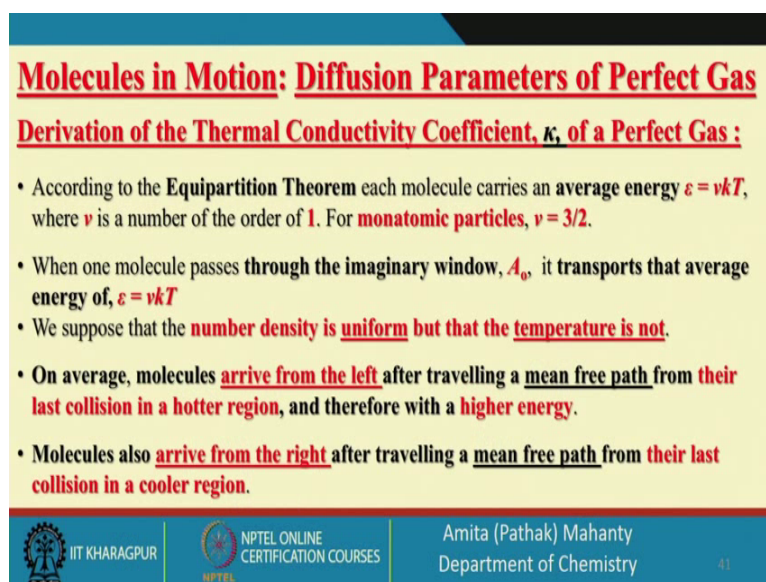


Molecules in Motion
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Lecture - 40
Molecular motion in gases (Contd.)

Welcome to the last lecture on Molecules in Motion, we are continuing with the parameter of derivation of the various diffusion parameters for a perfect gas and that too from the kinetic theory. This derivation was not initially taken though this and this derivation was not listed in the part of your syllabus, but I thought we have taken similar kinds of derivation so, it could be included here.



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Molecules in Motion: Diffusion Parameters of Perfect Gas

Derivation of the Thermal Conductivity Coefficient, κ , of a Perfect Gas :

- According to the **Equipartition Theorem** each molecule carries an **average energy $\epsilon = \nu kT$** , where ν is a number of the order of **1**. For **monatomic particles**, $\nu = 3/2$.
- When one molecule passes **through the imaginary window, A_0** , it transports that average energy of, **$\epsilon = \nu kT$**
- We suppose that the **number density is uniform** but that the **temperature is not**.
- On average, molecules **arrive from the left** after travelling a **mean free path from their last collision in a hotter region**, and therefore with a **higher energy**.
- Molecules also **arrive from the right** after travelling a **mean free path from their last collision in a cooler region**.

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So, what we have? We have the lecture when the last class was which we talked about was the derivation of the thermal conductivity coefficient Kappa in which we are talking about the energy being transported through collision.

And for that what we had taken that each molecule is carrying a average energy of say E equal to $\mu k T$. Where μ is the parameter on depending on the type of molecule which we have and k is the Boltzmann constant, T is the temperature, μ is going to be 3 by 2 if you have mono atomic gas particles.

So, μ is to be designated is to type of particles which we are having molecules which type we are having either mono atomic dynamic atomic or complex which we have taken up in details. What we have taken in assumption is the number density is uniform throughout the system only parameter which is changing in the process is the temperature.

Let the temperature is changing atom molecules are moving from one region to the other, then what they are doing that actually transporting energy along with them. So, if each of the molecules are carrying or particles are carrying certain amount of energy the total energy transfer transported by them will be the average energy of the molecules carried by each molecule into total number of molecules which we have.

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Molecules in Motion: Diffusion Parameters of Perfect Gas

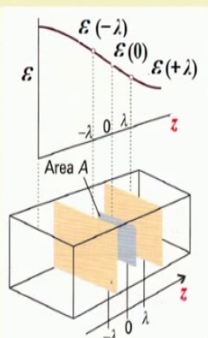
Derivation of the Thermal Conductivity Coefficient, κ , of a Perfect Gas :

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

$$= Z_w A_0 \Delta t, \text{ with } Z_w = \frac{1}{4} N \bar{c}$$
- Therefore, the **flux of energy** from left to right, $J(L \rightarrow R)$, arising from the supply of molecules on the left, at $z = -\lambda$ will be:

$$J(L \rightarrow R) = \frac{\frac{1}{4} A_0 \bar{c} \Delta t N \varepsilon(-\lambda)}{A_0 \Delta t} = \frac{1}{4} \bar{c} N \varepsilon(-\lambda)$$
- Therefore the average energy transported at $z = -\lambda$, can approximately be written as:

$$\varepsilon(-\lambda) = vk \left[T - \lambda \left(\frac{dT}{dz} \right)_0 \right]$$



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And on finding out to find out the number of particles which have transporting, we look into diagram like this. Where area of interest is A, we are looking into this region only we are saying that the particles are moving with the relative speed \bar{c} and in time Δt the travel distance of $\bar{c} \Delta t$. So, all the molecules in the region in the volume element A into $\bar{c} \Delta t$ is going to be colliding into the surface.

And the number average number of impact the collisions that can happen in this region can be given by $\frac{1}{4} N \bar{c}$. And total number of molecules contained in this has to be multiplied by the volume element that is the volume element is that is the distance into area and that is area A naught into \bar{c} into Δt .

So, this is going to be the total volume in element, all molecules containing in this region will become actually colliding on the surface to find out the flux of the particles which are moving from either left side or the right side. When they are moving from left side you see as I projected on the distribution of energy verses distance brought, then this plot at λ minus is going to be at higher energy and the flow of energy is always going to be from higher to lower.

So, if I what restrictions I have put that the molecules are moving only one free path mean free path distance to come into collision at the area of interest. So, the mean free path we have designated to be as λ . So, this is the distance the molecules are travelling to hit on the window.

So, the molecules which are travelling from left to side left side towards the window or from the right side towards the window have to have travelled a transverse that length distance of only one mean free path that is λ . So, when them so, what we are going to be looking is to what is the net flux which is what is the flux of particles coming from left hand side left hand side? What are the particles coming from the right hand side?

And when we are going to be meeting at the area of interest the net flux in the window is going to be the addition of the one moving from the left side to right side plus the flux of particles with particular energy moving from right side to left side. So, if I want to find out the average energy transported I need to know what is going to be the transported energy. Transported energy at λ minus Z equal to Z λ minus is nothing, but the energy associated with at any position is going to be $\mu k T$.

So, this is $\mu k T$ minus what $\mu k T$ into λ , the λ is distance at which it is travelled into the change in temperature with distance. So, what you have? The change in temperature into distance into the position gives you the lo[cation]- location at which your finding out what? The energy so, it has to be multiplied by k μk Boltzmann constant.

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Molecules in Motion: Diffusion Parameters of Perfect Gas

- Similarly, the **flux of energy** from right to left, $J(L \leftarrow R)$, arising from the supply of molecules on the right, at $z = +\lambda$ will be: The **two opposing energy fluxes** are therefore

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

- Average energy transported at $z = +\lambda$ is :**

$$\bar{\epsilon}(\lambda) = vk \left[T + \lambda \left(\frac{dT}{dz} \right)_0 \right]$$

- From the **two opposing energy fluxes**, we get the **net energy flux** : $J_z = J(L \rightarrow R) + J(L \leftarrow R)$

$$J_z = \frac{1}{4} \bar{c} N \left\{ \bar{\epsilon}(-\lambda) - \bar{\epsilon}(+\lambda) \right\}$$

$$J_z = \frac{1}{4} \bar{c} N vk \left\{ \left[T - \lambda \left(\frac{dT}{dz} \right)_0 \right] - \left[T + \lambda \left(\frac{dT}{dz} \right)_0 \right] \right\} \Leftrightarrow J_z = -\frac{1}{2} vk \lambda \bar{c} N \left(\frac{dT}{dz} \right)_0$$

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So similarly, we have for both the expressions the average energy transported at lambda equal Z equal to plus lambda, this is going to be positive sign. So, let total opposite energy flux which we have and meet and the window of interest A_0 will be nothing, but the flux moving from of particles having certain amount of energy E moving from left to right to that of the flux of particles moving from right to left.

If you remember the right side is always a cooler side, so, cooler side molecules cannot move to the higher hotter region. So, thus expressions which we write will be always having negative sign, flux is not a negative value, but what we are trying to say the flux movement is actually towards the reverse from left side to right side. When we are talking from left side to right side, left side represents much hotter region. The particles moving from hotter region and cooler to cooler region is spontaneous so, this will be positive and this will be giving a negative term.

If you look at this is a positive this is the term which I am associating with the location see at lambda plus and this was at lambda minus and substituting these values what I do get? I get this to cancelled off, I get twice of this value into whatever is constant outside. So twice of this value means I am going to get a 2 cancelling off, 2 by 1 by 4 will be half and why do I get a minus sign? I get a minus sign because, I have a minus here generated and this is also minus. So, if I have this totally evaluation the flux is going to be 1 by 2 μk into lambda c into N .

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Molecules in Motion: Diffusion Parameters of Perfect Gas

- Thus, the **net energy flux of the molecules** will be: $J_z = J(L \rightarrow R) + J(L \leftarrow R)$

$$J_z = \frac{1}{4} \bar{c} N \left\{ \varepsilon(-\lambda) - \varepsilon(+\lambda) \right\}$$

$$J_z = \frac{1}{4} \bar{c} N v k \left\{ \left[T - \lambda \left(\frac{dT}{dz} \right)_0 \right] - \left[T + \lambda \left(\frac{dT}{dz} \right)_0 \right] \right\} \Leftrightarrow J_z = -\frac{1}{2} v k \lambda \bar{c} N \left(\frac{dT}{dz} \right)_0$$


- As before, multiplying by factor of $\frac{2}{3}$ to take long flight paths into account, and so arrive at:


$$J_z = -\frac{1}{3} v k \lambda \bar{c} N \left(\frac{dT}{dz} \right)_0$$

Thus we get, the **energy flux** is proportional to the **negative of Temperature Gradient**


- By comparing the above with the **phenomenological equations of Thermal Conductivity**:

$$J(\text{energy}) = -\kappa \left(\frac{dT}{dz} \right) \quad \text{and} \quad J_z = -\frac{1}{3} v k \lambda \bar{c} N \left(\frac{dT}{dz} \right)_0 \quad \text{we get:} \quad \kappa (\text{Thermal conductivity coeff.}) = \frac{1}{3} v k \lambda \bar{c} N$$

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So, what we can compare now you compare these two equation with the phenomenological equation of that energy and temperature gradient is this is how it is related energy flux is proportional negative gradient of temperature. This is how it is related and what we have got from the net flux? We have net on the net flux as 1 by 2 mu k lambda c N dT by Dz. If I compare these two, before comparing I can rectify this we can multiply by 2 by 3 for correction for taking into account long flight path of the molecules which we have discussed in the last class.

We have say in that the distance which we are looking into for the molecules are ions to hit on the window of interest is con[sider]- may be considered low, but sometimes what happens these molecules which are at close this is of condition with the surface actually has a taken a long flight. And this on the process should have been buried or grounded as they have underground previous collision ok.

So, to take into that that into account the to account for the long flight path which should be lowering the flux of the particle. So, I have multiplied by 2 by 3 into this whole thing gives you 1 by this parameter. If I compare this then you can get the value of thermal conductivity.

This is also minus sign, this is also minus sign so, this is my value of Kappa and the Kappa is thermal conductivity it is nothing, but $\mu k \lambda$ into relative mean speed into the number density ok.

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Molecules in Motion: Diffusion Parameters of Perfect Gas

- By comparing the above with the phenomenological equations of Thermal Conductivity:
we got: $\kappa(\text{Thermal conductivity coeff.}) = \frac{1}{3} \nu k \lambda \bar{c} N$
- Again, N (number density) $= N/V = n N_A/V = N_A [A]$ where, $[A]$ is the molar concentration of A
 $\therefore \kappa(\text{Thermal conductivity coeff.}) = \frac{1}{3} \nu k \lambda \bar{c} N_A [A]$
- Again for a perfect gas follows from $C_{v,m} = \nu k N_A$ (since, $R = k N_A$)
 $\therefore \kappa(\text{Thermal conductivity coeff.}) = \frac{1}{3} \lambda \bar{c} C_{v,m} [A]$
 $\therefore \kappa = \frac{1}{3} \lambda \bar{c} C_{v,m} [A]$ where, $\lambda = \frac{kT}{\sqrt{2} \sigma p N_A}$ since, $[A] = n N_A/V = N_A RT/p = kT/p N_A$
 $\Rightarrow \kappa = \frac{\bar{c} C_{v,m}}{3\sqrt{2} \sigma N_A}$

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Now, comparing the now you can if you put the number density here in this expression and this number density is nothing, but the total number of molecules in the volume total volume of the container v . Then total volume of the container V we can rewrite that in terms of what do you say? This is the V is the total number of I want to find out total number of mole. then I can multiply that total moles into the Avogadro number divided by N .

This replacing and the number of molecules by the number of moles, then V by N is nothing, but the concentration A ok. So, V by N is the concentration, so, this V by $N A$ it is actually the reverse.

So, we have A equal to V by A so, A is the molar concentration right you have a look at this how is it A coming to A coming A is equal to V by N . So, if it is V by N then A is going to be in the numerator right. So, I can come put that in terms of the Avogadro number into the A the molar concentration. Again you can these are simplifications you can further do it, take your time and do it yourself, I repeating it does not matter it does not make any sense because, I have derived this probably in if you do it you will also remember.

Now, put the values of the molar specific mole molar specific heat which is again defined as μ into R into Avogadro number, R which is actually R and μ into R which I can change into R be replaced by Boltzmann constant into Avogadro number. So, R is replaced by Boltzmann constant into Avogadro number. So, this with thermal conductivity can be replaced in terms of C_V , you just see you can replace this value and this value with the C_V the molar specific heat at constant volume.

So, you can put that now you can do for the simplification in terms of the collision diameter. Collision if you see κ this is the expression where λ is to be if you we have done that previously λ is kT by \sqrt{T} root 2 collision cross section area into the pressure into that Avogadro number.

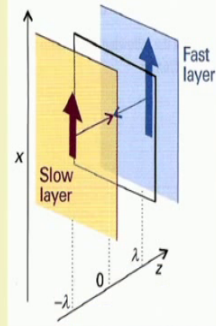
If you look at the simplification of A , instead of A if you write down this then you come to this expression, where you can put in the kT value here and N value here and if you divide by Nm on numerator and denominator you get this value. You do it, in until you do it will not be able to because, when I do it I become clear, but it is very difficult to make you understand until you are doing parallelly with me ok.


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Molecules in Motion: Diffusion Parameters of Perfect Gas


Derivation of the Viscosity Coefficient, η of a Perfect Gas :

- The calculation of the viscosity coefficient (η) of a gas, examines the net x component of momentum brought to a plane from faster and slower layers on the average travelling a distance of one mean free path (λ) away in each direction.
- As shown in the Figure, the molecules travelling from the right to left (moves from a fast layer to a slower one) and transports to their new layer at $z = 0$, a momentum = $mv_x(\lambda)$
- Similarly, the molecules travelling from the left to right (moves from a slower layer to a fast one) and transports to this new layer, a momentum = $mv_x(-\lambda)$






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The last one is the viscosity coefficient, of a perfect gas. So, for this calculation what we have to look is the viscosity coefficient of the gas at as the next x component of momentum brought to the plane. This is the plane of interest at say z equal to value

λ equal to 0 and this location what was happening? The x component of momentum is brought to the plane from faster moving to the slower moving layers ok.

This is the faster to the slower. So, if I moving from faster to slow on the average travelling at distance of say λ that is the mean free path in each direction. So, move in the x component of momentum is transferred to a plane from faster to a slower one on the average by travelling either λ distance on the positive side or in the negative side ok so, this is what it is going to look like.

As shown in the figure molecules travel from right to left move from faster to slower ok. So, as we move from right to left we move from faster to slower right and when you are talking about flow of liquid, when we say the one the layer which is at in contact with the container is actually supposed to be stationary that is the slowest.

So, you can see in a take the container as a towards this side. So, what we have? We have a molecule travelling from right side to left side moves from a faster layer to a slower layer. And in the process transports in the moment and the x component of momentum to a new layer at x equal to 0 and the total momentum which is transferred is $m \times$ at λ ok.

So, similarly molecules moving from the left side, this is the left side to right side, since, simply it is the slow moving to a fast moving which is not possible. So, we always get a negative sign to represent that the other way round is more spontaneous; that means, from fastest to slower is what is what was spontaneous.

Transport to this μ at z is equal to λ equal to 0 is the position where it is going to be moving that is the window per interest. And amount of moment momentum x component of momentum transferred as we have moving from this side to this side is going to be mine m say $m v^2$ at number x equal to minus λ .

So, as faster moving comes from faster moving layer to the layer which is at x equal to z equal to 0 moving so, it comes from a faster moving layer to a slower moving layer. When you come from the right hand side we come from the higher momentum region to a lower momentum region, then we transfer the momentum the momentum transferred will can be taken as $n \times$ at λ equal to $x z$ equal to λ .

So, the distance which is travelled from right to left is the λ , distance that is the minimum distance which can travel that is the mean free path, only those we are considering which is travel only one mean free path.

Similarly, we can have the molecules move from left to right; here it is more in from the colder slow moving to the higher moving which is not really logical. But, transports to a new layer what is the amount of momentum which is transported? It is $m \times \lambda$ at z is equal to minus λ z is equal to minus λ .

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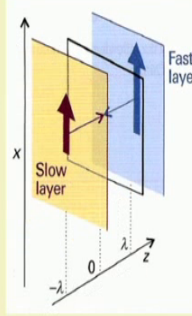
Molecules in Motion: Diffusion Parameters of Perfect Gas

Derivation of the Viscosity Coefficient, η of a Perfect Gas :

- Assuming that the **density is uniform** in all the layers,
- And the **collision flux is** $= \frac{1}{4} N \bar{c}$
- Therefore, those molecules arriving from **right to left, $J(L \leftarrow R)$** , will **on the average carry a momentum:**

$$mv_x(\lambda) = mv_x(0) + m\lambda \left(\frac{dv_x}{dz} \right)_0$$

- Therefore, those molecules arriving from **left to right, $J(L \rightarrow R)$** , will **bring in an average momentum:**

$$mv_x(-\lambda) = mv_x(0) - m\lambda \left(\frac{dv_x}{dz} \right)_0$$


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Now, the assuming that the number density is uniform throughout all the layers, the collision flux is given as $\frac{1}{4}$ by 4 number density into the mean free path. And molecules arriving from the left to the right sorry, from the left to right from left to arriving from right to left, from this side to this side will on the average carrier momentum of how much at this position what is the momentum?

That is the $m v_x$ at λ z equal to λ and that is going to be something which is going to be the momentum at x equal to z equal to 0, into some distance where the velocity gradient is velocity gradient is in this direction.

So, velocity gradient \times into z because, that is what momentum is getting transported so, what we will see to find out the average momentum carried by the molecules when they are moving from right hand side to left hand side that means, from higher faster and

moving layer to slow moving layer, what is happening? What is happening is this if you see the total number of total momentum which is good undergoing change.

It is at this point what is the momentum change it is the change the momentum at this point that is $m \times v$ at $x = z = 0$ plus depending on location of the λ you can take depending on the concentration if the concentration is uniform what we say? This slope of change of and the velocity the change of velocity with distance along this into the distance which are travelled gives you the more or less location of your energy or momentum.

So, the momentum along this say right hand side to left hand side, this side will be the average energy which is the molecules are going to carry while moving from say N_0 to N plus left right to left right to left. And value- the value will be the momentum at x equal to $z = 0$ that is this value plus the slope of change of velocity with z there were $v \times$ velocity with z into the distance λ into m .

Before the molecules arrived from the left for those molecules arriving from the left to right, will be bringing in an average momentum of what? It is first corresponding to say right hand side to left hand side; here we are corresponding to the energy corresponding to from left hand side to right hand side.

So, from left hand side to right hand side the molecules, which is going to be arriving at the interest of windows z is at $z = 0$ will be nothing, but mass into velocity. And x component of it at the condition of $\lambda - \lambda = 0$ equal to the momentum at $z = 0$, minus the slope of the say velocity in with distance the graph, the slope of that into the velocity and the mass of the gas into the what you call mean free path.

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Molecules in Motion: Diffusion Parameters of Perfect Gas

Derivation of the Viscosity Coefficient, η of a Perfect Gas :

- The **net flux of x-momentum** in the **z-direction** is therefore be:

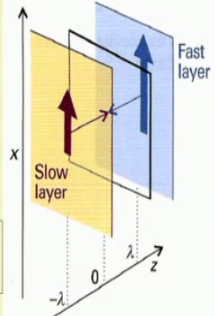
$$J_z = J(L \rightarrow R) + J(L \leftarrow R)$$

$$J_z = \frac{1}{4} c N \left\{ [m v_x(-\lambda)] - [m v_x(+\lambda)] \right\}$$

$$J_z = \frac{1}{4} c N \left\{ \left[m v_x(0) - m \lambda \left(\frac{dv_x}{dz} \right)_0 \right] - \left[m v_x(0) + m \lambda \left(\frac{dv_x}{dz} \right)_0 \right] \right\}$$

$$J_z = -\frac{1}{2} c N m \lambda \left(\frac{dv_x}{dz} \right)_0$$

The **flux of x-momentum** is proportional to the **negative of the velocity gradient**



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If I can take the net flux which is the x component of moment in the z direction can be taken as the flux at z direction is nothing, but the flux of the particles having the momentum $m x$ along this, $m x$ average energy of transferring the momentum of $m x$ at a distance say λ . λ is the mean free path one mean free path distance from the last collision.

So, what we have? We have this and now we want to find out the net flux of the x component momentum at the window of our interest that is z equal to 0 at this location. What will be that? If you see if you write down the what is the momentum transfer when molecules are moving from the left hand side to the right hand side.

And what is the moment of materials particles from right hand side to left hand side? Right hand side always being say faster, so, right hand side will always import higher momentum to that of the component which is slower at λ minus x z minus λ .

So, if you take this flux, flux means this flux means flux at the say left to right hand side and here right hand side to left hand side. If I take two location, two position at the position is of are interest that is z equal to 0, at this position z component of the momentum can be given as the net of this and this what happens?

If see this is going to cancel off again you are left with twice of this and twice of this with a negative sign. So, this is also negative, this is also negative so, you have left with

twice of this is a twice of that will give you 1 by 2 you to multiplied by 2. So, it becomes 1 by 2 and you get a negative sign because, they are negative.

The so, here what we have the flux of x momentum is proportional to the negative of the velocity gradient c , what we are getting? We are again approaching a phenomenological equation where we are having the flux proportional to the negative velocity gradient.

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Molecules in Motion: Diffusion Parameters of Perfect Gas

- By comparing with the phenomenological equations of **Viscosity**:
 $J_x(\text{x-component of momentum}) = -\eta \left(\frac{dv_x}{dz} \right)$ and $J_x = -\frac{1}{2} c N m \lambda \left(\frac{dv_x}{dz} \right)$ we get: $\eta = \frac{1}{2} N m \lambda c$
- As before, multiplying by factor of $\frac{2}{3}$ to take long flight paths into account, we arrive at:
 $\eta = \frac{1}{3} N m \lambda c$
- Now by using $Nm = nM$ and $[A] = n/V$, above expression
 $\eta = \frac{1}{3} N m \lambda c = \frac{1}{3} \left(\frac{N}{V} \right) m \lambda c = \frac{1}{3} \left(\frac{nN_A}{V} \right) m \lambda c \Rightarrow \eta = \frac{1}{3} M \lambda c [A]$
 $\eta = \frac{1}{3} M \lambda c [A]$ where, $\lambda = \frac{kT}{\sqrt{2} \sigma p N_A}$
 $\Rightarrow \eta (\text{coefficient of Viscosity}) = \frac{mc}{3\sqrt{2}\sigma}$
- Applying, N (number density) $= N/V = nN_A/V = N_A [A]$ where, $[A]$ is the molar concentration of A

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So, if I compare the two expressions, if we compare the two expressions we have this as the constant this constant can be taken to be this one right that is what I have written. Now, again we are if we take into account the long flight paths into consideration, then we have we the flux will be reduced. So, for that we have to multiply by $\frac{2}{3}$ by $\frac{2}{3}$ the correction factor. The correction factor if you multiply by this then you get $\frac{1}{3}$ rd Nm into the root mean square velocity into the it is the relative mean velocity and this is the what you call that mean free path.

So, you can further modify this in terms of various parameters in terms of N_A and molecules which is mole[cule]- molar concentration of the molecules and you can do that by substituting the lambda values as well. Lambda is the mean free path and you get expression like this. So, you these are also expressions which are modification simplified, but this is the one which you get from directly from the without further manipu[lation]- manipulation of the equations. You play around with the equations to get various expression in terms of molar mass, in terms of a molar concentration. Also you

can do it in terms of the molecular mass into the say diameter of the cross section diameter.

So, all of these you can see, you can utilise to find out the various values of the parameters which is associated with the phenomenological equation. What we have done today? We have taken all the diffusion parameters like diffusion coefficient, we have done the thermal conductivity coefficient, we have taken the viscosity coefficient.

And we have tried to put in very crudely, but we have tried to put in use the using the kinetic theory model. We have to try we have tried to put in the expression for each so, that we can justify how it is got. So, this these are previously taken how they are changing if you get to discussed, please go through those because the very important parts there are This is only a derivation; proudly if you understand then you do not even need to think about it much.

But, how each of the parameters, how temperature pressure is affecting each of the say diffusion parameters is very important. You have got the expression here and is this from expression what do you extrapolate and can think.

Please do such problems; please try to solve problems using this particular diffusion parameters. Because, numerical will be on this type of question these type of expression because, when you try to keep your units uniform so, that if you are having unit problem. Then the values of η or κ whatever d you are going to get will be not proper If you are not maintaining the units properly for each of the parameters which you have in the expression.

This more or less covered what we are supposed to be doing in this syllabus, please do more problems, please solve from equations. Whatever I have done here in the class and previously it is mostly taken from 2 books Atkins and physics chemistry by Atkins, Peter Atkins and physical chemistry by Castrol you can go through them. But, please try to solve more some few problems, please go through the transparency by each line because, each line conveys a lot of information and all the best.

Thank you so much.