Advanced Chemical Thermodynamic & Kinetics
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Lecture – 11
Transport Phenomena – I

Hello everyone. So, in today's lecture in this topic we will start about the Transport Phenomena. Now, what you mean by transport phenomena?

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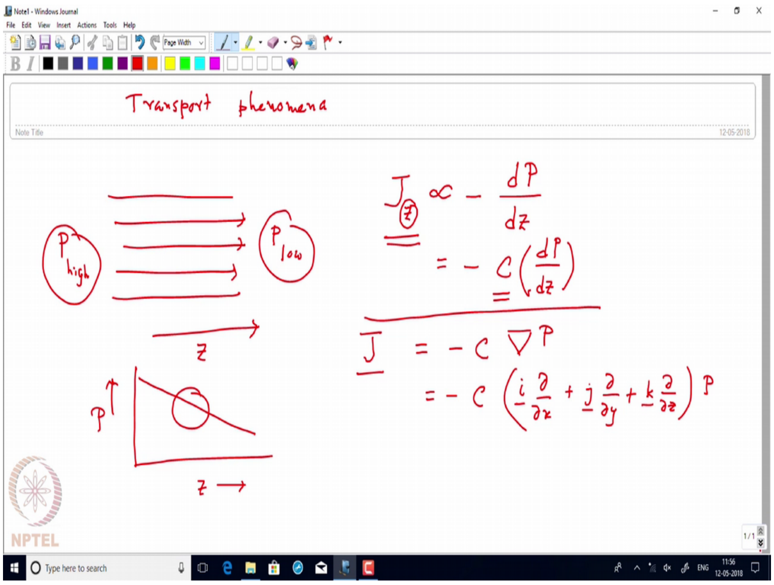

So, as the name suggests transport phenomena means it is the transport of certain quantities. For example, this certain quantity can be say for example, heat or say just a mass and all these things we can actually have or we can formulate under a generalized formulation that we are going to discuss.

Now, when you talk about transport it can be transport through gas or in a gaseous medium on transport through liquid which means, actually transport in handling involves a fluid medium. Now, because the fluid actually flows and then we talk about the generalized transport equation, where transport of something again the something can be heat or something can be a mass actually flows due to gradient of some other quantity. For example, if you have a temperature gradient like you have a variation of temperature then you will have a flow of heat.

Similarly, if you have a concentration gradient then actually you will have a flow of mass and these are very obvious like why things flow if I have a temperature gradient. But so, we are not going to discuss at the microscopic way how it is happening we will give some picture. But what we are going to do is a rather phenomenological approach, in the sense we know that there is a gradient of some quantity and something is actually transporting or being transported across this gradient.

Now, how do you approach this problem? Now, think about a very simple problem that I have a tube and some water is suppose flowing through this tube or suppose instead of water let us think about I have a pipe and then some gas is flowing. And, the gas is flowing from say due to the pressure difference where I have a P high and P low something like that. So, the pressure on this right hand side is low than the left hand side and that is why the gas is flowing from left to right.

Now, in this case I can actually define a quantity which is some transport quantity and I will call it as in general J. Now, J is known as flux I mean we will connect it later and why it is called as flux and what is the importance of flux, how you can derive it. Now, this J is this transport of this quantity the flux it can be again flux of heat, it can be flux of mass something like that. And, in general flux means the quantity being transported per unit area per unit time and that I am saying will be proportional to some; in this case actually it is proportional to the gradient in the pressure.

Now, if everything is one-dimensional I can just write it this is nothing, but the pressure gradient as a function of z. So, if this is the z direction so, that is why I am writing suffix z. So, transport of along z or the flux along z of that quantity is proportional to the pressure gradient along z. And we then write the proportionality constant as C which will define later, what is this constant and how will you evaluate this constant.

Now, as you can see that in this equation the pressure gradient in the positive z direction is negative because, pressure is higher here and pressure is lower here. So, usually the whichever quantity you are talking about either it is a mass or its heat that flow from the high temperature gradient or high concentration gradient to the low concentration gradient or low temperature gradient something like that. So, if we plot the gradient if the gradient is linear for example, if we had plotted pressure versus z; I will see if I am increasing the z the pressure is following.

Of course, it is an oversimplification because I have written it as the gradient is a linear function, but whatever it is I see it is a negative quantity. The slope the slope is equal to the gradient which means actually then by definition the flux will be negative by our mathematical formulation, but by definition the flux cannot be negative. So, in order to keep the formulation consistent what we do is that we introduce a negative sign here. So, that this constant also is positive my left hand side the flux is also positive and d P d z is negative, but if I take negative of d P d z that is positive. So, this will be our general formulation.

Now, although flux the way we have written it is a scalar, but strictly speaking actually it is a vector quantity. And because, it is transport in a particular direction and truly speaking if you want to write it properly in vector notation. We have to consider the gradient of pressure where, actually these gradient is nothing but the special gradient which is itself is a vector i del del x plus j del del y plus k del del z of P. Where, this i j k are the unit vectors along the three Cartesian coordinates.

But, we will be using only very simple notation in the sense that will be just restricting ourselves as if it is an one-dimensional gradient and everything is flowing in a particular direction. Now, next thing so, this equation is known as Poisson's equation and the next thing we are going to understand is what is this flux. In the sense that whatever we have told so, far that it there is some quantity called flux and this flux as we have denoted it as; flux did in this case actually we are talking only along flux along z direction which we wrote as J suffix z.

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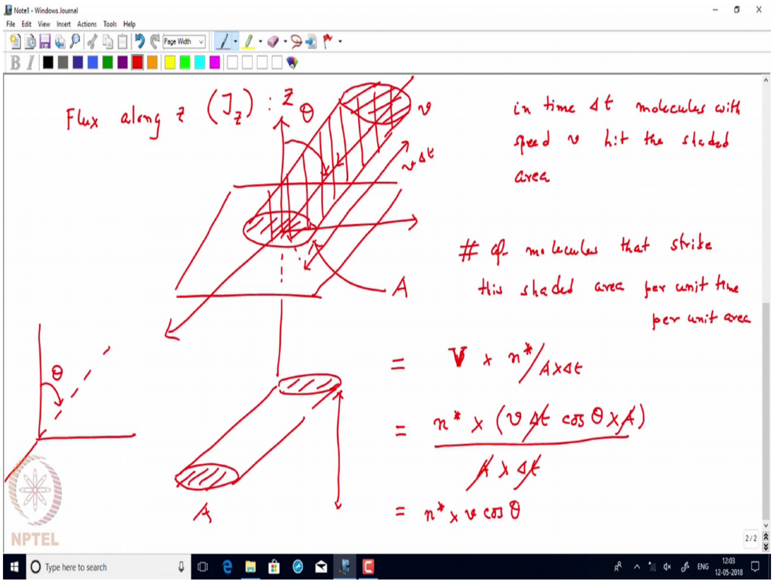

Now, this has as we said that it has a molecular origin although, again we are not using any explicit nature of the molecules we will be using it very classically in the sense. And, we are only doing it phenomenologically and we are just describing the phenomena, if the molecules move how the flux will what will be the mathematical expression for the flux.

Now, suppose I have some arbitrary surface in my system and all I want to calculate is how many molecules is crossing this surface per unit area per unit time because, that quantity is related to the flux. Now, also all we want to do is that we want a jet projection of that quantity because we are only considering the flux along z axis or z axis. Now, let us draw a picture. So, what we are saying here suppose we have some surface. Suppose, this is the particular area that we are considering and let us say that that cross sectional area of this particular shaded region is A and this is the positive z axis, this is my coordinate system.

And then of course, I have actually this three-dimensional coordinate system; I am only considering the flow along z axis. And suppose, some molecule is coming at some angle and hitting this surface hitting this said suppose, this molecule has a speed of say v ok. Now, the question we are asking is that how many molecules are going to pass through this surface per unit area per unit time. In order to understand that let us suppose, that the molecule or set of molecules have speed say v in this direction which is striking this area and which are coming from top.

Now, we can say that what is the say in time delta t how many molecules will actually with the velocity v will strike this particular area. So, this is very simple to calculate because, we can always say that the molecules which are within the distance of v into delta t. So, they will come and hit this surface because, v is my speed and delta t is the time speed into time interval is nothing, but the distance traveled. So, those molecules which are actually lying within this cylinder which cylinder this cylinder and has a speed in that direction and the magnitude of the speed is v will actually come and strike this particular shaded region which is has a cross section of A. So, this is as simple as that.

So, then I can also calculate the total number of molecules because, I have to calculate the total number of molecules passing through this area per unit time per unit again divide by the area to get the per unit area concept. So, in time delta t molecules with speed v say hit the shaded area. That, was our starting point and then which means the number of molecules which are basically we want to calculate the number of molecules that strike this shaded area that will be nothing, but whatever are the molecules those molecules which are basically lying (Refer Time: 11:09) cylinder.

So, I how do a calculate it? I have to calculate the volume of the cylinder and times the density of the molecule. So, how to calculate the volume of the cylinder? Now, see that this cylinder is a slant cylinder it has something like this, it has a cross sectional area. The base area is A and it has a slant like this something like this.

Now, let us assume the cylinder has this axis and this axis is making an angle theta with respect to the positive z axis. So in our spherical polar coordinate concept so, this is nothing, but the azimuthal angle which is the inclination with respect to the positive z axis so, the vertical height of the cylinder we can easily calculate if the distance is v into delta t, the vertical height will be v into delta t into cosine theta. So, the volume of the cylinder v times the density of the molecules that will be nothing, but v times n star let me actually replace the v first. So, v is nothing but now, the base area times the vertical distance and the vertical distance as you just said it is v delta t into cos theta. Let me write that n star first. So, I will write n star times instead of v I am writing small v which is the velocity, this v is the volume capital v delta t into cos theta.

Now, this is basically the height times the base area will be the following. So, this quantity is volume of the slant cylinder. Now, all we are interested is not the number of molecules that right this shaded area, but we want to calculate a quantity which is per unit time and basically per unit area. So, that can be easily figured out. So, we just have to divide it by area times the time. So, it has to be divided by A times delta t. So, I will just get these arbitrary things cancelled and all I will be left is nothing but n star into v into cos theta.

Now, we have a situation here. We actually assumed that all the molecules which are coming have a very unique speed, which is v. Now, that is not correct because we know that at any time for a gas molecule; let us assume that this is a gas molecule were talking about we will have a Maxwell-Boltzmann distribution of speeds. And not only that this molecules the speed of course, we have a speed distribution, but think about it these molecules are also coming from different direction. Because, we just took a particular region, particular angle at angle theta it is inclined with respect to the positive z axis, but there could be actually other angles. So, we have to consider those angular distribution also.

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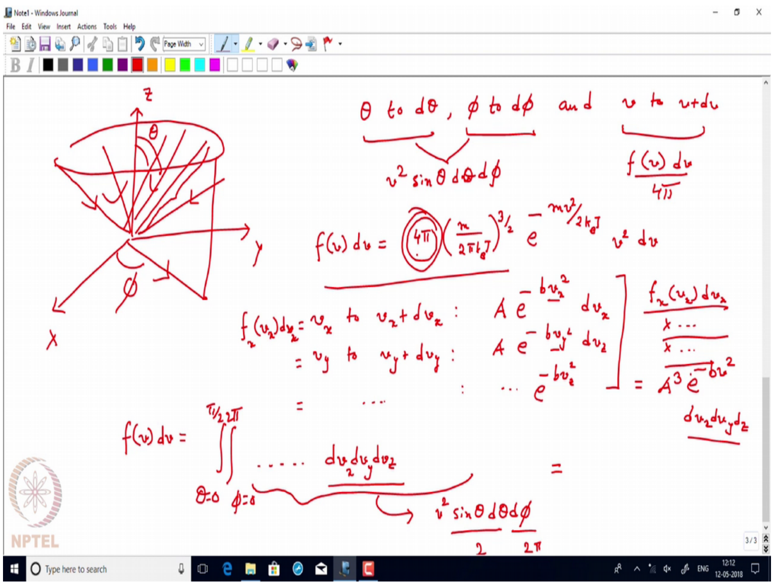

So, what we have now right now saying is that we just told that some set of molecules which are lying with in the distance P into delta t. And, for those molecules I calculate the number of molecules which have that condition which have velocity v and how many of them are crossing per unit area per unit time that is what we have calculated so far. But then as I said the molecules will have a distribution of speed and secondly, these molecules are also coming at different directions.

They can come from here also, they can come from here and not only that so, the inclination angle will be very different. And not only that as you can see the molecule can come from a same angle, but from a very different direction. In the sense that their projection on this X Y plane that angle is also going to change. So, we have to actually integrate over these two angles also.

So, what we are going to do right now is to make a more general form. In the sense that I am saying that I will have I am going to calculate some flux which is let us say from theta to d theta, if we value the angle little bit. As well as the other angle phi to phi plus d phi and if I have a velocity distribution, if I go to v to v plus d v. What will be the quantity?

Now, already we know that this from theta to theta plus d theta and phi to phi plus d phi we rotate our vector. Then we generate a cross section area and we know that from the knowledge of our spherical polar coordinate system that this area comes out to be sine theta d theta d phi. And with r squared thing, but they then actually there is nothing called r, it is actually a velocity space we are talking about. So, this volume will be basically v square into this and if you want to take a distribution of molecular speed. So, that means, actually we have to multiply the entire thing by the Maxwell-Boltzmann distribution of molecular speed.

Now, we have a problem here because if you remember when we write the Maxwell-Boltzmann distribution for molecular speed, we write basically 4 pi into some constant which is m by 2 pi k B T. You can actually go back and check this Maxwell-Boltzmann distribution, e to the power minus m v square by twice k B T into v square d v. So, it basically says what is the fraction of molecules or what is the probability of molecules of having speed in the range v to v plus d v. When you say speed it is independent of the direction, but now actually we are going to use the Maxwell-Boltzmann distribution, but we are again imposing the condition that there is a directionality.

Now, if you remember if you have studied this thing how this 4 pi factor comes, you will readily realize that when you derive the Maxwell-Boltzmann distribution we first considered a velocity distribution, like say velocity for v x or something like that, what will be the probability for v x to v x plus d v x. And that we got something like some constant into e to the power of minus some constant into b v s squared something like that.

So, then what one does is that then we consider the isotropic nature of the gas molecules. And then, we say that the y distribution will also be something like this and similarly for the z distribution also. So, together then we see that if we take the multiplication because we know that the x component distribution and the y component distribution and the z component distribution, these are also a probability distribution. And since, the distribution at any direction is independent of the other direction we take the total distribution as a multiplicative thing.

And then we just simply do this multiplication v x d v x into v y into d v x d d v z. Then all this individual distribution give you something like A cube e to the power minus b and then the all these exponential terms will actually add up. Because, exponential a plus into exponential b into exponential c is nothing, but exponential a plus b plus c. And that way v x squared plus v y square plus v z square give you v square and then you were left with some volume element which is d v x d v y d v z.

And then in the next step you integrate this volume element, in the sense that you say that all I want to calculate is a speed distribution independent of the direction. And that you calculate from this quantity which we just wrote here, but you integrate now over all the spherical polar angle in the velocity space. Now, what we are right now doing we are doing a quick here we are saying that so, let me just write it what do you had done. So, we take theta from 0 to pi by 2 phi from 0 to 2 pi and then integrate this function into d v x d v y d v z. And, instead of d v x d v y d v z we use the spherical polar value which is v squared sin theta d theta d phi.

And this differential value now integrate and if you integrate it you can easily see that the integration of sin theta d theta over 0 to 2 pi will give you 2. And integration of our d phi over 0 to 2 pi will give you 2 pi and this gives you this 4 pi factor. Now, we do not want to introduce exactly or use that exactly the Maxwell-Boltzmann distribution here because, the Maxwell-Boltzmann distribution is already integrated for the different angles it is a speed distribution. So, we want a similar distribution up to here, in the sense that we want will integrate it once again.

So, we want a speed distribution which is dependent on the direction and then we will further integrate just like we did for the Maxwell-Boltzmann distribution. So, long story short what we are going to do is we are going to actually multiply it by a distribution function for this velocity. But, which is not actually Maxwell-Boltzmann distribution, but rather which is Maxwell-Boltzmann distribution divided by the 4 pi factor.

Because, this 4 pi factor comes after you integrate over the all possible variations because if I write it that will be our original Maxwell-Boltzmann distribution as you can see. So, this divided by 4 pi is nothing, but our original multiplication of the distribution functions along three different directions where it kept the volume element has dependent on theta and phi. So, long story short what we are going to do here, we have already seen an expression for the flux along z. And what we are going to do is that we are going to take this flux, multiply it by the spherical polar volume element.

If I go change it from v to v plus d v r to r plus d r that way and then, what we will get we get a surface element differential surface element which you obtain from going from theta to theta plus d theta and phi to phi plus d phi. And, that will be equal to something like v square sin theta d theta d phi and plus we are going to have one Maxwell-Boltzmann distribution. So together now we are going to add these two things and we are going to see actually what we are going to get with this plus. Please do not forget that we already have a v sitting here.

So, if you do it carefully so, then what we are going to get and remember this Maxwell-Boltzmann distribution what I just said; if I change theta to theta plus d theta and phi plus phi plus d phi and as well as change v to v plus d v. So, v plus to v plus d v means there will be a distribution function, but then I will not take the; there is a v square in the distribution function.

Because, if you remember that we will get this 4 pi v squared term after the integration of theta and pi. So, what we have to do is that division by 4 pi v square. So, I have to take only this part of the Maxwell-Boltzmann distribution. So, like m by 2 pi k B T whole to the power 3 by 2 e to the power minus m v square into d v, but I will not I do not need to write it because we will see that why you do not need to write it.

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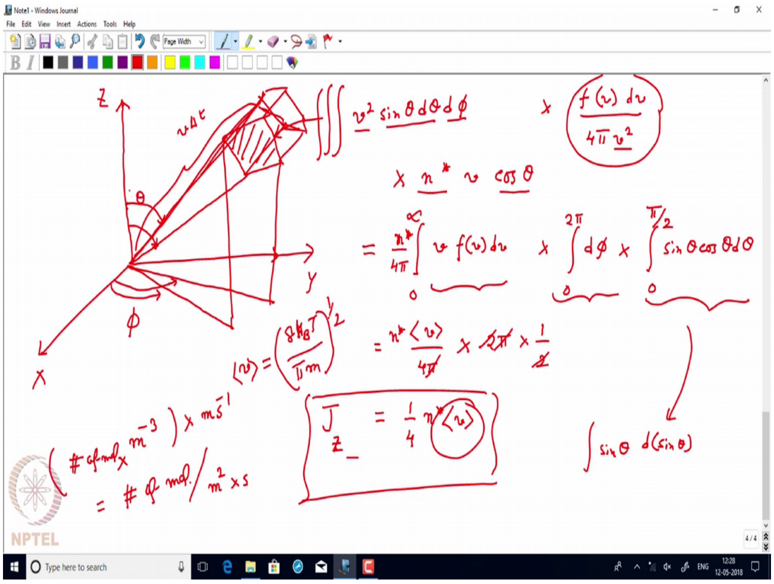

So, let us first try to draw the coordinate system which we just discussed. So, we are talking in terms of the spherical polar coordinate system and first we calculated the number of molecules which are coming in a particular direction. Now, particular direction means it had a particular inclination angle which was theta and it also has a particular angle phi. But, we do not want these molecules coming in this particular angle; we want to actually have molecules coming from all different angles. And for that you have to calculate suppose, I am saying that molecules are coming let us say from all different angles.

So, how I do that? So, I have to vary the angles suppose I change this theta to theta to theta plus d theta is a small angular increment and this is basically the small angle is d theta. Let me just draw it more clearly. So, this is theta and this is theta plus d theta and similarly I can also sweep an another angle from pi to say phi plus d phi. So, let us say this is the phi to phi plus d phi angle.

So, together what we are going to see here is that we will actually sweep an area going from theta to theta plus d theta and phi to phi plus d phi and this area is v squared sin theta d theta d phi. So, that is the area, but then what I am saying here my speed is also varying; meaning this axis if you remember what we had is the distance and this distance is nothing, but v into delta t now, that is also varying.

Now, I am saying that I will also vary v to v plus d v. So, if I do that then I just have to multiply it by d v and then I will get a differential volume element, the way I have drawn it and that will be just multiplication by d v. In this case it is d v into delta t, but we are dividing it by delta t at end of the day. So, it does not matter really. So, what we have is this quantity. Now, the same way we also derived the Maxwell-Boltzmann distribution and then what we did we just integrated over the sin theta d theta.

But, we will not integrate it first and then again use the values we will first use the probability distribution in a general form because, our flux also depends on the angle and this all this distribution. So, we will use the distribution where actually all these things are present times I have to also this include the speed distribution which is f v to f v plus d v. But keeping in mind that we can actually associate the d v like here because we are considering a range of speed but, we have to divide by 4 pi v square because that was the total volume after integration.

So, this is basically my distribution function and that is a probability function. And, that we are now going to multiply with whatever we got for a single speed in a single in a unique direction and that was if you remember that was something like n star into v into cos theta. So, just do it I will just multiply by n star into v into cos theta and then we will integrate it. Now, so integrate it for what? It to integrate it for theta phi and v, again theta is this angle and as you can see that theta is going from all possible angles. Similarly, phi is also going from all possible angles. Now, what we can do here we can play a trick here now, let us have a look here what we have just derived.

Now, you can see that I have for this v square and this v square will cancel. So, I have the Maxwell-Boltzmann distribution. So, for the v integral it is nothing, but v into f v d v and the integral of v between and the range of speed is basically 0 to infinity. And then, there is a 1 over 4 pi now this is nothing, but the expression for the average velocity average speed sorry. So, we will write it as average speed divided by 4 pi, we do not need to actually explicitly use the Maxwell-Boltzmann distribution.

And then, what we are left with we are left to it this d phi that is a straightforward integration between the limits 0 and 2 pi and then we are left with the theta integration. We have sin theta d theta plus we have a cos theta and this cos theta is coming because we had a generalized formulation, where actually the cylinder was a slant cylinder for an arbitrary molecule coming with an angle theta. So, that is why we will have here sin theta cos theta d theta and that integration is between 0 and pi. Now, I did not tell this. So, you can think about it this integration will not depend 0 and pi. Why? Because, what I am saying is basically a flux now, flux as a direction.

Now, you can think that my entire coordinate system the in the X Y plane I have an X Y plane here, this is the Z axis. And suppose, this X Y plane actually divides the system into two halves and then I am considering the flux which is the net downward flux. So, I do not need to consider the flux which is coming from the bottom. So, you can think about it this is a sphere and I have divided the sphere into two halves by the X Y plane. So, I have two hemispheres. Now, I am only considering the molecules which are coming from the top and crossing this thing because flux has a directionality.

So, I am talking about crossing the surface which is lying along the X Y plane. So, I am talking about directionality for flux all on causing the plane. Now, you might argue that there will be also molecules coming from the bottom, we will do it later. First, we are considering the net downward flux and from this actually what the way we will integrate it; we just integrate it from 0 to pi by 2. Because, for a hemisphere if you remember my inclination angle will be just up to the X Y plane. So, this angle the maximum angle is pi by 2 not pi.

So, that is why we did not use the Maxwell-Boltzmann integrated Maxwell-Boltzmann distribution. We just used up to the point before the integration which gives us this 4 pi v square that is basically, surface area of the sphere of radius v. So, that part we did not do because we will integrate over the hemisphere. But we took the probability distribution in the most general that depends up to on theta and phi. And that part is nothing, but 4 f v d v divided by 4 pi v square by simple argument and then we used it. And this pi integration readily gives you the 2 pi and this integration now, we can think about it.

What is this? This is sin theta cos theta d theta. Now, cos theta d theta is nothing, but d of sin theta. So, this integration is also very easy. So, it is just integration of sin theta and d of sine theta it is x d x kind of integration. So, the integrand is x square by 2 in this case is sin squared by 2. Now, sin square evaluated between pi by 2 and 0 sin pi by 2 is 1. So, sin square phi by 2 is also 1 and sin 0 is 0. So, 1 minus 0 is 1 and the integrant was remember it was 1 by 2 because it is x square by 2.

So, we will get half factor here. So, what we will get is nothing, but we will get one half factor and then if you see here these 2 and 2 cancels, these pi and pi cancels. So, what we will get is one-fourth, we had an n star also here I did not write it. So, I will have a n star over 4 pi this n star and I will have a n star into v. So, I will have one-fourth n star into average velocity. So, this is basically the expression for my flux up to this point, but this flux is the net downward flux.

So, I can actually write a minus sign for that because it is just the flux describing the downward thing. So, up to this I have somewhat general expression for the flux. Now, let us quickly check what is the dimensionality? In the sense that the what we just got is the flux is connected to n star 1 4 is a number. So, n star is a density, if you remember that we just calculate the total number of molecules by taking the volume of the cylinder multiplied by the density.

Now, density means per unit so, 1 over centimeter cube or 1 over meter cube. So, let us use actually the meter cube notation. So, it will have something so, it is basically number of molecules times meter cube that is the dimension of n star. And, what is average velocity it is just a velocity and average velocity will be meter per second kind of thing. So, together what we are getting the dimension is number of molecules or number of particles in some cases times you will have meter to the power minus 2 and second to the power minus 1.

So, which is nothing, but number of molecules per unit square area per unit time. So, that is what the definition of the flux and it is not surprising that we have got the correct definition. Secondly, this average velocity which we wrote here you know the expression for the average velocity it is 8 K B T by pi m for using Maxwell-Boltzmann distribution. Now, we will see that we will just make this expression more; I mean we will just make it more and more correct. Because, as you see that we did not calculate here the net there are also downward flux. But, then we have to consider that the molecules are coming from top molecules are coming from bottom also, but is there any net flux across the surface.

Now, for an isotropic system like suppose I have a chamber I have a container and I have a gas which is in perfect equilibrium. Now, if we consider any plane you will see the net downward flux and net upward flux are same. So, in that case it will be 0, but if there is any concentration gradient or pressure gradient along the z axis then the flux will be very different. And, in that case actually you can have a net flux going in a particular direction that we are going to right now calculate.

Now, in order to do that we need to understand we need to actually model the system and we can model the system, as if that the system I have different planes. And, I am considering flux along a particular plane that is the way we did it like the X Y plain and we are considering this plain. Now, we will consider along z axis where which is our axis of choice along which axis we are calculating the flux. We will first say that let us, think that along z axis I have multiple layers and I will just choose one particular layer and consider the flux across that layer. So, let us now proceed.