Microscale Transport Processes

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Lecture No # 26

Scaling Dimensions and Issues

Good morning. In today's class, we are going to start with discussion on Scaling Dimensions and Issues for small systems, now there there are certain factors which we need to look into.

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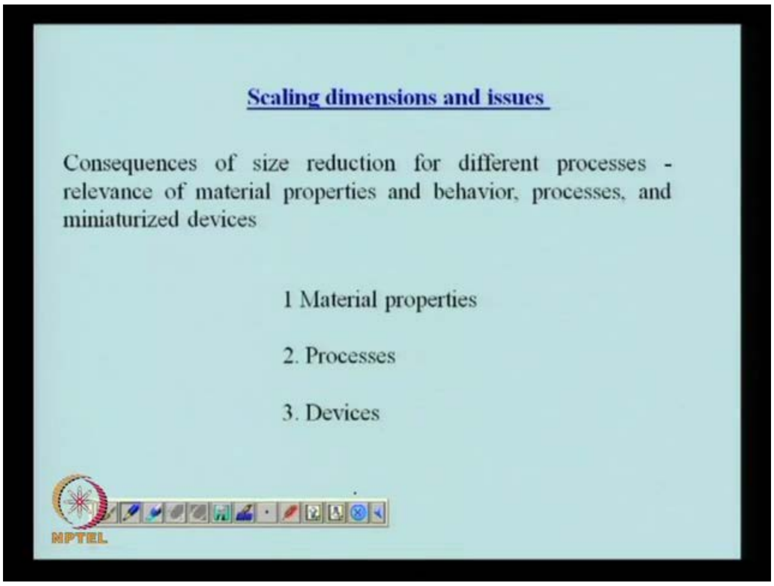

Scaling dimensions and issues

Consequences of size reduction for different processes - relevance of material properties and behavior, processes, and miniaturized devices

1 Material properties

2. Processes

3. Devices

And we we can see that when we reduce the size of any any device, the different processes will behave differently and there would be some relevance of these dimensions, reduction in dimensions on various factors present in the process. For example, one of the interesting ways by which a process can behave differently is that, the material properties of that of of of the fluid present in the system may behave differently when the sizes are reduced to a certain level.

So, in in today's class, we will see principally how the reduction in dimension of a system can result in substantial changes in the material property, changes such that many of the equations which were applicable for bulk flow will no longer be applicable for such systems, we would also see that measurement of any property or the properties may show statistical fluctuations which cannot be ignored.

So, depending on where you measure a specific property, let us say the density, the concentration of of a fluid you make a different result, you would also see that there are certain, all the gases present can be divided into two categories what is what is known as a dilute gas and the densed gas. The equations of motion for example, Navier-Stokes equation may not be applicable in some such systems where the sizes are very small or where the pressure is relatively low and so on.

So, there is definitely a need to de market the region where these equations, the continuum concept is applicable and a region where these assumptions, this continuum assumption will start to show significant deviations. So, what should we do? There are different ways to treat systems which are in which are in different different zones of continuum, I mean in some cases the continuum theory is completely valid in which it is partially valid and in another, it may not be valid at all.

So, we would like to see the approaches to handle systems which may not agree, which may not adhere to the continuum assumption. And secondly, we would also like to see the processes which would come up, which would which you are relevant in in in small systems and how the efficiencies of the processes are going to be affected by a reduction in size, and what kind of devices one can one can, what that kind of devices that are fabricated which takes into account the changes in material properties, the enhanced for example, separation efficiency of any chemical process and the limitations of such devices and so on. But in today’s class, we will mostly concentrate on the material properties or rather the changes in material properties brought about by reduction in the in the dimension of the system.

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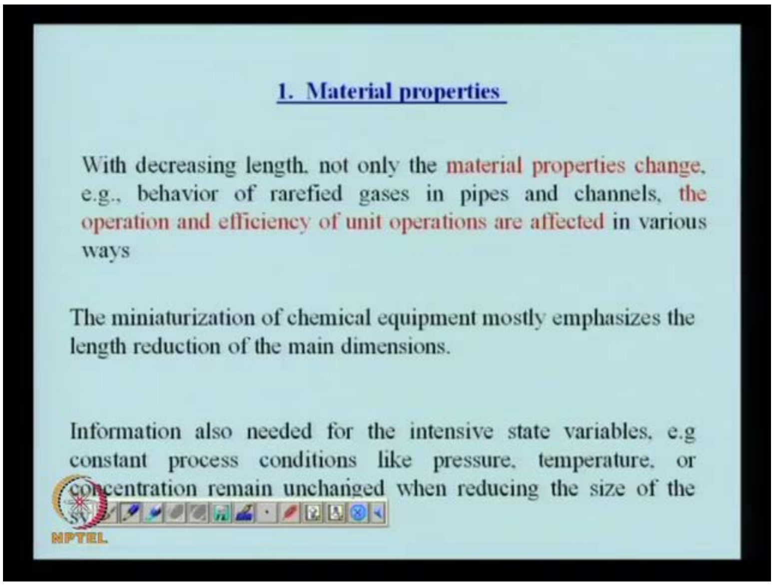

1. Material properties

With decreasing length, not only the material properties change, e.g., behavior of rarefied gases in pipes and channels, the operation and efficiency of unit operations are affected in various ways

The miniaturization of chemical equipment mostly emphasizes the length reduction of the main dimensions.

Information also needed for the intensive state variables, e.g constant process conditions like pressure, temperature, or concentration remain unchanged when reducing the size of the

So, if we go to our next slide, we can see that with decreasing length, not only the material property is change, the behavior is going to be affected which in turn would result in the, in a change in the efficiency of many of the unit operations, fluid flow, heat transfer or mass transfer in various devices in in different ways. When we talk about miniaturization of a chemical equipment, we we generally specify it in terms of the reduction in length, but we also require the information about, let us see how would the pressure or the temperature in such a small system may vary with time and with position. So, you would like to see the effect of reduction in size on on on such systems.

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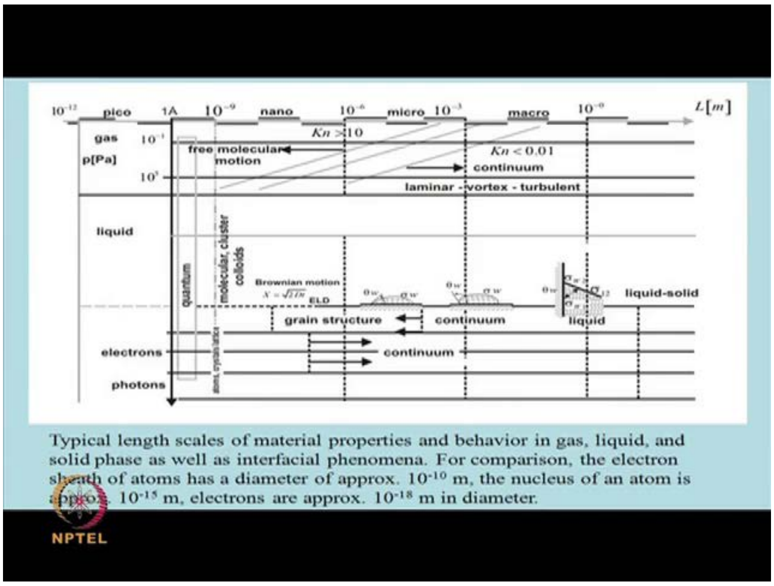

Typical length scales of material properties and behavior in gas, liquid, and solid phase as well as interfacial phenomena. For comparison, the electron sheath of atoms has a diameter of approx. 10^{-10} m, the nucleus of an atom is approx. 10^{-15} m, electrons are approx. 10^{-18} m in diameter.

So, this is figure which tells us something about the different processes in where one is going to be important. For example, if you look at this portion, this is the region for a gas in which continuum assumption is going to be maintained. So, no matter where you measure any property of that gas, of of that fluid, your your property is going to be, your property will not change with reduction in size and this K n refers to Knudsen number which I will again explain later later in a greater detail. And you would see that the value of the Knudsen number can be used can be used to denote, whether we are in the continuum region or in the other extreme where the molecules of the fluid of the gas in this case do not interact with each other and that region can be termed as free molecular motion.

So, in free molecular motion, the molecules do not come in contact, they do not collide and they do not essentially see the presence of the, of another molecule in there. So, it can traverse the entire dimension, entire dimension of the small device without encountering another molecule in its path. So, this is going to be characterized by a large value of the Knudsen number. So, starting with the continuum limit which is valid for Knudsen number about less than 0.01, to when Knudsen number equal is greater than 10, we go from continuum to free molecular motion and if you if you see the top axis, the continuum limit is more or less going to be going to be maintained for macro systems.

So, all the system systems that we see around us the macro systems, they follow continuum assumption nicely and for such systems, the use of Navier-Stokes equations, the use of the no-slip boundary condition in no temperature jump at the liquid-solid interfaces, so this temperature temperature continuity will be maintained.

So, we already know how to tackle such systems, complete solution of Navier-Stokes equation with no-slip boundary equation or no temperature jump at the at the solid-liquid or solid-fluid interface. But when we come to progressively higher value of Knudsen number and we would see that one of one or more assumptions involved in continuum continuum hypothesis will start to breakdown. So, we are going to see, what what such processes are, in nowhere here in the in the rest of the slide, we have some information about the sizes and where, whether it is in the macro scale or in the nanoscale and I think we have discussed this in our previous classes as well, so I will skip this part.

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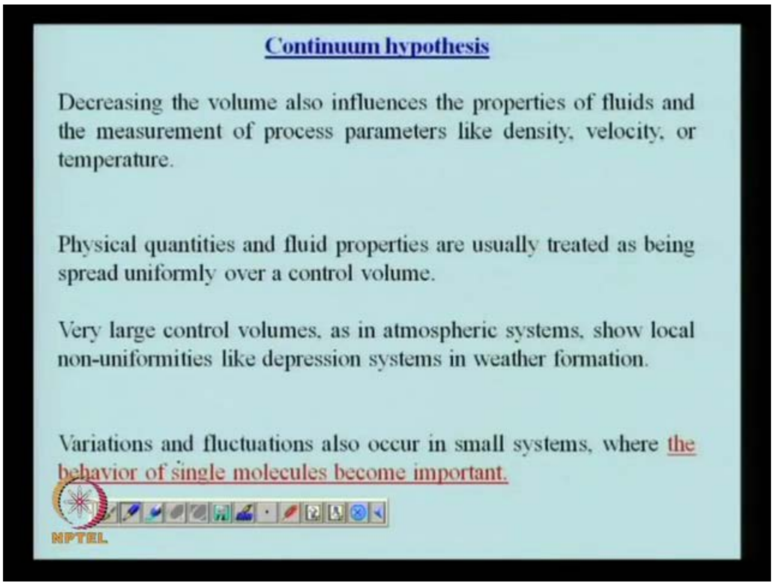

Continuum hypothesis

Decreasing the volume also influences the properties of fluids and the measurement of process parameters like density, velocity, or temperature.

Physical quantities and fluid properties are usually treated as being spread uniformly over a control volume.

Very large control volumes, as in atmospheric systems, show local non-uniformities like depression systems in weather formation.

Variations and fluctuations also occur in small systems, where the behavior of single molecules become important.

Now, what is continuum hypothesis? If we if we if we start reducing the volume, it is of of any system at some point of time, it start to influence the properties of the fluids and the measurement of process parameters like density, velocity or temperature will be affected by the reduction in size of the reduction size of the system.

Now, physical properties and fluid properties are usually treated as being uniform over a control volume. So, no matter what is the control volume size, we will we will assume that the physical properties do not change, but if we think of a very large control volume, then you can have special or temporal variation of properties.

So, at the, at one end of the spectrum, I have a situation in which the physical property or thermo physical condition for example, the pressure could be widely different from from another location and the best example of some such situation is atmosphere. So, atmosphere is such a large system that you can have variation in pressure depending on where you are.

So, inside this room, the pressure is uniforms everywhere, but if you go 10 kilometers from here, the pressure may vary. So, for very large systems as well, you may see a change in the in the properties of the system. On the other hand, if I keep on reducing the size of this room smaller and smaller, a point would come where the dimensions of that control volume, the reduced control volume could be comparable or would be would be close to the mean path of the molecules present in it, not only that, not only it is not going to depend only on the size, but will also depend on the pressure.

So, even for a very small system, you may have enough number of molecules present in the control volume which would let you use the continuum hypothesis. But we understand that when you go from very large systems to very small systems, you are going to have situations in which, let us say the pressure can vary or the size will start to dictate or will start to effect the physical property of the system, it is the in between size where the continuum hypothesis will be will be valid in most of in for most of the temperature and pressure conditions.

So, is this as I said, the behavior of single molecules will become important when we think about variations in properties, also the fluctuations due to the presence or absence of a one molecule or a number of molecules in the measurement volume that you have. So, if your measurement volume is 1 micron into 1 micron into 1 micron cube, then if your pressure is really low, then the number of molecules can vary significantly inside that 1 micron cube.

So, you may have a fluctuation due to the absence of, absence or presence of molecules in such a control volume.

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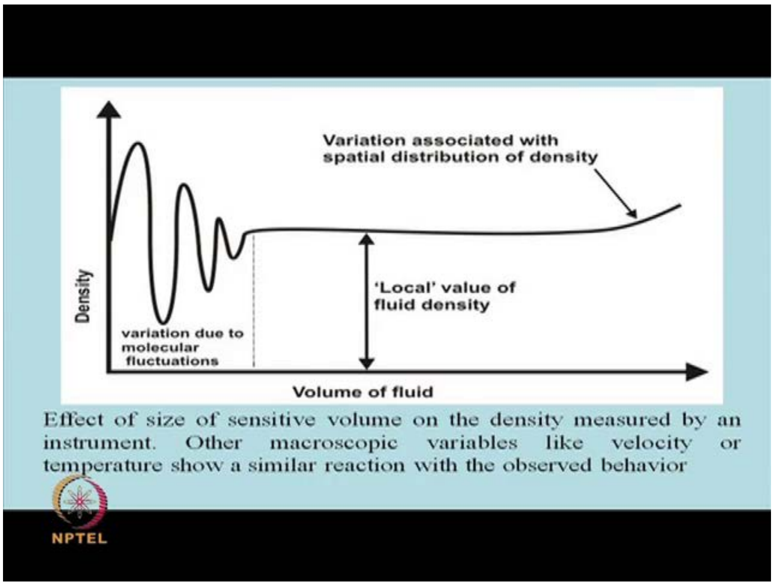

Effect of size of sensitive volume on the density measured by an instrument. Other macroscopic variables like velocity or temperature show a similar reaction with the observed behavior

So, the next figure is a, what I have a already discussed that you have very large size effect and very small size effect. So, one let us say, we are talking about the density change, density as a result of pressure change and here we have a density change as a result of molecular fluctuation, but this is the region that we normally had associated with, where the local value of the fluid density as you can see remains constant.

So, this effect of the size of sensitive volume on the density is usually measured by an instrument. So, depending on the amount of volume that is necessary to measure a property by the instrument, its its reading may vary when you reduce the size of the system.

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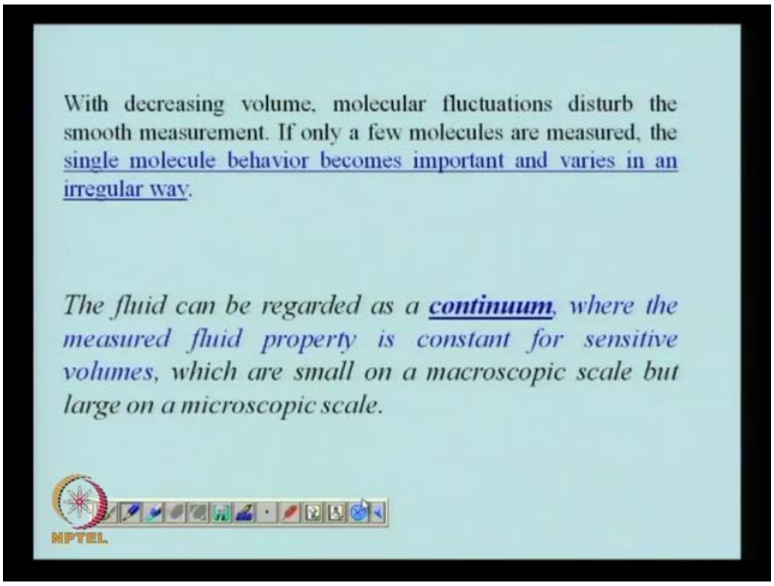

With decreasing volume, molecular fluctuations disturb the smooth measurement. If only a few molecules are measured, the single molecule behavior becomes important and varies in an irregular way.

The fluid can be regarded as a ***continuum****, where the measured fluid property is constant for sensitive volumes, which are small on a macroscopic scale but large on a microscopic scale.*

And we would see that how this is going to affect the the the continuum hypothesis. So, when we start reducing the volume, the molecular fluctuations would start to disturb the smooth measurement. So, you are not going to get a one value of pressure, but you would rather get a fluctuating pressure that can vary widely from one instant to another.

So, when you when you reduce the system to such an extent that you are measuring only a few molecules at a time, then the single molecule behavior will become extremely important and will vary in an irregular way. And we would like to see that, whether how to, how we can how we can express such variations using using non using non conventional approaches other than continuum assumption.

So, the definition of a continuum as you can see is that, a fluid can be regarded as a continuum where the fluid properties that you measure will be a constant for sensitive volumes that is the volume necessary to measure that property with the instrument that you were using. And the volume of that which is used to measure the property is small on a macroscopic scale, but large on a microscopic scale. So, you would I would give you can example of what we call about a macroscopic scale small, but microscopically it is large.

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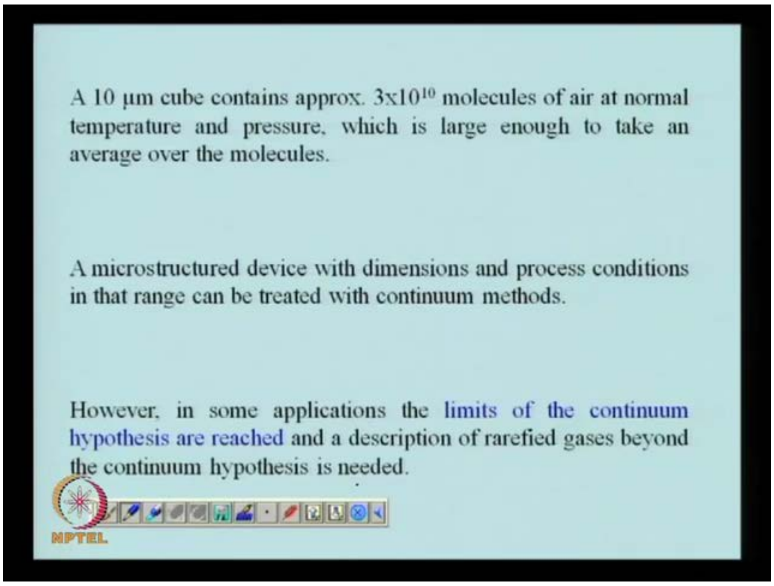

A 10 μm cube contains approx. 3×10^{10} molecules of air at normal temperature and pressure, which is large enough to take an average over the molecules.

A microstructured device with dimensions and process conditions in that range can be treated with continuum methods.

However, in some applications the limits of the continuum hypothesis are reached and a description of rarefied gases beyond the continuum hypothesis is needed.

So, let us say we take a take air and we try to see, the number of molecules which are present in air at normal condition. So, you think about a 10 micron cube, instead of the one micron cube example that I have given you it is it is a cube found of 10 micron by 10 micron by by 10 micron. And if you calculate the number of air molecules present in such a cube at normal pressure and temperature, you would see the air of the order of 10 to the power 10, so it is a huge number of molecules.

So, the effect of molecular fluctuations on any measured property will not be felt if your measurement volume is 10 micron by 10 micron by 10 micron. So, for all practical purposes, these statistical fluctuations are going to be insignificant in such a system at normal pressure and normal temperature. But what happens, if we reduce that pressure or the temperature that is something, or if we reduce from it to from the micron level to nanometer level.

So, would it still be, a situation would it still represent a situation in which the properties are going to be independent? The (()) sensitive volumes are going to still going to be so large that the number of molecules present in it are going to be very very large of the order of 10 to the power 8 and so. So, here you see the sensitive volume of 10 micron cube is very small when we talk think about macroscopic scale, but it is still large when we talk think about the microscopic scale, because of number of molecules present in such a system is so large.

So, if you if you if you if you think of a microstructure device whose dimensions and process conditions are of the order of 10 micron, 1 atmosphere and let us say 25 degree centigrade, then in that range, the fluid present in the microscope in that microscopic device would would obey would obey the continuum assumption in all the methods and models available for continuum situation would be valid in such systems. So, we would, but we are more interested in this class is about the limits of the continuum hypothesis where they are going to be reached, where the continuum assumption will not hold good, and a description of the gases which are also termed as rarefied gases beyond the continuum hypothesis.

So, you would like to see, how, where to draw the line, how to present a quantitative way to decide about whether you have reached the one limit or the other of continuum.

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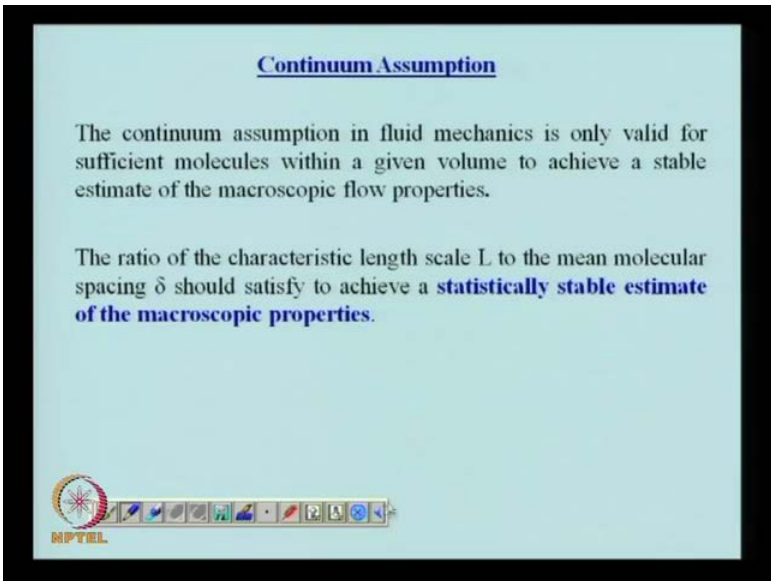

Continuum Assumption

The continuum assumption in fluid mechanics is only valid for sufficient molecules within a given volume to achieve a stable estimate of the macroscopic flow properties.

The ratio of the characteristic length scale L to the mean molecular spacing δ should satisfy to achieve a **statistically stable estimate of the macroscopic properties**.

So, the continuum assumption in fluid mechanics is only valid when you have sufficient number of molecules present in a given volume so that you achieve a stable estimate, stable which is which is not, where there is not fluctuations of the microscopic of the macroscopic flow properties.

So, the pressure, temperature, etcetera will remain constant throughout your measurement. So, this length scale that we have that we need the ratio of the characteristic length scale to the mean molecular spacing should be large so as to obtain a statistically stable estimate of macroscopic properties. So, the mean molecular spacing should be quite small compared to the length of it and a number has been, it has been found that when you have the number in in in within in such a way that L by delta where L is a characteristic length of the device. And if you have the molecular spacing delta, if it is if it is greater than certain numbers, then we can assume that we do not have any statistical fluctuations present in the system.

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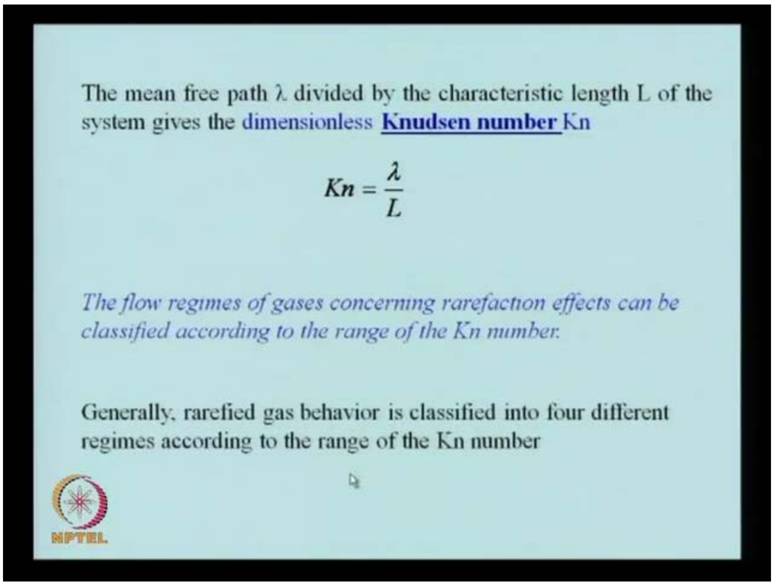

The mean free path λ divided by the characteristic length L of the system gives the dimensionless **Knudsen number** Kn

$$Kn = \frac{\lambda}{L}$$

The flow regimes of gases concerning rarefaction effects can be classified according to the range of the Kn number.

Generally, rarefied gas behavior is classified into four different regimes according to the range of the Kn number

This another way to another way to say, when I am going to reach the limit of continuum is to define a number which is a Knudsen number, which is defined as the mean free path of the gas molecules when they are divided by the characteristic length of the system, we get a dimensionless number which is known as the Knudsen number. And depending on the values of Knudsen number, one can decide whether, where we are in terms of the rarefaction effects on the flow regimes of the gas present in it. So, for different values of

Knudsen number, we can classify the flow regimes to say that, this obeys continuum and this does not.

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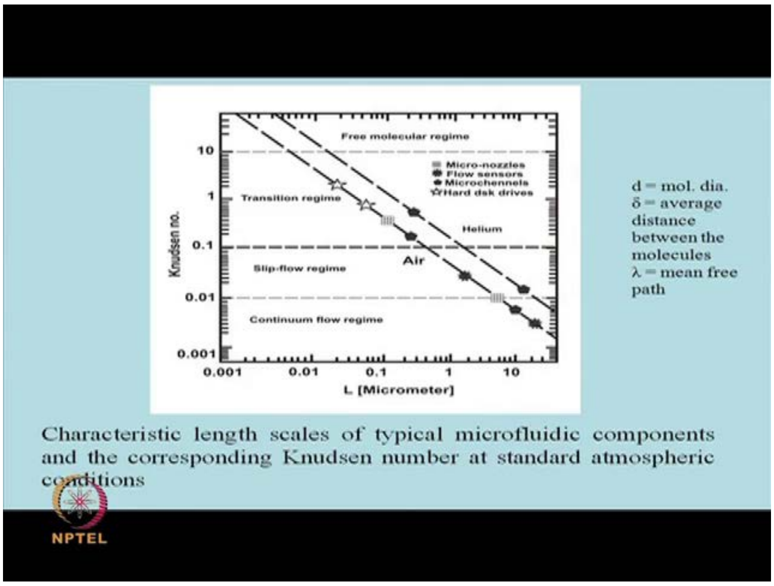

d = mol. dia.
δ = average distance between the molecules
λ = mean free path

Characteristic length scales of typical microfluidic components and the corresponding Knudsen number at standard atmospheric conditions

This figure is an interesting figure where we have on the left, the Knudsen numbers are plotted and you can see that, it is a logarithmic plot where the Knudsen number can vary from 0.10 1 into the 10 to the power minus 3 about 10. And in the in the y axis, in the bottom y axis it is the length in micron, the length scale of the device in micron and your d, if you see the right hand side over here, the d is the molecular diameter of the gas present, delta is the average distance between the molecules and lambda is the main free path.

So, the mean free path is the distance each molecule has to travel in at, before it comes to contact with another molecule. But at one instant of instant of time, delta is distance between two molecules, average distance between the two molecules present in such a device. So, here you would see that for small values of Knudsen number, the continuum flow regime, we can assume that it is continuum flow regime. That means, the properties are going to be more or less constant and you are going to have no slip conditions, validity of no slip conditions and so on. Between a Knudsen number 0.01 and 0.1, we have slip flow regime, we will discuss about that all of all these in more detail and then when the Knudsen number is of the order of 1, you get a transition regime which is in between slip flow and free molecular regime which is which is valid, which is classified for a Knudsen number of for a Knudsen number of greater than 10.

So, in between free molecular regime and slip flow regime, we have the transition regime. So, now we will take each one of them one by one and we will see how, what what would do they imply in terms of the applicability of the equations that we know or in terms of new equations or new methods of measurement or new modeling approaches that are to be undertaken in order to explain, or in order to describe in detail the flow of a fluid or variation of the property of the fluid in such a small system.

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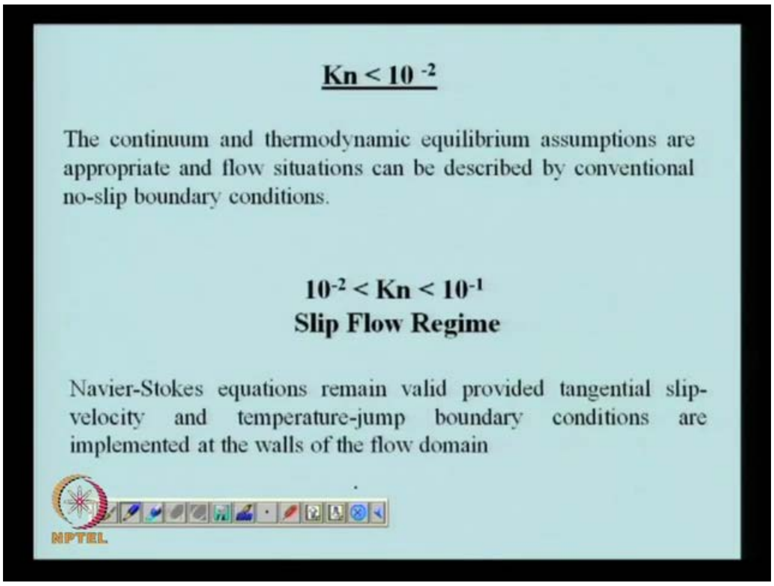

$Kn < 10^{-2}$

The continuum and thermodynamic equilibrium assumptions are appropriate and flow situations can be described by conventional no-slip boundary conditions.

$10^{-2} < Kn < 10^{-1}$

Slip Flow Regime

Navier-Stokes equations remain valid provided tangential slip-velocity and temperature-jump boundary conditions are implemented at the walls of the flow domain

So, we will first start with, like situations in Knudsen number is less than 1 into 10 to the power of minus 2, now this refers to complete validity of continuum model. So, the continuum model says that you, when you measure a property, that property will not vary based on molecular fluctuations, you can use many of the equations that are that are valid for macroscopic macroscopic systems such that you can use Navier-Stokes equation to describe the flow inside such as small, inside a system.

And you are also going to have no slip boundary condition at the solid, solid fluid interface and if you think of the energy equation, then you can you can you can assume you can assume without any error that the temperature on the solid side of the interface is equal to the temperature of of the fluid side of a interface. So, in other words, the temperature is going to be continues function even at the interface without a jump of temperature or pressure at the solid fluid interface.

So, any systems in which the Knudsen number is less than 10 to the power minus 2 can safely be assumed to follow continuum models, all equations which are valid in macroscopic systems, all boundary conditions which are normally taken to be taken to be true, taken to be valid for macroscopic systems.

Next, we come to the point where Knudsen number is between 10 to the power of minus 2, greater than 10 to the power of minus 2, but less than 10 to the power of minus 1. Here some models, some equations for example, Navier-Stokes equation will still remain valid even though it cannot be, it cannot truly be said that it is it is it is a, it follows continuum model completely. But there are certain certain alterations or certain approximations need to be introduced in to Navier-Stokes equation for, to be used in slip-flow regime. And as the name suggests, you have to assume that there is a slip between the gas molecules and the solid at the interface.

So, as long as a slip model or a slip flow is assumed, as temperature jump is assumed at the fluid solid interface, Navier-Stokes equation can be used without any problem. So, this is a very common situation in micro fluidic devices, the slip-flow regime and they become important when the Knudsen number is in this range, between 10 to the power minus 2 to 10 to the power minus 1.

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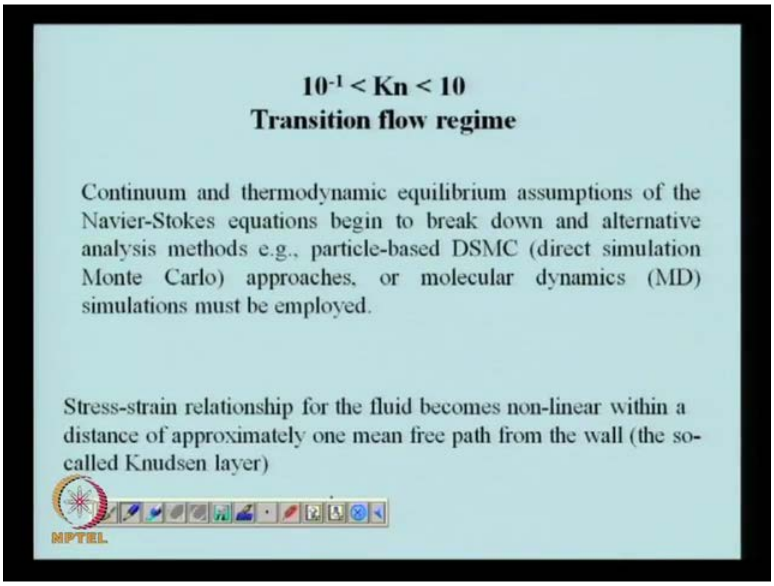

$10^{-1} < Kn < 10$

Transition flow regime

Continuum and thermodynamic equilibrium assumptions of the Navier-Stokes equations begin to break down and alternative analysis methods e.g., particle-based DSMC (direct simulation Monte Carlo) approaches, or molecular dynamics (MD) simulations must be employed.

Stress-strain relationship for the fluid becomes non-linear within a distance of approximately one mean free path from the wall (the so-called Knudsen layer)

Then comes that the third flow regime, which is known as transition flow regime. In this flow pattern, in this in this situation, the continuum and the thermodynamic equilibrium assumptions of the Navier-Stokes equation will start to break down and need to find alternative analysis methods, it could be molecular dynamic simulation or Monte Carlo simulation. So, you are not going to, you will not be able to use continuum models such as Navier-Stokes equation even with the introduction of slip flow, because you not only have the continuum limit is going to be going to be exceeded, you are going to have a breakdown of the thermodynamic equilibrium at the interfaces, but still the, it cannot be called a free molecular flow.

So, this is transition flow and this is also quite common in micro systems. So, another interesting phenomenon which one would come across in such systems is that, the stress strain relationship will behave in a non-linear fashion within a distance of about one mean free path from the wall, so this is called the Knudsen layer. So, if you cross the Knudsen layer, the stress strain relationship will no longer remain linear. So, this is the additional complication which one has to take into account while modeling a flow in the transition regime.

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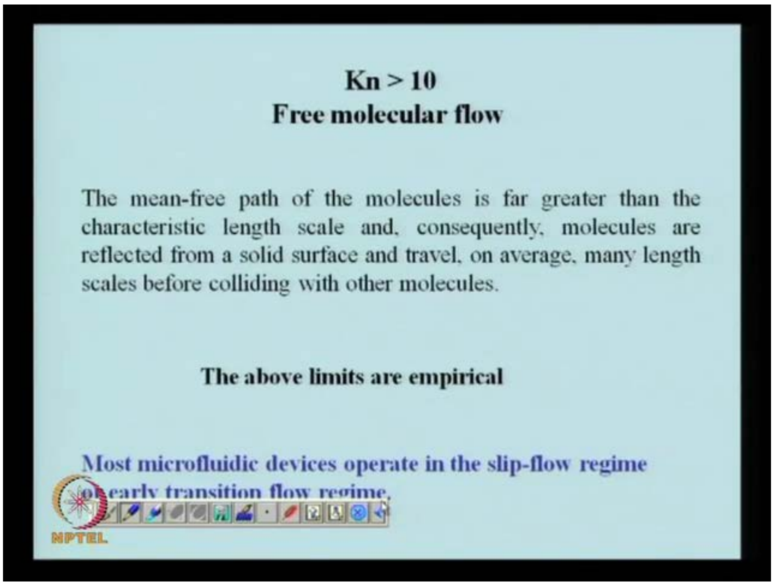

Kn > 10
Free molecular flow

The mean-free path of the molecules is far greater than the characteristic length scale and, consequently, molecules are reflected from a solid surface and travel, on average, many length scales before colliding with other molecules.

The above limits are empirical

Most microfluidic devices operate in the slip-flow regime or early transition flow regime.

And finally, for large values of Knudsen number, we come to a situation which is known as the free molecular flow.

So, here the mean free paths of the molecules are far greater than the characteristic length scale. So, your characteristic length may be 0.1 micron, but your mean free path of the, because of the pressure and the temperature conditions of the of the of the gas which is present in such a micro device, it could be 10 micron. So, you have a large difference between the size of the system and the mean molecular free path. So, the mean free path is will be much more than the size of the system, therefore a molecule which gets deflected which gets reflected from from the device surface will reach another, will reach the other end of the device before it comes in contact with another molecule.

So, that is why, it is called the free molecular flow of gases in such a system. And as you can clearly see, the continuum assumption, the continuum approximation does have no meaning for see in situations like this. Because you you just have few molecules in a device, in to the size of the molecule the device is very very large and to the separation between the molecules, the device length is very large I am sorry, it is other way around so that you you do not any collision of the molecules, very few collisions of the molecules in between.

So, all these above limits, we must need to know or much need to emphasized that all these limits are empirical. So, this is, this would just give an idea where, what would be the nature of the flow by looking at the values of Knudsen number alone. So, the value of the Knudsen number, only the value of the Knudsen number will indicate where your system can be, it is not a definite thing that you would say with certainty that for a Knudsen number of value equal to 0.1, it is going to be in the slip-flow regime, fortunately that most of the micro fluidic devices, either operate operate either in the slip-flow regime or in the early transition flow regimes.

So, many of the continuum models will be applicable if we add the flow slip flow at the at the solid gas interface. So, the equations will remain the same, the boundary conditions need to modified in order to use these these, in order to analyze such situations.

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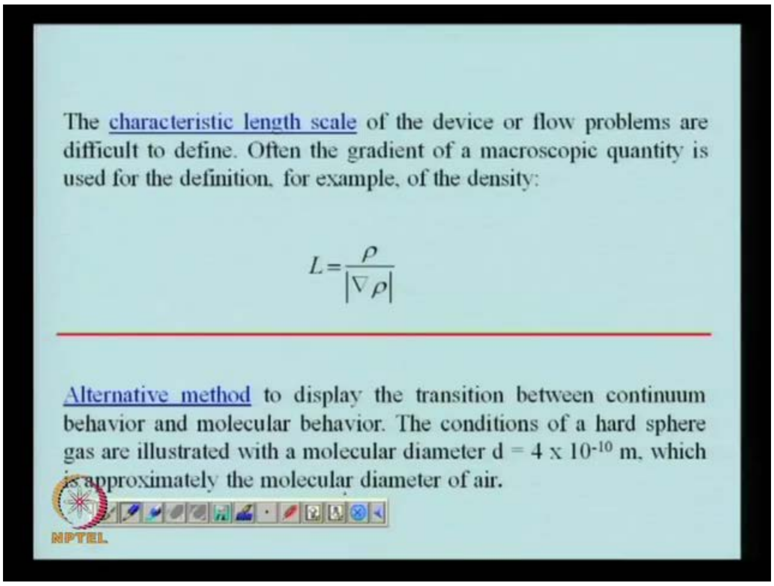

The characteristic length scale of the device or flow problems are difficult to define. Often the gradient of a macroscopic quantity is used for the definition, for example, of the density:

$$L = \frac{\rho}{|\nabla \rho|}$$

Alternative method to display the transition between continuum behavior and molecular behavior. The conditions of a hard sphere gas are illustrated with a molecular diameter d = 4×10^{-10} m, which is approximately the molecular diameter of air.

Now, now the question may come is, what is a length scale, is it the smallest length of a device that is going to be treated or that is going to be termed as the characteristic length, or is it something else?

So, in order to circumvent the problems associated with the definition of characteristic length, this definition is sometimes used, it is the property divided by the gradient of the property which has dimensions of length are sometimes called the characteristic length, so so there is an alternative. So, we we this is up to this point is classification of systems based on Knudsen number alone, but there is an alternative method which displays the transition between continuum and the molecular behavior in a more detailed, in more fundamental way where we know precisely which of the assumptions of continuum approximation, continuum model is going to be violated and what can be done to address those violations.

So, it is more in depth study of the variation of the transition from one regime to another which I am going to present next. So, for this I take an example where, example it is a, we we will assume that it is a hard sphere gas and with the molecular diameter of 4 into 10 to the power of minus 10 meter which is approximately that which is approximately the molecular diameter of air.

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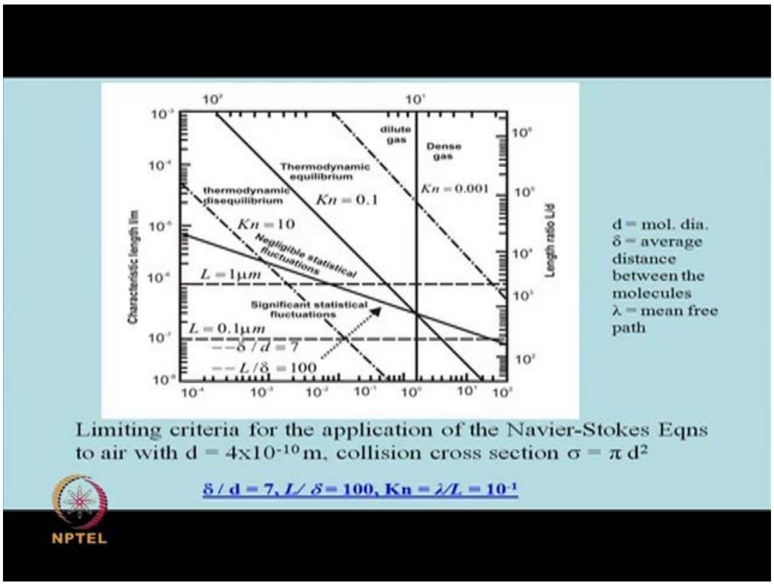


d = mol. dia.
δ = average distance between the molecules
λ = mean free path

Limiting criteria for the application of the Navier-Stokes Eqns to air with $d = 4\times10^{-10}$ m, collision cross section $\sigma = \pi d^2$

$\delta / d = 7, L/ \delta = 100, Kn = \lambda/L = 10^{-1}$

And with that we have plot, this plot tells us gives us more insight into the process where on the x axis, we have the characteristic length L to be defined in a way that that that that could be, it could be the smallest system dimension or the property divided by the gradient of the property as I have said before. On the top y axis, it is the intermolecular spacing normalized by the molecular diameter. So, delta is the average distance between the molecules and d is the molecular diameter. So, it is the intermolecular spacing normalized with the diameter of the with the molecular diameter. On the right x axis, right y axis, we have the length ratio L system dimension normalized by the molecular diameter again.

So, these, this two are the same, one is in only length and this is normalized length and the x axis, the bottom x axis it is the variation it is it is the variation of the physical property, physical situation, it could be the pressure, it could be the density where density normalized by density at some standard condition p 0. So, here you would see that the flow regime, the nature, the situation, the condition of the system is different based on where you are located.

So, for example, this gas where delta by d is 7 and and smaller is called dense gas. So, this line denotes this line denotes whether you are in dense gas regime or in the dilute gas regime and these dotted lines these dotted lines are for different values Knudsen number.

(Refer Slide time: 32:00). So, of this line is for a Knudsen number of 0.001, this is for 0.1 and for 10 and so on.

So, based on the value of Knudsen number you would see we would see where we are going to have the continuum labeled. Now, if you if you think of this, if you if you see line, this is for L by d characteristic length divided by sorry L by delta characteristic length divided by the average distance between the molecules, this line refers to when L by delta is equal to 100 and so on. And here you see that the size, actual size of the device, so this line corresponds to L equal to 0.1 micron and this line corresponds to L equal to 1 micron and so on (Refer Slide time: 32:57).

So, by looking at the figure and by by noting where you are, let us say, you are at this point, your process conventions are such that your system is located at this point. So, you can say it is it is on the right hand side of this line, so it is a dense gas and your Knudsen number is less than 0.001. So, definitely you are you are within the thermodynamically equilibrium assumption often of often continuum model; at the same time, since you are above this L by delta equal to 100 line, since you are above this regime, then there is going to be negligible statistical fluctuation of properties in here.

So, location a position over here satisfies the dense gas assumption, it satisfies the thermodynamic equilibrium assumption and it ensures that there is no molecular, no statistical fluctuation in the property. So, a system over here must be, would be such that continuum approximation, continuum model, continuum equations can be used without any without any second thought, without any problem.

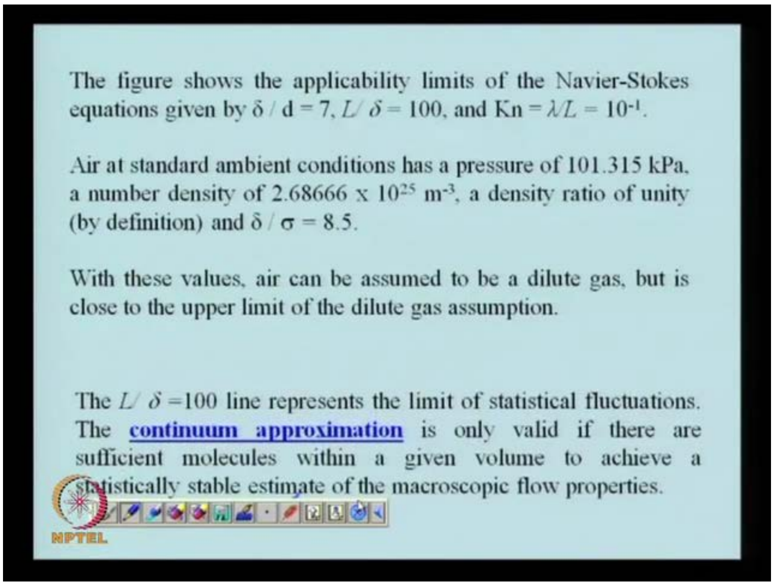
But on the other hand, if you are at a different location , let us say if you are over here if you are over here (Refer Slide Time: 34:33) , then you are in the dilute gas range, the thermodynamic equilibrium assumptions of continuum flow will not be will not be maintained, will will be violated. But you are above the statistical statistical fluctuation line such that the properties are not going to be not going to be, they they are not going to be any molecular effect on the properties, but still one assumption of Navier-Stokes equation is not going to be valid.

But if you are over here (Refer Slide Time: 35:08), or any other any other point over here, then you you you will be, your your thermodynamic equilibrium and no statistical fluctuation assumptions of continuum flow, continuum model, both are going to be violated and definitely, you have to think of molecular simulations, molecular dynamic simulations or Monte Carlo simulations or even free molecular flow to model flow in such a such a system.

So, this figure essentially tells you, give you a complete picture of where you are in terms of the validity of the different assumptions associated with continuum flow model. So, it does not say that you only have to look at value of Knudsen number, it also tells you that you have to look at the ratio of L by d that is the length scale sorry L by delta length scale divided divided by the average distance between between the molecules, you also have to look at whether it is a dense gas or it is a dilute gas (Refer Slide time: 36:07). So, this gives you more complete picture of the, of various processes of various approximations, whether they are valid or not in such systems.

So, the, this is just description that I have already already told you that, what is the x axis y axis and z and the right x axis and the top y axis. Now, we see that the zone of applicability of Navier-Stokes equation is given by delta by d equal 7, L by delta has to be in the in the upper upper half of that line corresponding to L by delta and Knudsen number should be equal to 10 to the power minus 1 or smaller.

(Refer Slide Time: 36:25)



The figure shows the applicability limits of the Navier-Stokes equations given by $\delta / d = 7$, $L / \delta = 100$, and $Kn = \lambda / L = 10^{-1}$.

Air at standard ambient conditions has a pressure of 101.315 kPa, a number density of 2.68666×10^{25} m^{-3}, a density ratio of unity (by definition) and $\delta / \sigma = 8.5$.

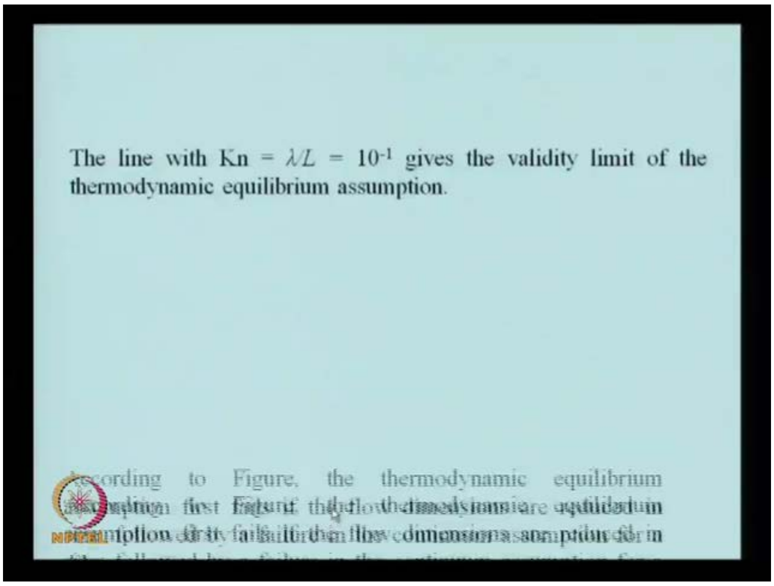
With these values, air can be assumed to be a dilute gas, but is close to the upper limit of the dilute gas assumption.

The $L / \delta = 100$ line represents the limit of statistical fluctuations. The **continuum approximation** is only valid if there are sufficient molecules within a given volume to achieve a statistically stable estimate of the macroscopic flow properties.

And if you think of air, you would see that it has a number density at 1 atmosphere pressure of 2.6 into 10 to the power of 25 in a meter cube size and density ratio which is about 8.5. So, with these values, one can say that air is a dilute gas, but it is close to the upper limit of dilute gas assumption. And this L by delta equals 100 line which is this line, L by delta equals 100 line, it represents the limit of statistical fluctuations, you have to have sufficient number of molecules within a given volume to achieve a statistically stable estimate of the macroscopic flow properties.

So, in order to have in order to for continuum approximation to be valid, your system or your conditions should be such that your L by delta is above that 100 mark line; that means, your L by delta should be above this line (Refer Slide Time: 38:10). So, you do not you cannot see it over here, but it simply tells you that this is the condition that needs to be maintained for you to use for you to use the continuum approximation, this side of the line, this side of the line and this side of the line (Refer Slide Time: 38:30). So, it is essentially gives you more or less, this being the region where the continuum approximation is going to be valid (No audio from 38:49 to 38:59).

(Refer Slide Time: 38:57)



The line with $Kn = \lambda/L = 10^{-1}$ gives the validity limit of the thermodynamic equilibrium assumption.

According to Figure, the thermodynamic equilibrium [illegible]

So, there are certain other interesting things, which you would see that if you are a dilute gas (Refer Slide Time: 39:04), if your situation is over here and you keep on reducing the size of the system, then the first problem that you are going to encounter in using continuum approximation is that your thermo dynamical equilibrium is going to be violated, and then you are going to come to you are going to come to this point where the there would be significant statistical fluctuation in the properties.

So, that is how a dilute gas, when you are going to reduce the system size, how it is going to behave. On the other hand, if you start with the dense gas, then you are going to cross this limit first that is the statistical fluctuation limit is going to be crossed first, and then you are going to come to the to the thermo dynamical limit. So, for dilute gas it is a thermodynamic equilibrium condition which would be violated first, where as for the case of dense gas, it is just a molecular fluctuation which is going to be violated first. So, this is how the two systems will behave differently.

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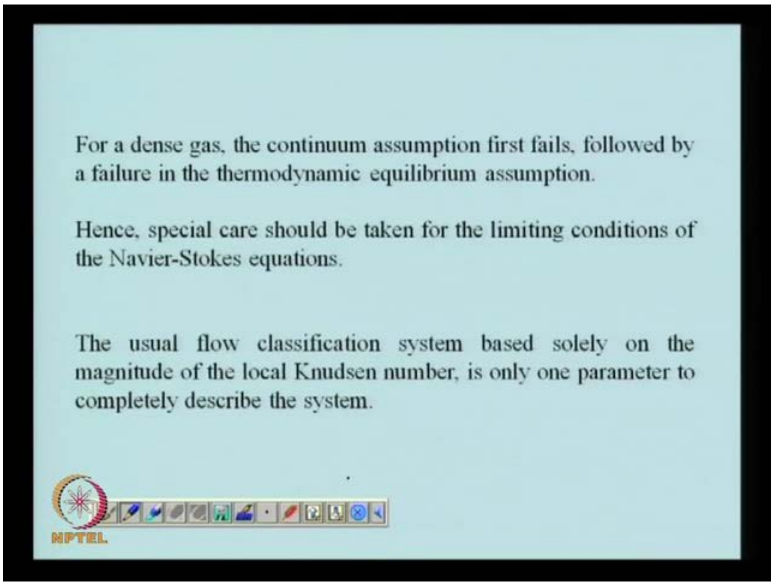

For a dense gas, the continuum assumption first fails, followed by a failure in the thermodynamic equilibrium assumption.

Hence, special care should be taken for the limiting conditions of the Navier-Stokes equations.

The usual flow classification system based solely on the magnitude of the local Knudsen number, is only one parameter to completely describe the system.

And so, one should take a special care for the limiting conditions to use, the limiting conditions of the Navier-Stokes equation and as the you can see now that the Knudsen number, the magnitude of the Knudsen number is just one parameter, one of the many parameters, one of the 4, 5 parameters which I have mentioned that describes the nature of the system.

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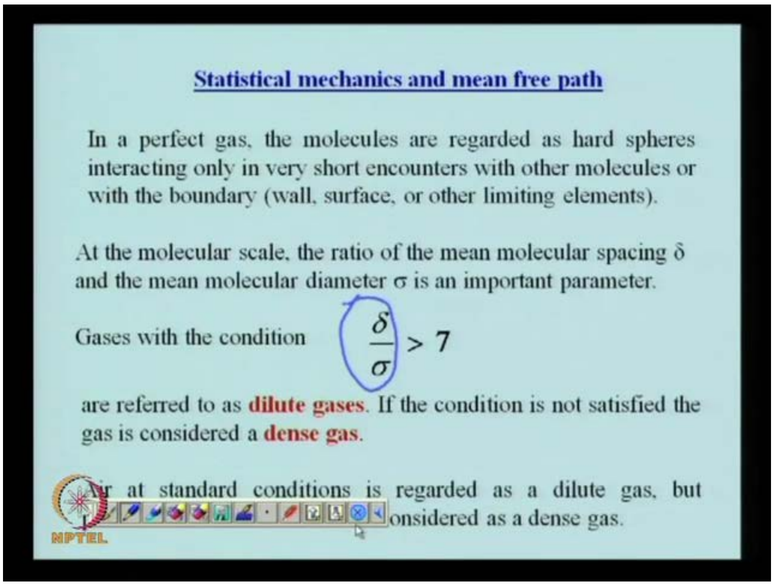

Statistical mechanics and mean free path

In a perfect gas, the molecules are regarded as hard spheres interacting only in very short encounters with other molecules or with the boundary (wall, surface, or other limiting elements).

At the molecular scale, the ratio of the mean molecular spacing δ and the mean molecular diameter σ is an important parameter.

Gases with the condition $\frac{\delta}{\sigma} > 7$

are referred to as **dilute gases**. If the condition is not satisfied the gas is considered a **dense gas**.

Air at standard conditions is regarded as a dilute gas, but onsidered as a dense gas.

Now, we come to our next part which is the statistical mechanics and mean free path, usually gases with this condition that delta by sigma greater than 7 where delta is the mean molecular spacing. And mean molecular spacing and sigma is the main molecular diameter, this is going to be an important number, delta by sigma and gases with the condition delta by sigma greater than 7 are treated as dilute gases and if the condition is not satisfied, then the gas is called dense gas.

So, air is at standard conditions, it is a it is a regarded as dilute, it can calculated, it can be shown to be as dilute gas, but at a lesser pressure it is going to be at sorry at higher pressure, it is going to behave as a dense gas.

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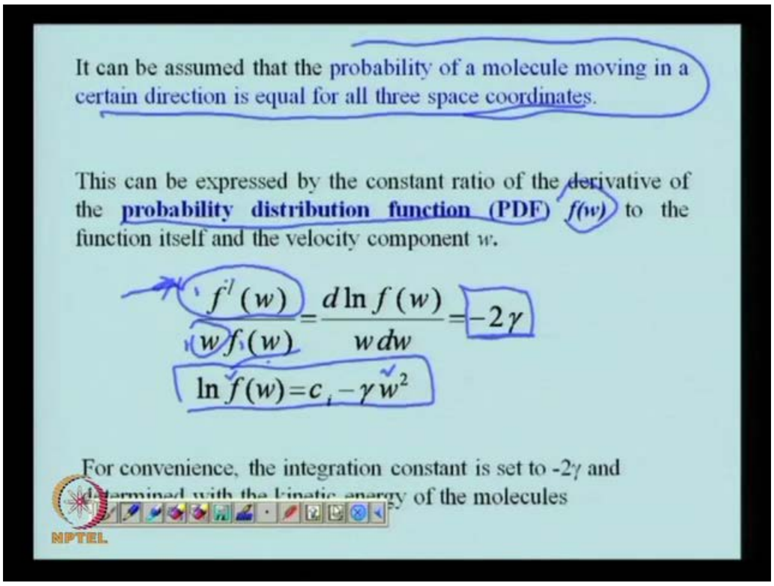

It can be assumed that the probability of a molecule moving in a certain direction is equal for all three space coordinates.

This can be expressed by the constant ratio of the derivative of the **probability distribution function (PDF)** $f(w)$ to the function itself and the velocity component w.

$$\frac{f'(w)}{w f(w)} = \frac{d \ln f(w)}{w\,dw} = \boxed{-2\gamma}$$

$$\boxed{\ln f(w) = c_1 - \gamma w^2}$$

For convenience, the integration constant is set to -2γ and determined with the kinetic energy of the molecules

Now, it is assumed that the probability of the molecule moving in a certain direction is equal in all space co-ordinates. And that can be only be true, if this important parameter, probability distribution function or PDF denoted by f w if we if we if we, if the derivative of the probability distribution function to the function itself and the velocity component if it is expressed in this form. In other words, the derivative of the of the probability function distribution function to the function itself, the ratio of these two and the velocity; if this ratio if it can be if it can be a constant which for convenience we express as minus 2 gamma.

If this condition is specified, then the probability of the molecule moving in a certain direction is equal in all space, three space co-ordinations. So, for this assumption to be valid, the variation, the derivative of the probability distribution function to the function itself and the component of velocity in in any direction would have to be a constant. And on integration, one can obtain this relation between the probability distribution function and the velocity in that component where c is the constant of integration.

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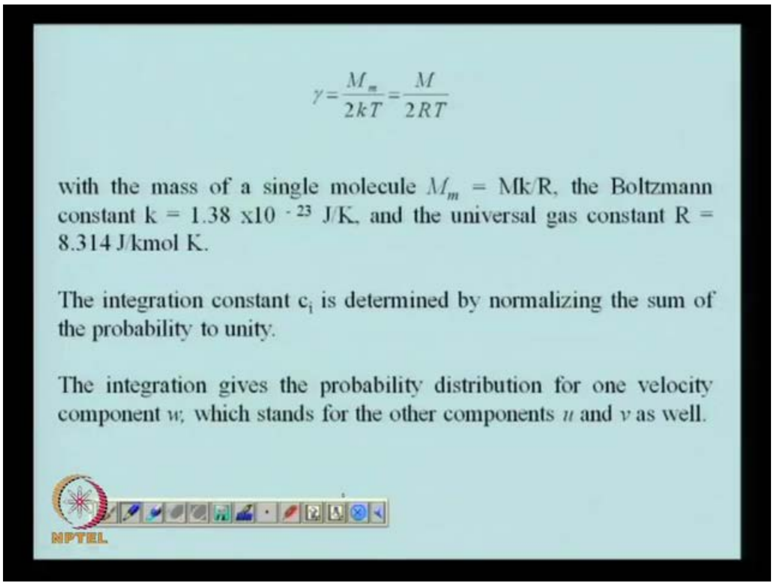

$$\gamma = \frac{M_m}{2kT} = \frac{M}{2RT}$$

with the mass of a single molecule M_m = Mk/R, the Boltzmann constant k = 1.38 x10 $^{-23}$ J/K, and the universal gas constant R = 8.314 J/kmol K.

The integration constant c_i is determined by normalizing the sum of the probability to unity.

The integration gives the probability distribution for one velocity component w, which stands for the other components u and v as well.

And this integration in this integration constant can be evaluated and one can obtain the integration constant by normalizing the sum of the probability to unity. And therefore, you can obtain gamma from the kinetic theory the and this is the relation for gamma and the integration constant can be obtained. So, this integration gives the probability distribution of one velocity component which is w, the other components in other direction u and v can be calculated in a similar fashion.

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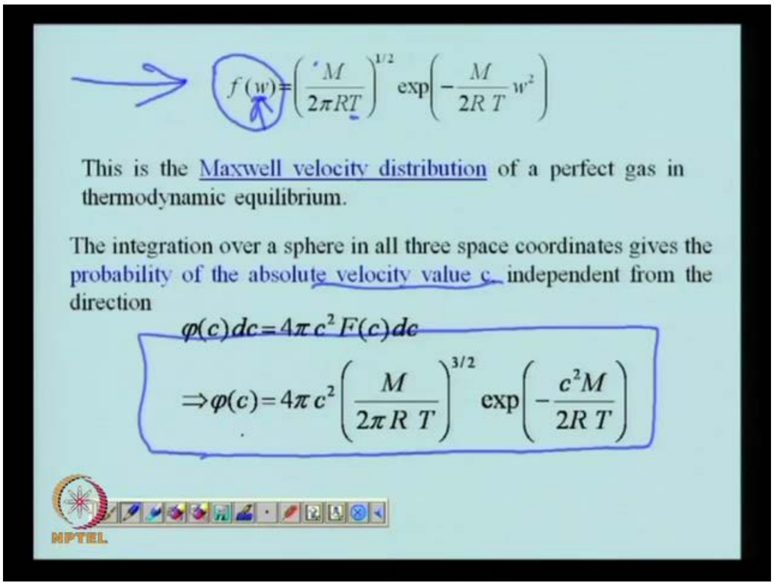

$$f(w) = \left(\frac{M}{2\pi RT}\right)^{1/2} \exp\left(-\frac{M}{2R\,T} w^2\right)$$

This is the Maxwell velocity distribution of a perfect gas in thermodynamic equilibrium.

The integration over a sphere in all three space coordinates gives the probability of the absolute velocity value c, independent from the direction

$$\varphi(c)dc = 4\pi c^2 F(c)dc$$

$$\boxed{\Rightarrow \varphi(c) = 4\pi c^2 \left(\frac{M}{2\pi R\,T}\right)^{3/2} \exp\left(-\frac{c^2 M}{2R\,T}\right)}$$

Which, this is the probability distribution of one velocity of the velocity in one specific direction w.

So, as you can see that it depends on the mass, but more importantly it depends on the on the on the temperature and so on. So, this distribution of velocity is known as the Maxwell velocity distribution of a perfect gas which is in thermodynamic equilibrium. Now, if you integrate this probability distribution function in all three spaces co-ordinate, it gives the probability of the absolute velocity, so this is this is this is this is the one component (Refer Slide time: 44:35).

So, this is the probability of the velocity in one component where as c is the absolute velocity or the probability of the absolute velocity which is independent from direction and this expression is the probability of the absolute velocity of a gas, of a perfect gas which is in thermodynamic equilibrium. So, let us, this is extremely useful in some of the calculations, specially when they are used in conditions where the continuum approximation may not be valid.

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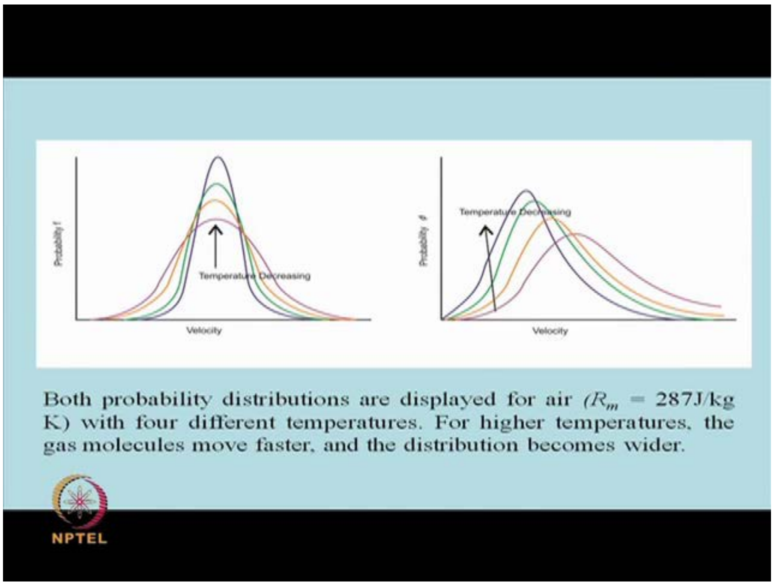

Both probability distributions are displayed for air (R_m = 287J/kg K) with four different temperatures. For higher temperatures, the gas molecules move faster, and the distribution becomes wider.

So, these two are well known figures where the probability is plotted against velocity at different values of temperature and you can see that the probability distributions, these probability distributions are for air and for higher temperature, the gases are going to move faster and the distribution is going to be wider and wider. So, these are at higher temperature. So, these are at higher temperatures and you can see that they they are and they becomes more wide, the velocity increases and so on.

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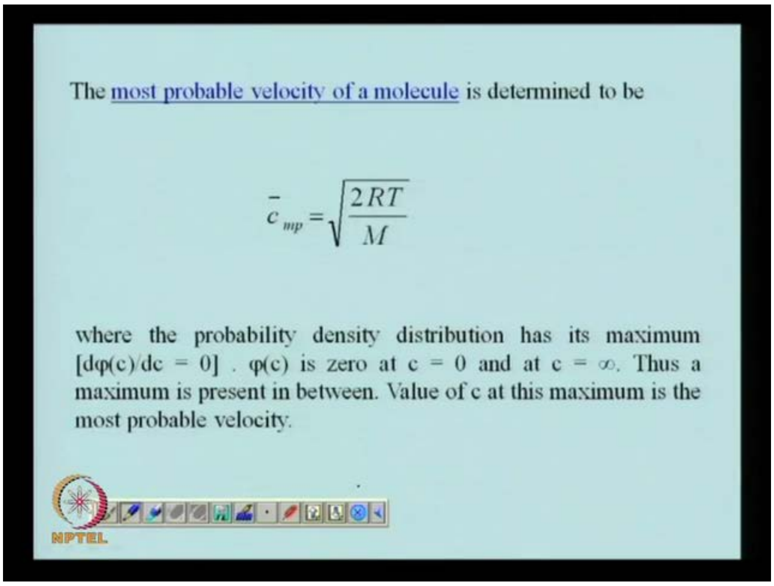

The most probable velocity of a molecule is determined to be

$$\bar{c}_{mp} = \sqrt{\frac{2RT}{M}}$$

where the probability density distribution has its maximum [dφ(c)/dc = 0] . φ(c) is zero at c = 0 and at c = ∞. Thus a maximum is present in between. Value of c at this maximum is the most probable velocity.

There are certain velocities which, there are two or three different definitions of a velocity which one has to know for the case of air, let us say for a for any gas. The most probable velocity is denoted as c m which can be calculated, which can be expressed as root over 2RT by M, R is the gas constant, T is the absolute temperature and M is the mass of the gas. So, this is the most probable velocity of a molecule and the most probable velocity of a molecule can be obtained by differentiating the probability density distribution and see where it has the maximum where it has the maximum. So, whenever you have the maximum probability, the velocity that you obtain at that point is known as the most probable velocity of a molecule.

Now, if you see the distribution of phi c it has a, it is equal to 0 at c equal to 0 and at c equal to infinity. So, somewhere in between there is a maximum and that maximum value of c at this maximum is the value of velocity at this maximum is denoted by the most probable velocity.

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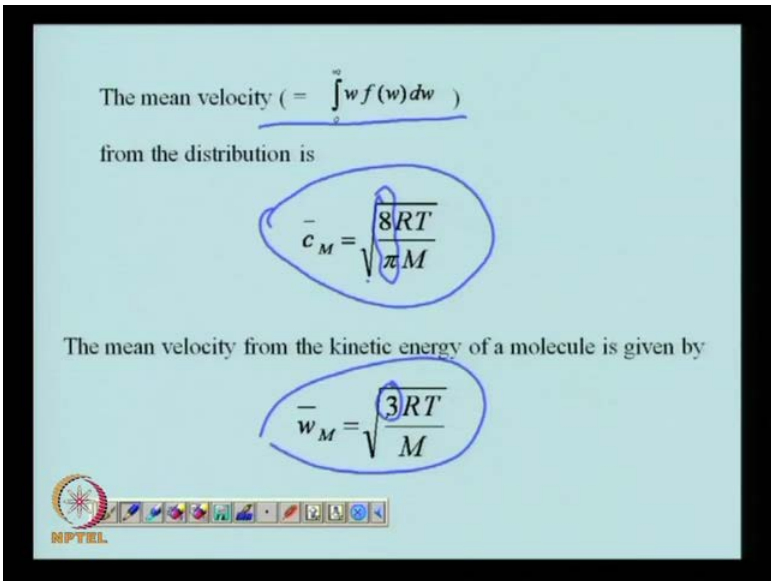

The mean velocity (= $\int_0^\infty w f(w) dw$)

from the distribution is

$$\bar{c}_M = \sqrt{\frac{8RT}{\pi M}}$$

The mean velocity from the kinetic energy of a molecule is given by

$$\bar{w}_M = \sqrt{\frac{3RT}{M}}$$

You also something which is called a mean velocity, where the mean velocity can be obtained as as as I have given in the formula and the distribution is this (Refer Slide Time: 47:08). So, this this is 8 by pi and when you compare this mean velocity with that from the that predicted from the kinetic theory, then you get this is essentially the same, all the thing is this is 3 where as this is 8 by pi. So, that is the only difference in between these two, so you can either express it in terms of probability distribution or in terms of kinetic theory only, and the mean velocity are, can be obtained as this.

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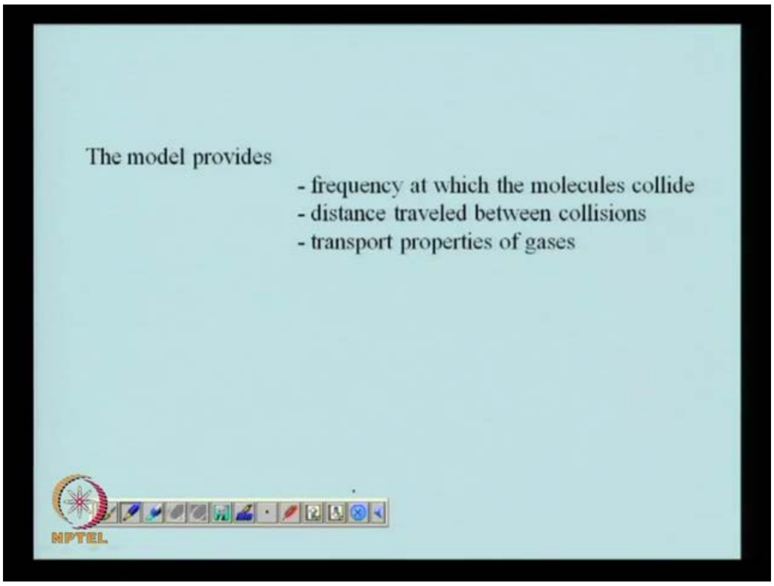

The model provides

- frequency at which the molecules collide
- distance traveled between collisions
- transport properties of gases

So, this model essentially provides us with a frequency at which the molecules are going to collide, the distance which are traveled between collision and the transport properties of the gases and there is to something else to see is that, this also tells us like, what will be the effect of the temperature.

For example, as temperature increases, the velocities are going to increase and we all know that from the kinetic theory, increase in temperature energizes the molecules so that they would move faster with more kinetic energy. And the time of collision would also be less, since the value of w is going to be more. So, the two molecules that the time difference between collisions, between molecules are going to be small at higher temperatures and so on.

So, it is physically consistent with our understanding and it gives us gives us a compact expression to calculate the velocities of the molecules as as as as at a certain temperatures, at certain conditions.

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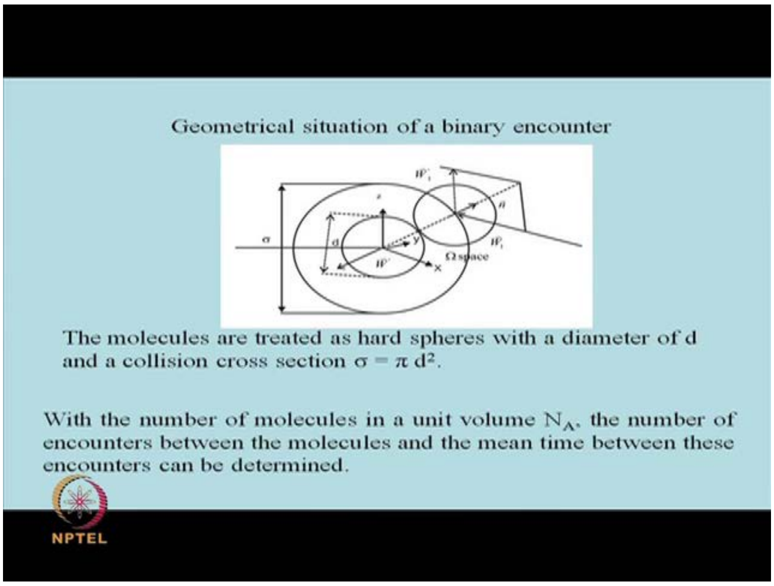
Geometrical situation of a binary encounter

The molecules are treated as hard spheres with a diameter of d and a collision cross section $\sigma = \pi d^2$.

With the number of molecules in a unit volume N_A, the number of encounters between the molecules and the mean time between these encounters can be determined.

And finally, there is one more model which you probably are aware of, it is the, if we assume that the molecules can be treated as hard spheres and we would like to see the binary encounter of the one molecule with the other and we specify the number of molecules in a unit volume and we try to calculate, what is the number of encounters between molecules and the mean free path mean free mean time between these encounters, one can obtain the relations that the average length between two collisions utilizing the expressions for the mean free path one can obtain to be this.

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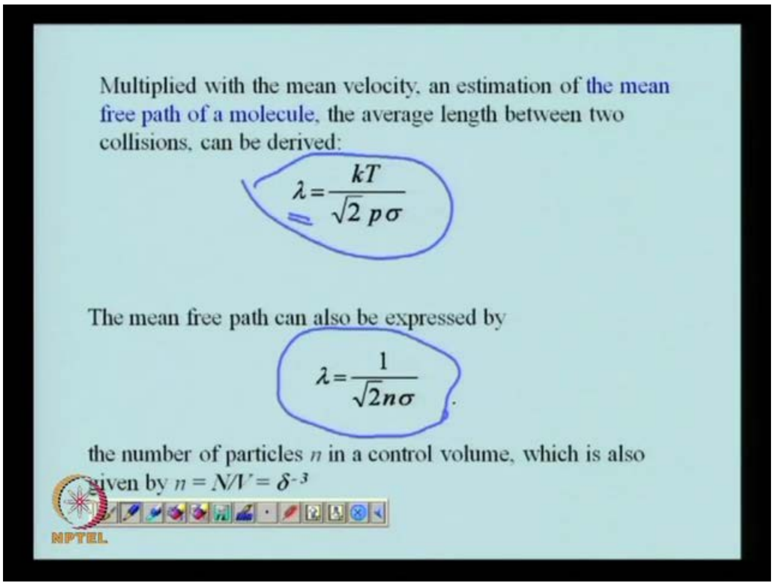

Multiplied with the mean velocity, an estimation of the mean free path of a molecule, the average length between two collisions, can be derived:

$$\lambda = \frac{kT}{\sqrt{2}\, p\sigma}$$

The mean free path can also be expressed by

$$\lambda = \frac{1}{\sqrt{2} n\sigma}.$$

the number of particles n in a control volume, which is also given by $n = N/V = \delta^{-3}$

So, here lambda is the average length between collisions and it can also be expressed expressed as in this form and these are again very useful relations which tells us the interrelation between conditions in the gas, the sizes of the gas. And the concept of mean free path in kinetic theory is extremely important, specially when we are going to analyze the free molecular flow regime (Refer Slide Time: 49:32).

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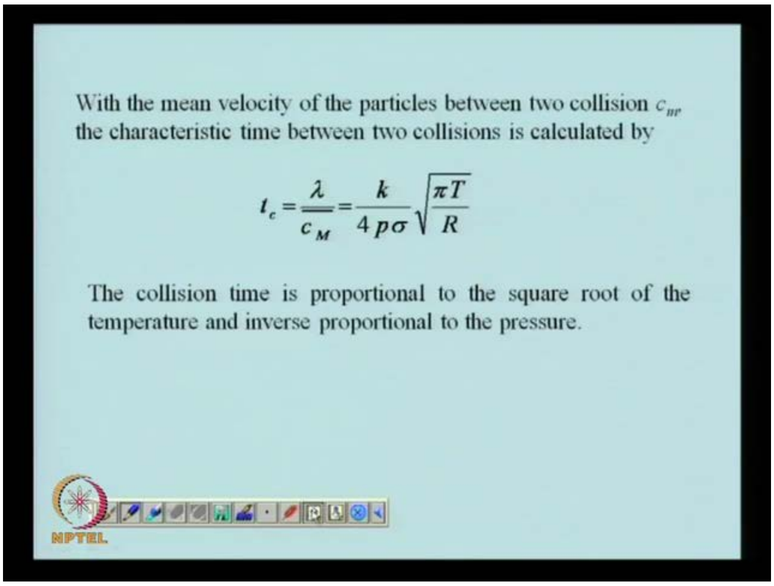

With the mean velocity of the particles between two collision c_{mr} the characteristic time between two collisions is calculated by

$$t_c = \frac{\lambda}{c_M} = \frac{k}{4p\sigma}\sqrt{\frac{\pi T}{R}}$$

The collision time is proportional to the square root of the temperature and inverse proportional to the pressure.

And finally, when we know the mean free path of the particle mean velocity particles between two collisions, the characteristic time between two collisions can be evaluated and as you can see, the collision time is proportional to the square root of temperature and inversely proportional to the pressure.

So, if I like to summarize what we have covered in this class is that, we understood that this is extremely important to know where exactly our system is in terms of its adherence to the continuum flow, continuum condition. We know that when the lengths, dimensions are reduced, the properties may vary, the properties may fluctuate, the thermodynamic equilibrium conditions which are imperative in Navier-Stokes equation for example, one of the continuum flow, continuum models are going to be violated.

So, it is, sometimes we try to decide about the condition of one of a of the system based on one parameter only which is Knudsen number. But the value of Knudsen number, though indicative of the condition of the system is does not give the complete picture. So, smaller values of Knudsen number tells us that the system is closer to the continuum condition, where as Knudsen number greater than 10 will tell us that it is a free molecular flow situation.

But besides that, we also have to look at, what is the value of L by L by delta, that is, if the value is greater than 100, then we know that at the statistical fluctuations of the due to the presence of molecules, due to the presence of the effect of the individual molecules will be significant. So, when we think of the figured that to that to I have I have shown you, it is it it it is it is marked by a specific region in which the in which the molecule can be treated, in which it can be treated as obeying the continuum law.

So, one has to see, whether it is a dense gas, whether it is a dilute gas, one has to also look at situations, let me go back to that graph before I conclude today’s lecture right. So, one has to see where they are located and the region would be above this thermodynamic equilibrium line (Refer Slide Time: 52:55). So, it should be this region, you have to have above this line.

So, this is the region which roughly tells us about whether or not we, the continuum continuum flow model is going to be valid and there are different ways to treat systems in which you have slip flow, in which you have transitions between slip flow and the free molecular flow and in free molecular flow. So, finally, looking at the statistical distribution of velocities in a system, we have obtained the expressions for the most probable velocity, we have obtained the expression for the collision time between two molecules and we have seen the variation of these as a function of temperature and other other parameters of the system.

So, this gives us the picture of these scaling dimensions where the effect on material properties is going to be significant based on the size and the pressure temperature conditions of gases present in it, thank you.