Thermal Physics

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Lecture-06
Topic-The Mean Free Path of a Gas Assembly

Hello and welcome back to this NPTEL course on thermal physics. In today's lecture we will be talking about mean free path. Now why it is important to discuss the collision and mean free path in a molecular gas assembly. So, the situation is something like this, let us say I am standing or I am inside a room in one corner of the room and I have a bottle of perfume something like a deodorant or could be bottle of some other perfume whatever and you are standing on the other corner of the room which with our mutual distance is something like of the order of 5 meters or 10 meters may be depending on the size of the room but it is of the order of meters.

Now in the last weeks lecture what we have seen is the mean velocity of a gas assembly at room temperature is of the order of 300 meters to 500 meters per second we have calculated computed it for oxygen I remember the numbers were of the order of 400 meters per second depending on the molecular mass and other temperature room temperature can also fluctuate it will be somewhere between 300 and 500 meters per second, average speed.

Both all the 3 like mean speed, the RMS speed, what was it most probable speed or everything was of that order. So, when I open the bottle of perfume in one corner of the room what happens the gas particles evaporate from the surface they are not exactly monomeric particle but nonetheless they are gas particles and this gas particles let us assume that they have average velocity of 200 meters per second very low compared to other elemental gases.

But even with that speed in order to cover a distance of 5 meters to 10 meters it should take less than a second the fraction of second, so when I open the bottle of perfume you should smell it almost immediately but in reality what happens it takes a finite time depending on let us say the room is totally closed; there is no flow of air, it will still reach you but maybe depending on the situation maybe in 15 seconds, maybe 20 seconds maybe sometimes a minute, it will reach you.

So, the gas particle which I am releasing at one corner of the room is taking a much longer time and as opposed to what predicted by kinetic theory to reach the other corner. Now what does it mean? So Clausius first came with the hypothesis that this is happening because the gas molecules are not taking a linear path and they cannot take a linear path, there are collisions.

And of course this is one of the prime assumptions of kinetic theory that there are collisions between gas molecules. Collisions are elastic; they are colliding with themselves; they are colliding with the wall container of the wall and they give rise to pressure. So, at first we will be just considering the collision among themselves. So, when this happens the gas molecules has to take their bound to take a zigzag path.

So, they cannot go from one end to the other end of the room uninterrupted, they have to suffer many different collisions but still they make a progress primarily because in this case because see the perfume is one type of molecule which is not present in the room before I open the bottle, moment I open the bottle there is a finite density of perfume molecules in one corner and in order to gain equilibrium they have to disperse throughout the room and finally it has to be equilibrated.

So, this is something that we will be discussing later on in a more elaborate manner when we will be discussing diffusion, this is something called molecular diffusion, but in the path they are constantly suffering collision and that is why it is important to compute something called the mean free path of a gas molecule for a given gas assembly.

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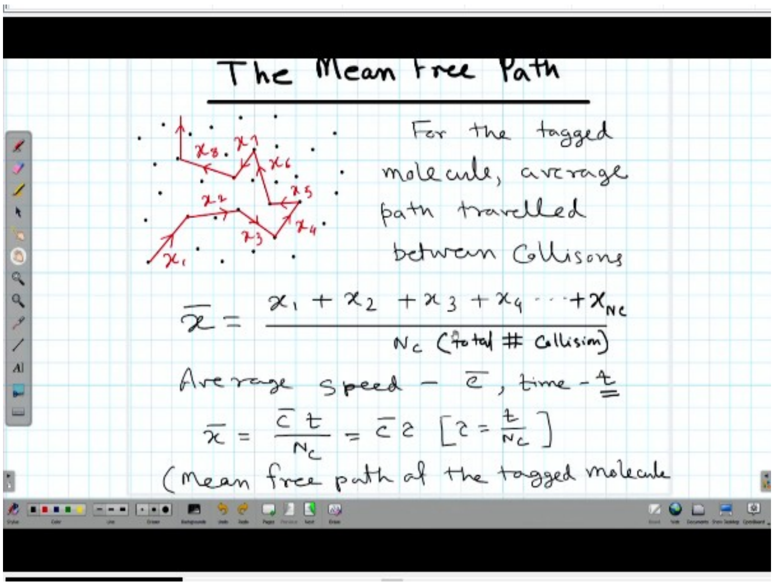

The Mean Free Path

For the tagged molecule, average path travelled between Collisons

$$\bar{x} = \frac{x_1 + x_2 + x_3 + x_4 \cdots + x_{Nc}}{N_c \text{ (total \# Collisim)}}$$

Average speed – $\bar{c}$, time – $\underline{\underline{t}}$

$$\bar{x} = \frac{\bar{c}\, t}{N_c} = \bar{c}\, \tau \quad \left[\tau = \frac{t}{N_c}\right]$$

(Mean free path of the tagged molecule

So, let us come to this in a let us take it up in a more systematic manner, so here the black dots represent the gas molecules in some arbitrary gas assembly. Now what we have done here we have just tried to trace the path of one such molecule which is let us say starting from here it will go here then take another collision go there, take another collision in this direction this will take another collision and it will keep moving like this.

And in between collision it will transverse or travel a path x 1, x 2, x 3, x 4, x 5, x 6, 7, 8 so on and so forth, it will keep moving all the time. So, let us assume that somehow we managed to tag one gas molecule and I can very accurately measure the distances x 1, x 2, x 3 up to a certain number and let us say altogether I have N such numbers Nc such numbers. Nc being the total number of collision.

So, finally we have to have x and c. Now the average distance traveled between 2 successive collision; the average for this tagged molecule will be the average of all these numbers, so x 1 plus x 2 plus x 3 all the way to x and c divided by Nc; Nc being the total number of collision. And if the molecule travelling and please remember that this molecule every collision will change its velocity, change its speed actually, velocity in a sense because it will change both the direction and the magnitude of the velocity.

So, what we can do is we can compute if we start from this position and end here let us say. So, the overall time taken by this molecule if for Nc number of collision is t then we can compute and the total distance that has been travelled is some x prime or something then we can calculate the average speed c bar of this molecule. So, for this particular molecule what we can do is we can write the x average as c bar times t divided by Nc which is c bar times tau.

What is tau? Tau is t by Nc, t being the total time taken and Nc being the number of collision. So, tau is the average time taken between 2 successive collisions. So, that is how we can compute the mean free path of the tagged molecule. But this is only for one molecule in the gas assembly we have typically Avogadro number of molecules 10 to the power 23 number of molecules.

So, for each such molecule if we can compute the free path and the mean and then we take average of that then we get the mean free path for the entire gas assembly and that let me tell you it is a humongous task. I mean you already have an idea I mean what I am talking about. So, this is absurd I mean we cannot do that.

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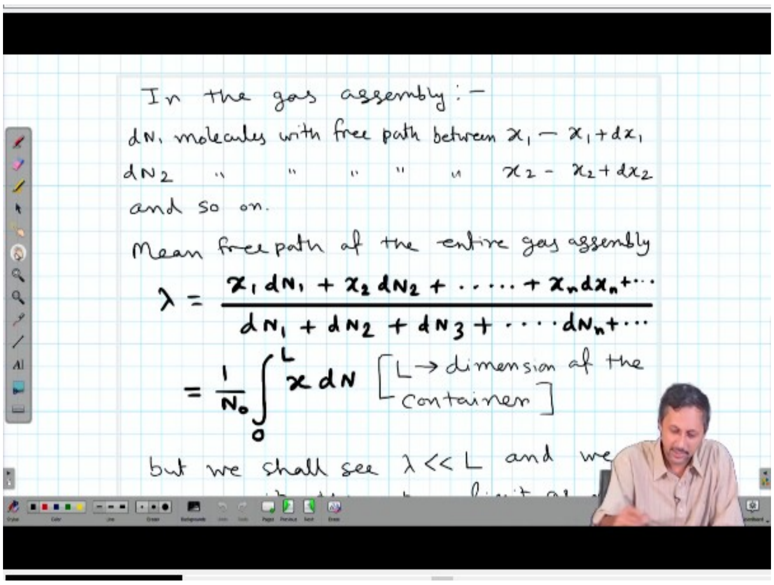

In the gas assembly :-

dN_1 molecules with free path between $x_1 - x_1 + dx_1$

dN_2 " " " " " $x_2 - x_2 + dx_2$

and so on.

Mean free path of the entire gas assembly

$$\lambda = \frac{x_1 dN_1 + x_2 dN_2 + \cdots\cdots + x_n dx_n + \cdots}{dN_1 + dN_2 + dN_3 + \cdots dN_n + \cdots}$$

$$= \frac{1}{N_0}\int_0^L x\, dN \quad \left[L \to \text{dimension of the container}\right]$$

but we shall see $\lambda << L$ and we

So, instead what we can do is we can kind of formalize it in a more systematic manner. So, what we can do is in a gas assembly we can define dN 1 as the molecule with free path between x 1 and x1 plus dx 1, dN 1 is the number of molecule in this range, dN 2 similarly is the molecule the with free path between x 2 and dx 2 and so on. So, the mean free path by definition of mean free path it will be x 1 dN 1 d plus x 2 dN 2 of all the way to x n dx n divided by d N 1 plus dN 2 plus dN 3 all the way to dN n and so on.

So, the integration I mean because if the numbers are large number of such assemblies are large enough we can replace this summation with an integration and we can write the lower one will be the total number of molecules in this case we are just writing it N 0, there is a reason for it instead of N we are writing N 0 because later on introducing N in a slightly different way.

Then it will be integration x dN and the integration limit is 0 to L. Now why L, L being the typical dimension of the container, the gas molecules are inside some container some tank or something, so if it has a dimension of 1 feet by 1 feet by 1 feet the maximum value of x can be only 1 feet or maybe the diagonal length whatever it is, but it is of the order of L. Now we shall see later that the mean free path for a standard gas assembly which is let us say some elemental gas at STP that is standard pressure and temperature.

This is very, very, very small as compared to the length of the container typically. So, just to put things in perspective the typical length of the container is of the order of 1 meter or let us say 0.1 meter whatever ye 1 meter of the order of that it could be less than that would be more than that and the mean free path we will see that it is of the order of 10 to the power minus 7 meters 10 to the power minus 8 meters which is time. So, for all practical purpose we get lambda is much, much less than L and the upper limit of this integration in effect becomes infinity.

So, the integration lambda is actually integration 1 by N 0, 0 to infinity x dN. So, this is the integration we have to compute in order to compute, in ordered to find out lambda for a gas assembly. Now so in order to compute this integration this is only theoretical up to this point, in order to compute this integration what we have to do? We have to get an expression for dN in terms of x.

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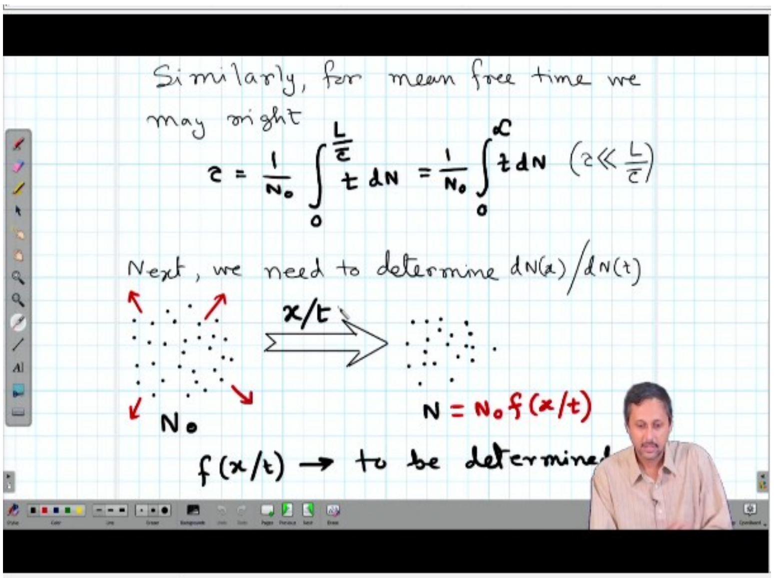

Similarly, for mean free time we may wright

$$\tau = \frac{1}{N_0}\int_0^{L/\bar{c}} t\, dN = \frac{1}{N_0}\int_0^{\infty} t\, dN \quad \left(\tau \ll \frac{L}{\bar{c}}\right)$$

Next, we need to determine $dN(x)/dN(t)$

$f(x/t) \rightarrow$ to be determined

So, how do we do that and similarly and before we go there similarly the mean free time can also be computed in a similar manner as tau is equals to 1 by N 0. Please remember it is not for 1 molecule but the mean free time or actually probably what I should do is I should not confuse you by writing tau here, I should write t bar for a single molecule then I think you get a better feel. So, this is t bar and x bar for 1 molecule t bar for 1 molecule lambda for the assembly similarly tau is for the assembly.

So, tau will be averaging over all these t bars which is nothing but 1 by N 0 integration 0 to L by c bar, c bar being the average speed of the assembly which we get from the Maxwell's distribution anyway and t dN. So, once again as tau becomes very less compared to this quantity L by c bar we can write this as 1 by N 0, 0 to infinity t dN. So, either way in order to compute lambda and compute tau we have to find out a way of determining dN x or dN as a function of t.

So, to that time what we do is we start looking into this physical picture, we have a gas assembly. Let us say it is open and so it is exactly like the perfume bottle moment you open the perfume bottle the perfume molecules get released and they are traveling across the room. Now they initially start off as a group as a big group because I get the strongest smell of course. If I have the bottle in hand I get the strongest smell, so there are the number density is maximum.

As the travel across the room travel, across the atmosphere they start colliding with each other among themselves and there are molecules that are knocked out of that group and so this is again this is not the best model to describe a physical system but this is where we start and as they travel they start losing molecules due to collision.

So, let us say they start with a number N 0 to begin with here and finally they end up after a distance x or a time t they end up having N number of molecules which is N 0 multiplied by some function of either x or t because as we see if we look at the gas assembly we immediately after that when the x or the t is very small then N is approximately equal to N 0. But as we go away from the initial position or as we go advanced in time N becomes small compared to N 0. So, f is the function that is that to be determined, we do not know what is x.

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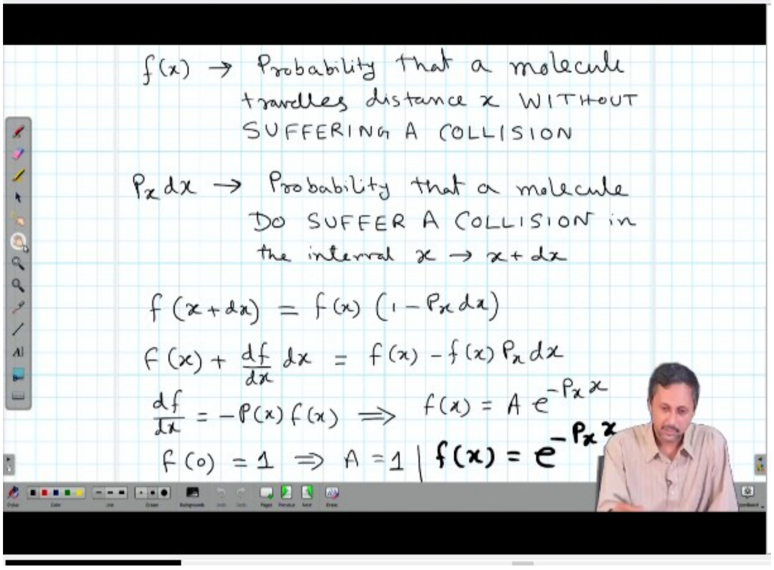

$f(x) \rightarrow$ Probability that a molecule travelles distance x WITHOUT SUFFERING A COLLISION

$P_x dx \rightarrow$ Probability that a molecule DO SUFFER A COLLISION in the interval $x \rightarrow x + dx$

$$f(x+dx) = f(x)(1 - P_x dx)$$

$$f(x) + \frac{df}{dx} dx = f(x) - f(x) P_x dx$$

$$\frac{df}{dx} = -P(x) f(x) \Rightarrow f(x) = A e^{-P_x x}$$

$$f(0) = 1 \Rightarrow A = 1 \quad | \quad f(x) = e^{-P_x x}$$

Now what we do is we define and so basically what we realize from there that f has something to do with the collision probability. So, we have to have we start with N 0 number of molecules in an assembly and then we multiply this with f which is a function equivalent of with a function and then get N number of molecule that still survives presumably without a collision in this assembly.

So, basically f is a function that gives you the probability that a molecule travels a distance x without suffering a condition in that assembly. So, please understand this because N 0 multiplied by f gives you N which is still existing, still surviving in this assembly f is essentially the probability of not suffering a collision over a distance x. So, we are just computing f x for now similar manner we can do it for f t also. I will just show you how to do it for f x, same logic same type of calculation you can apply and you can find out f t.

But later on we will see that f t is not needed separately we can do that of course I mean but we will see later the tau and lambda they are strongly correlated to each other. So, we can either work with f t or either what with f x any of this will do anyway. Now at the same time we introduce a new parameter P x dx where P x dx is actually the probability that a molecule do suffer a collision in this interval x to x + dx. So, let me try to explain this in more detail.

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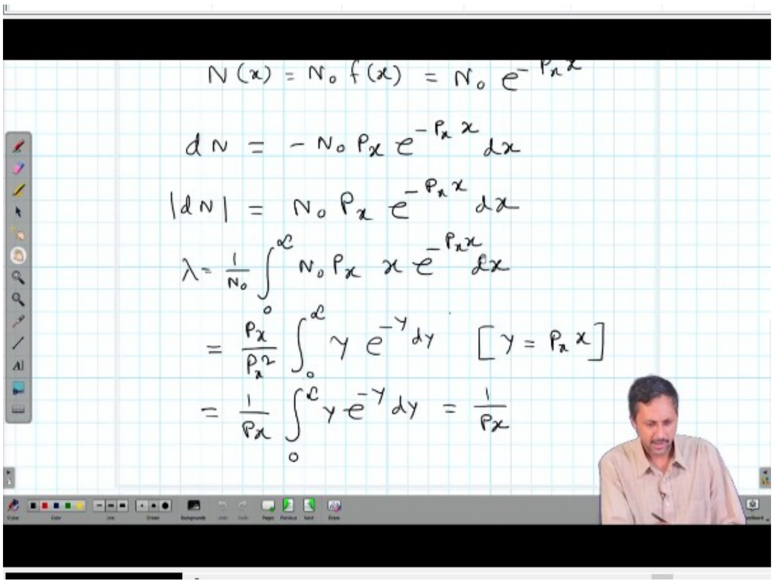

$$N(x) = N_0 f(x) = N_0 e^{-P_x x}$$

$$dN = -N_0 P_x e^{-P_x x} dx$$

$$|dN| = N_0 P_x e^{-P_x x} dx$$

$$\lambda = \frac{1}{N_0} \int_0^\infty N_0 P_x \, x e^{-P_x x} dx$$

$$= \frac{P_x}{P_x^2} \int_0^\infty y e^{-y} dy \quad [y = P_x x]$$

$$= \frac{1}{P_x} \int_0^\infty y e^{-y} dy = \frac{1}{P_x}$$

So, we have this gas assembly, they are colliding, let us say this one collides with this one and gets knocked out. What is the probability that it will suffer a collision in this distance, just the probability is given by P x dx. What is the probability that it will not suffer a collision? This is given by a probability 1 minus P x dx. That is because the total probability has to be 1.

Now the function f x talks about probability of not suffering a collision of the up to a distance x. So, the function f x plus dx is probability of not suffering a collision up to a distance x plus dx now what will be that? That will be a product of f x multiplied by 1 minus P x dx because f x is not suffering a collision up to x and this one is not suffering a collision for next Dx. So, the probability that is f x plus dx that is not suffering a collision up to a distance x plus dx is a product of f x and 1 minus P x dx.

So, this is exactly what we have done here f x plus dx is f x into 1 minus P x dx. Now we expand f x plus dx in a Taylor series only up to the first term then we simplify f x, f x cancels out, we have df dx = minus P x f x which on integration gives you f x = A e to the power minus P x x. Now we have to realize that f 0 at x = 0 f = 1 because the place where we start we have N 0 number of molecules, go back to this picture at x = 0 or t = 0, f has to be equal to 1.

So, there is no collision, no at the beginning or at the initial distance there is no collision, total number is equal to N 0. So, N at x = 0 = N 0. So, that gives you A = 1, so the function f x is simply e to the power - P x x. P x is undetermined at present, we do not know what is P x. So, we write f x N x = N 0 f x. Similarly N t also we can write N 0 f t where t has to be determined we can do that in a similar manner, just the way the same treatment can be applied for time also.

So, N 0 e to the power minus P x x. Now we compute d N. What is d N? d N is minus N 0 P x e to the power minus P x s dx. So, the number we are interested only in the magnitude and this magnitude will be this without the negative sign here. Now let us go back to the expression for lambda. Lambda = 1 over N 0 0 to L x d N, we already have computed an expression for d N, we just plug it in here, we simply plug it in here and we get lambda = 1 over N 0 0 to infinity N 0 P x x e to the power minus P x x dx.

Substitute y = P x x and you will find out that. This simplifies to P x by P x square integration 0 to infinity y e to the power minus y dy. So, why it is fantastic, ye so lambda = 1 over P x integration 0 to infinity y e to the power minus y dy. This is a standard integral you can find out this integral and it will give you 1. So, lambda = 1 over P x if you compute this integral you will see that it will give you 1 only.

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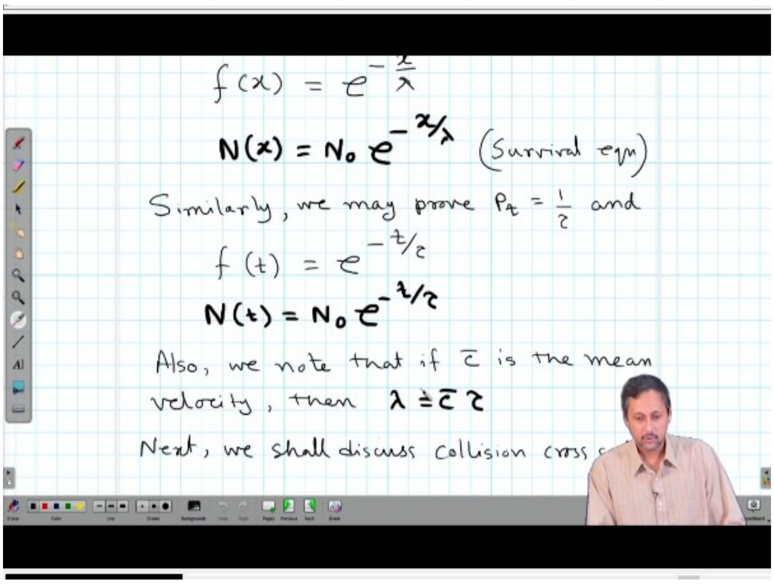

$$f(x) = e^{-\frac{x}{\lambda}}$$

$$N(x) = N_0 e^{-x/\lambda}$$ (Survival eqn)

Similarly, we may prove $P_t = \frac{1}{\tau}$ and

$$f(t) = e^{-t/\tau}$$

$$N(t) = N_0 e^{-t/\tau}$$

Also, we note that if $\bar{c}$ is the mean velocity, then $\lambda \doteq \bar{c}\,\tau$

Next, we shall discuss collision cross

So, finally we get the full expression for f x which is f x = e to the power minus x by lambda, so N x = N 0 e to the power x by lambda which we call the survival equation. This gives you the number of molecule that will survive in a group even with collision over a distance x and lambda at present it is undetermined. We have used the definition of lambda the mean free path in order to find out the survival equation but we have not derived lambda yet. Lambda has to be determined in a different manner. Similarly for time as I have said the exact same treatment is valid for time also.

So, we can always define a probability which is the probability of collision in the time t to t plus dt and we can find out that f t the function that says the survival function f t is nothing but e to the power minus t by tau. That that P t = 1 over tau and the survival equation for time will be N t = N 0 e to the power minus t by tau. Now let us go back to this relation here you see x bar = c bar t bar. In the similar note we can say that lambda = c bar tau. So, our job we have to determine lambda but before that let me introduce something a new parameter called the collision cross section.

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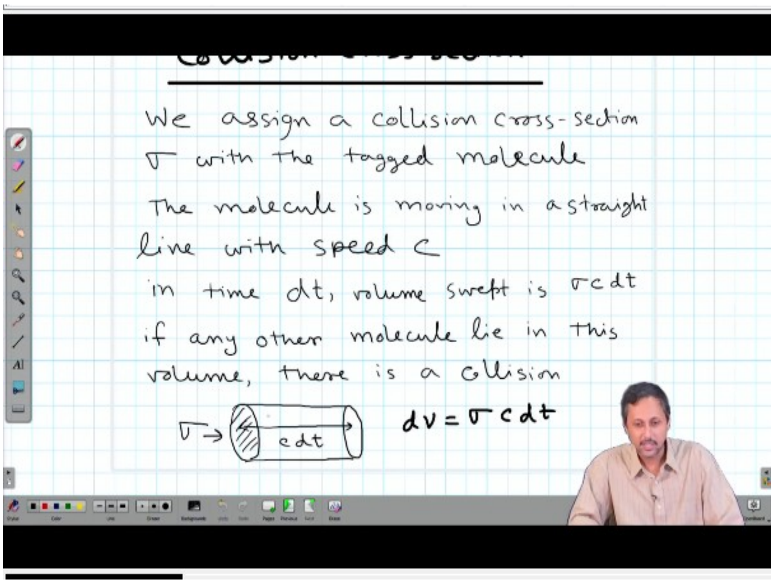

We assign a collision cross-section σ with the tagged molecule

The molecule is moving in a straight line with speed c

in time dt, volume swept is $\sigma c dt$

if any other molecule lie in this volume, there is a collision

$dv = \sigma c dt$

Now what is the collision cross section? Let us say a molecule is traveling through space. If a molecule is traveling through space it will collide with other molecules and then we can define something called the collision cross section which gives a effective cross section that this molecule have when it is traveling through space. Now at present at first glance it seems like that this collision cross section is exactly like the cross section of that molecule.

But later on we will see that there are it is not exactly that but that is something to do with the actual cross section of this molecule but it is sometimes more than that, we will come back to that in the next lecture. But for now what we are going to do is we are just going to assign a collision cross section and we call it sigma. We just name it sigma. Now once again we are looking into a tagged particle and we assume this is a zeroth order approximation in which we assume that only the tagged particle is moving through space all other molecules are stationary.

Now this is a very bad approximation, I can tell you I mean it is not nowhere close to the actual picture but this is a zeroth order approximation that is where we start with slowly and slowly we will build on that. Now let us say this molecule is moving with a speed c and it has a collision cross section sigma. Now in a small time interval dt how much will that move or what is the volume swept by this particle? Let us say this is my collision cross section, c is the speed of the molecule and it is traveling a length c dt in the small time interval dt.

So, the volume that is swept is nothing but dv = sigma c dt. So, this is the volume inside this cylinder here. Now if and only if there is another molecule present in this volume there is a collision, if there is no molecule present there is no collision. But assuming that there are sufficient number of molecules present so that there is a collision inside this volume. The total number of collision has to be proportional or has to be a function of the density of the molecule as well, the density of the gas assembly as well.

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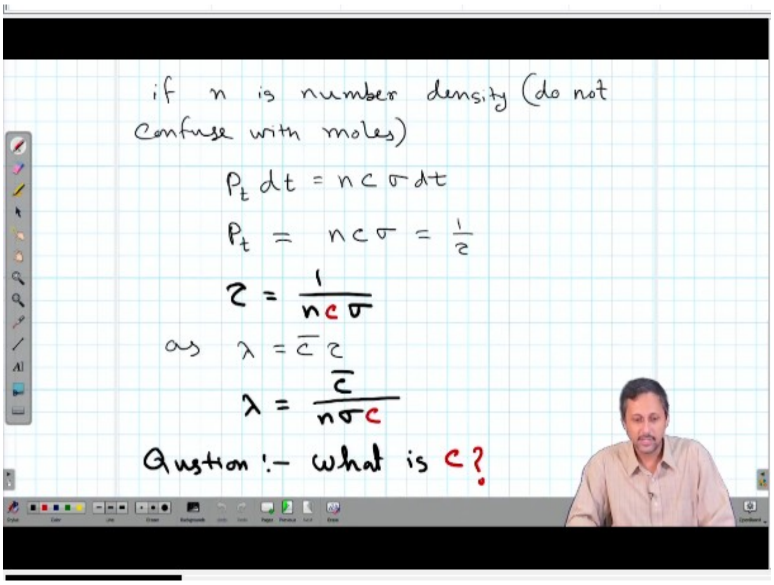

if n is number density (do not
Confuse with moles)

$$P_t\, dt = n c \sigma\, dt$$

$$P_t = n c \sigma = \frac{1}{\tau}$$

$$\tau = \frac{1}{n c \sigma}$$

as $\lambda = \bar{c} \tau$

$$\lambda = \frac{\bar{c}}{n \sigma c}$$

Qustion :- what is c?

So, that is why we get if n is the number density of the gas molecules and please do not confuse it with the number of moles so far we have used N only for number of moles. But in this treatment n is the number density of molecules. So, that means if we have N number of molecules with a volume v, so n is simply capital N by v. So, the probability of having a collision in the time interval dt = n c sigma dt.

Why n c sigma this volume is sigma c dt, sigma c dt then it will be sigma or rather I would just write d v here and dv is equal to sigma c dt and n being the number density. So, how many collisions in the small time interval? That is exactly sigma c dt times n, that is the number of other particles that is present in this volume which is traveled or which is covered in the small time interval dt by this one molecule we are talking about.

So and this is nothing but P t dt. Please remember the in our treatment what was P x dx that the probability that a molecule do suffer a collision in this interval x to x plus dx. Similarly, P t dt is the probability that a molecule do suffer a collision in the interval t to t plus dt. So, they are basically the similar parameters one in space the other one is defined in time. So, this is nothing but and we see that dt cancels out from both sides and we have P t = n c sigma which is equal to 1 over tau as we have seen P t = 1 over tau.

We have not computed that explicitly I will just leave it to you for that computation the way we have proved that lambda = 1 over x. similarly, we can prove that P t is equal to or tau is equal to 1 over P t or P t = 1 over tau. So, then we get a relation tau = 1 over Nc sigma. Now what is this c. C is the speed of the tagged molecule. So, we get a relation and we remember that lambda = c bar tau.

We just wrote that here, it has to be the relation so we get lambda = c bar n sigma by c. I have written c in red just to make it distinct from c bar; c bar being the mean velocity, c is something. So, now the question is what is c? What is an appropriate expression for c? It is it exactly similar to this means velocity c bar here or it is something else. So, we will start here from the next class and we will compute an expression for c under the first order approximation, the second order approximation and we will find out a proper expression for the free path. So, that is where we stop today we will continue from here in the next lecture bye.