

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

Lecture-09
Topic-Pressure and Molecular Flux from Mean Free Path

Hello and welcome back to another lecture on this NPTEL course on thermal physics. Now today, as promised we will be discussing about the pressure expression, how to get the pressure expression from mean free path? And we will also discuss how it compares with the pressure expression that we got from the standard kinetic theory of gas that is by using Boltzmann distribution sorry Maxwell distribution of molecules speed.

Now what is pressure? We know that the particles they with each other when similarly they also with the container of the wall the gas particles. Now this collision they are elastic collision but that means there is no loss of energy, but definitely there is a transfer of momentum. So, that means every time a gas particle hits the wall of the container it will transfer a tiny amount of momentum on that container wall.

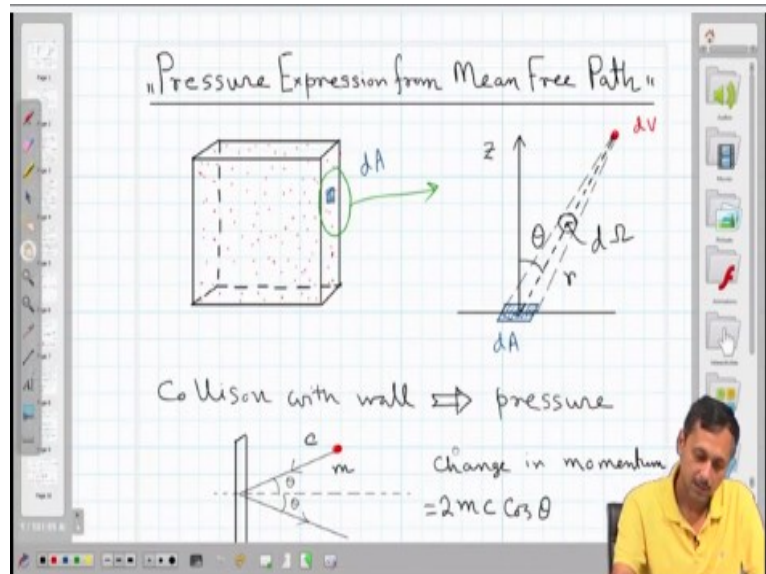
Now, please remember that there are literally almost infinite many number of gas particles, we are generally talking about the numbers of the order of 10 to the power 23 unless and until we are dealing with a very low pressure or extremely high pressure situation. In very low pressure the density can come down to below 10 to the power 10 . And for extremely high pressure situation the number density can go up to 10 to the power 30 but these are very special cases.

But in general for all examples that we take the number densities typically stays in the range of 10 to the power 20 to 10 to the power $25, 26$ in that range. So, that is a huge number of particles, very large number of particles and each of these tiny particles transferring a tiny amount of momentum when they are colliding actually results in the pressure inside the container. Actually we do not realize some time that we are always under immense pressure due to the atmosphere and it is exactly happening exactly because of that.

So, that the air column that is present in the atmosphere the air particle that is present around us, they keep continuously bombarding us with they collide with us continuously and from all directions. So, that is why we experienced and uniform pressure upon our body all the time, we just do not realize that because we are so used to it. Similarly for the container, it is not only one side of the wall, but all the portions of the wall that is exposed the inside part of the container, they experience equal amount of pressure.

Because the molecular distribution, the speed distribution, whatever you might call it is uniform all throughout. Now in this lecture what we are going to do is? We are first going to consider the concept of mean free path; I mean we all know we have already discussed the concept of mean free path. And we want to see how that concept can be applied in order to compute the pressure of a gas particles deciding inside a closed container.

(Refer Slide Time: 04:02)



Now in order to do that we have adopted the following geometry. We have just drawn a cubic container here and please remember that I am just giving it a cubic shape just for illustration purpose, there is absolutely no necessity that it is a cube. I mean it could be of any shape and size any arbitrary shape and size, it does not matter because finally what we are interested in is that tiny surface area, surface element I would say that has a cross section dA .

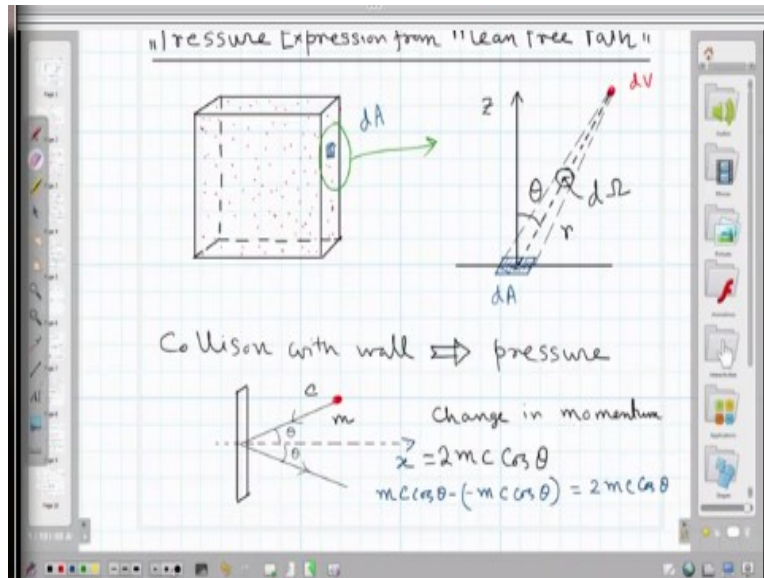
Now in the next figure on the right hand side what I did was? I am representing this dA in a slightly different manner with a vertical coordinate system. So, I am assuming that this z if I just try to draw this z keeping the orientation intact, the z will be somewhere here, something like this. But anyway it does not matter, we are just because I am taking a element from here the z will be vertical if I take an element from the bottom side the z axis is horizontal.

Because I am choosing the element from here but if I choose an element in the bottom for example if I choose an element here the z will be vertical anyway, it does not matter. It just a arbitrary surface element and it is a coordinate system that we are setting with respect to that surface element. So, now what do we consider? We considered that the element is lying at the origin and the z axis is perpendicular to that surface of that element.

Now the next thing is there is a small elemental volume dV which contains certain number of gas particles. We do not know what is that I mean I should not say we do not know but we know exactly what is the number of gas particles inside that volume, that number is n times dV , n being small n being the number density. And we are assuming uniform distribution as of now we are not we are considering that the system is in absolute equilibrium with the surrounding and within itself.

So, we assume that the density is uniform all throughout. So, the tiny volume we know exactly how many molecules it contains. Now, the parameter of interest it is a solid angle $d\Omega$. And $d\Omega$ we will derive I mean we already know we have derived an expression for this in one of the one of our previous classes I guess, if not anyway I do not remember exactly but we will just discuss this in a moment.

(Refer Slide Time: 07:10)



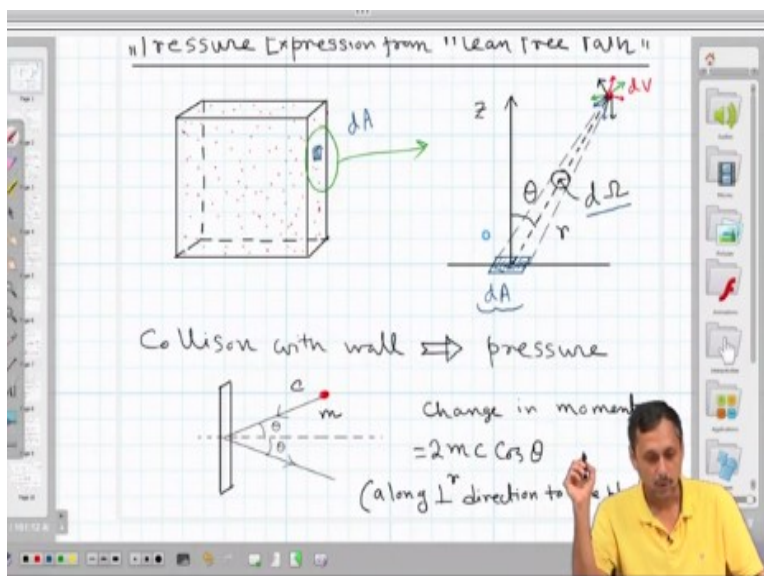
Now when it comes to the elemental description of collision, let us assume that there is a surface on which this particle marked in red has a collision. This is our particle of mass m and with speed c ; I should not call it speed because for this particular case we know exactly which direction it is going. But let us say it has a velocity with a magnitude of c in this particular time. And this particular direction makes an angle θ with the normal to this particular surface of interest.

So, when it collides what happens is it will change its momentum, I have just given the final expression for change in momentum here but actually I can break it into 2 parts. I can write the momentum along this if I call it for example, the x axis, so along x axis or minus x axis, the momentum should be $m c \cos \theta$ when it is coming in, so it comes with a minus sign. And after reflection the momentum is once again $m c \cos \theta$, this will be plus.

So, total change in momentum we are just considering the change it is not about the magnitude the total change in momentum will be $mc \cos \theta$ minus of minus $m c \cos \theta$ because please remember this one is incoming momentum and this one is outgoing momentum at the x component and they are in the opposite direction. So, there is already a relative minus sign between them and because we are considering the change there is an additional minus sign, so all together we get $2 mc \cos \theta$. So, I should not write change in momentum only, I should write

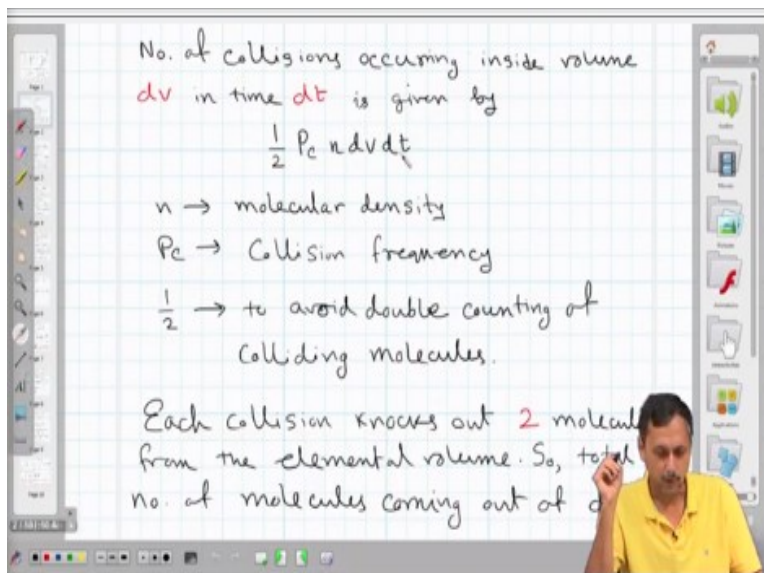
change in momentum in the perpendicular direction. Anyway I hope you understand what I mean to say here. So, the total change in momentum along the perpendicular direction is given by this.

(Refer Slide Time: 09:36)



So, I should just write along perpendicular direction to the plane. So, we have a construction that is given here and we have a magnitude of change in momentum for any particle which makes an angle theta with the vertical of a surface area.

(Refer Slide Time: 10:10)



Now let us move on from here. So, number of collision that is occurring inside this small volume element dv x time dt is given by half P_c , look at this expression. So, $n dv$ is the number of gas particles inside this tiny volume and the time is given by dt . So, it has to be as the number of

collision is proportional to the time interval, so it has to be multiplied by dt . And then we have P_c which is the collision frequency. Now collision frequency gives you basically $P_c dt$ gives you the number of collision per unit volume, so $P_c dt$ gives you the number of collision in the time interval dt .

So, then this has to be multiplied, so $n dv$ basically multiplied by $P_c dt$ gives you the total number of collision and we have an additional factor half here. Because please remember the 2 particles they collide and if we count the number of particles, so there is a factor. So, basically there is a possibility of double counting. So, if we are just computing the number of particles that has to be divided by 2 in order to get the total number of collisions because 2 particles collide gives you 1 collision. So, then comes this factor of half, so altogether this is half $P_c n dv dt$.

Now because this volume dv is so tiny here. So, we assume that each particle or each collision will actually knock out both the participating particles from the small volume. Similarly another collision will knock out 2 more particles, almost arbitrary direction similarly another collision will knock out 2 more particles, so all in arbitrary directions. Now total number of such particles that will be coming out of this small volume is this quantity multiplied by 2 which is essentially $P_c n dv dt$. And as I have already mentioned, this particles will be going in all the directions uniformly. Because the distribution is uniform molecular speed is uniformly distributed in all possible directions.

So, the total number of particles that will be coming out of course will travel in all possible directions. Out of that how many particles will travel towards this small surface area dA that is the question we have. Please remember, please understand that the total when we talk about all directions, so we talked about a solid angle of 4π , total solid angle of 4π . Now out of that 4π only the particles that will be within this solid angle $d\Omega$ this only those particles will travel towards this surface element dA .

(Refer Slide Time: 13:44)

$2 \times \frac{1}{2} P_c n dv dt$
 Since these molecules are heading uniformly to all directions, the number that is travelling towards dA is
 $P_c n dv dt \frac{d\Omega}{4\pi} = N_0$
 the elemental solid angle $d\Omega = \frac{dA \cos \theta}{r^2}$
 Applying survival equation, the total number hitting the elemental area
 $N = N_0 e^{-r/\lambda} = P_c n dv dt \frac{dA \cos \theta}{4\pi r^2} e^{-r/\lambda}$

So, all we have to do is we have to multiply this number of particles which is this $n P_c n dv dt$ with $d\Omega$ by 4π . The 4π is the total solid angle, so $d\Omega$ by 4π gives you the fraction of particle that will travel towards this particular surface area and we call it N_0 . So, these are all, up to this, this is very elementary, nothing difficult about it. It is just that we have a long expression here but every term of this expression is totally understandable.

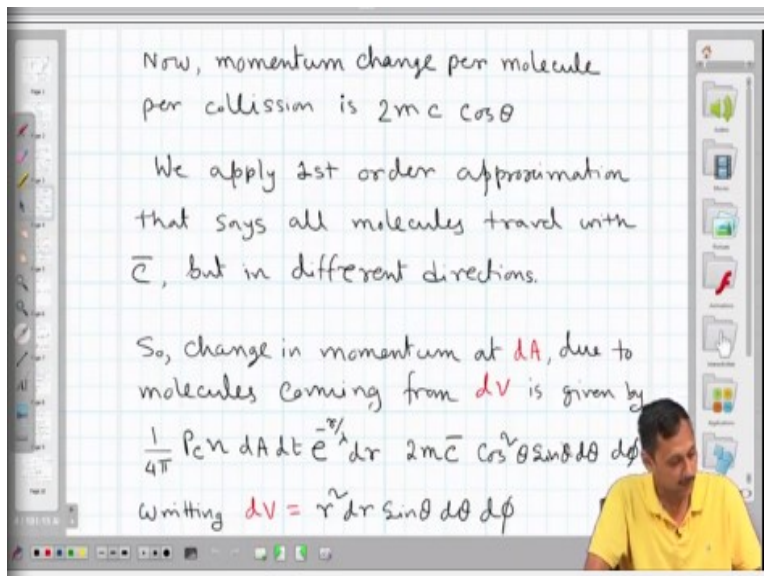
Now what is the expression for $d\Omega$ here? Next we have to substitute for $d\Omega$ and $d\Omega$ is given by $dA \cos \theta$ by r^2 . And that is the standard definition of solid angles, I really do not remember if we have discussed it already, if not. If yes, fantastic, if not please take any of the standard textbook of thermal physics, there this one will be derived. The expression the $dA \cos \theta$ by r^2 will be explained in detail.

Now next what do we do? We apply the survival equation. Survival equation will tell you how much of this particles will actually reach the surface area dA . Because what happens is it has to travel a finite path, so it will start from here and it will travel along this path, we call this distance as r that is as it is already mentioned here. So, it has to travel a distance r in order to reach the surface element dA .

So, we know according to the survival equation $N = N_0 e^{-r/\lambda}$, where λ is the mean free path of this gasses. So, N is essentially this quantity N_0

multiplied by e to the power r by λ which is given by $Pc n dv dt$ and we have substituted $dA \cos \theta$ by r^2 of course there is a 4π here, so it will be $4\pi r^2$ whole multiplied by e to the power minus r by λ . I hope this is readable once again very simple $Pc n dv dt dA \cos \theta$ by $4\pi r^2$ whole multiplied by e to the power minus r by λ .

(Refer Slide Time: 16:26)



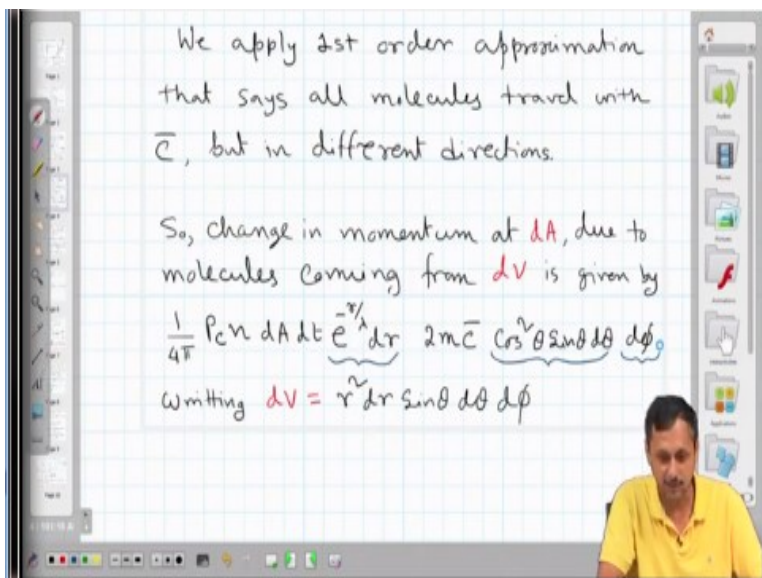
So, we have already discussed what is the momentum change per collision. So, all these particles which will come towards the small surface area dA will have a collision with dA . Now each collision will transfer $2mc \cos \theta$ amount of momentum that we have already discussed here $2mc \cos \theta$. So, altogether the total change in momentum will be this quantity whatever is written here multiplied by $2m \bar{c} \cos \theta$, why \bar{c} because once again we are working in first order approximation.

What is first order approximation? If you remember when we discussed about deriving the expression of mean free path we talked about 0th order, 1st order and second order approximation. In 1st order approximation, we assume that the molecules are travelling with a uniform speed \bar{c} that is the mean speed but in all possible directions, exactly the situation as we are discussing here. So, this is the first order approximation.

So, the change in momentum is simply given by this quantity multiplied by $2m \bar{c} \cos \theta$. Now please understand that there is a volume element dv present here and in order to compute this, so

next what do we do? We just write out dv in spherical polar coordinate and in spherical polar coordinate dv is given by $r^2 \sin \theta dr d\theta d\phi$. So, you see there is a $\sin \theta$ here, there was a $\cos \theta$ from here itself. $\cos \theta$ from this expression of $d\Omega$ and there will be another $\cos \theta$ from the expression of momentum change, that is $m\bar{c} \cos \theta$. So, it will be $\cos^2 \theta \sin \theta d\theta d\phi$. So, we have just grouped it one by one.

(Refer Slide Time: 18:39)

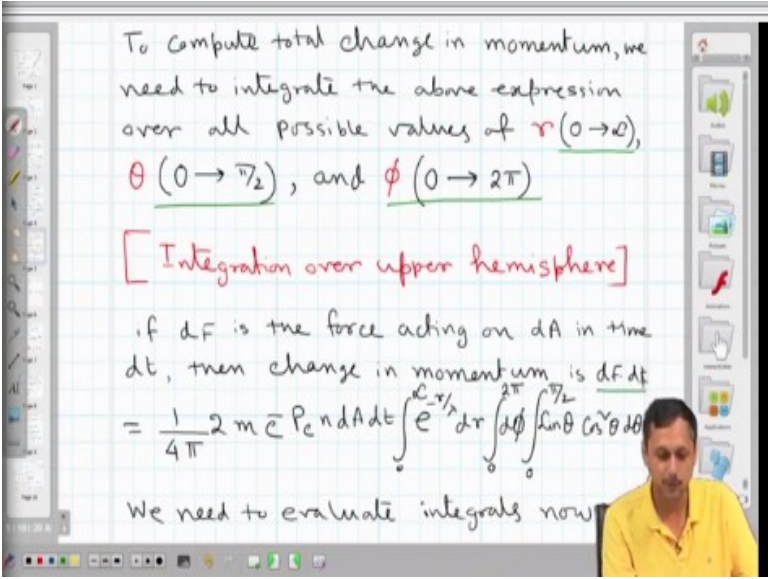


So, we have $e^{-r/\lambda} dr$ there is $2m\bar{c}$ is the constant, we have $\cos^2 \theta \sin \theta d\theta d\phi$ and we have $d\phi$. Next is in order to get the total number of particles, so this is an expression basically for momentum change. So, if we have to compute the momentum change for all possible such volume elements; please remember with this m value whatever this number whatever we are computing this expression is only for this small dv .

And there are volume elements here, such volume elements here, here, here everywhere surround, I hope it is clear that we are just considering only small, small volume element. So, essentially what we have to do is we have to compute an integral and that integral will be for this upper hemisphere. So, what should be the range of r ? r should be 0 to infinity in practice the range of r is typically the dimension of the container but as we have discussed already, this L is so much greater than the mean free path λ that for all practical purpose we can think of that integral is from 0 to infinity.

So, there will be 3 integration one on r , one on θ and one on ϕ , r integral will go from 0 to infinity, θ and ϕ , please remember please understand that θ and ϕ should be on this upper hemisphere only. Because, the possible range of θ is 0 to $\pi/2$, so this is my possible range of θ , I cannot go beyond $\pi/2$. Because beyond $\pi/2$ the space beyond $\pi/2$ is actually outside. So, and for ϕ , ϕ is 0 to 2π .

(Refer Slide Time: 20:51)



To compute total change in momentum, we need to integrate the above expression over all possible values of r ($0 \rightarrow \infty$), θ ($0 \rightarrow \pi/2$), and ϕ ($0 \rightarrow 2\pi$)

[Integration over upper hemisphere]

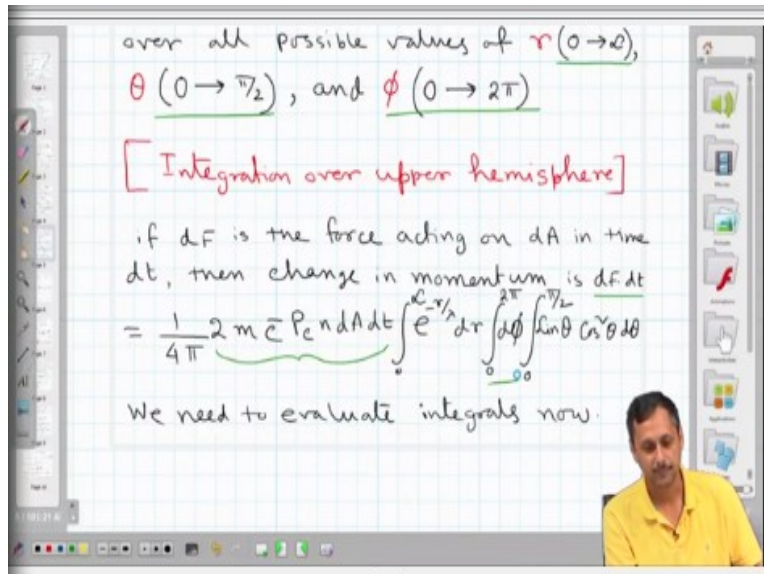
if dF is the force acting on dA in time dt , then change in momentum is $dF dt$

$$= \frac{1}{4\pi} 2m \bar{c} P_0 n dA dt \int_0^\infty e^{-r/\lambda} dr \int_0^{2\pi} d\phi \int_0^{\pi/2} \sin\theta \cos^2\theta d\theta$$

We need to evaluate integrals now

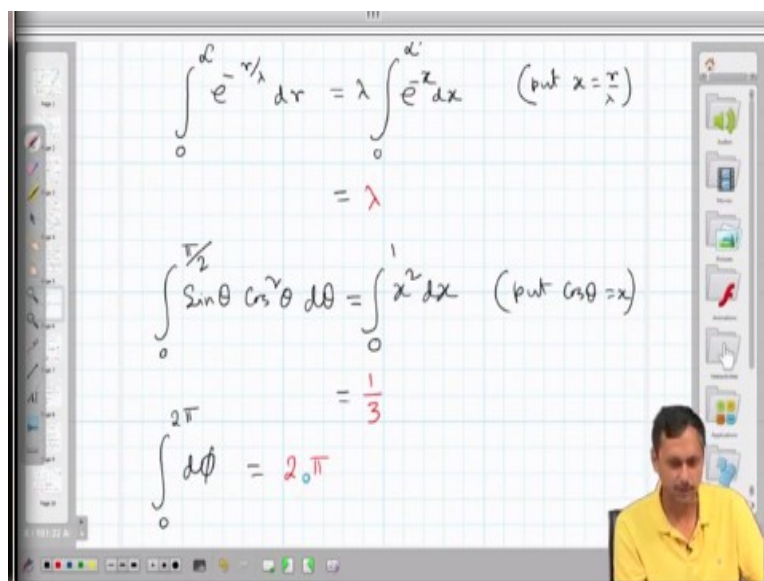
So, upper hemisphere corresponds to the r range of 0 to infinity, θ range of 0 to $\pi/2$ and ϕ range of 0 to 2π , so this is my upper hemisphere. Now if dF is the force acting on dA due to collision in a time interval dt , then the total change in momentum can be written as $dF dt$. Unfortunately, I should not call it unfortunate but so I am basically deliberately avoiding writing dp .

(Refer Slide Time: 21:24)



Because p stands for pressure, p stands for momentum, so I am just not writing that, instead I am writing $dF dt$, $dF dt$ is basically 4 multiplied by time which is essentially the change in momentum which is given by $\frac{1}{4\pi} 2mc \bar{P}_c n dA dt$. And so, these up to this everything is constant you see, this entire part is constant. And then the integration will be 0 to infinity to the power minus r by λ dr 0 to 2π $d\phi$ 0 to $\pi/2$ sine θ cosine squared θ $d\theta$. Now, so basically we have to evaluate these 3 integrals, the middle integral is the simplest it will simply give you 2π .

(Refer Slide Time: 22:14)



The first integral is also trivial, you see if you simply put x is equal to r by λ the integration reduces to λ times 0 to infinity to the power minus x dx , this will give you 1 you do not

even need to do any integration by parts, a simple proper integration of exponential function will give you 1 for this. So, you have $\lambda \sin \theta \cos^2 \theta d\theta$ from 0 to $\pi/2$. Here it will be if we substitute for x is equal to $\cos \theta$, this integration will be $x^2 dx$ from 0 to 1 which will give you one third and 0 to 2π , this integration will give you 2π only.

(Refer Slide Time: 23:05)

$$dF dt = \frac{1}{2\pi} m \bar{c} P_c n dA dt \lambda \cdot \frac{1}{3} \cdot 2\pi$$

$$= \left(m n \frac{\bar{c}^2}{\lambda} \lambda \cdot \frac{1}{3} \right) dA dt$$

$$\left[P_c = \frac{1}{\bar{c}} = \frac{\bar{c}}{\lambda} \right]$$

$$\text{So, pressure } p = \frac{dF}{dA} = \frac{1}{3} m n \bar{c}^2$$

This is **different** from one obtained from kinetic theory!

$$p = \frac{1}{3} m n \bar{c}^2 \quad [\bar{c}^2 = c_{r.m.s}^2]$$

So, substituting we get $dF dt$ which is the change of momentum in time dt is $\frac{1}{2} \pi m \bar{c} P_c n dA dt$. Once again this was already there the prefactor, now we have $\lambda \frac{1}{3} 2\pi$ and you see this 2π , 2π nicely cancels out, this 2π and this 2π . And finally we have $m n \bar{c}^2$ by $\lambda \frac{1}{3}$, why there is a \bar{c}^2 ? Please remember that P_c is the collision probability which is given by $1/\tau$. So, P_c is the collision probability in time, so $P_c dt$ is the number of collision in time interval dt . So, we have this is equal to $1/\tau$ the mean free time which is $\bar{c} \lambda$.

So, the pressure expression finally what we get is $dF dA$ is $\frac{1}{3} m n \bar{c}^2$. Now, this one is different from what we get from the kinetic theory. From kinetic theory, we get p is equal to $\frac{1}{3} m n c^2$ where c^2 basically is the $c_{r.m.s}^2$ velocity square. There is a difference \bar{c}^2 and c^2 this is the square of the mean speed and this is the square of the $r.m.s$ speed, why this happens? Let me tell you very briefly.

(Refer Slide Time: 24:43)

After a rigorous treatment by applying kinetic theory (Maxwell Speed distribution)

$$dF \cdot dt = \frac{2m \cdot dA}{4\pi} \int_0^{\pi/2} \cos^2 \theta \sin \theta d\theta \int_0^{2\pi} d\phi \int_0^\infty c dt \int_{c=0}^\infty C dN_c$$

$$= \frac{m \cdot dA \cdot dt}{3} \int_0^\infty c^2 dN_c \Rightarrow n \overline{c^2}$$

$$p = \frac{dF}{dA} = \frac{1}{3} m n \overline{c^2}$$

So, the similar treatment applies for kinetic theory and finally the momentum change can be written in an integral of the form $2m \, dA$ divided by 4π integration 0 to $\pi/2$ by $2 \cos^2 \theta \sin \theta \, d\theta$, exactly the same what we get 0 to 2π $d\phi$ also the same what we have got from mean free path. Then we have the r , it is a slightly different treatment, you can look into any standard textbook.

So, basically we have 2 integration one in r which goes from 0 to $C \, dt$ and one integration on dN_c , dN_c being the Maxwell speed distribution, $C \, dN_c$ ranging from c is equal to 0 to infinity. So, first we evaluate this integration which will give you $C \, dt$ and then in the next step the dt comes out and C goes into inside this integral and we have $c^2 \, dN_c$ which eventually gives you $n \, \overline{c^2}$ average. So, basically this integration is the origin of the r.m.s speed. So, this is the expression we get from Maxwell distribution.

(Refer Slide Time: 26:03)

kinetic theory (Maxwell Speed distribution)

$$dF dt = \frac{2m dA}{4\pi} \int_0^{\pi/2} \cos^2 \theta \sin \theta d\theta \int_0^{2\pi} d\phi \int_0^\infty c dt \int_{c=0}^\infty c dN_c$$

$$= \frac{m dA dt}{3} \int_0^\infty c^2 dN_c \Rightarrow n \overline{c^2}$$

$$p = \frac{dF}{dA} = \frac{1}{3} m n \overline{c^2} \quad (\text{From Maxwell distribution})$$

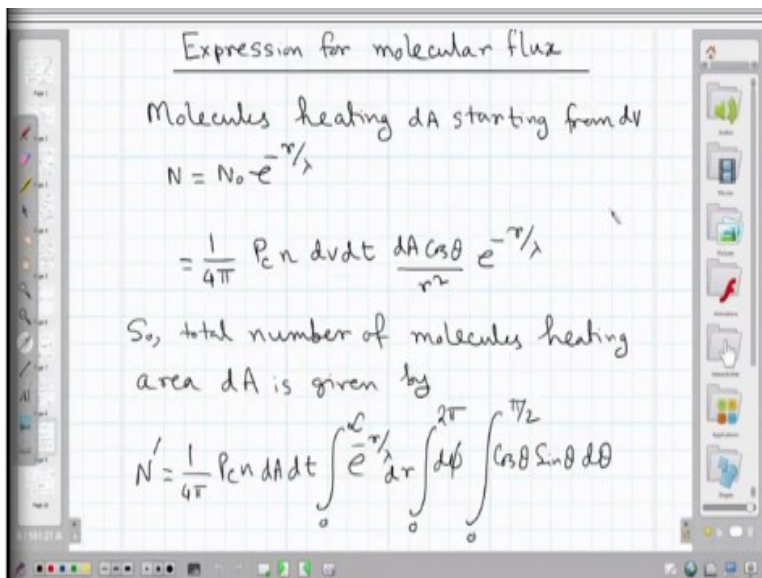
Now if you ask me between this 2 expression, the one we have got from the mean free path concept and one we have got from the kinetic theory, which one is correct? First of all, let me tell you that they are very close to each other, I mean \bar{c} is $\sqrt{8 KT / \pi m}$ and $\overline{c^2}$ is $3 KT / m$. And they are not very far from each other of course they are different there is a 15% difference in the number. So, the 2 expressions are distinctly different, now which one is correct? For me, I am bit confused, I am not sure which one should we accept.

All the standard textbooks, all every standard textbook have used this expression $\frac{1}{3} m n \overline{c^2}$, which you can get even from very elementary consideration of kinetic theory. For example, if you look into Zemansky. In Zemansky this expression has been derived even without going into the details of Boltzmann distribution function. So, it looks little more fundamental in nature as compared to this one but when we incorporate the mean free path concept that also looks physically very sound.

So, between these 2 I have seen that most of the textbooks have chosen this one but I will not immediately discard this one. So, I request you to keep this discussion alive in the forum, share your opinion. First of all look into any standard textbook where this expression has been derived. This expression this derivation which I have shown you, you will not get in many books, some of the book will have it. Anyway, I have given you a detailed discussion then let us discuss it over

the forum and try to figure out which one is the more accurate expression of pressure between these two.

(Refer Slide Time: 28:24)



Expression for molecular flux

Molecules hitting dA starting from dV

$$N = N_0 e^{-r/\lambda}$$

$$= \frac{1}{4\pi} P_c n dv dt \frac{dA \cos \theta}{r^2} e^{-r/\lambda}$$

So, total number of molecules hitting area dA is given by

$$N' = \frac{1}{4\pi} P_c n dA dt \int_0^\infty e^{-r/\lambda} dr \int_0^{2\pi} d\phi \int_0^{\pi/2} \cos \theta \sin \theta d\theta$$

Now before we end the class, let me quickly take you through this another expression for molecular flux, which is essentially the number of molecules hitting unit area of the wall in unit time. So, exact same treatment instead of momentum change will be, so will be basically considering the number of particles that has originated from dV and hitting this area dA . So, exactly the same treatment, we first have to compute the total number of molecules that is coming out as a result of collision from this elemental volume dV here.

And out of that $d\Omega$ by 4π is travelling towards dA and eventually the number that is reaching dA is that whole whatever the expression we have multiplied by e to the power minus r by λ , exactly the same treatment. And finally we have to compute the, so you see, just taking you through the steps. So, finally N will be equal to N_0 to the power $-r$ by λ , so it will be 1 over 4π $P_c n dv dt dA \cos \theta$ by r square e to the power minus r by λ . So, once again total number that is hitting the area is when this quantities integrated over the upper hemisphere that means r is equal to 0 to infinity, ϕ is equal to 0 to 2π and θ is equal to 0 to π by 2 , once again this integrations are all familiar.

(Refer Slide Time: 30:05)

$$N' = \frac{1}{4\pi} P_c n dA dt \cdot \lambda \cdot 2\pi \cdot \frac{1}{2}$$

$$= \frac{1}{4} \bar{c} n dA dt \quad \left[\text{writing } P_c = \frac{\bar{c}}{\lambda} \right]$$

So, no. of molecules hitting unit area in unit time

$$\phi = \frac{N'}{dA dt} = \frac{1}{4} n \bar{c}$$

Exact same expression obtained from kinetic theory!

of great importance in transport studies

We just put it and we finally get one fourth $\bar{c} n dA dt$, once again by writing P_c is equal to \bar{c} by λ . And see there is a λ in the denominator and there is a λ here, so these 2 λ s, so when I write P_c is equal to \bar{c} by λ this λ and that λ will cancel out, leaving us $\frac{1}{4} \bar{c} n dA dt$. So, number of molecules that is hitting unit area in unit time is simply ϕ is equal to N' divided by $dA dt$ which is $\frac{1}{4} n \bar{c}$.

Now surprisingly exact same expression is obtained from elementary treatment with kinetic theory also. In this time there is no discrepancy, there we get the molecular flux proportional to the mean speed not the r.m.s speed. So, if we start from either kinetic theory or from mean free path concept, we get to the exact same expression but when it comes to the fresher expression there is a difference.

Anyway so, we will keep this discussion alive in forum as promised and this particular expression ϕ is equal to $\frac{1}{4} n \bar{c}$ is of great importance when will be discussing the transport studies, which will be discussed in the next week. So, we are closing this lecture with this comment and see you very soon on the next lecture, thank you.