Thermal Physics
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Lecture-07
Topic-Expression for Mean Path

Hello and welcome back to another lecture of NPTL course for thermal physics. Now, in the last lecture, we have discussed about mean free path in details and also the terms like collision probability both in terms of energy as well time and distance. And we have established a relation between these 2 parameters that is tau that is a conditional frequency in time and lambda which is the mean path which is in distance.

So, basically lambda gives you the average distance over the entire gas assembly in terms of the average distance of a particle can travel inside this gas assembly without suffering a collision. Similarly, the mean free time lambda is the average time between 2 successive collisions and strictly speaking like the Maxwell's velocity speed distribution function, they also have a distribution. So, these are the average value what we are talking about.

So, for example, in a Maxwell distribution speed distribution case we have seen that the maximum numbers of molecules stay in the vicinity of the top of the distribution curve that is close to the mean velocity or close to the mean speed or most probable speed, but, in principle there are molecules or there are gas particles which have zero velocity and there are gas particles which has nearly infinite velocity nearly zero and nearly infinite velocity. So, these are possible similarly, the mean free path and mean free time or the inverse of pollution frequency whatever you call it, these are actually the average over the entire assembly.

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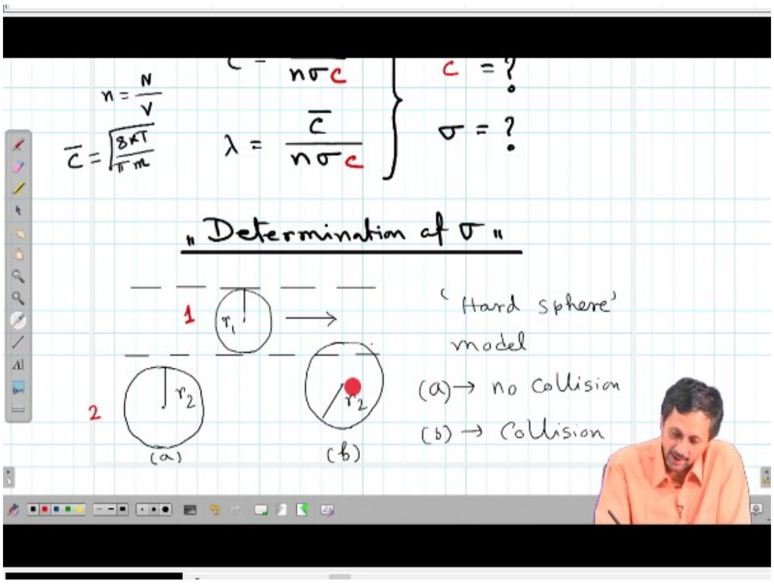

Now, if we go back to the mathematical derivation we did in the last class and we look back into this relation we see we have derived 2 relations lambda tau = 1 by n sigma c and lambda = c bar divided by n sigma c. Now, n is the number density n is do not confuse it with the moles n is the number density. So, n is simply equal to capital N by V. That is the total number of molecules in the gas assembly divided by total volume and sigma is the collision cross section.

c bar is the average the mean velocity from the Maxwellian distribution and we know that c bar will be equal to root 8 kT by pi m. So, this is what we have already derived I am not going into the detail discussion of this term once again, but what is important that there are 2 more parameters in this expression. One is the c which is marked in red and one is this sigma which is the collision cross section.

Now, the question is what are the values of sigma and what are the values of this c which I should once again write in red, because this is more or less the convention I have followed. So, what is this c and what is this signal? Now, sigma as we know this is the collision cross section and very soon we will start with by determining an expression for sigma in terms of the molecular parameter.

Question still remains what is c? c is the speed with which our molecule moving in an on an average. So, let us first discuss about sigma and we try to determine an expression for sigma, then we will come back to c. So, in order to determine sigma, let us focus on this following picture. Let us assume this there is a gas particle let us name it gas particle 1 which is moving with an uniform speed or in this particular direction and there is the second particle, we call it the particle 2, it has a radius r 2 whereas, the first one has a radius r 1 and this is somewhere in the space.

Now, look at this picture carefully. So, this dotted line actually that marks a cylinder. Cylinder that is stressed out in space by this particular molecule 1 and if and only if there is a overlap of this cylinder, which is marked by these dotted lines and with the second molecule there is a collision. So, we have drawn the second molecule in 2 different positions, position 1 position a and position b.

In position 1 or position a, the second molecule lies outside this cylinder of influence and there is no position and in position b in case b or rather I should say, case a and case b. In case b, the second molecule, somehow the volume of that molecule has an overlap with the cylinder of influence of the molecule bond. So, in that case, there will be a collision. Now, mathematically speaking, we have this is the hard sphere approximation where we assume that in during the collision, the volume of the cylinder or volume of the gas molecule does not change.

Now, in reality, what happens is we have one molecule here and the second molecule coming in the collide and once the collide, there is a shrinking in volume. So, basically it is an elastic deformation because molecules are finally, I mean, although we look at it as if they are hard sphere, but they are not there, they have electron cloud in the outermost shell and the electrons they interact and I should not say that the contract like what happens to molecules in a collision between 2 tennis balls for example, the contract.

I am not saying they do that, but of course, there are some sorts of interactions. And there is some atomic deformation or molecular deformation present and we are ignoring that in this particular hard sphere model we are totally ignoring that. So, all we care about is in position a, there is a no collision in position b there is collision. Now, if the respective radiuses are r 1 and r 2 of molecule type 1 and molecule type 2.

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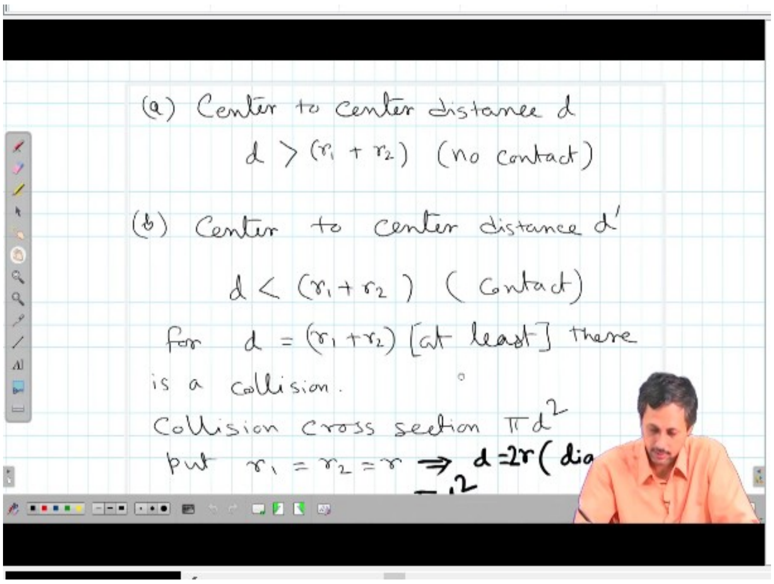

(a) Center to center distance d

$d > (r_1 + r_2)$ (no contact)

(b) Center to center distance d'

$d < (r_1 + r_2)$ (contact)

for $d = (r_1 + r_2)$ [at least] there is a collision.

Collision cross section πd^2

put $r_1 = r_2 = r \Rightarrow d = 2r$ (dia

Then we can write in position center to center distance d is greater than r 1 and r 2. When d is greater than r 1 and r 2 there is no contact between them. And in position 2, let us go back these equal to the center to center distance d being the center to center distance. So, center to center distance at the point of collision when this molecule will come to this particular position okay or rather this molecule will come to this particular position it will be something like this and the center to center distance becomes less.

Of course, it cannot be less because these are hard sphere. So, what happens is it comes to contact and then it deviates in another direction. So, that is exactly what is written here that for d = r 1 + r 2 there is a collision. So, in hard sphere approximation the collision cross section is defined by pi d square. So, this is now, let us assume that these molecules are inside the same gas assembly. So, they are basically the same molecule just for illustrative purposes I have put r 1 and r 2, but they have equal radius.

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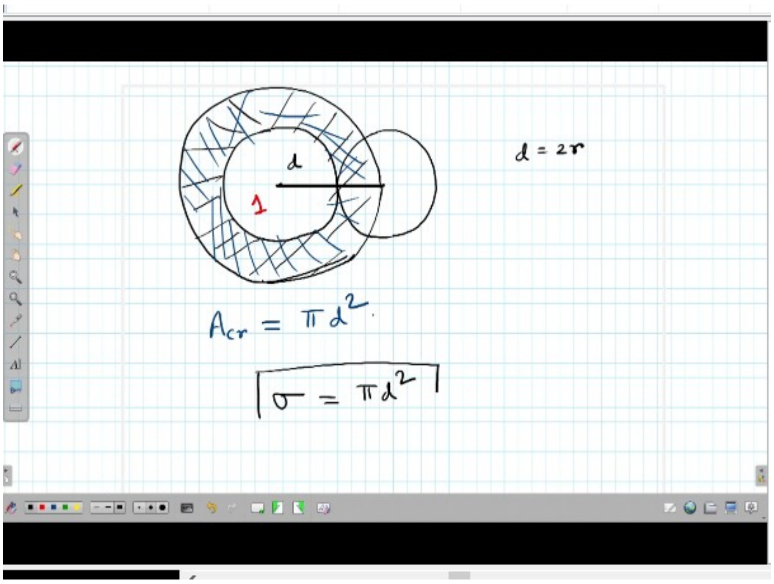

So, what happens is when there is let me try to draw this quickly. So, that I give you a better understanding. So, I have one molecule drawing is never that great you have to bear with it, you have one molecule and the second molecule can come in contact with the first one, if and only if the center to center distance is d, which is 2r. Now try to assume this. We draw a circle of radius, not radius r, but radius d, it is a hypothetical circle.

So, any molecule the center of that molecule, if that comes within this circle, there is a collision. So, this basically, the effective cross section of this molecule 1, so let us call it molecule 1. So, this shaded area, I will just mark it with blue maybe this shaded area is actually the effective cross section of this molecule as it travels through space. So, this area is given by a or rather, we will call it a cross section is equal to pi d square. I hope this makes sense. Now, let us go back. So, we just written this expression here, probably I will make some changes in this text, because the text sometimes gets bit confused, confusing here, maybe.

So, I will make slight changes and then, but anyway, from this picture itself, you get a better feel for it. So, now, we know that this is nothing but sigma. So, basically, we get sigma = pi d square. So, out of two parameters of interest, one was sigma and another was c. So, we have got an expression for sigma here. Now, next up is c. So, you would like to see what are the possible values or what are the possibilities in which way we can find c.

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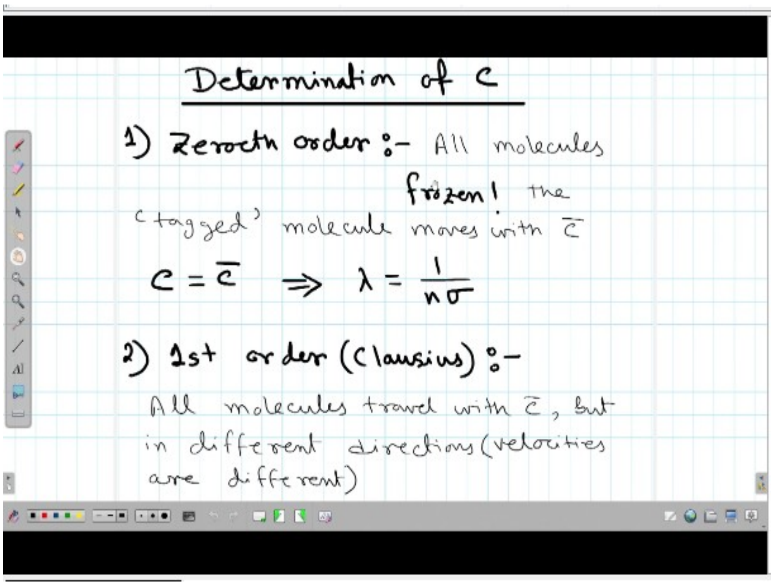

Determination of c

1) Zeroth order :- All molecules frozen! the 'tagged' molecule moves with $\bar{c}$

$$c = \bar{c} \Rightarrow \lambda = \frac{1}{n\sigma}$$

2) 1st order (Clausius) :-

All molecules travel with $\bar{c}$, but in different directions (velocities are different)

So, the first approximation is zeroth order, in the zeroth order approximation you see that all molecules are frozen. So, that is exactly how we first described or determine the expression for lambda. So, we have assume that all the molecules are frozen and only one molecule the so called tact particle is moving and this is exactly the same way we have computed this one also the collision cross section also.

We have assumed that these molecules are more or less frozen and this is the only one that is moving just for the better understanding, but in principle, even if all the molecules are moving, this picture does not change. If and only if in the center to center distance equals to this to 2r only then there is a collision. So, the minimum distance that the collision cross section remains by the square.

But once again, let us go back to the zeroth order approximation when we assume that all the molecules are frozen and our tact particle is the only one that is moving through space. Now, in this case and that one is moving with the average speed c. And blankly we just put c = c, c average or c mean and then going back to this expression, what happens this c bar over here and c bar over here cancels out and we have lambda is equal to 1 by pi d.

Also we can write an expression for tau, tau will be 1 by n sigma c bar we can do that. Now, this one gives you an idea, I mean, of course, it gives you an idea, but this is an oversimplification by all means, we cannot make all molecules frozen. And we cannot assume that even if there is only one molecule moving that is moving with the average speed. So, it is a vast oversimplification of the situation. But anyway, it gives us an idea of what should be there, what is an approximate, what could be an approximate expression for lambda?

Now, next comes the first order approximation and this was given by Clausius none other than the great Clausius. So, he assumed. So, let us make all the molecules move and for simplicity, we just say that they all of them move in different directions, there is no restriction that they have to move in one particular direction, but they move with the average speed c bar, that is a mean speed of the gas assembly. So, basically he did not assume any distribution of the speed, but he has assumed uniform speed, but different velocity of the gas assembly. Now, then the calculation becomes kind of simple let us see.

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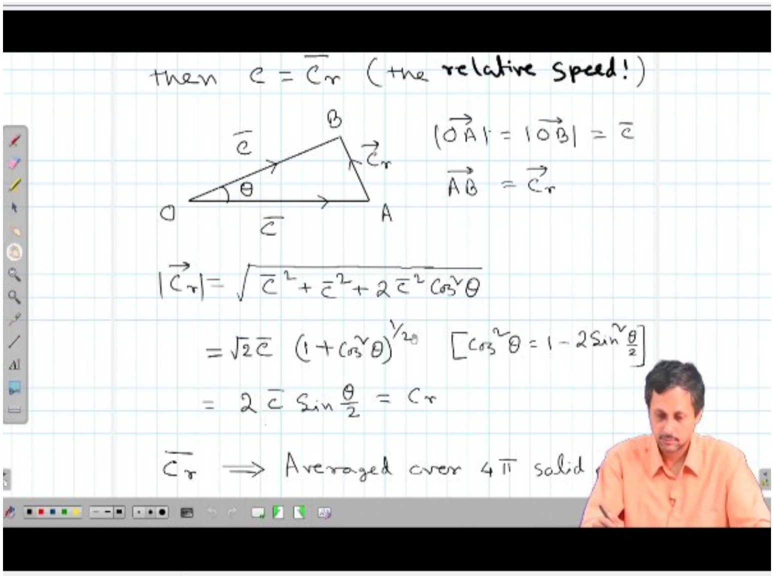

then $c = \overline{c_r}$ (the relative speed!)

$|\vec{OA}| = |\vec{OB}| = \bar{c}$

$\vec{AB} = \vec{c_r}$

$$|\vec{c_r}| = \sqrt{\bar{c}^2 + \bar{c}^2 + 2\bar{c}^2 \cos^2\theta}$$

$$= \sqrt{2}\bar{c} \left(1 + \cos^2\theta\right)^{1/2} \quad \left[\cos^2\theta = 1 - 2\sin^2\frac{\theta}{2}\right]$$

$$= 2\bar{c}\sin\frac{\theta}{2} = c_r$$

$\overline{c_r} \Longrightarrow$ Averaged over 4π solid

So, the calculation, what happens is, what we have to do is we have to determine the relative velocity between two particles, if two particles are moving in two different directions, they have a relative velocity and the c in the expression for lambda what we have to put is that relative velocity. Now, let us consider this situation, let us say we have two molecules both moving with the same speed c, but in different direction.

So, what we have to do is, we have to in order to find out the relative velocity, we have to you know come back to this basic vector diagram, we have put one velocity OA here the other velocity OB is in this arm and the angle between them is theta simple. So, the relative velocity C r is nothing but this vector AB and from vector diagram, we immediately see that AB = OB – OA, right? Oh sorry, there should be a minus sign here, my mistake. OB minus

OA. Now, if written in terms of proper vector components, the magnitude of c r is so, I probably should elaborate a little more on this so, that you understand it better.

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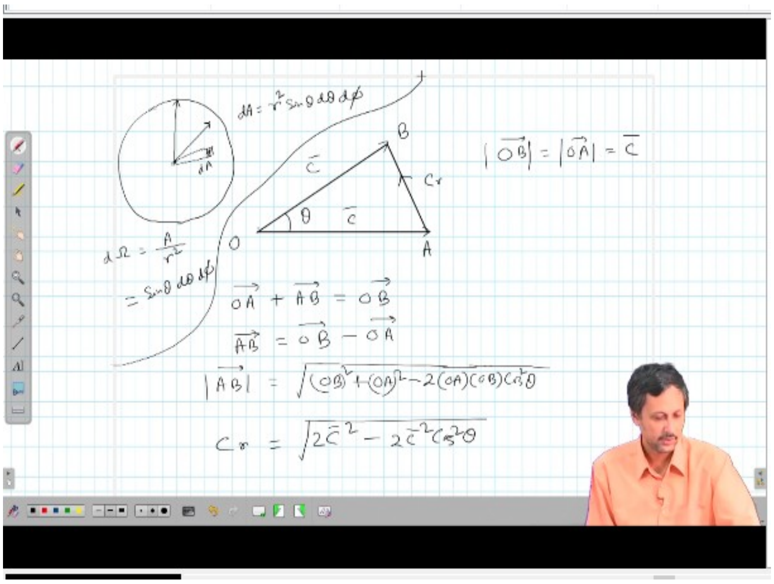

$$dA = r^2 \sin\theta \, d\theta \, d\phi$$

$$d\Omega = \frac{A}{r^2}$$

$$= \sin\theta \, d\theta \, d\phi$$

$$|\overrightarrow{OB}| = |\overrightarrow{OA}| = \bar{c}$$

$$\overrightarrow{OA} + \overrightarrow{AB} = \overrightarrow{OB}$$

$$\overrightarrow{AB} = \overrightarrow{OB} - \overrightarrow{OA}$$

$$|\overrightarrow{AB}| = \sqrt{(OB)^2 + (OA)^2 - 2(OA)(OB)\cos^2\theta}$$

$$c_r = \sqrt{2\bar{c}^2 - 2\bar{c}^2\cos^2\theta}$$

So, we have one vector, I have the second vector same magnitude a different direction and the third vector is disconnecting. So, basically OAB, so OA + AB = OB. So, this is the simple vector equation. So, AB is nothing but OB – OA and OB mod = OA mod = c bar and this is c r. So, this is c bar, this is c bar and this is c r. So, from this equation we see that AB mod is nothing but OB square plus OA square and the angle is theta minus 2 OA OB cos square theta.

And this is nothing but so basically c r = 2 c bar square because this is c bar, c bar minus 2 c bar square, this is cross square theta. So, simplifying you can take 2 c bar square common from these 2 terms and then you can take it out of the route putting root t root 2 c bar = 1 + cos square theta whole to the power half. Now, we write cos square theta using this trigonometric identity as cos square theta = 1 – 2 sine square theta by 2 and very simply, we have c bar or c r magnitude = 2 c bar sine theta by 2**.**

Now, this is for only one specific value of theta and Clausius assume that gas molecules are moving in all possible directions relative to each other. So, what we have to do is even in this simplified assumption, we have to find out the average value of c r, which will be averaging over all the possible theta values. And once we do that, so, c r average is basically what we have to do is we have to do it for this all entire 4 pi solid angle.

Why 4 pi solid angle? Because I will just try to make you understand here. So, let us say one molecule is our reference molecule is sitting at the center. So, the other molecule can make or let us say this one has a velocity component in this direction. Now, what are the possibilities of other different directions we have? We can have anywhere on this figured actually. The other velocities the second molecule can be anywhere on the sphere and what is the total area of the sphere in terms of solid angle this is 4 pi.

So, what we have to do is, we have to average it over this entire 4 pi solid angle divided by 4 pi. So, the element and please remember that the radius of the sphere is fixed. So, any element on this will be r sine theta d theta d phi and r is fixed and once we try to compute the solid angle due to this particular area. So, it will be r sine theta d theta d phi. So, this will be d omega= 4 pi by A, it will be A over. So, this is dA, the area here dA over r squared. Sorry this will be r squared, A over r squared. So, this is nothing but sine theta d theta d phi, right.

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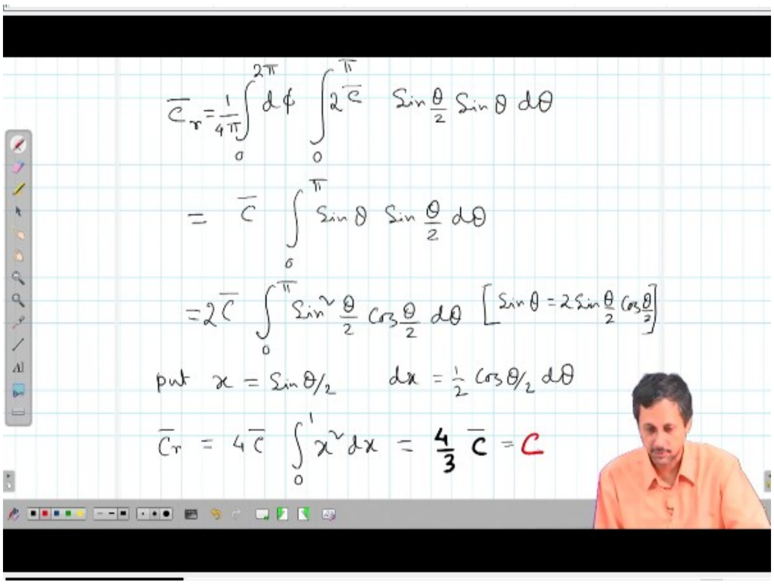

$$\bar{c}_r = \frac{1}{4\pi}\int_0^{2\pi} d\phi \int_0^{\pi} 2\bar{c}\ \sin\frac{\theta}{2}\sin\theta\, d\theta$$

$$= \bar{c}\int_0^{\pi} \sin\theta\ \sin\frac{\theta}{2}\, d\theta$$

$$= 2\bar{c}\int_0^{\pi} \sin^2\frac{\theta}{2}\cos\frac{\theta}{2}\, d\theta \quad \left[\sin\theta = 2\sin\frac{\theta}{2}\cos\frac{\theta}{2}\right]$$

put $x = \sin\theta/_2$ $\quad dx = \frac{1}{2}\cos\theta/_2\, d\theta$

$$\bar{c}_r = 4\bar{c}\int_0^{1} x^2\, dx = \frac{4}{3}\bar{c} = C$$

So, this is exactly what we are doing, we are integrating over d phi and integrating over sine theta d theta multiplied by 2 c r sine theta by 2 over 0 to pi, right. So, that is the range of theta I hope you understand that, but let me tell you anyway, theta can vary between this angle which is 0 to this angle which is wanting to do which is 180 degree which is phi and phi can have altogether 2 pi full circle value. So, we have 2 pi coming from here, 2 coming from here. So, 4 pi is in the denominator both all nicely cancels out leaving behind c r 0 to pi sine theta, sine theta by 2d theta.

Further simplification is done by writing sine theta = 2 sine theta by 2 cos theta by 2 which is 2 c 4 0 to pi sine square theta by 2 cos theta by 2 d theta and by a very simple substitution we get this integration as 4 times 0 to, 2 times 0 to 1 x square dx which is finally gives us four third c r. Sorry, c r, four third c bar I should write not c r, because c r is this one. These are all c bar my mistake right, basically c r average so, this will be c r average, this is c bar. So, from here this is c bar, c bar, c bar here also c bar and that is c bar. So, now this is nothing but our c, which we are looking for.

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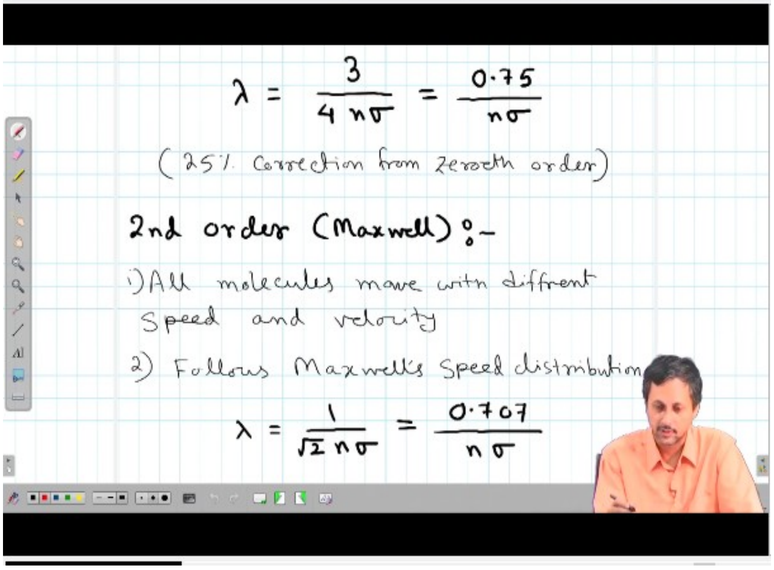

$$\lambda = \frac{3}{4 n\sigma} = \frac{0.75}{n\sigma}$$

(25% Correction from zeroth order)

2nd order (Maxwell) :-

i) All molecules move with different speed and velocity

2) Follows Maxwell's Speed distribution

$$\lambda = \frac{1}{\sqrt{2}\, n\sigma} = \frac{0.707}{n\sigma}$$

So, going back to this expression, we will have to simply substitute. So, we go back to this expression once again. We have to simply substitute c with four third c bar and the final expression that we get is lambda = 3 4 n sigma, which is 0.75 n sigma which is a 25% correction over the zeroth order approximation. Now, the next one is the second order approximation, which is a very involved discussion where it is by Maxwell's actually.

Now Maxwell assumes that all molecules move with different speed and velocity when I say different speed and velocity that means different magnitude and direction. So, everyone is going in a random manner, just the way we think of Maxwell speed distribution function. So, basically all the molecules have different speed and basically different velocity because they are colliding with each other moving in different directions. And then the gas assembly also follows the maximal speed distribution law.

And we are not going into this detail calculation, these are worked out in the book, if all the textbooks have mentioned, if you are interested, you can go through it, it is almost like in the textbooks itself, it is a 2 to 3 page calculation not going through it, but finally, we get an expression which is lambda = 1 by root 2 pi n sigma which is 0.707 n sigma. Now, with a very simplistic model and a simple averaging, we can get 0.75 and with a much more complicated calculation much more complicated involved mathematics we get 0.707 and the ratio of this 2 is 94% is 0.94.

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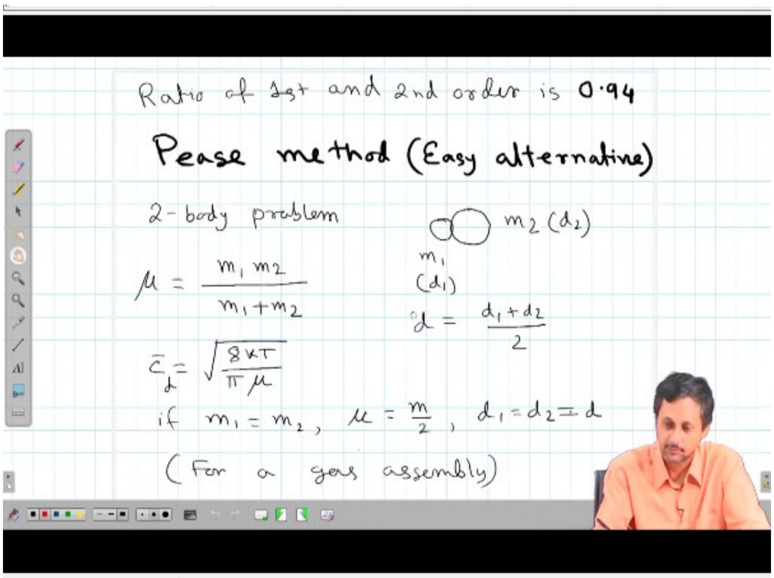

Ratio of 1st and 2nd order is 0·94

Pease method (Easy alternative)

2-body problem

$m_2 (d_2)$

m_1
(d_1)

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$d = \frac{d_1 + d_2}{2}$$

$$\bar{c}_d = \sqrt{\frac{8kT}{\pi \mu}}$$

if $m_1 = m_2$, $\mu = \frac{m}{2}$, $d_1 = d_2 = d$

(For a gas assembly)

So, the first order approximation is almost 94% accurate as compared to the more detailed second order approximation. Now, it so, happens that, although we do not want to go into the details of this derivation, there is a very simple way of deriving the exact same expression and that was by piece. So, it is an easy alternative, we get the same expression and but again it might look over simplified to you, I also think that way, but anyway I thought I will discuss it.

So, what Pease did was he essentially, you know, treated the molecular impact as a 2 body problem. Now, in a 2 body problem, we have 2 molecules m 1 and m 2 with radius d 1 and d 2. So, the d between them we are diameter d 1 and d 2, so, that d will be the impact distance d will be d 1 + d 2 divided by 2 because it is a 2body problem, the effective mass has to come into picture.

So, this system will have an effective mass mu which is given by m 1 m 2 divided by m 1 + m 2. So, for this 2 body case, the mean speed of the gas assembly will be simply reduced to root over 8 kT by pi mu instead of pi m. Now, once again if we are talking about the uniform gas assembly, where there is only one type of gas molecule present, we simply have m 1 = m 2 and d 1 = d 2 = d then mu becomes m by 2.

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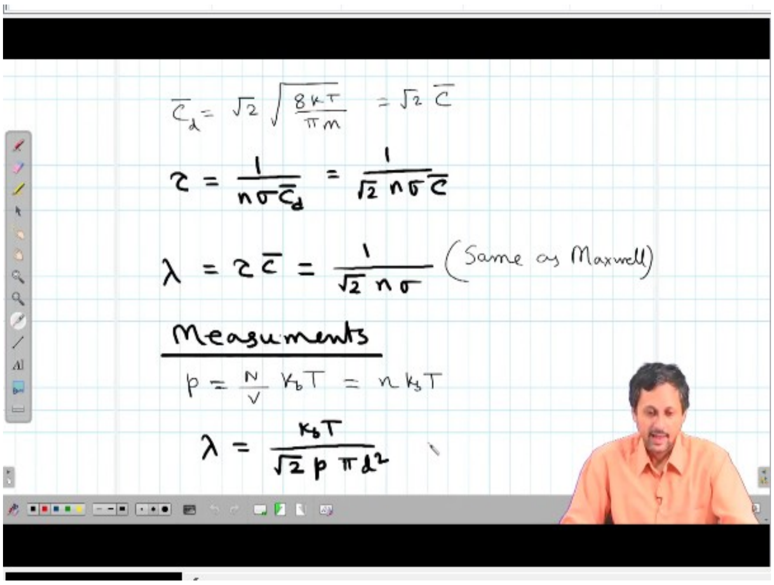

$$\bar{c}_d = \sqrt{2}\sqrt{\frac{8kT}{\pi m}} = \sqrt{2}\,\bar{c}$$

$$\tau = \frac{1}{n\sigma\bar{c}_d} = \frac{1}{\sqrt{2}\,n\sigma\bar{c}}$$

$$\lambda = \tau\bar{c} = \frac{1}{\sqrt{2}\,n\sigma}$$ (Same as Maxwell)

Measuments

$$p = \frac{N}{V}k_bT = nk_bT$$

$$\lambda = \frac{k_bT}{\sqrt{2}\,p\,\pi d^2}$$

And c d that is the 2 body diameter so, this is the 2 body mean speed of the system, it just becomes root over m kT by pi m but because m is replaced by m by 2 there is an extra factor of root 2 comes out here, which is root 2 c bar. C bar is the mean speed of the Maxwell distribution and this very simple treatment gives you the exact same expression of tau and lambda which we get from the Maxwell's detailed more elaborate calculation and that is root over 1 by 2 n sigma.

So, now we see that what are the actual or what are the detailed physical way of dealing with these problems? We have also come up with proper expressions for the mean free path lambda and the mean free time tau of course, they are related by the simple relation that lambda = tau times c bar. C bar being the mean speed of the Maxwell's speed distribution function. Now, it comes to measurement.

How do you measure that experimentally, because as I keep repeating the same thing over and over again unless and until you can measure something, the theory is not proved? So, mean free path and all everything is good, but how to measure it experimentally and basically how to measure it experimentally. In the next class, we will have a discussion on that, but let me quickly tell you that there is a very simple way of writing this expression for lambda and tau in terms of the measurable parameters that is pressure, volume and temperature.

Remember, especially for an ideal gas, the ideal gas equation is PV = N k B T, so, this is the familiar form PV = N K b T, all I did is I just took this remove this V from here and took it into the denominator, then N by V = n in this expression and this expression. So, P = n k B T. So, all we have to do is we have to substitute for n with P by K b T and we write lambda = K b T divided by root 2 P pi d square.

If we have an idea of the molecular diameter and if we know the temperature and the pressure of the gas assembly, then we can very easily measure the mean free path. And once we know mean free path also we can know mean free time, because this is just a factor of c bar between them. And c bar is the mean speed, which is totally determined once again from this parameters?

Because if you recall, c bar is nothing but root 8 kT by pi m. If we already know kT, we are we are good and all we need to know is m. So, all we need is the temperature of the gas assembly, the pressure of the gas assembly, the diameter of the molecule and the mass of the molecule in order to estimate the value of lambda and tau., So, that is why we stopped today. In the next lecture, we will be talking about how to determine the parameters lambda experimentally in a proper experiment how do we measure that and we will also solve some problems. Thank you.