Advanced Chemical Thermodynamic & Kinetics
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Lecture – 12
Transport Phenomena – 2

So, as we just defined our system let us first draw what we mean by these layers.

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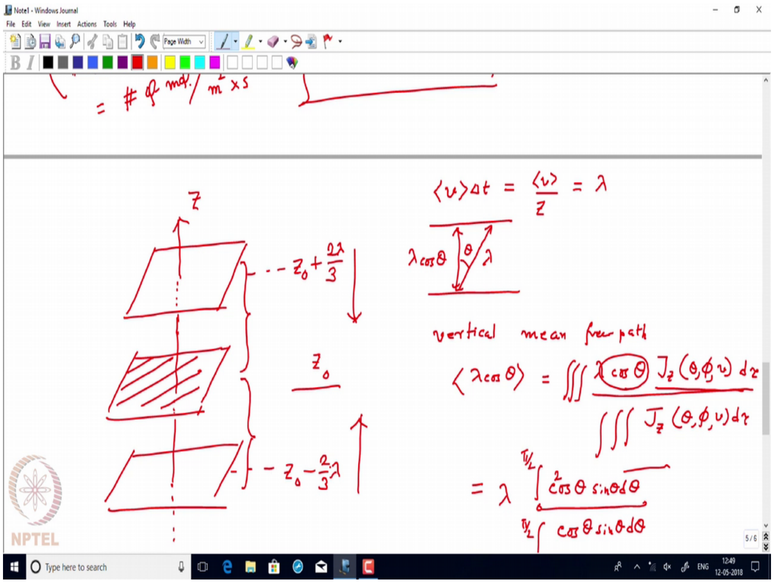

$= \#\ \text{of mol.}/m^2 \times s$

$\langle v\rangle \Delta t = \frac{\langle v\rangle}{z} = \lambda$

vertical mean free path

$$\langle \lambda\cos\theta\rangle = \frac{\iiint \lambda \boxed{\cos\theta}\, J_z(\theta,\phi,v)\,d\tau}{\iiint J_z(\theta,\phi,v)\,d\tau}$$

$$= \lambda \frac{\int_0^{\pi/2} \cos^2\theta \sin\theta\, d\theta}{\int_0^{\pi/2} \cos\theta \sin\theta\, d\theta}$$

So, as we just said that let us suppose that the system is composed of some layers or we can think that they are arbitrarily that along z axis there are some layers. So, let me actually draw the z axis like this so, that you get a feeling of the 3D version. So, this is the z axis. Now, suppose we are talking about flux across this particular layer which I have denoted at the middle.

So, this particular layer and let us say the position along the z axis it is around some origin let us say I am calling it as z 0 it is not be 0, some position along z. So, I want to calculate that the net flux across the surface. Now in order to do that we can do two ways so, there are some molecules which are coming or particles which are coming from vertically from top and some molecules which are coming vertically from bottom.

Now, what do you mean by these layers there? So, these layers are something which are actually line a distance which is equal to the mean free path between mean free path of the molecules, which means actually this makes sense. Because, if we want to calculate the flux we are saying that from this layer and to this layer the molecules are coming without any collision. And that basically, connects us to the definition of mean free path. Because by definition mean free path is nothing, but the part a molecule makes because between two successive collisions because, if you have a collision in between these two layers the trajectory may gets drifted and we would not be able to calculate it nicely.

So, the assumption here is that assumption we are actually considering the layers act basically distances, which are acting the mean free path distance of the mode system. Now, what is a mean free path? The mean free path you can easily calculate, see if the velocity is suppose v and you can easily say that these average velocity times delta t which is nothing but the average velocity divided by the number of collisions for if the collisions are between the same type of molecules and that we actually define my mean free path in kinetic theory of gases.

But here we have a conceptual problem because, this does not have any orientation inherent to it; meaning if you remember correctly for the generalized orientation we said that the cylinder is actually in a slanted position. So, what we have to do; we have to actually calculate the vertical distance between these two layers. So, what I am trying to say here suppose these are the distance between these two layers and all I know is basically this is the lambda. But what I want to calculate is the vertical distance which is nothing but in our definition it is lambda cos theta because this was the theta.

So, then again I have to think about that there is an average of these thetas. So, I have to again calculate the average of that mean free path. So, the vertical mean free path or the vertical distance between these layers, if I just call it as a vertical distance or the vertical mean free path, vertical mean free path that would be nothing, but the average of this lambda cos theta. Now, average over what? Average over basically all possible distribution; now, when you take the distribution what we have derived so, far is a quantity if you remember of this entire thing the z thing. But if we just say that this up to this point this quantity whatever we are just writing.

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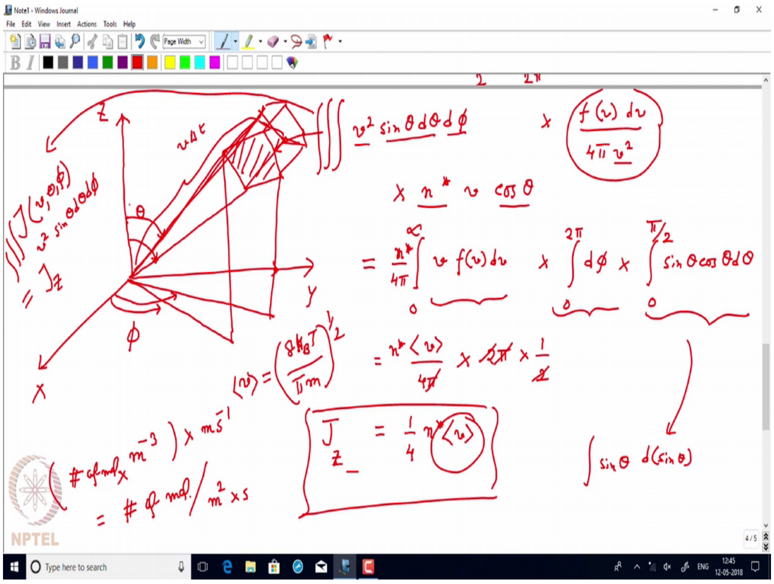

$$\iiint v^2 \sin\theta \, d\theta \, d\phi \times \frac{f(v)\,dv}{4\pi v^2} \times n^* v \cos\theta$$

$$= \frac{n^*}{4\pi}\int_0^\infty v f(v)\,dv \times \int_0^{2\pi} d\phi \times \int_0^{\pi/2} \sin\theta\cos\theta\,d\theta$$

$$\int \sin\theta \, d(\sin\theta)$$

$$= \frac{n^*\langle v\rangle}{4\cancel{\pi}} \times \cancel{2\pi} \times \frac{1}{\cancel{2}}$$

$$\langle v\rangle = \left(\frac{8k_BT}{\pi m}\right)^{1/2}$$

$$\iiint J(v,\theta,\phi)\, v^2 \sin\theta\, d\theta\, d\phi = J_z$$

$$\boxed{J_z = \frac{1}{4} n^* \langle v\rangle}$$

$$(\#\text{ of mol} \times m^{-3}) \times m s^{-1} = \#\text{ of mol.}/m^2 \times s$$

So, this if I write it as say some J which is dependent on v theta and phi and then we had to multiplied it by v square sin theta d theta d phi and if we integrate all this thing then we get J z value. So if we define it in that way so, this is nothing, but this mean free path also has to be weighted by the flux because flux is nothing, but again probability distribution.

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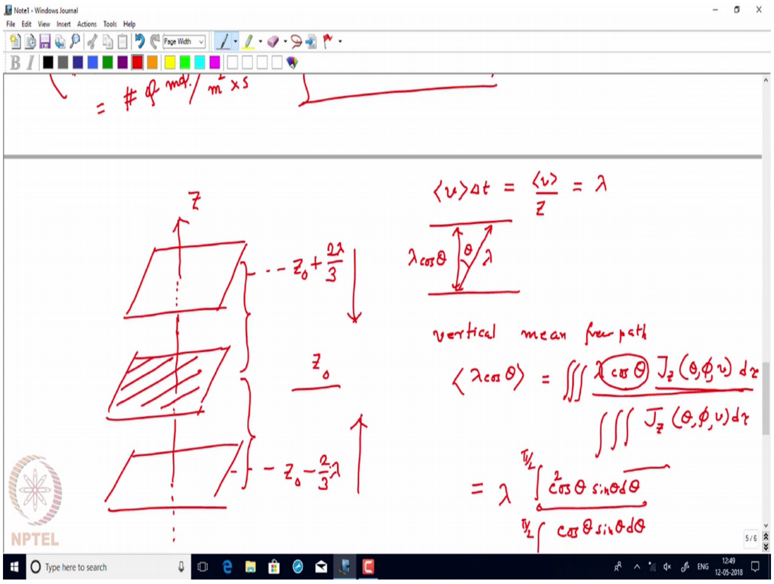

$$= \#\text{ of mol.}/m^2 \times s$$

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$$= \lambda \frac{\int_0^{\pi/2} \cos^2\theta \sin\theta\,d\theta}{\int^{\pi/2} \cos\theta\sin\theta\,d\theta}$$

So, you are basically integrating it with respect to theta phi and v and with all this integration d theta d phi d v with this square and all this term. But that I am supposed writing it as d tau and divide it by if the J z is not a normalized probability distribution, we have to also divide it by the integration over J z.

Now, this is rather simple integration because as you can see the all we have to do is the theta part integration, but again we have to be very careful because within J z we know that what was J z remember that we had a sine theta d theta and cos theta. So, that we integrate it, but now actually we are taking another cos theta because you are taking the projection for lambda. So, all other things like d phi and d v part we do not need to consider because, we have the same thing in the numerator and the denominator then they will cancel out.

So, lambda by definition is not dependent on theta that is a constant that is coming directly from our mean free path, but in this case it is the angular mean free path. And then, all we are left to it is basically an integration after we integrate out the v and phi part. So, we will have a cos theta and remember it will be basically cosine squared theta sin theta d theta divided by for the J part it will be basically cos theta sin theta d theta. And, this integration is again from 0 to pi by 2 for the reason we just discussed.

Now, how to evaluate this integration it is also very easy and if you follow these things so, this integration will be nothing, but you can use actually does again the tricks you can write actually sin theta d theta in terms of say d of cos theta with a minus sin because d of cos theta is minus of sin theta. So, ultimately it will be a cos cube theta divided by 3 evaluated between 0 and pi by 2 and the denominator will be the same; we have already integrated that part out. It will be cos square theta for the same reason sin theta d theta we take as minus cos theta, you just write cos theta d theta sin theta sin d of sin theta either way is fine and then it will be evaluated like this and there was a lambda.

So, what will get ultimately is basically this fellow will be two-third you can easily check it. So, it will be nothing, but of two-third of lambda. So, what we learned is that, this distance if this is at this plane is located at z 0 the middle plane. This is located at z 0 plus 2 lambda two-third lambda and this is located as z 0 minus two-third lambda. So, now all we are saying is that we have to calculate the net flux across this surface which is at the center, which is lying at the middle, which is basically at z 0 for the molecules which are coming from top from a layer which is a line at z 0 plus two-third of lambda.

And, from molecules which are going up which is lying which are coming from a layer which is lying at a distance z 0 minus two-third lambda.

So, now how will I calculate it? It is also very easy we will just use just a phenomenological notation; in the sense that we are saying that let us calculate the net flux. And, this net flux will be like net positive flux which is going in the plus z direction and also subtract net negative flux. Now, remember that the positive flux which is going in the upward direction is coming from the lower layer. So, these molecules are going upward from this layer. So, if I call it as a say layer number 1 this is 2 and this is 3. So, it is coming from the layer number 3 and the downward flux is coming from layer number 2.

So, you have to be very careful. So, for the positive flux it will be nothing, but we will use the definition it is one-fourth average velocity. Now, J are the flux which is the positive flux coming from the bottom layer which means actually it is nothing, but this quantity n star. And now, before write something else let us first say that I write it as J z is a one-fourth n star into v average. But suppose, this is basically the J z let me write it once again one-fourth v average into n star. So, that basically tells you what are the number of molecules which are moving in the upward or some direction.

Now, suppose each molecule is carrying something. What is this something? Suppose, each molecule is carrying some momentum or each particle is carrying some momentum. So, the flux we will have also in instead of the number of molecules per unit time per unit second, it will be the momentum transferred per unit time per unit per unit square area. So, which means I have to multiply it by some quantity and this quantity will differ from one problem to another problem. Meaning, when we are doing talking about say viscosity not viscosity it is say diffusion, viscosity is a little bit complicated because it will be the x component of velocity we will discuss about it. Suppose, we are talking about the diffusion simply so, then it is simple.

So, it is just the number of particles itself it is the concentration gradient. So, q is does not make sense, but if it is a heat transfer equation then actually the q is basically the amount of heat carried by each particle per unit area per unit time. So, then the q that the dimension of the q will be the dimension of heat which is dimension of energy; something will associate with that and so, in this case we just leave it as n star into q and that quantity is changing. Now, in order to calculate the net flux we have to now calculate what is the value of this n star q at for positive z, again it is coming from bottom.

So, it means actually what is the value of n star q at z 0 minus two-third lambda minus what is the value of this n star q at z 0 plus two-third lambda. Now, the textbooks we recommended for you some textbook actually write to this quantity n star into q as rho suffix q, but we are not using that notation. Because, rho itself is used and many places as density so, we do not use that. So, we will just keep it as n star into q. Now, what we will see here is that now, that I do not know because it will depend on the gradient of that quantity, which quantity; q.

Now, n star is a density and if you remember that there could be a density gradient plus there will be there could be a gradient of a particular this property itself the q itself. And, the gradient is along the z axis that is why the flow is happening. If the gradient is 0 so, these two quantities will be identical and then it will be just the same. So, there will be no net flow. So, now let us first define what is what will be this gradient.

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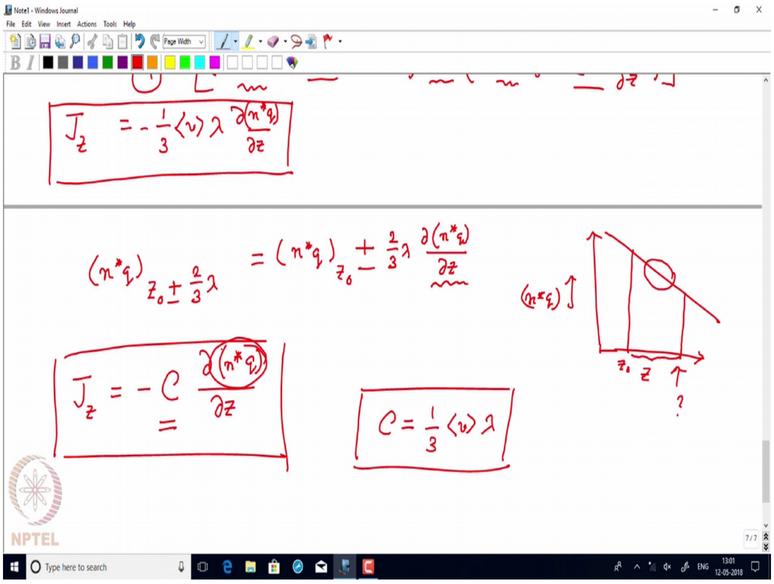

$$\boxed{J_z = -\frac{1}{3}\langle v\rangle \lambda \frac{\partial (n^* q)}{\partial z}}$$

$$(n^* q)_{z_0 \pm \frac{2}{3}\lambda} = (n^* q)_{z_0} \pm \frac{2}{3}\lambda \frac{\partial (n^* q)}{\partial z}$$

$$\boxed{J_z = -C \frac{\partial (n^* q)}{\partial z}}$$

$$\boxed{C = \frac{1}{3}\langle v\rangle \lambda}$$

So, what we are asking this question what is the value of this n star into q at z 0 plus two-third lambda or minus two-third lambda. Now, we can say that fine let us say this gradient, the way it is changing in the positive x axis positive z axis sorry this gradient of this quantity which is n star q is changing along z linearly. So, if it changes linearly then it is a very simple equation it is nothing, but y equal to m x minus c; m x plus c, where actually m itself is a negative quantity because the slope is negative.

So, that way you can say that fine so, I can say that it is nothing, but the intercept the intercept means that its value at z 0 minus, for plus actually will have a minus because the gradient is changing in the positive direction. But since, we have already taken that into account because, we are considering the flux coming from bottom minus common flux coming from top.

So, in that sense we can write it as this is nothing but the rate of change and the rate of change is nothing, but the slope or the gradient along z. And now, if you have a gradient so, basically suppose this is the z 0 value and this is at some point, I want what is the value here. So, what I have to do that I have to take this gradient or the slope which itself is a negative along z and multiply it by where I am taking this fellow right.

So, in this case it is nothing, but evaluated at a distance which is two-third lambda away from that. So, this will be the value and then you can actually use another bracket maybe or we can just leave it like that so, this is for plus and this is for minus. So, again the positive or negative sign is already inherent here. So, we can actually go back and write the expression for our quantity which is z or the flux along net flux along z axis. So, it will be one-fourth average velocity and then first the net upward motion net upward flux sorry. So, it will be n star q evaluated at z 0 and there was a minus sign remember because, upward is coming from the lower bottom layer.

So, I have to consider minus two-third lambda into this gradient del of n star q del z minus I have to subtract the net downward plots which is nothing, but n star q at z 0 plus it will now, have a plus because it is coming from the top layer. So, it will be plus two-third lambda into the same quantity which is del n z sorry del n star q del z. So, as you can see the this constant term cancels out and all will be left to it so, you can see here this is minus two-third lambda it is plus two-third lambda with a minus sign here so, it will be minus of four-third of lambda. So, this 4 and 4 this 4 will get cancel out.

So ultimately, we will get minus one-third v average lambda times the gradient of this quantity del n star q del z. And, this will be the equation for the net flux. Now, you can see now this is a very generalized equation. So, what we did let me again summarize we just define the quantity flux and we defined it is the quantity which is being transported per unit area per unit time. So, in order to define that we just considered a surface arbitrary surface located in our bulk system bulk macroscopic system.

But, we give a molecular picture how basically let us this calculator is the number of molecules because, it is the molecules which are carried carrying that property. It may be momentum, it may be heat, it may be something else. It may be the number of molecules itself in that case it is just the equation for diffusion. So, then in that case q will be just 1 there is no extra quantity. Now, we said that phenomenologically the Poisson's law was nothing, but that if we just remember the first slide we wrote. So, that was nothing, but some constant and multiplied by the gradient of that quantity and Poisson's equation it was a gradient of pressure.

And, we wrote it as del p del z. So, in this case actually we can write it something like this so, gradient of that particular quantity along z axis. Now, we see very interesting thing what we see here if we compare these two equations, we can actually get expression for this constant. And, this constant as I said is basically nothing, but one-third v average into a mean free path. So, that we see actually what are the consequences of this constant. So, this is known as this constant will be the coefficient of that particular process.

For example, if you talk about say viscosity this will be the coefficient of viscosity in that case. But, it will depend on what quantity we are talking about what is the q in that case and how that derivative we can take out. So, that will go through in detail, but before that let us just try to understand what we just learned and, then I will try to basically recapitulate what we just discussed.

So, we first talked about these layers that there is a particular layer and across that layer some flux I mean we are going to calculate some flux. And, then you consider that at a particular angle the molecules are coming and hitting this surface, but then you consider the all possible distributions of the surface, but only from one side because we are considering the flux along a particular direction. So, say a net downward flux or net upward flux something like that and for that actually we took the integration for the azimuthal angle, where the theta to be 0 to pi by 2.

And, then we considered also Maxwell-Boltzmann distribution, but we actually cleverly said that I will take the distribution function divided by 4 pi v square because, Maxwell-

Boltzmann distribution was already integrated as over theta and phi. But we do not want to integrate it; we want to actually use the Maxwell-Boltzmann distribution before the integration happened going from velocity distribution to play speed distribution; at that connection where I had the distribution of speeds. But it is still an angle dependent because, in our derivation we saw that there is a velocity distribution and that we cleverly introduced it use the Maxwell-Boltzmann distribution as well as the fact that we have to integrate over all these possible angles.

And when you do that then, we figure out that we get a very simple expression in terms of the average velocity and it is nothing but one-fourth of the one four times the density times average velocity. But, this is just the number of particles a number of molecules which are moving. If we are interested in the flux of a certain quantity that is carried by the molecules so, then you have to also multiply by the quantity itself. So, carried by each molecule and then we said that fine it is basically a flux along a particular surface. But, then you have to consider the net flux along the surface and then along we since, our problem is we have kept it very simple one-dimensional along the choice of axis was z axis along z axis.

So, we said that let us consider a layer along z axis across which we want to calculate this flux and then we said that what are the other layers that we have to consider. So, then we said molecules which are coming from immediately above and immediately below that we are considering. But, then we had a problem in defining, what is the location of those layers which are like above and below? So, by definition this is basically within the mean free part of the molecules. But, then the way we define the problem that the molecule can actually come at an arbitrary angle. For that actually the mean free path is lambda, then the vertical angle will be lambda into cos theta and then again took the average of this mean free path.

And, we figure out that it will be basically two-third of lambda that is the mean free path. So, the layers are lying actually above two-third lambda and below two-third lambda something like that and the above layer corresponds to the downward flux and the below layer corresponds to the network upward flux. And, then what we said is that we wanted to calculate the net upward flux which is the flux due to the bottom layer minus flux due to the top layer. And, we connected that quantity with a gradient and we assumed a very simple gradient relationship. In the sense that we said that the gradient is actually varying linearly which may not be the case, which might have a very complicated variation.

And then, this gradient if it varies linearly so, then you can actually just use a linear equation and then we inserted that thing. And you can show that now the flux can be directly connected to the gradient of that quantity times mean free path times the average velocity. Now, we will stop here and now we will build upon on this particular topic. And, we will discuss about specific cases like what will be the expression for heat transfer, what will be the expression for momentum transfer, what will be the expression for say just a transfer of molecules, which is diffusion?

And, we will consider all this physical process again these are all developed phenomenologically. And, before you go through all these topics I will advise you that you go back and read the text books which are recommended to you or you can actually go back and see my YouTube video lectures for the earlier course. Where, I actually derived the Maxwell-Boltzmann distribution from the very first principle; distribution of velocities. Then you will have an idea about this velocity distribution, how basically from speed distribution we get the velocity distribution.

Now, before I conclude this part I will just make few remarks. So, here during this entire derivation we made some explicit assumptions. In the sense that we said first of all these molecules are still kind of rigid spheres just like Maxwell-Boltzmann distribution in applied and without any intermolecular interaction.

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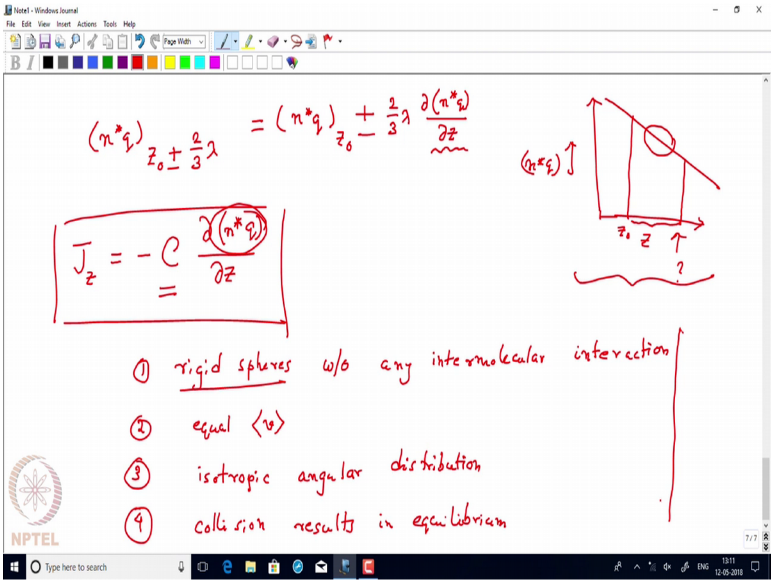

$$(n^*q)_{z_0 \pm \frac{2}{3}\lambda} = (n^*q)_{z_0} \pm \frac{2}{3}\lambda \underbrace{\frac{\partial(n^*q)}{\partial z}}$$

$$\boxed{J_z = -\underline{\underline{C}} \frac{\partial \boxed{(n^*q)}}{\partial z}}$$

① rigid spheres w/o any intermolecular interaction

② equal $\langle v \rangle$

③ isotropic angular distribution

④ collision results in equilibrium

So, that is definitely an assumption and that is why all the all these derivations which we did will hold true for gaseous system or the attractions or repulsion gas in a very dilute condition of course, will be very minimal not in condensers. Because in that case the intermolecular process will be very high, number 2 is that we said that the molecules have actually equal speed which is something like equal average velocity. In reality it would not be true although, we took actually Maxwell-Boltzmann distribution of speed.

But then you can thing that the mean free path will be very different for each molecule and we took the average and then you took a mean free path for something and then you took the average. So, it is not a very rigorous derivation in that sense and number 3 is we also assume that it is basically isotropic in nature and there is no angular variation. So, isotropic angular distribution in the sense that along the theta and phi we just did not say that there is any gradient so, gradient is acting only along z. So, it is a linear in specifically a gradient varying only along one-dimension.

So, that entire problem is kind of one-dimensional although we are saying a three-dimensional it is a three-dimensional system. But a gradient always happens in the one direction that is why the flow, either in heat flow or diffusion whatever it is mass flow in case of diffusion that flow also happens in one direction. But in reality you might have a gradient which also happen very annually so, then you have diffusion problem over a particular solid angle. And so, this is a real life examples, but are real life situations or scenarios. But we are not discussing those situations you are making our analysis very simple. And, the fourth thing is that the collision each collision results in equilibrium; equilibrium of what it is equilibrium with respect to interchange of the property being transferred.

Now, this is a very important thing what we said is that there is a mean free path of the molecules and they are coming from the above layer, but then actually the molecules are also colliding. Because, mean free path is directly connected to the collision because it is the path between two collision effects and during the collision the property also should change. But, we are actually assuming the, whatever collisions is happening the collisions are happening in such a large number; that those collisions are actually setting the system again in the equilibrium. So, that exclusively although each collision is changing for example, of molecules moving this direction and it collides with another they another molecule and it is a direction and the magnitude of the momentum can of course, can change or not change.

But we are saying that for a large number of molecules or large ensemble of molecules or particles it does not matter because, everything gets averaged out. And, even with the collisions the equilibrium is always maintained or even immediately after the collision the equilibrium is established. So, these are the assumptions. So, we made here and those assumptions actually make this I mean analysis very simple. Because, all we want to do is to understand the physics behind the transport phenomena in a very simple way. And, again at the very beginning we said that for a right I mean way of doing it is that you have to consider the angular distribution.

You have to consider the proper gradient, you have these are all vector quantities although we are dealing it dealing with these as if they are scalar quantities so, which are not correct. But as long as we assume that it is a one-dimensional problem it is perfectly fine because, if you just analyze properties of vector along a particular direction so, it is just a scalar. So, because if there is no other component. So, we will just stop here and in the next part we will introduce you to the particular problems like mass flow or heat flow which are connected to basically diffusion and heat transfer.