Chemical Kinetics and Transition State Theory
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Lecture 06
Maxwell-Boltzmann distribution: how fast are molecules moving?

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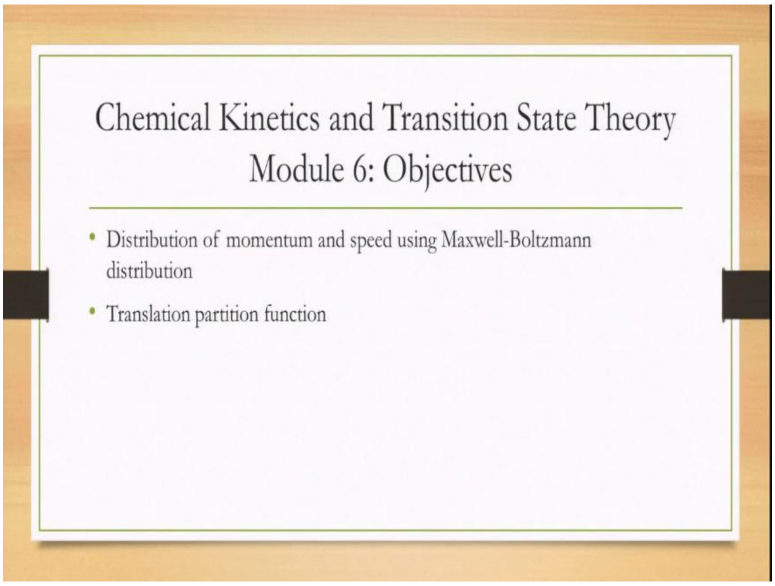

Hello, and welcome to module six of Chemical Kinetics and Transition State Theory. Today, we are going to look at the distribution of speed and velocities. In last module we had looked at the Boltzmann distribution itself, but what can we do with that Boltzmann distribution is what we are going to look at today. In doing so, we will also cover up one important topic that will be important later on which is the translational partition function.

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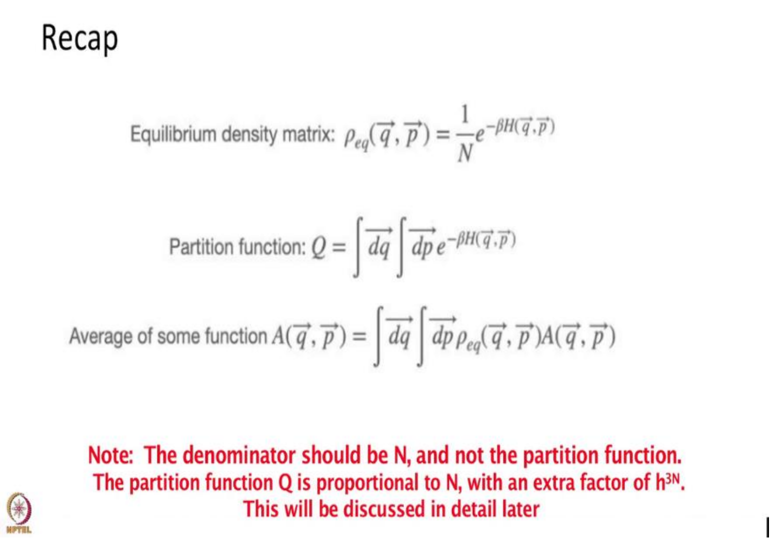

So, a quick recap of module five we had given you a partial derivation of calculating the equilibrium density matrix, it is given by this Boltzmann distribution $e^{-\beta H}$ where H is the Hamiltonian divided by Q and Q is called the partition function, which is an $\int d\vec{q} \int d\vec{p}$ $e^{-\beta H}$.

And we also discussed how do we calculate average of any property. If I have any quantity, let's say A as a function of some q and p in general, to find the average of A, I must integrate over all p and q ρ which gives me the probability of being at q and p multiplied by A, which gives me the value at q and p. So, in the last module, we looked at a few examples, which is average momentum and average kinetic energy.

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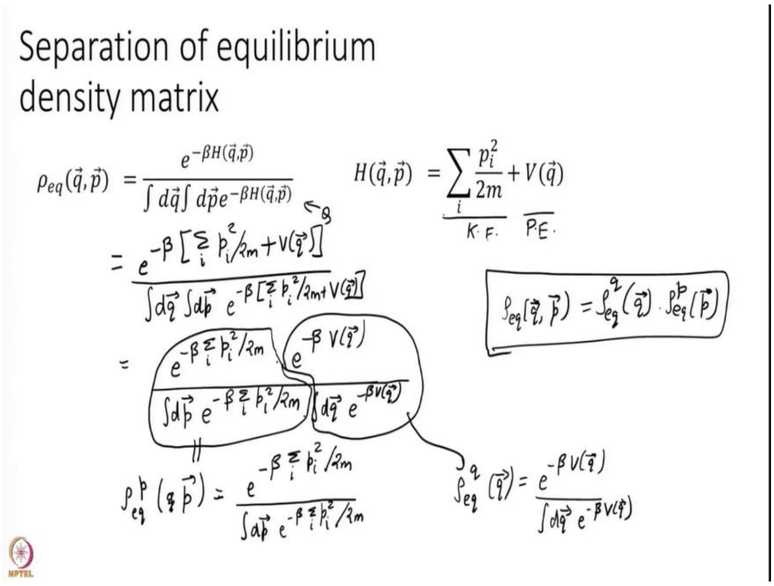

So, before moving forward, let us do one thing, which is going to be useful. So, I have written down the definition of our ρ_{eq}, which is what we derived in the last module $e^{-\beta H}$ divided by what this integral is basically the Q and I have written the Hamiltonian explicitly, which is the kinetic energy plus the potential energy, so I want to just substitute this H in this ρ_{eq} and see if we can simplify this equation a little bit.

So, if I substitute what I get is, so I write H as $\sum_i \frac{p_i^2}{2m} + V(\vec{q})$ divided by $\int d\vec{q} \int d\vec{p}$ $e^{-\beta \sum_i \frac{p_i^2}{2m} + V(\vec{q})}$. I write the same big summation here and summation in exponential can be converted into a product of exponentials.

So, I write the same thing as $e^{-\beta \sum_i \frac{p_i^2}{2m}} * e^{-\beta V(\vec{q})}$ divided by, and I will do the same separation in the denominator, I will write the momentum first because I have momentum first in the numerator. So, just to be consistent, we write it as this my bad it should be an integral not a summation.

So, let's remove the summation let's put in the $\int d\vec{q}\, e^{-\beta V(\vec{q})}$. So, some of you notice that we have separated the terms as a function of p and as a function of q. So, this part we will define to be $\rho_{eq}^{p}(\vec{p})$, only p, note there is no q dependence in this and this portion I will define of $\rho_{eq}^{q}(\vec{q})$, there is no p dependence in this one.

So, in total, I am writing this $\rho_{eq}(\vec{q},\vec{p})$ in separable form of $\rho_{eq}^{q}(\vec{q}) * \rho_{eq}^{p}(\vec{p})$, where $\rho_{eq}^{p}(\vec{p})$ is defined here and $\rho_{eq}^{q}(\vec{q})$ is defined here.

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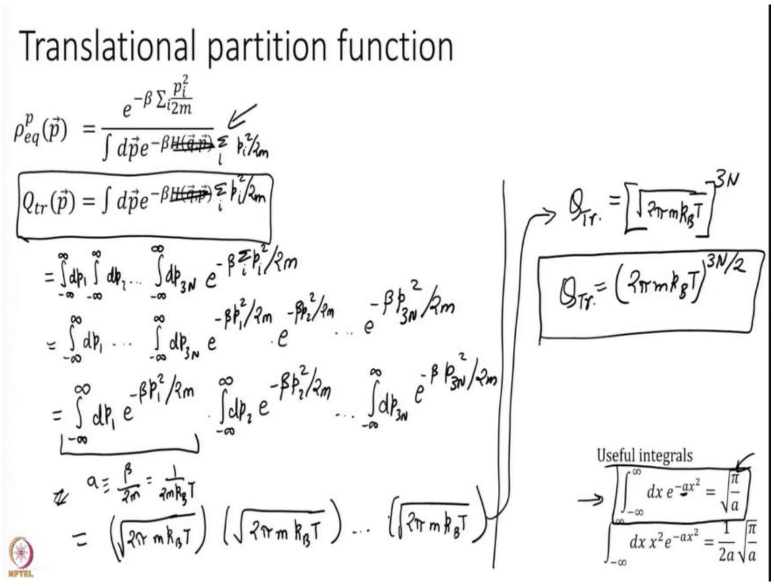

So, let us look at the equilibrium function for p for a moment, we can actually simplify it a little bit more. So, I have rewritten the $\rho_{eq}^{p}(\vec{p})$ right here. Now, the denominator that we have here my bad, this should be $\sum_i \frac{p_i^2}{2m}$, this should be $\sum_i \frac{p_i^2}{2m}$. So, this denominator that we get is called the translational partition function, why translational because it is simply kinetic energy.

So, this is the partition function when V of q is zero for a free particle. So, this partition function is called the translational partition function and we can actually simplify it and calculate it, you can find an closed form answer for this. So, let's try to do that. So, this thing first of all note that $\int d\vec{p}$ is the same thing as $\int_{-\infty}^{\infty} d\vec{p}_1 \int_{-\infty}^{\infty} d\vec{p}_2$ till $\int_{-\infty}^{\infty} d\vec{p}_{3N}$, remember, we have 3N momenta 3N positions, why 3N? N is the number of particles for each particle I have x, y and z. So, I have p_x p_y p_z for particle one, p_x p_y p_z for particle two, they are on so forth. So, I have 3N momenta.

So, this is what I have that I have to calculate, well, we note that I can simplify this integral as $e^{-\beta \sum_i \frac{p_1^2}{2m}} * e^{-\beta \sum_i \frac{p_2^2}{2m}}$ till $e^{-\beta \sum_i \frac{p_{3N}^2}{2m}}$. So, I have again taken the exponential, exponential was a sum form so, I can take it into a product form.

Now, I note that this is equal to. So, I separate all the terms out and take them the corresponding integral. So, let us look at each integral separately first separated out all the integrals, all are independent integrals and I can evaluate them one at a time. That's the beauty of this.

And this one integral is called a Gaussian integral from all over all space -∞ to +∞ that integral form is known, I have provided you the formula and again throughout the course, any integral which is complex, we will provide you, you do not have to memorise any of this and this is not really a maths course.

So, this thing, here we note that in my formula I provided you this a. So, if a here will be $\frac{\beta}{2m}$. Yeah, it is the constant before my variable, which is nothing but $\frac{1}{2mk_BT}$. So, this thing becomes equal to $\sqrt{2\pi m k_B T}$, so I am simply using this formula here $\sqrt{\frac{\pi}{a}}$. So, $\sqrt{\frac{\pi}{a}}$ but a note is one over something so I get this thing. But I get the same integral when I solve for p_2. In fact, I will get the same for all 3N of them.

So, if I multiply these together what I get is or I just write slightly differently. So, now we have derived the formula for the translational partition function, this will be useful later on. So, we keep it for now. And once we use it, I will remind you of this, for now this is nothing but the denominator of $\rho_{eq}^{p}(\vec{p})$.

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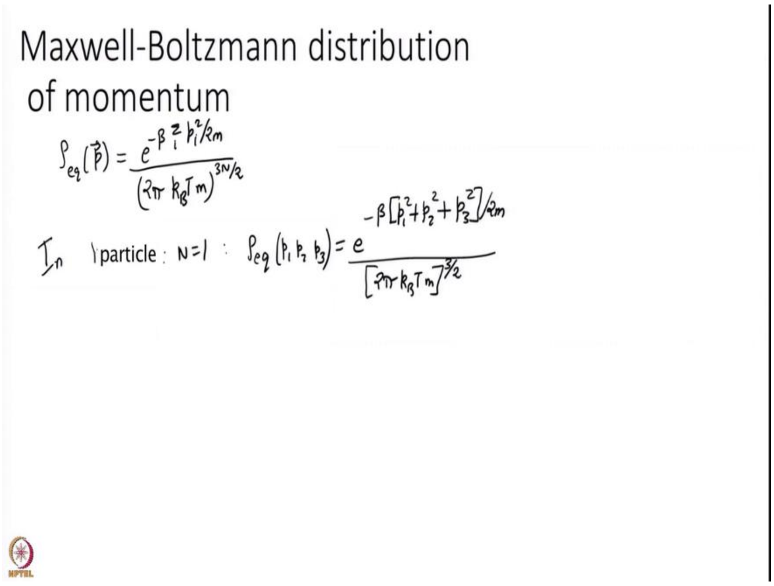

So, now finally, I get

$$\rho_{eq}(\vec{p}) = \frac{e^{-\beta \sum_i \frac{p_i^2}{2m}}}{(2\pi k_B T m)^{\frac{3N}{2}}}$$

So, let us just look at it in one dimension only. So, for this I get ρ_{eq}. For N=1, I still have three momentums p_x p_y p_z and in our notation we refer p_1 as p_x, p_2 as p_y and p_3 as p_z and here I will substitute N=1 so I get this. So, that is a distribution of momentum in one dimension.

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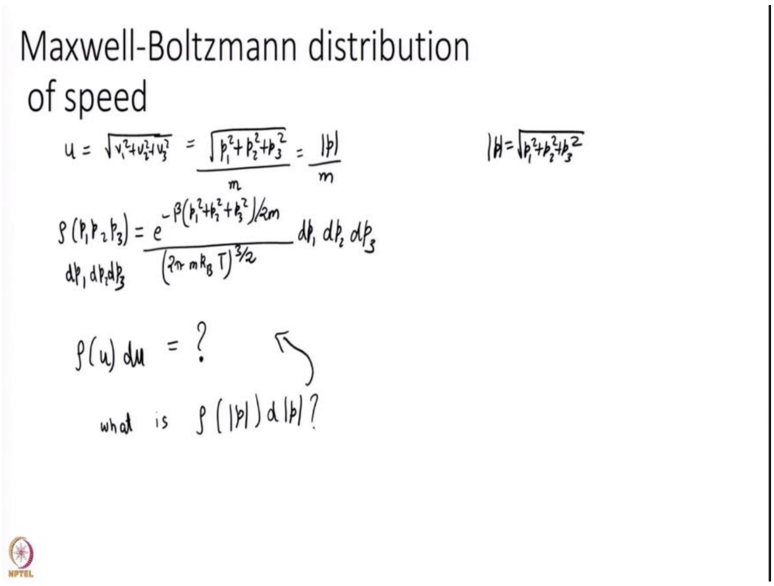

I am trying to figure out what will be the distribution of speed? After I do not care what is the value of momentum in different directions x, y and z, speed is a more natural quantity, I want to figure out how fast is a particle moving? Yeah, that's a very natural question to ask. So that is what I am trying to figure out. So, let's get to that. First of all, let us be formal and define speed, speed is nothing but $\sqrt{V_1^2 + V_2^2 + V_3^2}$, where V_1, V_2, V_3 are the velocities in x, y and z direction.

But I write it in the language of momentums and I call this as $\frac{|p|}{m}$, where $|p|$ is this, so I am trying to find a distribution of u and how do I do that? Alright, so let us just look at ρ once more of p_1, p_2, p_3 this is equal to $\frac{e^{-\beta\frac{p_1^2+p_2^2+p_3^2}{2m}}}{(2\pi k_B T m)^{\frac{3}{2}}}$ just from last slide.

The important thing to remember when converting between distributions so I am going from a distribution of p_1, p_2, p_3 to a distribution of u, when you do that, in whichever field not only kinetics or thermodynamics quantum dynamics wherever remember the volume element that is very important.

So, I will start writing that a little bit more explicitly. So, this is really what this probability density anyway mean in a very small volume of size $dp_1*dp_2*dp_3$, what is the probability of finding the system there? So, I am asking you the question, what is the probability ρ(u)du is equal to. We will actually start with slightly different question, which is what is $\rho(|p|)d|p|$. Because here I have everything in the language of momentum. So, I will start with momentum and then I will go back and answer this question.

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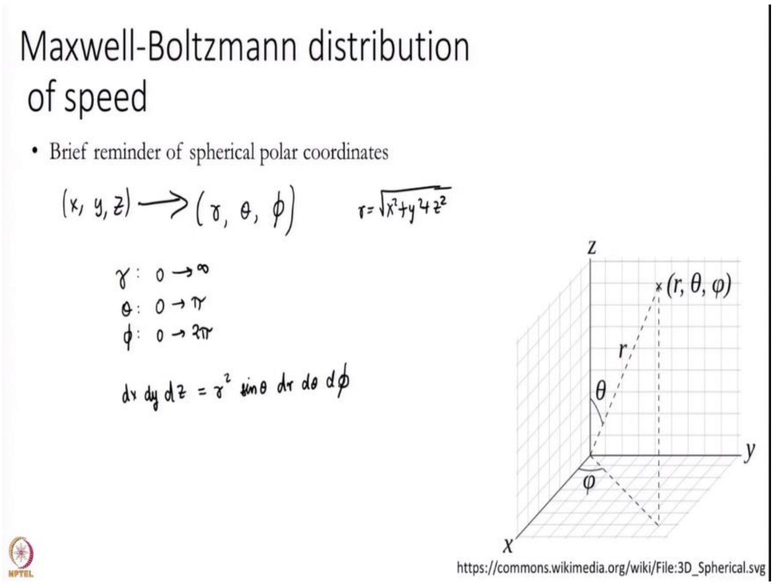

Now, to calculate this, I will have to remind you a little bit of what is called the spherical polar coordinates, you must have seen this in some form or another, it occurs in many many different contexts. So, imagine you have three dimensions x, y and z. I define a new coordinate system which is called r, θ and ϕ, r is nothing but what we are looking were in the previous slide, θ is the angle that the vector r makes with the z axis and ϕ is the angle that the projection of the vector r on the xy plane makes with the x axis.

So, few important properties that I want to remind you of r goes from zero to infinity, θ goes from zero to π and ϕ goes from zero to 2π these are the limits and more importantly, what is the volume element in this. So,

$$\text{dxdydz} = r^2 \sin\theta \, dr d\theta d\phi$$

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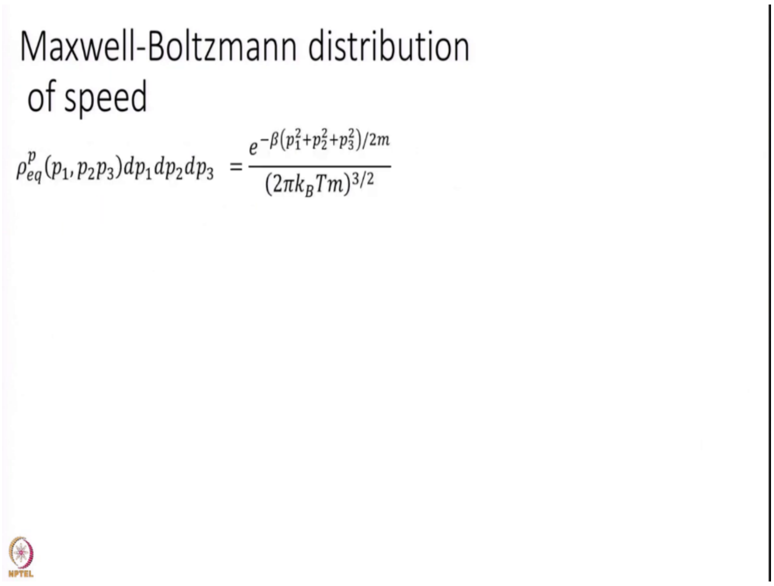

So, now the ρ_{eq} I had already written in the last slide I have forgotten to write dp_1 dp_2 dp_3. I want to find ρ^p_{eq} $(|p|, \theta, \phi) d|p| d\theta d\phi$ that's my first challenge. So, that you can see $\frac{e^{-\beta|p|^2/2m}}{(2\pi k_B T m)^{\frac{3}{2}}}$ once more $|p|$ is nothing but $\sqrt{p_1^2 + p_2^2 + p_3^2}$.

And now, we introduce the volume element that we talked about in the last slide, which is $|p|^2 \sin\theta \, d|p| d\theta d\phi$, but this is not what we wanted, right, we wanted $\rho^p_{eq}(|p|)$. I do not care which angle θ and ϕ it is, anyway θ and ϕ are arbitrary they depend on the axis choice.

So, what I am going to do is I integrate over all of θ and all of ϕ. So, because I want the average value of θ and ϕ, again the range of θ is zero to π, ϕ is zero to 2π and I write this whole thing here and I write d$|p|$ separately I should have a d$|p|$ here as well. So, what I do is, I take the terms that are independent of θ and ϕ outside the integral and then I integrate over θ and ϕ.

So, for θ you know I have sin θ, for ϕ I have dϕ I leave it as a homework for you to prove this is equal to two and this is equal to 2π. These are very easy integrals you should be able to do so, in total, I get

$$\frac{4\pi|p|^2}{(2\pi k_B T m)^{3/2}} e^{-\frac{\beta|p|^2}{2m}}$$

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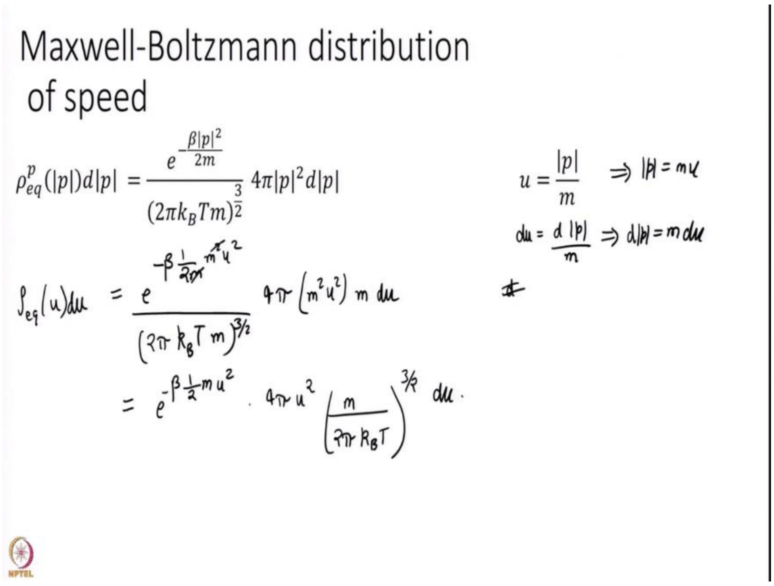


So, I calculate this $\rho^{p}_{eq}(|p|)$ I just copied it from the last slide but I wanted ρ of u, not p, for our will let us not very hard now, I note that

$$u=\frac{|p|}{m}$$

and so

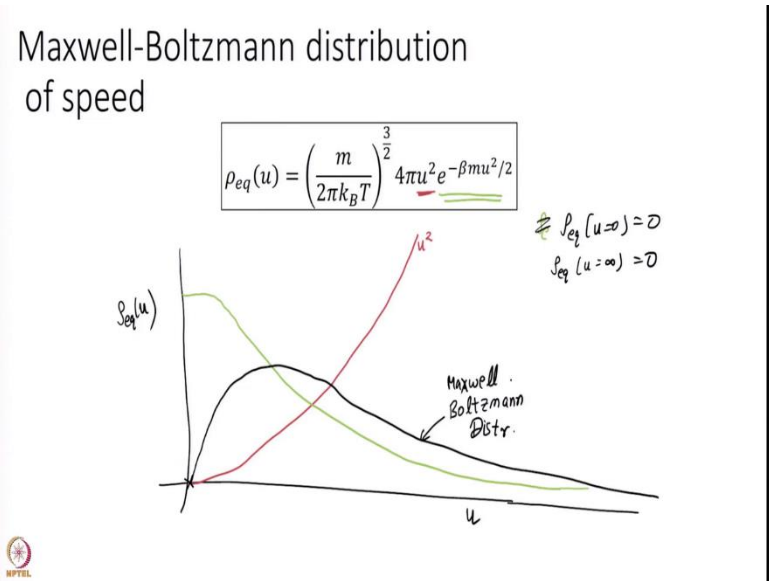
$$du = \frac{d|p|}{m}$$

. And so, we just substitute these quantities here $|p| = mu$, d$|p|$ = mdu. So, this becomes equal to

$$\frac{e^{-\beta m^2 u^2/2m}}{(2\pi k_B T m)^{\frac{3}{2}}} 4\pi m^2 u^2 m du$$

. This is $\rho_{eq}(u)du$.

So, I just simplify this a little bit this m cancels with this just massaging a little bit here and there, I get $4\pi u^2$ and I just transform this into this form you can quickly verify whether I have written it correctly or not make sure you can do this if I have made a mistake then please correct me.(Refer Slide Time: 21:46)



So, this is the final form I get for the Maxwell Boltzmann distribution it's a very famous distribution it is named after these two outstanding scientists Maxwell and Boltzmann who have contributed immensely towards statistical mechanics. So, let us just look at one thing you let us make a plot of it. So, I just want to look at as a function of u, how does $\rho_{eq}(u)$ look like?

So, well if you look at it, this function is a product of two different functions, one is u^2. So, u^2looks like this. I am just qualitatively trying to find how the curve will look like and the other function is this Gaussian and this Gaussian looks like this. This will keep on going till it reaches zero at infinity. Very qualitatively, I am not being very precise here.

So, if I take a product of these two, my question is what will you get, so I would recommend pause the video, take a moment and multiply this on yourself do not take help of any computer or anything and make a plot. Hopefully, you pause the video and make the plot by your own self.

So, the point to note is that ρ_{eq}, I should change the colour $\rho_{eq}(u = 0)$ = 0. If I put u=0, this red thing goes to zero and $\rho_{eq}(u = \infty)$ = 0 because the green thing goes to zero. So, I start with zero here and I must end with zero as well. So, I get a function that increases initially and then over time decreases and goes to zero. So, this is the Boltzmann, Maxwell Boltzmann distribution.

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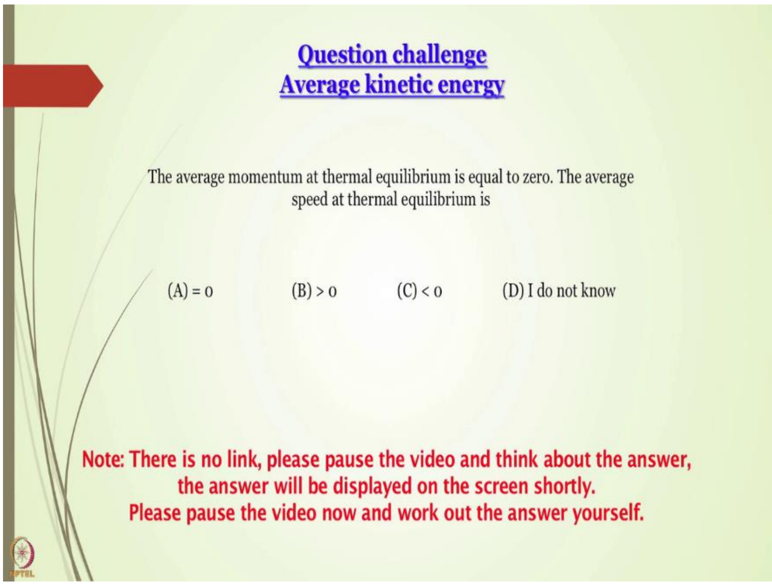

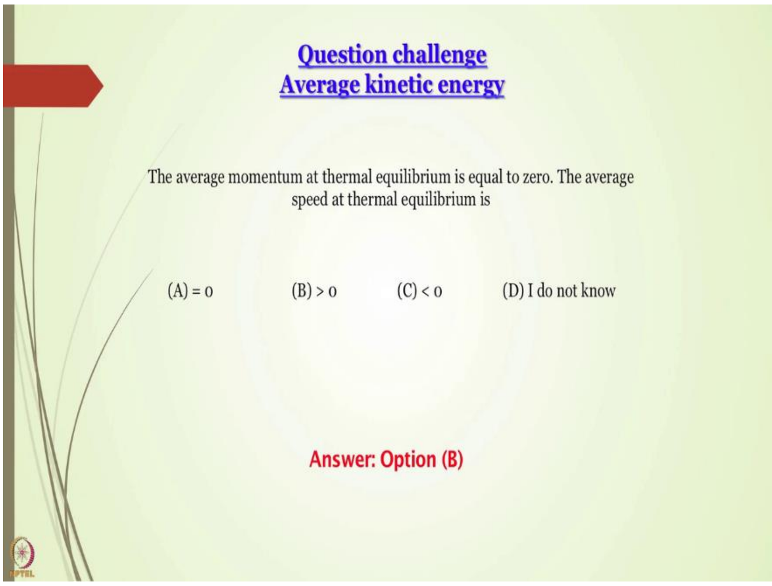

So, I have a challenge to you a question. You have this distribution good. In the previous module, we calculated the average momentum and we showed it is equal to zero. What is your guess? What will be the average speed? Will it be zero, greater than zero or less than zero? So, please go to this link that is provided here and upload answer there. This is completely anonymous, this is for your own good and you will get any immediate feedback based on your answer.

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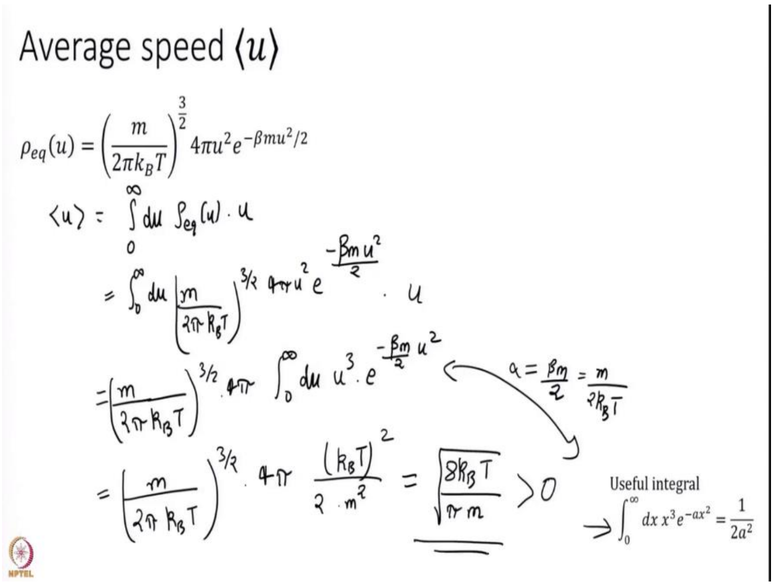

So, hopefully all of you have answered this question based on whatever you think it is right. Let us try to solve it now. So, the <u>, well how do I find <u>, it's the same trick $\int du\, \rho_{eq}(u)u$. Now, the question is, what is the limit for u? Is it -∞ to ∞ or zero to ∞? It is zero to ∞. Remember that u is magnitude, it can never be negative, you are only dealing with that overall quantity.

And so, we substitute all of this big formula here, $4\pi u^2 e^{\frac{-\beta m u^2}{2}} u$. So, we take all the constants out of the integral. And what we are left with is $\int_0^\infty du * u^3 * e^{\frac{-\beta m u^2}{2}}$. And again, as before, we will provide you the integrals when you need the integrals, this is slightly complex integral. And so, we have provided you the answer here on how to solve.

So, to match these two, my a = $\frac{\beta m}{2}$. So, I get

$$\left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} * 4\pi * \frac{1}{2a^2}$$

a is I will write this as m over 2 k_B T because I have k_B T in this equation. So, m^2 into $(k_B\, T)^2$. So, you can go ahead and simplify this equation and show this is equal to $\sqrt{\frac{8k_BT}{\pi m}}$. So, this is clearly greater than zero.

So, by the way, you didn't had to do the maths to tell whether it is greater than zero or not see, speed is a positive quantity. So, if I am averaging over a lot of particles over positive numbers only, well, you are going to get some positive number. So, it cannot be zero, it cannot be less than zero, I have some speed of some particle which is positive. And so, you can formally show it is equal to this.

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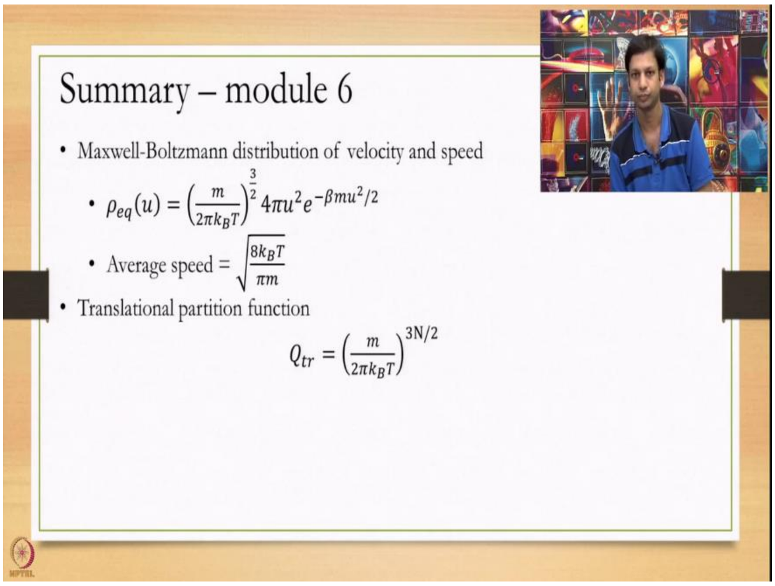

So, in summary, today, we have looked at the Maxwell Boltzmann distribution of speed, it's a very important distribution and this will be very useful in the coming modules when we discuss kinetic theory of collisions. We have shown that the average speed is equal to $\sqrt{\frac{8k_BT}{\pi m}}$.

Please do not memorise any of these as and when needed, we will always be providing you equations. This is not a memory, going to be a memory test. This is not going to be a mathematics test. Finally, one another thing just keep in mind for future. We have also derived what is called a translational partition function as $(\frac{m}{2\pi k_BT})^{\frac{3N}{2}}$. Thank you very much.