Transport Processes I: Heat and Mass Transfer

Prof. V. Kumaran
Department of Chemical Engineering
Indian Institute of Science, Bangalore

Lecture – 17

Diffusion: Momentum diffusion coefficient

In the last couple of lectures, we were discussing the process of molecular diffusion and I had given you some idea about the physical origins of molecular diffusion. Diffusion takes place only when there is a variation or a gradient in the density of whatever is being diffused. So, for example, the diffusion coefficient for mass will depend upon the variation in concentration, that for energy will depend upon the variation in the energy density and that for momentum will depend upon variation in the momentum density. I had shown you the diffusion coefficient for mass of the basis of a molecular picture in the previous lecture.

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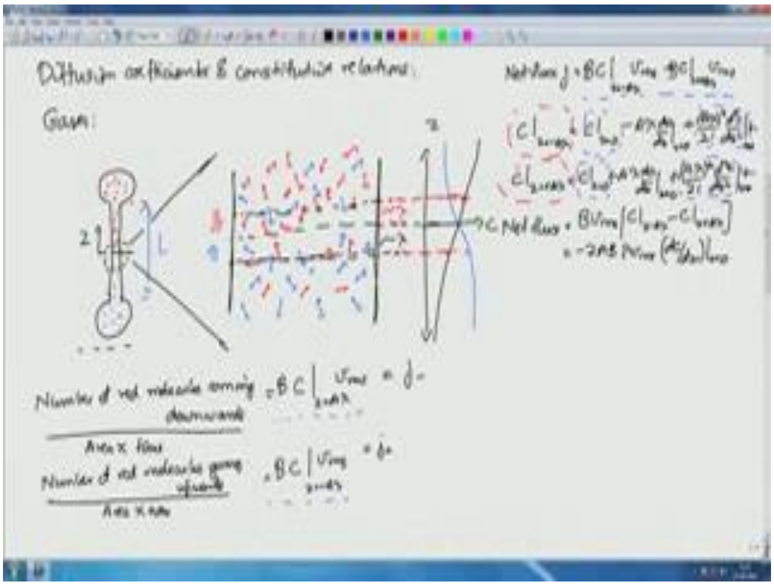

The basic idea is that when you have a surface across which there is a variation in the concentration of a particular species. In a gas for example, the molecules that are moving downwards are moving from some distance above this surface, molecules are moving upwards or moving from some distance below the surface. Since the concentration above the surface is higher than the concentration below the surface, you have a net transport of mass downwards, if the concentration is higher above the surface .The flux due to that as usual is proportional to the fluctuating velocity times the density of mass or the concentration and if we take the difference in flux between above and below the surface, it is proportional to the difference in concentrations between that location above and below the surface.

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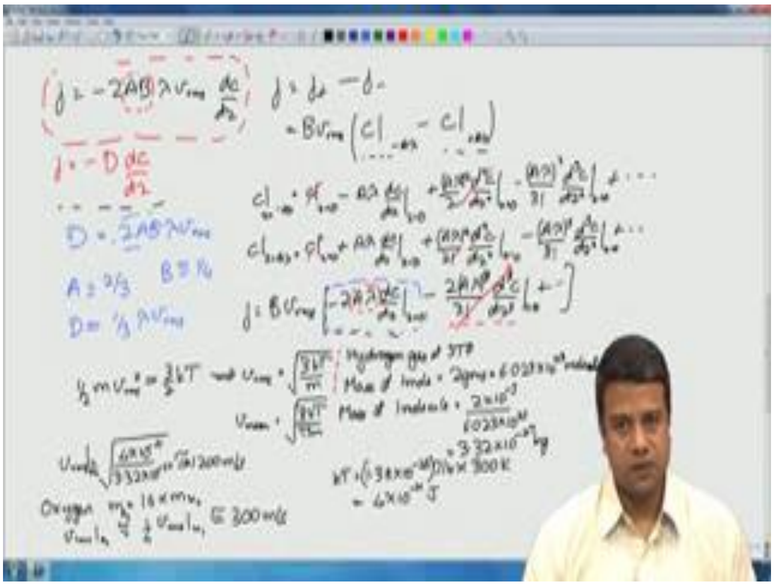

And now if we expand these concentrations above and below the surface in a Taylor series expansion, in the distance from the surface and we subtract those; we get the first term that is proportional to the gradient of the concentration, the first derivative times the mean free path, so that is a concentration difference; the derivative times the mean free path because the distance between the locations above and below the surface is comparable to the mean free path that times the fluctuating velocity and that straight away gives us what is the diffusion coefficient, if we compare that with the Fick's law for diffusion.

Diffusion coefficient has the mean free path times the root mean square of the fluctuating velocity, subject to some constants which are not yet known, which are dimensionless and of order 1. So, all these diffusion coefficients will scale as the mean free path times of fluctuating velocity and in the last lecture we had made an attempt to actually determine what is the magnitude estimate of the mean free path and the fluctuating velocity. Fluctuating velocity is comparable to the speed of sound, it is about 300 meters per second in air oxygen nitrogen, it is much larger for hydrogen because the hydrogen molecules are much smaller about 1200 meters per second.

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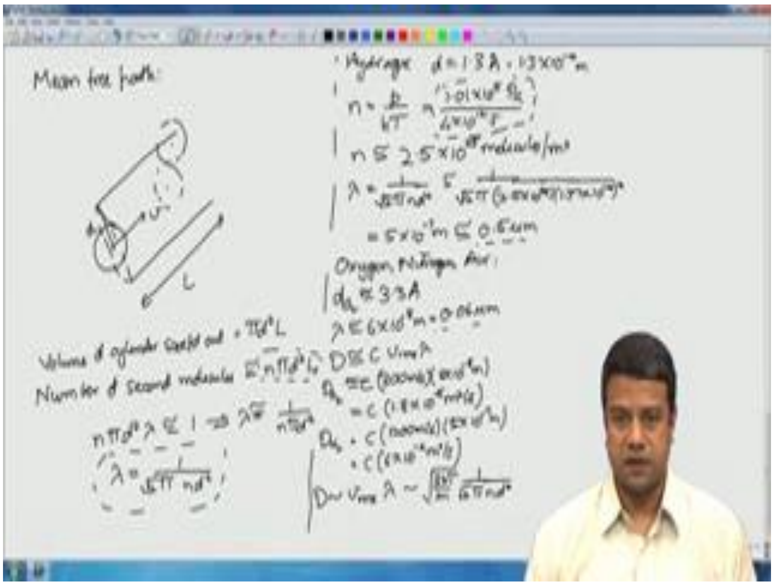

We had also made an estimate of the mean free path by looking at the volume swept out by a molecule as it is translating through the gas and on the basis the volume swept out we calculated the number of second molecules that are there and when that is approximately one we know that the mean free path is comparable to the length that has travel and we got this expression for the mean free path up to within a dimensionless constant.

And we had evaluated the values of these for oxygen for example, the mean free path is about a 10th or less of a micron for hydrogen is about half a micron. So, that is roughly the magnitude and on that basis you can get out what is the diffusion coefficients, they are approximately 10 power minus 5 meter square per second for oxygen nitrogen and so on. You can get more exact expressions for the diffusion coefficient using more exact calculations in kinetic theory of gases.

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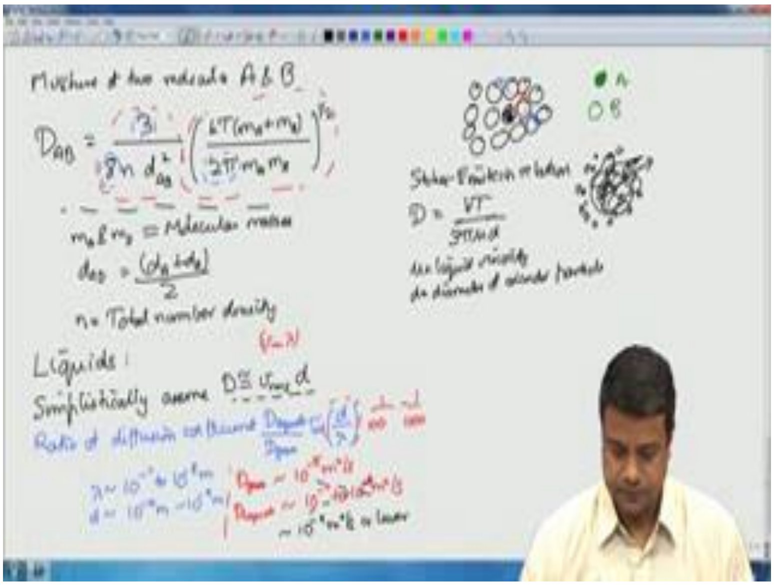

Mixture of two molecules A & B

$$D_{AB} = \frac{3}{8 n d_{AB}^2}\left(\frac{kT(m_A+m_B)}{2\pi m_A m_B}\right)^{1/2}$$

m_A & m_B = Molecular masses

$d_{AB} = \frac{(d_A+d_B)}{2}$

n = Total number density

Liquids:

Simplistically assume $D \cong v_{rms} d$

Ratio of diffusion coefficient $\frac{D_{liquid}}{D_{gas}} \sim \left(\frac{d}{\lambda}\right)$

Stokes-Einstein relation

$D = \frac{kT}{3\pi\mu d}$

The diffusion coefficient that you will get, so if I had a mixture of two molecules A and B the diffusion coefficient D AB for spherical molecules in kinetic theory of gases to within about 2 percent or so accuracy is of the form 3 by 8 n d AB square into k T by 2 pi m a, m d to the half. You can see this is approximately the same as what we had earlier 1 by n b square is approximately proportional to the mean free path that we calculated earlier k t by m to the half is proportional to the mean square fluctuating velocity, but the kinetic theory calculation gives you the constants as well, again this expression the constants present in this expression where m a and m b are the molecular masses of the two species, d AB is the mean diameter d a plus d b by 2 and n is the total number density.

And you can get a similar expression in case you had only one species, if the masses and the diameters of the two species are equal, then you just have d AB is equal to d and m a is equal to m b; so that will be the diffusion coefficient. So, this is the exact expression but to within a multiplicative constant, we got the same expression from the product of the mean free path and the fluctuating velocity of the molecules and in all of these cases the diffusion coefficient scales approximately as the product of the means free path and the fluctuating velocity.

Now, if you go to liquids the situation is different; if you have to simplistically assume the diffusion coefficient is equal to v; r m s or times the molecular diameter. In the case of liquids, I told you that the molecules are all closely packed so the microscopic molecular scale in this case, the distance between molecules is the molecular diameter itself. So, if you have to assume that this scales is the molecular diameter times the root mean square velocity. In gases, I told you that the mean free path is of the order of 0.06 to about 0.5 microns. So, it is approximately 0.1 micron; 0.1 microns is about 100 nanometers. So, the only thing that changes here is that instead of, in the case of gases instead of having v; r m s times lambda, I have now v r m s time to d. So, is the molecular diameter is much smaller, you would expect that the ratio of the diffusion coefficients D in liquids by D in gases, will be approximately the molecular diameter divided by the mean free path.

The ratio of the molecular diameter in the mean free path in gases the molecular diameter the mean free path is of the order of 0.01 to 0.1 micron that is 10 power minus 8 to 10 power minus 9; sorry 10 power minus 8 to 10 power minus 7 meters. So, lambda goes as 10 power minus 7 to 10 power minus 8 meters, the molecular diameter typically goes as 10 power minus 10 meter, it goes as 1 angstrom to 10 angstroms to 10 power minus 9 meters. So, you would expect this ratio to be of the order of 1 in 100 to 1 in 1000, I told you that D of gases goes as 10 power minus 5 meters square per second which means that by this calculation D in liquids should go as 10 power minus 7 to 10 power minus 8 meter square per second. Turns out that this is not quite accurate, the diffusion coefficient in liquids actually goes as 10 power minus 9 meter square per second or lower. For example, in water the diffusion of small molecules hydrogen, oxygen etcetera will be proportional to 10 power minus 9 meter square per second.

For larger molecules the diffusion coefficient is even less, it is of the order of 10 power minus 11 to 10 power minus 13 meter square per second; that is four orders of magnitude smaller. So the diffusion coefficient in liquids is actually overestimated by a simple estimate like this, it is actually much lower than what you would expect from just taking the product of the root mean square velocity and the molecular diameter or from the root mean square velocity is the same, whether it is liquids or gases it scaled as square root of 3 k t by m; only the diameter is much smaller than the mean free path.

The reason that this kind of an estimate does not give you an accurate answer is because if you look at a liquid; the molecules are all very closely spaced and so if one molecule has to move in any particular direction, you require that other molecules have to move out, when you have a dense packed cluster of molecules; if any molecule has to diffuse in any particular direction, all the other molecules had to move out of the way. So, there has to be some cooperative motion, so at all of these molecules can diffuse; after all mass diffusion has to take place by the physical motion of the molecules.

If we had two molecules A and B, so one molecule is A and the other molecules are B; diffusion of molecule A requires that the A molecules have to actually moved and without the molecules moving, you cannot have mass diffusion and for this reason mass diffusion is a much slower process because it requires in a densely packed liquid with molecules, it requires that there has to be cooperative motion amongst the molecules so that there can be mass diffusion.

And for this reason the mass diffusion coefficient in liquids is much smaller than what you just expect just on the basis of the mean free path and the fluctuating velocity. There is no simple formula of this kind that can be used in liquids, what is used is what is something based upon what is called the Stokes Einstein relation, the diffusion coefficient is equal to k t by 3 pi m u b. This expression actually is for the diffusion of a colloidal particle in a liquid which contains small molecule because of the collisions of the liquid molecules on this particle, liquid molecules are in a state of constant motion therefore, they are constantly exerting a force on this molecule, on this colloidal particle. There are instantaneous asymmetries in the force because at any instant in time, you may not have equal number of molecules on either side or equal forces on either side that actually results in a diffusive motion of this molecule; it is called thermal diffusion of this molecule or Brownian motion.

For this the diffusion coefficient is written as k t by 3 pi m u d, where m u is equal to the liquid viscosity and d is equal to the diameter of the colloidal particle. This is an exact expression if the diameter of the colloidal particle is much larger than the diameter of the molecule. So, that instantaneously the each colloidal particle is interacting with many such molecules; however, it can be used also to determine to estimate the diffusion coefficient for the molecules within this liquid. So, this expression where k t is a thermal energy and 3 pi m u is the viscosity of the liquid and d is the diameter of the colloidal particle.

This can be usefully employed in order to find out what is the diffusion coefficient. So, I have tried to explain to you the physical mechanism of mass diffusion in liquids and in gases. In gases because the distance traveled between successes interactions was large compared to the molecular diameter. Diffusion takes place primarily due to the free flight, the ballistic motion of molecules between collisions across the surface and in that case we were able to determine the diffusion coefficients based upon the mean free path and the molecular diameter to a very high degree of accuracy.

Whereas in liquids the diffusion coefficient is much slower than what you would simplistically assume and the reason for that is because when the molecules are densely packed, the diffusion of a molecule in any one particular direction requires cooperative motion of all the other molecules around and that is a much slower process because mass diffusion can take place only due to the physical motion of molecules, due to the physical motion of the solute molecules across the surface and that is a much slower process, so that is a brief introduction to mass diffusion.

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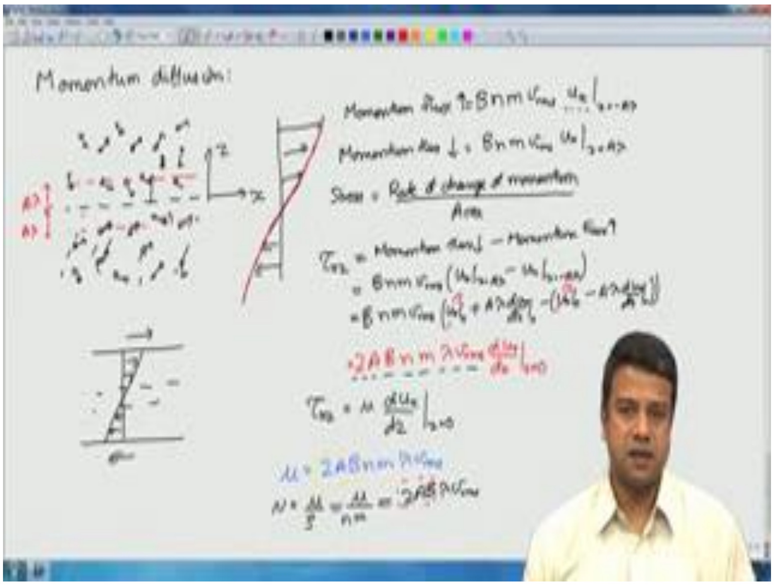

Now, let us come to momentum description; let us say, we have a surface here and we have molecules with some fluctuating velocities and let us consider that there is also a mean velocity. So, I need to put a coordinate system here, so I will take this as the x direction, this as the z direction; z direction is across the surface perpendicular to the surface, it is in the z direction that momentum diffusion is taking place and there is some velocity variation across the surface, variation in the mean gas velocity across the surface due to some applied flow for example, this could be a small section of the flow between two plates; here two place like this, you will end up with having a mean velocity across the surface and I will just consider the small sectional here. So, there is a variation in the mean gas velocity across the surface and the mean velocity in the x direction; the variation is in the z direction.

Due to this variation what is going to be the momentum flux across the surface. Now at each location in this flow, the mean velocity of the molecules is equal to the mean velocity at that location and that is varying with position. Now if I look at the molecules that are crossing this surface, the molecules that are coming downwards are coming an average from a distance comparable to the mean free path above the surface, whereas, the molecules that are going upwards are going from a distance comparable to the mean free path from below the surface.

Due to this there is going to be a net transfer of momentum across the surface because the average momentum of the molecules below the surface is different from the average momentum of the molecules above the surface and this is going to result in a net flow of molecules across the surface, so how do we compute that. Now what is the momentum flux going upwards, it is going to be equal to the mass flux times the average momentum of the molecules that are crossing the surface. So, it is going to equal to the mass flux which is equal to the number density, times the mass of a molecule times the v r m s fluctuating velocity, mass flux is just the mass density times the root mean square the fluctuating velocity. The mass density is the number density times the molecular mass, times the mean velocity of the molecules at a location z is equal to minus A lambda, that is the approximate expression for the momentum flux going upwards and of course, this is just a proportionality. So, I have a proportionality constant here of order one in order to get the total momentum flux across the surface.

What is the momentum flux downloads, it is going to be equal to B n m v r m s, the mass flux times the velocity at a location z is equal to A lambda. Now what is going to be the stress due to this transport? The stress on the surface below the surface; on the volume below the surface. Stress is equal to rate of change of momentum per unit area; here I will make a slight distinction from what I had done earlier in the case of mass transfer. I will define the stress to be positive, if it increases the momentum of the volume that is below the surface, the stress to be positive if it increases the volume of the momentum below the surface that is if it increases the momentum of the volume for which the outward perpendicular within the plus side direction. So, tau x z is the momentum change per unit area in the x direction, the momentum is in the x direction because the velocity in the x direction, the transfer direction is in the z direction; I will define it as positive if it increases the momentum of the volume below; the volume whose use outward unit normal is in the plus side direction.

So, this is going to be equal to the momentum flux downward minus the momentum flux. so that is the rate of change of momentum per unit area; per unit time which is a force per unit time rate of change of momentum per unit time is a force. So, that is the net rate at which the force is being exerted on the volume below whose outward unit normal is in the plus side direction. That is the way stress is defined tau x z is the rate of change of x momentum, x momentum because I considered the mean velocity in the x direction; at a surface whose outward unit normal is in the plus side direction. It is the outward unit normal in the plus side direction; that means that you are considering the increase in momentum of the volume below the surface.

So, this I can once again get, so I get B n m, v r m s into u x at z is equal to A lambda minus u x at z is equal to minus A lambda; that is the (Refer Time: 24:18) momentum flux. So, this will be equal to B n m; v r m s and once again if I use a Taylor series expansion for the variation of the mean velocity, I told you that we can include just the first term in the expansion provided the mean free path is much smaller than the macroscopic scale. So, if I do the Taylor series expansion and include only the leading the first derivative; I get u x at 0 plus A lambda u x by d z at 0 minus u x at 0 minus A lambda d u x by d z and once again the constant term actually gets cancelled and I will get A B n m lambda v r m s d u x by d z x z is equal to 0; the factor of 2.

So, there is the expression shear stress and from this we have to determine the viscosity. So this is the expression for the shear stress, this contains the coefficients A B n m lambda v r m s; compare that with Newton's law of viscosity; tau x y is equal to tau x z; my apologies d; u x by d square is equal to 0, this gives me the expression for the connection the viscosity to A B and n m lambda v; r m s, therefore, the viscosity goes as some constant; times n m lambda v r m s.

This is a dynamic viscosity, we had earlier defined the momentum diffusivity as the kinematic viscosity, as the dynamic viscosity divided by the density and we know that the dynamic viscosity; the density is the mass density is equal to the number density times the molecular mass and this just becomes equal to 2 A B lambda here. So, we are getting the same expression for the kinematic viscosity as the mass diffusivity to within these multiplicative constants, which could be different; give these multiplicative constant could be different because the average location from which these molecules are coming may depend upon what quantity you are calculating.

The v r m s it is of course, not dependent on that, but when you do the a more exact calculation; you will find that these coefficients here A and B do depend upon, whether you are looking at mass diffusion or momentum diffusion; however, both of these diffusivities are proportional to the mean free path times v r m s fluctuating velocity and this shows the analogy between mass and momentum diffusion. Both of them are proportional to the root mean square velocity times the mean free path. In both cases the reason is that in both cases transfer of mass or momentum takes place due to the physical transfer of molecules across the surface in a gas. The transfer due to intermolecular interactions is much smaller in a gas because the molecules move distance is large compared to their diameter between collisions.

And due to that the physical mechanism of mass and momentum transfer are the same between liquids and gases and for that reason the dependence of the mean free path and the molecular fluctuating velocity ends up being the same whether it is a liquid or a gas I am sorry whether it is mass transfer or momentum transfer.

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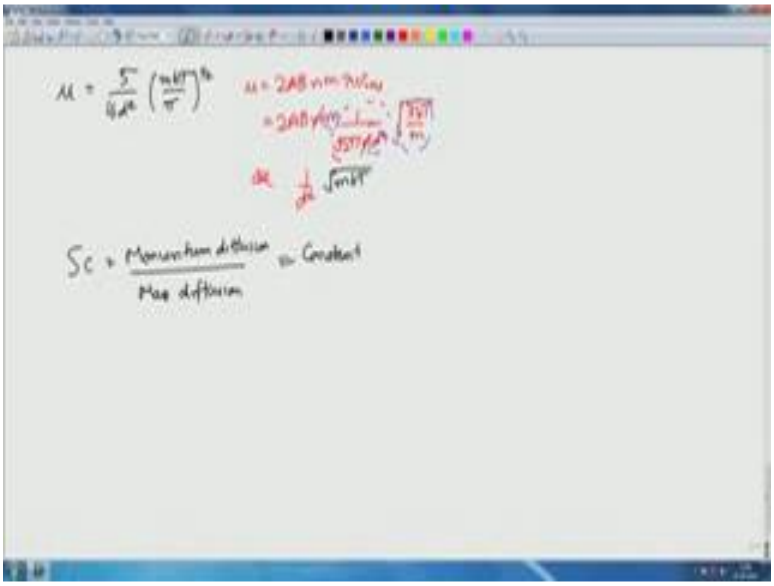

$$\mu = \frac{5}{16 d^2}\left(\frac{mkT}{\pi}\right)^{1/2}$$

$$\mu = 2AB\, n m \lambda v_{rms}$$

$$= 2AB\, nm \frac{1}{\sqrt{2}\pi n d^2}\sqrt{\frac{3kT}{m}}$$

$$\mu \propto \frac{1}{d^2}\sqrt{mkT}$$

$$Sc = \frac{\text{Momentum diffusion}}{\text{Mass diffusion}} \sim \text{Constant}$$

You can get more exact expressions for the dynamical viscosity using kinetic theory of gases. You get an expression of the form 5 by 16 d square, m k T by pi to the half; note that I had earlier said that the dynamic viscosity scales as 2AB n m lambda v r m s. So, this has to be of the form 2AB n m, lambda is 1 by root 2; pi n d square and v r m s is root of 3 kt by m and therefore, in the dynamical viscosity you see that the number density dependence actually cancels out.

Basically because as the number density increases, the number of molecules crossing a surface does increase; however, as the number density increases; the distance of the molecules move decreases as 1 over the number density and it is for this reason that the viscosity and gases was independent of the number density and it will be it go as some constant times m, sorry if you work this out; it will go as, it will be proportional to 1 over d square that it is coming out of here and then if I have this mass and this root of kt by m and therefore, the product of these two will be giving something that goes as root of m k t divided by d square.

So, there is the dependence of the viscosity on the molecular properties in a gas and the kinematic viscosity has the exact same dependence as the mass diffusion coefficient and I told you the physical reason for that and it is for this reason that the ratio of momentum, the spit number which is the ratio of momentum diffusion to mass diffusion is approximately a constant in the kinetic theory of gases.

So, next lecture I will start off with comparing this with the situation in liquids and then we look briefly at thermal diffusion and then we will proceed to actually solving problems. So, I will continue with this topic of diffusion of mass momentum and energy, I have completed mass diffusion; I will see a little bit more about momentum diffusion and then a little bit about energy decision and then we will go on to actually solving problems. So, with this I will see you in the next lecture, we will continue this topic.

Thank you.