

Thermal Physics
Prof. Debamalya Banerjee
Department of Physics
Indian Institute of Technology, Kharagpur

Lecture -2
Maxwell's Law for Speed Distribution of Gas Molecules

(Refer Slide Time: 00:33)

$\rho \rightarrow$ Number of molecules of the specific type per unit volume
at steady state $\rho \rightarrow$ constant

So $\rho = N f(v_x) f(v_y) f(v_z) = \text{const.} \text{---(2)}$

Differentiating (1) and (2), we have

$$v_x dv_x + v_y dv_y + v_z dv_z = 0 \text{---(3)}$$
$$\frac{f'(v_x)}{f(v_x)} dv_x + \frac{f'(v_y)}{f(v_y)} dv_y + \frac{f'(v_z)}{f(v_z)} dv_z = 0 \text{---(4)}$$

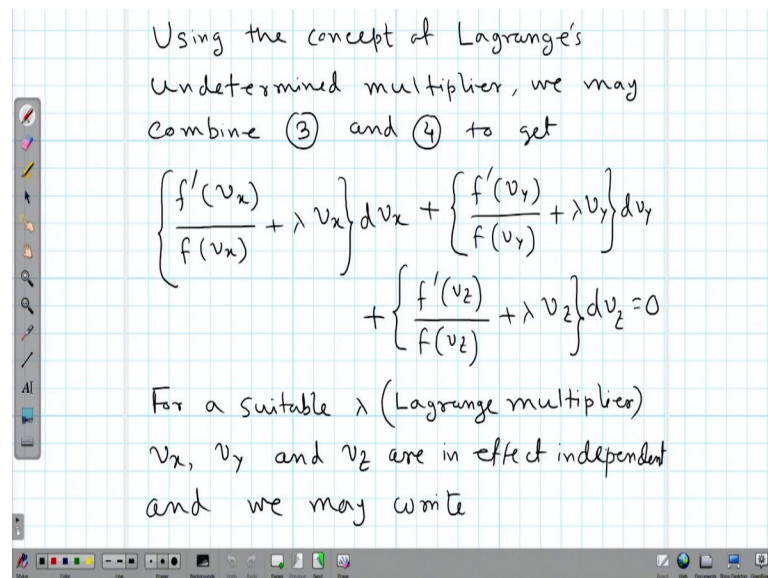
Eqn (1) is the constrain condition that makes only 2 of v_x, v_y, v_z independent

Welcome back. So, we have we will start from the position where we have left it in the last class. So, in last class if you recall there were two equations that is where we ended up we have the first equation which is the we got this idea taking a derivative of the velocity and then there is a second equation. Now the first relation essentially is originating from this constraint condition that we square v_x squared plus v_y squared plus v_z square is equal to c squared which is taken as constant.

Because we are talking about a fixed felicity we want at present we want to see the distribution of components for a given velocity. Now and so because there is a constraint condition in differential form and there is a relation also in form of a differential I mean it is in differential form. All 3 coefficients of dv_x , dv_y and dv_z cannot be independent of each other because there is a constant condition as mentioned in the upper relation.

So, the way in order to handle this we have to use Lagrange's undetermined multiple. Now if you are not familiar with how Lagrange is undetermined multiplier works I would request you to go back to your mathematics lectures or if you have taken a classical physics course already probably it is discussed when you were in the foundation of you know the basics of Lagrangian dynamics was discussed but mostly it is found in mathematics book.

(Refer Slide Time: 02:15)



Using the concept of Lagrange's undetermined multiplier, we may combine (3) and (4) to get

$$\left\{ \frac{f'(v_x)}{f(v_x)} + \lambda v_x \right\} dv_x + \left\{ \frac{f'(v_y)}{f(v_y)} + \lambda v_y \right\} dv_y + \left\{ \frac{f'(v_z)}{f(v_z)} + \lambda v_z \right\} dv_z = 0$$

For a suitable λ (Lagrange multiplier) v_x , v_y and v_z are in effect independent and we may write

So, we will switch to. Now for today's content we first start with the concept of Lagrange's undetermined multiplier I mean sorry not the concept but the application of Lagrange's undetermined multiplier. So, basically we add 3 and 4 at first we multiply equation 3 with a constant lambda. Now lambda is totally arbitrary because equation 3 is what essentially is zero.

So, we can multiply anything with zero and that still remains zero and then we added with equation 4. So, basically we are adding something with zero. So, we are not violating any mathematical law and once we, you know, separate the I mean we or rather we want to we will or rather once we you know put everything under dv I mean with the fact that dv x in one bracket and dv y in another bracket and devise it in another bracket we get this particular relation.

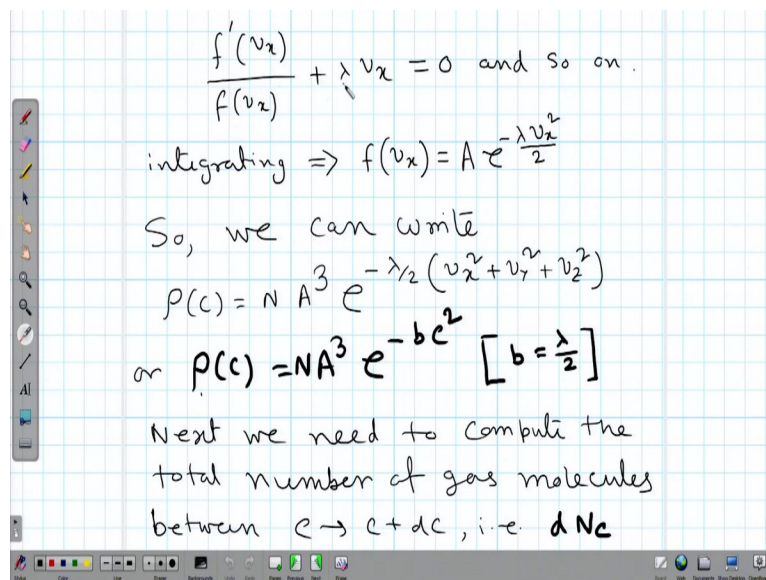
Now as we have already mentioned there are 3 variables and there is one constant conditions out of that 3 variable only 2 can be independent. Now because we have this Lagrange's undetermined multiplier in hand what we can do is also in other words in mathematical words if

we have let us say okay let me quickly write this if it makes any sense. So, let us say we have a situation where we have $c_1 dx_1 + c_2 dx_2 + c_3 dx_3 + \dots + c_n dx_n$ and if this is equal to zero.

In order to have all x_1, x_2, x_3 accent if all these coordinates are independent we can say that c_1, c_2, c_3, c_n are individualized that is when we have every coordinate as independent. So, now go back let us go back to our situation we have something with dv_x plus something with dv_y plus something with dv_z equal to zero and we know that dv_x divided out of this 3 only 2 independent. So what we can do here is we can so out of this 3 coefficients only 2 will be zero sorry yeah 2 will be individually zero the third one will be not but we have this Lagrange's undetermined multiplied in hand.

So, by using what we can do is we can make the third relation that coefficient also equal to zero because this lambda let us assume that dv_x the coefficients of dv_x and dv_y were already zero for dv_z we have this lambda in hand and we can always choose a suitable value of lambda. So, that this whole thing becomes zero. Now once we do that that we are free to do that because lambda is anyway undermined.

(Refer Slide Time: 06:22)



$$\frac{f'(v_x)}{f(v_x)} + \lambda v_x = 0 \text{ and so on.}$$

$$\text{integrating} \Rightarrow f(v_x) = A e^{-\frac{\lambda v_x^2}{2}}$$

So, we can write

$$p(c) = N A^3 e^{-\frac{\lambda}{2} (v_x^2 + v_y^2 + v_z^2)}$$

or $p(c) = N A^3 e^{-b c^2} \quad [b = \frac{\lambda}{2}]$

Next we need to compute the total number of gas molecules between $c \rightarrow c + dc$, i.e. dN_c

We get 3 all 3 coefficients like this one and this one and this one individual equal to zero. So, we can write an equation for example for the first one we can write if prime v_x of divided by $v_x +$

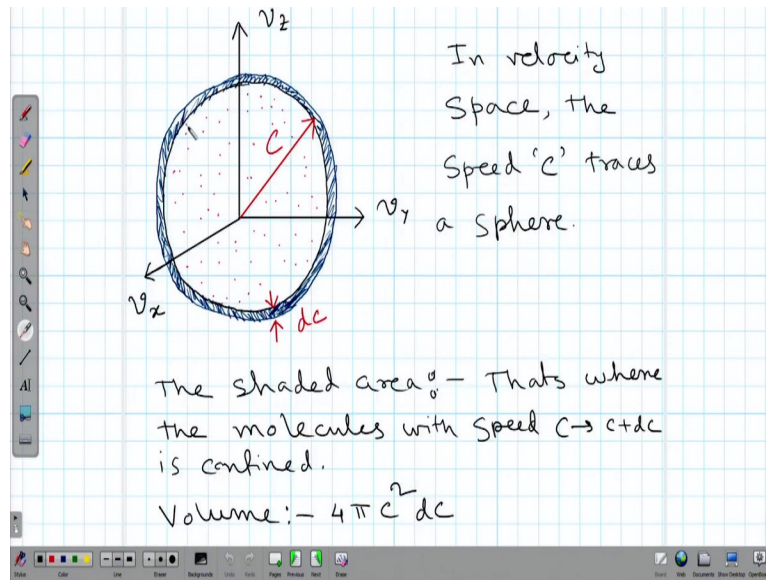
λv_x is equal to zero and these relations are very easily integrable absolutely without any problem we can integrate those and we can get $F(v_x)$ is equal to a to the power minus λ v_x squared weight right.

But and also we have to remember that the we have very similar expression for $f(v_y)$ and $f(v_z)$ because all 3 equations are identical all 3 coefficients of this equation are identical. So, if v_x functional form $f(v_x)$ is known a is also known and we have ρ_c is equal to $N A$ cubed it would be and please remember is the constant the same constant we are using all in all 3 case for all 3 functions. So, ρ will be N times remembered ρ was $f(v_x) f(v_y) f(v_z)$ times m right.

So, that product will be simply $N A$ cubed to the power minus λ by 2 v_x squared plus v_y squared plus v_z square. Now writing v_x squared plus v_y squared plus v_z square is equal to c squared and defining v is equal to λ by to a new constant we write ρ_c is equal to $N A$ cube to the power minus $b c$ square. Now next we want to compute these 2 constants A and b and finally we would like to go to we would like to compute dN_c which is the total number of molecule in the gas assembly okay that has a speed between c to c plus sorry I will just bring it up a bit.

So, finally we want to compute dN_c which is the number of gas molecules in the range c to c plus dc right. Now the question is how to compute A and b ? Probably for this relation okay oh sorry let us first focus on dN_c how to compute dN_c using this relation.

(Refer Slide Time: 08:39)



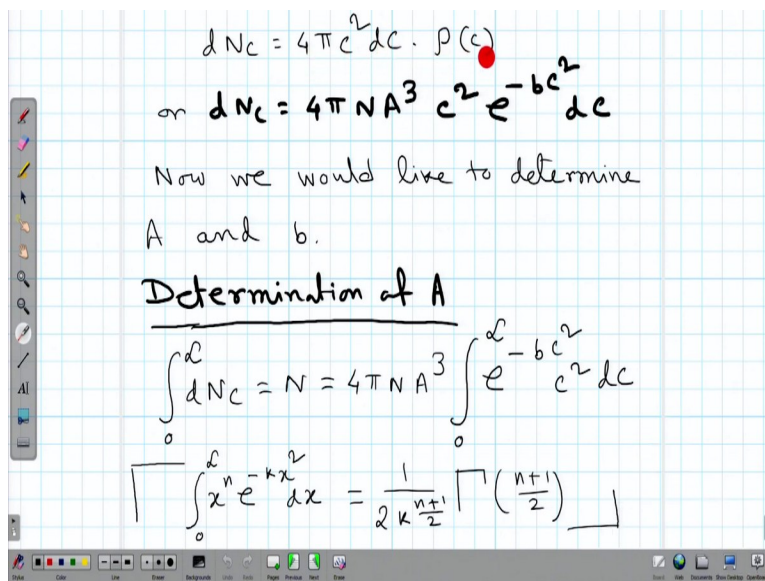
So, once again we assume that in velocity space the molecule moving on. Now if we want to compute the total number of molecule that has a speed c please remember it is not velocity anymore it is a speed. Speed is what speed is simply a magnitude. So, once we want to compute the speed we basically have sea okay I have given it I mean I have drawn it like a vector but it is frankly speaking it is not a vector is simply a scalar.

So, all the molecules which will have a speed c will lie on the surface of this sphere and what do we want to compute? we want to compute the number of molecules in the range c to c plus dc because of course we cannot really calculate the exact number of particle molecules that are moving with c we always have to define a range T c small range okay. In the speed c to c plus dc essentially means that this number essentially means the number of molecules in the velocity space which will lie inside this thin shell.

You see this shell is mark the shell has a thickness dc so we have a sphere of a radius c which is a hollow sphere and then there is a spherical cell of thickness dc whatever molecules or whatever gas particles are inside this spherical cell they will have the speed between c to c plus dc . Now what is this volume thin volume this is simply $4\pi c^2 dc$. I hope you are all familiar with this treatment of spherical cell if not just try to understand okay it is nothing very complicated just try to understand look at this picture over here and you will realize why the volume is $4\pi c^2 dc$ quality.

So, and we already have this expression for rho. So, we have density expression we have the expression for volume.

(Refer Slide Time: 10:47)



$$dN_c = 4\pi c^2 dc \cdot p(c)$$

$$\text{or } dN_c = 4\pi N A^3 c^2 e^{-bc^2} dc$$

Now we would like to determine A and b.

Determination of A

$$\int_0^\infty dN_c = N = 4\pi N A^3 \int_0^\infty e^{-bc^2} c^2 dc$$

$$\int_0^\infty x^n e^{-kx^2} dx = \frac{1}{2k^{\frac{n+1}{2}}} \Gamma\left(\frac{n+1}{2}\right)$$

So, the final number is not nothing but dN_c is equal to $4\pi c^2$ times $p(c)$ which is dN_c equal to $4\pi N A^3 c^2 e^{-bc^2}$. Now this is our expression for the famous Maxwell velocity distribution and next what we want to do is we want to determine the constants A and b. Now that determining one of the constant is I mean both the constants are easy one is very straightforward the one we are going to take a first.

All you have to understand that if we integrate this dN_c for all possible velocity starting from zero to infinity we should get the total number of molecules or total number of particles gas particles present that is N. So, integration zero to infinity dN_c is nothing but N and this integration you can write as $4\pi N A^3 \int_0^\infty e^{-bc^2} c^2 dc$ right.

So, just from this expression you can write. Now this class of integration is a special class of integration called the Gaussian integration which has this following form zero to infinity $x^n e^{-kx^2} dx$ is equal to $\frac{1}{2k^{\frac{n+1}{2}}} \Gamma\left(\frac{n+1}{2}\right)$ where gamma is a

special class of function called the gamma function.

So, I am not going into the details of this but once we compare we see this N here is equal to 2. So, N is 2 and minus kx squared is minus vc squared okay. So, if we can make A 1 to 1 correspondence the integration this integration gives 1 over 2 between the power 3 half gamma 3 half there are standard tables for gamma function you can always look up.

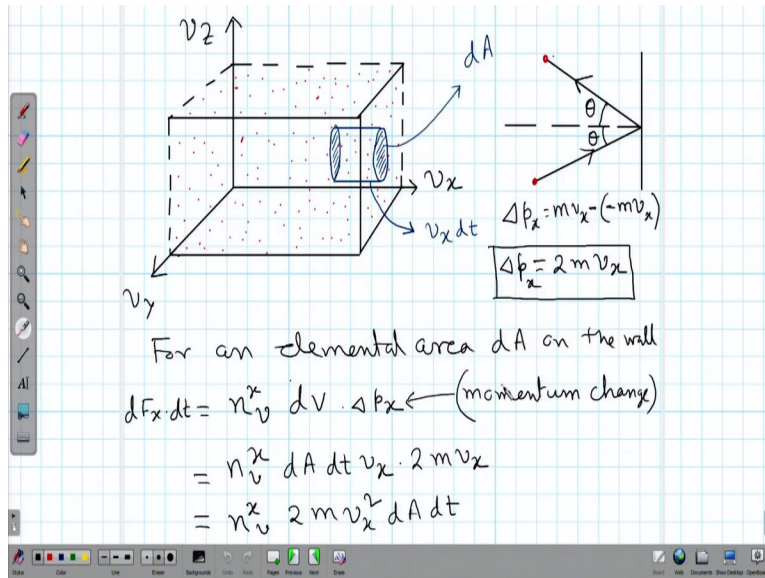
(Refer Slide Time: 13:00)

$$\begin{aligned} \text{So, } N &= 4\pi N A^3 \frac{1}{2 b^{3/2}} \Gamma\left(\frac{3}{2}\right) \\ &= 4\pi N A^3 \frac{1}{2 b^{3/2}} \frac{\sqrt{\pi}}{2} \\ \text{So, } b^{3/2} &= A^3 \pi^{3/2} \\ \text{or } A &= \sqrt{\frac{b}{\pi}} \\ \text{To find out } b, &\text{ we need to use} \\ &\text{the pressure expression derived} \\ &\text{from elementary kinetic theory} \end{aligned}$$

Gamma fraction is allowed gamma is allowed only thing is gamma of minus integer is not allowed any other real and imaginary function a real and imaginary number can have I mean a value in the common function table. So, 3 half is there you can compute that you can have a look at that tables which are freely available on internet and the value is root pi by 2 simplifying we get this relation that A is equal to root of b by pi. Now to find out b, now that means what instead of 2 constants we have A and b here we can express A in terms of b.

So, all we have to do is we have to find out b from by some by some other means and for that we need to use the elementary treatment of pressure from kind of using kinetic theory.

(Refer Slide Time: 13:57)



Now let us go back to our first picture which we have drawn we have drawn a similar figure a cube or you know parallel parallelogram that is containing the gas and here we just representing this in the velocity space or actually you should not actually we should make it x y and z not v x v y V z sorry there is a small mistake. So, it will be simply x y and z . Now strictly speaking this is not exactly the oh yeah that is fine we have already drawn the right handed coordinate this is fine right.

So, yeah I have written v x here ideally it should be x in this direction y in this direction but just for the sake of simplicity I know it is wrong but let me write why here and x here as I have already written all the expressions in terms of v x knowing that it is wrong it is not exactly the right handed coordinate system we are familiar with this is the left handed coordinate system but that is okay I mean it is just a representation not very; we cannot we can afford to do this take this liberty.

Now just focus on this elemental area dA on the surface let us say this is the axis although frankly speaking it might be why but does not matter. So, let us say this is the elemental area. Now any particle this marked in red that is hitting wall and going back. Now this phenomena is responsible for pressure. Please understand this pressure in a gas container is primarily because the molecules are being bombarded on the boundary wall.

Now let us assume this particle is moving in this direction with an angle θ and it will require in another in this direction with another making this angle θ . So, altogether there will be a deviation of 2θ . So, but because these are elastic collisions that is one of the basic assumption of kinetic theory the total change in momentum will be only along the x direction and this will be Δp_x is equal to $m v_x$.

Let us say it has velocity components v_x, v_y, v_z only the x component will change its direction because these are elastic collisions right. Now if we try to find out the total force or impulse of force in a time interval short time interval dt on this small area dA that will be given by dF_x times dt that is the impulse and it will be given as $n \cdot dV \cdot \Delta p_x$. Now the first term is the number density.

I will explain that little in with some little more detail dV is the volume of the cylinder which has a site of one of the sites the cross section area dA and the length of $v_x dt$ because if we are considering a short time interval dt only the gas molecules these are within this distance can strike the wall anything that is lying outside this distance will not be able to reach the wall in the short interval. So, this explains a lot I mean sorry this explains why this is why this dV can be written as $dA \times dt \times v_x$.

Δp_x is already the momentum change is $2m v_x$ please do not mix it up with the pressure because unfortunately for pressure and momentum we have to write the same we are family we write p small p . So, I am just trying to put a Δp_x and please note that this is momentum nothing to do with pressure as of now okay. So, anyway we put the value of Δp_x as $2m v_x$. Now coming back $2m v_x$ what is that? This is the total number or number density that means the total number of molecules in this assembly with the speed with the with the x component of velocity v_x divided by the volume.

So, in brief $n v_x$ is $dN v_x$ by V , right $dN v_x$ is something that we have already defined. So, I have just substituted for $dN v_x$ in the next slide.

(Refer Slide Time: 19:08)

$$dp_x = \frac{dF_x}{dA} = 2m n_v^x v_x^2$$

$$p_x = \sum dp_x = 2m \sum n_v^x v_x^2$$

$$n_v^x = \frac{dN_{vx}}{V} = \frac{N}{V} f(v_x) dv_x$$

Also, we note that $p_x = p_y = p_z = p$

$$\therefore p = 2m \frac{N}{V} \int_0^\infty f(v_x) v_x^2 dv_x$$

$$= \frac{2mN}{V} \int_0^\infty e^{-b v_x^2} v_x^2 dv_x$$

You will in a moment. So, now we want to compute the pressure what is pressure? Pressure is now you see this dt sorry this dt from this side and dt from this side cancels out nicely and finally we have the pressure expression which is dF_x by dA that is force per unit area which is $2m n_v^x v_x^2$. Now and this is only for this, this is this elemental pressure dp_x on this area right. Now if we want to compute the; but anyway does not matter because we are taking the derivative. So, pressure at this point pressure on this surface and pressure on this entire face will be exactly the same.

But also but we have to remember that this is only for those molecules for which the velocity has a x component of v_x what about the others other molecules? There are many different speed ranges different velocity ranges. So, we have to sum up over all possible velocities in this manner. So, it will be p the total pressure p_x which is equal to $2m \sum n_v^x v_x^2$. Now we substitute for this n_v^x sub superscript x is equal to dN_{vx} by V which is nothing but N by V $f(v_x) dv_x$.

Let us go back quickly where is it right yeah remember this expression from the last class dN_{vx} is equal to $N f(v_x) dv_x$ similarly dN_{vy} and dN_{vz} was defined. So, we are just using this expression and finally also we have to note that p_x is equal to p_y is equal to p_z that means the pressure in all directions are equivalent that is only one pressure right. So, it does not matter whether we measure it along x axis y axis z axis.

So, the final pressure we instead of $p \times v$ we can write p this is nothing but $\frac{2}{3} \frac{m N}{v}$ divided by v and integration zero to infinity $\int v \times v \times \text{square } dv$.

(Refer Slide Time: 21:51)

$$pV = \frac{2}{3} m N \sqrt{\frac{b}{\pi}} \frac{1}{4} \sqrt{\frac{\pi}{b^3}} = \frac{m N}{2b}$$

Comparing with $pV = N k_b T$

$$\frac{m}{2b} = k_b T \Rightarrow b = \frac{m}{2 k_b T}$$

So, $A = \sqrt{\frac{m}{2\pi k_b T}}$

$$dN_c = 4\pi N \left(\frac{m}{2\pi k_b T} \right)^{3/2} e^{-\frac{mc^2}{2k_b T}} c^2 dc$$

Writing $\frac{dN_c}{N} = F(c) dc$

$$\Rightarrow F(c) = 4\pi \left(\frac{m}{2\pi k_b T} \right)^{3/2} e^{-\frac{mc^2}{2k_b T}} c^2$$

Now if we compute this integral once again we get this Gaussian type of integral and this integral I mean we have already computed this what is the value here we know the value is $\sqrt{\pi}$ by $4b$ to the power $3/2$ right. So, we just substitute for this. So, $\sqrt{\pi}$ by $4b$ cube one over 4 and we get $\frac{m N}{2b}$. Now and instead of p we just what do we do? We just take this v from here and multiply with p . So, finally we compare it with the ideal gas equation $p v$ equal to $n k_b T$ where n is the total number of molecule we simply get b is equal to $\frac{m}{2 k_b T}$.

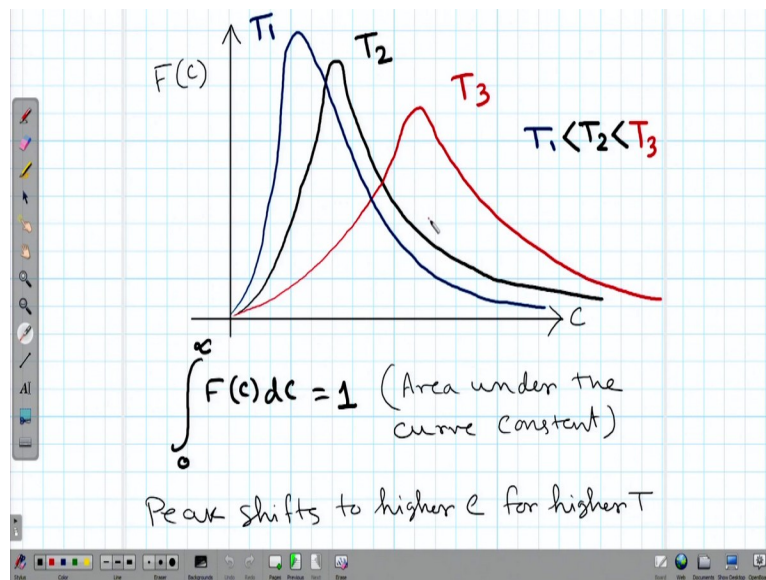
Now we have A in terms of we already know A is equal to $\sqrt{\frac{m}{2\pi k_b T}}$. So, we have b is equal to $\frac{m}{2 k_b T}$ or b by π yeah b by π right. So, A is equal to $\sqrt{\frac{m}{2\pi k_b T}}$ and the final expression Maxwell's velocity distribution expression is this dN_c is equal to $4\pi N \left(\frac{m}{2\pi k_b T} \right)^{3/2} e^{-\frac{mc^2}{2k_b T}} c^2 dc$. Now we can write this as dN_c by N which is nothing but you know density number density of molecules in the speed range c to $c + dc$.

And we write this as $F(c) dc$ where $F(c)$ is this function. Now this is an interesting function we have one term which is constant in terms of speed but the coefficient the this term which is constant in

terms of speed but changes with temperature and we have this term and this term which this term which is dependent on both speed and temperature and we have this term which is only speed.

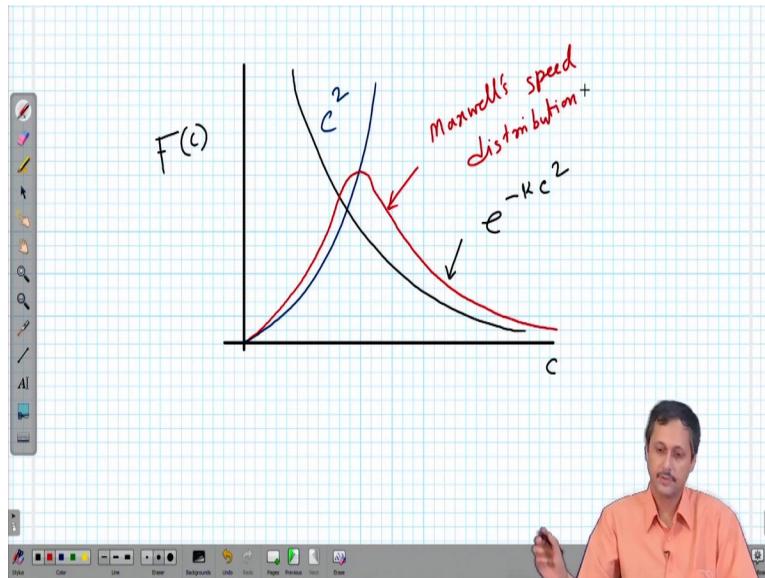
Now look at this term as the sorry look at this term as the speed increases this is going up as c squared and look at this term as the speed increases this is decreasing exponentially. So, for now if we take temperature as a constant quantity this term will be dominant at high values of c and this term will be dominant for small values of c and look at this black curve here.

(Refer Slide Time: 24:24)



So, it will be something like this okay let me quickly go back to this our class rough document skate and what we can do is I can try to draw this quickly for you.

(Refer Slide Time: 24:40)



So, this is my x this is my c . So, in $F(c)$ we have one term which goes as c squared right ok. We have one term that is that goes as c square and we have one term that falls off as okay no not like this maybe like this yeah fall off as e to the power minus c squared I mean some constant times c squared keeping the temperature constant some constant times. So, the overall range should be an overall summation should be something like.

At some point it should turn back and start going right. So, this is my Maxwell's speed distribution right. So, now in this part what I have tried is I tried to draw these 3 lines corresponding to 3 different temperatures. When I draw the previous one I did not I mean I consider temperature to be constant right. But then when temperature increases see what happens this coefficient changes the I mean this factor also changes.

So, overall there is a shift. Now you think of why with increasing temperature they should be going right and why with decreasing temperature it should be going left but I think if you just give it a thought you can find it out. So, I have given I have drawn it for 3 different temperatures T_1 , T_2 , T_3 but also the note that not only it shifts to the right or to the left but please remember the integration zero to infinity $F(c) dc$ is equal to one it has to be because what is $F(c)$? $F(c)$ is nothing but $F(c) dc$ is nothing but $dN(c)$ by N .

So, integration $F(c) dc$ is mean from zero to infinity means integrating the $dN(c)$ from zero to

infinity and dividing it by N which will be N by N which will be equal to one. So, the area under the curve should be constant okay. So, if the peak shifts to the right it should also smear out a bit. So, that the idea remains constant similarly if it shifts to the left it should be little sharper the decrease should be little sharper.

So, that the area under the curve remains the same. Now for today's lecture we will end here in the next class we will try to define 3 quantities or 3 different speeds which is the mean speed the root mean square speed and the most probable speed for this velocity distribution okay. So, goodbye for now.