Micro and Nanoscale Energy Transport

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Lecture - 20
Kinetic Theory of Energy Carriers Part-1

Good Morning. Until the last week we focused on the Equilibrium part of energy transport. The case where we are looking at quantized energy states and the corresponding calculation of distribution function from which, we have an understanding about the internal energy of this particular system and therefore, from which we can also estimate the heat capacities. So all this is kind of Equilibrium thermodynamics.

So, this gives important information about one of the thermo physical properties. This is the specific heat capacity or the volumetric heat capacity and if you want to solve heat transfer problem; however, this is not sufficient. So, we need to also estimate the other important thermo physical property, which is the thermal conductivity.

So, thermal conductivity is again very difficult property to evaluate for different materials. Now people do lot of experiments, but again we were talking about the effect of size, that is with the nano scale materials we can actually see that the thermal conductivity changes with the reduction in the size of the material. So, therefore, how do we fundamentally understand property called Thermal conductivity, again we have to apply some elements of non equilibrium heat transport.

So, one of the simplest ways of studying is thermo physical property will be by using what is called as Kinetic theory. So, the next one or two classes, we will devote our time to using simplified model based on kinetic theory, to derive the expressions for example, the Thermal conductivity as well as heat transport is concerned and the molecular viscosity as for as the flow or the hydrodynamic concerned. So we will see that these are not bad approximation, these are reasonably good.

Later on when we do more rigorous non equilibrium transport phenomena, using the Boltzmann transport equation, from which will again derive the rigorous expressions for thermal conductivity and so on. So, there you will find it is quite similar and only that the Boltzmann transports equation gives more detailed picture, including the size effects. So,

depending on the thickness of the medium you are considering, you can actually capture the size effects of the thermal conductivity, which cannot be however captured using the Kinetic theory.

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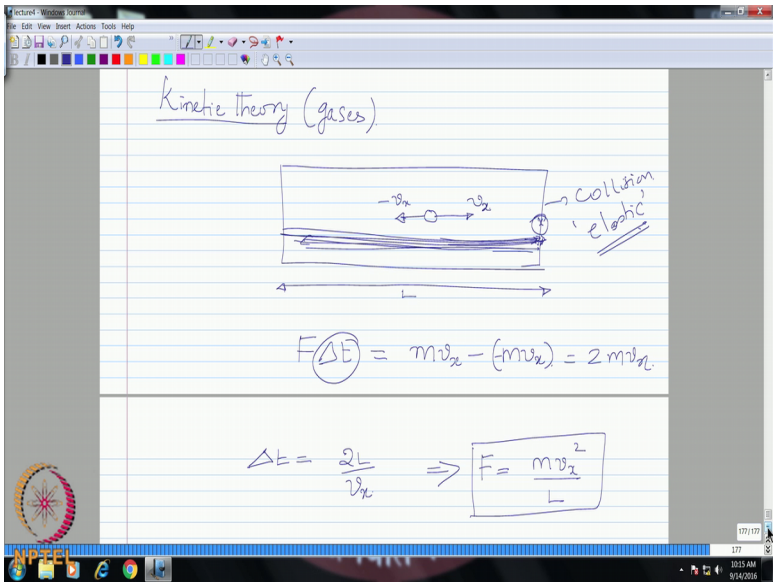

Therefore, just to give a kind of a model to understand how we can get a model for predicting the thermo physical property like thermal conductivity, we will apply some elementary kinetic theory concepts.

So therefore, we start looking at the simplified model based on the Kinetic theory, in this model we are talking about a molecular picture again. So you can visualize a container which is rectangular and the length of this along the Cartesian x direction is capital L.

So, you can picture molecule gas molecule. So, primarily the kinetic theory is applied only for gases, now we cannot use this for liquids for example, because the rarefaction is mostly seen observed in case of gases and therefore, when we extend this to other energy carriers like electrons or phonons, we can only simply use it as it is, assuming this a phonons gas and an electron gas model. So this is a mainly for rarified gases, but can be extended to other energy carriers and very approximate manner, but of course, you cannot use it for liquid molecules.

So, if you just considered a picture of gas molecule in a container, this has and assuming also the motion is translational in only one dimension; that means, it can move either

along this way or along this way. So in the positive direction its velocity is v x, negative direction it is minus v x. So, I mean these are basically corresponding to the random motion of these gas molecules. So it can be defiantly travel in translational directions and also the fact that if you are increasing the temperature of this medium, the kinetic energy will go up and also this velocities momentum will also go up.

However, what I am interested is the force exerted by this gas molecule on the right wall, at the end x equal to l to look at the force exerted by this molecule when it collides on to the right wall. So therefore, if I just apply simple Newtonian mechanics to understand this problem, what we can write is that the impulse which is the force times delta t. So, the delta t is basically the time between successive collisions, on to this particular wall right. So it will just first collide then come back it might collide here and again it will travel back and again collide. So, that that time difference between 2 successive collusions on to this is basically your delta t and the resulting change in the momentum.

So, in the positive x direction you have m v x and in the negative x direction you have minus m v x. So it just comes in hits here the positive momentum, then it again rebounds back with a momentum minus m v x. So therefore, the change in the momentum is m v x minus of minus m v x. So therefore, we have 2 times m v x. So, we are assuming again this collusion is perfectly elastic. So it rebounds with the same momentum in the opposite direction.

Therefore, in this particular case we can substitute the fact that, the time between the successive heats delta t. So once it heats them come back travels the other direction and again comes back here. So how much distance is traveled between 2?

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Basically, it is 2 L. Therefore, we have 2L upon v x this is a velocity, assuming the velocity is constant. So if you substitute into the above expression, you have F is equals to m v x square by L. So, this is the expression for the force on the right wall, due to the motion of this gas molecule with the velocity v x in one direction. If you want to extend this to all the 3 velocities v x, v y and v z, so we can replace therefore, v x with the absolute velocity v.

So, v is related to the individual components. So, this is a vectorial summation. So, we have v square equal to v x square, plus v y square, plus v z square and therefore, assuming that v x is equal to, v y is equal to, v z.

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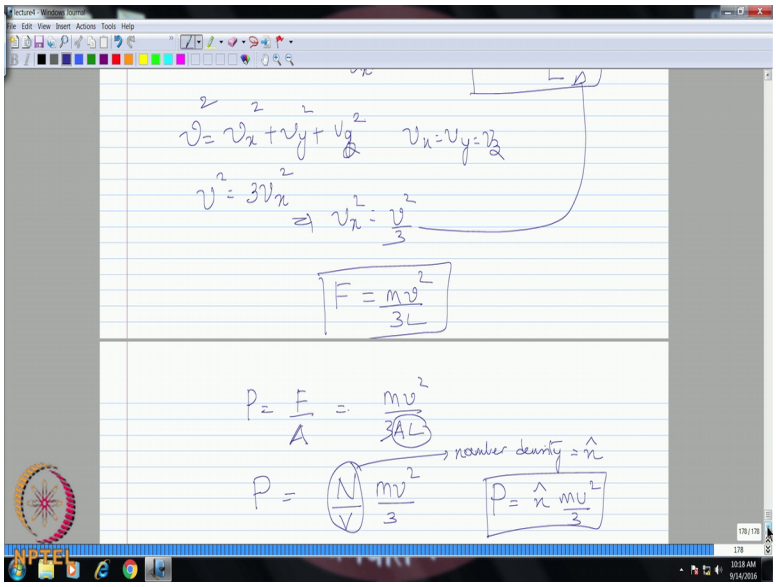

The velocity is uniform in all the 3 directions, we can just say that v square is equal to 3 times v x square or we can replace v x square as v square by 3, this can be put in to this expression we can rewrite force as m v square by 3L.

So, now we have expression for force, we can calculate what is the pressure due to the collusion on to that wall which is nothing but force per unit area, to the area of cross section we will just say it A, so we have m v square by 3AL. So therefore, if you have n such molecules, that is where you really understand pressure, single molecule I mean it is not really the conventional pressure measurement, if you have n number of molecules therefore, you have N times m v square by 3 and the product of a times l is what is the volume the volume of that container.

Therefore, this N by V is nothing but, the number density. So, this is the number density of molecules or number of molecules where unit volume of the container. So therefore, if you write this as small n cap as the number density, you have n cap m v square by3. Now, if you want to relate this to the kinetic energy of the gas molecule.

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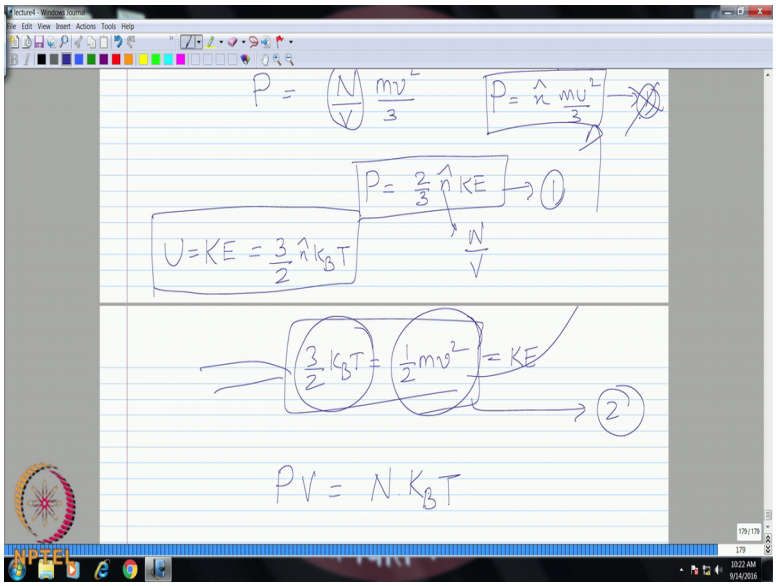

So, we can go ahead further and we can write this as 2 by 3, n cap times kinetic energy, half m v square is the kinetic energy. So we can multiply and divide by 2, so that you can write this in terms of kinetic energy.

If you look at our Maxwell Boltzmann distribution, for the case with translational kinetic energy, the kinetic energy in that case that we calculated U that is nothing, but your internal energy. Internal energy contribution was coming only translational kinetic energy. If you remember if you go back what was the expression that we got for U from the Maxwell from the Maxwell Boltzmann distribution. So we integrated F times, this kinetic energy into d and then over all the velocities d v x, d v y, d v z from minus infinity to plus infinity. So you have 3 by 2.

Student: (Refer Time: 13:33).

3 by 2 and K B T.

So, if you are looking at system with only one molecule, then it is just 3 by 2 K B T, which is equal to half m v square. This is the energy translational kinetic energy of single molecule. So this is equal to your contribution coming from the Maxwell Boltzmann. So, this is basically your equal partition theorem, which says that if your molecule is having a velocity v x. So in each direction you have a contribution of 1 by 2 K B T quantity of energy. So therefore, you are talking about v x square, plus v y square, plus v z square.

So you have all the 3 components. So each direction you have half K B T. Therefore, you have 3 by 2 K B T is your total quanta of energy.

So therefore, we can always use this expression to calculate what is your velocity of the gas molecule at a given temperature? So this is usually required in order to know what the correct velocity is. So that you can therefore, substitute into this and calculate your pressure at a given temperature.

So having known this we know now that 2 things, one this is your Kinetic energy, Kinetic energy is a function of temperature, also the fact that your pressure can also be written as a function of temperature. So how can we do that? So simply we substitute this so let us call this as 1 and let us call this as 2. So use let us call this as 1. It is already this is in terms of kinetic energy. So substitute 2 into 1 and again rewrite pressure in terms of temperature.

So I am going to rewrite this n cap as capital N by V again. So, you have P V is equal to N times 2 by 3, Kinetic energy is equal to 3 by 2 K B T. So therefore, that cancels you have N into K B T where N is the total number of molecules.

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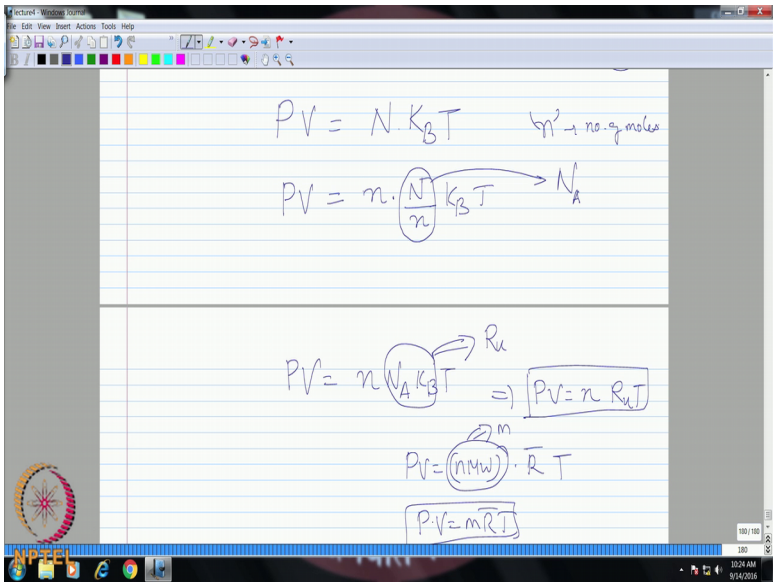

So, now what I am going to do is divide and multiply by the number of moles while called this num n as number of moles. So, I have distinguished from the number density

as n cap, number of moles is n so therefore, I have n times N by n K B T. So therefore, my number of molecules divided by number of moles what is this?

Student: (Refer Time: 17:17).

Avogadros number this is your Avogadro number, we can write this as [noise] subscript a. So this is again a constant value to therefore, PV is equal to n number of moles times N A K B T and N A K B is nothing but.

Student: Universal gas.

Universal gas constant R u; so therefore P V is equal to n into R u times t. Therefore if you multiply and divide this by molecular weight, molecular weight of the gas, so therefore the P V is equal to n times molecular weight, now n times molecular weight will be the mass of the gas. Times this is your real gas constant, times temperature. So this is nothing but your mass of the gas, the mass of the gas molecular weight is usually given as kilogram per kilo mole.

So you multiply by the number of moles that will give you the mass of this gas in the entire container. So therefore, your P V is equal to M RT is derived from the kinetic theory. So, this is nothing but kinetic theory we are assuming one gas molecule collision, we are extending this to n number of gas molecules and then we are relating your internal energy or kinetic energy to temperature and then we are linking this to the pressure and therefore pressure is also function of temperature.

So therefore, what we can conclude from this exercise is that, if you look at both pressure as well as temperature. So what the Kinetic theory says is if you look at the ideal gases, these are ideal gases because we are not considering the interaction between the gas molecules. So they are all acting independent.

So we are simply able to scale it to n number of molecules, but if you are looking at this ideal gas system, both the pressure and temperature are therefore functions of, kinetic energy of the molecule. So fundamentally, this is you have only kinetic energy of the molecule, this is your fundamental energy from which you derive your other macro scale properties like pressure and temperature.

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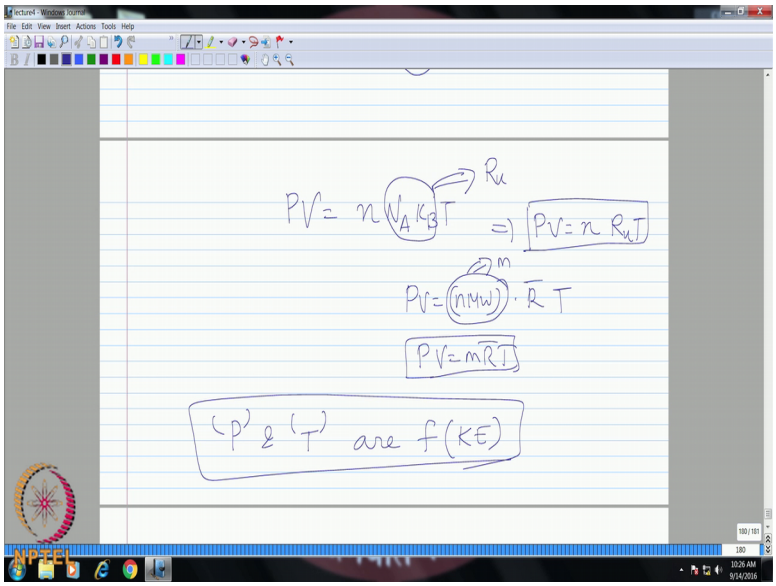

So, the kinetic theory says, based on this inference you can say that, according to kinetic theory both macro scale properties such as pressure and temperatures are only functions of kinetic energy. So, this I think many of you might have already done this. So you may know how to derive the ideal gas equation of state and this is already known, but this is basically the foundation of what we are going to do now.

So, the next important concept is that, if you are considering collision of molecules or energy carriers, you should understand how to calculate the mean free path or the average distance that these molecules are energy carrier's travel before colliding with each other. So this is another important concept that is obtained by using the kinetic theory.

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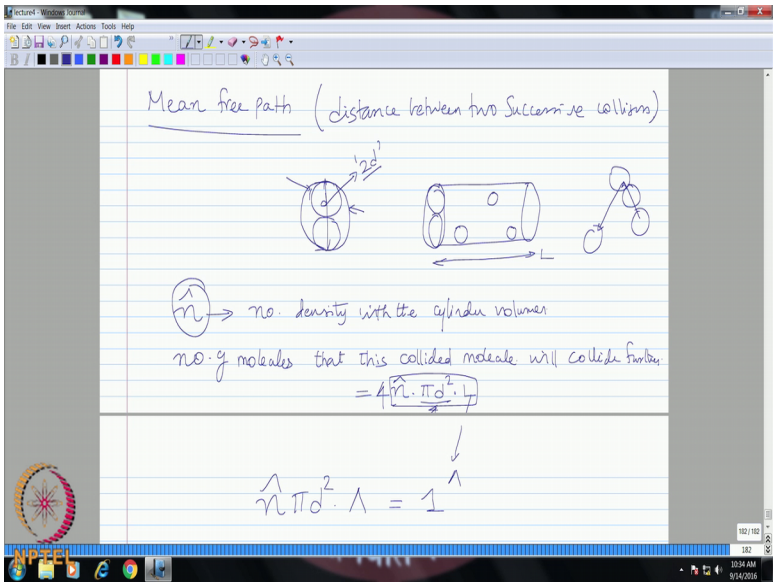

Therefore, a simple model of calculating mean free path will be to assume that you 2 molecules which have come together and collided with each other. So in this picture you can draw represent this effective molecule that is a picture of 2 molecules, in the collided state with an equivalent circle and you can extend this in the third dimension to a cylinder.

So if you look at the 2d picture of these 2 molecules, the effective shape of this is represented by a circle and you can probably have now you have these molecules here together and then you can have molecules into the depth of the cylinder.

So therefore, the let us say the diameter of each molecule is d. Therefore, this diameter here, therefore, effective diameter will be 2d and into the depth we can project this to a cylinder of length L. So that means, you have a picture where you already have a system of collided molecules and now we have to look at how this go propagate and collide with other molecules in the third direction into the cylinder. So therefore, now based on this we can define the number density of molecules within this particular volume. So, let us again denote this is your number density or number concentration within the cylinder volume.

So, the next step is to find out how many number of particles; this is your number this is your total number of molecules within the system. So how many number of molecules that this one particle. For example can collide with in this volume, so the next step is to

calculate number of molecules that, this particle means we are already looking at 1 collided, 2 collided molecules here. Because the way we are going to define the mean free path is the distance between 2 successive collisions, so you are talking about a 3 molecule picture here. So, first these 2 molecules collide and then they have to travel a certain distance to collect. So therefore, you have 2 successive collisions and you are looking at the effective distance.

Student: (Refer Time: 25:26).

So, the this is a simplistic model, the model here says that already we have looked at one collision, now the next collision that will happen will give you the mean free path. So, we have already considered a picture where we are representing these 2 collided molecules with an equivalent diameter and we are going to now find out what will be the distance travelled to collide with the next molecule and that will directly give you a mean free path. So therefore, number of molecules that this collided molecule will collide further.

So you have to therefore multiply this number density with the volume. So, that will be n into pi d square times L. So you have for example.

Student: (Refer Time: 26:41).

This is your n cap correct.

Student: (Refer Time: 26:47).

I think this should be this should be 2 d.

Student: (Refer Time: 26:53).

This should be four d square; however.

Student: (Refer Time: 26:54).

I think the way that the simplistic model can be assumed; yeah you can also include this factor. Yeah for example, let us include it right now. So, in the end we will have another factor which will account for the relative motion.

Student: 4 by 4 cancel.

4 by 4 cancels yes, you are talking about pi d square by 4 yeah correct that is correct this cancels. So effectively you will have only n cap pi d square into L. So if you are talking about calculation of mean free path. So you want to talk about this particular picture, now colliding with one more molecule. So, effect effectively what it means, is it has to therefore, travel a distance of mean free path to collide it with another molecule; that means, this has to be equal to 1, I hope this is clear.

So, we have defined this model in such a way that, it will directly give you for the mean free path if it collides with one more molecule. So, effectively you can have so many numbers of molecules within this volume and you already have a picture where 2 molecules are collided, now if this goes ahead collides with one more molecules, then you will get your mean free path.

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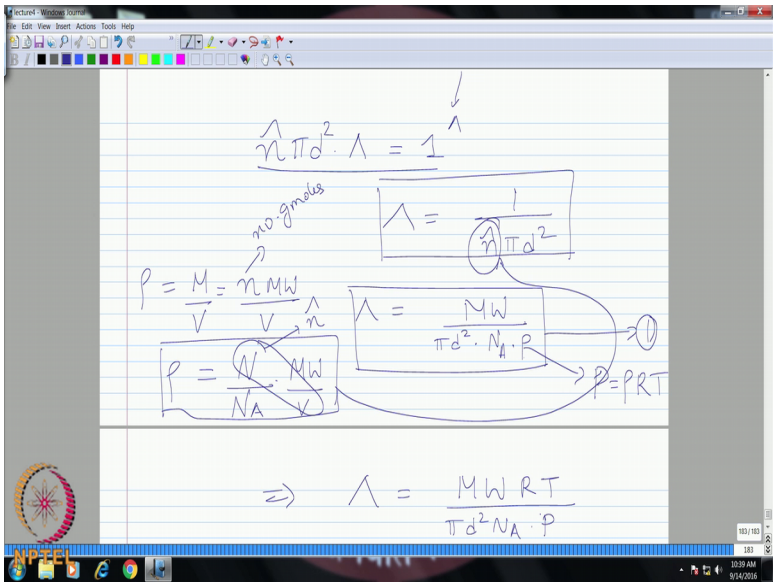

Therefore, there are different ways of deriving the mean free path definition; this is one of the simplest ways I have formed. In some textbooks they give a slightly more rigorous way, but leads to the same expression. So, your mean free path will be 1 by n cap pi d square.

So now, we have to bring about the proper way of representing this n cap here. So how do we do that, now we can we can also relate this in terms of the Avogadros number. So, the easiest way to there is 2 or 3 ways to juggle around. One way is to write this in terms

of molecular weight. So you will have an expression such as, Molecular weight divided by pi d square into the Avogadros number times' rho.

So I am using the fact that, in this case my rho is equal to mass per unit volume which is equal to number of moles times molecular weight by unit volume and again which is equal to, if I replace my number of moles with the Avogadros number I can read rewrite this as number of molecules divided by the Avogadros number, times molecular weight by volume. So 0049 am just doing some jugglery here, in the end therefore I can replace this n by v which is nothing but my n cap, in terms of row N A and molecular weight.

So, this expression is substituted for n cap and therefore I get this one. So, this n is number of moles. is it clear just do not get confused between n and n caps because some in the textbook they have you stand, somewhere n cap. They do not use n cap, they use n for number of mole somewhere it is density so on. I hope this part is clear I am writing row in terms of Avogadros number molecular weight and my number density and just simply substituting for number density in terms of therefore, density and molecular weight. So let me call this as equation number one.

So now I can write, I can use the ideal gas equation of state, therefore replace my rho in terms of P and RT. So my expression for mean free path will become molecular weight times RT by pi d square NA times pressure.

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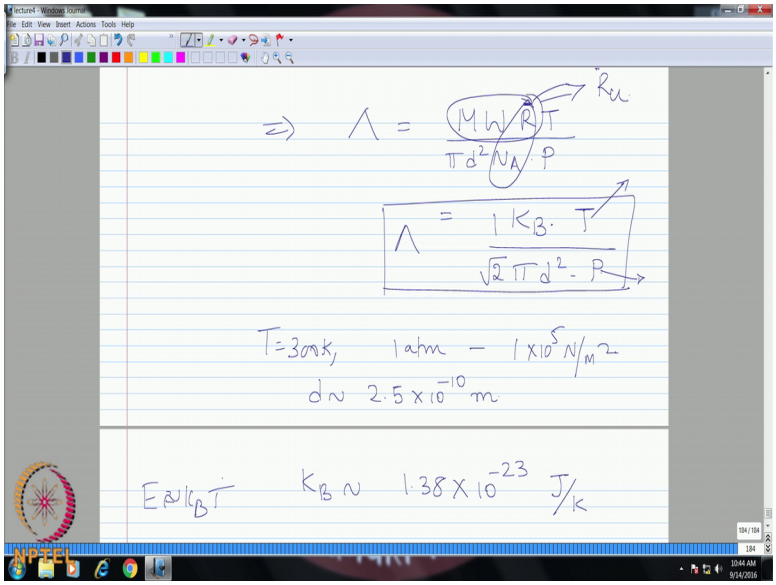

So now what is R by NA KB Boltzmann constant? So this can be written as therefore, my Boltzmann constant, times t divided by pi d square p. So, I think we have K B T by pi d square p.

Student: (Refer Time: 33:52).

So, this is your real gas constant here.

Student: (Refer Time: 34:25).

Therefore, this can be written as your R u. So therefore, now R u by NA becomes KB. So finally, we have therefore, we can relate the expression for mean free path as a function of temperature and pressure. So, we have 2 macro scale properties which we have evaluated before, one was the temperature, which we can evaluate from this expression and the other was pressure, which we can evaluate from this expression here. So, both are functions of kinetic energy.

So, once you get the expression for pressure and temperature, so we can simply substitute that into this and calculate what the mean free path is for that particular energy carrier. So just to do a simple example; Now this is your fundamental expression; however, there is a correction to this because we are assuming that this system of 2 collided molecules is going to move and hit the other molecule, but there is also a relative motion, the other molecule is also moving already. So therefore, in order to account for that correction the effective mean free path is going to now be reduced because this molecule will be moving, this molecule is also moving. So, it does not have to move that much like this expression.

So, to correct for that relative motion we have to have a factor of one over root 2. So, these will therefore be accurately giving you the correct mean free path between the two sets of molecules which are moving. So this is your more rigorous expression, even if you do not use it you will get an approximate order of magnitude value, but to make it more accurate, you use the factor of 1 over square root of 2.

So therefore, now based on this expression you can calculate; what is the mean free path of gas molecules at room temperature and atmospheric pressure? So room temperature you can assume as 300 Kelvin and one atmosphere. This is 1 into 10 power 5 Newton per

meter square and also the effective diameter for the gas molecules can be assumed to be 2 point 5 into 2 point 5angstrom, 2 point5 into 10 power minus 10 meter.

What is the value of Boltzmann constant 1 point?

Student: 38 into 10.

3 8 into10 power minus 23 what is the unit.

Student: Joule per k.

Joule per; so simple thumb rule is this should be equal to K B T.

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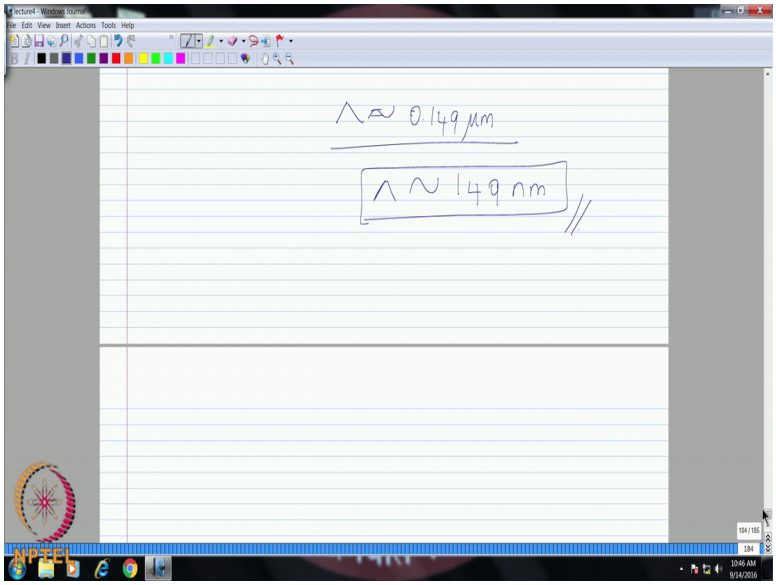

Student: Point 149 microns.

This is substitute you are getting how much point 149 microns that is how much it is 149 nanometers approximate. So, if you are looking at the mean free path of gas molecules, at room temperature and pressure, so this is your mean free path. Now if you want to extend this to other systems and other energy carriers however, this is going to be a little bit tedious because we do not know this effective diameter d.

Therefore, this is suitable expression mainly to estimate mean free path of gas molecules. So when we use the Boltzmann transport equation, there we will understand how to rigorously estimate this value for the other energy carriers also, but kinetic theory

primarily is for gas molecules. So this part is giving you now the next important parameter, which is your mean free path between 2 successive collisions. Now therefore, from this let us go to application of this kinetic theory to a case of heat conduction.

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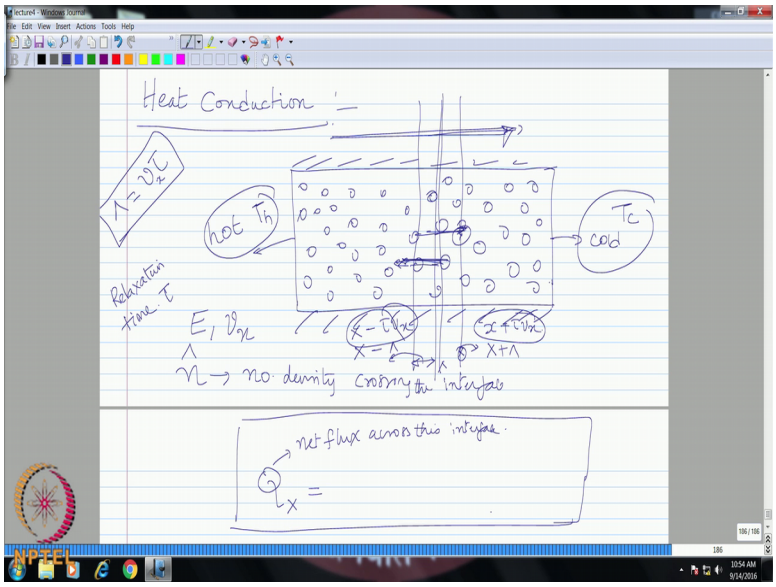

Once again we will consider the case of gas molecules we can probably extend this to other phonon gas or electron gas. So you have molecules in a container, randomly dispersed. But now when we solve the heat conduction, we have therefore to look at the transport of these molecules due to the application of a temperature gradient. So, we are going to heat one end of this container, maintain this at a hot condition T h and the other and the cold condition temperature T c.

So, we can insulate the top and the bottom walls such that effectively the heat transfer is happening in only this direction from left to right. So far we have just looked at kinetic theory, without understanding what the temperature gradient is and therefore, how effectively the molecules will move on and so on. But now we have maintained a prescribed temperature gradient, which we are expecting that because of due to which we have motion of gas molecules in this direction and how do we apply the kinetic theory to calculate the heat flux for this system.

So, the first step here is to look at an interface, some imaginary interface you can just draw a line vertical line, which will allow flux of these particle density to move across. So, you can have some particles which are going in this way, some particles which are

going in this way, effectively there should be a flux which is moving from left to right. Which means that therefore, there is a conduction of heat, and therefore these molecules are effectively moving in this direction to conduct this heat does not mean all the molecules have to move in that direction, you can have molecules moving this way this way, but effective flux, the net flux of these molecules crossing this interface should be from left to right. So therefore, from the kinetic theory picture therefore represent again n as the particle number density crossing the interface; you can put this interface anywhere that you want, but whichever interface it is, is n is the number density which is crossing the interface.

So, the heat flux along the positive x direction is given by, therefore you have motion of the particles, so we can just draw about this interface at a distance of equal to mean free path. So, this is your mean free path, therefore if you call this as x, so this will be x minus your mean free path and this distance as x plus your mean free path. So that means, you have a flux of this particle before they collide with the next particle, it will travel a distance of x plus gamma in the x direction and similarly in the minus x direction before it collides with the other particle it travels x minus gamma.

So, if you want to relate gamma with your velocity, we have to introduce another parameter called the Relaxation time. So we have already introduced mean free path, this relaxation time is denoted by tau, which talks about the time scale between the successive collusions. So therefore, if you no tau how can we write the mean free path as a function of tau.

Student: (Refer Time: 45:46).

If you assume the velocity of this gas molecules is V x, therefore we can say that the mean free path is related to the relaxation time as V x into tau or in other words it tells you converts your length scale to your time scale and vice versa.

Therefore, we can replace this as x minus tau times V x, this is your x plus tau times v x. So what I asked you to do now, we do not have time to complete this exercise. So based on this picture I have given you your n is you can also write this as n cap to be consistent number density crossing the interface, you can calculate what is your net flux across this interface. That means, you are looking at the molecules which are going across this interface and reaching this point and similarly across this interface and reaching this

point, the difference between these 2 in terms of transporting your corresponding value of energy. The molecules which are going from here to here are carrying certain amount of energy with that.

Similarly the molecules going from across from this to this side is also transporting certain amount of energy, but the net flux should be in this direction; that means, the net energy transport should be from the left to right. So, you try to write down let us say that the energy of each of these molecule is E this is your kinetic energy and you also know the velocity V x.

So therefore, you can write down the net energy flux going in positive x direction, net energy flux going the negative x direction and therefore the net flux across the interface using that. So you please do that exercise and we will start from that point tomorrow. So the kinetic theory as such, it is a very simplistic argument.

So we are just simply looking at the picture of molecules and we just look at how much of energy flux can cross a particular interface before it can collide and transfer the energy to the other molecule and so on. By this we can still derive a reasonably approximate expression for thermal conductivity and same way we can extend this to also dynamic viscosity, we can use this to derive the expression for dynamic viscosity based on this the Newtonian model tau is equal to u d u by d y.

Similarly, we can use this for deriving the expression for mass diffusivity that is the flicks law of diffusion. So, all the diffusion phenomena including momentum diffusion, mass diffusion, energy diffusion, heat diffusion can all be derived in a kind of an empirical way using this kinetic theory.

By tomorrow we will be able to also look at the Newton shear stress relation that is momentum diffusion also and kind of conclude the kinetic theory and move ahead with the non equilibrium transport.

Thank you.