Molecules in Motion
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Lecture – 39
Molecular motion in gases (Contd.)

Welcome, to another chapter or another lecture on Molecules in Motion. What we had began in the last class we will we could not finish, in fact, we are just begun and we have to end the discussion.

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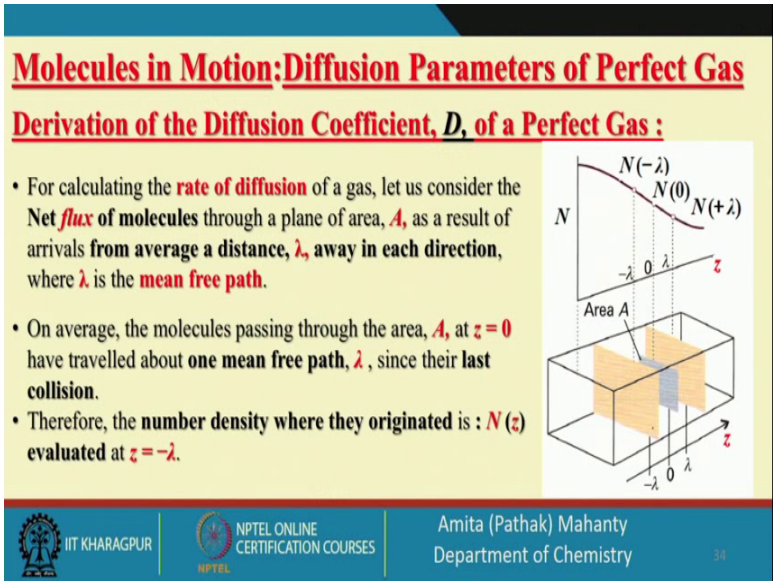

And, the discussion was on finding out the definition expression for diffusion coefficient of a perfect gas using the kinetic theory of gases. When you are talking about kinetic theory of gases this was the expression this was the question we had taken up which we have not discuss in previously remember the distribution of the graph of our interest is a window of area A. We are looking at the particles which is reaching the window after travelling a distance of one mean free path; that means, after travelling a distance of lambda; that means this lambda is the distance travelled between since the last collision of the molecule.

So, if you had a collision here, the next collision will be here on the window of interest and if that has to happen then the molecules have to travel a distance lambda, ok. So, that is how the mean free path is defined. So, what we are looking into we are trying to define

the diffusion coefficient for that the rate of diffusion of a gas is considered for that for that we have to calculate the net flux of molecules that is passing through this window.

As a result of arriving from a distance of say lambda minus; that means, from left side to right side also by travelling a distance lambda plus; that means, from right side to left side. When I am travelling when the molecules are travelling from the left side to right side then you see if I project that into the distribution of number of molecules with distance then you see the lambda minus correspond to a location where the number of number density of the molecules is higher compared to that or the region of the window. So, I take that as 0 where lambda is equal to taken to be the origin.

So, if this is the distance which is going to travel when it is travelling from say minus lambda; that means, left hand side to right hand side that means it is moving from a higher concentration of the numbers to a lower concentration. And, how was that number concentration taken, we have discussed that in the last class. But, here again I am going to say when I am looking at the molecules moving I am looking at specific window area A, I am seeing in the next flux that is passing through that in a window of area A as a result of molecules travelling a distance of one mean free path from either direction.

One mean free path means that the next whatever collision they had previously the next collision will happen on the window of interest, ok. So, this is the distance it is going to travel between the collision; that means, the next this collision should with the wall should happen at a distance lambda and this is the distance which we are looking into.

And, if I want to find out the number density at the various locations and what is the number density in this place what is the number density at this place and this place what we had taken.

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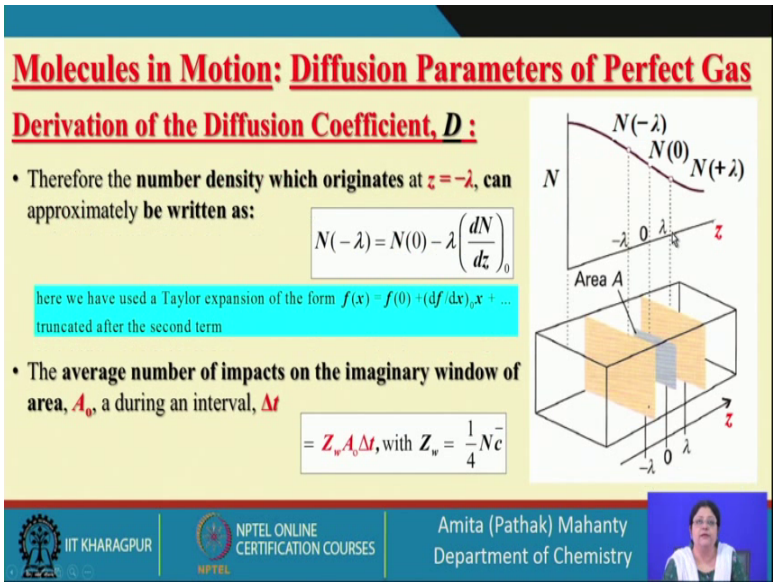

We had taken the Taylor series expansion of the Taylor series which we said the number of number density of the particles or molecules at this region; that means, at lambda equal to at z equal to minus lambda is going to be a position which going when to be a value which is equal to the number density at z equal to 0 plus or minus; here what I have? I have minus the slope of say the change in number density with the distance the slope is decreasing.

So, I have a slope which is decreasing; that means, that I at any of this position what do I find out what is going to be the value of number density it is going to be slope of this curve; that means, change of number density with distance it is which is actually when into that location because each at each location you have to find out you can get the number concentration of the particle. So, what is going to be that I say like that distance be lambda. So, we can have a higher series then truncate the whole series at only the first differential and what I see it is the number density at minus this point if the number density this minus the slope of that plot which is already a minus into the lambda the distance it is travelled.

And, this is located doing the we are doing it as 0 means Z equal to is 0 at considering that and the condition. Now, the number of impact which is happening on the surface is the number of frequency of collision which is there on the wall which is nothing, but the

number of Z w into the area of interest into delta time t and if I want to find out what is going to be the flux of these collisions on the molecule on the surface of the wall.

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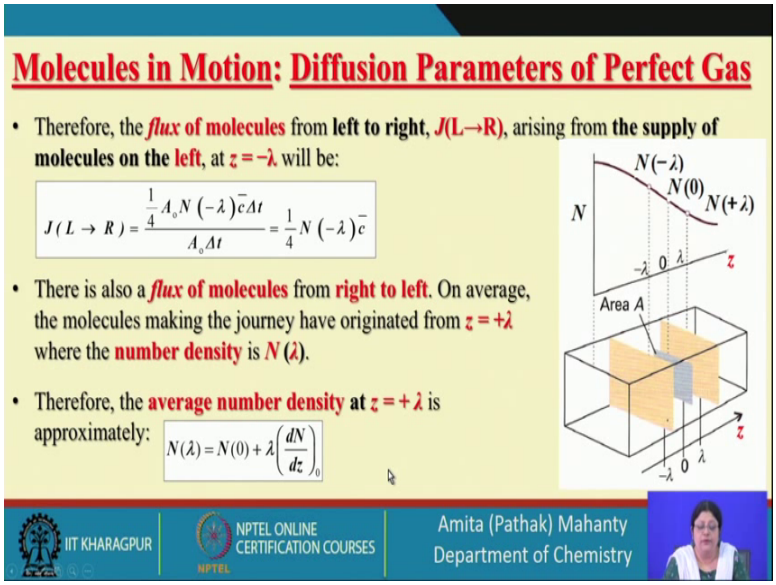

Then, I should divide this by A 0 by 80 and then the total number which you have here to total number of molecules which is going to be cover coming to this position will be what, will be the total number of molecules contain in this volume element. What is the volume element the molecules are moving with the mean relative speed of c bar and in delta time t. So, c bar delta t is the distance and this is the area A or A 0. So, A 0 into c bar delta t is the volume element this is what we have taken and if this is the number density which you are talking about. So, that we have to be multiplied and if that as the if you take the expression previous expression it is 1 by 4 and if you divided by the area of interest I mean the time taken that gives you the flux and flux and as the molecules are moving from left side to right side.

So, what you get you get a expression of 1 by 1 by 4 number density at minus lambda into the relative mean speed. So, therefore, there is also a flux of molecules which is moving from the right side to the left side, the average molecules making the journey have the originated from z equal to plus delta lambda when. So, we have if we want to find out the number density at say at this point and this point what will that be it is gone all of this is move to this side. So, I can remember this is of a lower concentration, ok.

Movement it is what we are looking is from right hand side to left hand side I am looking at moving from this site to this side, ok. So, what I have according to the Taylor series I have the molecules at the z equal to lambda this is a molecule at z equal to lambda number density will be the number density at z equal 0 lambda equal to 0 into the slope of the number density with distance this slope into the lambda, this distance is travelled. So, we have now you see.

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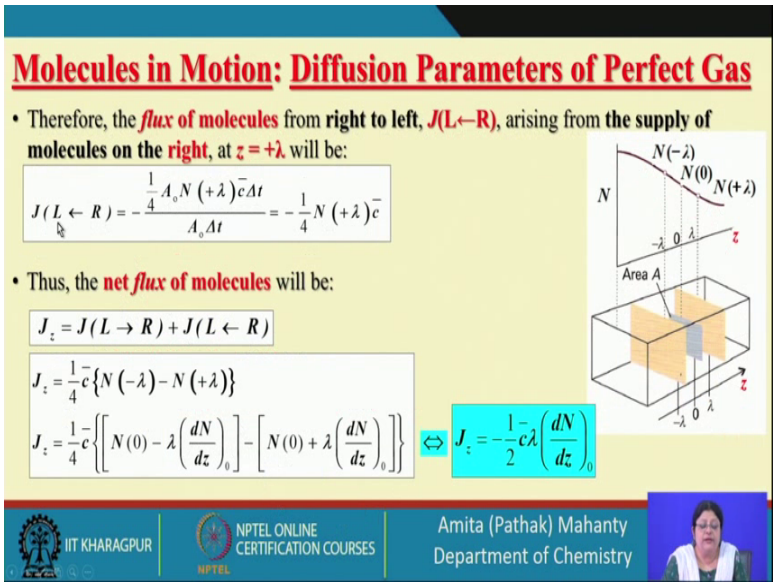

Similarly, you can be invade the flux for that and flux for that will be what the flux for that will be 1 by 4 again here you have the positive lambda value of lambda is positive here see the again this will cancel up I hope you understand this because we have been talking this for quite some time now. How to find the flux? Flux is the total parameters whatever molecules and or atoms which are undergoing the transport process divided by the area of interest into the time interval delta t.

So, this is the number of molecules which is going undergoing impact with the wall and impact with the wall how many molecules are going undergoing the impact with the wall; all the wall molecules which is contained in this volume element. What is this volume element? The molecules are moving with the mean speed in relative mean speed of c bar and in delta time t. So, this is the distance, this is the distance into the area of interest whatever is contained in this volume element will be moving and how many

what in that volume element what is the number density, that is going to be the number density at lambda minus, minus lambda.

And, according to the number of impact which we have I have 1 by 4. So, I am reduced to having 1 by 4 N minus lambda c bar, ok. The flux of molecules from right to left now I have taken left to right now take right to left, what should I have this is the value of number density at lambda plus value; that means, this position. Now the flux of molecules from right to left arise from the supply of molecules on the right; that means, this side will be having a negative sign and so, if I want to find out the because this is if I take this movement as positive. This movement should be negative this movement has to be positive because it is according to the from lower higher concentration to lower concentration and here the movement is from the lower concentration of higher concentration so, it is opposite.

So, we have to take a indication that whenever we are talking about movement from right side to left side we have supply of molecules from right side to left side at z equal to plus lambda the values will be 1 by whatever you had for the minus a lambda case, for this case the number of a number density at minus lambda that will be 1 by 4 into the relative mean speed, but you will have a minus sign.

So, to find out what is the net flux at the window which is of our interest what we need to know? We need to we have to add two flux; flux which is moving from left side to right side; that means, moving from higher concentration to lower concentration plus the flux which is moving from lower concentration to higher concentration. What does this negative thing mean? Negative flux cannot be negative it is meaning that it is moving on the opposite side it cannot move from the lower concentration to higher concentration side.

So, if I have to find out the what is the flux the net flux I have to take I have taken this is the flux value from the left hand side to right hand side the value at left hand side to right hand side was 1 by 4, c bar I can say common minus is coming from this one for the particles for the number density at lambda plus, ok. So, this is the flux I get this is the flux at when you are moving from right to left and what is the flux which you have when you are moving to right left to right this is the expression, ok. Now, you minus this and

plus this we will get all the things can be taken common only the number densities at the lambda minus minus the number density at lambda plus.

Now, we substitute the values of number densities if you see the number densities was given to be something like this, ok. So, substitute this for the position lambda equal to z equal to lambda plus and z equal to lambda minus. So, this is corresponding to lambda minus. So, it is number of density at x equal to z equal to 0 minus lambda into the slope of the number the change of number density with distance that is z minus what you have you have you have the number density at x equal to z equal to 0 and the differential of plot of number density with distance into lambda.

So, if you see this if these will cancel of what you are getting? You are getting this is going to cancel of you getting twice of this. This is also minus, this is also minus you will get a minus sign and twice of this. Twice of this number density with distance, slope of that twice of that into lambda into the relative mean speed and overall you have 1 by 4 outside. So, 1 by 4 multiplied by 2 becomes 1 by 2. So, 1 by 2 with a negative sign this is the flux along the J.

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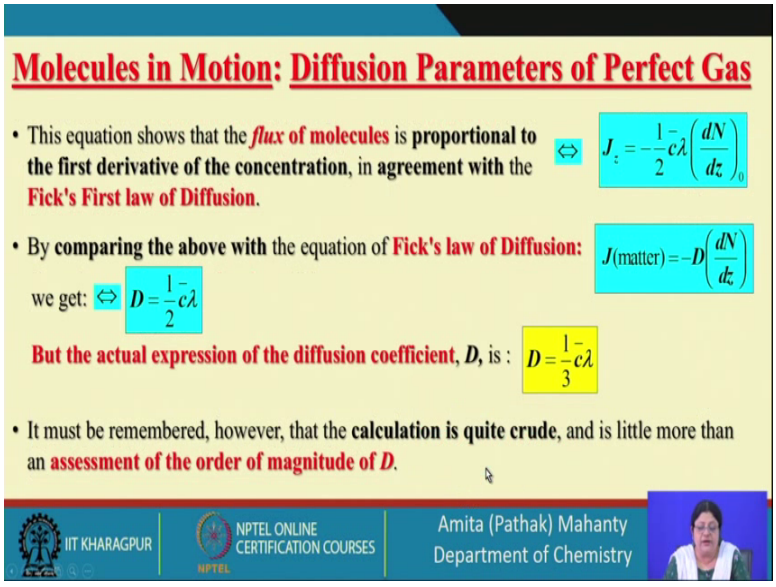

Now, if you look at this equation more carefully you will see that the flux of molecule is the expression is saying the flux of molecule is proportional to the flux derivative of the concentration, and that to a negative sign. And, this nothing, but the Fick's law of diffusion Fick's first law of diffusion. If you compare the Fick's first law of diffusion and

the expression which we have derived just now, what do we have? This is the Fick's first law and this is the expression of flux of molecules which we have derived. So, this is both of them have negative sign, this is these are negative concentration gradient, this is the number density gradient for flow of matter or flux of matter, then we can compare and see that the D can be equated to half relatives mean speed into lambda. This is the expression we get from the kinetic theory.

But, what happens is when if you see the table you will see that the value is 1 by 3 lambda into the mean speed the relative speed c bar. So, how do we get that value what is the reason why we get 1 by 2 not 1 by 3 remember all these calculations are very crude this is these are only used to find out the magnitude of order of D not exactly the precise value of D.

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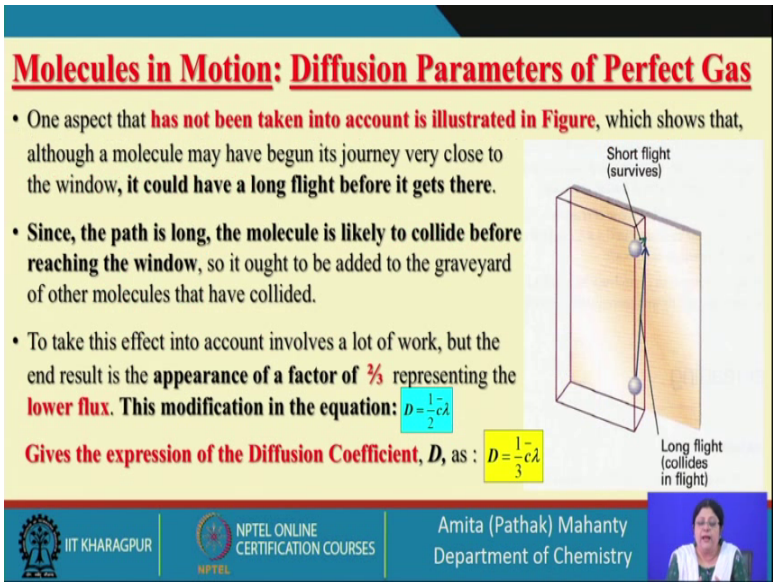

What happens in when you if you look at this diagram, if you have taken account of the molecules which are undergoing collision and if you are trying to find out the flux the aspect which we have not taken into account or neglected if the if you see this the molecules may have a began a long distance a journey very far away very a molecule may begun it is journey very close to the window, it may actually may have a very long flight

So, if it is actually it is flying from here to here, but it the collision is taking place close to the window, ok; that means, if this is within the if this is lambda, but in spite of the

fact that it is lambda it is actually having a very long flight. Since the path is long the molecules is likely to collide before they reach the window. If the path is too long then there are possibility there are n number of possibilities that the particles will be moving a long distance and if the particles are moving in long distance is not possible that they will reach the window without colliding so, there are chances of colliding.

So, what we are looking at, we are looking only at the particles which are supposed to be very close by and within the distance lambda. We are not we have overlook the fact that this molecule which we are looking into may have a very long flight and it ought to have gone into the graveyard of the molecules that have collided. And, because if you have collided and lost that is we do not consider those sort of particles.

But to take effect of these accounts which we have not let done we have not considered a molecule which may have gone to a long distance before coming to the collision point which the collision distance is from the wall maybe small, but it is gone through a very long flight, but we have neglect that we have only consider them to be reaching the flight reaching the window distance which is covered maybe probably 1 lambda, but actually it may have collided before and should have been ideally gone to not to be considered.

So, for this effect to be taken into account what we have seen it has been seen that if you take a factor of 2 by 3 and multiplied with the values which you have then you get the realistic values which is supposed to be lower flux than what you get what you get from the calculations. So, the equation which you have for the D is 1 by 2 into the mean free path into the concentration and relative speed relative mean speed, but actually what you get if you multiply with this by 2 by 3 then 2 gets cancelled you get 1 by 3 mean relative mean speed into the mean free path.

So, this is the value which is more appropriate which is what is lifted in the if you can see I do not have it in this lecture, but if you see in the previous lecture there you will see the expression for D is something like this. And, that is because we have taken into account the long flight molecules which would otherwise have should have contributed, but actually should have been going to the should have been buried because they probably go undergo a collision before reaching the window.

So, if I to have a correction factor of 2 by 3 multiplied by the whatever um flux we have generated if you can do that if you do that multiplication it has been seen that you go

closer to the value which you observe so, this D value is here. Now, D equal to 1 by 3 and that is the more acceptable value.

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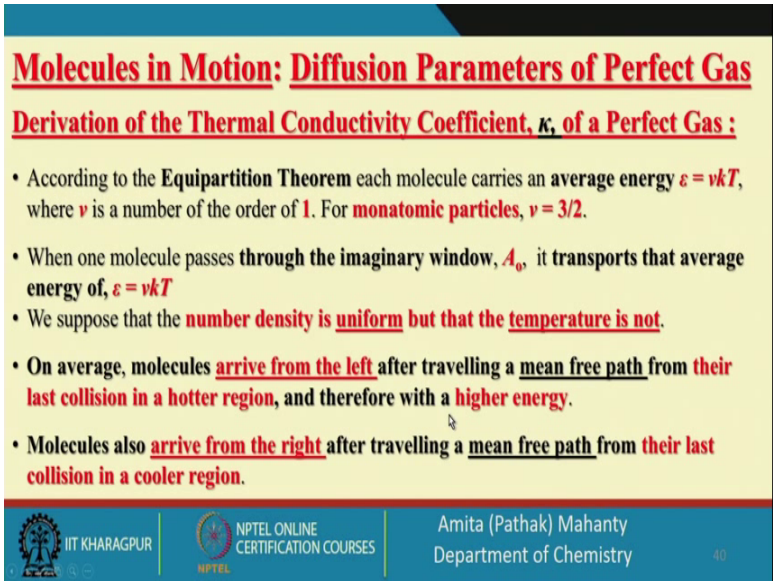

Now, we have; what we have done, we have derived the expression for diffusion coefficient based on the kinetic model and based on the condition that we are looking into number of particles moving through a volume element, where the volume element is actually considered as the window of whichever molecules reach the windows contained in the area or volume surrounded by what do you say what is the it is moving with a speed say relative mean speed of c bar and in time delta t. So, c bar into delta t is the distance between the window and area of the window.

These multiplication of A into the distance c bar delta t is the volume element we are talking about locating the molecules located in this volume element will collide with the surface of the window and that is how we are looking into how the collisions are getting impacted. And, from that impact of the collision we are calculating the various parameters. We have calculated the diffusion coefficient now consider let us consider the thermal conductivity coefficient.

For considering the thermal conductivity coefficient, we have to remember that we are looking into the molecules which are propagating or getting transported, but each of them will carry some certain energy. So, according to equipartition theorem what you have the average energy which is going to be carried by the molecules is going to be

epsilon k T, right and I put a nu because depending on whether the molecule is diatomic or monatomic or complex molecules the nu of that energy should be changing.

So, according to partition theory you have the average energy to be e equal to nu k T; nu k T nu is the one which is you write down 3 by 2 kT 5 by 2 kT. So, nu for a diatomic molecule and for monatomic molecules will be different. So, we do not want to distinguish between what is the condition of the nu value because it depends from it will be different for a monatomic to a diatomic to a complex molecule we will keep it as nu, ok.

For monatomic particle molecule the nu will be 3 by 2, right. So, the molecules passing through a imaginary window A 0 it transports the energy or the average energy which is going to be transported by those molecules is going to be number of molecules into the average energy carried by them what is the average energy carried by them e that is equal to nu k T, where k is the Boltzmann constant and T is the temperature in Kelvin.

Suppose, what we are assuming the number density is uniform there is no distribution no concentration or number density difference in the medium only change is in the medium is the temperature, ok. So, when we are talking about the thermal when we want to derive the thermal conductivity coefficient we have to assume that the number or the concentration of the particles is uniform throughout the medium only difference is the temperature, and all the molecules when passing through the window A will transport the total energy equivalent to what each of the molecules are carrying average energy carried by each of the molecule into the total number of molecules, right.

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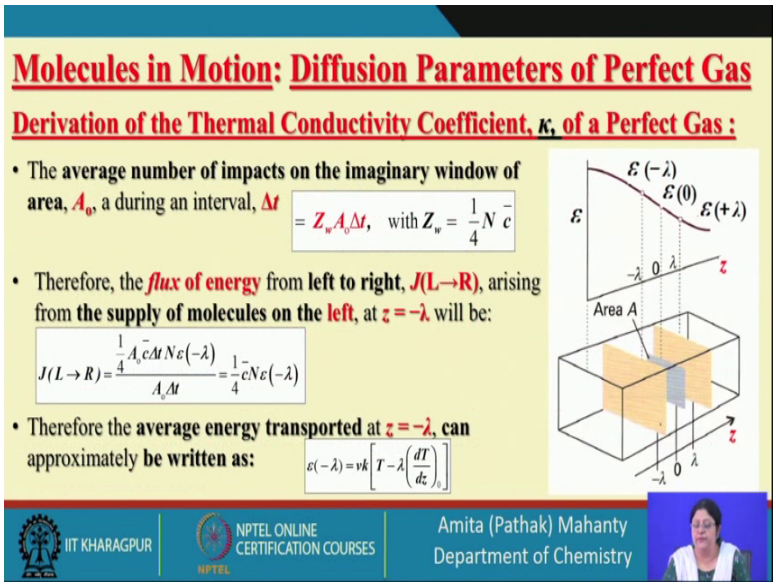

So, on the average the molecules arrive from say left hand side. Let us see what we have we can have from left hand side and from right hand side see left hand side I am putting that as lambda minus means if you are having a location where the energy is higher. Energy will be always again flow from higher to lower. So, what we have? We have, sorry. So, what we have? We are having an average molecules right from the left after travelling a mean free path distance from their last collision in a hotter region and therefore, the energy that they are higher in energy understood.

So, whichever particle which is coming from the left hand side and travelling a mean free path distance lambda that is the time which they had last collided was anywhere and next collision would have been in the window of interest. So, that is going to be this distance going to be lambda and I designate that as plus lambda so, a minus lambda. So, whenever the molecules are moving from left and travelling a mean free path distance from left to right and that means, it is moving from the higher energy to lower energy region.

Molecules similarly will arrive from the right side travelling a same mean free path distance from the last collision, but that will be from a cool edition, right. This will be much cooler region. So, this molecules when they are travelling they will be going it is not possible for the molecules to move from the colder region to high energy region. So,

this will be always having a negative sign indicating that the flow is spontaneous in the reverse direction.

The number average of the impact which you have on the wall it is going to be given by 1 by 4 N capital N into the mean relative speed. So, if I want to find out the flux of energy from left to right, the flux of energy from left to right this is the left to right arises from supply of molecules from the left side and left side will be always at a higher energy. So, if I can see what is going to be the total number of flux of energy which is going to be associated on that impact I have to see what is the total number of number molecules present here and each of the molecules is having a average energy of nu k T.

So, I have to multiply the total number of molecules which is present in this volume element into nu k T and what is the total number of molecules which is present in the area of interest they are the A is the area of window, c bar is the distance at the mean relative speed which they are travelling in delta time t. So, A 0 into c bar into delta t is the total volume element. So, this is the total volume element, and into the total number of molecules this is the number density and each of the molecules will have a energy e, ok. So, this energy is now evaluated at lambda equal to x equal to minus lambda I am taking a movement from a distance of lambda from the left hand side.

So, from the left hand side this is the total number of collisions per unit area gives you the flux. So, flux is 1 by 4, c is the mean velocity relative speed into the number density into the energy associated the average energy associated includes at z equal to minus lambda. Now, if we want to find out the average energy which is getting transported we had talked about the number of molecules which is getting transported. Now what is the average energy which is getting transported? Average energy which is transported is the energy here plus if you have this energy associated at z equal to 0 and then you take the energy at this point with any point here will be the slope of distance which is the temperature difference between these two regions; that means, dT by dx into the in position at which is this happening.

So, what is that the total the average energy transported will be at x equal to minus lambda; x equal to minus lambda is this position, have a look at this. This will be nothing, but it will be e at 0 T, ok. What is e; e is nu k T. So, instead of writing e as 0 we have because it does not make sense to have a 0 temperature. So, so what we have taken

is instead of writing like we have written here we written here 0 instead of writing 0, what we have taken is the energy at t that is nu k T minus the nu k T into lambda into the changing slope of the temperature versus distance.

So, this is the change. How the change is taking place in temperature with distance into the location at which you are looking at the temperature that is lambda that into the nu k will be giving you the energy at any distance lambda and that should be a energy at T, that means, nu k T minus this value, right.

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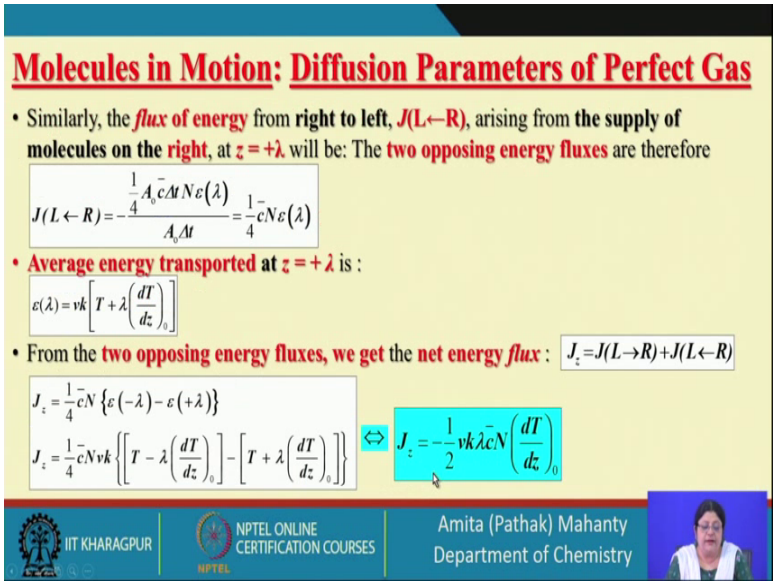

Similarly, the flux of energy from right to left can be also evaluated right is the one where you have molecules moving from a cooler region to a hotter region which is actually not possible. So, we always get a negative sign, ok. So, there will be a negative sign here, ok. So, right to left will be always having negative sign into the c bar number density into energy at a distance x, z equal to lambda. The two opposite flux of energies are therefore, these are the two opposing flux which we have at my flux of energy at lambda minus and at lambda plus. We can evaluate and then we get this value.

We will talk about this a little further in the next class we will begin with the flux of energy and go take over the expression for the coefficient of viscosity a we will ultimately take coefficient of viscosity, but we will first talk about the thermal conductivity.

Thank you so much.