this is the then I am going to play certain tricks is the following I notice that this quantity which is sum in the exponent. Now sum in the exponent can also be written as a product, right? sum in the here you understand know that this is u and u is the sum so sum in the exponent is nothing but a product okay.

So now and the product is there all in all when all these things there are N (N – 1)/2 correct okay. So, this is I can write that quantity as that quantity right okay. Now comes a very important thing that look at this thing now $e^{-\beta \sum u(r_{ij})}$ and look at this my potential so when r goes to infinity then if $u(r_{ij})$ goes to 0 then this quantity goes to 1 and this is I now decompose that when I decompose these things, I will find that a very large number of terms comes in.

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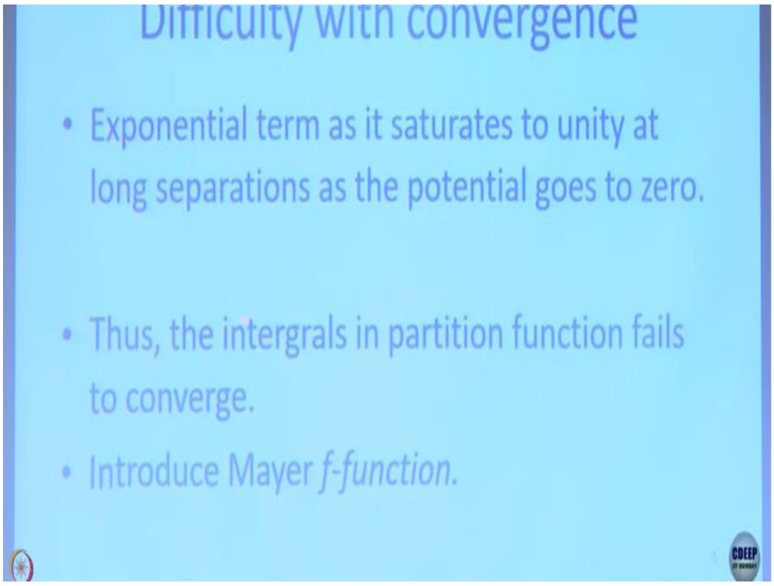

Difficulty with convergence

- Exponential term as it saturates to unity at long separations as the potential goes to zero.
- Thus, the intergrals in partition function fails to converge.
- Introduce Mayer *f-function.*

So, this is a problem that is why I introduced a Mayer- f function. But let me go through this now.

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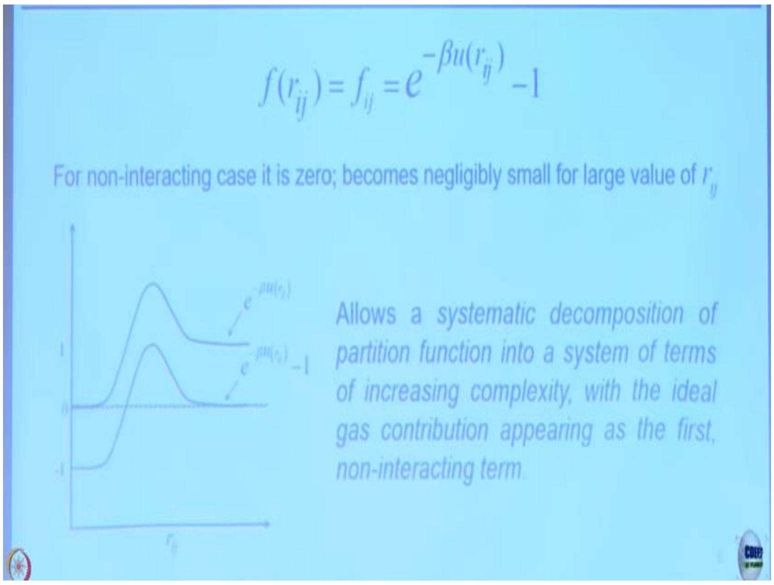

$$f(r_{ij}) = f_{ij} = e^{-\beta u(r_{ij})} - 1$$

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 we will go to this now.

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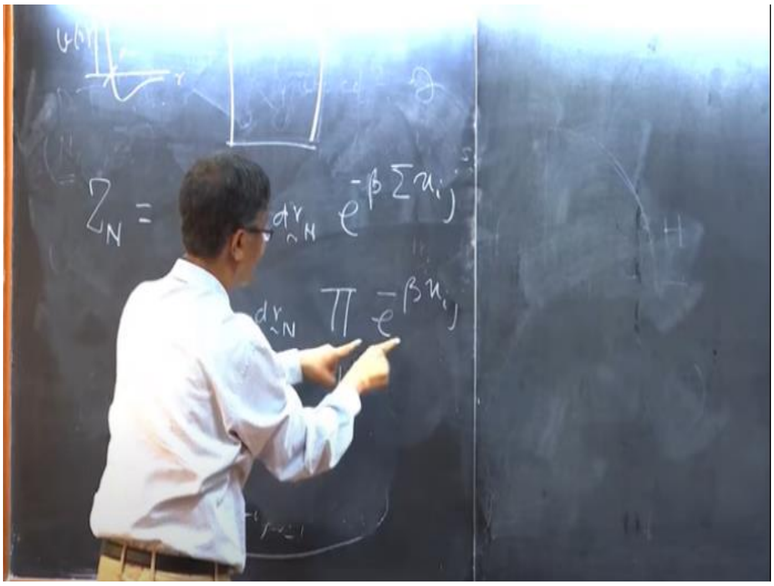

So $Z_N = \int\int ... \int dr_1 ... dr_N e^{-\beta \sum u(r_{ij})}$. Okay now this is the sum over all the particles which I am now writing $Z_N = \int\int ... \int dr_1 ... dr_N \prod_{i<j}^{N(N-1)/2} e^{-\beta u(r_{ij})}$. This then here the difficulty I face I tell you if I keep it like that these integral here does not converge so Mayer then did the following trick Mayer listen carefully what Mayer did he said okay I it this is the this is the difficult part I introduce the function f which is the this function.

Now if I do that function then this simple mathematical trick means that I have to replace $e^{-\beta \sum u(r_{ij})}$ here, this is a beautiful trick actually it is two different things that it does and as I told you this is essentially the start of the graph theoretical language in physics and chemistry, you go you bring this here. Now this simple trick allows the following advantage $u(r_{ij})$ goes to infinity here and $e^{-\beta\sum u(r_{ij})}$ goes to 0.

But however, when r goes to infinity these goes to 0, this goes to 1. However, if I take - 1 out then when r goes to 0 this r is the goes to infinity and goes to 0 like here and it goes to - 1. But when $r_{ij}$ goes to 0 then this goes to 0 this goes to 1 then it goes to 0. So, by this transformation you are removing the divergence okay and this is allowing a systematic decomposition of partition function which is fairly trivial, but we will see how it goes to graph theory.