Introduction to Molecular Thermodynamics
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Lecture – 37
Classical Statistical Mechanics

Welcome today we are going to discuss the classical statistical mechanics and it is application to ideal and non-ideal systems, for the ideal systems we are specifically going to discuss the case of an ideal gas, where the ideal gas is comprised of n number of non-interacting particles which may be atoms or molecules, but we are going to model Them as classical particles. Classical structures less particles looking like a billiard ball and then in the second part of my lecture we are going to talk about the non-ideal system where the interaction between these constituent particles of the gas cannot be neglected.

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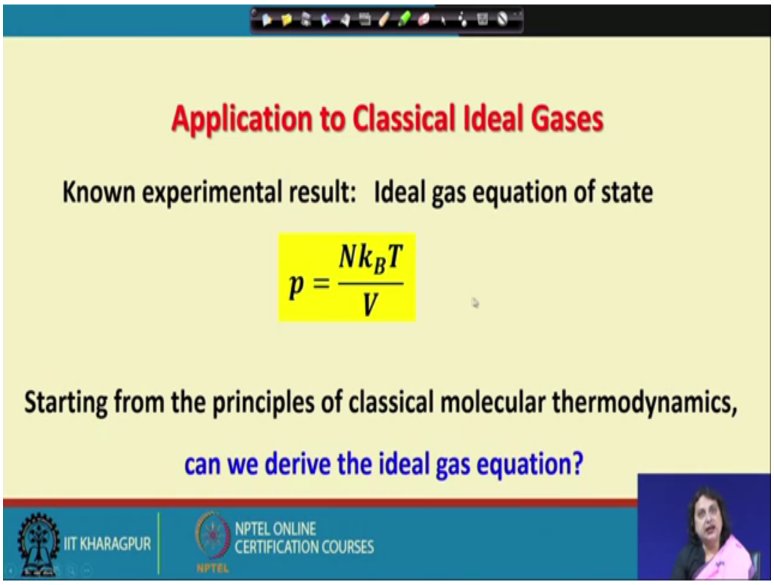

Application to Classical Ideal Gases

Known experimental result: Ideal gas equation of state

$$p = \frac{Nk_BT}{V}$$

Starting from the principles of classical molecular thermodynamics,

can we derive the ideal gas equation?

So, let us start with the discussion of classical ideal gases where as we already know; that the well-known experimental result gives us the pressure of the gas in terms of the temperature and the volume at which this gas is present. And in this case the gas is assumed to be comprised of capital N particles which are the either the atoms or molecules depending on what the gas are, but in the classical description all the particles are being assumed to be a spherical structure less particle. And the aim of our discussion here is starting from the principles of classical molecular thermodynamics can we derive the ideal gas equation and, in this process, can we try to understand what is the molecular origin of this kind of an expression or the relationship between pressure temperature and volume of a classical ideal gas.

So, when we adopt the language of classical statistical mechanics so; obviously, we start by defining the macro state of the system. I will continue the discussion in the canonical ensemble where we assume that at the macroscopic level the system is present at a given temperature, volume and number of particles.

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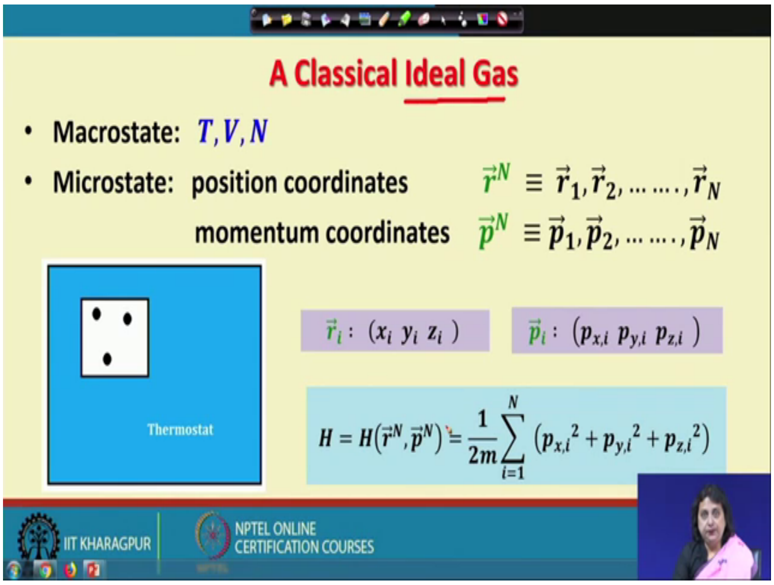

A Classical Ideal Gas

- Macrostate: T, V, N
- Microstate: position coordinates $\vec{r}^N \equiv \vec{r}_1, \vec{r}_2, \ldots\ldots, \vec{r}_N$

  momentum coordinates $\vec{p}^N \equiv \vec{p}_1, \vec{p}_2, \ldots\ldots, \vec{p}_N$

$\vec{r}_i : (x_i \; y_i \; z_i)$

$\vec{p}_i : (p_{x,i} \; p_{y,i} \; p_{z,i})$

$$H = H(\vec{r}^N, \vec{p}^N) = \frac{1}{2m}\sum_{i=1}^{N}(p_{x,i}^2 + p_{y,i}^2 + p_{z,i}^2)$$

Accordingly, the microstates are given in terms of the position coordinates and the momentum coordinates of the capital N particles

Now, here I have used this shorthand notation as I have introduced in the last lecture, which actually is corresponding to capital n 3 dimensional vectors given like this. Now each vector is corresponding to a 3-dimensional position vector. So, we are looking into the microscopic state for a system where each particle is present in 3 dimension and therefore, it is coordinate has 3 components like the x coordinate, y coordinate and the z coordinate.

Accordingly, for each particle I will have one momentum vector which is giving me the x y and z components. So, there are 3 numbers associated with each momentum coordinate for each particle and therefore, the microstate together is described in terms of

6 n numbers. And with this idea in mind then what we do is this is a typical visualization of the microscopic state of the system, where I have highlighted only a few of these structure less balls that represent my constituent atom or molecule.

So, these atoms or molecules they do not know that the others exist. Each of them is free to move around in this box which is having a volume V and the total number of these particles is constant and, in this system, that the system is capable of exchanging thermal energy with the surrounding and therefore, it is in thermal equilibrium with this thermostat; maintaining the temperature of the system at a given value t.

So, for this particular description we have adopted as I have mentioned already the notation that for the ith particle the position coordinate is associated with 3 numbers x, y and z. X i, y i and z i representing the x y and z coordinate respectively of the ith particle. Similarly, p i is a collection of 3 numbers px i py i and pz i for the momentum the for the components of the 3 dimensional momentum p i.

So, under such condition if it so happens that I am talking about an ideal gas, I can write down the classical Hamiltonian and this classical Hamiltonian is going to be like this as each of the particles are independent of each other there is no potential energy of interaction between the different particles. And therefore, the overall Hamiltonian is going to be comprised of the individual Hamiltonians of the of each particle. Now each particle is nothing but a structure less ball.

As a result, in the Hamiltonian there is only one term for each particle that is the momentum term each momentum term once again is going to have contributions from the 3 components px py and pz. Accordingly, we can write down the Hamiltonian of the system which is a function of all the 3 N position coordinates and 3 N momenta coordinates as a summation over these momentum terms. And divide it by 1 by 2 m, where m is the mass of each constituent particle now once we understand this then.

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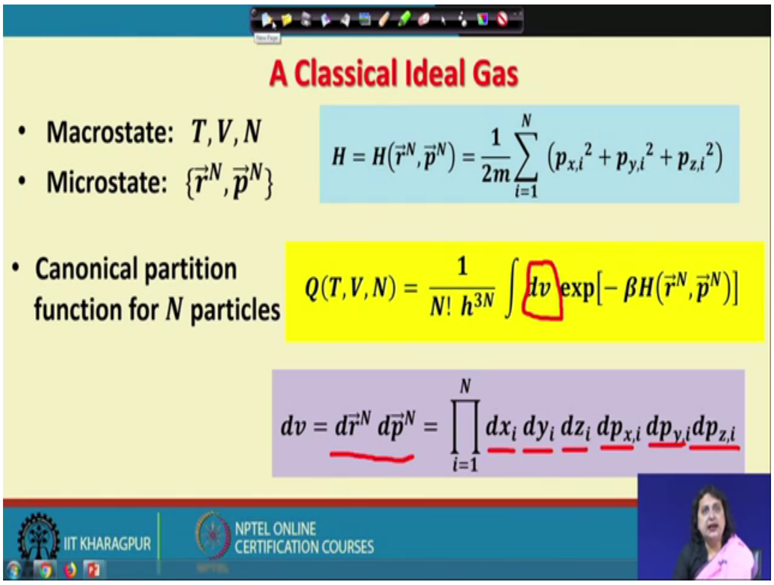

A Classical Ideal Gas

- Macrostate: T, V, N
- Microstate: $\{\vec{r}^N, \vec{p}^N\}$

$$H = H(\vec{r}^N, \vec{p}^N) = \frac{1}{2m}\sum_{i=1}^{N}(p_{x,i}^2 + p_{y,i}^2 + p_{z,i}^2)$$

- Canonical partition function for N particles

$$Q(T,V,N) = \frac{1}{N!\, h^{3N}} \int \boxed{dv} \exp[-\beta H(\vec{r}^N, \vec{p}^N)]$$

$$dv = \underline{d\vec{r}^N\, d\vec{p}^N} = \prod_{i=1}^{N} \underline{dx_i}\, \underline{dy_i}\, \underline{dz_i}\, \underline{dp_{x,i}}\, \underline{dp_{y,i}}\underline{dp_{z,i}}$$

Basically, we can go ahead and write down the canonical partition function for the N particles. So, that is by definition given by this. I would like to remind you here that this is the generalized expression where in order to have the correct expression correct derivation we have introduced this factor involving in the Plancks constant. So, that I have no problem in going to the limit where the quantum effects are important and this term N factorial takes care of the fact that I have capital N identical particles in the system

So, one we understand this then basically we can write down here the explicit form of what I have written by dv. So, dv is in a shorthand notation given by this volume element in there this is a infinitesimal volume element in the 6 n dimensional phase space. And if I write them down explicitly it contains dx I dy idz I this is for the position coordinates of the ith particle and d px i dp y i and the pz i these are the momentum coordinates of the ith particle.

And I have 6 such terms appearing for each of the N particles. So, as a whole these is this integration is a 6 N dimensional integration over the phase space of the system. Now once I understand this then let us go ahead and try to see how the canonical partition function would look like for an ideal gas, where I have only 2 particles. So, capital N is equal to 2.

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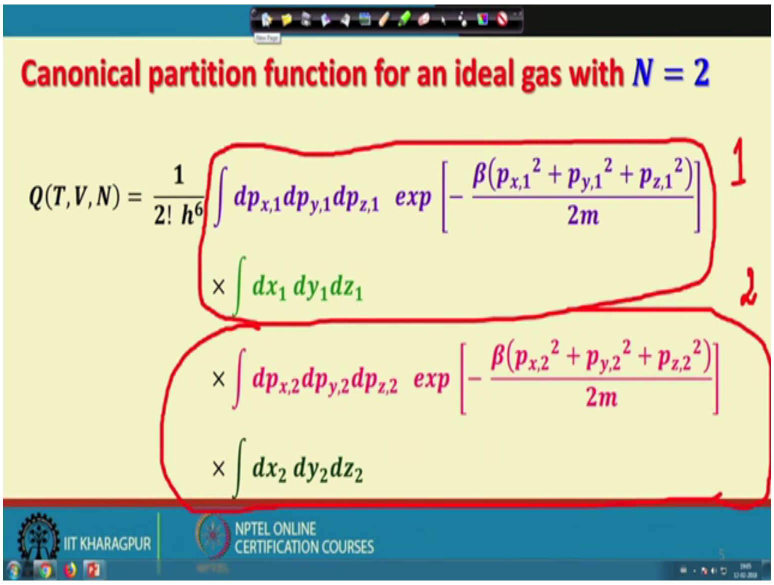

Canonical partition function for an ideal gas with $N = 2$

$$Q(T,V,N) = \frac{1}{2!\,h^6}\boxed{\int dp_{x,1}dp_{y,1}dp_{z,1}\ exp\left[-\frac{\beta\left(p_{x,1}^2+p_{y,1}^2+p_{z,1}^2\right)}{2m}\right] \times \int dx_1\,dy_1dz_1}\ 1$$

$$\boxed{\times \int dp_{x,2}dp_{y,2}dp_{z,2}\ exp\left[-\frac{\beta\left(p_{x,2}^2+p_{y,2}^2+p_{z,2}^2\right)}{2m}\right] \times \int dx_2\,dy_2dz_2}\ 2$$

So, here what I have done is I have explicitly put in the contribution coming from the Hamiltonian of each of the particles. And written out the phase space integration over the 6 into 2 that is, 12-dimensional phase space. Now the first term that you see here that is involving the particle 1 and this is integration over all possible values of momentum of particle 1 and the integrand contains e to the power of minus beta p square by 2 m, where I have one contribution coming from the x component another contribution coming from the y component and the third contribution coming from the z component.

For the particle 1 there is another term here over it is x y and z coordinates, but the integrand is nothing but 1; and that is because what you had in the Hamiltonian was term dependent only on px py pz and there was no term dependent on x 1 y 1 z 1. And therefore, here the integrand is 1 and together as I see that I have these 2 integrations corresponding to my particle number 1.

Now, similarly I have written out the expression for the integration corresponding to the particle number 2. So, as I see because of the independent nature of momentum of particle 1 and particle 2, I have 2 independent contributions. So, I can simplify and rewrite this canonical partition function for n equal to 2 in the following manner.

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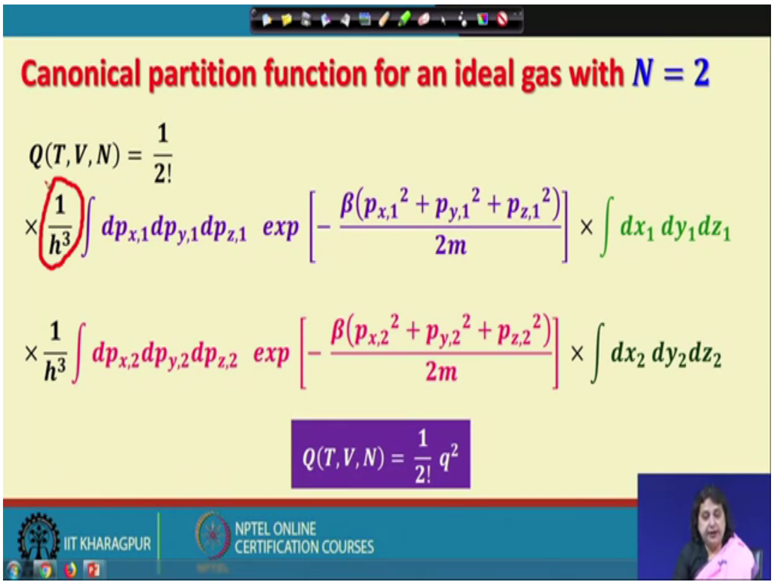

Canonical partition function for an ideal gas with $N = 2$

$$Q(T,V,N) = \frac{1}{2!}$$

$$\times \frac{1}{h^3} \int dp_{x,1} dp_{y,1} dp_{z,1} \; exp \left[- \frac{\beta(p_{x,1}{}^2 + p_{y,1}{}^2 + p_{z,1}{}^2)}{2m} \right] \times \int dx_1\, dy_1 dz_1$$

$$\times \frac{1}{h^3} \int dp_{x,2} dp_{y,2} dp_{z,2} \; exp \left[- \frac{\beta(p_{x,2}{}^2 + p_{y,2}{}^2 + p_{z,2}{}^2)}{2m} \right] \times \int dx_2\, dy_2 dz_2$$

$$\boxed{Q(T,V,N) = \frac{1}{2!} q^2}$$

I have this 1 by 2 factorial term to take care of the fact that I have two identical particles. Now I have written out one term that is shown here that depends only on the particle 1 and here I have written out another term which depends only on the particle 2, right? So, what I understand is if I have 2 particles which are not interacting with each other, then the overall canonical partition function is going to have one contribution dependent entirely on the coordinates and momenta of particle 1.

And another set which depends only on the position and the momentum coordinates of the particle 2. As a result what I can do is, I can very easily write down that the entire Q T V N is going to be given by q square divided by 2 factorial where small q is this integration term for any given particle.

And now, as you can see that in state in addition to these integrals I have included here this term 1 by h cube. So, that is because for every degree of freedom I would like to have the correct derivation of a quantum mechanical analog, as a result for every particle I will pre-multiply by 1 by h cube. So, that my normalization constant even in the quantum limit is correct.

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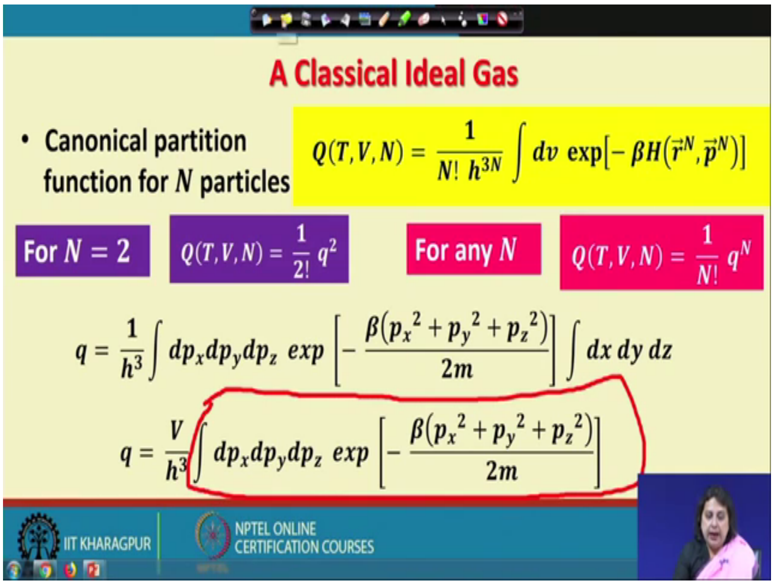

A Classical Ideal Gas

- Canonical partition function for N particles $Q(T,V,N) = \frac{1}{N!\,h^{3N}} \int d\nu \, \exp[-\beta H(\vec{r}^N, \vec{p}^N)]$

For $N = 2$ $Q(T,V,N) = \frac{1}{2!} q^2$

For any N $Q(T,V,N) = \frac{1}{N!} q^N$

$$q = \frac{1}{h^3} \int dp_x dp_y dp_z \, exp\left[-\frac{\beta(p_x^2+p_y^2+p_z^2)}{2m}\right] \int dx\,dy\,dz$$

$$q = \frac{V}{h^3} \int dp_x dp_y dp_z \, exp\left[-\frac{\beta(p_x^2+p_y^2+p_z^2)}{2m}\right]$$

So, noting all these therefore, I can now very easily say that yes; this is the generalized expression for the canonical partition function for N particles in the where the Hamiltonian depends on the position and the momentum coordinates of all the capital N particles. We demonstrated how it looks like for the very simple case where my system is comprised of 2 identical non-interacting particles.

So now, if I try to write down what capital Q is for any N if your system is comprised of capital N identical non-interacting classical particles then we can say that Q T V N is going to be given by 1 by N factorial to take care of the fact that all the particles are identical. And then small q to the power of n this part which tells us that what happens if I have independent contributions from each of the capital N particles

Now if I write down then for capital N particles, what happens what is the expression for small q this is what I will get. So, all I have done is I have written out for any general particle the single particle canonical partition function which by definition is an integration over all possible the phase space momentum components of that particle px py and pz.

And also, integration over dx dy and dz; in the case of a classical ideal gas the integrand dependent on x y z is equal to one while the integrand dependent on px py pz is given by e to the power of minus beta into the kinetic energy term. And therefore, what I can argue is I can now understand that if I do this integration, what are the values to which x y and z can vary? Of course, if my integrand is 1 this is nothing but the integrated value that I have the value of the integral is nothing but the volume of the system. And therefore, I can take the volume out and write small q as V by h cubed and I am left with the momentum integration as written out explicitly in terms of px py and pz.

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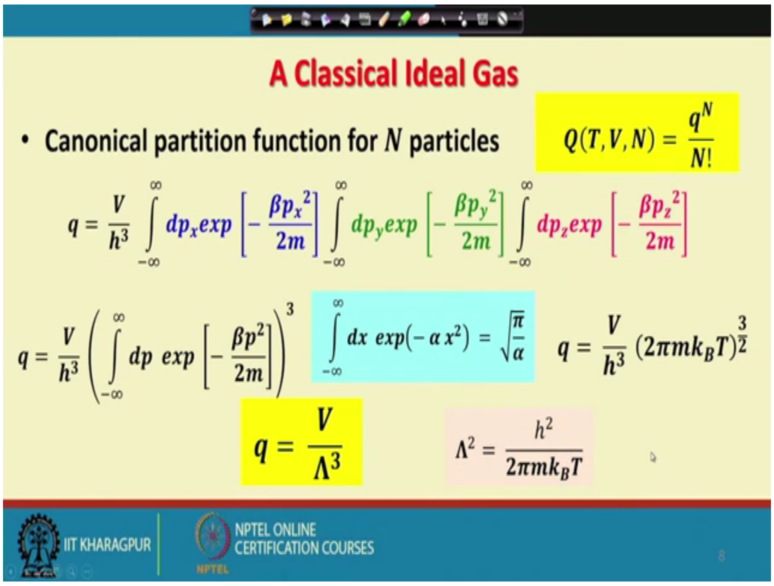

A Classical Ideal Gas

- Canonical partition function for *N* particles

$$Q(T,V,N) = \frac{q^N}{N!}$$

$$q = \frac{V}{h^3} \int_{-\infty}^{\infty} dp_x exp\left[-\frac{\beta p_x{}^2}{2m}\right] \int_{-\infty}^{\infty} dp_y exp\left[-\frac{\beta p_y{}^2}{2m}\right] \int_{-\infty}^{\infty} dp_z exp\left[-\frac{\beta p_z{}^2}{2m}\right]$$

$$q = \frac{V}{h^3}\left(\int_{-\infty}^{\infty} dp\ exp\left[-\frac{\beta p^2}{2m}\right]\right)^3$$

$$\int_{-\infty}^{\infty} dx\ exp(-\alpha x^2) = \sqrt{\frac{\pi}{\alpha}}$$

$$q = \frac{V}{h^3}(2\pi m k_B T)^{\frac{3}{2}}$$

$$q = \frac{V}{\Lambda^3}$$

$$\Lambda^2 = \frac{h^2}{2\pi m k_B T}$$

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And what we do next is we do some further simplification and this simplification is that; I split each of the exponential functions and right this momentum integral as 3 independent integrations. The first one being this one that is integration over the px values the second one is the integration involving the py values and the third one is involving the integration over the pz values. Now as you understand this px py p z is the dummy indices, right?

As a result, I can say that all these 3 integrations are actually the same integrations and therefore, I should be able to write that small q is nothing but this V by h cubed into this integration it is value raised to the power of 3 because I have 3 identical integrals being that are being multiplied together. So, once I know this then I can go back and try to see what kind of integration do I have here. I would like to remind you that we have seen such integrations before and this integration is of the form where you have as the integrand e to the power of minus alpha x s square. And we know that this integral when integrated from minus infinity to plus infinity values of x gives me root over of pi by alpha.

Now, in this case I understand what is my alpha, alpha is equal to this quantity therefore, I can actually estimate this integration and find that my small q is going to be given by an expression like this now; obviously, this combination of terms is familiar and that is exactly what we have used here. We have written out small q as capital V divided by lambda q where capital lambda is the thermal (Refer Time: 17:56) wavelength. And it is defined in terms of the plancks constant h and it is related to the mass of every constituent particle of the system and it is also dependent on the temperature at which the gases present.

Now, as you can see that we have achieved something spectacular. We are talking about a very large number of particles and we found that capital Q that is a 6 N dimensional integral. And we could simplify this entire expression here by saying that for an ideal gas system capital Q can be reduced to small q to the power of N by N factorial, where small q is nothing but a 3-dimensional integral. And when we evaluate this 3-dimensional integral because of the simplicity of the system that I have an analytical expression regarding the single particle canonical function canonical partition function can be obtained.

Therefore, if I know small q I can go back use this expression and find out capital Q and this tells me very simply that; now that I know the canonical partition function for these N particles I should be able to work on the thermodynamics of a system comprised of capital N identical non-interacting classical particles, and see if I can reproduce known experimental results on the ideal gases. So, that is what we are going to examine next.

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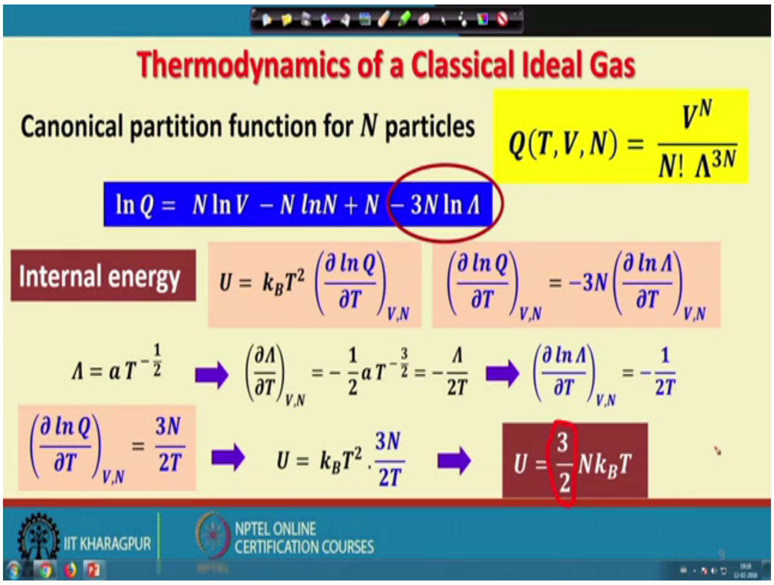

Thermodynamics of a Classical Ideal Gas

Canonical partition function for N particles $Q(T,V,N) = \frac{V^N}{N!\,\Lambda^{3N}}$

$$\ln Q = N\ln V - N\ln N + N - 3N\ln\Lambda$$

Internal energy $U = k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{V,N}$ $\left(\frac{\partial \ln Q}{\partial T}\right)_{V,N} = -3N\left(\frac{\partial \ln \Lambda}{\partial T}\right)_{V,N}$

$$\Lambda = aT^{-\frac{1}{2}} \Rightarrow \left(\frac{\partial \Lambda}{\partial T}\right)_{V,N} = -\frac{1}{2}aT^{-\frac{3}{2}} = -\frac{\Lambda}{2T} \Rightarrow \left(\frac{\partial \ln \Lambda}{\partial T}\right)_{V,N} = -\frac{1}{2T}$$

$$\left(\frac{\partial \ln Q}{\partial T}\right)_{V,N} = \frac{3N}{2T} \Rightarrow U = k_B T^2 . \frac{3N}{2T} \Rightarrow U = \frac{3}{2}Nk_B T$$

So, this is the result that I am going to start from and let me start from the internal energy. So, once again this is a quick reminder that the internal energy of the system is related to the derivative of ln Q with respect to temperature keeping volume and the number of particles constant. Now if I use this expression of Q, I can very easily write down that ln Q is comprised of these terms, where I have assumed that capital N is a very large number like the avogadro number and therefore, I can very easily utilize the (Refer Time: 20:27) approximation.

And now as you see that I am interested in the temperature derivative of ln Q under the condition where the volume and the number of particles are constant. And therefore, I understand that in this expression there is only one term which has any dependence on temperature and that is, through the dependence of temperature of the thermal (Refer Time: 20:52) wavelength lambda and therefore, if I want to find out del ln Q del T under the condition of constant volume and number of particles I am essentially going to look at minus 3 N into del del T of ln lambda keeping volume and number of particles constant.

Now, if I look back at the explicit temperature dependence of lambda on temperature it is something like this, where a is a constant when v and n are held constant therefore, I can say what is del lambda del T is under such conditions that turns out to be minus lambda by 2 T. Now if I bring this lambda to the left-hand side what shall I get I will have 1 by lambda del lambda del T and that is nothing but del ln lambda del T keeping volume and number of particles constant. Therefore, this quantity turns out to be minus 1by 2T. So, the mathematics is simple and now I am going to combine these 2 relationships first del ln Q is related to del del T of l n lambda under such condition; and del del T of r ln lambda is given by minus 1 by t. I combine these 2 equations and what I get is I end up determining del del T of ln Q in in terms of N and T.

And when I use this expression and put it back here what I get is u is kbt square multiplied by this quantity. So, that is 3 N by 2T and that tells me that sure what I have obtained is that the internal energy of the system comprised of capital N structure less classical particles that are not interacting with each other that is, capital N k b T multiplied by 3 by 2, right?

And therefore, what I understand here is that the internal energy is comprised entirely of the kinetic energy of each of these structure less classical particles present in the system. They are moving about in the box at a temperature T, and it has each particle has 3 degrees of freedom in the x y and axis. So, each degree of freedom contributes half kt energy to the overall internal energy.

So, capital N such particles contribute 3 N by 2kT total amount of energy to the internal energy of the system. And this once again is what we have known as the result from the equipartition theorem. And when we were working with the explicit structure this is the term that came from the translational motion of each of the center of mass at a temperature T within the volume V. and I had capital N identical non-interacting particles.

Now, the next thing is we will go back and examine what happens to the pressure.

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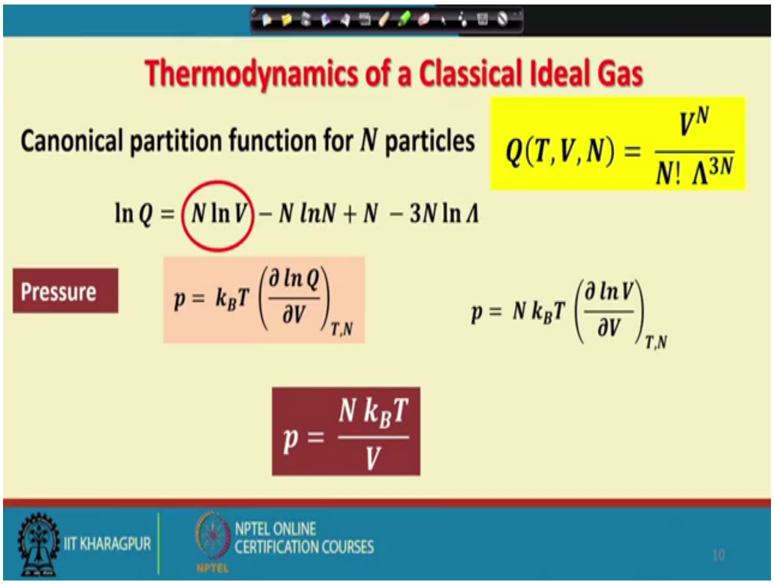

Thermodynamics of a Classical Ideal Gas

Canonical partition function for N particles $Q(T,V,N) = \frac{V^N}{N!\,\Lambda^{3N}}$

$$\ln Q = \boxed{N\ln V} - N\ln N + N - 3N\ln\Lambda$$

Pressure

$$p = k_BT\left(\frac{\partial \ln Q}{\partial V}\right)_{T,N}$$

$$p = N k_BT\left(\frac{\partial \ln V}{\partial V}\right)_{T,N}$$

$$p = \frac{N k_BT}{V}$$

So, once again very quickly let us remind ourselves that pressure is related to the del del V of lnQ. And if I look at l n Q that is only one term that explicitly depends on volume. So, keeping temperature a number of particle constant all other terms here are going to be constants of volume therefore, I can very easily write down that p is equal to N kbT this N going out as a constant, then del del V of ln V under the condition of constant temperature and number of particles and this is something that you can very easily do, and find out that the pressure is nothing but what we have learned from our experimental data.

So now we have been able to combine many different approaches that approach of kinetic theory of gases, the approach where we attached the explicit microscopic states of the molecules or atoms; that are constituting the ideal gas and here. I have represented the particles of the gas just as structuralist classical balls. In all these cases what I find is the system comprised of this capital N identical known and interacting particles will have energy that is equal to 3 N by 2k T. And the pressure is entirely from the collision of these structuralist particles with the walls of the container and while doing so it does not really know that other particles are exist in the system. And therefore, it is as if the entire volume is available to the system and you get the ideal gas equation.

So now, that we have shown that the ideal gas equation is actually related to the description of the system over all possible microscopic states and that is an average from all possible microscopic states; taking into consideration the translational motion of the molecules only, but interestingly what happens is in the real world we have not only in the ideal gases, but also the real non-ideal behavior.

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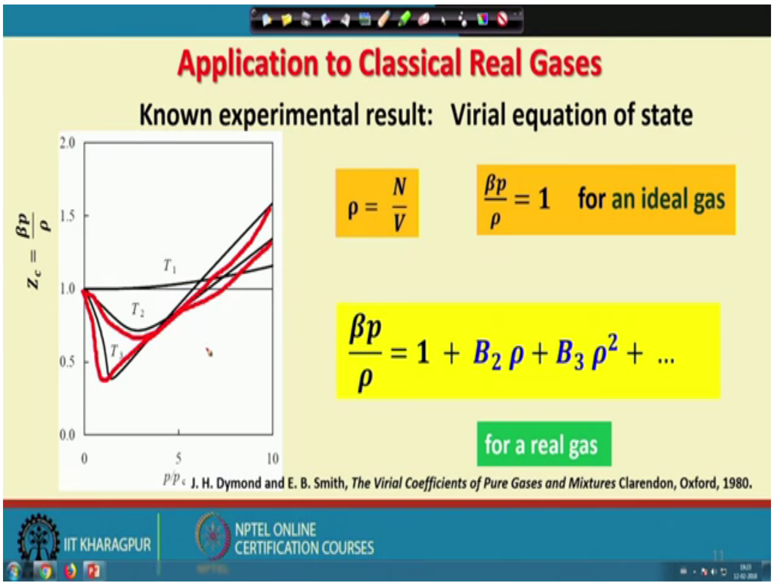

Application to Classical Real Gases

Known experimental result: Virial equation of state

$\rho = \frac{N}{V}$

$\frac{\beta p}{\rho} = 1$ for an ideal gas

$$\frac{\beta p}{\rho} = 1 + B_2\rho + B_3\rho^2 + \ldots$$

for a real gas

J. H. Dymond and E. B. Smith, *The Virial Coefficients of Pure Gases and Mixtures* Clarendon, Oxford, 1980.

And this such non-ideal behavior is generally represented in terms of the compressibility factor, which is defined here in terms of beta p by rho. So, rho is the number density. So, what happens is if I plot this compressibility factor as a function of pressure this is some reduced pressure in certain scale, then it is possible to show that z c must be equal to 1 for an ideal gas. So, that is the outcome of the ideal gas equation, but for a real system we do see that there are market deviations from this constant behavior. As you see that at different temperatures the compressibility value will show you many different values which are rather different from the ideal gas value of unity.

Now, whatever we have done so far did not take into account the interaction between the particles constituting the gaseous system. So, in the next lecture let us take up that problem and try to understand, how we can introduce the concept of interaction between the different particles in a gas in a real gas and explain why the equation of state should be an equation like this, where in addition to the ideal gas term. I will have additional terms that are expected to be reflecting directly the effect of underlying intermolecular interaction.

Thank you.