Introduction to Molecular Thermodynamics
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Lecture – 38
Classical Statistical Mechanics

Welcome back, we are discussing the application of classical statistical mechanics to understand the properties of ideal and non-ideal gases

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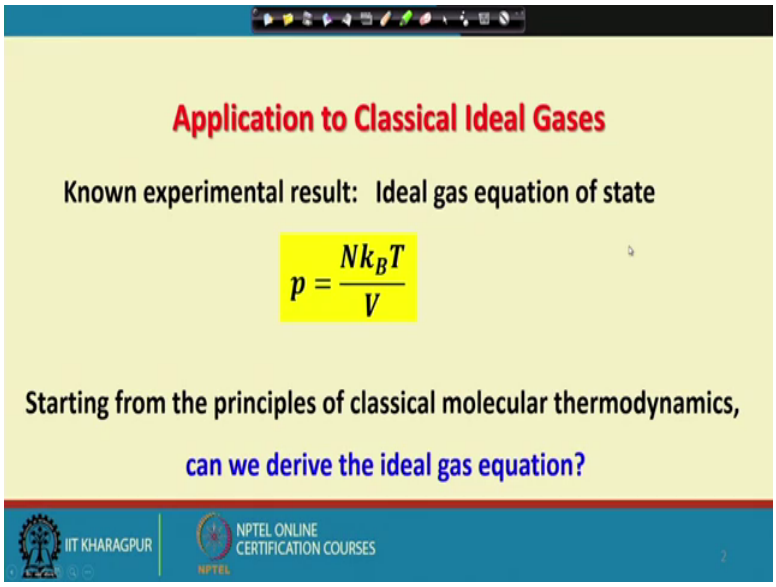

We have already seen that for the classical ideal gas, it is indeed possible to start from the basic principles of classical molecular thermodynamics and derive the ideal gas equation.

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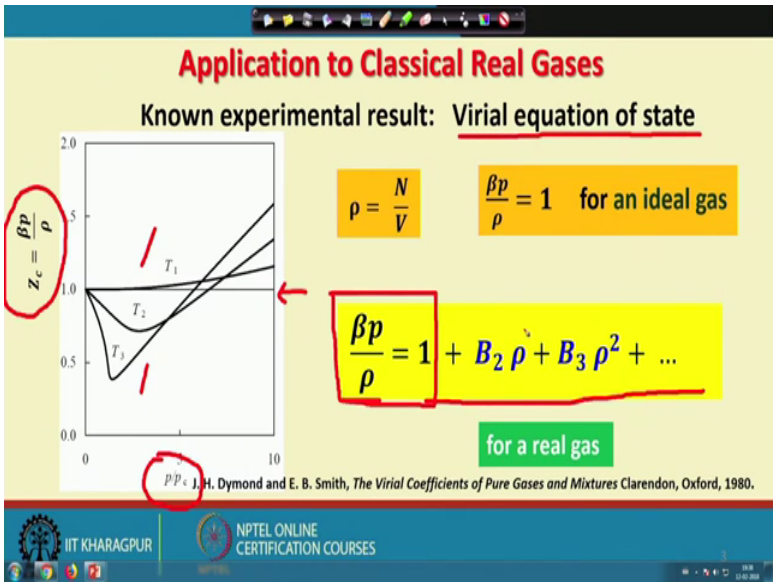

So, in this lecture I am going to focus on the real gases, where I assume that the real gas is comprised of structure list particles between and the interaction between the particles is not negligible. Now, how do I know that a particular system is different from an ideal gas? This is most easily understand understood by plotting what is known as a compressibility factor, and this is shown here that Z c is beta P by rho that is plotted as a function of pressure.

And as expected from the ideal gas equation this factor is supposed to be equal to one, but in many cases it is found that the real gases exhibit market deviation from unity as a function of pressure and the deviation whether it is positive deviation or a negative deviation depends on that not only on the nature of the gas, but also for a given type of gas at what temperature such measurements are being made.

Based on these observations Kemmerlin and Owens proposed equation of state for the real gases. And this is known as the Virial equation of state for real gases and it expresses the quantity beta p by rho in a power series summation in number density rho.

So, as you see that this part describes the ideal gas behavior and for real gases you have additional terms dependent on rho and rho square and the coefficients B 2 and B 3 these are known as the virial coefficients and they reflect the deviation from the ideal gas behavior. So, in this lecture we are going to particularly focus on this second virial coefficient and we are going to look at the behavior of B 2 as a function of temperature.

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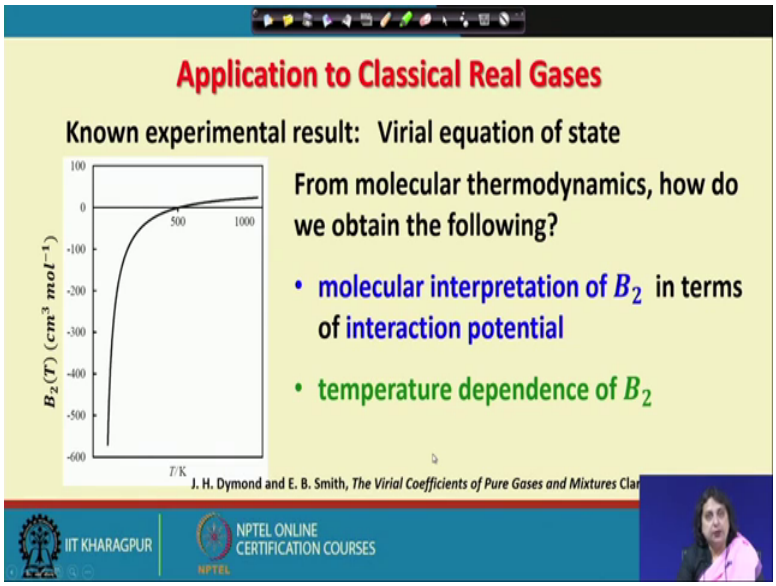

So, this is the result from experimental data, where B 2 has been plotted as a function of temperature and the observation is B 2 is a very large negative number for small values of temperature, as you increase temperature B 2 also increases and it goes to more positive values and beyond certain temperature it goes to positive values and the question that we are asking here is as follows.

Using the principles of classical statistical mechanics that, we are implementing within the framework of molecular thermodynamics. Can we give any molecular interpretation of the second virial coefficient B 2.Especially we will be interested in knowing how B 2 depends on the underlying interaction potential that is the potential energy term on the Hamiltonian on the system. And secondly, we would also like to understand why B 2 depends this way on temperature. So, let us next try and understand these two questions one by one.

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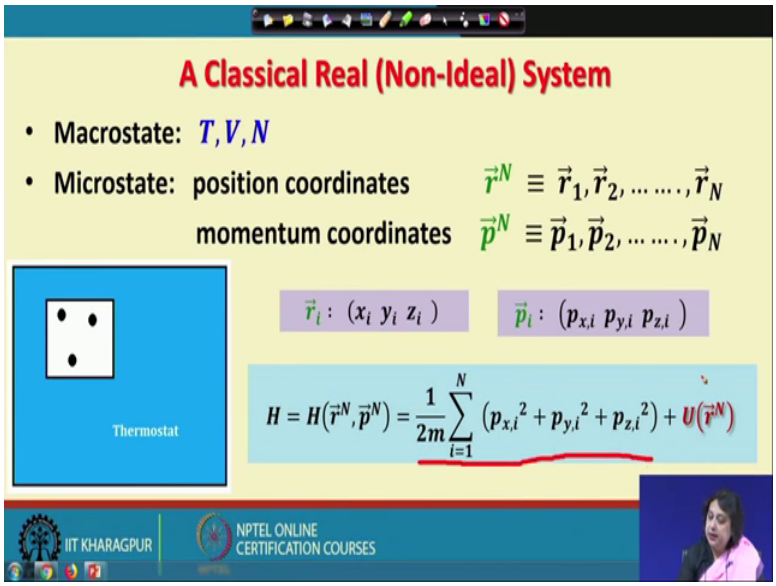

Now, once again we are going to adopt the kind of representation that we have already discussed in the case of ideal gases. So, the first thing is we are working in the canonical ensemble, we have 6N positional coordinates position and momenta coordinates of these 3 r belonging to particle 1 position and 3 r belonging to particle 1 momentum.

So, in general we are going to use a condensed notation like this. So, r i is a position vector of the ith particle having the component x i, y i and Z i similarly these three numbers corresponds to the X, Y, Z component of the ith particle of the momentum of the ith particle in three dimension.

Now, if I write down the Hamiltonian of this system, what I find is here as before I have the kinetic energy terms for the total capital N particles, but now I have an additional term U and this is the potential energy that contains information regarding the interaction between all the capital N particles present in the system and therefore, what we will say is we are going to try and write down the canonical partition function for this system.

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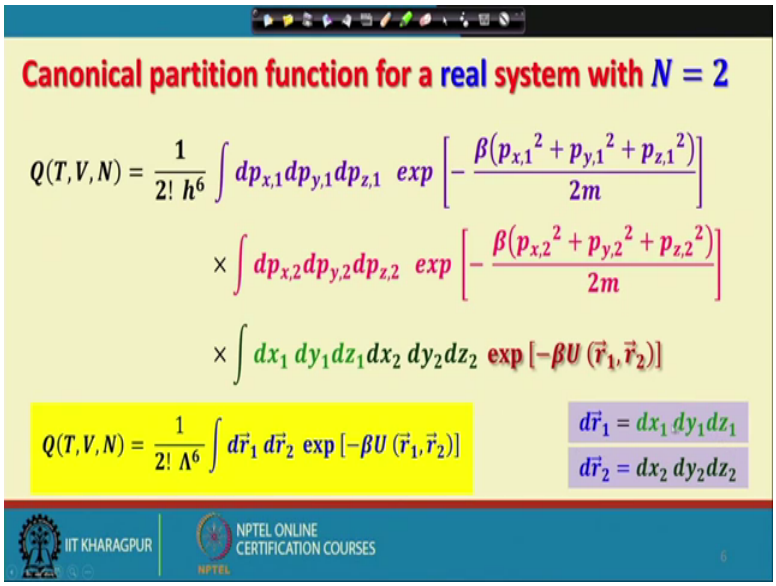

To keep our discussion simple let us first write the canonical partition for only two particles. So, in that case as we have seen before, we can explicitly write out the 6 into 212 dimensional integral form of the canonical partition function and here unlike the ideal gas case, I now see that in addition to the momentum integrations.

Now, I have one integration which has the integration being performed with over the coordinates of particle 1 as well as the coordinates of particle two and the integrant is e to the power of minus beta U where u is the total potential energy of the system involving the two particles located at the position vectors r 1 and r 2.

Now, as you see then; obviously, I can generalize this kind of observation in a much more condensed notation, where I would say that if I carry out the momentum integration that is something that we have already worked out. Then these all these terms can be simplified into one term which corresponds to the yes the thermal the (Refer Time: 07:33) wavelength.

So, that is what appears over here and I am left with this integration, which I have written down here using a condensed notation where my d r 1and d r 2 are essentially d x 1, d y 1, d Z 1 and d x 2, d y 2, d Z 2.

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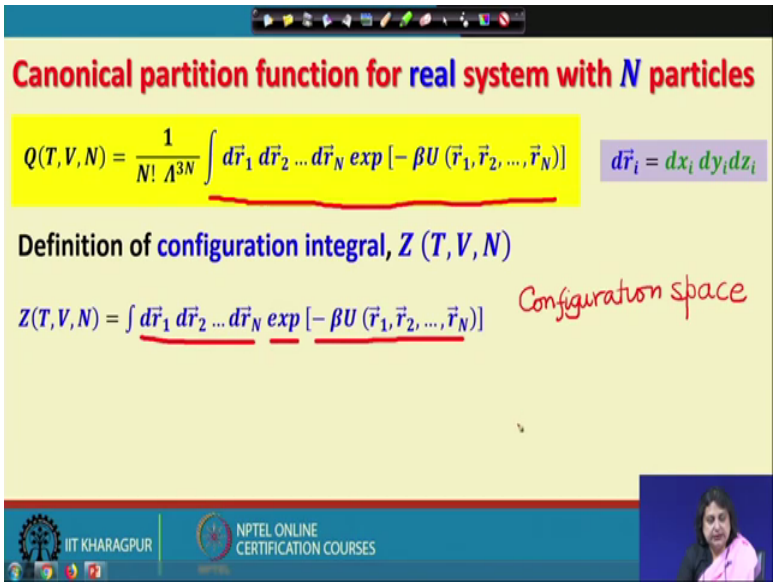

Now, once I understand this, then I do realize that now the major difference from the ideal gas case is appearing because of the presence of the non-trivial dependence of this integrand on the positions of the capital N particles present in the system, through the appearance of the potential energy term.

Now, let us now introduce a new function, which we will call the configuration integral this is given this symbol Z and just like q it also depends on TV and N. So, this quantity the configuration integral is defined as whatever additional integration that I am getting for the non-ideal case.

So, I have in the integrand e to the power of minus beta U, that is U is the total potential energy of the capital N particle system multiplied by minus 1 by k t when the system is present at temperature T and then I am going to integrate over the entire configuration space, which is the part of the phase space, where I do not take into account the momentum of the particles rather I integrate only over the position coordinates of the particles.

Therefore, the space that is the 3 N dimensional space that expand by r 1, r 2 to r N is known as the configuration space. Because the name follows from the fact that it depends on the configuration of the system, that is in terms of the position vectors of the N particles and it does not depend on what the their association momenta are. Therefore,

it is; obviously, a subspace of the total phase space and once I understand this definition, I can go ahead and write and write this expression in a more condensed notation.

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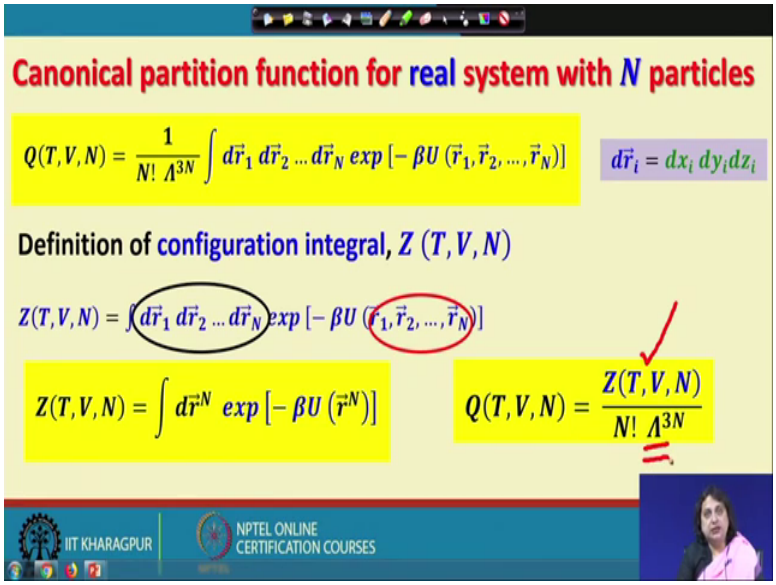

So, that Z that configuration integral is given by e to the power of minus beta U integrated over the entire configuration space.

And then I find that for the entire canonical partition function it is nothing, but this configuration integral divided by N factorial into lambda to the power of 3 N. So, now, I see that for an interacting system, if I want to calculate the canonical patrician function, in that case it requires me to understand what this configuration integral is and at a given temperature.

If I know the mass of each of the constituent particles, then I can find out lambda and capital N is fixed for a given system as a result knowing Z, I should be able to evaluate what capital q is. So, that is what we will look at next.

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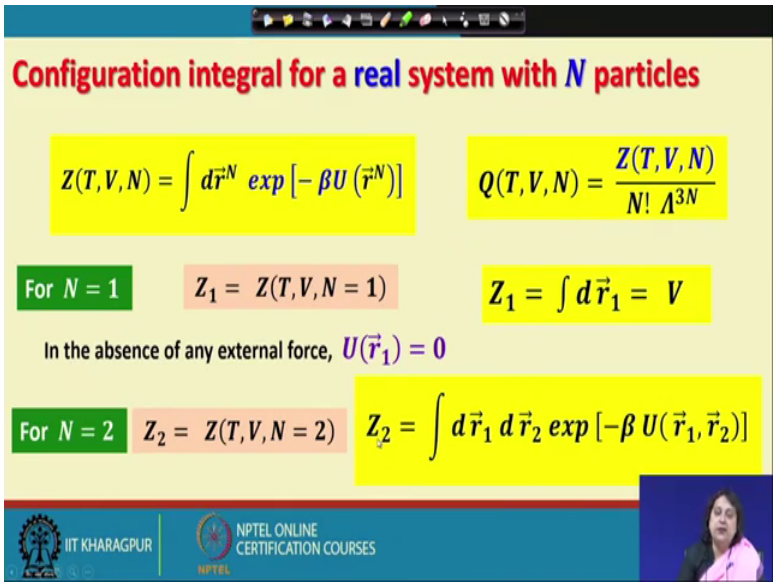

So, when N is equal to 1 if I have only one particle present in the system, then what shall I have a Z would be the value of the configuration integral, when N is equal to 1. So, if I write down the definition of Z 1 this is nothing, but integral d r 1 and so, when you have only a single particle in the absence of any external force field, then you can very easily assume that the self-energy of this single particle is equal to 0.

Therefore, I would not have n e to the power of minus beta U term because U is equal to 0. So, e to the power of minus beta U equal to 1 and I know that since this particle is contained within the volume V. So, integral over d r 1 must give me back the volume of the system.

Now, what happens if I have two such particles? Then the configurational integral is given the symbol Z 2 and by definition this is the same Z, T, V, N, but now computed with N equal 2. So, if I write out what explicitly would be the expression for Z 2 it is this. So, Z 2 is the configuration integral of a system comprised of two particles 1 and 2.

Let us say the these two particles are present at position coordinates r 1 and r 2 in the 3 dimensional space, then Z 2 is defined as e to the power of minus beta U r 1 2where U r 1 r 2 is the total potential energy of these two particles and integrated over the entire configuration space. So, taking this examples and trying to understand what the configuration integral is helpful.

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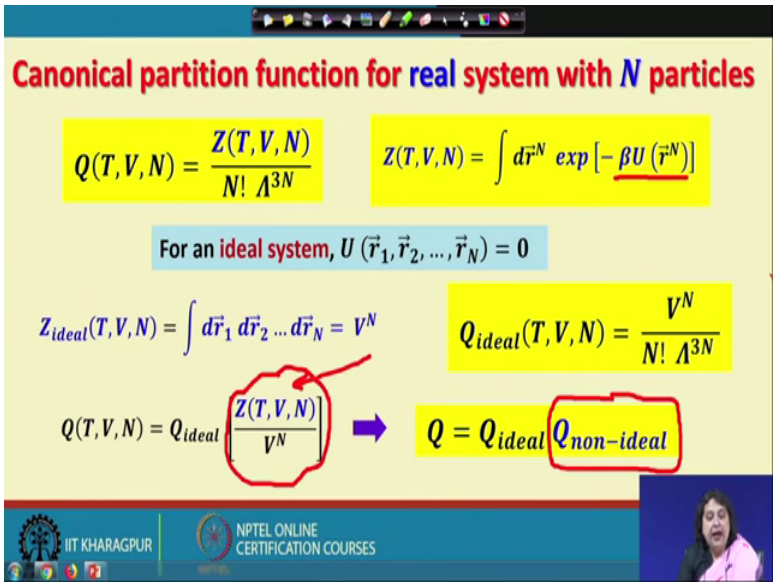

Because for the real system with capital N particles these will appear at different stages or the other the simplest system of course, is the ideal gas case where the N particle potential energy is equal to 0 because there is no interaction between the different constituent particles in the system.

So, in that case Z ideal is nothing, but V to the power of N and therefore, Q ideal as we have seen before is nothing, but V to the power of N divided by N factorial into lambda to the power of 3 N. Now what I am going to do is, I am going to write out the total canonical function for the real system, in terms of the ideal gas partition function multiplied by another function, which depends on the configuration integral and I have adjusted this V to the power of N term over here.

Now, why would I like to do this? Actually this expression is highly instructive because it shows me that I have the signature of the ideal gas behavior entirely contained with this term Q ideal and whatever non ideal behavior is appearing here, it is contained entirely within this term that I have marked as Q non ideal why is that so?

Because Q non ideal is the term is appears within this bracket and that contains the configuration integral and configuration integral is the one which depends on the potential energy of the system and therefore, I would say that by using this definition I have this extremely important relationship that I can express capital Q of our real system

as capital Q for the ideal part and capital Q for a non-ideal part dependent on the inter particle interaction in the system.

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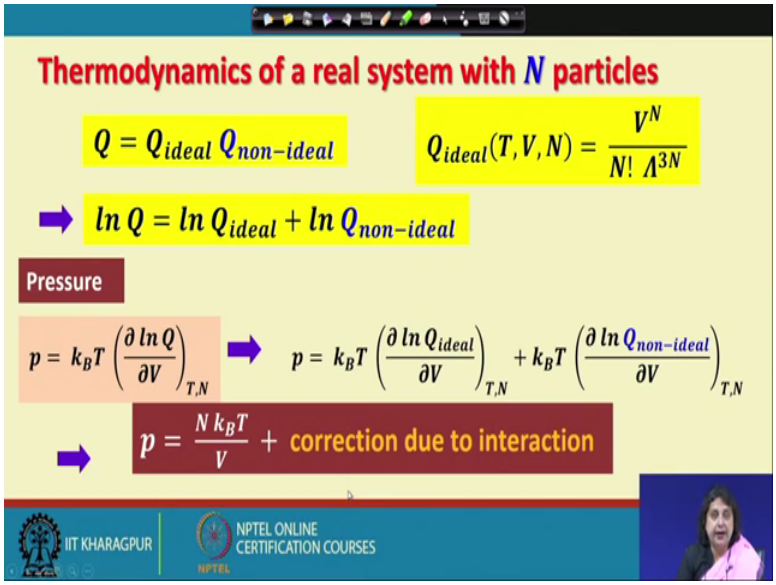

Now, the consequence of this expression is that, if I take algorithm on both sides then I find that l n Q has two additive terms, one that is coming from the ideal part the other term which is a correction coming from the presence of non-negligible interaction between the particles and therefore, if I look into the thermodynamic properties like pressure say, I can very easily say that now pressure will have two independent terms.

The first term is the one that is obtained from Q ideal and the second term that is obtained from the Q non ideal or in other words what I am trying to say here is that from the first term I will be obtaining NK B T by V as we have already seen plus there will be some corrections due to the presence of non-negligible interaction in the real gases. So, now, we have established that whatever correction that will be there in the pressure of an ideal gas, this is going to be additive in nature.

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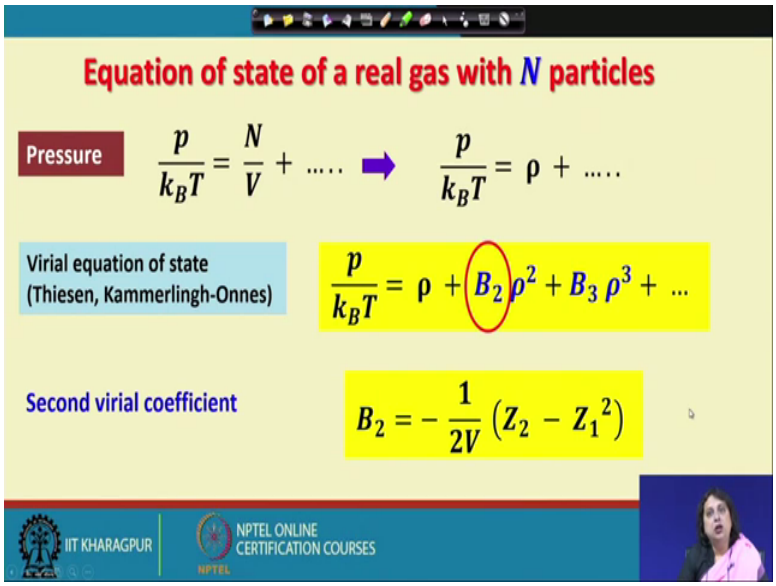

Then we can ask the question like what are these terms going to be. So, what we have done is we are now rewriting this expression as p by k T equal to N by V plus other terms which means that, if I write it out in terms of rho then it turns out to be p by k T equal to rho plus the additional correction terms appearing from the interactions.

Now, this tells me that if I follow the virial equation of state as I have shown you before, I actually understand that p by k T is now given by some term like this where the first term is rho that is the leading term and then I have additional additive correction in the form of B 2 rho square plus B 3 rho cube and soon. If the density is not too high in that case what I can do is, I can neglect this term and trunked this correction at the level of rho square ok.

Now, as you see then here B 2 must be related to the underlying interaction in the system and here I have this term rho. Now if it is an ideal gas, I see that the contribution is rho and in this correction term the dependence on rho comes in the form of rho square actually one can derive and explicit expression for B 2 by expanding pressure in a infinite power series in rho.

In this introductory course I am not going to work out this derivation rather what I am going to do is, I am going to present to you the result from classical statistical mechanics that tells us what the second virial coefficient is and the second virial coefficient can be

shown to be related to Z 2 and Z 1 ok. So, what is Z 2 and Z 1? If you remember these are the configuration integrals for two particles and one particle respectively.

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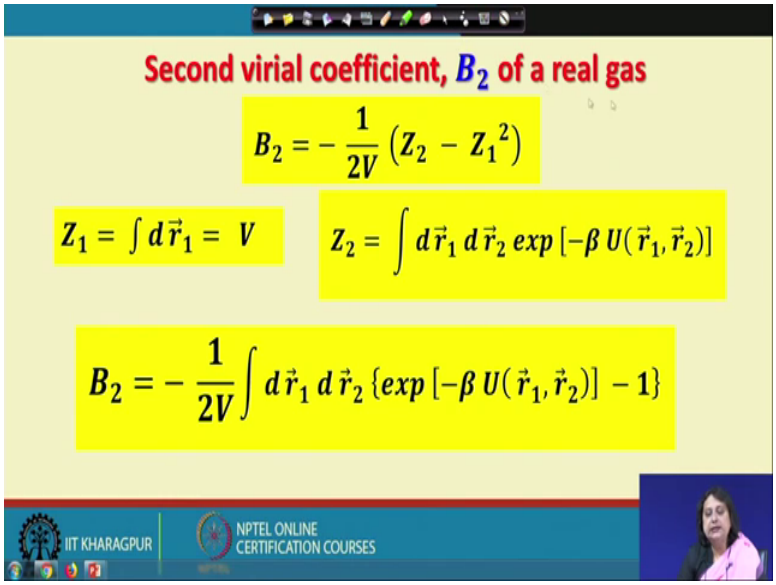

So, what we have got here is this, that B 2 can be expressed in terms of Z 2 and Z 1 and if I put these expressions back, then it is possible that I can write Z 1 square as integral d r 1 d r 2. So, I put it back and then my integrand becomes e to the power of minus beta U and then minus 1.

Now, this particular expression is something that I we can use because this is nothing, but a simple six dimensional integration in the configuration space of two particles right.

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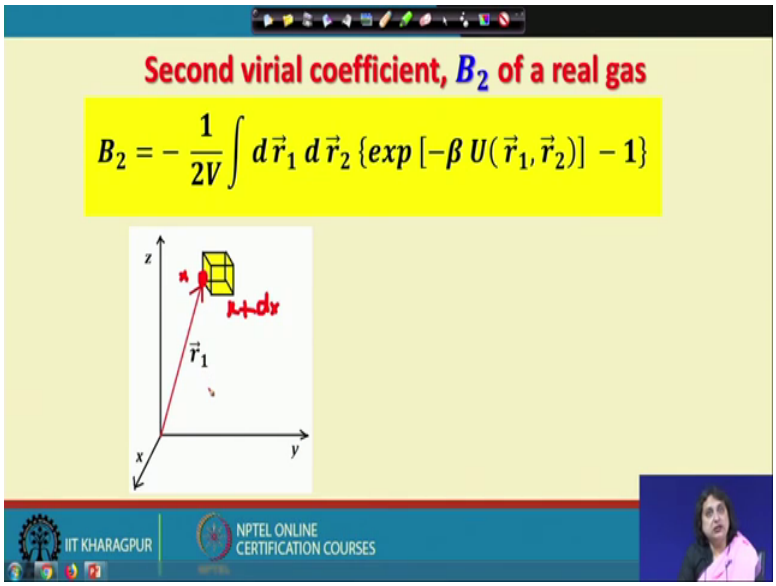

So, if I want to do that some more algebraic simplification may be necessary and for this purpose let us try and understand the geometry of the problem as being presented over here.

So, this is the X, Y, Z quotation coordinates in the 3 dimensional space and let me say that this is the position of my particle 1 right. So, its position coordinate is given by this vector r 1 whose X, Y, Z components are x 1y 1 and z 1.

Now, if I allow this particle to be present anywhere within this small volume element, which is bounded by x values between x and x plus d x y and y plus d y and z and z plus d dz, then what I am looking for is the particle being located somewhere within this volume element, and this volume element is expected to be much much smaller than the volume of the box in which this each of this particles are present.

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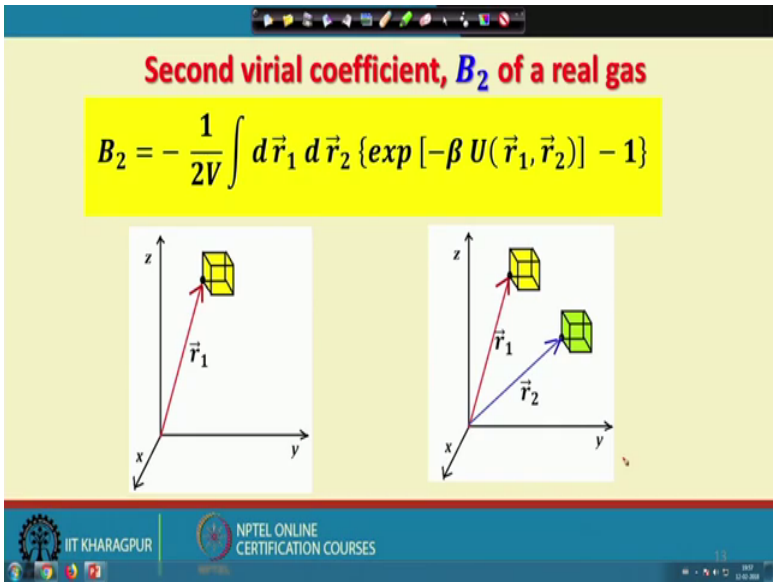

Now, extending this picture to two particles therefore, I am now talking in terms of the same X, Y, Z coordinates and this is the origin and I am measuring the position of particle 1 and particle two here with respect to the origin using the position vectors r 1 and r 2.

And I am thinking of finding the particle 1 somewhere within this volume element which is my d r 1 and particle two within this volume element that is given in terms of d r 2.

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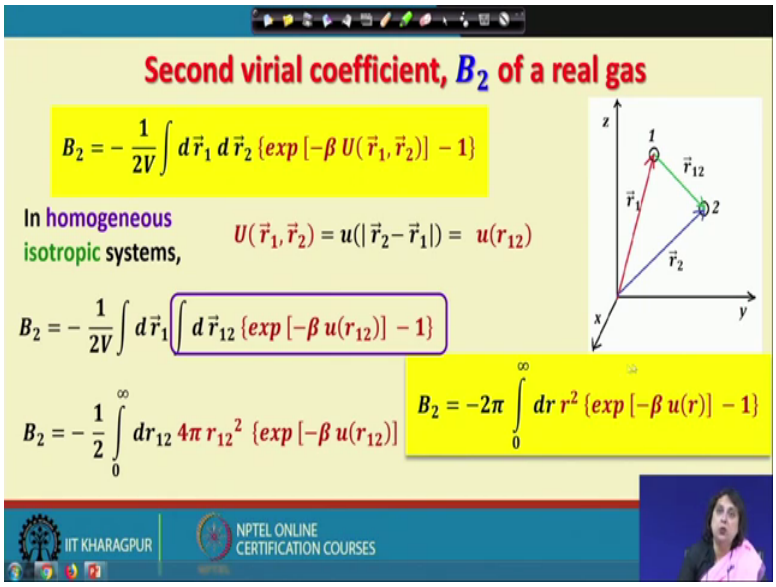

Now, when I think about estimating the second virial coefficient for a real gas, then I understand that in this case I will really have to worry about what this function the potential energy function is, when the two particles are present at positions r 1 and r 2 respectively. Because my integrand is e to the power of minus beta U minus 1 now if I look back at this kind of picture I find that for r 2 and r 1 defined like this, there is another vector which is defined here which connects the centers of the two particles 1 and 2.

And in general it so, happens that when we are dealing with simple homogeneous isotropic systems, it does not matter in which part of the system I am measuring the interaction potential between these two particles, the interaction potential is going to be dependent only on the magnitude of the vector separating the two particles and therefore, I can replace this potential energy term by a simple scalar quantity u, which its magnitude depends on the magnitude of the distance separating the through particles 1 and 2.

Now, if I put it back in the expression that I have written for B 2,now I have the following expression. As you see that the second integral it is completely dependent on r 1 2 and does not explicitly depend on what d r 1 what anything to do with r 1 and therefore, I can carry out this integration and; obviously, this is nothing, but v.

So, v and v cancels and I am left with this integration where I see that dr 1 2 that is d x 1 2 d y 1 2 and d Z 1 2, I will juts replaced it with the simple spherical polar coordinates and I find that this is nothing, but four pi r 1 2 square d r 1 2, but; obviously, this r 1 2 this index can be dropped and I can very easily write down, that this is the simplified and useable expression for the second virial coefficient of the real gas.

Now, what does it depend on it depends on u of r and beta. So, what is beta? Beta is 1 by k t. So, it depends on the temperature at which the particles interacting particles are present what is u? U is the interaction energy between two particles, which are separated by a distance r.

Therefore, if I know at what temperature the system is present I know the factor beta. If I know what u of r is then I should be able to find out the integrand which is this factor multiplied by r square and carry out this integration and therefore, I should be able to evaluate what B 2 is. Therefore, at this stage it was found that for real gas if I have some

model of the pair interaction of the pair interaction potential between the particle 1 and two that is u of r then I should be able to find out what B 2 is.

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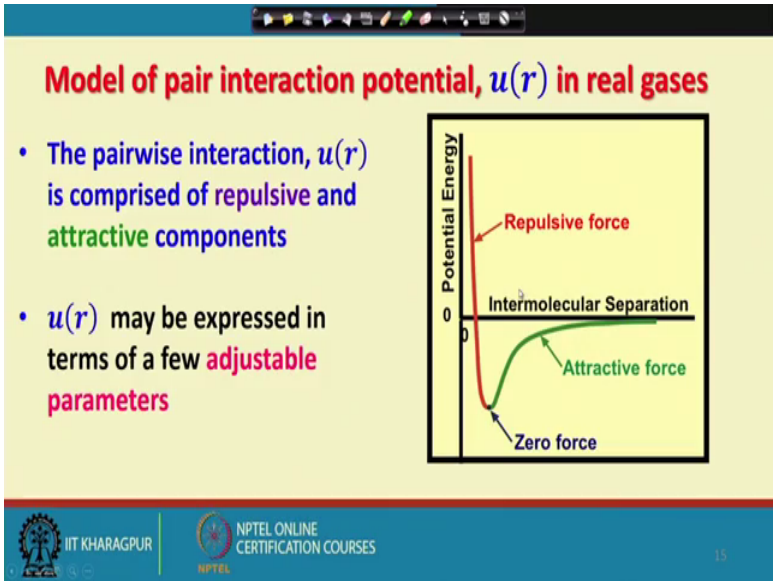

So, this actually brought us to the discussion of is it possible to model the pair interaction u of r in a gaseous system. Now, think of two gas molecules or atoms of real gas which are interacting with each other. Now, if they are coming very close together the surrounding electron density of each of the particles will evidently repel each other.

So, at very short distance inter particle distances I must be having a repulsive interaction between the two particles when they are far apart from each other in that case, you should have no interaction and in between because of the presence of induced dipole moment induced dipole moment kind of interaction there will be some attractive component.

So, this is what we are looking for. We are looking for the pair wise interaction that is comprised of a repulsive part and an attractive part and it should such that a balance should be maintained such that, there is a minimum in the potential energy which says that this is the configuration for which the interaction between the two particles is most attractive and below this the interaction becomes mostly repulsive and way from this separation the interaction rapidly goes to 0.

Now, this actually is a very general description of inter molecular or inter atomic interaction. Of course, the nature of how steeply this part would vary or how fast this part will go to 0 will depend on what kind of system we are talking about. So, basically then we are looking for a model of this u of r in such a way that I can express u as some algebraic function of r and there would also be present some adjustable parameters, which will vary from system to system.

So, with this idea in mind let us now examine a few cases where the expression for u as a function of r is known and what it tells about the expression for B 2 in those systems.

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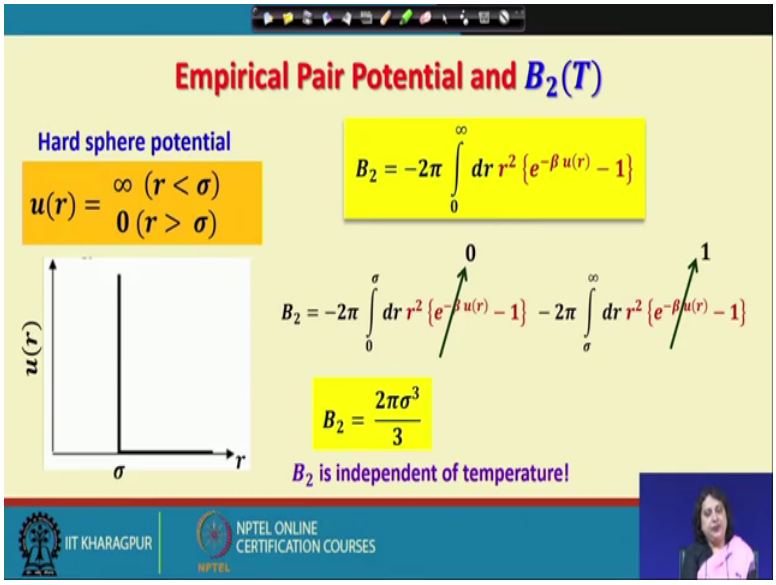

The first example that we take is the simplest case of an empirical pair potential. Now why do I say empirical because this is the kind of form of u that we are proposing are showing here this is empirical, this has not been rigorously defined rather one proposes a form in terms of certain arbitrary parameters and then tries to justify some of the parameters, which appear in the expression of u. The first and the simplest expression for an empirical pair potential is the hard sphere potential.

So, how does the hard sphere potential look like? This is the interaction between two hard sphere particles and if I try to push together to still bolls, they would behave as hard sphere particles. So, you can assume that when they are far apart from each other there is no interaction, but if they touch each other these are hard impenetrable balls and therefore, u of r can be represented in the following form.

This is infinity when r is less than sigma and equal to 0 when is r is greater than sigma. So, sigma is the hard sphere diameter and if I plot this, expression over here it is like at r less than sigma u of r becomes infinity r greater than sigma u of r becomes 0.Now I am going to use this expression and put it in the expression for B 2 and while doing that I realize that there are two distinct length scales one is 0 to sigma and sigma to infinity. So, we explicitly write out this integrant in these two limits.

So, in a state of going from 0 to infinity, I am now using two limits 0 to sigma and sigma to infinity because of the discontinuous nature of the interaction potential as shown. Now because of the kind of behavior u of r given if you look into this integrand what I have is r square into e to the power of minus beta ur minus 1 in the limit between 0 to sigma, I know that u of r is infinity. So, this term will become e to the power of minus infinity which is 0 therefore, in the integrand I am left with d r minus r square and therefore, this integral can be evaluated.

Similarly, if I look back into the second part of the integration, in the limit sigma to infinity I have u r is equal to 1 u r is equal to 0 and therefore, this term becomes equal to one as a result the integrand vanishes therefore, if I evaluate this I find that B 2 is given by 2 pi by 3 into sigma cube, where sigma is the hard sphere diameter of the molecule, but it says that B 2 is independent of temperature.

So, the hard sphere model which is essentially are repulsive potential of interaction gives the interaction between two particles in entirely in terms of a steep repulsive potential. It is in capable of producing the temperature dependence of the second virial coefficient

So; obviously, the next step would be introduce an attractive interaction between the particles in the intermediate separation.

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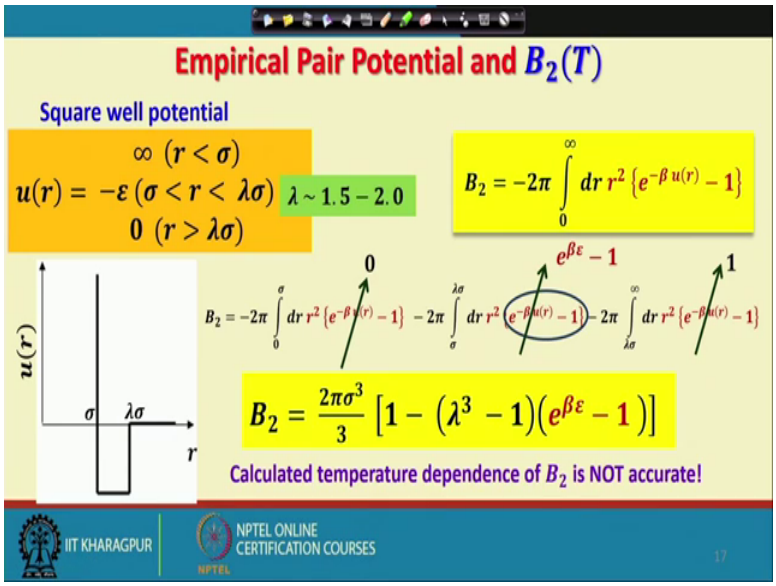

That is exactly done by considering the square well potential and here it has three distinct regions first at very small distances less than sigma, u as like hard sphere case it is infinity and for r greater than lambda sigma, there is no interaction. In an intermediate range between sigma and lambda sigma the interaction is a constant negative number.

And therefore, if I plot this potential as a function of r, where lambda varies from typically from 1.5 to 2.0you see that this is the nature of the square well potential. There is an attractive square well between the length scale sigma r equal to sigma to r equal to lambda sigma and hence the name square well potential. So, unlike the hard sphere system, we not only have a repulsive part we also have an attractive part in the interaction potential.

Now, if I put this back into the expression for B 2, now you see that I will have to evaluate the integral in 3 distinct regions; one is between 0 to sigma, another one is between sigma to lambda sigma and the other region is between lambda sigma to infinity and that is because in the integrand, the beta ur behaves differently.

Now, if I now once again examine how beta ur varies in each of these limits I find that this term as before goes to 0 this term as before goes to one making the integrand vanish and I have this intermediate region, where this term is replaced by a factor e to the power of beta epsilon minus 1 which is independent of r and this term can be taken out of the

integration, and when you do the integration you find that now B 2 is given not only in terms of the hard sphere term, but a term which depends on temperature.

So, that tells us very very importantly that a combination of repulsive as well as attractive interaction is very very important in describing the temperature dependence of B 2. But if you compare the values of B 2 as predicted for a given temperature, we find that the square well potential fails to reproduce the accurate values of B 2 then; obviously, the question is whenever we used a combination of repulsive as well as attractive interaction, we were in the right track, but we did not do it completely right.

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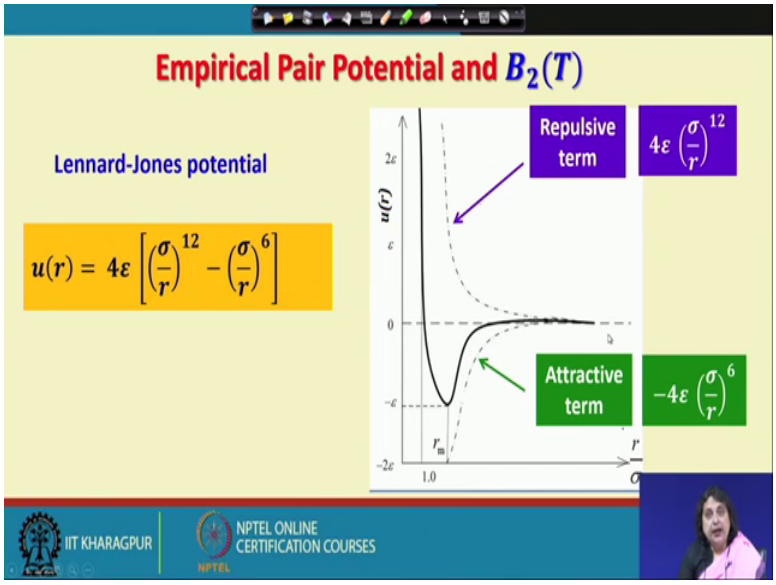

And therefore, the Lenard-Jones potential is introduced which once again is comprised of two terms the first part is an repulsive part, which is shown here and there is a second part which is the attractive term, which is present here. And when these two terms as shown by the dashed lines are combined then we find that the net interaction provides us the r dependent variation as we originally envisaged.

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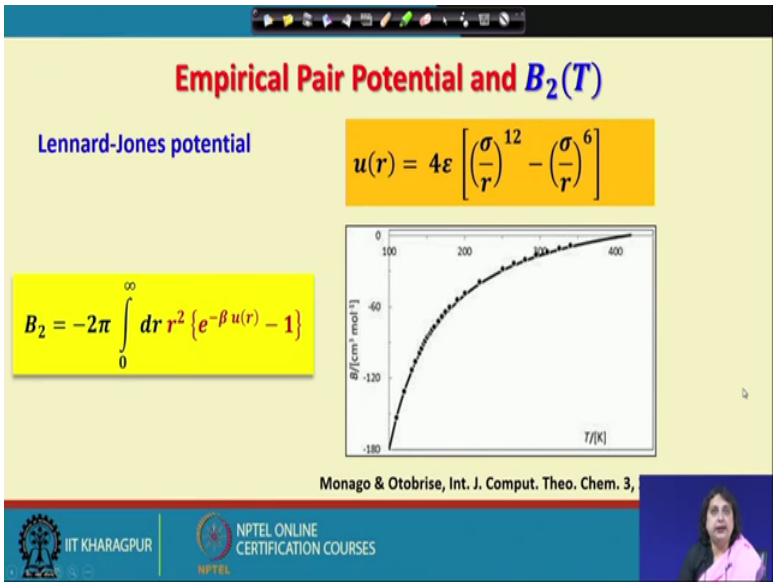

And when you put this back into the expression for B 2 r and compare them with the experimental data, you find that for system such as argon where the molecules are non polar in nature and there I find that the predicted values of B 2 match very well with the experimental data.

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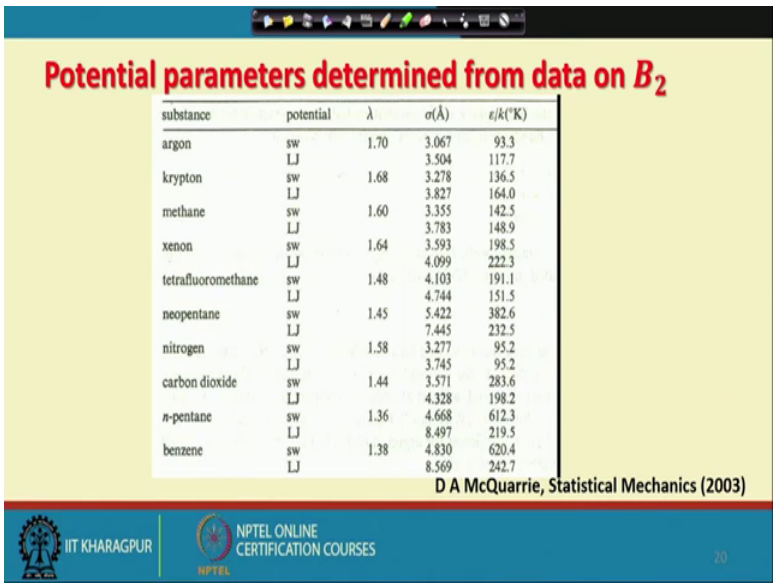

substance	potential	λ	σ(Å)	ε/k(°K)
argon	sw	1.70	3.067	93.3
	LJ		3.504	117.7
krypton	sw	1.68	3.278	136.5
	LJ		3.827	164.0
methane	sw	1.60	3.355	142.5
	LJ		3.783	148.9
xenon	sw	1.64	3.593	198.5
	LJ		4.099	222.3
tetrafluoromethane	sw	1.48	4.103	191.1
	LJ		4.744	151.5
neopentane	sw	1.45	5.422	382.6
	LJ		7.445	232.5
nitrogen	sw	1.58	3.277	95.2
	LJ		3.745	95.2
carbon dioxide	sw	1.44	3.571	283.6
	LJ		4.328	198.2
n-pentane	sw	1.36	4.668	612.3
	LJ		8.497	219.5
benzene	sw	1.38	4.830	620.4
	LJ		8.569	242.7

So, actually what has happened is once you know that B 2 is related to the pair potentials, people actually use the reverse of the problem they use the data on virial coefficient and find out potential parameter from B 2.For example, we have seen in the

square well potential the parameters are lambda and sigma in the case of the Lennard-Jones potential we require sigma and epsilon. So, using the data at different temperatures from B 2,for systems like argon, krypton, methane xenon all these non-polar systems it is possible to extract these potential parameters and then use them in describing the interaction potential of the molecules the atoms constituting these gaseous systems.

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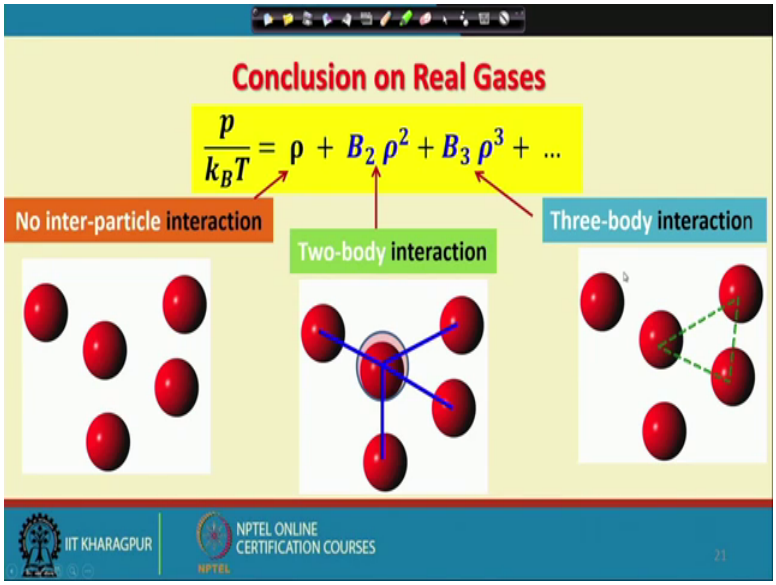

So, let us conclude on what we have learnt on real gases. We have found out that the experimental measurement on real gases with small to moderately high densities and expansion of this form is possible. And we found that the first term is actually an ideal gas term where the picture is that the gas is a collection of such some spheres like this spherical particles structure less spherical particles like this, which do not interact with each other.

Then we had the second term appearing here, which is dependent on two body interactions therefore, if I ask this question let us consider this particular molecule or atom of the gas. Then what is its total energy of interaction with the other molecules present? This is given in terms of the two body interaction term u which is dependent only on the distance between the two particles therefore; the total interaction energy of this particle with the other particles will be a sum of all these two particle terms.

Although I have not shown to you, but it can be shown that the B 3 that is the third virial coefficient is related to 3 body interactions, where the interaction of this particle with its

neighbors or the other particles in the system is computed in terms of three particles taken as together and all such triplets triplet interactions taken together, will give you the an interesting contribution to the overall energy of interaction.

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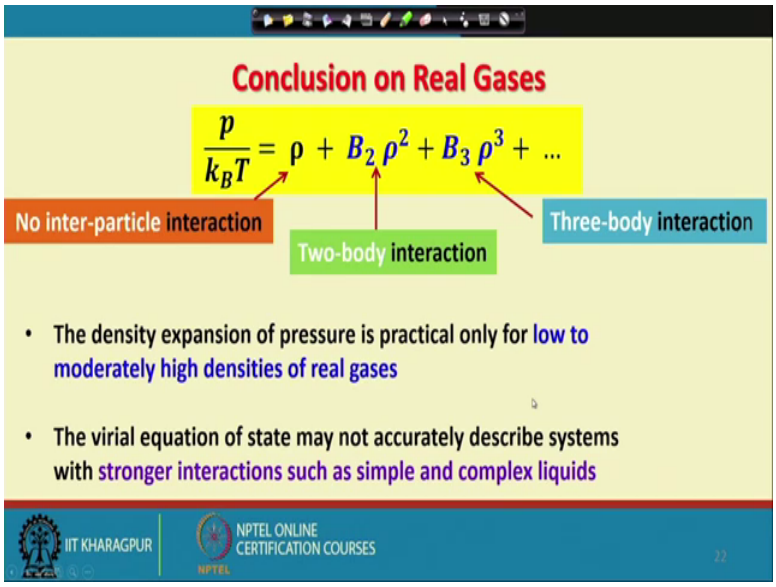

However, this kind of resolution into two body and three body interaction and a density expansion in terms of the pressure is practical only for low to moderately high density for real gases therefore, although the virial equation of state is extremely useful in gaining inside into how the underlying intermolecular inter atomic interactions are going to affect the thermodynamic properties, the virial equation of state is not that useful in systems which exhibits stronger interactions like simple liquids like liquid argon or complex liquids like water.

So, in the next lecture we are going to describe the steps that are adopted to modify this entire picture in such a way that we can indeed extract useful information even for strongly interacting systems like simple and complex liquids.

Thank you.