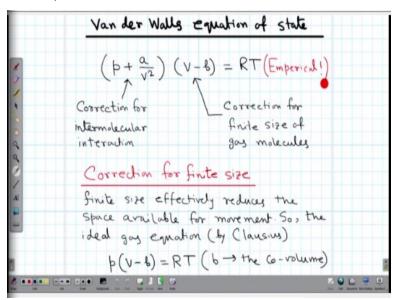
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# Lecture-25 Topic-Van der Waal's equation of State

Hello and welcome back to another lecture of this NPTEL course on thermal physics. Now this is the last lecture number 25 that is the last lecture of week 5. And for today's lecture, we will continue from where we have left in the last class. That is, so last class we have been discussing real gases and in the last class we have switched our attention to one particular equation of state that is used to describe real gases, that is Van der Waal's equation of state.

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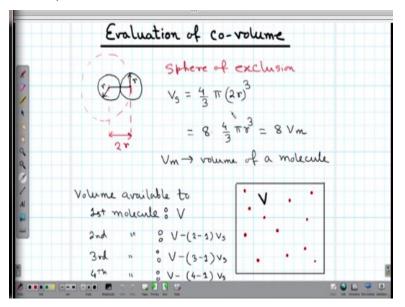
So, let us focus on that, we have the Van der Waal's equation which is p + a by v square times v minus b is equal to RT. Now it was proposed in 1873 and at that time this was purely an empirical equation. The primary reason why Van der Waals' equation came into action because it could explain the experimentally observed behaviour of real gases in certain experiments better.

And then it turns out that these two terms actually they have some physical significance this correction terms actually which is v minus b and p plus a by v squared, this is one correction and

this is another correction to volume and they have a reason or logical reasoning behind this. That we have discussed in the previous class itself that there are two major correction that leads to from the ideal gas assumption that leads to this the Van der Waal's equation for real gas. One is the correction for finite size that means the finite size of the gas molecule effectively reduces the space available for movement.

So, the ideal gas equation, this modification was first proposed by Clausius few years before Van der Waal's finally came up with his equation of state. That in an ideal gas equation the term v has to be replaced by v minus b, where b is called the co-volume. This is actually not exactly equal but somehow correlated to the total volume occupied by all the molecules of the gas assembly. So, this is by Clausius p times v minus b is equal to RT.





Next we have to go through this following exercise, so that we can correlate this or we can find out an expression for b and we can correlate this to the volume of the actual gas molecules. So, the concept of sphere of exclusion is something that is not very new to us, if you remember while discussing collision cross section for gas molecule, we have discussed about the surface of exclusion. This was primarily an 1D phenomena and the 1D phase of a molecule when visible from one particular direction is actually a circle. But in this case, the collision or the, so in principle that was an 1D phenomena but this is not. Here the collision can take place from all possible directions. In reality in that picture also collision can take place from all possible directions but there we have assumed that the movement of molecules in only one direction with an average speed c, right. So, that is where we have taken the surface of exclusion or circle of exclusion, here we have to consider the sphere of exclusion.

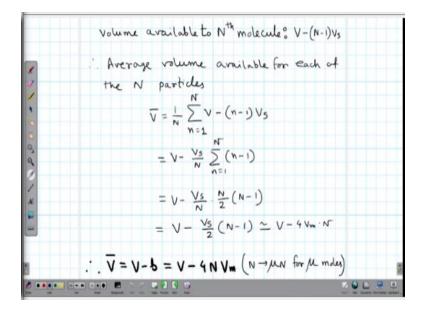
So, the concept is the same, the closest separation between the two molecules centers two similar molecules are 2r. So, there is a volume that is four third pi 2r cubed these volume around every molecule where the other molecules cannot come without suffering a collision. So this volume which is eight times the molecular volume, remember this cross section was four times the molecular cross section because that was pi r square.

Now here it is 2r cubed, so the factor of 8 comes out and we have V s is equal to 8 times V m. So, this is the volume in which 1 molecule will not allow any other molecule to come in. Now let us assume that the first molecule is inside this box, we first place a single molecule, let us say this molecule of gas. When this molecule comes in, for this particular molecule the entire volume is available, so the volume available to the first molecule is V.

When we include the second molecule into picture, let us say this one then there is already 1 molecule. Now the second molecule can explore all the space except for V s that is the volume of exclusion for the first molecule. So, it is the available volume for the second molecule is V minus 2 minus 1 V s. Now what is V? I am just writing it 2 minus 1 because this actually gives you a sequential order in this.

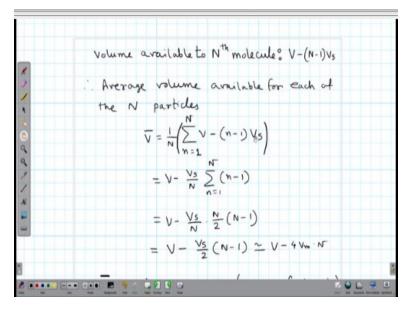
So, for the third molecule, it is actually V times  $2 \le 2 \lor s$ . So, we just write this as 3 minus 1 V s because when there is the third molecule is coming in the first and the second molecule is already there and a total of 2 V s space is not available to the third molecule. Similarly for the fourth molecule, already 3 molecules are there, so 3 V s space volume is not available, we just write this as 4 minus 1 times V s.

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So, if we just follow this logical progression, then volume available to the Nth molecule is V times or V minus N minus 1 times V s. So, average volume available to each of these N particles or N gas molecules is V average which is 1 over N sum over V minus n minus 1 V s, where n runs from 1 to N, N being the total number of molecule available in the gas assembly. So, if I execute this sum, the first see this V is a constant here, so this V can immediately be taken out of this bracket.

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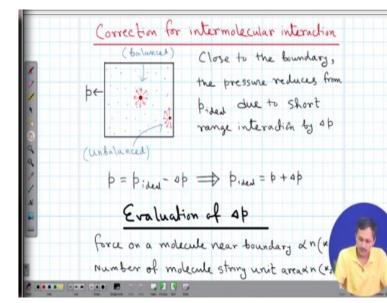


So, by the way there is a parenthesis all over there is a parenthesis. So, you see the first term which is V. So, if I open this bracket it will be or open this term it will be simply V times sum over n is equal to 1 to N which gives you n, n and this will cancel out with this n in the

denominator. And the first one will be V simply, for the second term V s once again is the constant it will come out, so V s minus N sum over n is equal to 1 to N n minus 1. And this sum will be nothing but N by 2 times N minus 1. And once we assume that, once we simplify this, this N and this N will cancel out and what we have is V minus V s times V s by 2 N minus 1 which is approximately equal to.

So, N is such a large number, so we can actually neglect N with respect to N and we can write V - 4 times V m times N. So, this is the average volume available to per molecule. Now compare it with this relation or which is there actually, compare it with V minus b. So, b is nothing but 4 times N times V m, V m being the molecular volume. Now let us assume and this calculation is for 1 mole of molecule. Let us say, so we can say for 1 mole of molecule N is equal to N A the Avogadro number.

Now if we have mu such moles present in this gas assembly, then we can simply multiply this with mu. So, in that case N will be mu times N A, so the scaling is simply with this quantity mu here. So, for mu moles instead of writing V minus b, we have to write V minus mu b, where b is equal to 4 N V m. So, N being the number of molecules present in this gas assembly. So, 4N times V m is actually the four times the total combined volume of all the gas molecules.



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Now this is for the second term that is the volume term this correction will work. For the pressure term what will happen and why there is a correction needed in the pressure term? So, once again, let us go back few slides. So, this term has a correction for intermolecular interaction, this we have already taken into account, now we have to understand this. The situation is as follows, we have once again I have drawn a box where the blue particles are the gas molecules here.

So, these are the gas molecules, now let us focus on 2 molecules 1 at the center, 1 close to the side of the box. Now in the kinetic theory of gas we have always assumed that there is no intermolecular interaction. And during this exact motion they come close they collide with each other in a perfectly elastic manner and that is it. But here we assume that there is actually but in reality we do not assume actually.

In reality, there is a weak interaction between the molecules. Now for this molecule which is placed somewhere in the center of the box, this weak interaction will be equal from all the directions. Because molecules are surrounding it evenly from each direction and the overall force will balance out, cancel out. So, at the center this molecule kind of behaves like an ideal gas when it comes to intermolecular interaction.

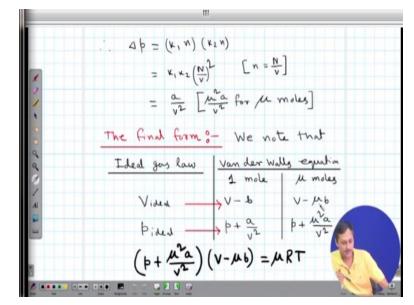
But for the molecule here which is towards the edge of the container close to the wall of the container, you see there is hardly anything on the between this one and the molecule. And, so the interaction so there will be kind of a pullback, pullback towards there is a force which will try to pull it inside the box. So, what will happen? It will collide with the wall with a lesser force as compared to an ideal gas.

So, that means there will be a pressure reduction and that pressure reduction if I denote it by delta p. So, the actual pressure p is p ideal minus delta p, p ideal being if the gas is ideal the pressure that it would have been putting on the container wall and delta p is the correction term. So, we can write p ideal is equal to p plus delta p. Now our job is to determine or find out an expression for this delta p.

Now pressure depends on two things or this force rather depends on two things, this delta p is the correction due to the force, the net force acting on this molecule. Of course, we have to understand or this is kind of very intuitive that this will have a term proportional to the density of the molecules if we have a molecular density of n inside this box, so higher the value of n the force of attraction will be more.

So, there will be a term force one molecule near the boundary of course in the central part this force will balance out, so it will not affect. But we are concerned only about the gas molecules which are close to the boundary because finally they have higher chances to collide directly with the wall. So, there will be 1 term which is the force on a molecule which will be proportional to n, so let us call it k 1 n. And there will be another term that is the due to the number of molecules striking unit area. We know that the pressure actually consists of two terms.

One is the force with which it hits that basically the momentum transfer and the number of molecule that hits the unit area. Now if you remembered the expression for number the molecular flux actually was one fourth N c bar. So, it is proportional to n, c bar being let us assume that c bar is a constant, so this is also proportional to n. So, we are not going into the details of this proportionality constant, we just call it k 2 n. So, these two effects and in the pressure expression if you recall, we have to multiply one with the other.



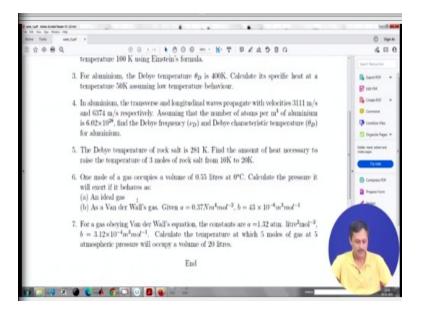
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So, basically in the pressure expression, there will be a correction factor which is a multiplication of both, so let us call it k 1 n times k to n. So, which is once again is a k 1, k 2 is a constant and n can be written as N by V, N being the number of molecule in the gas assembly. So, we can simply put all the constant together inside this a, and we can write delta p is equal to a by v square where a has all the proportionality constants.

Now in case of we have mu moles of gas present, then once again this N and mu they are linearly correlated to each other. So, as we have N square here, we will have a mu square in the proportionality constant coming in. Once again comparing to this pressure term or volume term, we have a scaling with mu and in the pressure term because it is proportional to N.

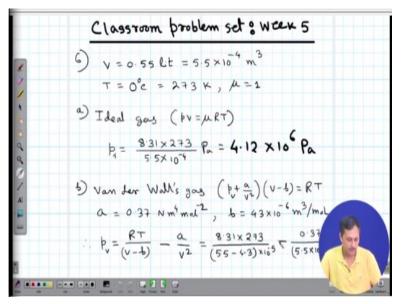
So, that is why we have N is replaced by mu N for mu moles and for pressure as the constant a is correlated to N square, so a is replaced by mu square the expression. So, in the final form we have in the ideal gas law, so what is ideal gas law? Ideal gas is V ideal, p ideal is equal to RT. So, V ideal has to be replaced by V minus b or V minus mu b and p ideal has to be replaced by p plus a by V square or p plus mu square a by V square.

And we know in the right hand side instead of RT if we have mu moles of an ideal gas we have to write mu RT. So, pv is equal to mu RT that is the ideal gas law, we just have to make this proper substitution and the general form for mu moles is p plus mu square a by v square times V minus mu b is equal to mu RT. So, this is the Van der Waal's equation of state for mu moles or real gas. So, now what do we do? We just solve two problems and then we proceed further. **(Refer Slide Time: 18:20)** 



So, problem number 6 and 7 from the classroom problem set I hope you already have this in your hand. Now for the first problem it is for 1 mole, so we can use the 1 mole formula, 1 mole of a gas occupied a volume of 0.55 litres at 0 degrees centigrade. Calculate the pressure it will exert if it behaves as an ideal gas and as a Van der Waal's gas given that a and b values are there. So, let us first quickly calculate it for the ideal gas, it is a very straightforward simple calculation.





Because V in terms of meter cubed which is 5.5 to 10 to the power minus 4 meter cubed and T is equal to 0 degree centigrade, which is 273 Kelvin, mu is equal to 1, so this is for 1 mole of gas. So, the ideal gas which is pv is equal to mu RT, so, we get p i is equal to 8.31 into 273 divided by 5.5 into 10 to the power minus 4 Pascal which is 4.12 into 10 to the power 6 Pascal.

And for the Van der Waal's gas, we have to use this constants a is equal to this, b is equal to this. So, a and b are given, so all we have to do is we have to use the proper relation which is p v, v is stands for the Van der Waal's pressure, a by v square, so in the Van der Waal's expression v being the container volume. So, the interpretation of v is exactly the same for ideal gas law and the Van der Waal's law.

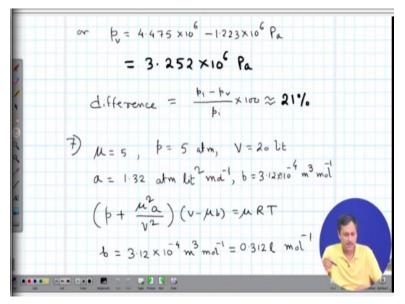
Similarly the interpretation of p is also exactly the same, these are the measured pressures. So, if we have an ideal gas in this particular situation we measured the pressure and we get 4.13 into 10 to the power 6 Pascal. And then what are given a is equal to 0.37 Newton meter to the power 4 mole to the power minus 2, b is equal to 43 into 10 to the power minus 6 meter cubed per mole. The units, unit of b is straightforward because b has to be the units of volume per mole which is there. Unit of a is also not very difficult to understand, so basically it has to be in simple terms this has to be the dimension of pressure this whole quantity. So, it has to be some pressure unit multiplied by volume square per mole square. So, because if you remember in the full expression there is a mu square here. So, when we have mu moles we have a mu square here.

So, it has to be mu mole to the power minus 2 which is there and pressure times volume square is actually has the dimension of N m to the power 4 Newton meter to the power 4 in SI units. You can work it out yourself and find out whether it is correct or not. If you find any problem with this unit here, please comment in the forum, we will try to discuss, correct. So, next is we have to open up this bracket and we can write p v is equal to, so basically I take v minus b here.

So, RT by v minus b minus a by v square and all we have to do is, we have to put in the numbers here and compute. So, once we put in the numbers, so there is a unit conversion here, so what I did? This is just for convenience, you see b is given as 43 into 10 to the power minus 6 meter cubed and V is given us 5.5 into 10 to the power minus 4 meter cube. So, what I did is instead of minus 4 I just wrote 55 into minus 5 meter cubed and instead of 43 into minus 6 I just wrote 4.3 into 10 to the power minus 5 meter cubed.

So, the power of 10, the order of magnitude matches and we have 55 minus 4.32 into 10 to the power minus 5. So, this is 1 term and the second term is straightforward, this is 0.37, it is already given. All we have to do is we have to put volume in SI units because this is given in SI units which we already did here. So, this is the volume in SI units here. So, all we have to do is, we have to put this number.





And see the value here is 4.475 into 10 to the power 6 minus 1.223 into 10 to the power 6. So, the correction term here is actually has a relatively large order of magnitude. The first this and this if I put b is equal to 0, the first term actually gives 4.12 into 10 to the power 6 but we are getting 4.47 the e is something. So, of course b has reduced, so we are getting, so something higher than 4.12, so we are getting 4.47.

And for the second term, you see it is 1.223 into 10 to the power 6, so it is almost one fourth of this term. So, the correction term in this particular case is almost 25% as compared to the actual term. Or if not 25 if I compare it with this 1.223 with 4.12, it is 12, so 35% almost even higher. So, this is the first problem we have in this direction. So, I just computed the difference just to show you.

So, p i minus p v divided by p i into 100 gives you the percentage difference between the ideal pressure and the Van der Waal's pressure computed on this particular system and this turns out

to be 21%. So, there is a 21% difference in terms of pressure when we consider Van der Waal's intermolecular interaction and change in available volume as compared to the ideal gas condition, which is by no means negligible, it is not 2%, it is 21%.

So, we see Van der Waal's equation the correction terms has considerable impact on the ideal gas equation. Now the next problem or the last problem for this week classroom problem. We have a gas which is obeying Van der Waal's equation, the constants once again a and b are given but this time you see it is in a slightly different unit. So, this one is meter cubed per mole inverse but the unit of a is atmosphere litre square mole to the power minus 2 which is also.

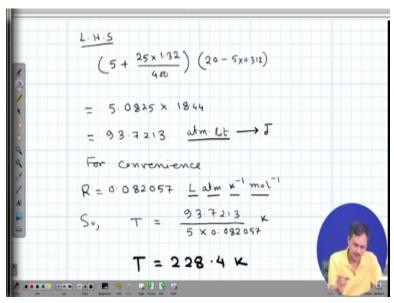
Because litre is a standard unit for volume and atmosphere is also not a very standard but accepted unit for pressure. So, that is okay, the dimension wise it is correct. Now we have to calculate the temperature at which 5 moles of gas at 5 atmosphere pressure will occupy a volume of 20 meters. So, we have 5 moles of this given gas, it will occupy a volume of 20 litres and the pressure of this system will be exactly 5 atmosphere at what temperature? This is the question. So, for this we first summarize the problem here.

So, here mu is equal to 5, p is equal to 5 atmosphere, V is equal to 20 litres, a is equal to 1.32 atmosphere litre square mole to the power minus 1, b is equal to 3.13 into 10 to the power 4 meter cubed mole to the power minus 1. And you see if I look at this expression here is p plus mu square a by v squared times v minus mu will be equal to mu RT, we have to calculate this T. So, this is the unknown in this case, because the final the pressure and volume, volume is given in litres and pressure is given in atmosphere, it is advantageous to work with this particular unit. So, what I can do is, I can simply convert this unit from meter cubed mole inverse to litre per mole and this will give us advantage.

And this conversion is very straightforward, so 3.13 into 10 to the power minus 4 meter cubed per mole is actually 0.312 litres per mole. So, this conversion is just decimal conversion factor of 10 to the power 3, you can check it out. Anyway, I might make mistakes, so check it yourself but probably this is right. But I strongly suggest that you do it yourself because I might make mistakes in this conversion. Next is we have to put these values here, so I have to put p is equal

to 5 atmosphere, mu is 5, a is equal to this 1.32 and v square will be 20 litre whole square. And once again this is 20 minus mu is 5 and b is equal to 0.312.





So, once we put that the left hand side is see the denominator is straightaway it is 20 into 20 which is 20 square which is 400, 25 because mu square into 1.32 and this is 20 minus 5 into 0.312. So the first term is 5.0825 and the second term is 18.44 and the multiplication is 93.7213 and what should be the unit of this one? The unit of this one should be atmosphere litre. So, this one is in atmosphere the pressure term is in atmosphere and the volume term is in litres, remember that. So, we have a new unit, on the right hand side what do we have? On the right hand side we have mu RT.

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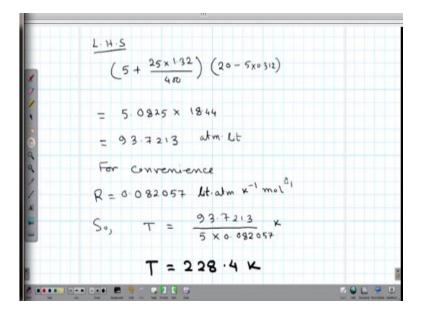
J' AJK MIU difference = thi - the x 100 = 21%. M = 5, b = 5 atm, V = 20 lit a = 1.32 atm lit<sup>2</sup> md<sup>-1</sup>,  $b = 3.12 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}$  $\left(b + \frac{\mu^2}{\nu^2}\right) \left(v - \mu b\right) = \mu RT \left[R - J x^2 - \frac{1}{\nu}\right]$ to = 3.12 × 10 m mol = 0.312 ( mol 

Typically the unit of R is Joules calorie inverse Kelvin inverse mole inverse, so this is the typical unit, v minus mu b, so it is actually per mole. So, this mole and this mole will cancel out, right. So, either we have to take this unit and convert it to Joules because what happens is? See, when I multiply it with number of moles, this mole and mole cancels out it becomes Joules per Calorie per Kelvin.

So, either we have to convert this litre into atmosphere into Joules or what else we can do? We can do that of course; we can just convert the unit of R and express R as litre atmosphere per calorie per mole. These units are available, it is not something very new, it is there, you can find it even in Wikipedia or any standard textbook of thermodynamics there should be a table where the value of R for different, not so standard units like non-SI units will also be given.

Because in engineering people uses this units all the time. So, I have expressed R in litre atmosphere per Kelvin per mole and this is 0.082057. So, I have just taken it from a standard table. This saves you some trouble all I have to do is otherwise what is the possibility? Otherwise we have to make this conversion the atmosphere litres to Joules which is also absolutely doable, you should get the same answer at the end. So, once I put this 93.7213 divided by 5 into 0.082057, you see litre atmosphere actually I should write the exact same thing for litre what I have written here.

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So, I have, so litre atmosphere calorie inverse and you see units cancel out nicely and we have Kelvin which is 228.4 Kelvin. So, I hope this helps you in understanding the Van der Waal's equation. See our objective for today's lecture was to give you a physical interpretation of this 2 correction terms in Van der Waal's equation. The first term in pressure is due to intermolecular interaction and the second term is due to finite volume of gas molecule.

And then we solved two problems which will help us to understand the impact of this correction better. For example, we have seen that there is 21% correction in terms of the ideal gas volume when we apply Van der Waal's equation. Now this is where we stop for this week's lecture and in the next week what we will do is, we will continue from here, we will look into more applications of Van der Waal's equation. And we will go in details on how to determine this constants experimentally, the constant a and b from the experimental data, till then thank you and good bye.