Fundamentals of Transport Processes

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Module No. # 02

Lecture No. # 06

Mechanisms of diffusion-1

Welcome to the sixth lecture in this lecture series on fundamentals of transport processes. As promised, this lecture is going to be about diffusion.

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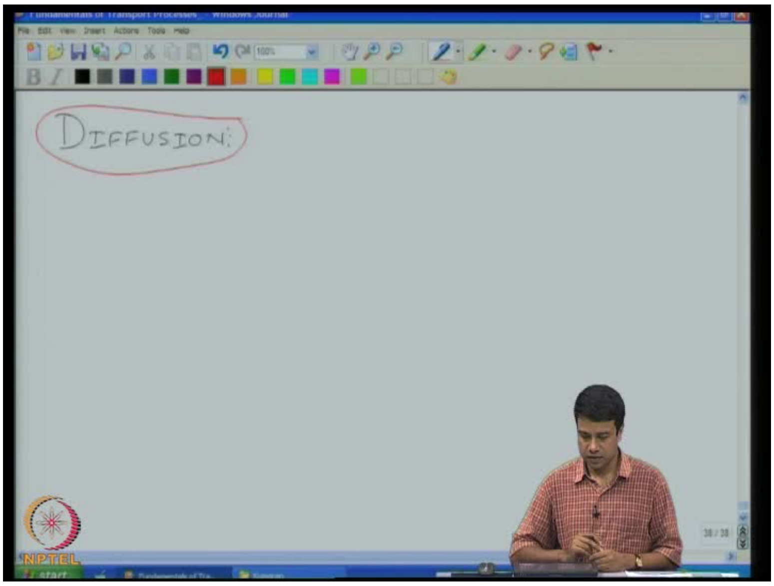

Fundamentals of transport processes - two mechanisms - convection and diffusion. I had earlier explained to you, why diffusion is so important.

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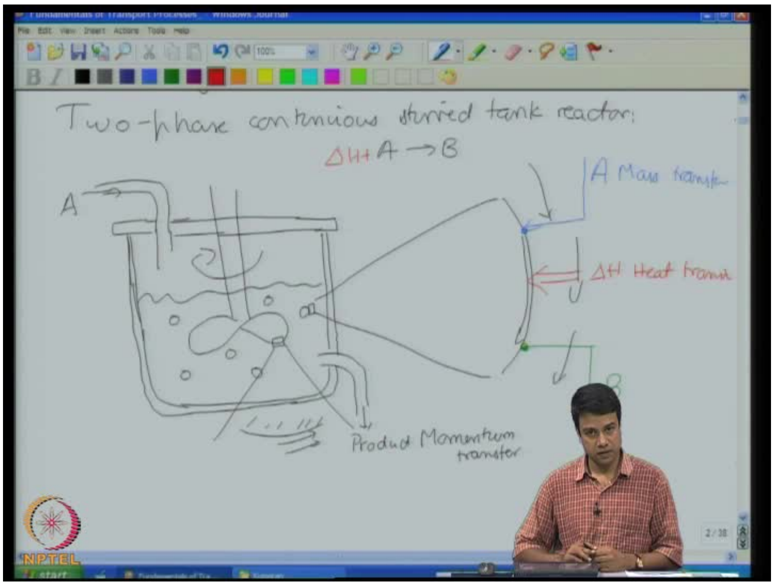

Let us just go over that once again. In the problem of the reactor, solid catalyzed reactor, the transport of mass of the reactants to the surface and the transport of products from the surface, the transport of heat and without that transport, the reaction is not going to take place.

If you look closely at the surface itself, the fluid flow does not penetrate the surface because the surface is an impenetrable surface. Therefore, the fluid flow has to be tangential to the surface; a fluid flow tangential to the surface is not going to transport mass or heat to the surface. It is going to transport only along the surface. For the mass to go to the surface, you need have transport that is perpendicular to the surface; that transport can take place only due to diffusion.

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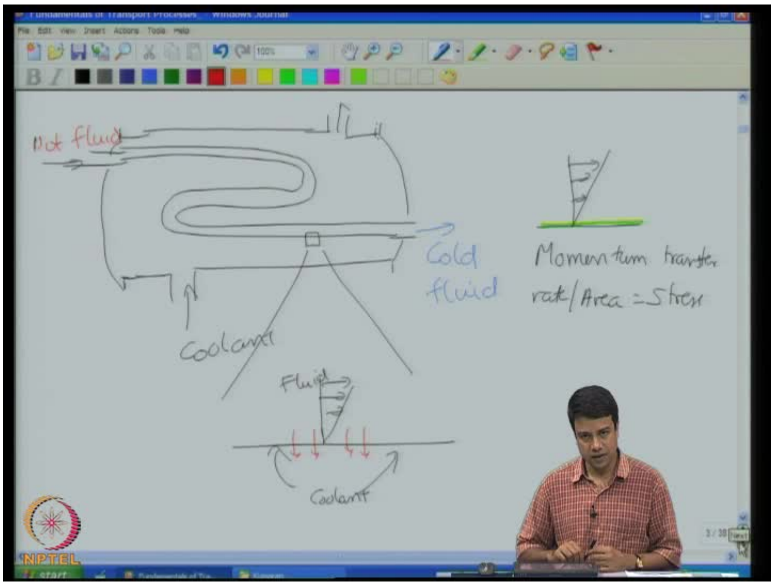

So, ultimately, there has to be diffusive transport for the material to be transported to the surface. In the case of the heat exchanger, there is convection of hot fluid into the heat exchanger. So, there is heat coming in with that hot fluid by convection, but that heat has to go across the surface to the coolant. Across the surface, there is no fluid flowing. Fluid flow is only along the surface. Therefore, transport across the surface ultimately has to take place due to diffusion.

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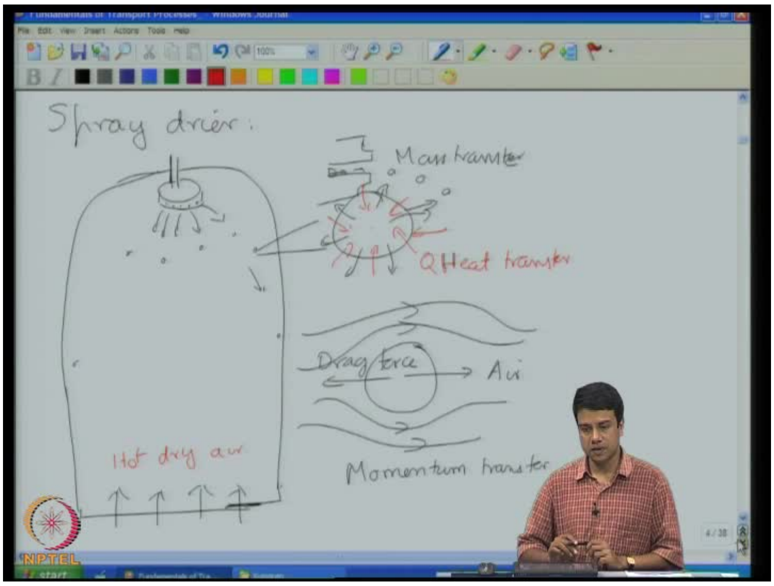

Similarly, in the problem of spray drier that I had talked about, the mass that is transported from the catalyst surface to the outside or the heat that is transported into the droplet, both of these had to be transported due to diffusion because there is no fluid penetrating the surface. So, there is no fluid velocity perpendicular to the surface. Transport perpendicular to the surface has to happen due to diffusion.

Same is the case of momentum transfer. There is no fluid going in or going out. So, it carries no momentum with it. The only force that is exerted is due to the drag force on the surface, the shear stress that is exerted on the surface as well as the pressure forces.

This transport of momentum by shear stresses has to happen due to diffusion. So, ultimately, regardless of whether convection is dominant or diffusion is dominant, if you go very close to the surface, the transport ultimately has to take place due to diffusion.

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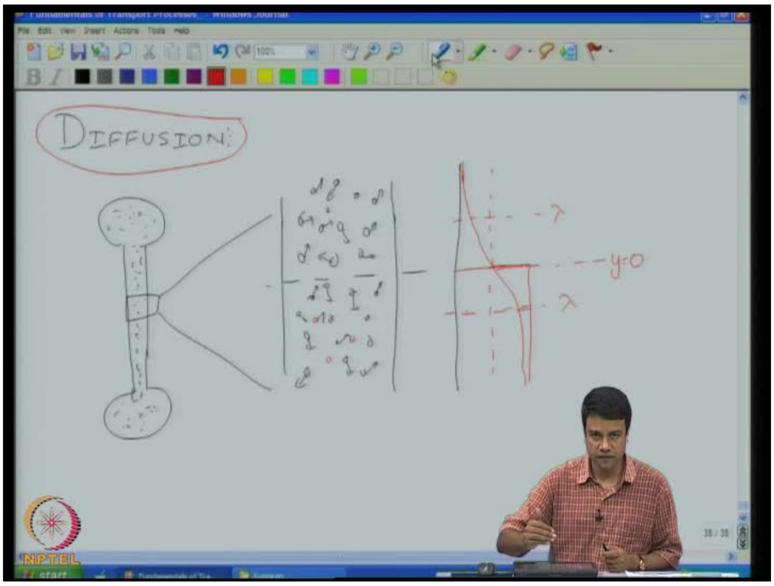

So, what is diffusion? Diffusion is the transport of material due to the fluctuating motion of the molecules without any mean velocity. Convection takes place when there is a mean motion of the fluid; diffusion takes place due to the fluctuating motion without any net mean motion in the fluid.

Let us take a simple example of mass diffusion. Let us assume that we had 2 cylinders with a stop cork in between it. So, this one was filled with molecules of gas; this one was filled with molecules of the same gas, but with a little bit of aromatic molecules added in here and there.

Initially, the 2 compartments are separated, but at some time we remove the separation between the 2 compartments. So, if I remove the separation between the 2 compartments, these molecules are going to be in fluctuating motion. So, if I look at some local location over here and I expand it out.

I have these black molecules here and I have black molecules below as well with a few red molecules thrown in and all of these molecules have fluctuating velocities.

As time progresses, these red molecules are going to diffuse around and inevitably some red molecules are going to cross the surface and go from above to below. There are no red molecules above; so, there is no equal transfer down and because of that, there is going to be net transfer of molecules from below to above

So, if I plotted the concentration field as the function of distance, for the red molecules, initially there are no red molecules above, so, I will get concentration that looks something like this. There is concentration of red molecules below, but there is no concentration above. As time progresses, these molecules will slowly diffuse across. I will get a field that looks something like this and if I wait for a very long time, the system gets completely mixed up and the concentration is the same everywhere.

As long as there is a concentration difference between below and above, there is going to be a flux of molecules. Note there is no mean motion of the molecules themselves; molecules themselves are only in a state of random motion. So, there is no change in the center of mass. However, there is a flux of molecules because of the fluctuating velocity of the molecules coupled with the difference in concentration.

When you reach the final state, where the concentration is the same throughout, there is once again no flux of molecules. So, flux of molecules requires a change in concentration across the length.

At a molecular level, why does diffusion take place? The simplest example to consider is that for a gas. So, in this particular case, let us look at the molecular transport. All of the molecules are having some random fluctuating velocity and because of that there is a constant motion of the molecules across the surface.

Now, in a gas, the molecules move a distance comparable to the mean free path between successive collections. So, molecules that are going above from below are going from a distance comparable to the mean free path below the surface whereas, the molecules that are coming from above downwards are going some distance comparable to the mean free path from above the surface.

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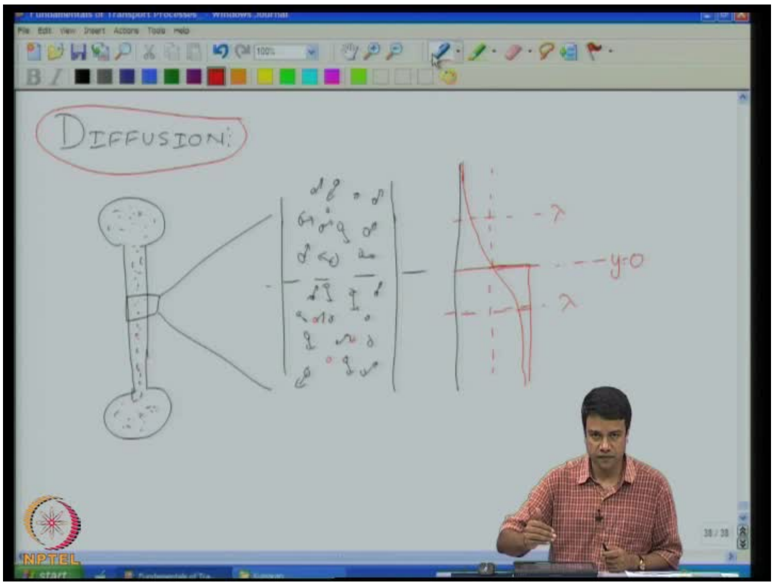

If I take this as the location where y is equal to 0, the molecules coming from below are coming from a distance approximately y minus some lamda times a constant, a distance comparable to the mean free path below the surface. Molecules going from above to below are coming from a distance comparable to the mean free path above the surface.

There is a difference in the concentration between these two. The concentration of red molecules is higher below and lower above. Therefore, you have more red molecules going above and less red molecules coming below and that ultimately is what is causing diffusion. So, there are two things: one is fluctuating velocity of molecules and the other is the concentration of the molecules at the point from which they come, the point at which they originate in the case of gases.

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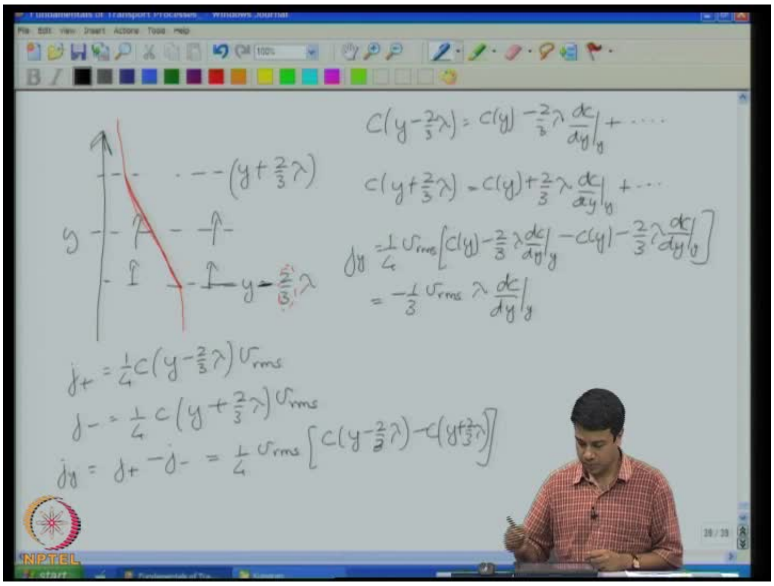

$$C(y-\tfrac{2}{3}\lambda) = C(y) - \tfrac{2}{3}\lambda \frac{dc}{dy}\Big|_y + \cdots$$

$$C(y+\tfrac{2}{3}\lambda) = C(y) + \tfrac{2}{3}\lambda \frac{dc}{dy}\Big|_y + \cdots$$

$$j_y = \frac{1}{4} v_{rms}\left[C(y) - \tfrac{2}{3}\lambda \frac{dc}{dy}\Big|_y - C(y) - \tfrac{2}{3}\lambda \frac{dc}{dy}\Big|_y\right]$$

$$= -\frac{1}{3} v_{rms} \lambda \frac{dc}{dy}\Big|_y$$

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

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

$$j_y = j_+ - j_- = \frac{1}{4} v_{rms}\left[C(y-\tfrac{2}{2}\lambda) - C(y+\tfrac{2}{3}\lambda)\right]$$

So, let us look at it more closely. This is my y coordinate. I have given a location and the concentration has some variation about this location. I should draw in the other way. concentration has some variation about that location.

Now, the molecules that are going upward are coming from some distance of the order of mean free path below the surface. We can do more detailed calculations and find out exactly how much they are coming? It turns out that they come from a distance minus 2 by 3 times the mean free path lamda.

So, the molecules from here are the ones that ultimately cross the surface. What is the flux of molecules going upwards? The flux of molecules is going to be equal to the concentration of molecules at y minus 2 by 3 lamda. This factor 2 by 3 comes from more detailed calculation which we shall not concern ourselves over here. We will just assume that it is some constant factor; it is comparable to the mean free path of the same order of the magnitude as the mean free path. So, that gives me concentration times the root mean square velocity of the molecules.

Molecules are coming from a distance comparable to the mean free path below. So, the flux will be this concentration times v rms, not exactly v rms because there will be some multiplication factor. So, it will have some factor a in front of it times C times at y minus 2 by 3 lamda times v rms. Once again, more detailed calculations show that this factor is actually one-fourth. I will not able to do the calculation to show that right now, but for the present we will just assume that they are coming the flux is proportional to the concentration times the root mean square velocity times the constant.

That concentration is not at the location y, but at a location below the surface. The distance between the location and the surface is comparable to the mean free path and more detailed calculations show that y is equal to 2 by 3 lambda.

So, that is the flux going from below to above. What about the flux going from above to below? The flux of molecules going from above to below come from a distance of the order of mean free path above the surface.

Therefore, the flux going downwards will be equal to one-fourth C into y plus 2 by 3 lamda times the root mean square velocity. Total flux - what goes above minus what goes below, if the y direction is directed upwards. If you assume that this is positive y upwards, y is upwards, positive in the upward direction, then the total flux j in the y direction is equal to j plus minus j minus - what goes up minus what comes down.

So, this will be equal to one by fourth v rms into C at y minus 2 by 3 lamda minus C at y plus 2 by 3 lamda. Now, continuum description as I discussed in the last lecture is valid only when the macroscopic scale is large compared to the microscopic scale, the mean free path in this case.

So, when the macroscopic scale is large compared to the microscopic scale, then this distance which we are interested in, the variation over distances, the distance range over which we want to find out variations is large compared to the mean free path. In that case, I can do a Taylor series expansion of the concentration about the location y. It is C at y minus 2 by 3 lambda is equal to C at y minus 2 by 3 lambda into dC by dy y plus higher order terms.

C at y plus 2 by 3 lamda is equal to C at y plus 2 by 3 lambda dc by dy y plus other terms. So, locally over distances comparable to the mean free path, if you assume the concentrated field is approximately linear, the variations and concentration takes place over much larger distances. So, locally the concentration field looks linear over distances comparable to the mean free path. Then we can use this Taylor series expansion and with this, the total flux j y take this and dark j y will be equal to one by fourth v rms into C at y minus 2 by 3 lambda dC by dy y minus C at y minus 2 by 3 lamda times dC by dy.

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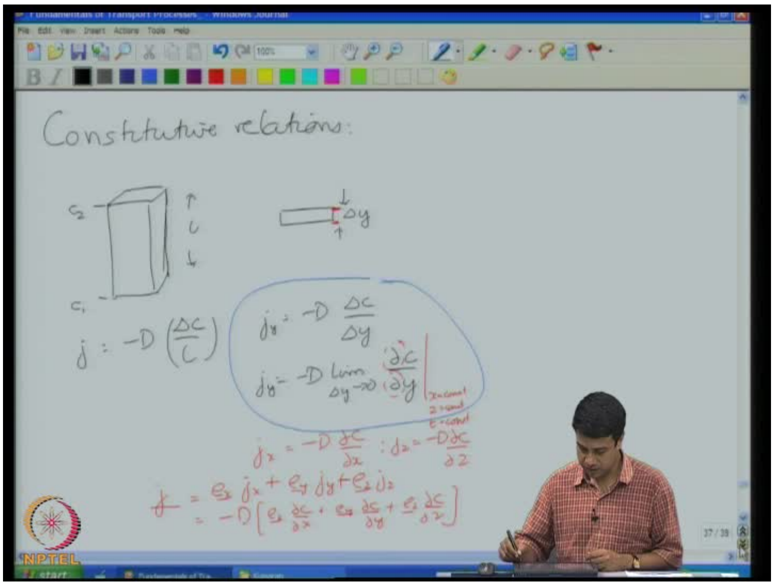

Constitutive relations:

$$j = -D\left(\frac{\Delta C}{L}\right)$$

$$j_y = -D\frac{\Delta C}{\Delta y}$$

$$j_y = -D\lim_{\Delta y \to 0}\left.\frac{\partial C}{\partial y}\right|_{\substack{x=const\\ z=const\\ t=const}}$$

$$j_x = -D\frac{\partial C}{\partial x} \; ; \; j_z = -D\frac{\partial C}{\partial z}$$

$$\mathbf{j} = e_x j_x + e_y j_y + e_z j_z = -D\left[e_x\frac{\partial C}{\partial x} + e_y\frac{\partial C}{\partial y} + e_z\frac{\partial C}{\partial z}\right]$$

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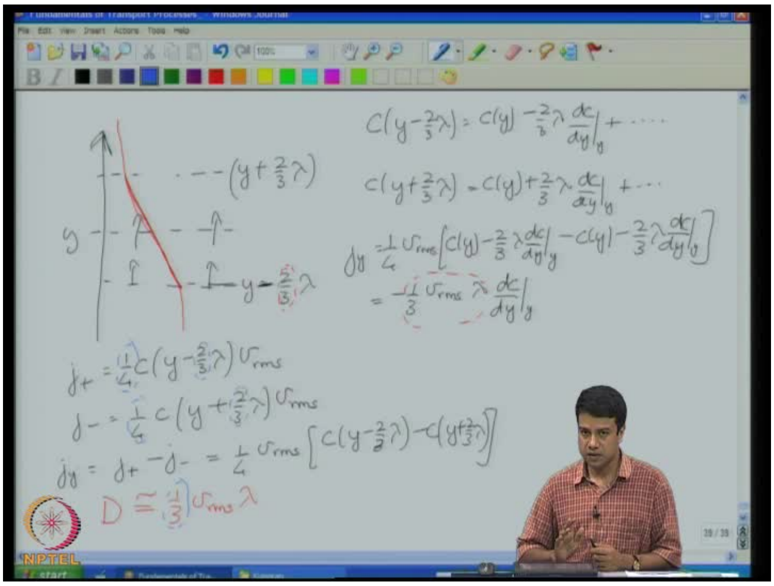

$$C\left(y - \tfrac{2}{3}\lambda\right) = C(y) - \tfrac{2}{3}\lambda\left.\frac{dc}{dy}\right|_y + \cdots$$

$$C\left(y + \tfrac{2}{3}\lambda\right) = C(y) + \tfrac{2}{3}\lambda\left.\frac{dc}{dy}\right|_y + \cdots$$

$$j_y = \frac{1}{4}v_{rms}\left[C(y) - \frac{2}{3}\lambda\left.\frac{dc}{dy}\right|_y - C(y) - \frac{2}{3}\lambda\left.\frac{dc}{dy}\right|_y\right] = -\frac{1}{3}v_{rms}\lambda\left.\frac{dc}{dy}\right|_y$$

$$j_+ = \frac{1}{4}C\left(y - \tfrac{2}{3}\lambda\right)v_{rms}$$

$$j_- = \frac{1}{4}C\left(y + \tfrac{2}{3}\lambda\right)v_{rms}$$

$$j_y = j_+ - j_- = \frac{1}{4}v_{rms}\left[C\left(y - \tfrac{2}{3}\lambda\right) - C\left(y + \tfrac{2}{3}\lambda\right)\right]$$

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

Finally, this will give me minus 1 by 3 v rms lamda times dc by dy. So, this is the flux equation. Compare with the flux equation that we have got in the previous lecture. In the previous lecture, we got j y is equal to minus D times dC by dy, D is the coefficient in front of the gradient, in front of the concentration gradient; concentration gradient here, flux here, the co efficient in between this the diffusion coefficient.

Therefore, the diffusion coefficient in this case, will be one-third v rms times lamda. Two things: one the flux depends upon the variation of the concentration with respect to position. Therefore, there is a diffusive flux only when there is a variation of concentration with respect position; this is called the gradient of the concentration field.

I told you that the Fick’s law relates the mass density to the rate of change with position of the mass density - the concentration. So, the proportionality constant in that case has to have dimension of length square per unit time. You can easily see that v rms times lamda has dimensions of length square per unit time.

Velocity has the dimensions in length per unit time; lamda has dimensions of length. So, this is the diffusion coefficient calculated from microscopic prospective with an approximation.

We had made 2 approximations here. One was that flux was equal to this factor of one-fourth times v rms and the second approximation related to the distance from where the molecules came. A more exact calculation can be done and the only thing that changes is this coefficient in front here.

We will discuss this coefficient little later, but the dependence on the root mean square velocity and the mean free path in a gas remains exactly the same. So, in all cases, for all gases, the diffusion coefficient has to be proportional to v rms times lambda because diffusion occurs due to the fluctuating motion of the molecules. That fluctuating motion depends upon the root mean square velocity and the diffusion takes place over a distance comparable to the mean free path because that is the microscopic scale.

So, it is going to be sensitive to the variations in concentration over a distance comparable to the mean free path. The change in concentration over a distance comparable to the mean free path is going to be equal lamda times dC by dy and that is why the diffusion coefficient has this form.

Next, so, how do we estimate this diffusion coefficient? We have to know what is v rms and we have to know what is lamda. We will go through that for a gas in order to justify why the diffusion coefficient that are actually measured in experiments have the values that they have.

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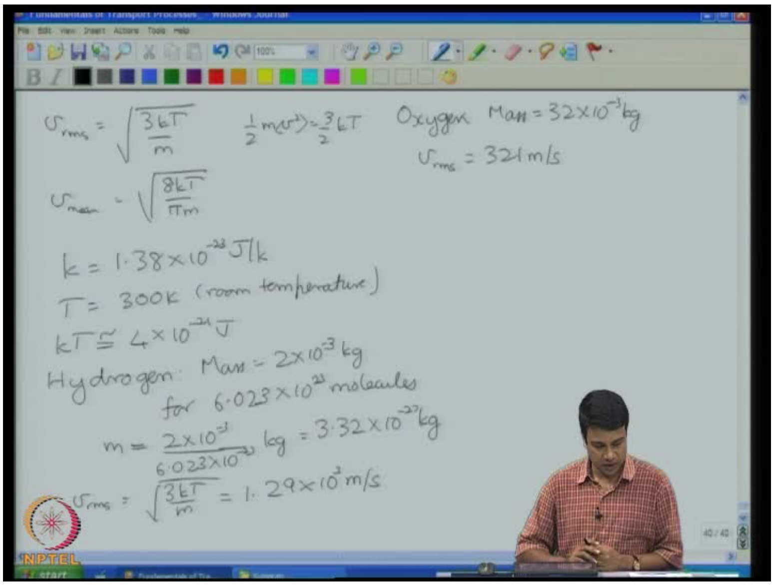

$v_{rms} = \sqrt{\frac{3kT}{m}}$ $\frac{1}{2}m\langle v^2\rangle = \frac{3}{2}kT$

Oxygen Mass $= 32\times10^{-3}$ kg

$v_{rms} = 321$ m/s

$v_{mean} = \sqrt{\frac{8kT}{\pi m}}$

$k = 1.38\times10^{-23}$ J/k

$T = 300$K (room temperature)

$kT \cong 4\times10^{-21}$ J

Hydrogen: Mass $= 2\times10^{-3}$ kg

for 6.023×10^{23} molecules

$m = \frac{2\times10^{-3}}{6.023\times10^{23}}$ kg $= 3.32\times10^{-27}$ kg

$v_{rms} = \sqrt{\frac{3kT}{m}} = 1.29\times10^{3}$ m/s

So, in kinetic theory of gases, you can define mean square velocity in different ways. v rms is defined as square root of 3 k T by m; 3 k T - this comes from the equipartition of the energy relation, half m v square is equal to 3 by 2 k T.

So, this is approximately the root mean square velocity of the molecules in a gas. I can define a different velocity, which is the mean. This comes out to be is equal to square root of 8 k T by pi m. This averaging is done in a spherical coordination system in the velocity space that need not concern us too much over here. The constant in both cases do not turn out to be very different.

So, what is the root mean square velocity for normal gases? Let us try to estimate that. k is approximately 1.38 times 10 power mines 23 joules per Kelvin. If we take T as approximately 300 kelvin at room temperature, then k T will be approximately 4 into 10 power minus 21 joules; that is an estimate of k T, the energy scale in the system at room temperature approximately.

What about the molecular mass? The molecular mass of course, varies. This is the mass of a molecule. For example, if you take the example of hydrogen, the mass of 1 mole is 2 grams; 1 gram mole is 2 grams. Therefore, the mass is equal to 2 into 10 power minus 3 kilogram for 6.023 into 10 power 23 molecules.

From that, you can get the molecular mass is equal to 2 into 10 power minus 3 by 6.023 into 10 power minus 23 kilograms, which according to my calculation turns out to be about 3.32 into 10 power minus 27 kilograms. So, this is the mass of 1 molecule. On that basis, I can find out what is v rms; it is equal to square root of 3 k T by m. With these figures, my calculation shows me that this is about 1.29 into 10 power 3 meters per second.

So, this is the fluctuating velocity of a hydrogen molecule in a hydrogen gas. If you take for oxygen molecule, for example, for oxygen, mass is equal to 32 into 10 power minus 3 kilograms. So, the mass is 16 times that for hydrogen. Therefore, the rms velocity will be about 1 by 4 times that of hydrogen and my calculation shows me about 321 meters per second.

So, this is the magnitude of the fluctuating velocity of the gas molecules. We can see that they are quit large. A thousand meters per second for hydrogen, more than a kilometer a second for oxygen, it is about 321 for nitrogen and air, it will be roughly about the same the numbers, will be approximately the same because the molecular mass of nitrogen is not very different from oxygen.

Your will also notice that these velocities are also approximately equal to the speed of the sound. In air, we know that the speed of sound is 330 meters per second and the rms velocity turns out about 321; in hydrogen, the speed of sound is about 1290 meters per second and that is what we have got for v rms. So, the molecules are fluctuating with velocities that are comparable with the speed of sound. So, the rms velocity of molecules in a gas is comparable to the speed of sound and the estimates are between 100 to a 1000 meters per second approximately.

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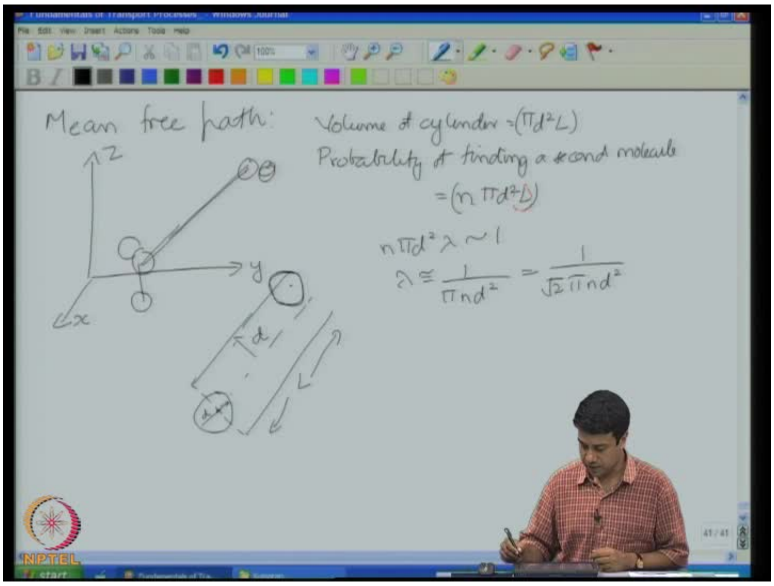

Mean free path:

Volume of cylinder $= (\pi d^2 L)$

Probability of finding a second molecule

$= (n \pi d^2 L)$

$n \pi d^2 \lambda \sim 1$

$\lambda \cong \frac{1}{\pi n d^2} = \frac{1}{\sqrt{2} \pi n d^2}$

So, the next thing that we need is the mean free path. Now, this is a little more complicated and I will try to go slowly through it, but it is a useful calculation because it gives us some physical insight into why the numbers turn out to be the way they are.

So, a typical molecule will undergo collision with other molecules and will go along a straight line path for some time and it will undergo another collision with some other molecule. Now, this molecule will travel in straight line between successive collisions. So, as it is traveling in the straight line, it sweeps out a cylindrical volume.

So, as these molecules travel in a straight line, it sweeps out a cylindrical volume. This molecular diameter is d; it sweeps out a cylindrical volume of radius equal to d, such that if the center of second molecule is lying within this cylinder, there will be a collision between 2 molecules. If the center of the second molecule is lying within the cylinder, there will be a collision between the 2 molecules.

So, as it is traveling with its root mean square velocity, it is sweeping out this distance. If it travels some length L, the volume of cylinder swept out is going to be equal to pi d square times L and of course, as it sweeps out a longer and longer cylinder, the probability that it will collide is going to increase and why is that going to increase? It is because the probability of finding the second molecule within the cylinder increases.

Therefore, let us estimate what is the probability of finding the second molecule within a cylinder of the length L.

The probability of finding a second molecule is going to be equal to the number density of molecules times pi d square L and n is number density of molecules - number per unit volume - pi d square L is a volume. So, the products of these two becomes just a number

So, as the number of second molecules is increases, there is a greater and greater chance of collision. The probability that the molecule will all most certainly collide happens to be 1, when L is equal to the mean free path because it cannot go much beyond the mean free path. It is very rare for a molecule to go very much larger than the mean free path before it collides.

Therefore, it is going to reach, it is going to undergo a collision and this probability becomes approximately 1, when this distance L is equal to the mean free path lamda. Therefore, I have n pi d square times lamda is approximately 1. So, it is going to collide it is going to cover its mean free path when this is approximately 1. Therefore, lamda has to be approximately one by pi nd square.

So, this is a simple estimate that was based upon single molecule traveling in a straight line between successive collisions. You can do a more detailed calculation and you will get the mean free path is 1 over root 2 pi nd square.

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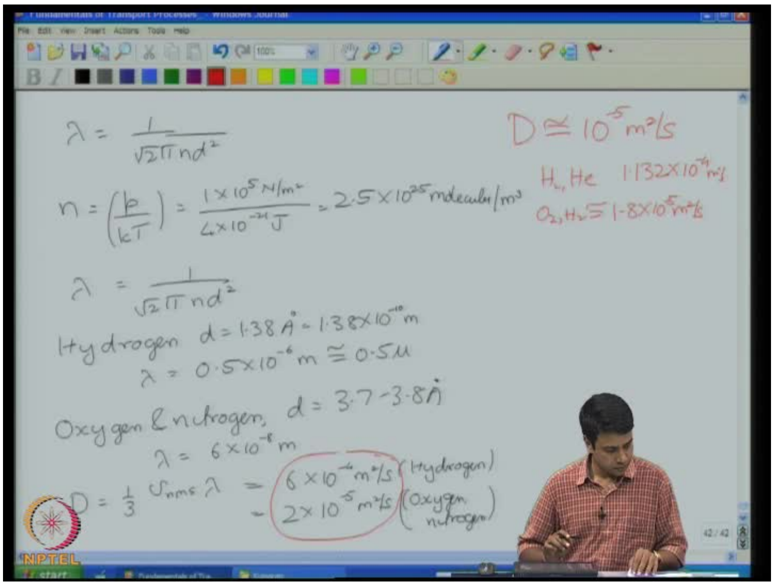

$$\lambda = \frac{1}{\sqrt{2}\pi n d^2}$$

$$n = \left(\frac{p}{kT}\right) = \frac{1\times10^{5}\,N/m^2}{4\times10^{-21}\,J} = 2.5\times10^{25}\,\text{molecules}/m^3$$

$$\lambda = \frac{1}{\sqrt{2}\pi n d^2}$$

Hydrogen $d = 1.38\,\mathring{A} = 1.38\times10^{-10}\,m$

$\lambda = 0.5\times10^{-6}\,m \cong 0.5\,\mu$

Oxygen & nitrogen, $d = 3.7-3.8\,\mathring{A}$

$\lambda = 6\times10^{-8}\,m$

$$D = \frac{1}{3} v_{rms}\lambda = \boxed{\begin{array}{l} 6\times10^{-4}\,m^2/s \\ \sim 2\times10^{-5}\,m^2/s \end{array}} \begin{array}{l} (\text{Hydrogen}) \\ (\text{Oxygen nitrogen}) \end{array}$$

$D \simeq 10^{-5}\,m^2/s$

H_2, He $1.132\times10^{-4}\,m^2/s$

$O_2, N_2 \cong 1.8\times10^{-5}\,m^2/s$

So, that is the mean free path. Let us try to estimate what is mean free path? The number of molecules per unit volume is equal to p by k T, number of molecules per unit volume from p v is equal to n k T. So, if you take atmospheric pressure, the pressure is approximately 1 into 10 power five Newton's per meter square divided by k T which is 4 into 10 power minus 21 joules.

You can easily see that these has dimensions of one over volume and if I carry out this calculation, this number density becomes approximately 2.5 times 10 power 25 molecules per meter cube at standard temperature and pressure. So, this is the number density of molecules. The mean free path is going to be equal to 1 by root 2 pi nd square. For hydrogen, d is 1.38 angstroms which is approximately 1.38 times 10 power minus 10 meters and using this in this formula, I get the mean free path is equal to 0.5 into 10 power minus 6 meters or approximately 0.5 microns. One micron is 1000 of the centimeter. So, this is approximately 1 micron is about 1000 centimeter.

For oxygen and nitrogen, I think diameter is approximately 3.7 to 3.8 angstroms. If you put this into this formula, I will get lamda is approximately equal to 6 into 10 power minus 8 meters. So, this is approximately 16 nanometers and you can easily see that the diameter is about three angstroms and the mean free path is about 6 nanometer and that the mean free path is approximately 100 times the molecular diameters, in the case of gases.

So, this gives a range to the mean free path is between about 0.5 microns to 10 power minus 7 to 10 power minus 8. So, diffusion coefficient is equal to some constant; in this case, we got one-third v rms times lamda. For hydrogen, v rms was about 12100 meters per second and I am getting about 0.5 micron per lambda and on this basis, I can estimate the diffusion coefficient as approximately 6 times 10 power minus 4 meter square per second for hydrogen.

This is approximately 2 times 10 power minus 5 meter square per second for oxygen and nitrogen. So, this is the range of diffusion coefficient for most common gases. It is approximately Diffusion coefficient in all cases is approximately 10 power minus 5 meter square per second.

If you look for example, look for values in literature, Kastler reports that H 2 and He diffusion coefficient is about 1.132 into 10 power minus 4 meter square per second, while for oxygen, it is about 1.8 times 10 power minus 5 meter square per second.

So, this is the range of diffusion coefficient for most common gases and the reason that the diffusion coefficient has this range is because the mean free path goes from about 10 power minus 7 to 10 power minus 8 meters and the velocity varies between 100 and 1000 meter square per second. In fact, you can do more detailed calculations to get exact results for diffusion coefficient for let us say spherical rigid molecules.

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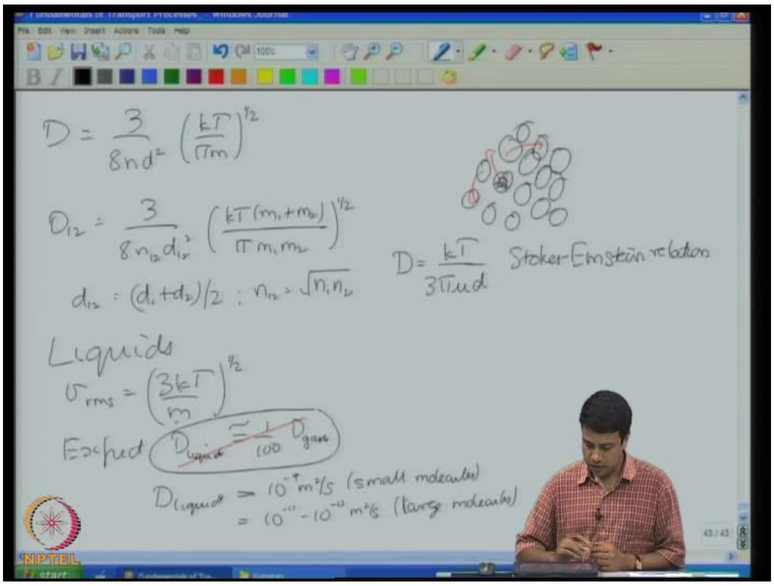

$$D = \frac{3}{8nd^2}\left(\frac{kT}{\pi m}\right)^{1/2}$$

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

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

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

Liquids

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

$$\text{Expected } \cancel{D_{liquid} \cong \frac{1}{100} D_{gas}}$$

$$D_{liquid} = 10^{-9}\,\text{m}^2/\text{s} \text{ (small molecules)}$$
$$= 10^{-11} - 10^{-10}\,\text{m}^2/\text{s} \text{ (large molecules)}$$

This turn out to be of the form D is equal to 3 by 8 nd square into k T by pi m power half. This is for a single component, where the number density is where the masses of the 2 molecules are not very different and if you have multi component diffusion - 2 species, this will be 3 by 8 n 1 2 d 1 2 square into k T m 1 plus m 2 by pi m 1 m 2 power half, where d 1 2 is equal to d 1 plus d 2 by 2 and n 1 2 is equal to square root of n 1 n 2. So, this is for multi component diffusion.

This explains why the diffusion coefficient have the values they do for gases. How about for liquids? So, for gases, I said the diffusion coefficient is of the order of 10 power minus 5 meter square per second. For liquids, the thermal velocity is the same.

The v rms, liquid’s v rms is still equal to 3 k T by m power half. The thermal velocity is the same whether it is gases or liquids. Only thing is in liquids, the distance between the molecules is small. Therefore, the molecules cannot move very far between successive interaction; that is the only difference between liquids and gases.

On this basis, the thermal velocities are the same, the mean free path in the liquid - distance between molecules, is about 100 times smaller than the mean free path in a gas as I just told you. Therefore, you would expect the diffusion coefficient also to be 100 times smaller. So, you would expect diffusion in liquids to be approximately 1 by 100 the diffusion coefficient for gases.

Turns out that this is not true; this equation it turns out is not true and the reason is the high density of molecules in a liquid. So, if I had molecules in a liquid, the motion of 1 molecule in any particular direction requires that all other molecules move out of the way.

So, diffusion in liquids is basically what is called cooperative processes. The motion of 1 molecule requires other molecules to move out. For most of the times, the molecules in a liquid are rattling within the cage that is made of the neighbouring molecules and occasionally there is a rearrangement, where one molecule moves out because the neighbouring molecules are moved in such a way as to permit the passage of the molecules.

Transport of mass requires the motion of molecules, the physical motion of molecules and for this reason diffusion in liquid is much slower process. In fact, if you calculate the diffusion coefficient in liquids, for small molecules, it is approximately 10 power minus 9 meters square per second which four orders of magnitude smaller than that in a gas.

For example, for hydrogen and water, the diffusion coefficient is 4 into 10 power minus 9. For larger molecules, if you had larger polymer molecules, protein and so on, this could be as low as 10 power minus 11 to 10 power minus 13 meters square per second, for large.

So, the diffusion coefficient in liquids is an exceedingly slow process because it involves the cooperative motion of many molecules and the diffusion coefficient in liquids is difficult to estimate just based on the mean free path consideration alone, but there is alternate ways to estimate that. One equation is what is called Stokes Einstein equation - k T by 3 pi mu times the molecules diameter. k T is the same k T, the thermal energy that we had before, mu is the viscosity of the liquid and D is the diameter of the diffusing particle; this called Strokes Einstein relation.

This relation is strictly speaking valid only for large collidal particles in a liquid, There is a requirement in deriving this relation that this diameter D has to be large compared to the molecular diameter so that the relaxation time of the large particle is much larger than the time scale on which these small molecules impact on the particle, but this can still be used to give an estimate of what diffusion coefficient of liquid should be

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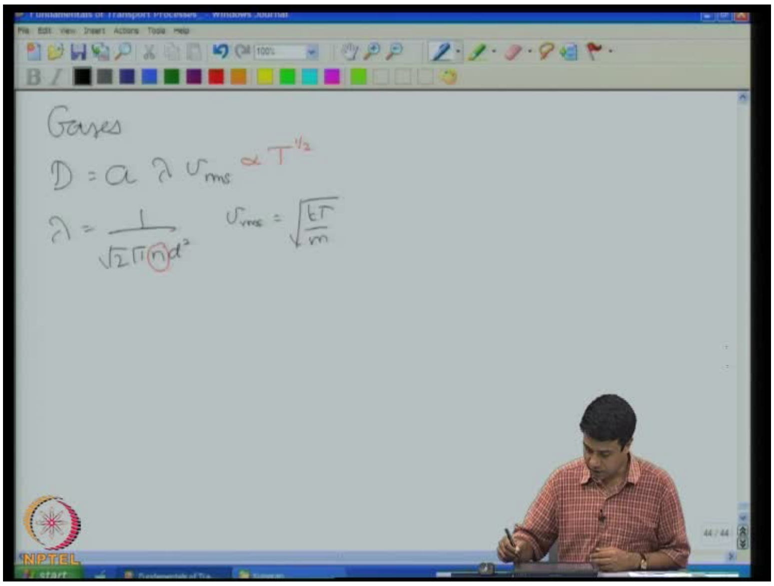

Finally, there is one other point to be noted here. In gases, D is equal to some constant, let us call that as a, times lamda times v rms, where lambda is equal to 1 by root 2 pi nd square and v rms is equal to square root of k T by m. That means, in gases, the diffusion coefficient increases with temperature.

The reason is because as you increase the temperature, the fluctuating velocity of the molecules increases and because of that the diffusion coefficient increases. The diffusion coefficient also increases as the number density is decreased; as n decreases, the diffusion coefficient increases.

That is because molecules travel longer distances between successive interactions. So, at a given surface, as you decrease the number density, the molecules of that point coming from much lower, where the concentration difference is much larger. That is the reason the diffusion coefficient increases as you decrease the number density and it increases proportional to T power half as the temperature is increased.

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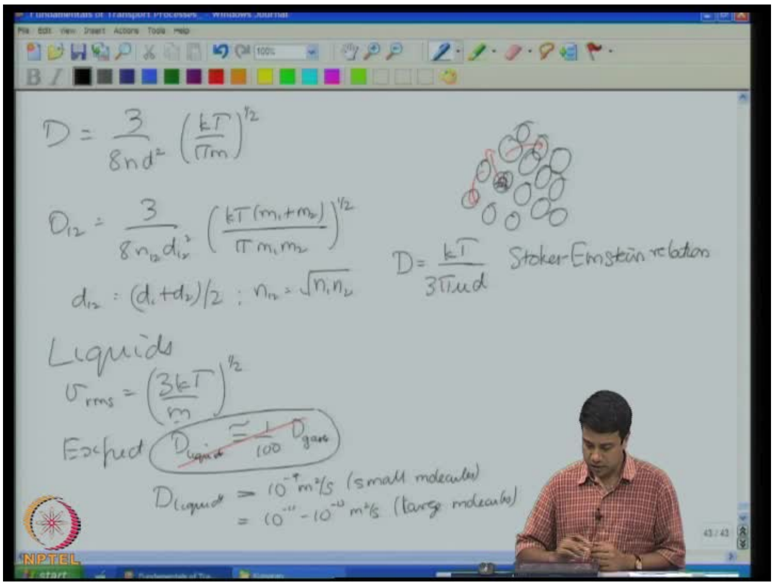

$$D = \frac{3}{8nd^2}\left(\frac{kT}{\pi m}\right)^{1/2}$$

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

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

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

Liquids

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

Expected $\cancel{D_{liquid} \simeq \frac{1}{100} D_{gas}}$

$D_{liquid} \approx 10^{-9}\ m^2/s$ (small molecules)

$= 10^{-11} - 10^{-10}\ m^2/s$ (large molecules)

In liquids, on the other hand, you can see from the Stokes Einstein relation, the diffusion coefficient has this form. So, it depends both upon the temperature as well as the viscosity. Typically, the diffusion coefficient will decrease as the temperature is increased.

Even though the temperature increases, the viscosity decreases. The diffusion coefficient increases as the temperature increases because the viscosity is decreasing fast and the temperature is increasing. When the viscosity decreases with increase in temperature, the diffusion coefficient will increase with the increase in temperature.

In this case, the power is actually larger than one because the temperature is increasing and the viscosity is decreasing. So, in both cases the diffusion coefficient does increase with temperature, but for different reasons in both cases.

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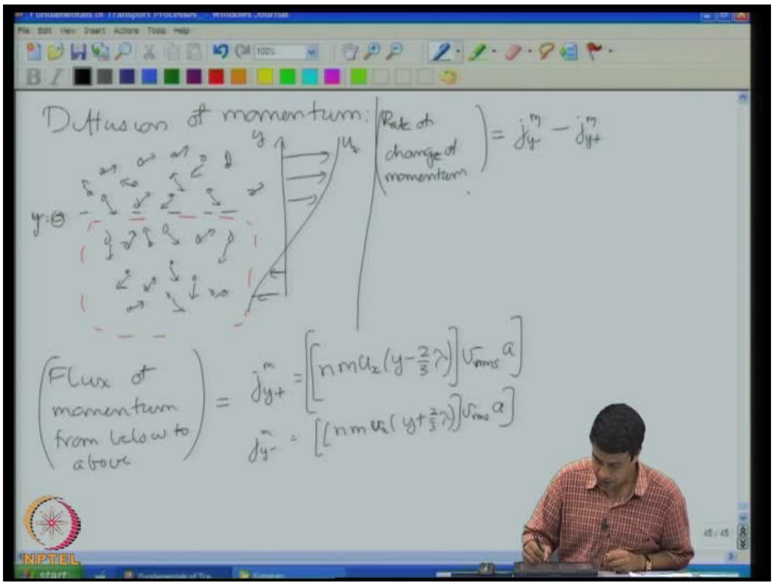

Diffusion of momentum:

$$\begin{pmatrix}\text{Rate of} \\ \text{change of} \\ \text{momentum}\end{pmatrix} = j^m_{y-} - j^m_{y+}$$

$$\begin{pmatrix}\text{Flux of} \\ \text{momentum} \\ \text{from below to} \\ \text{above}\end{pmatrix} = j^m_{y+} = \left[\left[n m u_x\left(y - \tfrac{2}{3}\lambda\right)\right] v_{rms}\, a\right]$$

$$j^m_{y-} = \left[\left[n m u_x\left(y + \tfrac{2}{3}\lambda\right)\right] v_{rms}\, a\right]$$

So, that gives us some physical insight into the diffusion of mass. Now, let us look at the diffusion of momentum. That is I am trying to get a relationship between the flux of momentum, which is the shear stress and the change in velocity across the surface. So, let us consider shear flow in which the velocity, this is the y direction, the velocity u x is varying along with position y. So, this is the location y is equal to 0 and I have molecules here and all of this have fluctuating velocities. However, there is also a mean velocity.

So, the molecules on top are moving with a small mean velocity towards the right; these molecules below are moving with a small mean velocity towards the left. The implicit assumption in all of these cases is that, the mean velocity is small compared to the fluctuating velocity of the molecules. As I told you earlier, the fluctuating velocity of the molecules is comparable to the speed of sound in the medium.

So, the assumption in all of these cases is that the mean velocity is small compared to the speed of sound. The ratio of mean velocity in speed of sound is called Mach number and we deal exclusively with low Mach number flows, where the mean velocity is small compared to the speed of sound.

So, if you take the volume below the surface and try to write an equation for the rate of change of momentum. Note that momentum has 3 components, but in this particular case you are assuming that the mean velocity is non-zero only in the x direction. So, momentum only has an x component; there is no y, z component. However there is a fluctuating velocity of the molecules in all directions. In particular, there is a fluctuating velocity of molecules in both x and y directions and that will prove to be important when we discuss diffusion.

So, now, what is the rate of change of momentum within this volume? When a molecule goes from below to above, the momentum of this volume decreases. When a molecule comes from above to below, the momentum of this volume increases. Now, we have to find out the flux of momentum from below to above and from above to below.

Flux of momentum from below to above, I will call this as j y momentum flux and this momentum flux is going in the positive direction. This momentum flux is going to be equal to the average momentum of the molecules below times the number of molecules traveling per unit time per unit area.

So, the average momentum of the molecules below this surface is going to be equal to number of molecules times mass of a molecule times v x at y minus 2 by 3 lamda is the value. So, this is the mean momentum. So I have to be careful here. I should use u x n into u x y minus lamda times the flux of molecules.

So, this is the momentum of molecules below times the flux of molecules, which is approximately v rms times some undetermined constant a. In the previous case, it was 1 by 4; you do not worry too much about what the exact numerical value of the constant is.

So, this is the momentum that is going from below to above. The momentum coming from above to below is going to be similar except that this is equal to nm times u x at y plus 2 by 3 lamda into v rms times proportionality constant.

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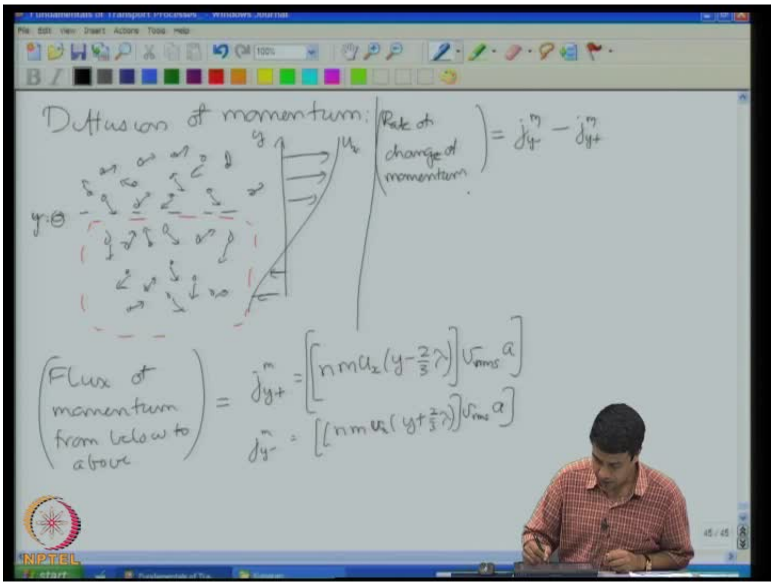

Diffusion of momentum:

$\begin{pmatrix}\text{Rate of} \\ \text{change of} \\ \text{momentum}\end{pmatrix} = j^m_{y-} - j^m_{y+}$

$\begin{pmatrix}\text{Flux of} \\ \text{momentum} \\ \text{from below to} \\ \text{above}\end{pmatrix} = j^m_{y+} = \left[\left[n m u_x\left(y - \frac{2}{3}\lambda\right)\right] v_{rms}\, a\right]$

$j^m_{y-} = \left[\left[n m u_x\left(y + \frac{2}{3}\lambda\right)\right] v_{rms}\, a\right]$

So, now, what is the rate of change of momentum? One has to be careful here, the momentum of this volume is increasing, when the molecules come from above to below whereas, decreases molecules goes from below to above.

So this is going to be equal to j m y minus minus j m y plus because what goes above is decreasing the momentum, what comes below is increasing the momentum. And if I take this

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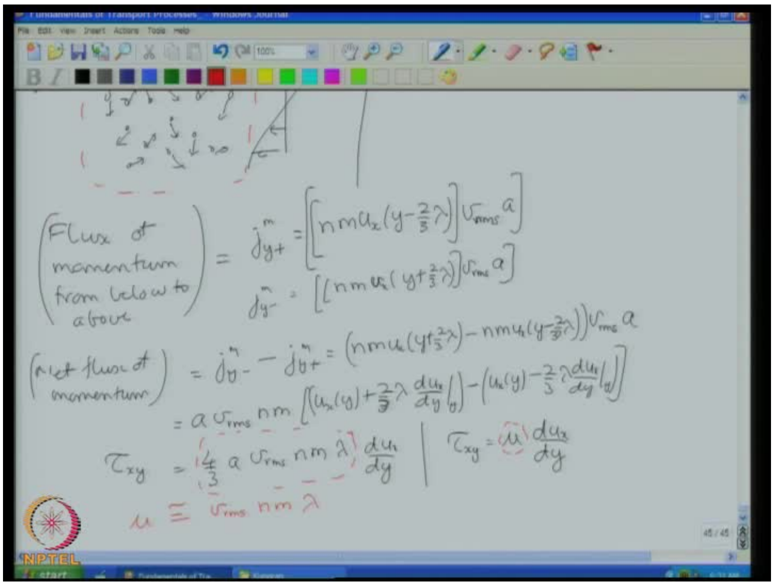

$\begin{pmatrix}\text{Flux of} \\ \text{momentum} \\ \text{from below to} \\ \text{above}\end{pmatrix} = j^m_{y+} = \left[\left[n m u_x\left(y - \frac{2}{3}\lambda\right)\right] v_{rms}\, a\right]$

$j^m_{y-} = \left[\left[n m u_x\left(y + \frac{2}{3}\lambda\right)\right] v_{rms}\, a\right]$

$\begin{pmatrix}\text{Net flux of} \\ \text{momentum}\end{pmatrix} = j^m_{y-} - j^m_{y+} = \left(n m u_x\left(y + \frac{2}{3}\lambda\right) - n m u_x\left(y - \frac{2}{3}\lambda\right)\right) v_{rms}\, a$

$= a\, v_{rms}\, n m \left[\left(u_x(y) + \frac{2}{3}\lambda \frac{du_x}{dy}\Big|_y\right) - \left(u_x(y) - \frac{2}{3}\lambda \frac{du_x}{dy}\Big|_y\right)\right]$

$\tau_{xy} = \frac{4}{3} a\, v_{rms}\, n m \lambda \frac{du_x}{dy}$ | $\tau_{xy} = \mu \frac{du_x}{dy}$

$\mu \equiv v_{rms}\, n m \lambda$

Therefore, net flux of momentum is equal to j y m minus minus j y m plus. This is going to be equal to nm u x at y plus 2 by 3 lamda minus nm times u x at y minus 2 by 3 lambda times v rms times this undermined constant. Once again, I can do the same Taylor series expansion. I assume that v rms is not changing too much because the temperature is not changing too much and the density - number density and mass of the molecules is approximately the same. So, this will give me a v rms nm into u x at y plus 2 by 3 lamda du x by dy at y minus u x at y minus 2 by 3 lamda du x by dy.

This is equal to 4 by 3 a v rms nm lamda times du x by dy. So, this is the flux of momentum. The flux of momentum is nothing, but the shear stress times tau xy. Newton's law of viscosity - tau xy is equal to mu du x by dy. So, clearly this coefficient mu is just everything that is sitting here in front.

The coefficient of viscosity is just the coefficient that appears in front of the velocity gradient; it is this coefficient. Therefore, the viscosity is approximately v rms nm times lamda. So, that is the viscosity of the molecular gas.

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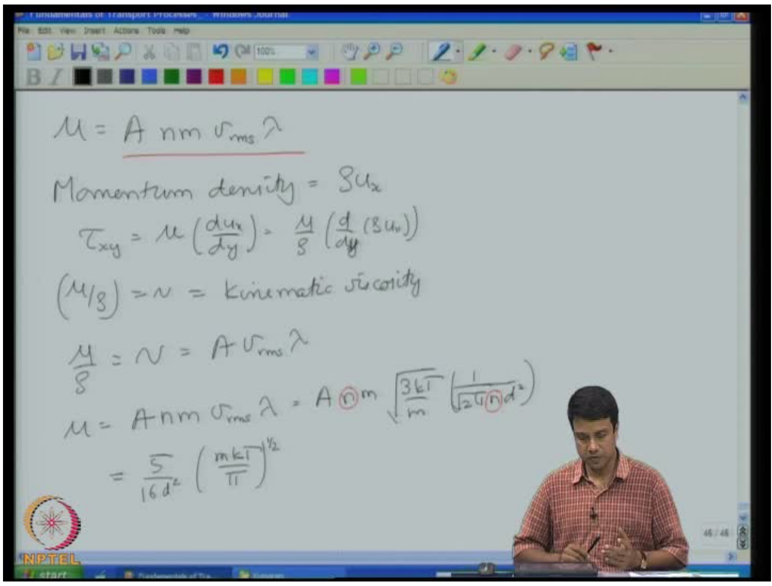

$$\mu = \underline{A\, n m\, v_{rms}\, \lambda}$$

Momentum density $= \rho u_x$

$$\tau_{xy} = \mu\left(\frac{du_x}{dy}\right) = \frac{\mu}{\rho}\left(\frac{d}{dy}(\rho u_x)\right)$$

$(\mu/\rho) = \nu =$ Kinematic viscosity

$$\frac{\mu}{\rho} = \nu = A\, v_{rms}\, \lambda$$

$$\mu = A\, n m\, v_{rms}\, \lambda = A\, \textcircled{n}\, m \sqrt{\frac{3kT}{m}}\left(\frac{1}{\sqrt{2}\pi\, \textcircled{n}\, d^2}\right)$$

$$= \frac{5}{16 d^2}\left(\frac{mkT}{\pi}\right)^{1/2}$$

So, therefore, the viscosity is equal to some undetermined constant. Let us call that as A nm v rms times lamda. The kinematic viscosity, we have discussed that earlier, when we write the diffusion equation. The flux of a quantity per unit area per unit time is equal to diffusion coefficient times the gradient of the density of that quantity. In this case, momentum; momentum density is just rho times u x in the x direction - momentum per unit volume. Therefore, equation that I had earlier is equal to mu into du x by dy. It can also be written as mu by row into d by dy of rho u x, momentum density, where mu by row is equal to nu is the kinematic viscosity. So, I have an expression for mu here. So, mu by row, row is the mass density. In the expression for viscosity here, n is the number of molecules per volume times m is the mass of the molecules. So, n times m is just rho, the mass density.

So, therefore, the kinematic viscosity is just some constant v rms times lamda. Kinematic viscosity is momentum diffusivity. Diffusivity of all mass, momentum and energy have to have dimension of length square by unit time. Clearly this has the dimension of length square by unit time, but it is more than that. In the case of mass diffusion, we found out that the mass diffusion coefficient was some constant times v rms times lamda; momentum diffusion constant is the same in this case, some constant v rms times lamda.

So, both the mass and momentum diffusion are approximately of the same magnitude in gases. That is no surprise. It is because the diffusion process for both mass and momentum are due to the physical motion of molecules in a gas.

So, in both cases we will get the momentum diffusion constant to be roughly of the same magnitude. The viscosity in the gas, I got it up to an undetermined constant here in a manner similar to diffusivity, I can do a more detailed calculation and that detailed calculation will give me the constants in the expression for the momentum diffusivity of the gas.

You can see here that viscosity is equal to A nm v rms times lamda and if I write out the expressions for v rms 3 k T by m and this is 1 over root 2 pi nd square. So, you can easily see that the number density at the bottom and the top cancel out and the viscosity is independent of density in gases.

If we do a more detailed calculation, we will get the viscosity is 5 by 16 d square into mkT by pi power half. So, this is what we get by more detailed calculation. We can see the dependencies are all correct. It has mkT power half and because there is mass here, one over mass here and this is 1 over d square. If I actually calculate the value of this, we will get L inverse T inverse, as we got from dimensional analysis.

So, for a gas, the viscosity increases with temperature proportional to T power half, for a dilute gas. The viscosity is independent of the density for a dilute gas. The reason it is independent of the density because the reason is momentum transport is proportional to the number of particles, but, the mean free path goes 1 over the number of molecules per unit volume; that cancels out and for that reason, it is largely independent on the number of molecules.

Next, we will go kinematic viscosity and the momentum diffusivity in liquids. In liquids, it turns out, when we discussed mass diffusivity earlier I told you the mass diffusivity in liquids much smaller than the mass diffusion in gases. The reason is because the diffusion of the mass requires the physical motion of molecules in liquid and that requires cooperative motion because for one molecule to travel, other molecules have to move out of the way.

Momentum diffusion does not require the physical motion of molecules and for that reason the momentum diffusion can happen much larger and much faster in liquids than mass diffusion. The excess momentum can be transmitted from one molecule to the other due to molecular interactions. It does not require the physical motion of molecules and for that reason, the momentum diffusion in liquids is much faster than mass diffusion liquids.

We look at the details in the next lecture. I will go through these arguments for diffusion of mass and momentum once again, complete the arguments for diffusion of energy in the next lecture and then we start looking simple configurations.

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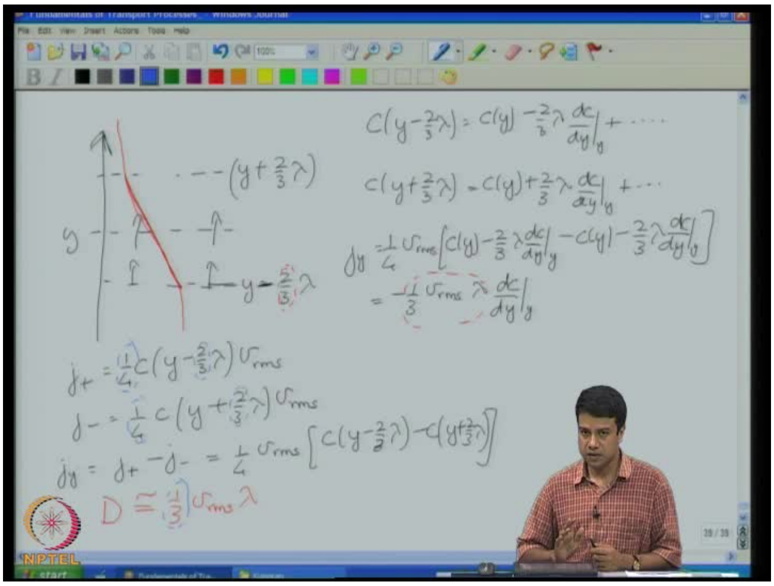

$$C(y - \tfrac{2}{3}\lambda) = C(y) - \tfrac{2}{3}\lambda \left.\frac{dc}{dy}\right|_y + \cdots$$

$$C(y + \tfrac{2}{3}\lambda) = C(y) + \tfrac{2}{3}\lambda \left.\frac{dc}{dy}\right|_y + \cdots$$

$$j_y = \frac{1}{4} v_{rms}\left[C(y) - \tfrac{2}{3}\lambda \left.\frac{dc}{dy}\right|_y - C(y) - \tfrac{2}{3}\lambda \left.\frac{dc}{dy}\right|_y\right]$$

$$= -\frac{1}{3} v_{rms} \lambda \left.\frac{dc}{dy}\right|_y$$

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

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

$$j_y = j_+ - j_- = \frac{1}{4} v_{rms}\left[C(y - \tfrac{2}{3}\lambda) - C(y + \tfrac{2}{3}\lambda)\right]$$

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

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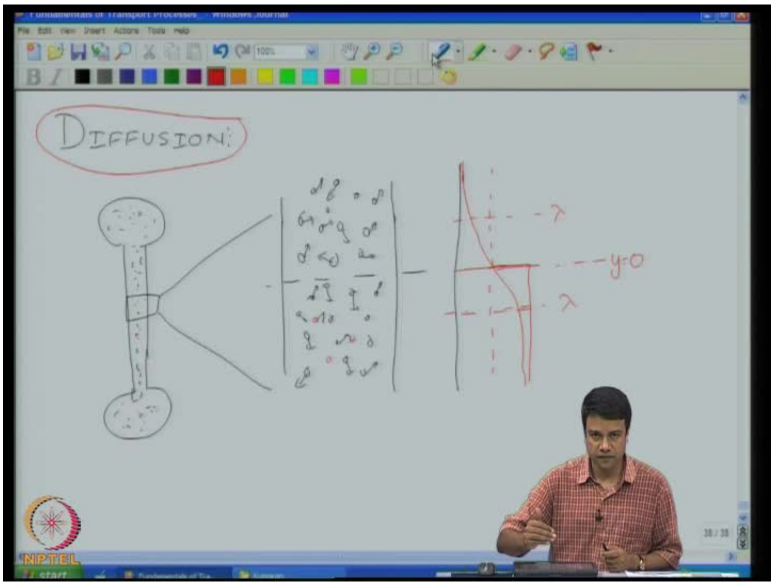

So, basically in this lecture what I have tried to convey to you is the physical understanding of diffusion and why it takes place. Diffusion takes place because you have changes in concentration across the surfaces. If I have more molecules below and less molecules above, there is no net flow, but because of the difference in concentration there is going to be a net motion of molecules. That is true, whether it is mass, momentum or energy. In the case of gases, the diffusion mechanisms are the same for all cases and we saw already the mass diffusivity and momentum diffusivity are approximately the same.

We will see later that energy diffusivity is also approximately the same. In liquids, they can be very different because the mechanisms are different. We will continue this discussion in the next class, will see you next time.