Molecules in Motion

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Lecture – 38
Molecular Motion in Gases

Welcome to another lecture on Molecules in Motion. We have almost covered most of the things which was supposed to be listed in your contents of the syllabus, but few things we will take up which was not essentially mentioned in the course content, but it is very much part of the understanding what we have.

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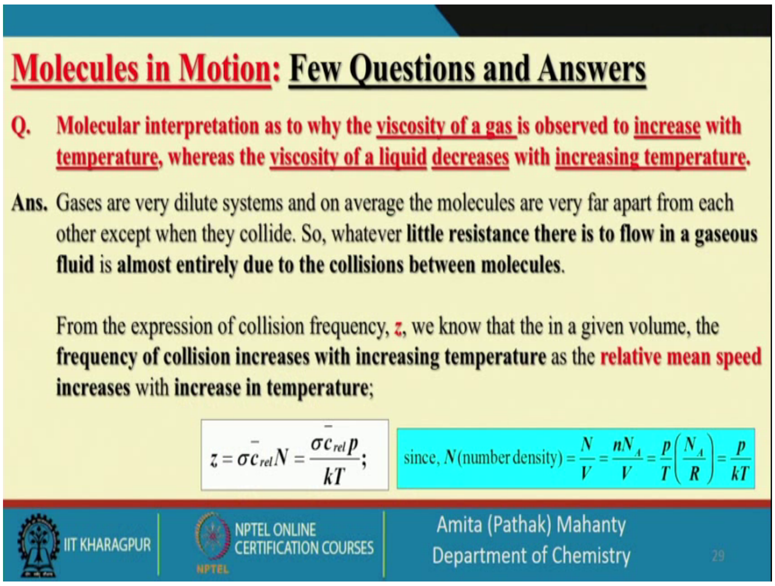

Molecules in Motion: Few Questions and Answers

Q. **Molecular interpretation as to why the viscosity of a gas is observed to increase with temperature, whereas the viscosity of a liquid decreases with increasing temperature.**

Ans. Gases are very dilute systems and on average the molecules are very far apart from each other except when they collide. So, whatever **little resistance there is to flow in a gaseous fluid** is **almost entirely due to the collisions between molecules.**

From the expression of collision frequency, z, we know that the in a given volume, the **frequency of collision increases with increasing temperature** as the **relative mean speed increases** with **increase in temperature**;

$$z = \sigma\bar{c}_{rel}N = \frac{\sigma\bar{c}_{rel}p}{kT};$$

since, N(number density) $= \frac{N}{V} = \frac{nN_A}{V} = \frac{p}{T}\left(\frac{N_A}{R}\right) = \frac{p}{kT}$

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So, starting with I would like to take a few questions which we have already discussed in detail actually, when we were talking about the viscosity of gases with viscosity of liquid we had a question which we had answered that time, but if you have a take a formal question like this, what is the molecular interpretation as to why the viscosity of a gas is observed to increase with increase in temperature? Whereas, for a liquid what happens the viscosity of the liquid decreases as we increase the temperature.

We will take two such questions we answer when we answer them and answer them in the form like it the second one same question may be of form in the form of a derivation which we have not taken initially. So, the molecular interpretation when we are talking about gases, what happens in the gas system? Gas the atom the molecules are far apart we can consider it as a system as a very dilute system and the on the average the molecules are very distance apart.

So, they and they are supposed to be only coming closer when they collide ok. So, whatever resistance they have in their flow; so when viscosity is a measure measurement of a measure of the resistance it is it experiences while it flows ok. So, whatever resistance it is offered in the flow of the molecules is going to be there in gaseous system is only because of the collision between the molecules. Essentially, we should understand what is the reason of say viscosity in a gas? Viscosity gas is free flowing, so, how do we justify having viscosity the viscosity is only when applicable or in can be thought to be as existing because, we are considering the collision of particles.

So, viscosity arises because the gas molecules undergo collision ok. So, from that expression of collision frequency I will not go in to the detail of the derivation, but I have given you the expression of the collision frequency z. Collision frequency for a given volume of a container, the frequency of the collision which is going to occur is going to be increasing with increasing temperature, as the as you see this is the expression for the frequency of collision. The more the number of collisions we have the more the resistance, so, viscosity should increase ok.

So, what happens when you having a high temperature? We have we are saying that viscosity of the gas increases with increase in temperature; that means; when I increase the temperature the number of collision increases, ok. So, the frequency of collision should be increased, right. So, this is the frequency of collision expression, this is the cross section of collision cross section which is equal to pi d square, where d is the distance between the two centres half the distance between the two centres of the atom or molecule which is colliding and supposed to be in touch with each other and this is the relative speed and this is the number density of the particles which we have.

So, number density if we if you have remember we had taken number density as number of molecules in the volume which is contained this is the definition of number density and if I want to consider say the total number of molecules then I multiplied the moles into the Avogadro number by the volume. Now, I this volume I which is fixed I replace it wi[th]- from the equation of PV equal to NRT and if I replace that by PV equal to NRT I get something like this.

So, I have this expression of N in which I put P by kT. So, you see T is in the denominator, despite that we have increased this is the frequency of collision we have a increase in number of collision with increase in temperature. That should be the eccentricity is inversely proportional it should not happen that way, but what then how do you justify the increase in collision increase in frequency of collision with increasing temperature.

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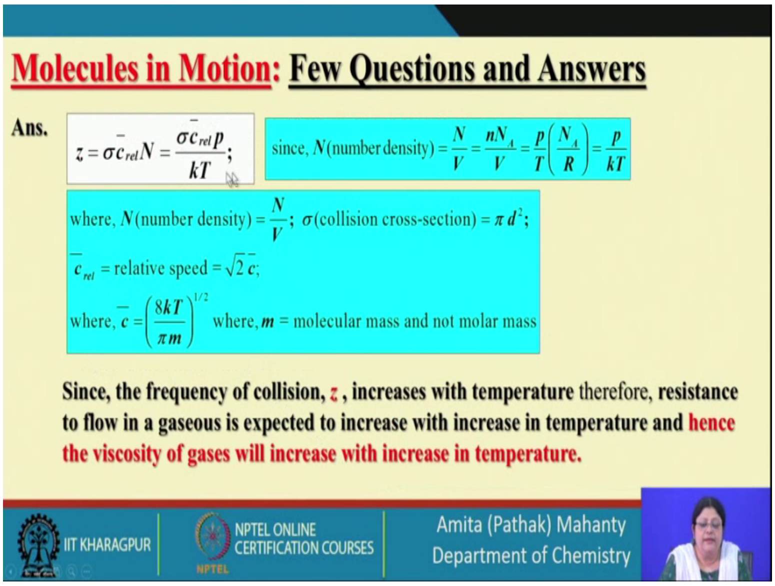

Molecules in Motion: Few Questions and Answers

Ans. $z = \sigma \bar{c}_{rel} N = \frac{\sigma \bar{c}_{rel} p}{kT}$;

since, $N(\text{number density}) = \frac{N}{V} = \frac{nN_A}{V} = \frac{p}{T}\left(\frac{N_A}{R}\right) = \frac{p}{kT}$

where, $N(\text{number density}) = \frac{N}{V}$; $\sigma(\text{collision cross-section}) = \pi d^2$;

$\bar{c}_{rel} = \text{relative speed} = \sqrt{2}\,\bar{c}$;

where, $\bar{c} = \left(\frac{8kT}{\pi m}\right)^{1/2}$ where, m = molecular mass and not molar mass

Since, the frequency of collision, z, increases with temperature therefore, **resistance to flow in a gaseous is expected to increase with increase in temperature and hence the viscosity of gases will increase with increase in temperature.**

What is important here, you see in this expression what is important here is the relative speed. What is relative speed? If you remember when we had taken the molecules to be identical then the mole[cule]- the relative speed was given to be under root into the mean speed. So, the mean speed is given to be 8 kT to the power half by m into pi, this pi become m becomes reduced mass when we have molecules which are colliding having two different masses. For simplicity we have considered the gas of one type, so, all the molecules are similar. So, we have taken this m as just to m and we have got the under root 2 here in the calculation of the relative speed.

So, what happens is the relative speed you see has a T term and this T term is associated with the speed associated with the molecules which are moving. So, as you increase the temperature what happens? The molecules start moving they have higher kinetic energy, they start moving with the higher speed. So, when you have higher speed the chances of collision becomes increased. So, the increase in temperature increases the number of collisions which is the gas molecules are undergoing and hence it is apparently increasing the resistance to the flow of the gas molecules. So, we can say that it is actually increasing the viscosity of the gas with increasing temperature right.

So, the whole thing comes from the concept of collision and collision going to is going to be related to the relative speed of the molecules which we are considering and each of them has a temperature factor directly in the numerator ok.

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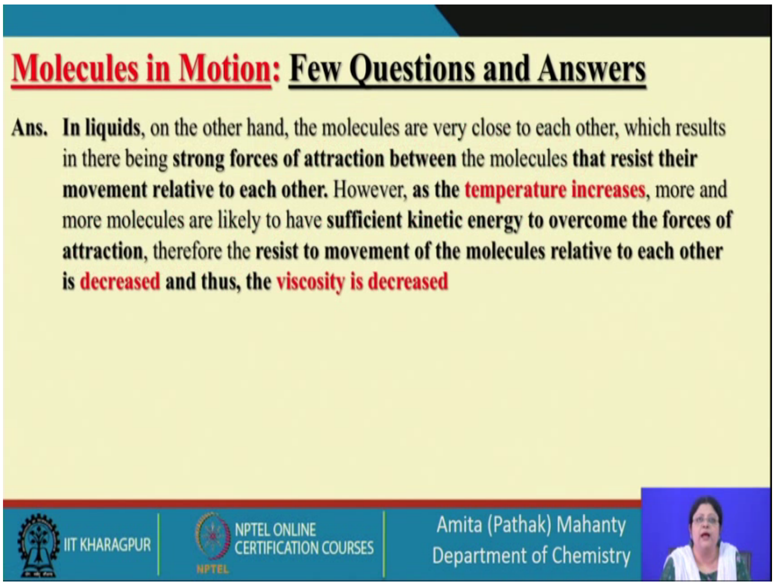

Molecules in Motion: Few Questions and Answers

Ans. **In liquids**, on the other hand, the molecules are very close to each other, which results in there being **strong forces of attraction between** the molecules **that resist their movement relative to each other.** However, **as the temperature increases**, more and more molecules are likely to have **sufficient kinetic energy to overcome the forces of attraction**, therefore the **resist to movement of the molecules relative to each other is decreased and thus, the viscosity is decreased**

So, this being the reason for the gases, what happens for the liquid? In liquid what happens we say that the in liquid the viscosity decreases with increasing temperature and what is the viscosity, this results tends to the flow of the fluid system ok. In liquid what happens on the other hand the molecules are much closer to each other which results in a strong attractive forces within the molecules or atoms ok. So, these since we have strong inter atom inter molecular forces in the form of attraction that causes them to move apart.

As you increase the temperature what you are giving, you are giving them sufficient kinetic energy to overcome these attractive forces and are able to move free. So, if they move they are moving freely, that means, the resistance is reduced; that means, the viscosity is it reduced right. So, what happens when in a liquid when you increase the temperature the molecules which are held together by inter molecular attractions then sufficient amount of energy to overthrow the attractive forces existing between the molecules and they start moving more freely. And that ever since that are moving more freely that means, the resistance to the motion of the molecules are decreased; that means, the viscosity of the system is decreased right. So, this is the this is one of the reas[on]- one of the questions which I was talking about.

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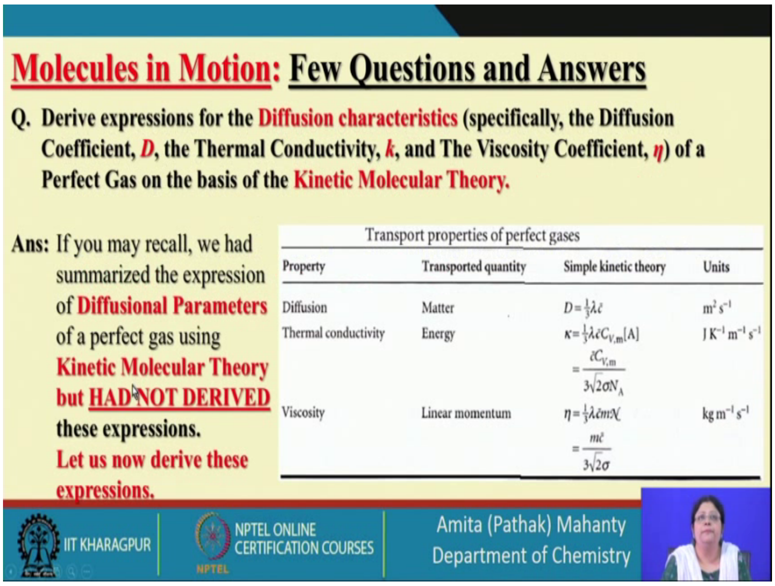

Molecules in Motion: Few Questions and Answers

Q. Derive expressions for the Diffusion characteristics (specifically, the Diffusion Coefficient, *D*, the Thermal Conductivity, *k*, and The Viscosity Coefficient, *η*) of a Perfect Gas on the basis of the Kinetic Molecular Theory.

Ans: If you may recall, we had summarized the expression of Diffusional Parameters of a perfect gas using Kinetic Molecular Theory but HAD NOT DERIVED these expressions. Let us now derive these expressions.

Transport properties of perfect gases

Property	Transported quantity	Simple kinetic theory	Units
Diffusion	Matter	$D=\frac{1}{3}\lambda\bar{c}$	$m^2\,s^{-1}$
Thermal conductivity	Energy	$\kappa=\frac{1}{3}\lambda\bar{c}C_{V,m}[A]$ $=\frac{\bar{c}C_{V,m}}{3\sqrt{2}\sigma N_A}$	$J\,K^{-1}\,m^{-1}\,s^{-1}$
Viscosity	Linear momentum	$\eta=\frac{1}{3}\lambda\bar{c}m\mathcal{N}$ $=\frac{m\bar{c}}{3\sqrt{2}\sigma}$	$kg\,m^{-1}\,s^{-1}$

Next one is we have not taken up this in the previous classes, this is the derive the question is you do not get theory question, but it is this is important part of the discussions we had previously, we have emitted this discussion and now I think is since it is part of question some questions which you have in some book. So, it is better to at least visit them in spite of the fact that you already know the expression and you should be knowing the expressions go through the slides you will see the expressions.

So, what we are going to be looking into the next question is derive the expression for diffusion characteristics or diffusion parameters specifically the diffusion coefficient D, the thermal conductivity Kappa, the viscosity coefficient eta for a perfect gas on the basis of kinetic molecular theory. So, if you remember in the kinetic molecular theory we had stopped the discussion on just having the phenomenological equations we did not go to derive the constant parameters which we obtained in the phenomenological equation.

What we are what we had given you is this table in which each of the properties was mentioned, what was being transported in that particular process was also mentioned and the diffusion parameter, diffusion characteristics the constant which was obtained from the from the phenomenological equation was just taken to be equation D, Kappa, eta. We had taken that we assume these are the equations, we have discussed this relationship, but we have never derived this relations we have said that this is not going to be discussed you take this to be known to us.

But, when we are talking about a course which is covered so much I think it is very relevant that we talk about how do we derive these diffusion parameters or diffusion characteristic for each of the cases. Like in diffusion coefficient, thermal conductivity, viscosity coefficient for a perfect gas using the same thought and processes which are arguments which we had while discussing the kinetic theory of kinetic molecular theory.

So, what we can recall, we have summarized these expressions of diffusion parameters of perfect gas using kinetic theory, but have not derived these expression now let us do the derivation right now. Have a look at these expressions these was tabulated previously the for a diffusion process the matter transported was the molecules the quantity start transported was matter or molecules and that conditions for which we have the phenomenological equation satisfied we had said that the proportionality of constant was known as the diffusion constant D which was given to be 1 by 3 lambda c bar that is relative speed mean relative speed and this is lambda is the mean free path.

Similarly, we had said for a property like thermal conductivity, the matter the quantity which was being transported was energy and the phenomenological equation the constant in that phenomenological equation was taken to be Kappa that is the thermal conductivity coefficient that was given in terms of c 1 by 3 lambda mean relative speed into C V molar specific heat into the concentration molar concentration of the gas molecules.

So, similarly we had for the viscosity we have two or three expressions you just have a look we are going to now visit this and see whether we are going to get these expressions from the logics which we had applied for other systems or we have even in the discussions of the kinetic theory of gases. So, what happens so, for the viscosity property if the property is viscosity what is getting transported is linear momentum what you have the phenomenon phenomenological equation was a gradient in velocity. The x component of the linear momentum was proportional to the velocity gradient in the z direction and that was given to be the constant of proportionality was given to be the eta then coefficient of viscosity.

So, we are going to be looking into each of them. Let us begin with the diffusion besides this is the most fundamental and once you understand the logic with how we derive the expression for diffusion of matter it is only going to be the concept will remain same as to how we derive the transport of energy and transport of linear momentum. Only thing is the factor which is where we are talking about number of molecules or the number of molecules and number density in case of transport of matter, here each of the molecules will have some associated energy. So, along with the number of molecules which is involved we have to take into account the associated average energy for that molecules.

Similarly, when we are talking about the number of transfer of linear momentum we need to know the number of molecules and need to multiply them with the total number of the tot[al]- linear momentum which we get, multiplied by the total number of molecules present will give you the tot[al]- average amount of the viscosity average amount of the linear momentum which is being transported. So, these are the three parameters which we are going to look into. Let us begin with the diffusion.

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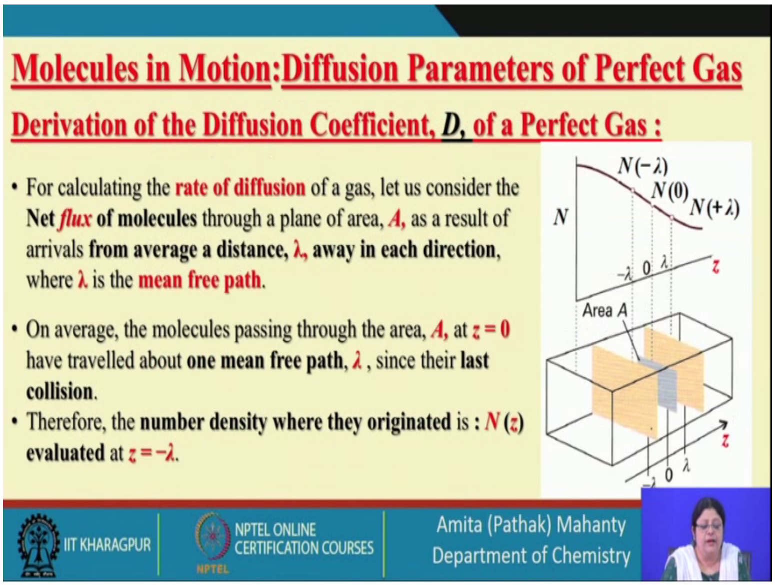

Molecules in Motion:Diffusion Parameters of Perfect Gas

Derivation of the Diffusion Coefficient, *D*, of a Perfect Gas :

- For calculating the **rate of diffusion** of a gas, let us consider the **Net *flux* of molecules** through a plane of area, ***A***, as a result of arrivals **from average a distance, λ, away in each direction**, where **λ** is the **mean free path**.
- On average, the molecules passing through the area, ***A***, at $z = 0$ have travelled about **one mean free path, *λ***, since their **last collision**.
- Therefore, the **number density where they originated** is : $N(z)$ **evaluated** at $z = -\lambda$.

For derivation of the diffusion coefficient D for a perfect gas, just have a look at this diagram. What as what does the Fick’s law say? Fick’s law says that the gas molecules or matter will move from a region of higher concentration to a region of lower concentration from high concentration the movement will be always towards the low concentration.

So, for calculating the rate of diffusion of a gas let us consider the net flux of molecules through a plane A 0 this is the A which is the window which we are looking into. We are going to see the net flux of flux of molecules which is passing through this area A as a result of arrival from a distance say lambda and lambda minus, if this side take as the axis as 0 along the z axis it can be x, y, z anyway, but as I take along say I will consider this as a z axis. What I am considering is find out the rate of diffusion what I am doing is I am trying to consi[der]- find out the flux of molecules through which is passing through this area A or A naught as a result of arrival from a distance of lambda in each of the direction.

Lambda is the mean free path it is the distance travelled after a recent collision the last after the last collision what is the distance travelled. So, what I am saying is after the collision the molecules that has travelled lambda distance is reaching this ok. So, similarly, molecules here reaching is only a distance which is equal to 1 lambda is coming from this side as well, either from right side this is the right side we are moving towards 0 or from the left side we are moving towards 0.

Now, consider this projection in this graph, this is the graph where you have the number of particles number of molecules in the y axis and x, y, z axis is corresponding parallel consider parallel to the one which we have here. So, consider if I project this as parallel to the window the window of this our interest if I project it on this graph of N versus x which is the number of graph between the number of particles moved with the distribution with the z axis.

So, if I could project this and I call this since this I am marked as 0, I mark this as 0, ok. So, the number of particles or molecules, the number density of molecules at 0, ok so; at let us take this as the origin. Now I can consider how many molecules are crossing this window and reaching this place and suppose the molecules are moving with the relative mean relative speed c bar so, they and the in delta time t. So, the distance they covered is going to be c bar delta t and the total volume contain in this area will be the area into of the interest window into c bar delta t because that is the distance delta velocity equal to distance by time.

So, if I want to find out the distance I multiply time into the velocity I get the distance, if the molecules are moving with the mean speed relative mean speed c bar then I multiply with that interval in which they have travelled delta t. And this delta t into c bar gives me the distance travelled and this distance is this one and in this area the total volume element will be this area into the distance travelled c bar delta t. So, A into c bar delta t is the total volume element of interest which we are looking into ok.

So, on the average molecules passing through A at 0 has to travel one mean free path lambda since it is last collision. So, I have assumed that to reach the window I will consider only the molecules which undergo one mean free path distance ok that is one lambda since the last collision. So, the number density they are where they originating let us say N z evaluated at z equal to minus lambda, what do we get?

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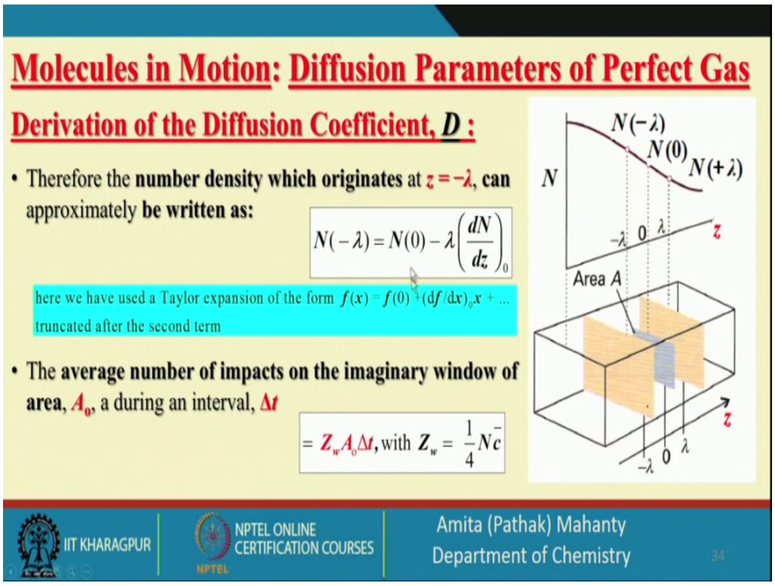

Molecules in Motion: Diffusion Parameters of Perfect Gas

Derivation of the Diffusion Coefficient, *D* :

- Therefore the **number density which originates** at $z = -\lambda$, **can** approximately **be written as:**

$$N(-\lambda) = N(0) - \lambda\left(\frac{dN}{dz}\right)_0$$

here we have used a Taylor expansion of the form $f(x) = f(0) + (df/dx)_0 x + \ldots$ truncated after the second term

- The **average number of impacts on the imaginary window of area,** A_0, a during an interval, Δt

$$= Z_w A_0 \Delta t, \text{with } Z_w = \frac{1}{4} N\bar{c}$$

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We get the number of num[ber]- the number density originated at z z equal to number lambda minus lambda can be given by a Taylor expansion series, where this is at 0 number density at 0 at lambda equal to 0, minus the lambda into the gradient of number density. And into x like it if you are taking a Taylor series if you want to take a Taylor series if you have a function like this and you want to evaluate the value then function f x is equal to f x value when x equal to at 0 or the origin plus the first differential of the f dash with respect to the variable into the variable.

So, and truncating the other values, if I compare these two compare that two that the number of molecules then I can write down the number density is at a distance one mean free path away from the origin of the centre of interest or window of interest is given to be the number density at minus lambda. Minus lambda means at this location; that means, we are going particles are going from this side to left side to right side and if you see left side minus lambda corresponding correspond to this ok.

So, minus lambda corresponds to this means the concentration or number density of this collision is going to be higher than this one ok. So, if we if the number coefficient number density of the molecules is going to be higher than this one compared to this one then what will happen the molecules will tend to move from higher to lower.

So, when I move from higher to lower what I am moving, I am moving from actually the if I you take this left side we are taking and this side as right side then you are moving from left to right when you are going towards the window ok.

So, when we are going towards the window from the left side to the right side then actually what we are moving is we are moving from a higher concentration of the number of molecules to that of the lower concentration. And mind you we are only considering the molecules which ha[s]- which are going to undergo only one mean path mean free path distant to reach the window of interest, that is A.

So, all distance with means this distance which is which they are going to transfer is going to be considering only one mean free path distance not beyond that ok. We can we are not talking about multiple integers of one mean free path, we are talking about the number of molecules which have undergone one collision the minimum collision is sorry, it is undergone at least one collision before reaching the which is going to reach make one collision to reach the window of interest. I am not I do not know whether I am able to make you understand.

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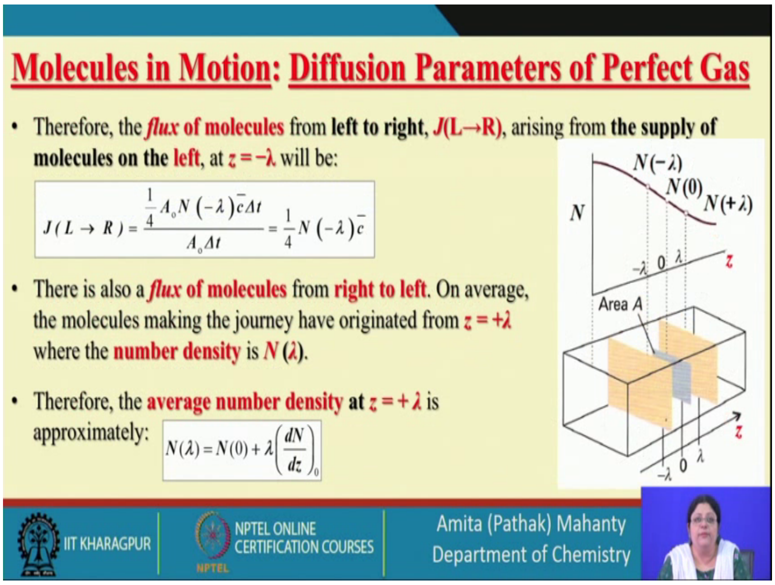

Molecules in Motion: Diffusion Parameters of Perfect Gas

- Therefore, the ***flux* of molecules** from **left to right**, **$J(L \rightarrow R)$**, arising from **the supply of molecules on the left**, at $z = -\lambda$ will be:

$$J(L \rightarrow R) = \frac{\frac{1}{4} A_0 N(-\lambda)\bar{c}\Delta t}{A_0 \Delta t} = \frac{1}{4} N(-\lambda)\bar{c}$$

- There is also a ***flux* of molecules** from **right to left**. On average, the molecules making the journey have originated from $z = +\lambda$ where the **number density** is $N(\lambda)$.
- Therefore, the **average number density at** $z = +\lambda$ is approximately: $N(\lambda) = N(0) + \lambda\left(\frac{dN}{dz}\right)_0$

What we are saying that on the average the molecules passing through the area A at z equal to 0, have to travel at least one mean free path that is since the last collision. That means, if you have the last free path having at any time and the molecules are still surviving and not gone lost it is energy, then it has to minimum travel one mean free path lambda distance to reach the window of interest.

This distance is lambda, ok so, this is the mean free path; that means, the distance travel between two consecutive collisions. If I have this last collision it happened sometime and the next collision is going to happen here then I say that mean free path is here is going to be lambda ok. So, this is going to be the next collision and then this was a time when it was previous collision.

So, distance it travel for from previous collision to the next collision is known as the mean free path. So, this distance is what is we are going to be interested and that should be one mean free path means, it should be colliding only once since the last collision ok. There should not be any shorter collision, there should not be any longer collision the distance should be with the average value of the should be equal to the mean free path of the molecules right.

So, having understood that I hope you have understood that for calculating the rate of diffusion of a gas let us let us consider the net flux of molecules which is passing through the area of window of interest of area of window of area A as a result of arrival from average distance lambda. This average distance is one mean free path away from the last collision away from each direction and where lambda is the mean free path. On the average molecules pass through the area A at z equal to 0, have travelled one mean free path since the last collision.

Therefore, the number density which they originated is can be given to be in terms of like something like this in terms of the Taylor expansion series. So, Taylor expansion series is given as the number density or any function at a given location is going to be the function at the origin minus or plus depending on what type of function you are taking it will be minus or plus the position of that distance which were travelled into the slope of the change slope of the change of the function with the distance.

So, if we if I have this expression applied to that of the number density, then number density at a location, where z is equal to minus lambda each equal to the number density at z equal to say condition where z is equal to 0 and will be minus the slope of the change of number density with distance into the lambda which is the distance which is travelled between the consecutive jump ok.

So, if I have this change in the number of molecules, then I can rewrite this as the number density which is which originates at x z equal to minus lambda. And can be approximately by using the approximation of truncated Taylor series expansion we have the N lambda at x equal z equal to minus lambda will be equal to the number density at x equal to z equal to 0 minus how the what is the slope of the number density with the distance z into the distance it is travelled and what is the distance travelled? Distance travelled is lambda. We could have written as this as x, but we know the distance which is it is travelling is lambda ok.

So, the number of impacts on imaginary window of area A in time interval delta t is given to be Z w, you have to look into the collision frequency and other things. Number of impacts of imaginary on the wall of area A is in time delta t will be nothing, but the say Z the whatever Z w on the hitting on the wall into A 0 into A t, ok. The Z 0 Z w is nothing, but 1 by 4 number density into the relative mean relative speed ok.

So, the flux of molecules moving from left to right say what is this left side? This is the left side left to right assigned from supply of molecules from left; that means, from higher concentration to lower concentration will be given as you see the flux is always going to be flux is going to be this divided by A into delta t per unit area per unit time. So, this is the number of molecules which is travelling, what is the number of they are travelling with the speed mean speed of c bar into the distance into delta t is the distance and what is the area this is the area and what is the number density which we have? We have number density at lambda minus equal to N minus this is actually signifying the number of number density at minus lambda. So, that is nothing, but 1 by 4 N at lambda minus into the relative mean speed right.

So, today we are going to be ending the section here I think I need to take up this a little bit more in detail, so that we can complete all the diffusion parameters in a perfect gas.

Thank you so much.