

Fundamentals of Transport Processes

Prof. Kumaran

Department of Chemical Engineering

Indian Institute of Science, Bangalore

Module No. # 02

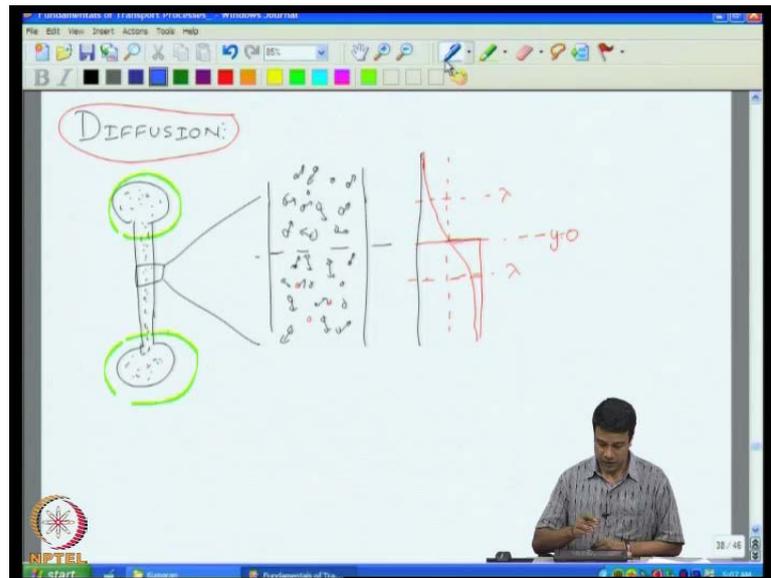
Lecture No. # 07

Mechanism of diffusion – 2

This is the course on fundamentals of transport processes and this is lecture seven, where we will continue our discussion on diffusion. Welcome.

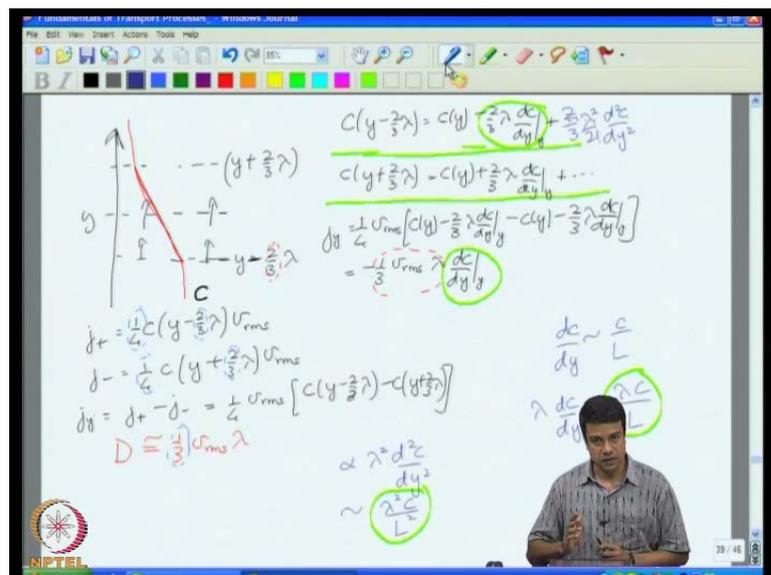
Last class we were discussing the fundamental mechanism of diffusion. As I said there are two mechanism of transport convection and diffusion. Convection is transport due to the mean flow of the fluid, whereas diffusion is the transport due to fluctuations in the molecules. **molecules** of both liquids and gases have fluctuating velocities due to thermal noise. And if there were gradients in temperature, this fluctuation will induce molecules to go from regions where they have higher concentration to regions where they have lower concentration. We took the simple example in the last class, of the diffusion between two chamber separated by a tube. And in the top chamber we have put in pure molecule of one component and in the bottom chamber, **we had** we had little bit of concentration of a solute mixed in, this red molecules are the solute molecules. And of course, diffusion takes place if we have the stop cork between the two chambers and instantaneously remove it. Then, all of these molecules are in fluctuating motion. So, there is no net motion of the center of mass. We are assuming that the concentration of the solid molecules is small enough, that the motion of these molecules does not affect the motion of the center of mass.

(Refer Slide Time: 01:18)



There are fluctuating but there are regions, where the solid is higher concentration is higher at the bottom and region where it is lower. And even though the fluctuating velocity of the molecules have no bias, there will be a net motion of molecules because below the molecules exist and they can travel upwards. Above there are no molecules that nothing travel downwards. Because, this is concentration gradient. This could be a transport of molecules. Fundamental mechanism of diffusion.

(Refer Slide Time: 02:36)



A little more quantitative. Why this diffusion takes place? If we have gradient in the concentration of the solid molecules, then the molecules that are, if we take any particular surface at y , molecules are going upwards and coming from a distance approximately a mean free path below the surface in a gas. Molecules that are coming downwards, are coming from position approximately one mean free path above. The concentration below is higher, the concentration above is lower. Therefore, the molecules on average will tend to flow upwards, if there is a lesser concentration above than below. Obviously, this mechanism works only when there is a concentration gradient. If the concentration are uniform, if there are no variation in the concentration, then the number of molecules going above from below, will be exactly equal to the number of molecules going below from above. There will be no net flux. So, there is no net transfer. Therefore, diffusion is the process driven by a gradient in the concentration. And it is due to the fluctuating velocity of the molecules.

We have done this calculation in the last lecture. On average from below, the molecules that go upwards, come from distance of the order of mean free path below the surface. Mean free path is λ and as I said that if you actually do the calculation, you will find they come from the distance of order 2 by 3 times the mean free path below on average. That is the flux going upwards is equal to the fluctuating velocity of the molecules, times the concentration at the location y minus 2 by 3 λ , times the concentration and times the velocity of the fluctuation.

The actual flux has numerical factor in front of it. Turns out to be one-fourth. And then, we have to do this important step, which was the Taylor series expansion of the concentration about the location y . This is important. I expanded in a Taylor series, in the concentration about the location y and I retained only the first term in that series expansion. That means, I am neglecting all higher terms. And when I did the expansion and then I put that expression in the flux, I got the term is proportional to the gradient in the concentration.

There are higher order terms. The reason we were neglecting them is because the concentration variation has a certain length scale associated to that. If there were concentration gradient between two plates, that length would be the distance between the plates. The flux coming out of the **spherical** particle, that length would be the radius of that particle. It has a length scale associated with that. if that length scale is large

compared to that mean free path, then the variation of the concentration with distance dc by dy is approximately proportional to c by that microscopic length scale. It goes as c divided by that microscopic length scale and you see, this goes as c divided by that length scale.

And therefore, this term here, this term here, λ times dc by dy goes as λc by l , where l is the microscopic length scale. There are higher order terms. I have the next higher order terms in the series, which is plus $\frac{2}{3} \lambda^2 \frac{dc^2}{dy^2}$. If I look at what next higher order term is, it is proportional to $\lambda^2 \frac{dc^2}{dy^2}$. Which is, approximately $\lambda^2 \frac{c^2}{l^2}$. So, this first term is ordered by λc , next term ordered $\lambda^2 c^2$. When the mean free path is small compared to the microscopic length scale l , then this second term is small compared to this first term, the third term is smaller still. In that case, because of that I can neglect the all higher terms. So, diffusion is the phenomenon, that can be described by continuing equations only when the macroscopic length scale is large compared to the mean free path of microscopic scale in the system.

We had looked it estimates of these velocities. See, there are diffusion coefficient that I have got here depends upon two things. It depends upon the root mean square velocity and the mean free path. As I said, diffusion coefficient has dimensions of length square by unit time. You get that out, by writing it as a product of rms velocity and the mean free path. Velocity has dimension of length per time, length is length and you get length square by time as the diffusion coefficient.

(Refer Slide Time: 08:24)

$v_{rms} = \sqrt{\frac{3kT}{m}}$ $\frac{1}{2}mv^2 = \frac{3}{2}kT$ Oxygen: $M_{O_2} = 32 \times 10^{-3} \text{ kg}$
 $v_{rms} = 321 \text{ m/s}$
 $v_{rms} = \sqrt{\frac{8kT}{\pi m}}$
 $k = 1.38 \times 10^{-23} \text{ J/K}$
 $T = 300 \text{ K (room temperature)}$
 $kT \approx 4 \times 10^{-21} \text{ J}$
 Hydrogen: $M_{H_2} = 2 \times 10^{-3} \text{ kg}$
 for 6.023×10^{23} molecules
 $m = \frac{2 \times 10^{-3}}{6.023 \times 10^{23}} \text{ kg} = 3.32 \times 10^{-27} \text{ kg}$
 $v_{rms} = \sqrt{\frac{3kT}{m}} = 1.29 \times 10^3 \text{ m/s}$

So, if I know both λ as well as v_{rms} , I can estimate what diffusion coefficient should be. And that is what, we set out to do next. v_{rms} from liquid partition of energy half $m v^2$ equal to $3/2 kT$. v_{rms} square root of $3kT/m$. And we estimated that as rounded 1200 meters per second, for hydrogen 330, for oxygen comparable to the speed of sound. So, you can take speed of sound approximately, as an estimate for root mean square of fluctuating velocity of molecules in a gas. Mean free path, we had an argument for that. Distance travel between successive collisions.

(Refer Slide Time: 08:55)

Mean free path:
 Volume of cylinder = $(\pi d^2 L)$
 Probability of finding a n^{th} molecule = $(n \pi d^2 L)$
 $n \pi d^2 \lambda \sim 1$
 $\lambda \approx \frac{1}{\pi n d^2} = \frac{1}{\sqrt{2} \pi n d^2}$

Thus, the molecule moves along its width and sweeps out a cylinder, diameter πd^2 where d is the diameter of the cylinder. If the second molecules come within the cylinder, that means, there is collision. And therefore, if the probability of collision approaches 1; that means, that is, molecule is inevitably collided. And therefore, the length of the cylinder is equal to mean free path and probability is approximately 1. And from that, we got $1 = \pi n d^2 \lambda$, n is the number of density, number of molecules by unit volume and d is the diameter.

(Refer Slide Time: 09:41)

The whiteboard shows the following calculations and values:

- $\lambda = \frac{1}{\sqrt{2} \pi n d^2}$
- $n = \left(\frac{P}{kT}\right) = \frac{1 \times 10^5 \text{ N/m}^2}{4 \times 10^{-21} \text{ J}} = 2.5 \times 10^{25} \text{ molecules/m}^3$
- $\lambda = \frac{1}{\sqrt{2} \pi n d^2}$
- Hydrogen $d = 138 \text{ \AA} = 1.38 \times 10^{-8} \text{ m}$
 $\lambda = 0.5 \times 10^{-6} \text{ m} \approx 0.5 \mu$
- Oxygen & nitrogen, $d = 3.7-3.8 \text{ \AA}$
 $\lambda = 6 \times 10^{-8} \text{ m}$
- $D = \frac{1}{3} v_{rms} \lambda = \begin{matrix} 6 \times 10^{-4} \text{ m}^2/\text{s} \text{ (Hydrogen)} \\ 2 \times 10^{-5} \text{ m}^2/\text{s} \text{ (Oxygen, nitrogen)} \end{matrix}$
- Summary values: $D \approx 10^{-5} \text{ m}^2/\text{s}$
 $H_2, He = 1.132 \times 10^{-4} \text{ m}^2/\text{s}$
 $O_2, N_2 = 1.8 \times 10^{-5} \text{ m}^2/\text{s}$

And from that, we got mean free path as approximately 6 into 10 power minus 4 meter per second, **am sorry**, we got the mean free mean path approximately 0.5 into 10 power minus 6 for hydrogen and 6 into 10 power minus eight meters for oxygen, nitrogen. 6 into 10 power minus 8 is about 60 nanometers, 600 armstrong. The diameter of the molecules is about 3 to 4 armstrongs. So, there is large separation between mean free path and molecular diameter.

And on this basis, we got the diffusion coefficient about 10 power minus 5 meter square per second for most gases at standard temperature and pressure. Lighter gases will have a higher diffusion coefficient because the diameter is smaller, they travel longer, their mass is smaller, their fluctuating velocity is larger. Therefore, they will have a higher diffusion coefficient. Heavier molecules will have the lower diffusion coefficient. next we look at fluids, at liquids.

(Refer Slide Time: 11:37)

$$D = \frac{3}{8n_s d^2} \left(\frac{kT}{\pi m} \right)^{1/2}$$

$$D_{12} = \frac{3}{8n_s d_{12}^2} \left(\frac{kT(m_1+m_2)}{\pi m_1 m_2} \right)^{1/2}$$

$$d_{12} = (d_1 + d_2)/2 ; n_s = \sqrt{n_1 n_2}$$

Liquids

$$v_{rms} = \left(\frac{3kT}{m} \right)^{1/2}$$

Effect $D_{liquid} \approx \frac{1}{100} D_{gas}$

$$D_{liquid} = 10^{-9} \text{ m}^2/\text{s} \text{ (small molecule)}$$

$$= 10^{-10} \text{ m}^2/\text{s} \text{ (large molecule)}$$

$$D = \frac{kT}{3\pi\eta d}$$
 Stokes-Einstein relation

And if you just simplistically estimate diffusion coefficient of liquids, you would say that would be about 10 to 100 times smaller than that for gases. Because, the mean free path in the liquid is approximately comparable to the molecular diameter. In a gas, it weighs about 10 to 100 times than the molecular diameter because the mean free path is lower. The root mean square velocity is still given by the liquid partition argument and because of that root mean square velocity of the molecules at the same temperature in liquids and gases are the same.

And therefore, you would simplistically say that the diffusion coefficient of liquid is about to 10 to 100 times smaller. Turns out that is not true. In liquids, small molecules diffusing in liquids, diffusion coefficient is actually 10 power minus 9 meter square per second, four orders of magnitude, smaller than gases. For large molecules it is even smaller. You can go all the way, 10 power minus 11 to 10 power minus 13, all in meter square per second. Physical reason for that, I explained in previous class. The liquids consists of molecules very close to each other. So, if one molecule wants to go in any direction, that the other molecules move out of way. Motion of one molecule is not just an motion of its velocity and mean free path,, but also the collective cooperative motion of the all other molecules around it, in order to allow it, go on particular direction. That accounts to the much smaller diffusion coefficient in liquids.

So, this is mass diffusion. I should emphasize once again, that this is only for tracer for mass diffusion where the concentration of the solute is small. So that, there is no real center of mass motion. We will come back to what happens, when there is center of mass motion, a little later.

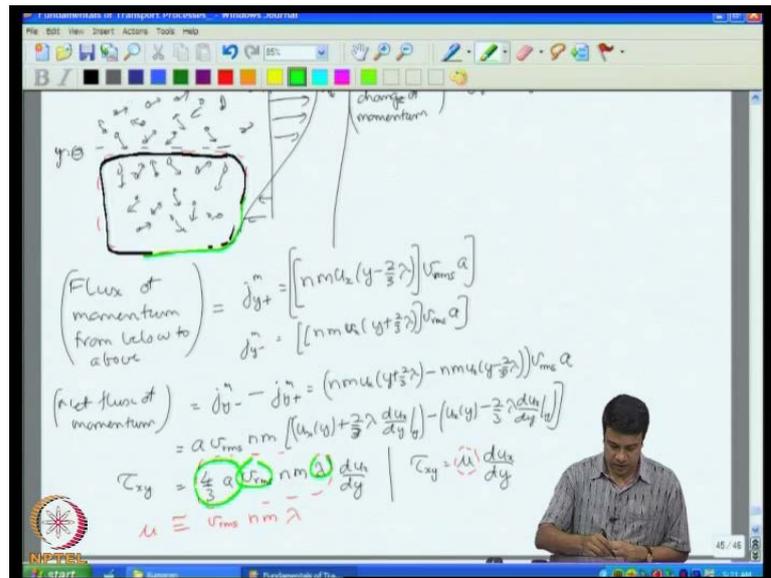
(Refer Slide Time: 12:56)

Handwritten equations on the whiteboard:

$$D = a \lambda v_{rms} \propto T^{1/2}$$
$$\lambda = \frac{1}{\sqrt{2} n \sigma d^2}$$
$$v_{rms} = \sqrt{\frac{kT}{m}}$$

So, in the case of gases, as I said the v_{rms} is proportional to the square root of temperature. The mean free path is independent of square root of temperature. It changes only with the number density of molecules. So, diffusion coefficient goes as temperature to the half.

(Refer Slide Time: 13:40)



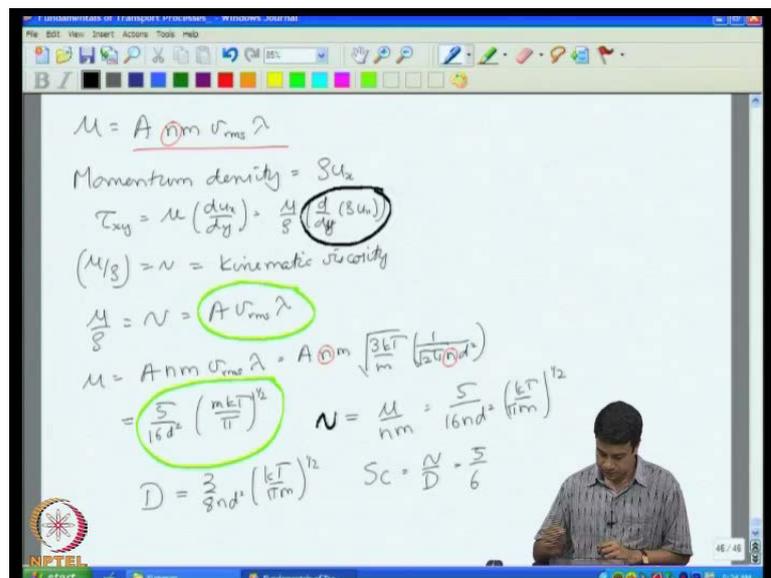
Next we look at diffusion of momentum, fundamental equation. A little bit different. Rate of change of momentum is equal to some of the net forces acting on the molecules, acting on the system. So, we took a fluid with a particular cross section, across which there was a velocity gradient. And if we take this differential volume, we take this volume, then there is an increase in momentum within the volume because faster moving molecules are coming down and decrease in momentum because molecules are going upwards; however, there is the mean velocity gradient, which means that on average the molecules that are coming downwards have a higher velocity than the molecules that are going upwards, because the velocity increases going upwards in this system. So, on average there is net momentum increase of this volume of fluid, because faster moving molecules coming downwards, slower moving molecules are going upwards. Therefore, there can be a transport of momentum, only when there is a gradient in the mean velocity.

And we deduced a very similar argument to calculate the fluxes. On average, the molecules that are going upwards, from below to above, they are coming from the distance of the order of mean free path below the surface; that means, the number of molecules going upwards is equal to root mean square velocity, times the density, times the velocity at the location approximately two-thirds of the mean free path below the surface. Molecules that are **coming upwards** coming downwards from above. On average they are coming from location above the surface.

Therefore, on average molecules that are coming downwards or coming from the location that is two-thirds of the mean free path above the surface. And what that means is that, the flux downwards is equal to $n m$ into the velocity at y plus $2/3 \lambda$, times the root mean square velocity, with some undetermined constants. We are only going to estimate the values, so do not worry too much about the undetermined constants. So, we take the difference between what is going upward and what is going downwards. And we ended up with an expression for the stress.

As some constant, some constant times the root mean square velocity times the mean free path. Times $n m$, n is number of molecules per unit volume, m is the mass of the molecules. Therefore, n times m is the density, **the number of**, the mass by unit volume times the du by dy . Therefore, the viscosity has approximately root mean square velocity times the mean free path, times the number density and the mass of a molecule. Therefore, the shear stress is the viscosity times the velocity gradient.

(Refer Slide Time: 17:28)



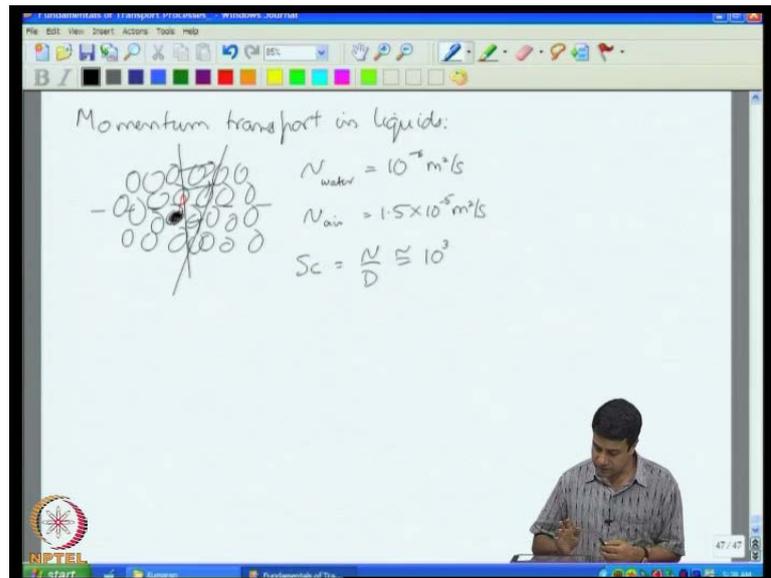
We could also express this, in the terms of the momentum density. ρu_x , where ρ is the mass density, n is the number of molecules into the molecular mass. And we have expressed in that term, we get the shear stress which is equal to μ by ρ times the gradient of the momentum density. If you recall, when we did the diffusion equation, many lectures ago. I said that diffusion coefficient, the flux of the quantity can be expressed as diffusion coefficient times the gradient of the density of that quantity,

quantity per unit volume. Flux of mass is equal to mass diffusion coefficient, times the gradient in density of mass of the concentration. Flux of momentum, momentum diffusion coefficient, times the gradient of the momentum density.

So, here we have gradient of the momentum density and sitting in front, is the momentum diffusion coefficient, which is just equal to the kinematic viscosity, μ by ρ . And it also has dimensions of length square per time and it is proportional to V rms time slab. Therefore, the momentum transport and the mass transport in gases have the exact, the same mechanism. So, in this case for example, the **the** viscosity is proportional to the mass density times the momentum diffusability. You can do more sophisticated calculations and actually, find out what those constants are using kinematic theory of gases. For monoatomic molecules in the very dangerous region, turns out that those constants 5 by 16 d^2 m $k T$ by π half. So, therefore, kinematic viscosity will be equal to μ by n times m , which is equal to 5 by 16 $n d^2$ into $k T$ by m in to π whole half. So, that is kinematic viscosity.

Recall the equation, the formula for the diffusion coefficient. The mass diffusion coefficient that I had got was 3 by 8 $n d^2$ $k T$ by πm power half. So, straight away from this, I can get the split number which is the ratio of the kinematic viscosity of the mass diffusability or ratio of momentum and mass diffusability. Split numbers equal to μ by d which is equal to 5 by 6 for dilute monatomic gases. So, because the mechanism of mass and momentum transfer in gases are the same, both require the physical transport of molecules across a surface.

(Refer Slide Time: 19:58)



Therefore, the diffusability that you get will also be the same. Now, how about momentum transport in liquids. So, anyway we discussed mass transport. I said that mainly, you would expect that the mass diffusability for liquid is about 10 to 100 times smaller than that in gases. Simply, because mean free path is smaller. The fluctuating velocity is approximately the same. Turns out not to be so. Turns out that physical motion of molecules, we require all molecules around it, to also move because the transport of solid molecules, it requires that particular molecule to diffuse through the fluid. So, it requires a physical motion of one particular molecule.

Momentum transfer does not require the physical motion of the molecule. If I have some surface and I have a liquids in which the molecules is separated by distances comparable to the mean free path. And I apply a velocity gradient across. For momentum, to get transferred in any one direction, it is not necessary that one particular molecule actually move in that direction. Because, this molecule can transfer momentum to the adjoining molecule. In that way, there can be momentum transferred. After all momentum can be transferred not just by the motion of a faster molecule across the surface but also because the faster molecules interacts with the molecules next to it and transfer some momentum. So, the transfer of momentum does not physically require the transport of the molecules and due to this momentum transfer in the molecules much higher than mass transfer in the liquids. Split number for liquid is **is is is** typically large. The **the** kinematic viscosity for water is approximately 10 power minus 6 meter square per second.

The kinematic viscosity of air is approximately 1.5×10^{-5} meter square per second. And there is not that much difference. I told you that kinematic viscosity in the mass diffusability for gases, all of same magnitude, all are approximately 10^{-5} meter square per second, where the kinematic viscosity of liquid is actually much larger than the mass diffusability of liquids. The reason is because, for momentum to be transported, you do not need the physical transport of molecules across the surface. It is sufficient that the forces are exerted by interacting molecules across its surface. Therefore, momentum diffusion is much faster process and actually the split number in liquids μ by d could be as higher as 1000. So, momentum diffusion in liquid is typically much faster than mass diffusion in liquids.

(Refer Slide Time: 23:21)

The whiteboard content is as follows:

Energy diffusion. Gases

Diagram: A coordinate system with a vertical y-axis and a horizontal x-axis. A temperature profile T is shown as a curve increasing with y . Arrows indicate the direction of energy transport.

$$j_+ \approx \frac{1}{4} e(y - \frac{2}{3}\lambda) v_{rms}$$

$$j_- \approx \frac{1}{4} e(y + \frac{2}{3}\lambda) v_{rms}$$

Net flux $j = j_+ - j_-$

$$= \frac{1}{4} v_{rms} (e(y - \frac{2}{3}\lambda) - e(y + \frac{2}{3}\lambda))$$

$$= \frac{1}{4} v_{rms} [e(y) - \frac{2}{3}\lambda \frac{de}{dy} - e(y) - \frac{2}{3}\lambda \frac{de}{dy}]$$

$$= \frac{1}{2} v_{rms} \lambda \left(\frac{de}{dy} \right)$$

So, that is as far as mass and momentum diffusion are concerned. Let us go on to the third topic. That is energy diffusion. Energy diffusion obviously takes place due to gradients in temperature. So, the physical mechanism for gases at least, this is same as physical mechanism for the mass and momentum diffusion. Which say I had a surface with molecules all-around of a gas, each having its own fluctuating velocity. And those have temperature gradient across is the function of this coordinate y . This is gradient in the temperature. Temperature is higher above and lower below. That is going to transport of energy. Mechanism is very simple. Because, the temperature is higher above, molecules that are coming down from above and **an average** on average higher energy, temperature is lower below. So, molecules that are going from below to above, on

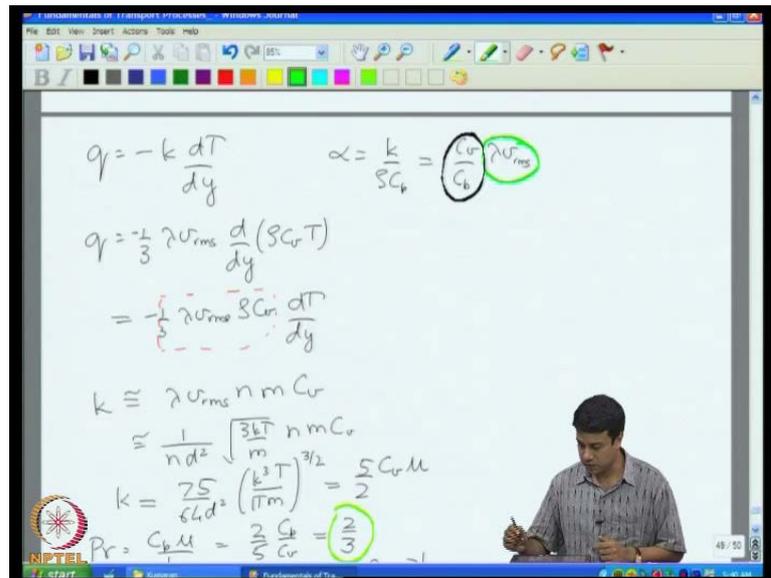
average have a lower energy. This is going to result in the net flux of energy across the surface.

So, let us once again calculate the fluxes. flux of energy going upwards, the flux of energy going upwards from the below the surface, this going to be equal to the energy below the surface. The energy at the location below the surface. If you assume that the system has a gas at constant volume, then the specific energy. That is going to be equal into the energy at y minus $2/3 \lambda$. This is the specific energy, the energy density at a distance y minus $2/3 \lambda$ in to the rms velocity, rms velocity across the surface.

The flux of energy that is going downwards from above, at time some constant which I said was approximately $1/4$. The flux of energy going below, comes from the distance of the order of the λ above the surface. So, this is $1/4 e$ in to y plus $2/3 \lambda$ in to V rms. So, the net flux is equal to flux going above minus the flux going below. The net flux j is equal to j plus minus j minus. So, the net flux equal to flux going above minus below this equal to $1/4 V$ rms in to e at y minus $2/3 \lambda$ minus e at y plus $2/3 \lambda$.

And I use the Taylor series expansion once again. And I use the Taylor series expansion once again for this. So, this is equal to $1/4 V$ rms into e at y minus $2/3 \lambda$ de by dy , at the location of y minus e at the location y minus $2/3 de$ by dy at the location y times the λ . If you put all of together, we get $1/3 V$ rms λ times de by dy where e is the specific energy, energy per unit volume. So, this now is the thermal diffusion coefficient, exactly the same in the form of the mass diffusion and the momentum diffusion coefficient, but this is the net flux. This is net flux of heat.

(Refer Slide Time: 28:24)



The equation that we usually use, is of the form heat flux is equal to minus k in to dT by dy. There is Fourier laws for heat conduction. So, in order to get this equation in this form, we have to write the energy flux as one-third lambda V rms in to d by dy of the energy density. Energy per unit volume. If the system at constant volume, then this will be mass density, times specific volume in to temperature. Mass density as I told you, is equal to number density is times molecular mass, with the negative sign. So, this is the approximately equal to minus 1 by 3 lambda V rms rho C v dt by dy. And this whole thing thermal conductivity k. So, the kinetic theory of gases, thermal conductivity is equal to lambda V rms in to the density. Density is number density, times the mass, times the specific volume.

So, that is the expression for the thermal conductivity. I said that mean free path was going as, n d square. V rms is square root of 3 k T by m. Then, I have n m and then C v. For a gas at constant volume C v is equal to 3 by 2 k, gas at constant volume C v is equal to 3 by 2 k. And of course there is a undetermined constant here, because that is approximately equal to I have add factors of order 1, which I have suppressed in this calculation. So, I can only get it up to 2 unknown constant. In kinetic theory of gases, you can do more exact calculation. Once again for monatomic gas, with the only translation decrease a freedom the expression that we get for thermal conductivity is , k is equal to 75 by 64 d square in to k cube by i t m. So that is the more exact expression you will get. This is also equal to 5 by 2 C v times the expression for viscosity. That two

term are not to be exact, because the expression for C_v , I had $5n$ by $16\sqrt{\pi}$. If I multiply that by 5 by 2 C_v is 3 half of monatomic gas I have 70 by 64 , 75 by 64 square.

So, this is the exact expression for thermal conductivity of monatomic gas of of spherical molecules. I can calculate, in the previous case when I did mass diffusion, I calculated for you the split number. I can now calculate for you the fatal number using this expression. The fatal number is equal to k by ρC_p . Fatal number is equal to ρ by C_p and I am sorry , the fatal number is equal to $C_p \mu$ by k , which is equal to 2 by 5 C_v by C_p . And C_v by C_p for monatomic gas is at 3 degree of freedom. C_v is 3 by 2 k and C_p is 5 by 2 k . The ratio γ is specific heat is 5 by 2 . So, this fatal number would transfer to the 2 by 3 for a gas of monatomic molecules, order 1 . It is approximately equal to 1 . The the ratio of the momentum, thermal diffusability of both approximately of order 1 . Reason is because both of these take place by same mechanism, the physical transport of molecules. For monatomic gases, number is approximately 2 by 3 . For larger molecules, number moves closer to, for larger molecules fatal number goes to 1 . That is because the ratio of specific heat is approximately 1 for larger molecules. So, this gives the prediction for fatal number should be for gases. The mechanism transport is exactly the same. For transporting mass, for transporting momentum, and for transporting energy in gases you require physical motion of molecules.

The reason is because the distance between large compare to the molecular sides. So, molecules cannot effectively transport momentum and energy just by an interactions, by long distance interactions. Because, the distance between the molecular are very long. Therefore, it is essential that molecules are transported in order for both, for all three, mass, momentum and an energy diffusion to take place. And because, you require a physical motion of molecules, the diffusabilities that you get for all, get same magnitude. For example, the diffusability α , thermal conductivity is going to be equal to k by ρC_p and ρk is equal to λV_{rms} times ρC_v . So, we get approximately C_v by C_p times λV_{rms} . This is the dimensional number and this thing, it is the same diffusion coefficient, we had earlier for both mass and momentum diffusability, mean free path times of fluctuating velocity. And because of this, the gases the transport mechanism are the same for both mass, momentum and an energy. And the diffusability

is also approximately the same. They expect numbers 5 by 6, the fatal number 2 by 3 for monatomic gases.

(Refer Slide Time: 35:36)

Thermal Conduction in liquids:
Liquid metals

$Pr = \frac{\text{Momentum diffusion}}{\text{Thermal diffusion}}$
 ≤ 1

Liquid mercury $Pr = 0.015$
Large organic molecules $10^{-4} < Pr < 10^{-2}$
Water $Pr \approx 7$

In the case of mass diffusion, we saw that the mass diffusability is much smaller. I am sorry. Then, the momentum diffusability in liquids, because the mass diffusability requires the physical transport of the solute molecules. Momentum diffusion does not take place in to interaction between the molecules. How about thermal diffusion in liquids? In liquids thermal diffusion can takes place in to different mechanisms depending upon the nature of the liquid.

For example, for liquid metals you do not require the physical motion of the molecule for energy conduction for temperature, for for for the transport of heat. It do not even require the molecule to transport heat from one molecule to other. The molecules in liquids, they have electron clouds, all over the, around them. And this electrons clouds can result in very fast, this electrons clouds is is internally shared by the all the molecules. And this can result in very fast thermal conduction. Therefore, the thermal conductivity of the liquid metals are very high because metals of transport basically took other transport due to the electron clouds which is shared by all the molecules. Due to that the fatal number which is the ratio of momentum diffusion by thermal diffusion, which is actually much smaller than 1. For example, for liquid mercury fatal number is above 0. 015; that means, the thermal diffusion is 60 times faster than momentum diffusion. As I told you,

momentum diffusion in liquids is faster still than the mass diffusion. So, because of this very efficient method of transport, the fatal number of the liquid is actually very small. In contrast, if you have large organic molecules, they do not transfer any energy quickly. The momentum diffusion in case of large organic molecules, the fatal number can anywhere below 10^4 to 10^2 , is very small. For the momentum is actually, γ must faster than the thermal diffusion. If water is example, somewhere between, fatal number is about 7 for water, somewhere in between. In this cases, thermal conduction is the different process. The reason is because the mechanism can be very different. In some cases, in liquids metal transport it is very fast, it takes place in to the electron clouds around the molecules. In other cases, the thermal conduction is very slow. Fatal number is actually very large times because it from 10^2 . **I am sorry**, this would be 10^4 to 10^4 , it could be as large as 10^4 or it could be small as 10^2 and normal liquids for somewhere between. Liquid metals are special cases and very insulating liquids are opposite special cases. So, this is the brief discussion of diffusion phenomena. Before, I leave this, I promise that I discuss the difference between diffusion in the case of dilute solution and normal multicomponent diffusion.

(Refer Slide Time: 40:02)

Multicomponent diffusion:

$n_1 = j_1 + C_1 U_{cm}$
 $n_2 = j_2 + C_2 U_{cm}$
 $(n_1 + n_2) = (C_1 + C_2) U_{cm}$
 $j_1 = -D \frac{dc}{dy}$

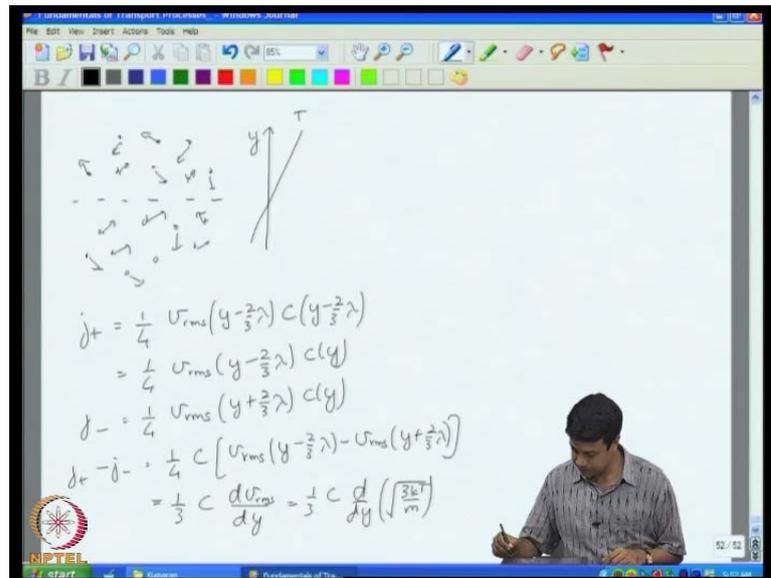
So, now, let me just briefly deal with that. I said, that diffusion is transport which does not require the motion of the center of mass. So, in that case, for example, when I had 2 **2** bulbs separated by some distance with a stop cork in between and the head molecules

and a few, tracer molecules on one side. Since, all of the black molecules are identical to each other, the motion of the tracer molecule did not affect the motion of the center of the mass very much.

On the other hand, if I had fusion between different molecules. Let say I had oxygen on one side. And much smaller hydrogen on the other side. The molecular mass of the hydrogen is 2 only whereas, oxygen is 32. So, initially mass on the left side is higher than the mass on the right side. But as diffusion progresses heavier molecular are going to the right and lighter molecules are coming to the left, due to the center of gravity, the system is actually going to the right. So, that represents the motion on the center of mass. Therefore, there is in addition to diffusion in this system, there is also convection, this system, there is also motion of center of mass. Now, how do you account for that? We have to write the fluxes little differently. I write the flux of one component.

Let us say this is one component 1 and this is component 2. I write the flux of one component. Then, as diffusion flux plus the concentration times the velocity of the center of mass. And I write the flux of the second component as the diffusion flux plus the velocity of the center of mass. Now, how do you calculate the center of the velocity of mass from the total transfer? n_1 plus n_2 is the total flux, total mass flux. And this one got to be equal to C_1 plus C_2 times the velocity of center of mass. From this, I can calculate the velocity of the center of mass. And then put that in here, I calculate total flux. Once you done that, the diffusion flux alone, the diffusion alone j_1 equal to minus $d C_1$ by dy . So, integration to the motion the center of the mass, this actually a flux relative to the center of mass, in multicomponent system both of these are simultaneously present and here to account for both of them. And finally, little bit of variety in this diffusion process. Can there be diffusion of mass due to temperature gradient? Can there be diffusion of energy due to gradient in the density?

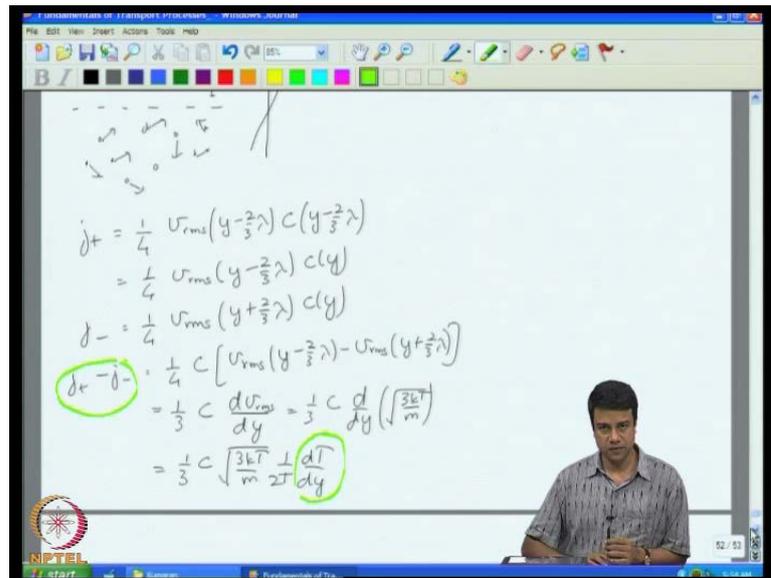
(Refer Slide Time: 44:06)



Turns out temperature gradient can in fact give you the diffusion of energy, a diffusion of mass. And the reason is as follows. When you have earlier done that problem, the diffusion of mass, the molecules which had fluctuating motion. I said that flux going upwards is equal to some constant. In that cases, I got one-fourth times the fluctuating velocity, times the concentration at location y minus 2 by 3 lambda. Now, if there were no concentration gradient, if there were no concentration gradient but there were temperature gradient, but there were temperature gradient with coordinate y . then for the flux going upwards, I would have to take the rms velocity at that location y minus 2 by 3 lambda. So, what I need to write is, this is equal to V rms times at y minus 2 by 3 lambda in to concentration at y minus 2 by 3 lambda. No concentration in the gradient.

Therefore, this is equal to 1 by 4 V rms at y minus 2 by 3 lambda. Include the concentration at y itself, because there is no concentration gradient. Flux going downwards will be 1 by 4 . The rms velocity at such some location above the plane, times the concentration y . Because, there is no concentration gradient but there is a temperature gradient. Therefore, the fluctuating velocity of the molecule is different. Add these two together, j plus j minus is equal to 1 by 4 c in to V rms at y minus 2 by 3 lambda minus V rms at y plus 2 by 3 lambda. So, this after doing all the manipulations that we have done for the previous cases, this will give me 1 by 3 c times d V rms by d y . The rms velocity is square root of k T by n . So, we get 1 by 3 C d by dy of square root of 3 k T by m .

(Refer Slide Time: 47:15)



Therefore, I can do the differentiation to get $\frac{1}{3} c$ into square root of $3kT$ by m in to $\frac{1}{2T} \frac{dT}{dy}$. When I differentiate T power half, I get $\frac{1}{2} T^{-1/2} \frac{dT}{dy}$. So, if I have a temperature gradient, I can generate a mass flux, there can be mass flux temperature gradient. In the similar manner, can there be an energy flux due to a gradient in the concentration and gradient in density. Of course, there can be a energy flux because the gradient in density. There is an average molecules going upwards. They are carrying the energy with them. Therefore, there is going to be energy transport due to fact that molecules which on average travelling upwards, the center of mass is travelling upwards, that is going to be an energy transport as well.

Can there be momentum transfer? No, because momentum is actually a vector. Because of that, there cannot be momentum transfer, unless molecules on average have a bias towards motion in one direction or the other. So, because of that there can be temperature, there can be mass transfer due to temperature gradient. There can be energy transfer due to density gradients, these are concentration gradients, these are called reciprocal relations, which relate fluxes of one quantity to gradients of one quantity. They are possible. And actually reciprocal relation relate in constant in those equations. However, in the present course, we not going to that discussion. We will not consider energy transfer due to concentration gradient, mass transport due to energy gradients. We restrict attention to the equation of mass. So, we now come to the end of our discussion on diffusion.

And next will go on to the actual core of the present course which is to **actually**, actually discuss how to solve equation of the transport of materials. So, that start in next lecture, lecture number eight. Before, we go there this basically completes the introduction part of this course. I first told you that what you trying to do in this course is solved for the fluxes urgently, due to gradient in certain quantities, the quantities that of interest to the mass momentum an energy. This are important in **in** physical situation.

For example, for a catalyst particle is not just if we have, if we have heterogeneous catalyst **catalyst** reaction happening in some reactor, it is enough to sufficient to just put in reactants and take the products out. And also to make sure that the reactants actually get to the surface where the reaction occurs. the product is out of the surface, heat is transferred as necessary. If it is Endothermic, heat has been transferred to the reaction location, if its exothermic heat has been transferred out of the reaction location. So, we are looking in detail, what happens at places where transport is actually takes place. In heat exchanger, for example, it is not sufficient to ensure that there is hot fluid coming in and cold fluid going out. So, we have to ensure that transfer across the surface. So, we focusing on those areas which are most crucial for the transport processes system occur.

Before, going there I first took you through the fundamentals of dimensional analysis. With the objective of giving physical interpretation to the dimensional numbers that we have been using all along. One class of dimensionless number are those dimensionless fluxes. I discussed those, the nusselt number, the track coefficient, the friction factor. Those are functions of other dimensionless groups. Broadly, classified as I told you, the ratio of the convection and diffusion or the ratio of two diffusabilities. Ratio of convection and diffusion Reynolds number for the momentum transfer, and peclet number for both heat and mass transfer. The ratio of two diffusabilities, split number, ratio of momentum and mass diffusion, the fatal number, the ratio of momentum and thermal diffusability.

And so, ultimately if you do the balance around the entire volume, you get average, the dimensionless fluxes, the dimensional heat flux, the dimensional mass flux, and the track coefficients of friction factor of momentum as the function of these dimensionless numbers. But, those were written for the entire system, the dimensional as heat flux is written as, was scaled by the average difference in temperature between the wall and the the fluid. Dimensionless mass flux has written as the average difference the

concentration between the reactor surface and far away. And these are written as scale velocities in the system. And our objective was go closer and look at what happens, very close to surfaces? And we wanted to write equations which told us how these quantities vary throughout the domain, not just between the surfaces and far away, throughout the entire domain.

And before we went there, I said we should look at diffusion. Take a look at what a mechanism in diffusion and why do diffusion coefficients have the kinds of numbers that they actually do? So, for example, in these lectures on diffusion coefficients, in gases the diffusion process occurs by the same physical mechanism for both mass momentum and energy transfer. And because of that, all diffusion coefficients and there being approximately given by the root mean square velocity times the mean free path in all three cases. I just told you that fatal number is **is is** 2 by 3, the split number is 5 by 6. The monatomic gases of hot particles in the transport processes is occurred due to different mechanisms. In the case of liquid metal, they have very fast thermal conduction but mono atomic is not as fast as mass diffusion.

In liquids it is typically much slower than either momentum or thermal diffusion. Mass diffusion is much slower because for a solid molecules to do it, diffuse through a liquid is necessary with surrounding molecules move out of the way. So, one molecule, the motion of one molecule does not require the motion of that molecule alone but the cooperative motion of a all other larger region. So, all other molecules move out of the way, this molecule can diffuse.

For that reason, mass diffusion is the very slow process. In the case of liquids momentum diffusion does not require the motion of molecules, physically it can take place due to the forces exerted by the one molecule to another. Therefore, momentum diffusion is faster.

Thermal diffusion, it depends on the mechanism by which thermal diffusion takes place. In liquid metal is very fast because of the transport of energy due to the electron clouds around the molecules. In the case of organic molecules is very slow, for the whole range. So, this completes our introduction to why we need fundamentals of transport processes. So, that was the first question that I asked in the very first lecture. What is it, we will be going to do? We look whether, we can get in simple systems around the single catalyst particle in a single tube cylindrical tube, near flat surface can we get the entire radiation

of the concentration temperature velocity fields, not just that the differences in the average value, for simple situation, in not a complicated situation, like heat exchangers and so on, for simple situations. If we can get that, exactly calculate why the dimensionless fluxes have that, the form have that they do in specialized situation.

So, we will start of on unit directional transport in the next class, where we will see transport only in one direction. Simple situation is actually transport between the two flat plate, they have the liquid between two flat plates, you heat one and other is cold, how does, how much energy goes through between the two? That is the simple example, because we know that temperature gradient is linear and the heat flux we can get quite easily; however, we can have more complicated situations, where it is not steady. In those case, how do we solve this problem. We will see in the next class. So, we start the unidirectional transport, in the next lecture. See you then.