**Thermodynamics for Biological Systems:
Classical and Statistical Aspects
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Lecture – 60
Partition function of Mono Atomic Gases

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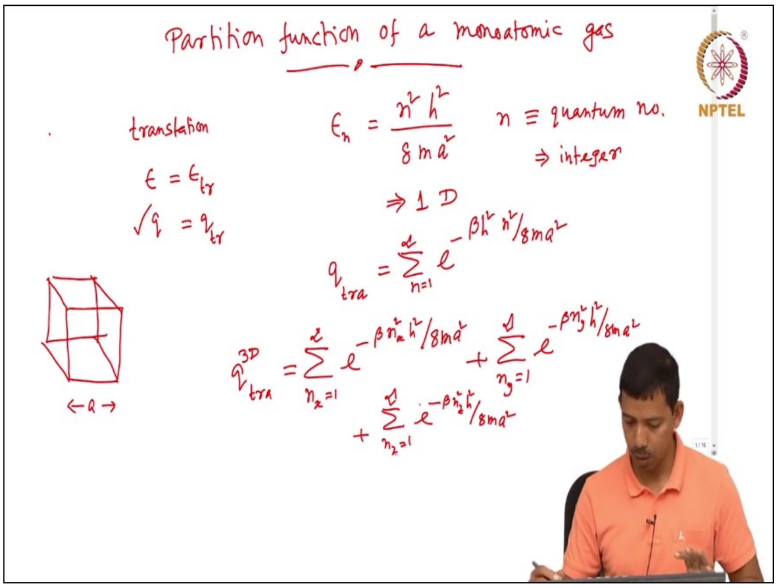

Now we will be basically looking at the partition function of a monatomic gas. So, what will be the partition function of a monoatomic gas? So, as I have shown you that partition function can be correlated to various common area quantities now we are taking a special case where we are trying to find out the partition function for monoatomic gas and from there on we will see how this partition function of monoatomic gas correlates to various thermodynamic quantities.

So, when it comes to a monotonic gas so you know this monoatomic system has only the translational motion. It has only the translation it has only the translation. It does not have if the system was a molecular system then, it will also have a rotational motion and it would also have a vibrational motion.

And therefore your total energy would turn out to be E translational plus E rotational plus E vibrational correspondingly your total partition function would look like as q translational product, q rotational product, q vibrational. But in this case we are talking about a much simpler system where we have no vibration, we have no rotation as well and therefore the energy contribution will have only the translational motion.

And therefore our q partition function will also have only the q translational. So, let us find out for the simple case what is our q. We assume that ours our gas is content in a cubic box of length a, so this is the cubic box of length a and monoatomic gas is basically kept in here. Now, if you recall your, your first-year chemistry. We you know that for a particle in a box system the energy was–

$$E_n = \frac{n^2 h^2}{8ma^2}$$

Where n is the quantum number.

It is a quantum number and it is an integer. So, this is the energy for a particle in a box. But if you remember this expression was for the movement of the particle in one dimension, in one dimension. Now if we make use of that formula here, our q translational, will be

$$q_{tra} = \sum_{n=1}^{\infty} e^{\frac{-\beta h^2 n^2}{8ma^2}}$$

This is in one-dimension, our gas is content in a cubic box and therefore the particle the gas particle can move in all XYZ direction. So, in that case our q translational in 3D would be

$$q_{tra} = \sum_{n_x=1}^{\infty} e^{\frac{-\beta h^2 n_x^2}{8ma^2}} + \sum_{n_y=1}^{\infty} e^{\frac{-\beta h^2 n_y^2}{8ma^2}} + \sum_{n_z=1}^{\infty} e^{\frac{-\beta h^2 n_z^2}{8ma^2}}$$

Here n is equal to integer 1 to infinity. So, this is q translational of 3D. Now, if you see is the part the gas is in cubic box and particle can go in X Y Z direction equally it can go to any direction with equal probability.

So, therefore we can write q thoroughly as our XYZ, all three directions are equally probable and they are, there they are the same. So, we can simplify this further. Let us see how we can simplify

$$q_{tra}^{3D} = \left(\sum_{n=1}^{\infty} e^{\frac{-\beta h^2 n^2}{8ma^2}} \right)^3$$

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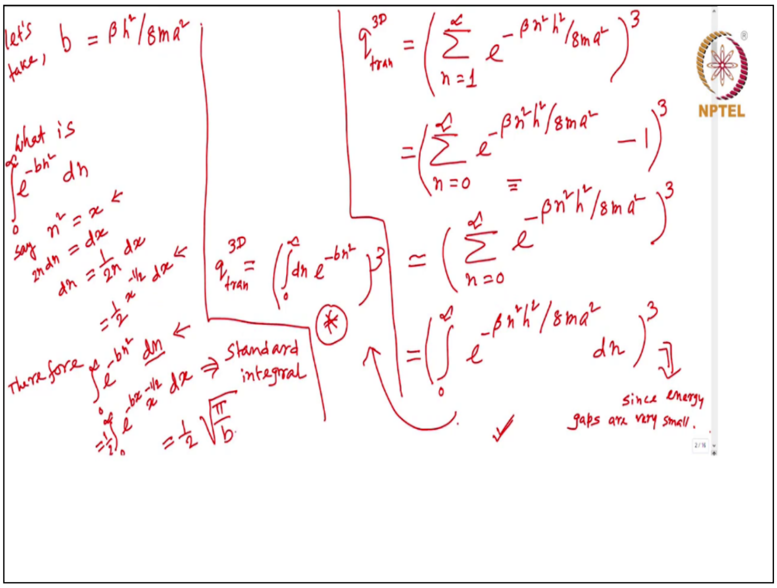

So, here our sum goes from n is equal to 1 because the quantum number is an integer and for the sake of mathematical simplicity, we want to change this limit from n is equal to 0 to infinity, how do we do that? so, we write as it is and then we simply put minus 1. Since e to the power 0 is 1, so just by when I put 1 into it was 0, so I get was 0 which is one and that one I am basically subtracting out here.

$$q_{tra}^{3D} = \left(\sum_{n=0}^{\infty} e^{\frac{-\beta h^2 n^2}{8ma^2}} - 1\right)^3 \cong \left(\sum_{n=0}^{\infty} e^{\frac{-\beta h^2 n^2}{8ma^2}}\right)^3$$

Now since this number, this number is much, much larger than 1 we can write this as n is equal to these are mathematical tricks, to make our calculation tractable. So, since 8m square to the power 3 since this quantity is much larger than 1 and therefore we can neglect 1. The second trick is since energy gap is very small you know, in in every system, in, in this case, in the quantum system, since there are many energy levels and the energy gaps are very small so we can assume we can replace this sum by integral.

$$q_{tra}^{3D} = \left(\int_0^{\infty} e^{\frac{-\beta h^2 n^2}{8ma^2}}\, dn\right)^3$$

So, this we can write as 0 to infinity e to the power minus beta n square h square by 8 m a square dn the power cube to the power 3 and we written with the logic that since energy gaps are gaps are very small, they are very small. So, you can you can assume that it is like a continuous energy states and therefore we change the sum to integral. Now how do we simplify this integral?

Let us say,

$$b = \frac{\beta h^2}{8ma^2}$$

Hence we can write

$$q_{tra}^{3D} = \left(\int_0^{\infty} dn\, e^{-bn^2} \right)^3$$

And

$$\int_0^{\infty} e^{-bn^2}\, dn = \frac{1}{2}\sqrt{\frac{\pi}{b}}$$

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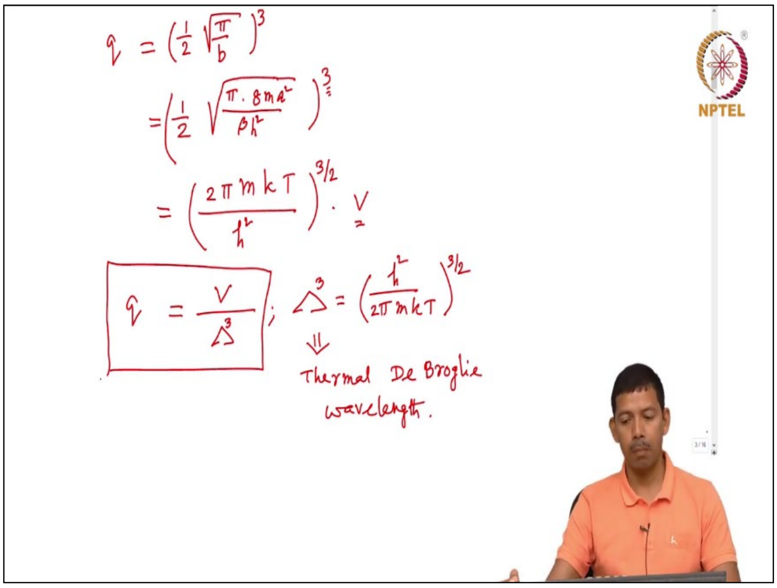

Therefore

$$q = \left(\frac{1}{2}\sqrt{\frac{\pi}{b}}\right)^3$$

$$q = \left(\frac{1}{2}\sqrt{\frac{\pi . 8ma^2}{h^2}}\right)^{3/2} . V$$

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

Thus,

$$\Delta^3 = \left(\frac{h^2}{2\pi mkT}\right)^{3/2}$$

And this lambda having a dimension of length is called the Thermal De Broglie wavelength, Thermal De Broglie wavelength okay. So, this is the expression what we are looking for and we got it finally for a monoatomic gas, the expression for partition function. So, the expression for expression of partition function for a monoatomic gas is nothing but volume divided by the cube of Thermal de Brogile wavelength.

So, now since we have the partition function of this mono atomic gas let us find out different thermodynamic quantities. So, the first thermodynamic quantity we can look for is the energy.

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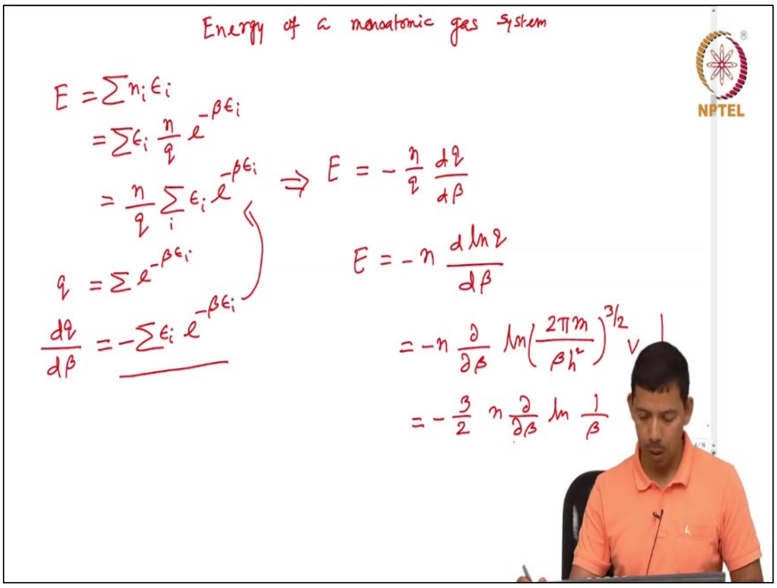

So what is the energy of a monoatomic gas system?

$$E = \sum n_i \varepsilon_i$$

$$E = \sum \varepsilon_i \frac{n}{q} e^{-\beta\varepsilon_i}$$

$$E = \frac{n}{q} \sum_i \varepsilon_i e^{-\beta\varepsilon_i}$$

We know that

$$q = \sum e^{-\beta\varepsilon_i}$$

$$\frac{dq}{d\beta} = -\sum_i \varepsilon_i \, e^{-\beta \varepsilon_i}$$

Putting this into above equation

$$E = -\frac{n}{q}\frac{dq}{d\beta}$$

$$E = -n\,\frac{d\ln q}{d\beta}$$

$$E = -\frac{3}{2}\,\frac{d}{d\beta}\ln\frac{1}{\beta}$$

This will gives us

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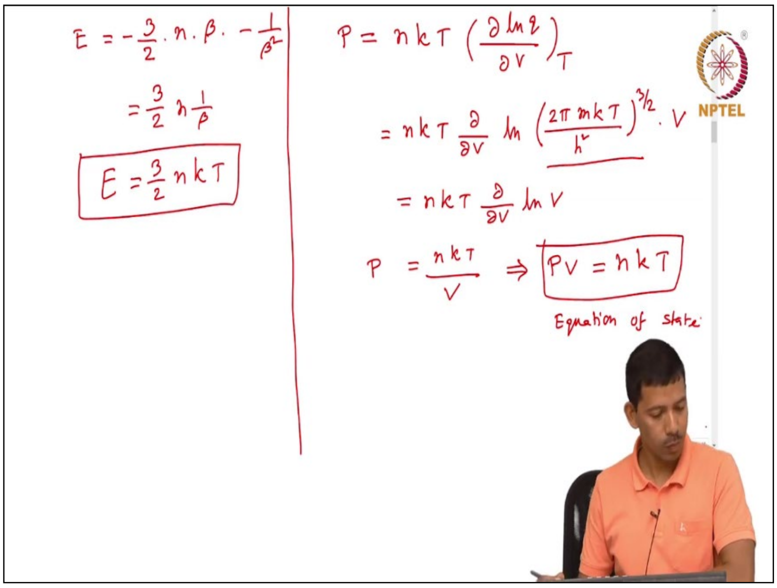

$$\boldsymbol{E = \frac{3}{2}\,nkT}$$

So, as you know as we have seen already E is total energy in terms of Boltzmann distribution law.

So we have started from the definition of partition function and then, we using that partition function definition we have come up with the thermodynamic expression what you know of the total energy of a monatomic gas system as 3/2 n KT.

What is the pressure of this system so pressure as you know from your thermodynamic law and which we already have used to get the relation with the partition function

$$P = nkT \left(\frac{\partial \ln q}{\partial V}\right)_T$$

$$P = nkT \frac{\partial}{\partial V} \ln \left(\frac{2\pi mkT}{h^2}\right)^{3/2} . V$$

$$P = nkT \frac{\partial}{\partial V} \ln V$$

$$\boldsymbol{PV = nkT}$$

That is your PV is equal to n KT which is the equation of state because an upstate offer of an ideal monoatomic gas system. So, what I want to point out here is that thermodynamics and statistical thermodynamics, they are they complement each other and thermodynamics statistical thermodynamics basically keeping with a microscopic information in terms of partition function here.

And that partition function can bring out not only the thermodynamic expressions but also can correlate to many classical equations our expressions you know how like PV is equal to n KT or the total energy is equal to 3 /2 n K_BT where K_B is the Boltzmann constant which I have written as K.