

Transport Processes I: Heat and Mass Transfer
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Lecture - 16
Diffusion: Estimation of mass diffusion coefficient

Welcome to this lecture number 16 in our course on fundamentals of transport processes. In the previous lecture we were discussing molecular diffusion and how we get the constitutive relations based upon molecular diffusion. The discussion the previous lecture was restricted to diffusion in gases, mass diffusion in gases.

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Diffusion coefficients & constitutive relations:
Gases:

Net flux $J = BC \frac{U_{rms}}{2A\lambda} - BC \frac{U_{rms}}{2A\lambda}$

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

$C \text{ Net flux} = BU_{rms} [C|_{z=L} - C|_{z=0}]$
 $= -2ABU_{rms} \left(\frac{dc}{dz} \right)_{z=0}$

Number of red molecules coming downwards $= BC \frac{U_{rms}}{2A\lambda} = \delta^-$
 Area \times time
 Number of red molecules going upwards $= BC \frac{U_{rms}}{2A\lambda} = \delta^+$
 Area \times time

I considered here a typical experimental configuration that is used for calculating the diffusion coefficient, you have two reservoirs with different kinds of gas molecules with a valve in between and when you open the valve, there is a transporter of gases across the surface, for the present we had considered that the molecular masses of the two gases are equal that is a simplification, but it makes our discussion easier.

If the molecular masses are equal, then there is no net motion across the surface there is no net mass transfer across the surface at constant temperature and pressure; however, since there is a variation in concentration, there will be a transfer of the red molecules downwards and a transfer of the blue molecules upwards and we had identified the cause for this transfer.

If you expand out this region here, you can see that for transfer across the surface the molecules that are coming downwards are coming on an average at a distance above the surface comparable to the mean free path because these molecules travel distances comparable to the mean free path between collisions therefore, the molecules that are coming downwards are coming originating at some distance above the surface, that distance is comparable to the mean free path. The molecules that are going upwards are originating at some distance below the surface, that distance is also equal to comparable to the mean free path.

There is no net transport, the total number of molecules coming down has to be equal to the total number of molecules going up, because there is no mean fluid velocity at any of these locations; however, because the concentration of molecules of type A above the surface is different from the concentration of molecules of type B below the surface, there will be a net transport of molecules from above to below because the total number of molecules at that surface above of A type is higher than the number of molecules surface below and that is going to cause a net transport of molecules. There will be an equal and opposite transport of molecules of type B in the opposite direction once again because the concentrations at these two locations are there. So, these are the diffusion fluxes due to the fluctuating velocities of the molecules. When I discussed convection, I had said that the convective transport of materials is equal to the mean velocity and if the flux is equal to the mean velocity times the mass density or the concentration.

In this case of the diffusive flux we have a similar relationship, except that is not exactly equal it is not the mean velocity, but rather the root mean square of the fluctuating velocity that should be taken to account. So, if the root mean square is a fluctuating velocity that is important in this case. So, therefore, the flux is equal to is proportional to the root mean square fluctuating velocity, times the concentration at that average location. Where B is a constant and A is also constant, it tells you what is the average distance above or below the surface from which these molecules originate.

So, the flux downwards is equal to b times the concentration at location above the surface, times the root means substituting velocity. Flux upwards is equal to some constant, times the concentration at the locations below the surface times the fluctuating velocity. Net flux is the flux going upwards minus the flux going downwards. So, I had

written that as this concentration at two different locations times the routines are saturating velocity the difference between these two.

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The whiteboard contains the following handwritten content:

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

$$= Bv_{rms} (C|_{z=A\lambda} - C|_{z=0})$$

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

$$D = \frac{2AB\lambda v_{rms}}{3}$$

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

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

$$C|_{z=0} = C_0 + A\lambda \frac{dc}{dz}\bigg|_{z=0} + \frac{(A\lambda)^2}{2!} \frac{d^2c}{dz^2}\bigg|_{z=0} - \frac{(A\lambda)^3}{3!} \frac{d^3c}{dz^3}\bigg|_{z=0} + \dots$$

$$C|_{z=A\lambda} = C_0 + A\lambda \frac{dc}{dz}\bigg|_{z=0} + \frac{(A\lambda)^2}{2!} \frac{d^2c}{dz^2}\bigg|_{z=0} - \frac{(A\lambda)^3}{3!} \frac{d^3c}{dz^3}\bigg|_{z=0} + \dots$$

$$j = Bv_{rms} \left[-2A\lambda \frac{dc}{dz}\bigg|_{z=0} - \frac{2(A\lambda)^3}{3!} \frac{d^3c}{dz^3}\bigg|_{z=0} + \dots \right]$$

Annotations on the whiteboard include:

- Red circles around $\lambda \frac{dc}{dz}$ and $\frac{\lambda^3}{L^3} \frac{dc}{dz}$.
- Red text: "only for $\left(\frac{\lambda}{L}\right) \ll 1$ ".

So, therefore, the flux was given by j is equal to j plus minus j minus, which is equal to B times V rms in to C at z minus A lambda, minus C at plus A lambda. Now each of these two we had expanded, we had written C at z minus A lambda equal to c I should like the second feed on 0, 0 here is equal to C at z is equal to 0, minus A lambda d c by d z and that is equal to 0.

And similarly C at z is equal to plus A lambda is equal to C f. So, those are the two expressions, now I have to take C at z minus A lambda, minus C x z plus lambda, when I subtract the two these terms will cancel out and ultimately you will be left with an equation for the diffusion flux that is of the form B V rms, minus 2 A lambda d c by d z and z is equal to 0, minus 2 A lambda the whole cube by 3 factorial, plus additional terms higher order terms. So, that is the expression for the flux.

Note that when we make the linear approximation in the previous lecture, what we had done was to neglect this term and higher order terms in comparison to this term which we resumed was going to be the largest term. So, we cut off the series at this first term when it is justified. If you look at this term here, it scales as the ratio of a mean free path, you mean free path is the molecular scale and the gradient is the gradient of the concentration, the gradient of the concentration is going to be equal to the difference in

concentration between these two locations, divided by this microscopic plants scale. The gradient of the concentration is going to be the difference in concentration divided by this length scale (Refer Time: 08:42) difference in concentration, the system size if you will therefore, this term here will scale as a mean free path times a difference in concentration is the first time here will scale us a mean free path times the difference and concentration divided by the system size.

The second term here will scale as the mean free path cubed because it is lambda cubed times the third derivative of the concentrations with respect to distance, ΔC by L cubed.

So obviously, this term can be neglected in comparison to the first term only for lambda by L , being small compared to 1. Only in that case will this term be much smaller than this done here because this causes lambda by L , the next term goes as lambda L the whole cube, the next time will go as lambda by L to the 5th power and so on. So, we can neglect the second term in comparison to the first only when the mean free path is much smaller than the distance over which there are concentration variations. Typically there will be concentration variations in a reactor for example, or distance is comparable to the particle size, the catalyst size or in the case of heat exchanger the temperature varies or distance comparable to the diameter of the tube. So, therefore, only when the mean free path is much smaller than this lens macroscopic land scale, is this valid and that is a point that I had emphasized in the last lecture as well. The continuum description is valid only when the system size is much larger than the molecular scales; in the case of gases the molecular scale is the mean free path, in the case of liquid the molecular scale is the particle diameter itself.

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

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

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

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

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

$$\frac{1}{2} m v_{rms}^2 = \frac{3}{2} kT \Rightarrow v_{rms} = \sqrt{\frac{3kT}{m}}$$

Hydrogen gas at STP
 Mass of 1 mole = 2gms = 2×10^{-3} kg
 6.023×10^{23} molecules
 $kT = (1.38 \times 10^{-23}) / 16 \times 300 \text{ K} = 4 \times 10^{-21} \text{ J}$

$v_{rms} = \sqrt{\frac{4 \times 10^{-21}}{3.32 \times 10^{-27}}} \approx 200 \text{ m/s}$
 Oxygen $m_2 = 16 \times m_H$
 $v_{rms, O_2} = \frac{1}{4} v_{rms, H_2} \approx 300 \text{ m/s}$

So, if that condition is satisfied, then we can neglect all these higher terms in the expansion, you can neglect all these higher terms in the expansion and retain only the first term and then we get this expression for the flux and just by looking comparing that with the standard fixed loss or for mass transfer, you can see that the diffusion coefficient is proportional to the mean free path times the fluctuating velocity.

So, therefore, if we know what is the mean free path and what is the fluctuating velocity, we can get some estimate for the mass diffusion coefficient. So, you will next try to calculate what are the mean free path and the fluctuating velocity in gas molecules in gases?

The fluctuating velocity in gases can be written in a few different ways; typically half $m v_{rms}^2$ is equal to $\frac{3}{2} kT$ for mono atomic gases from the equip partition of energy, which implies that v_{rms} is equal to root of $\frac{3kT}{m}$. So, this is the root mean square of the fluctuating velocity of the molecules, you can also define a mean velocity. The mean velocity of the molecules is sometimes defined as root of $\frac{8kT}{\pi m}$; this is what is called the mean molecular speed, these two differ only by a constant that is order one. So, for the present purposes we will use this definition of the root mean square fluctuating velocity. In any case we do have these constants here in this expression and these constants will change depending upon which value of the gas velocity that one

implies, in either case we can use any one of these in order to just get an estimate of the decision coefficient. So, I will use the root mean square of the fluctuating velocity.

How much is this velocity for example, if we take the case of hydrogen gas at room temperature I standard temperature and pressure, what is the mass of the hydrogen molecule? we know that mass of one mole is equal to 2 grams and one mole is 6.023×10^{23} molecules.

Therefore the mass of one molecule is equal to 2×10^{-3} grams is 2×10^{-3} kilograms, divided by 6.023×10^{23} ; this works out to approximately 3.32×10^{-27} kilograms. Now what is kT ? kT is equal to 1.38×10^{-23} there is a Boltzmann constant in Joules per Kelvin into at room temperature will take it is approximately 300 Kelvin, this is approximately 4×10^{-21} J.

Using these two you will find that V_{rms} equal to square root of 4×10^{-21} divided by it is approximately equal to 1200 meters per second approximately. You can see that quite easily. So, this is the root mean square velocity of the molecules in hydrogen gas. In oxygen gas for example, this is for H_2 , the molecular weight of oxygen m is equal to 16 times, m of oxygen is 16 to mass of hydrogen, it is 32 whereas, hydrogen is 2, which means that V_{rms} of oxygen is going to be approximately equal to $1/4$, you have one over square root of mass in the denominator, $1/4$ times V_{rms} now hydrogen, which will be approximately 300 meters per second.

Similarly, for air which contains nitrogen and oxygen it is approximately the same, approximately 300 meters per second. Approximately 300 meters per second is also the speed of sound in air 330 meters per second. So, therefore, the speed of the molecular fluctuating velocities is comparable to the speed of sound and that is no surprise because sound propagates through pressure waves through the air and the maximum velocity which those pressure waves can propagate has to be comparable to the molecule of fluctuating velocities. So, this the molecule of saturating velocity is V_{rms} for hydrogen is about 1200 meters per second, for oxygen it is about 300 meters per second.

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Mean free path:

Hydrogen $d = 1.3 \text{ \AA} = 1.3 \times 10^{-10} \text{ m}$

$$n = \frac{p}{kT} = \frac{1.01 \times 10^5 \text{ Pa}}{4 \times 10^{-21} \text{ J}}$$

$$kT = (1.38 \times 10^{-23} \text{ J/K}) \times 300 \text{ K} \approx 4 \times 10^{-21} \text{ J}$$

Volume of cylinder swept out $= \pi d^2 L$

Number of second molecules $\approx n \pi d^2 L$

$$n \pi d^2 \lambda \approx 1 \Rightarrow \lambda \approx \frac{1}{n \pi d^2}$$

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

Now, what about the mean free path? How do we calculate or rather estimate the mean free path? The mean free path is the distance between two inter molecular collisions. So, if you consider one molecule as it is moving with the translation velocity V , now this molecule it sweeps out a cylindrical volume, this molecule it will sweep out a cylindrical volume as it moves along, whose radius is equal to the molecular diameter such that if some other the center of some other molecule comes within the cylinder; that means, that the two molecules are collided; that means, the distance between these two has become the centers of these two molecules has become less than a molecular diameter; that means, that these two molecules have collided.

So, sweeps out cylinder of volume of cross sectional radius d and some length L , what is the total volume in the cylinder? Swept out is going to be equal to the cross sectional area πd^2 times L .

What is the number of second molecules in the cylinder has to be equal to the number density of the molecules times the volume of the cylinder, that is the number of second molecules in this cylinder. When the length is very small the number of second molecules is also very small. So, the probability that a second molecule has collided is very small; as the length becomes larger and larger you have many such molecules in this volume; that means, that this molecule has already collided.

When does the molecule translate approximately one mean free path, that is when the number of second molecules in this cylinder is approximately one; that is therefore, it has translated a distance equal to one mean free path when $n \pi d^2 \lambda$, it is approximately equal to 1. What that means is that, the mean free path λ is equal to $1 / n \pi d^2$. So, this is just an order of magnitude estimate, I said that the number of second molecules has to be approximately 1, for the molecule to collide on average and on that basis I would get caught the mean free path to within a proportionality constant. You can do a more exact calculation and if you do that you will find that the expression for spherical molecules for the mean free path is $1 / \sqrt{2} n \pi d^2$ sorry straight that as.

Note that n is the number density of the molecule; the number of molecules per unit volume. So, it is just a number per unit volume. So, therefore, if I have this expression for the mean free path, I can then calculate what is the mean free path in real gases; so, and I should correct myself. So, in order to estimate what is the mean free path I need to know what is the number density of the molecules and the diameter of the molecules. So, once again if we take the example of hydrogen, the diameter of the hydrogen molecules is approximately 1.3 angstrom is equal to 1.3×10^{-10} meters.

What is the number density of the molecules? The number density of the molecules has to be you know that n by v is equal to P by $k T$ from the ideal gas law, P is equal to if you recall the ideal gas law, it is usually written as P is equal to $N k T$ by V ; N is the number of molecules V used to volume. So, therefore, I can also write this as $n k T$ whereas, small n is the number of molecules per unit volume. So, from the ideal gas law you get the number density of the molecules or the number of molecules per unit volume.

So, pick n is equal to P by $k T$, once again at standard temperature and pressure, the pressure is 1.01×10^5 Pascals, that is an SI units atmospheric pressure is 10^5 pascals, which is newtons per meter square. Now what is $k T$? $k T$ is the 1.38×10^{-23} joules per Kelvin into 300 Kelvin. It is approximately 4×10^{-21} choose. So, this I have 4×10^{21} joules.

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Mean free path:

Hydrogen $d = 1.3 \text{ \AA} = 1.3 \times 10^{-10} \text{ m}$

$n = \frac{p}{kT} = \frac{1.01 \times 10^5 \text{ Pa}}{4 \times 10^{-21} \text{ J}}$

$n \approx 2.5 \times 10^{25} \text{ molecules/m}^3$

$\lambda = \frac{1}{\sqrt{2} n d^2} = \frac{1}{\sqrt{2} \pi (2.5 \times 10^{25}) (1.3 \times 10^{-10})^2}$

$= 5 \times 10^{-7} \text{ m} \approx 0.5 \mu\text{m}$

Oxygen, Nitrogen Air:

$d_{O_2} \approx 3.3 \text{ \AA}$

$\lambda \approx 6 \times 10^{-8} \text{ m} = 0.06 \mu\text{m}$

Volume of cylinder swept out $= \pi d^2 L$

Number of second molecules $\approx n \pi d^2 L$

$n \pi d^2 \lambda \approx 1 \Rightarrow \lambda \approx \frac{1}{n \pi d^2}$

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

$D \approx C v_{rms} \lambda \sim \sqrt{\frac{3kT}{m}} \frac{1}{\sqrt{2} \pi n d^2}$

$D_{O_2} = C (300 \text{ m/s}) (3 \times 10^{-10} \text{ m})$

$D_{N_2} = C (1.8 \times 10^4 \text{ m}^2/\text{s})$

$D_{H_2} = C (1200 \text{ m/s}) (5 \times 10^{-10} \text{ m})$

$D_{H_2} = C (6 \times 10^{-4} \text{ m}^2/\text{s})$

If I divide these two up, I will get a number density; n is approximately 2 point 5 into 10 bar 25 molecules per meter cubed. Pascal has dimensions of force per unit area or energy per unit volume and dividing it by energy. So, I just get a number per unit volume of these molecules and using that and the diameter of these hydrogen molecules, I can estimate the mean free path λ is equal to 1 by $n d^2$ is equal to 1 by 2 pi into 2 point 5 into 10 bar 25 into 1 point 37 into 10 power minus 10 whole squares. And this gives me mean free path of approximately 5 into 10 power minus 7 meters, which is approximately 0 point 5 micrometers, it is a half a micrometer.

So, that is the mean free path in a gas and for the container approximation to be valid, I told you in the last lecture that the system size has to be much greater than this mean free path which is about half a micron. So, continuum description in this case the case of gases will be valid only when distances are larger than half of my craft or so.

Similarly, you can do the calculation for oxygen, nitrogen air: for all of these things the number density remains the same, the number density is exactly the same because it depends only on the pressure and the temperature; however, the molecular diameter d of O_2 is approximately 3.3 angstroms. So, molecular diameter is larger x factor of 3 or so, therefore, the mean free path goes as one over the diameter square. So, it will be smaller by a factor of approximately 10 λ is approximately equal to 6 into 10 power minus 8 meters.

So, that is 0.06 microns for oxygen. So, now, we have got the mean free path we have got the molecular fluctuating velocity, from this we can estimate a diffusion coefficient. D is equal to some constant times V_{rms} times λ , we found that V_{rms} was approximately for the case of oxygen is restricted to 300 meters per second into 6×10^8 meters, if you work that out you will get a constant into approximately 1.8×10^{-5} meter square per second. So, that is the diffusion coefficient approximate diffusion coefficient for oxygen molecules translating in air. The diffusion coefficient for hydrogen molecules is slightly higher; diffusion for hydrogen molecules is equal to $C \times 1200$ meters per second into 5×10^7 meters. So, this will give me approximately a constant into 6×10^4 meter square per second.

So, that is roughly the range of diffusion coefficients for a very small gas molecules it will be about 10^{-4} , but for most gas molecules the diffusion coefficient is in the range of 10^{-5} meter square per second. So, there is a normal diffusion coefficient and this comes from a molecular calculation of the actual mean free path and the fluctuating velocity in a molecule in a gas.

Note that we had earlier said that the diffusion coefficient goes as V_{rms} times to the mean free path, which is $\sqrt{\frac{3kT}{m}}$ if the root mean square velocity and $\frac{1}{\sqrt{2} \pi d^2 n}$. So, this is the dependence, this is the dependence on the number density the molecular diameter and the molecular fluctuating velocity.

I will continue this in the next lecture to give you a more precise idea of what these diffusion coefficients mean. Everything that which I have done so far is only in gases, how does it translate into diffusion coefficients in liquids; once that is done then we will look at diffusivities for momentum and energy and we will get diffusion coefficients for those as well in a similar manner in gases in a more approximate manner in liquids and that will give us some idea how to treat diffusion in comparison to convection. So, I will continue with this diffusion calculation, the next lecture go to diffusion coefficient in liquids and then we will look at mass diffusion I am sorry momentum diffusion and energy diffusion. So, we will continue this in the next lecture, I will see you then.