Fundamentals of Statistical Thermodynamics

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Lecture – 54

Equations of state

Welcome back. We have discussed ideal systems at length during our discussion on statistical thermodynamics. Most of the expressions which we have derived belong to ideal system, ideal gases. But we know that even if we first talk about the gases, all the gases are not perfect gases or ideal gases. We may say that the ideality or perfection is approached under certain conditions. For example, when we talk about the gases, when the pressure is very very very low, the gases may start behaving ideally.

And when the system is not ideal, then there have to be some different sets of treatment for that. So, in today's lecture, we will talk about equations of state and in today's lecture, we will restrict our discussion to gases. We have been discussing many equations, many relations in terms of canonical partition function. And the canonical partition function which we designated as capital Q is a function of n number of particles volume and temperature.

So, this canonical partition function which is a function of volume, temperature, n number of molecules was connected to various thermodynamic parameters and one such connection was between pressure and canonical partition function. If you remember, we have derived this equation pressure is equal to k T times δ log Q by δ V at constant temperature. We can call this is an equation of state because what is an equation of state? When we talk about ideal gases or perfect gases, the ideal gas law, ideal gas equation or perfect gas law that is P V is equal to n R T, this is an equation of state for a perfect gas. So, we can call an equation of state as an equation which connects P V and T. The simplest case is P V is equal to n R T, but remember that this is only for an ideal gas.

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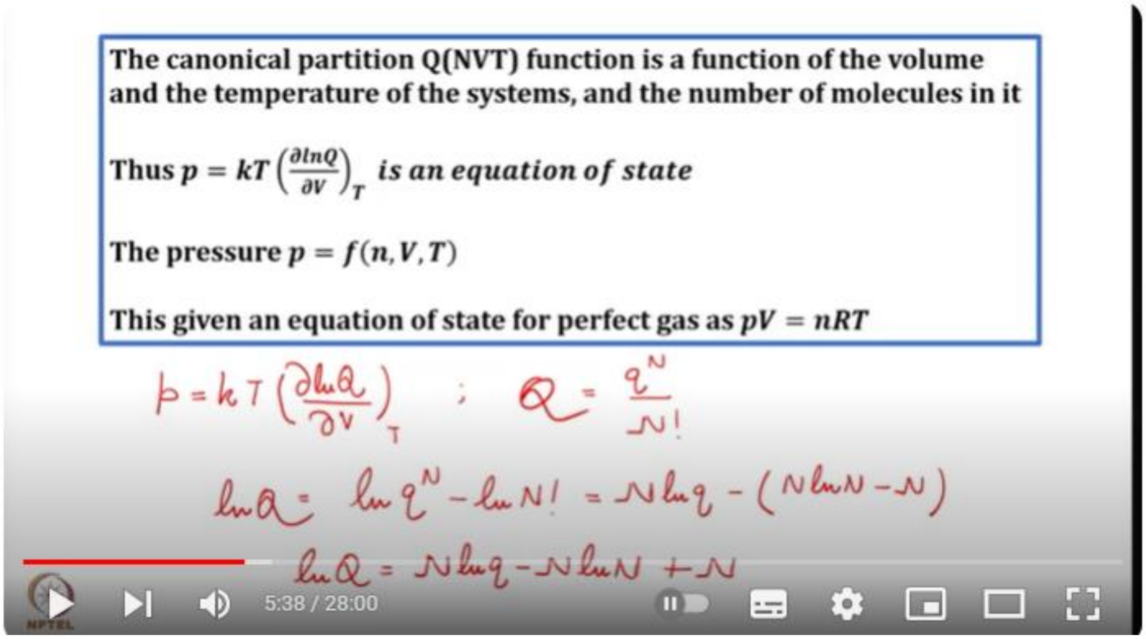

The canonical partition Q(NVT) function is a function of the volume and the temperature of the systems, and the number of molecules in it

Thus $p = kT\left(\frac{\partial \ln Q}{\partial V}\right)_T$ is an equation of state

The pressure $p = f(n,V,T)$

This given an equation of state for perfect gas as $pV = nRT$

$$p = kT\left(\frac{\partial \ln Q}{\partial V}\right)_T \quad ; \quad Q = \frac{q^N}{N!}$$

$$\ln Q = \ln q^N - \ln N! = N\ln q - (N\ln N - N)$$

$$\ln Q = N\ln q - N\ln N + N$$

Now, you come back to this expression p is equal to k T δ log Q by δ V at constant temperature. This is a purely general equation, we did not specify this that whether it can be used only for ideal gases or it can be used only for non-ideal system, we did not specify that. But let us first apply it to monatomic perfect gas, monatomic perfect gas. Let us do that and see what happens. What we have p is equal to k T δ log Q δ V at constant temperature.

Remember that if we are talking about monatomic system, we are only discussing perfect monatomic gas. Q canonical partition function in terms of molecular partition function is going to be Q raise to the power n over n factorial, because the molecules are not distinguishable. Therefore, we are going to use the connection of canonical partition function with molecular partition function which is used for indistinguishable molecules. Q raise to the power n by n factorial, then log Q is equal to log Q raise to the power n minus log n factorial. Can I write this as n log Q minus n log n minus n sterling approximation? That means my log Q is n log Q minus n log n plus n and let me write this on the next page.

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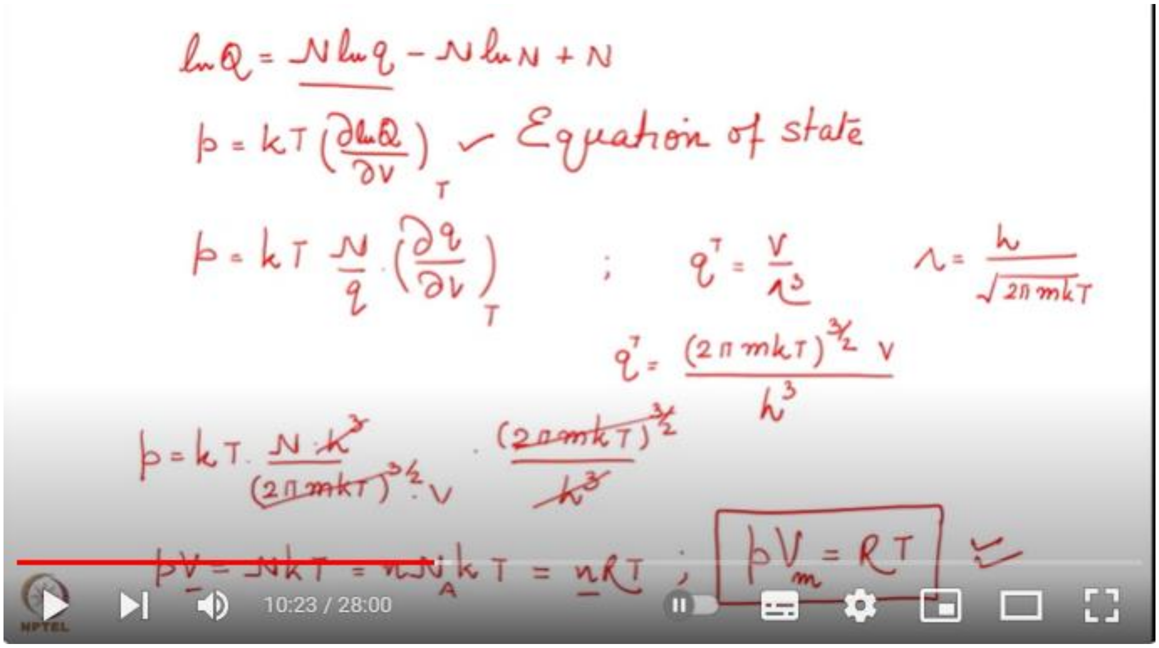

$$\ln Q = \underline{N \ln q} - N \ln N + N$$

$$p = kT\left(\frac{\partial \ln Q}{\partial V}\right)_T \checkmark \text{ Equation of state}$$

$$p = kT\,\frac{N}{q}\cdot\left(\frac{\partial q}{\partial V}\right)_T \quad ; \quad q^T = \frac{V}{\lambda^3} \qquad \lambda = \frac{h}{\sqrt{2\pi mkT}}$$

$$q^T = \frac{(2\pi mkT)^{3/2}\, V}{h^3}$$

$$p = kT\cdot\frac{N\cdot\cancel{h^3}}{\cancel{(2\pi mkT)^{3/2}}\cdot V}\cdot\frac{\cancel{(2\pi mkT)^{3/2}}}{\cancel{h^3}}$$

$$pV = NkT = \underline{n}N_A kT = \underline{n}RT \; ; \; \boxed{pV_m = RT} \checkmark$$

Log Q is equal to we have n log Q n log Q minus n log n plus n. This is what we derived that is log Q is equal to n log Q minus n log n plus n, but we are interested in pressure. Pressure is equal to k T δ log Q δ V at constant temperature and since we have already an expression for log Q, we can take derivative of log Q with respect to volume. So, when you take the derivative of this with respect to volume, this is the only term which may depend on volume n log n and this n these are constant. So, derivative of this these two quantities with respect to volume is going to be 0 ok.

That means the pressure is equal to k T, then we need to take derivative of this which is n by Q into δ Q δ V at constant temperature. Since we are talking about only monatomic perfect gas, so Q is equal to Q T is equal to V upon λ Q, where λ is equal to h over 2 π m k T ok. So, Q T is equal to then 2 π m k T raise to the power 3 by 2 into volume by h cube V upon λ^3. So, let us now put pressure is equal to k T n upon Q upon Q. I am going to write Q T which is 2 π m k T raise to the power 3 by 2 into V and here I have h cube.

This is n by Q then multiplied by δ Q by δ V at constant temperature. I need to take the derivative of this with respect to volume at constant temperature. Constant temperature means entire this factor becomes constant. So, let us write down. This becomes 2 π m k T over h cube, then δ V by δ V is 1.

Of course, this is raised to the power 3 by 2. This and this cancel, h cube and h cube cancel and then if I rearrange, I get P V is equal to n k T is n times n a that is number of molecule is number of moles times Avogadro constant into k into T k times n a is R is P V is equal to n R T. This gives me P V is equal to n R T because k times n a is equal to R. Now, I can consume n, I can take n on the other side and V by n I can write molar volume. So, I have PV_m is equal to R T.

This is the equation of state. We were saying that this is equation of state and by using that first restricting to ideal gases, we have shown P V is equal to R T or P V is equal to n R T. This is an equation which you have been using for a long time and we called it as equation of state, but this is applicable to ideal system, ideal gases. The gases may or may not be ideal. First of all, we should remember what is the definition of an ideal gas.

How do you differentiate between real gases or an ideal gas, right? Sometimes real gas you call as non-ideal gas. What is the difference between them? When I say ideal gas that means, no intermolecular interactions between them irrespective of the distance. When I say non-ideal gas or deviation from ideality that means, the attractive or repulsive interactions come into play when you vary your distance from very far to very close and if you remember at some point, we define π_T is equal to δ u δ v at constant temperature. This is equal to 0 for ideal gases and this is not equal to 0. I repeat this is not equal to 0 for non-ideal gases, ok.

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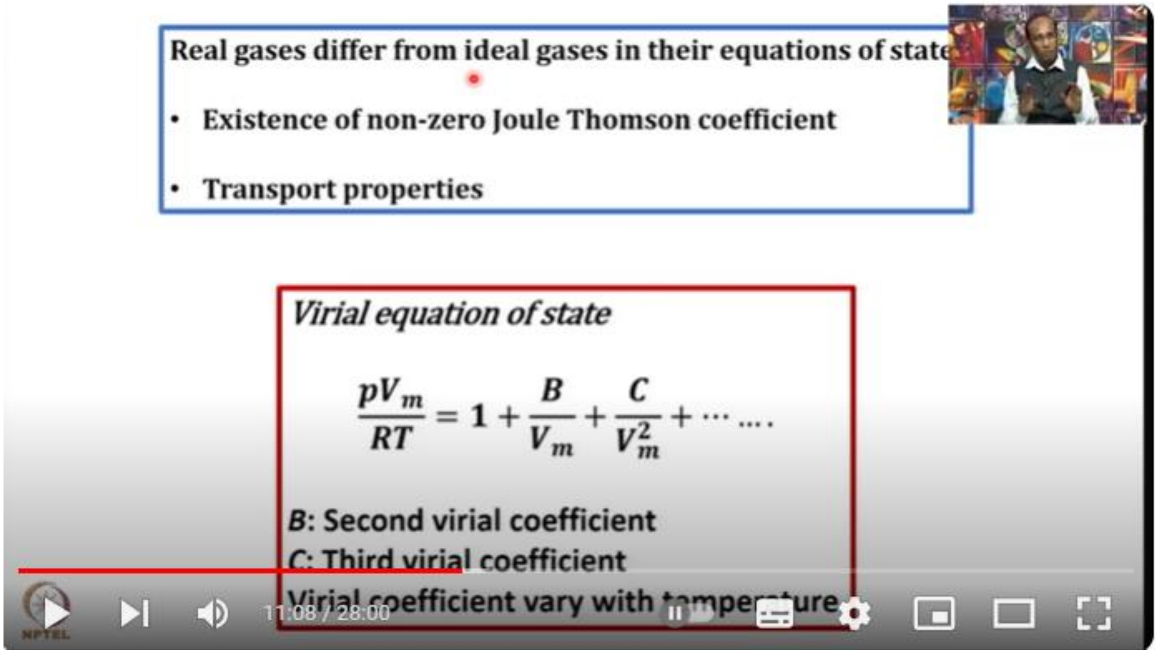

Real gases differ from ideal gases in their equations of state

- Existence of non-zero Joule Thomson coefficient
- Transport properties

Virial equation of state

$$\frac{pV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \cdots \ldots.$$

B: Second virial coefficient
C: Third virial coefficient
Virial coefficient vary with temperature

So, if we were to address the difference between real gases and ideal gases, there can be several points of differences. For example, one we talked about π_T. π_T is equal to 0 for ideal gas, π_T is not equal to 0 for non-ideal gas. Why? Because sometimes the gas molecules when you mix two gases and if these two gases are non-ideal, then they will interact with each other. So, interaction energy can also contribute to non-ideality.

There is existence of non-zero Joule-Thompson coefficient. There can be difference in transport properties. I repeat there is difference in transport properties and there can be existence of non-zero Joule-Thompson coefficient. So, therefore, how to address the deviation from ideality in gases? Looking back at what you study in class 11 or class 12, Van der Waals equation of state in which A and B were introduced which reflected upon the attractive and repulsive parts of the interactions. Here we will talk about the virial equation of state and we will talk about virial coefficients. PV_m upon RT which you remember was also called as compression factor, but here we are not going to talk in terms of compression factor. Here we are going to talk in terms of virial coefficients. Let us represent PV_m by RT is equal to 1 plus B by V_m plus C by V_m square plus so on so on. If B, C all these numbers or all these coefficients are 0, then you simply have PV_m is equal to RT, then it becomes an ideal gas. In this form of the equation B is called second virial coefficient, C is called third virial coefficient and so on.

Obviously, these virial coefficients are going to depend upon temperature. Why? Because when the temperature is increased, the intermolecular interactions between the gas molecules will also be affected. Therefore, these virial coefficients B, C etcetera these virial coefficients vary with temperature. So, our purpose is to somehow connect these virial coefficients with canonical partition function, then we can move towards bringing in non-ideality into our discussion.

Let us do that. But before doing that, let us recall some of our earlier learnings. One of the earlier learning was that the total kinetic energy of a gas of molecules is some of the kinetic energies of individual molecules even when interactions are present. When we only talk about kinetic energy, I am not talking about potential. The total kinetic energy of a gas of molecules is some of the kinetic energies of individual molecules even when the interactions are present. That means, now in a real gas, the canonical partition function must factorize into a part which is arising from kinetic energy that is going to be same as that for the perfect gas and another factor called configurational integral.

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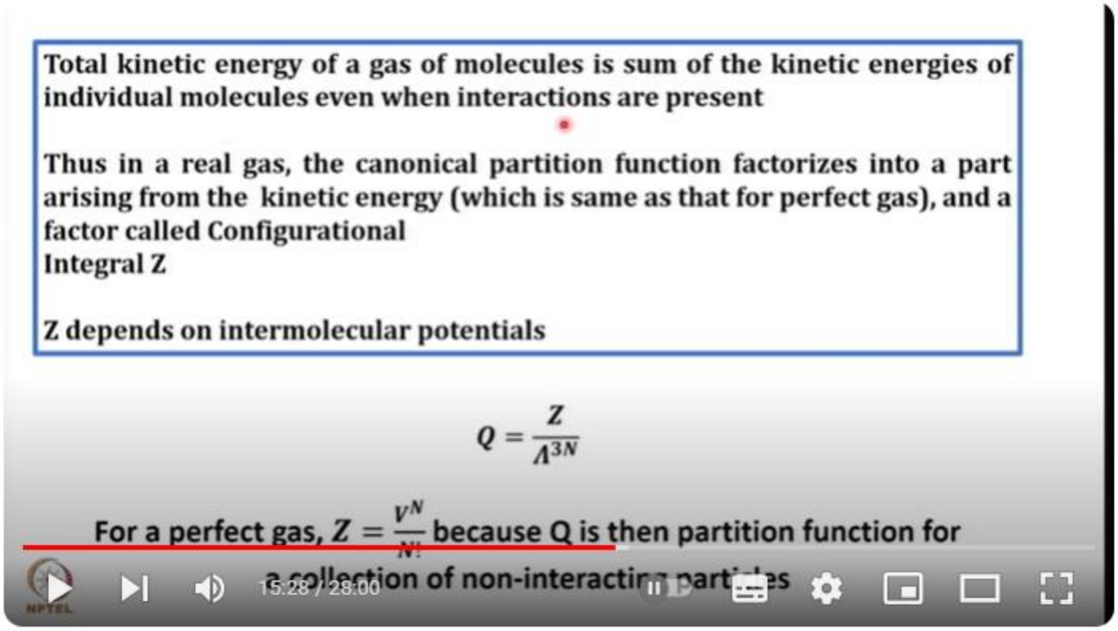

Total kinetic energy of a gas of molecules is sum of the kinetic energies of individual molecules even when interactions are present

Thus in a real gas, the canonical partition function factorizes into a part arising from the kinetic energy (which is same as that for perfect gas), and a factor called Configurational Integral Z

Z depends on intermolecular potentials

$$Q = \frac{Z}{\Lambda^{3N}}$$

For a perfect gas, $Z = \frac{V^N}{N!}$ because Q is then partition function for a collection of non-interacting particles

That is what is commented here. Thus, in a real gas, the canonical partition function factorizes into a part arising from the kinetic energy which is the same as that of perfect gas and a factor called configurational integral. This we will call as Z. Obviously, this Z which is configurational integral, it is going to depend upon intermolecular potentials. Now, this canonical partition function is represented as Z by λ raised to the power 3N.

For perfect gas, you have already studied that this is equal to V raised to the power N by N factorial where V is the volume of the container and this is according to this definition because Q is then partition function for a collection of non-interacting particle. That means, if Z is equal to V raised to the power N by N factorial, we are talking about perfect gas. We are talking about non-interacting particles. Alright, let us move ahead. From the ideal gases, now let us move towards the real gas.

When we talk about real gas, we are talking about intermolecular interactions. That means, we have to now in addition to the kinetic energy, we have to bring in the potential energy and let us represent potential energy as V^N . This potential energy of interaction is related to the configurational part Z which was if you go back, this configurational integral Z for ideal gas was V raised to the power N by N factorial, but for a non-ideal gas, this will be 1 over N factorial integration exponential minus beta V^N dr 1, dr 2, etc, dr N. What are these dr, dr 1, dr 2, dr this integration of each one is equal to volume. We are not getting into the derivation of these.

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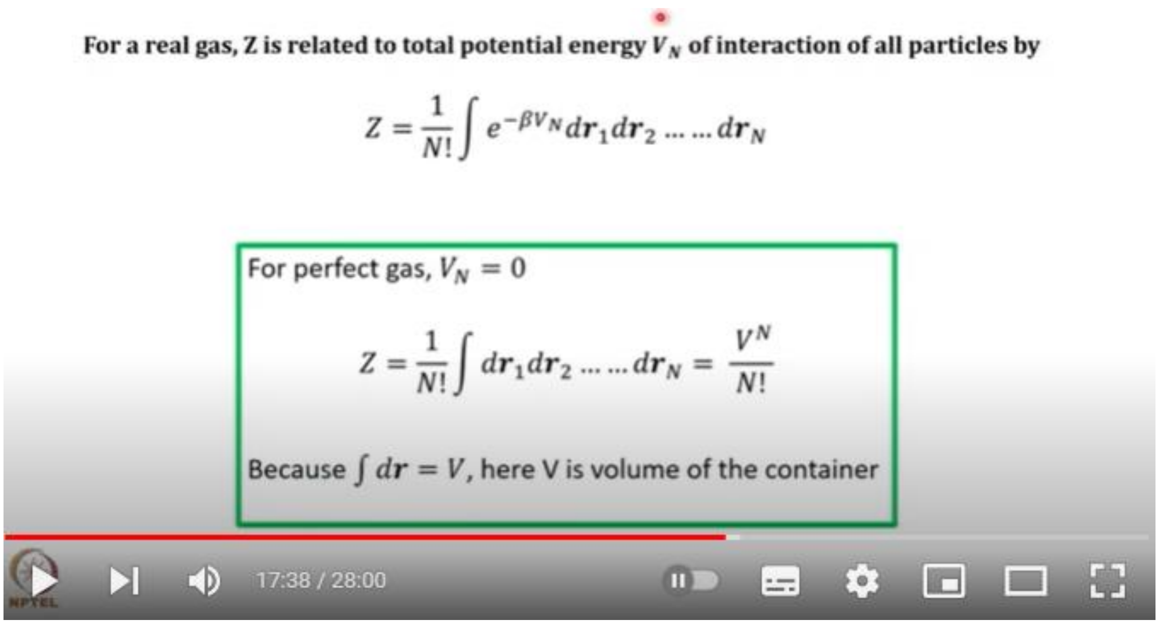

For a real gas, Z is related to total potential energy V_N of interaction of all particles by

$$Z = \frac{1}{N!}\int e^{-\beta V_N} dr_1 dr_2 \dots\dots dr_N$$

For perfect gas, $V_N = 0$

$$Z = \frac{1}{N!}\int dr_1 dr_2 \dots\dots dr_N = \frac{V^N}{N!}$$

Because $\int dr = V$, here V is volume of the container

You have learnt at some point, but we need to know in order to evaluate this, we need to know the potential. Though we are not getting into the derivation of this, but we can go reverse that we can show that this converts into the configurational integral for a perfect gas when you ignore the potential energy and when do you ignore the potential energy? When the interaction between all the particles is switched off to 0, perfect gas. If you put V^N equal to 0, then exponential 0 is 1. In that case, Z is equal to 1 by N factorial dr 1, dr 2, etc, and since each one is volume, then this is V raised to the power N by N factorial and this is what the configurational integral was defined for an ideal gas. Distinguish between this V^N and this V^N , this is the potential energy and this is the volume of the container ok. Now, let us consider only pairs of particles. You can consider two particle interaction, you can consider 3, 4, 5, you can keep on increasing and that will bring in more complexity, but for a simple example, let us consider the interaction between only pairs of particles. So, we will write Z_2, this is equal to 1 by 2 factorial exponential minus V_2 by k T d r_1 d r_2, and using this, again we are not going into derivation. The second virial coefficient turns out to be V is equal to minus N_A by 2 V into f integration of f dr_1, dr_2, where this f is expressed in terms of potential minus V_2 by k T minus 1.

N_A is Avogadro constant. So, that means, if we know the potential, somehow if we know the potential, then we can have B. This f is equal to minus V_2 by is called Meyer F function. Remember, this is called Meyer F function. Obviously, when you put V_2 equal to 0, then exponential 0 becomes 1, 1 minus 1 becomes 0 and if f becomes 0, that means, then in that case B also becomes 0 right. It says it goes to 0 when two particles are so far apart that V_2 equal to 0.

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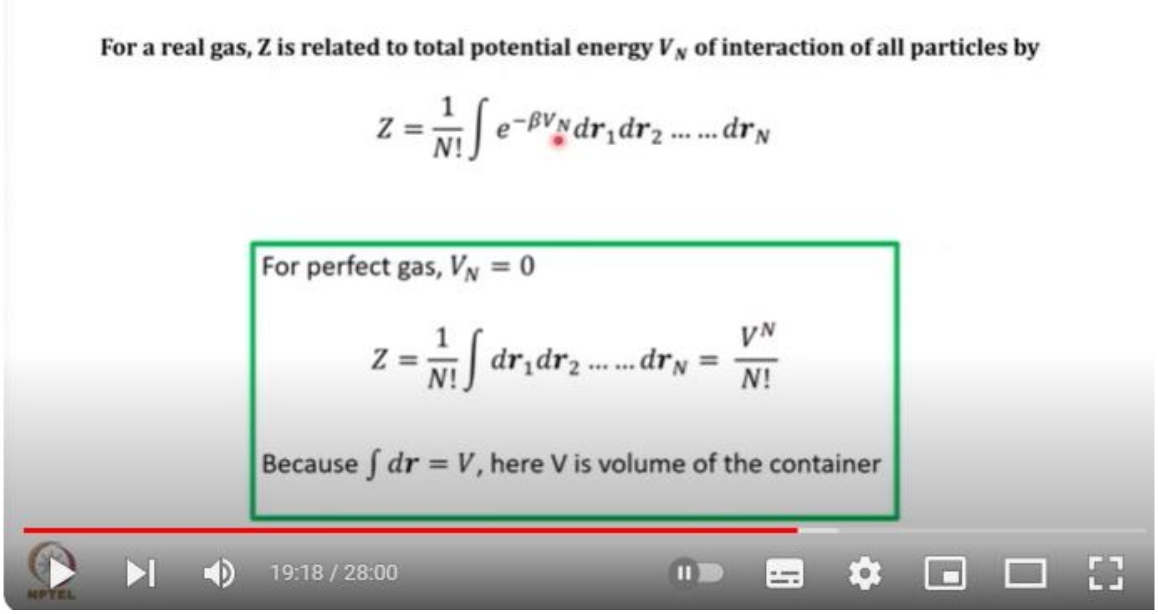

For a real gas, Z is related to total potential energy V_N of interaction of all particles by

$$Z = \frac{1}{N!}\int e^{-\beta V_N} d\boldsymbol{r}_1 d\boldsymbol{r}_2 \ldots\ldots d\boldsymbol{r}_N$$

For perfect gas, $V_N = 0$

$$Z = \frac{1}{N!}\int d\boldsymbol{r}_1 d\boldsymbol{r}_2 \ldots\ldots d\boldsymbol{r}_N = \frac{V^N}{N!}$$

Because $\int d\boldsymbol{r} = V$, here V is volume of the container

So, if you are talking about the particles, which are very far apart that there is no interaction between them, then the interaction potential energy is 0. V_2 is equal to 0. If V_2 is equal to 0, then your virial coefficient is also equal to 0. So, this explains that when the particles are very far apart, in that case this f f value turns out to be 0 and then you can see what happens to the value of B. Now, consider that the interaction intermolecular interaction depends only on the separation of the particles, but not on their relative orientation.

Please listen carefully. When the intermolecular interaction depends only on the separation of the particle's separation, let us represent by R, but not on their relative orientation. We can take an example for example, in closed shell atoms and tetrahedral or octahedral molecules. In that case, this equation B is equal to minus N_A over 2 V into f d r_1 d r_2, where f is this is the same equation that we discussed earlier. This B transforms to minus 2 π N_A 0 to infinity f r square d r and this can be evaluated numerically provided we have this Meyer f function, which is dependent upon the potential. You can have depending upon the potential energy; you can calculate you can evaluate the second virial coefficient numerically alright.

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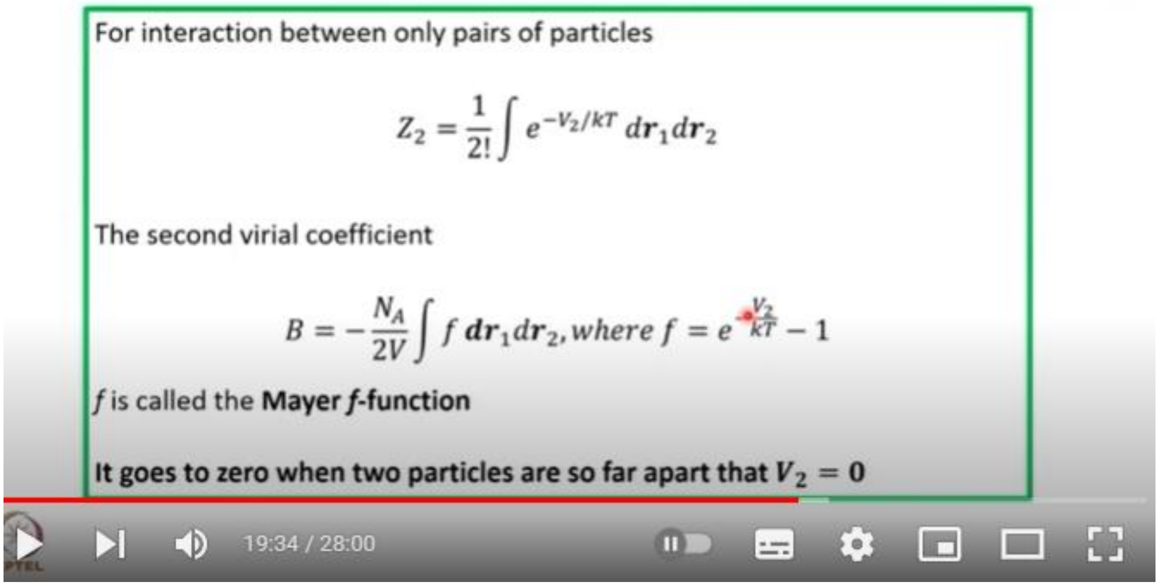

For interaction between only pairs of particles

$$Z_2 = \frac{1}{2!}\int e^{-V_2/kT}\,\boldsymbol{dr}_1\boldsymbol{dr}_2$$

The second virial coefficient

$$B = -\frac{N_A}{2V}\int f\,\boldsymbol{dr}_1 d\boldsymbol{r}_2, where\ f = e^{-\frac{V_2}{kT}} - 1$$

f is called the **Mayer *f*-function**

It goes to zero when two particles are so far apart that $V_2 = 0$

Now, what we have is the expression for B, which now we have derived for when the potential energy only depends upon their potential energy only depends upon their separation. So, consider hard sphere potential. This hard sphere potential is infinite when the separation of the two molecule R is less than a certain value. Remember the potential energy curve, it will go take a dip and then again it will increase. So, we are using the same principle that when the separation of the two molecules, which is represented by R is less than or equal to certain value right, then the potential becomes infinite.

For example, you see here if the potential energy for a certain values are less than sigma, it becomes infinite. Then you put V_2 equal to infinite over here exponential minus infinite 0, 0 minus 1 is minus 1 in that case f is equal to minus 1. So, if f is equal to minus 1, then B becomes you can connect this over here B becomes 2 π N_A R square d r from 0 to sigma, sigma is that minimum value, which turns out to be 2 by 3 π N_A times sigma Q. This is the case when the separation of the two molecules R is less than or equal to certain value. On the contrary if R is higher than sigma, let us say the molecule they are far apart, then you can take potential energy to be 0 in that case f also turns out to be 0.

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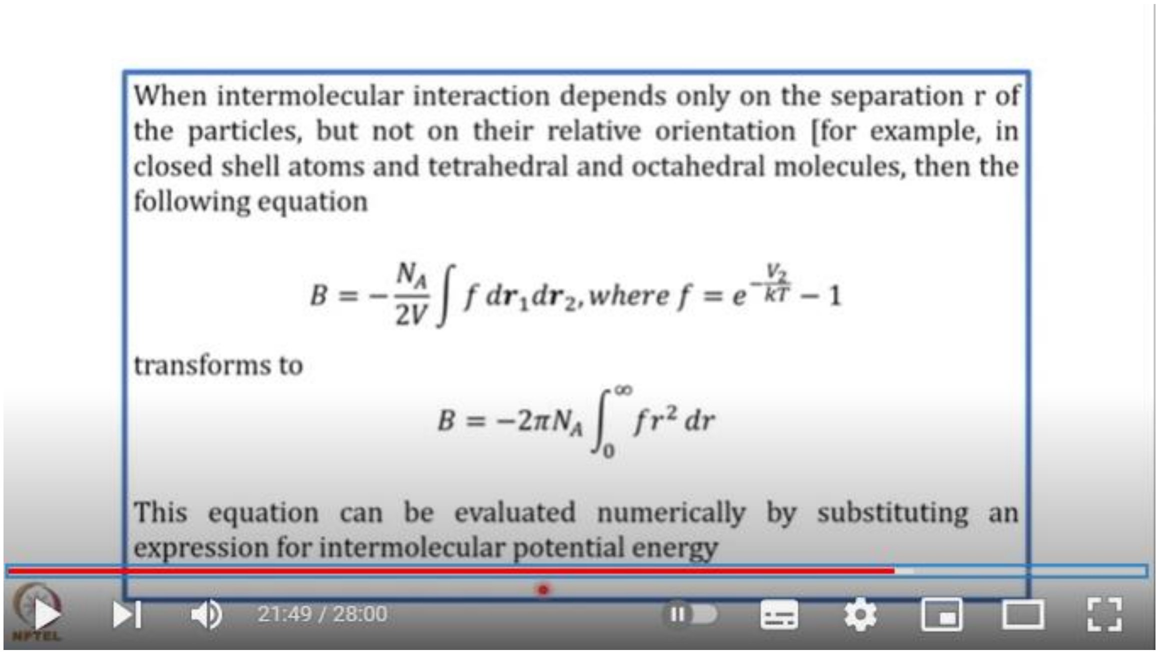

When intermolecular interaction depends only on the separation r of the particles, but not on their relative orientation [for example, in closed shell atoms and tetrahedral and octahedral molecules, then the following equation

$$B = -\frac{N_A}{2V}\int f\, d\mathbf{r}_1 d\mathbf{r}_2, where\ f = e^{-\frac{V_2}{kT}} - 1$$

transforms to

$$B = -2\pi N_A \int_0^\infty f r^2\, dr$$

This equation can be evaluated numerically by substituting an expression for intermolecular potential energy

So, what we have derived is that the second virial coefficient B is equal to 2 π N_A integration 0 to sigma R square d r, which takes up this form 2 by 3 π N_A times sigma Q. You remember that Van der Waals equation of state P is equal to R T over V_m minus B minus A over V_m square, where A took care of the attractive parts of the interaction and B took care of the repulsive part of the interaction. So, here also the hard sphere repulsive part of the intermolecular potential B that contributes to B in exactly in the same way, but the these are some of the extreme cases which we derived.

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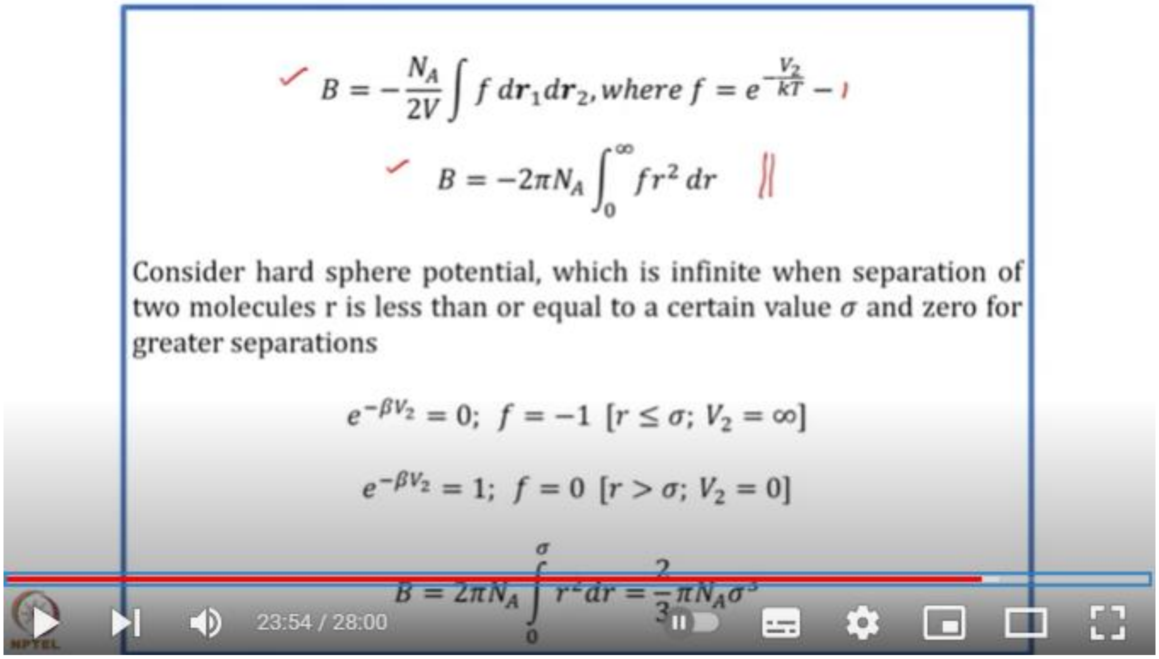

✓ $B = -\frac{N_A}{2V}\int f\, d\mathbf{r}_1 d\mathbf{r}_2$, where $f = e^{-\frac{V_2}{kT}} - 1$

✓ $B = -2\pi N_A \int_0^\infty f r^2\, dr$

Consider hard sphere potential, which is infinite when separation of two molecules r is less than or equal to a certain value σ and zero for greater separations

$$e^{-\beta V_2} = 0;\ f = -1\ [r \le \sigma;\ V_2 = \infty]$$

$$e^{-\beta V_2} = 1;\ f = 0\ [r > \sigma;\ V_2 = 0]$$

$$B = 2\pi N_A \int_0^\sigma r^2 dr = \frac{2}{3}\pi N_A \sigma^3$$

The question is can we find a potential the actual potential here we need to have the value of V_2 to evaluate the exact B C or any other virial coefficient. So, can a potential be found which when the virial coefficients are evaluated provides the full Van der Waals equation of state.

The answer is yes such a potential can be found. We have talked about second virial coefficient. Similarly, the extension of the discussion can be made to other virial coefficients and you will also require to have knowledge of how to find a potential which actually represents those intermolecular interactions, but that is beyond the scope of the current discussion. What I have discussed in this lecture is that the gases which do not follow ideality, which are not ideal, which are not perfect will show non ideal behavior and will undergo intermolecular interactions. How to incorporate those intermolecular interactions, how it is reflected into virial coefficients that is what we discussed in this lecture. I hope it was useful and it will form a basis for your higher level. Thank you very much. Thank you.