

Transport Processes I: Heat and Mass Transfer
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Lecture – 15
Diffusion: Mechanism of mass diffusion in gases

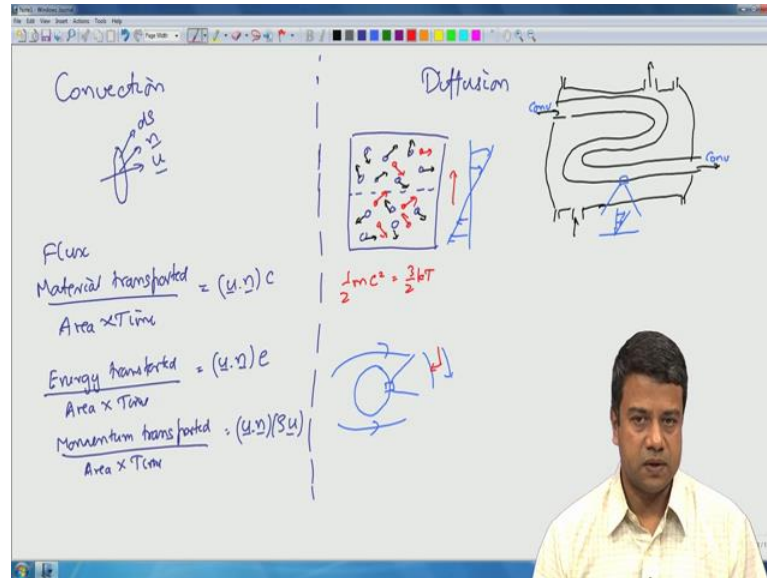
Welcome to this the 15th lecture in our series of lectures on fundamentals of transport processes. In the previous lecture I had given you a brief overview of how we will be analyzing transport phenomena and I said that we will consider the concentration, the temperature and the velocity as fields which are continuously varying functions of position and time and I had specifically given you an idea of how these fields are defined, on the basis of molecular properties such as the molecular density, the number of molecules per unit volume and their mass their momentum and the energy contained in those molecules.

So, before we go on to actually solving problems in transport phenomena based upon this continuum approximation, I would first like to give you a more fundamental idea of the molecular origins of the two transport processes that we will consider that is convection and diffusion. Both of these processes convection of course, as I said is the transport of material, energy or momentum due to the mean velocity of the fluid as a fluid moves along it carries along with it the mass momentum or energy that that it contains and therefore, it can transport it from one location to the other. So, if you transport the fluid it carries along with it its mass momentum and energy.

Diffusion is a molecular process, where there is a transport due to the molecular fluctuating velocities and I had try to give you a distinction between the fluid mean velocity and the molecular fluctuating velocity in the last lecture. The fluid mean velocity is just the average of all the velocities of all the molecules, the center of mass velocity if you will. The fluctuating velocities are the fluctuating velocities of the molecules due to their thermal fluctuations, the fact that whenever the temperature is greater than absolute zero, the molecules are always in a state of constant motion and that motion could actually result in transport of material; if there is variations in the density of mass momentum or energy, from this how do the equations for the fluxes arise the constitutive relations from a molecular description, how does one get the Fick's law

of a mass diffusion, the Fourier's law for heat conduction or the newtons law of a viscosity; that will be the subject of this lecture.

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So, the two main mechanisms as we know our convection and diffusion; now convection of course, is the transport due to the mean fluid velocity, if a fluid at any location has a velocity U that is the mean fluid velocity, this is actually a vector I will use a small u here. So, we do not get confuse later on. That is transporting material across an area $d s$, the flux which is the material transported per unit area into time, across the surface which has a unit perpendicular n , it is just equal to the velocity normal to the surface, times the concentration at that surface the mass density at that surface. You have to dot it with the unit normal because only the velocity perpendicular to the surface, transports material across the surface. The velocity that is tangents to the surface does not transport materials across the surface that is why you need to dot it with the unit pump. So, this velocity times this mass density concentration; you will see a mass transported per unit area per unit time.

Similarly you can do it for energy transporter per unit area into time, will be equal to $u \cdot n$ times the energy density, the energy per unit volume and same for momentum is equal to $u \cdot n$ into the momentum density momentum is a vector and the momentum density is just equal to the mass density times the fluid velocity, that is the fluid momentum density you note that momentum is a vector, so this is the flux due to

convection. Now what is the flux due to diffusion? That is what we are going to see in the next couple of lectures.

Why does diffusion take place? If I had let us say any container in which I had a variation in the concentration of some species, let us say I have a solvent which I showed by the light colour and I have a few solute molecules and let us say that as I have shown in this case the number density is the solute molecules of the concentration of the solute molecules is higher in the lower half of this container in comparison to the upper half. All of these are in a state of random motion, we will see a little later what their velocities are and what their distances that they move. So, all of these are in the state on the motion.

There is no net mean velocity we will assume for the moment that the some of the velocities of all the molecules is identically equal to zero. So, that there is no net mean velocity of the fluid. However, since these molecules are all in random motion and the number of molecules, the solute molecules; the red colored molecules in the lower half is higher than that in the upper half. If you wait for some time on average there's going to be a motion of the red molecules from below to above, in such a way that the concentration is equilibrated everywhere of course, the driving force for this is basically thermodynamic. Entropy prefers to make all the molecules be distributed equally in all regions of space and for that reason the molecules are going to be moving on average from below to above because their concentrations are different, if there were no concentration difference then there would be no average motion of molecules, but since the concentrations are different, there is a net average motion of molecules and that is what is called diffusion. And that diffusion flux of molecules takes place from regions of higher concentration to regions of lower concentration. So, that is the diffusion flux due to the molecular velocity fluctuations of the molecules.

Same thing holds for energy transport; if there were a temperature gradient in this system and let us say that the molecules below had a higher kinetic energy fluctuating kinetic energy on average in comparison to the average molecules above, as I will explained to you in the last lecture the fluctuating kinetic energy half $M C^2$, is just equal to $3/2 k T$, having the higher fluctuating kinetic energy implies a higher temperature therefore, the temperature below is higher the temperature above is lower. Due to the fluctuating velocities of these molecules, you will have transfer of higher energy molecules upwards

and transfer of lower energy molecules downwards. In gases the transfer takes place primarily due to the transfer of the molecules themselves. In liquids it could take place due to molecular interactions; in either case whether it is by molecular interactions or by the actual motion of the molecules, there has to be a net transfer of energy from below to above or from regions of high temperature to regions of low temperature and that is the heat flux due to the variations in temperature of the molecules.

Similarly, if you had a mean velocity field, the molecules above will have on average a velocity that is towards the right; the molecules below will have on average a velocity towards the left or the momentum towards the left. When there is a transport of molecules across the surface, molecules with higher velocity will come downwards and molecules with lower velocities will go upwards and that is going to cause a net transport of momentum, this transport could take place due to either the physical motion of the molecules across the surface or due to molecular interactions and this is what causes the stress of the momentum transfer across the surface.

So, therefore, transport of mass momentum and energy, due to the fluctuating velocity of the molecules. In gases it is primarily because the molecules move across a surface physically, in gases as I tried to explain to you in the last lecture the distance moved between interactions is much larger than the diameter of a molecule therefore, the transfer of energy across the surface of momentum or mass into molecular interactions is going to be much lower than the transport due to physical motion across the surface. In liquids the distance between molecules is comparable to the molecular distance and therefore, the rate of transport across the surface is going to be primarily due to molecular interaction. This mechanism is actually ultimately responsible for the transfer of heat mass or momentum in all the practical applications that we had seen. If you recall when we had done the problem of the heat exchanger, the fluid comes in and goes out in this transfer of energy, as I told you the fluid coming in and going out is due to convection. So, here you have convection.

However if you take a look at a small differential surface area at the surface, you have fluid that is being conducted past that surface and there is no fluid velocity perpendicular to the surface and therefore, ultimately transport across the surface has to take place due to diffusion, due to molecular diffusion. Similarly in the case of the catalyst particle that we had studied there is of course, a fluid flow around this particle that is either due to

impeller, due to exerted pressure differences across the fluid and so on. But; however, if you look at a differential surface element, there is no fluid flow perpendicular to the surface because of the no penetration condition and therefore, transfer ultimately has to take place due to diffusion perpendicular to the surface and that is why this diffuser transport is such an important topic.

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Diffusion coefficients & constitutive relations:

Gases:

Number of red molecules coming downwards = $BC \Big|_{z=A} U_{rms} = \delta^-$

Area \times time

Number of red molecules going upwards = $BC \Big|_{z=A} U_{rms} = \delta^+$

Area \times time

Net Flux $J = BC \Big|_{z=A} U_{rms} - BC \Big|_{z=B} U_{rms}$

$(C \Big|_{z=A} - C \Big|_{z=B}) - A \lambda \frac{dc}{dz} \Big|_{z=0} + \frac{(A \lambda)^2}{2!} \frac{d^2c}{dz^2} \Big|_{z=0} + \dots$

$(C \Big|_{z=A} - C \Big|_{z=B}) + A \lambda \frac{dc}{dz} \Big|_{z=0} + \frac{(A \lambda)^2}{2!} \frac{d^2c}{dz^2} \Big|_{z=0} + \dots$

Net Flux = $B U_{rms} (C \Big|_{z=A} - C \Big|_{z=B})$

$= -2AB \rho U_{rms} \left(\frac{dc}{dz} \right)_{z=0}$

So, let us look at how does one estimate the diffusion coefficients? So, I will talk about first diffusion coefficients and constitutive relations; first let us look at the case of transport and gases, let us say that I had some differential volume, so let me take specific equipment. The equipment that is often used to measure diffusion coefficient is this double bulb, where you have one particular molecule in one half in one bulb and another one in the other.

And then you typically you will have a stopcock across it, which is open so that now these molecules can mix with each other and you try to measure the time that it takes for the mixing to take place, once you open this wall between the two. Now if you look at this particular region and expand it, take a look at this particular region and expand it what you basically have is the surface across which diffusion is taking place and you have molecules on both sides, for the moment we will assume that these molecular masses are equal so that there is no center of mass motion as the molecules move across.

So, that if I plot for example, the concentration of one of these molecules is a function of distance that concentration is varying in somewhere. This let me call that as the z distance. So, the z distance will be the distance along here, the z distance is the distance perpendicular to the direction of diffusion. If you plot the concentration here let us say of the red molecules, this will be higher above and will be lower below, it will have some variation across the surface in a concentration and these molecules are all in a state of random fluctuating motion.

Now, if you look at the molecules that are actually crossing the surface, if you look at the molecules that are actually crossing the surface from below and from above. The molecules that are crossing the surface from above are coming not from the surface itself, but on average from some distance above the surface; the molecules that are crossing from above to below are coming on average from some distance slightly above the surface, some of them are closer some of them are further away, but on average they are coming from some distance slightly above the surface, this distance in the case of gases is of the order of the mean free path. So, this distance in the case of gases will be of the order of the mean free path, it is about two-thirds the mean free path, if you actually do a calculation based upon the distribution of velocities and so on, but in some number times the mean free path above the surface.

Similarly, the molecules that are crossing the surface from below to above are coming from some distance slightly below the mean free path to the surface that distance once again is of the order of the mean free path. Now there is no net change in the number of molecules from above to below or vice versa because for every molecule that goes from above to below, there is one that goes from below to above because there is no mean velocity therefore, the velocity fluctuations have to be equal, positive and negative therefore, the number of molecules that are coming from below to above is equal to the number that is coming from above to below.

However, since there is a higher concentration of molecules above the surface of the red molecules and a lower concentration below the surface, if actually plot the concentrations at these two locations for the red molecules these are different. Therefore, the number of red molecules coming down is higher because it is coming from above the surface, where the concentration is higher. The number of blue molecule, red molecules going up is lower because it is coming from below the surface where the concentration of

red molecules is lower and this difference is what is called is, what is it results in the diffusion flux of molecules.

So, let us try to write down an expression for the number of molecules coming downwards; this will be equal to the concentration of the red molecules, this concentration has to be at a location z is equal to some constant a times λ , I told you that constant is two-thirds, if you do an exact calculation ok. So, this is equal to the concentration at that location, times V_{rms} velocity, the root mean square velocity of the molecule V_{rms} ; we will come back to what that is. So, this is the concentration of that location above the surface, times the root mean square of the fluctuating velocity gives you the number of molecules coming downwards of these red molecules.

This is the number of red molecules coming downwards per unit area into time. So, this is similar to the convection flux except that instead of the fluid mean velocity, I have substituted the molecular fluctuating velocities of the molecules, the root mean square measure of the molecular fluctuating velocities of these molecules.

Now, number of red molecules going upwards; this I will call this as the flux coming downwards per unit area into time, it is going to be equal to the concentration, at the locations z is equal to minus λ because these molecules are coming on average from the location that is below the surface, I have taken z is equal to 0 as the location of that surface. Times V_{rms} , I will call this as the flux going upwards therefore, the net flux j will be equal to what comes down upwards minus what goes downwards. So, this is equal to C at z is equal to minus λ , times V_{rms} minus C at z is equal to plus λ , times V_{rms} .

I should note that typically in these expressions for the flux, if it would the mean velocity it would be an exact equality, since it is the fluctuating velocity the quality is not actually exact because you have molecular fluctuating velocities it will depend upon how you define the fluctuating velocity; whether it is the average velocity or the root mean square velocity and so on. So, in these expressions you also have another factor here which is a factor which is out of one, that is the expression for the flux. Now if I can make the continuum approximation, I told you previously that the continuum approximation is valid. So, long as the length scale for variation of the concentration is much larger than the molecular scale that limits the continuum approximation is valid.

In that case I can write the concentration at z is equal to minus A lambda, will be the concentration at z is equal to 0, minus A lambda $d c$ by $d z$ and z is equal to 0, plus A lambda square whole square by 2 factorial, d square c by $d z$ square (Refer Time: 24:34) is equal to zero, plus Taylor series expansion, at z is equal 2 minus a lambda, similarly at z is equal to plus A lambda, is equal to C at z is equal to 0.

So, if I can use the Taylor series expansion and substitute these expressions into this equation, I will get an equation for the net flux. So, therefore, the net flux is equal to BV rms in to C at z minus A lambda, minus C at z plus A lambda and if I substitute these expressions at z minus A lambda and z plus A lambda, you can see that the linear terms will all cancel out because I am taking the difference between these two concentrations the linear term will cancel out, the quadratic term will also cancel out, this is also positive in both cases and that will cancel out.

However the term that is proportional to the first derivative; the zeroth derivative and the second derivative will cancel out, because they appear with equal signs in both the expressions, the term with the first derivative will not in general cancel out and if I substitute that in there I will get minus $2AB$ lambda V rms, $d c$ by $d z$.

This once again (Refer Time: 26:27) is equal to zero. So, this is the equation for the net flux and now this equation for the next flux I can compare it with the equation that I get from the Fick's law of a mass diffusion.

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$$j = -2AB \lambda v_{rms} \frac{dc}{dz}$$

$$j = -D \frac{dc}{dz}$$

$$D = 2AB \lambda v_{rms}$$

$$A = \frac{2}{3} \quad B = \frac{1}{4}$$

$$D = \frac{1}{3} \lambda v_{rms}$$

So, I will just write this equation here, the expression that I got for the net flux was equal to minus $2 A B \lambda V_{rms}$, $d c$ by $d z$. If you recall the Fick's law of mass diffusion was equal to minus 2 minus. The negative sign because the mass is transferred from regions of higher concentration to regions of lower concentration. So, therefore, the concentration gradient is positive; that means, mass has been transferred in the negative z direction vice versa. So, comparing this you get an expression for the diffusion coefficient, the diffusion coefficient is basically $2 A B \lambda V_{rms}$.

I told you that A and B are some constants because when we argued that there is a net flux which is proportional to the concentration times V_{rms} it is proportional, if it was the mean velocity it would be an exact equality; however, since is the fluctuating velocity there is a proportionality constant. Similarly we had argued that the average location of the molecules coming from below to above is given by some constant times the mean free path. So, there are these proportionality constants in this expression for the diffusion coefficient.

But subject to that we also get a very definite value for the diffusion coefficient. So, these are actually dimensionless constants, times the mean free path times the root mean square of the fluctuating velocity of the molecules. So, that is the expression for the diffusion coefficient. As I had said earlier, diffusion coefficient has dimensions of the mean free path times the fluctuating velocity, which ultimately gives you length square per time; I told you that all the diffusion coefficients mass momentum and energy all have dimensions of length square per time.

And this expression here the mean free path that is a distance times of fluctuating velocity has the correct dimensions of length square per time. So, to within multiplicative constant, the expression for the diffusion coefficient is just equal to the mean free path in the gas times the root mean square fluctuating velocity and this is because as I told you in gases transport takes place primarily due to the physical transfer of molecules of more exact calculations will actually reveal that the coefficient A is approximately 2 by 3 for monatomic gases; B is approximately 1 by 4 . So, the expression for the diffusion coefficient will be to within a multiplicative constant about 1 by 3λ times V_{rms} . So, now, our task is to determine what is this mean free path and what is this molecular fluctuating velocity of the gases, of the molecules in a gas.

So, that is something that I will try to determine in the next lecture. As I told you both of these are properties of the gas they depend upon temperature pressure and. So, on, but based upon this we can get a very good estimate for what the diffusion coefficient should be, after that after I do that estimate I will then come back and discuss thermal diffusion as well as momentum diffusion in gases and once you have done that we will go and look at what are the expressions in liquids.

So, I hope I have given you some fundamental idea of why diffusion takes place at least in gases and how the diffusion coefficients depend upon the properties of the gas. Now our next task is to determine what is this mean free path and the root mean square fluctuating velocity that we will do in the next lecture. So, I will see you in the next lecture and I will continue this calculation in the next lecture.

Thank you.