Molecules in Motion

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Lecture - 07
Kinetic theory of gases (Contd.)

Welcome, to the course in Molecules in Motion. We are still discussing things subjects on topics on Kinetic theory of gases, and it includes a number of things I think which I would try to go into detail, but I do not know whether you will be interested in the mathematical part of the derivations.

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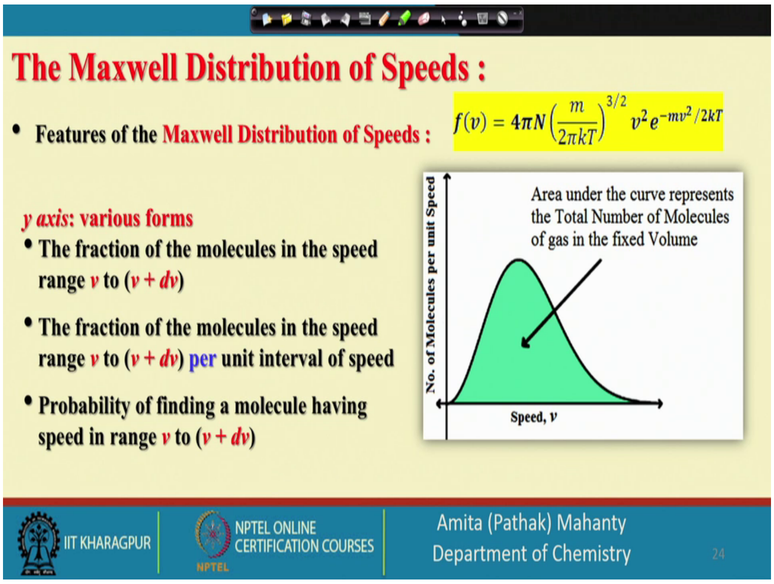

The Maxwell Distribution of Speeds :

- **Features of the Maxwell Distribution of Speeds :**

$$f(v) = 4\pi N\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT}$$

y axis: various forms

- The fraction of the molecules in the speed range v to $(v + dv)$
- The fraction of the molecules in the speed range v to $(v + dv)$ per unit interval of speed
- Probability of finding a molecule having speed in range v to $(v + dv)$

Area under the curve represents the Total Number of Molecules of gas in the fixed Volume

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In the last class, what we had talked about? We had talked about the distribution function for velocity distribution function, Maxwell-Boltzmann distribution, you can say Marx Maxwell's distribution you would usually Boltzmann distribution is associated with energy, but we usually say that it is a Maxwell-Boltzmann distribution. So, the distribution function we have derived we this is the expression which we have derived. I am go not going to go into the detail because we are going to now discuss the features of the Maxwell distribution function.

So, if you remember the representation of the x and y axis of the distribution function. So, it is a probability distribution. So, the total area is going to be summing up to one and the area under the curve represents that the total number of molecules of the gas and a fixed volume. So, the volume is a fixed the total number of gas molecules enclosed is fixed. So, the probability which we are evaluating will be always normalized to one.

So, the y axis is always not particularly different books follow different parameters. What we are looking into? We are looking into the probability densities along of finding a molecules in the speed range v and plus v plus delta v, but in some books you will find it is written in as the fraction of molecules in the speed having the speed in the range of this or in some books you can still find that the fraction of molecules in the speed range v plus delta v per unit velocity interval, or speed interval.

So, the per unit whenever you are talking about then you actually divided by the dc or dv whatever term you have and x axis is always the speed, ok. So, this is the feature which we are looking into and this is the function which we are going to evaluate and try to understand the various distribution.

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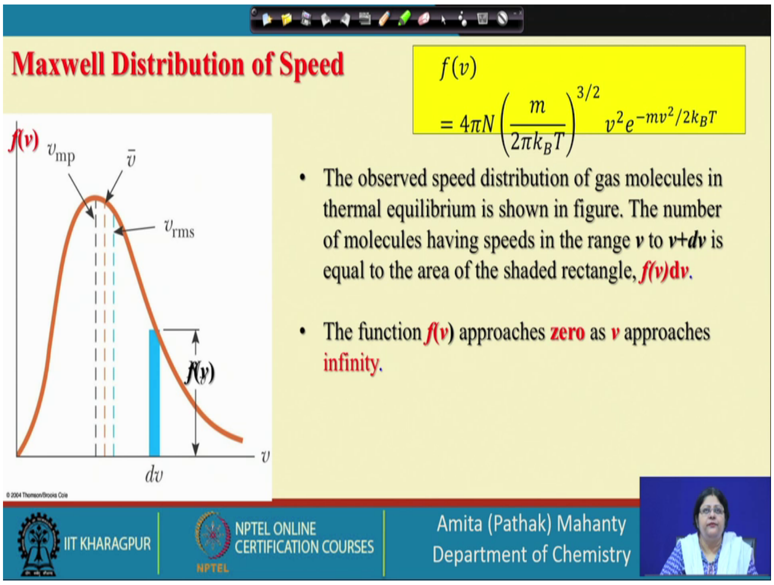

Maxwell Distribution of Speed

$$f(v) = 4\pi N\left(\frac{m}{2\pi k_BT}\right)^{3/2} v^2 e^{-mv^2/2k_BT}$$

- The observed speed distribution of gas molecules in thermal equilibrium is shown in figure. The number of molecules having speeds in the range ***v*** to ***v*+*dv*** is equal to the area of the shaded rectangle, ***f*(*v*)*dv***.
- The function ***f*(*v*)** approaches **zero** as ***v*** approaches infinity.

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So, what we have here? Here you see this is the distribution functions, sorry, that it is slightly distorted. So, I am not going to look into what the values are looking in showing I am just looking at the this is the distribution function, y axis this is the dv is the unit in which we are changing the velocity, this is the v axis and this is the unit in which we are interested the dv this is the velocity interval infinitesimally small velocity interval into which we are looking into.

So, that observes speed distribution of gas molecules in thermal equilibrium is shown in figure, ok. The number of molecules having in the speed in the range v plus delta v is equal to the area of the shaded triangle. So, what is the when I am talking about v plus v plus delta v, I am looking into this dv is the area of the shaded triangle, that is f of v into dv this is a area represents the f of v into dv. This is the interval, the infinitesimally fall small velocity interval and when I multiply in the distribution with this distribution function with the dv then I get f of v dv is the shaded area, ok.

So, the function f of v approaches 0 as v approaches 0, as v approaches infinity, sorry when will the f of v approach 0. You have this expression, from this expression you can see when will this approach 0. You have this expression the velocity is here in this term here it is there in the exponential term. So, where are the velocities included here it is square and here it is exponential, ok.

So, when we are talking about exponential term if this is the part which we are looking into then what should be the function approaches when will the function approach is 0. In this expression if you put in this function approaches 0 only when this is going to be approaching infinity this becomes very high. So, this is one of the features of the Maxwell's distribution or Maxwell's Boltzmann's distribution which we have taken the expression.

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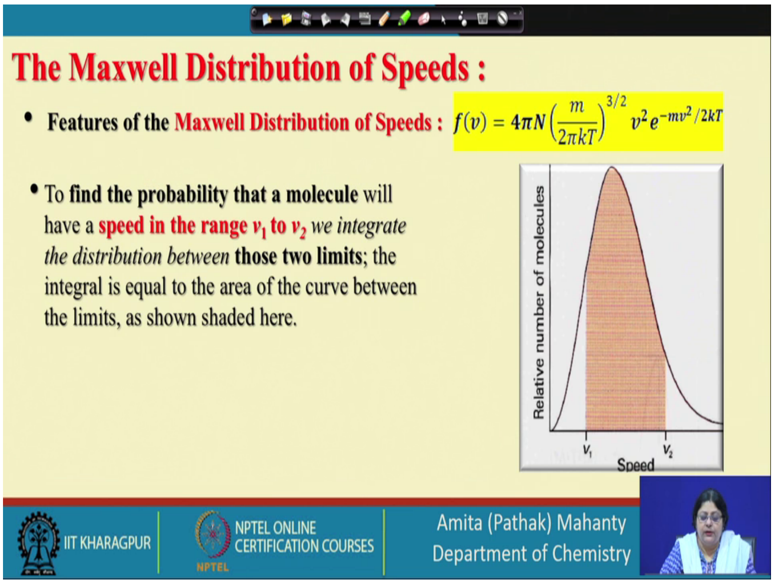

The Maxwell Distribution of Speeds :

- **Features of the Maxwell Distribution of Speeds :** $f(v) = 4\pi N\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT}$

- To **find the probability that a molecule** will have a **speed in the range v_1 to v_2** *we integrate the distribution between* **those two limits**; the integral is equal to the area of the curve between the limits, as shown shaded here.

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Now, and look into another feature of it. To find suppose I want to find the probability that a molecule will have a speed in the range say thirty to forty meters per second suppose this is the speed 30 and this is the speed 40 and I have a distribution function given by this. Here you see I have write it is written relative number of molecules the relative number also means that this the fraction of numbers, relative means I am taking a ratio of numbers or I am taking the probability function with respect to the total number of molecules. So, it is a division fraction it is a fraction basically, which we are representing the relative number of molecules which I am going to evaluate. So, I have to find out the probability that molecule will have a speed within the range v 1 to v 2 and we this v 1 and v 2 suppose I am saying this is 30 to 40 meters per second.

So, for finding out that what we do, we integrate from in distribution function within the two limits. These are the two limits v 1 and v 1 and v 2. So, this is 30 and 40. So, I put a line and adds you may draw the first I have the probability distribution curve now I fix the two values which I am looking into 30 meters per second and 40 meters per second. I mark that and integrate the area within these two limits.

So, when I get the when I integrate the area bet between the two limits then I get this shaded area and this shaded area of the curves is equal to the probability that the molecule will have a speed in the range say 30 to 40 meters per second or between v 1 to v 2. So, to find out the probability that the molecule will have speed in the range v 1 to v 2 we integrate the distribution between the two limits. The area and integration integral is equal to the area of the curve between the two limits and as is shown in the shaded here.

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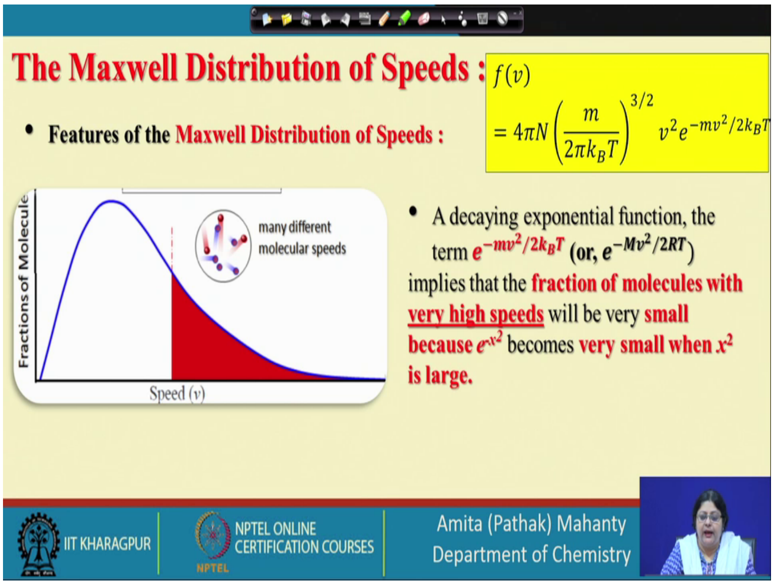

The Maxwell Distribution of Speeds : $f(v) = 4\pi N \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{-mv^2/2k_BT}$

- Features of the **Maxwell Distribution of Speeds :**

- A decaying exponential function, the term $e^{-mv^2/2k_BT}$ (or, $e^{-Mv^2/2RT}$) implies that the **fraction of molecules with very high speeds** will be very **small because** e^{x^2} becomes **very small when** x^2 **is large.**

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Now, what happens if you look at the expression of the distribution function, you see this the distribution function looks something like this. It is a decay function. Why it is a decay function? You see the expression here; the expression is e to the power raise something to the power minus and that is square suppose this is m is constant for the gas. So, it is the velocity which is changing and if it is a so, if the velocities are changing so, depending on the velocities I can say this is e to the power x minus x square, when I am saying the velocities are changing. So, this is e to the power minus x square I get is something like that.

So, the exponential decay function in terms of the value here which we have written already or in terms of the R if you multiply by the Avogadro's number both the Boltzmann constant with the multiplication with the Avogadro number gives you the R and small m multiplied with the Avogadro number gives you the molar mass.

So, this will be the other expression. So, what if this implies this implies the decay the exponent function implies that the fraction of molecules with very high speed very high speed means v is very large v will be very small, because this is exponential term this exp becomes very small when we are approaching these values are very high.

So, this is going to be if this is very high if this is very high then what you have, the fraction of molecules very will be very small because the e to the power expression is raised to the power minus x square and x square here is the velocity x is the velocity. So, velocity square, but it is a minus term.

So, what we what it implies? The fraction of molecules with very high speed will be very small when the speed of the molecules are very large here because this is the exponential term exponential in a term is a minus term that means, it is a decay and this decay term mainly indicates of all the number of molecules with very high speed will be very will be small will because it you are dealing with the exponential term and this exponential term is say e to the power minus x square, if I say this x represents the velocity then as the velocities are very large than the decay we have a decay. So, then the fraction of molecules with very high speed becomes small, just because it is a decay function.

So, next one what happens then again you look into the parameter. Here, we have already divided by the multiplied and divided the numerator by the Avogadro number. So, the factor 2 by M by 2 kT this there are two factors. You see e is dependent on the velocity and it is dependent on M by 2 kT 2 RT.

So, these are two parameters which is which we can separate out v squared term and m by 2 RT term. So, these the factor m by 2 RT multiplying v square in the exponent is large when the molar mass is large, for a fixed value of v. Suppose, I can have this fraction the factor m multiplied by v I have a factor I am multiplying this that velocity by another factor. This factor is dependent on the mass because it is capital N by 2 RT R is fixed. Suppose, I am talking about a given temperature for a given temperature I have this M f v multiplied by a term which is m by 2 by RT.

So, this factor m by 2 by RT multiplied by the v square in the exponent exponential term is large when the molar mass is large, ok. So, this exponential term it is a decay term remember it is going to give you a higher these value is lower will be the higher will be the decay and lower will be the value. So, what we have? We have a higher molecular weight factor multiplied into the exponential factor which is already having a v square. So, the exponential factor goes more rapidly towards 0, when the mass is large.

So, if you are dealing with large masses the decay will be faster. That i s, the heavy molecules are unlikely to be found at a higher speed, right. So, if you are doing a selection of the molecules if the if you are talking about higher molecular weight species what you have? You have them in the heavier molecules will not be found in the high speed region. So, because you here you are multiplying m by 2 kT into this and this is an exponentially decaying term, right. If it is an exponential decaying term if you have larger values the decay will be faster.

o, if you are having larger value the exponential goes rapidly towards 0, it approaches towards 0 very rapidly. That is, a heavier molecule that the heavier the molecule is faster is their decay. So, you will when we are talking about high speeds, these are the regions you can see it should be with the high speeds the molecular weight of the molecule gases which are having high molecular weight will be very less found in this region.

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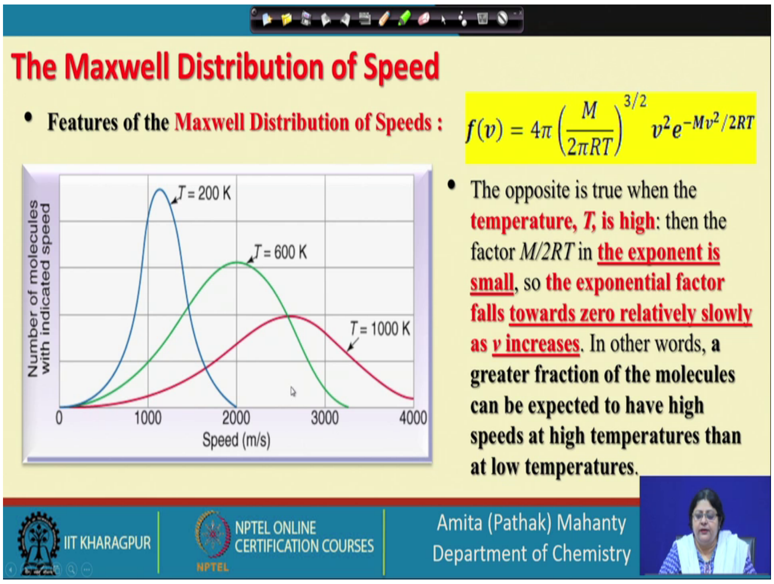

The Maxwell Distribution of Speed

- **Features of the Maxwell Distribution of Speeds :**

$$f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-Mv^2/2RT}$$

- The opposite is true when the **temperature, *T*, is high**: then the factor *M/2RT* in **the exponent is small**, so **the exponential factor falls towards zero relatively slowly as *v* increases**. In other words, **a greater fraction of the molecules can be expected to have high speeds at high temperatures than at low temperatures.**

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Another thing you can look into. You have seen 3 temperatures and temperature 20 of distribution function at 200, 600 and 1000. You see how the distribution function looks how is the peak changing and how the shape of the graph is changing.

Now, when the temperature is high when the temperature is high you see temperature is in the denominator of the exponential term. When the temperature is high then the factor M by 2 RT in the exponential is small. So, the exponential factor falls towards 0 relatively slow as we increases. So, as we increase the speed as we increase the speed which is going to be slower, when the temperature is when the temperature is high this factor which you are looking into in the exponent is small, this is high. So, the exponential is small and since the exponential is negatives an exponential. So, decay will be smaller.

So, the exponential factor towards 0, the exponential factor falls towards 0 relatively slowly, as we increase the speed. So, as the higher the speed which we are looking into higher the speed of the molecules which we have lower will be the rate at which they decay when the temperature is higher, as we increase the speed.

So, when you see that temperature 200, 600 and 1000 you are increasing the temperature. What you are increasing is, you are increasing the decreasing the exponential term and which is a negative term. So, the decay is reduced. So, what you have the exponential factor that falls towards 0 is relatively slow as you increase the temperature. So, you have a wider distribution in speed, understood?

So, in other words the greater fraction of molecules can be expected to have higher speed at higher temperature then at lower temperatures. Did you understand? It under in other words we are saying the greater fraction of molecules can be expected to have higher speed at higher temperature. The fraction of molecules with higher speed will be higher at higher temperature than that of the fraction which is at lower temperature, ok. So, as you see the broadness of the curve is going to be more sharp when you have lower temperature, but the total area if the gas is the same and use in you are using the same volume of the gas then the area under the curve will be all constant. So, all should be adding up to the probability equal to 1. So, this area under the curve will be always constant, but how the speed distribution is going to be shifting depending on the exponential term of the distribution function can be really easily understood.

So, two factors we have already discussed what we, one will be the when you have higher mass higher mass of the gases, if you are having higher mass the exponential decay will be faster because the number and the exponential factor is becoming high. So, the decay is faster. So, when you are having the fraction with high molecular weight will be always less when you are having going towards 0, that the when we are falling in the when the distribution is falling towards 0.

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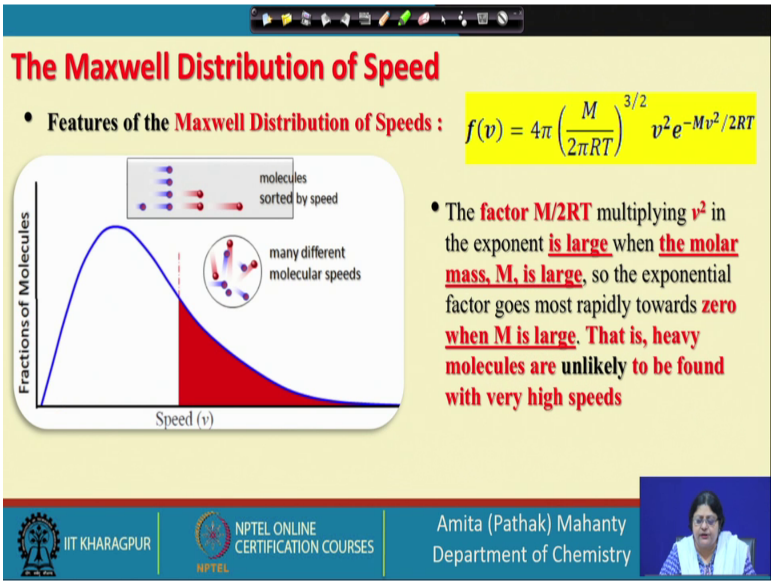

The Maxwell Distribution of Speed

- Features of the Maxwell Distribution of Speeds :

$$f(v) = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-Mv^2/2RT}$$

- The factor M/2RT multiplying v^2 in the exponent is large when the molar mass, M, is large, so the exponential factor goes most rapidly towards zero when M is large. That is, heavy molecules are unlikely to be found with very high speeds

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So, how will that look like I think I do not have that distribution function for two or three different masses.

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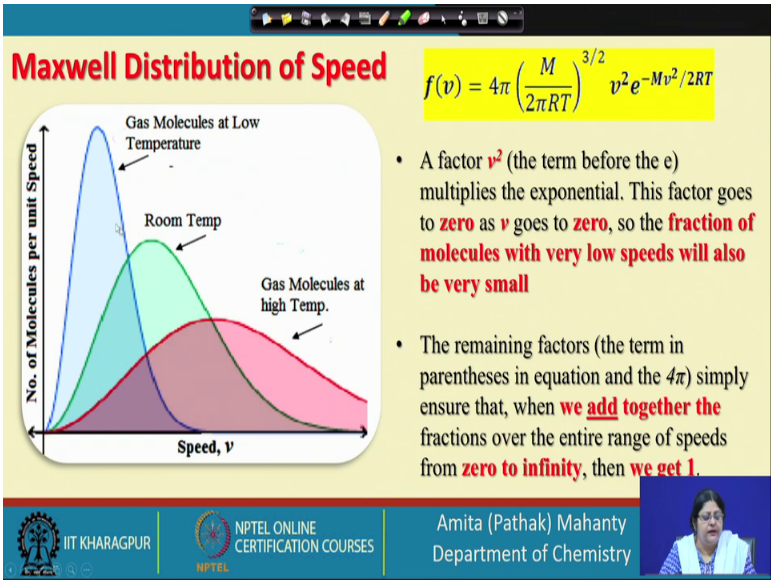

Maxwell Distribution of Speed

$$f(v) = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-Mv^2/2RT}$$

- A factor v^2 (the term before the e) multiplies the exponential. This factor goes to zero as v goes to zero, so the fraction of molecules with very low speeds will also be very small
- The remaining factors (the term in parentheses in equation and the 4π) simply ensure that, when we add together the fractions over the entire range of speeds from zero to infinity, then we get 1.

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Now, so, this is another look you can have which we have just now discussed; the gas molecules at low temperature, how the gas molecules look at room temperature and how the gas molecule distribution looks like at the high temperature. So, the factor v square the term which we have here is a multiplies the exponential. This factor goes to zero and the fraction of molecules with low speeds will also be small.

So, we have now taken two factors; one is this part and other this is other part. So, now, while if I take the factor v square into contribution not the exponential. So, from the factor v square what we have, v square multiplies by the with exponential term ok, the fact this factor goes to zero as we goes to zero. So, the fraction of molecules with very low speed will also be very small. The remaining factor the terms of parentheses of 4 pi and that is simply is ensures they when we add the fractions all over the range of the speed from zero to infinity then we get a value equal to 1.

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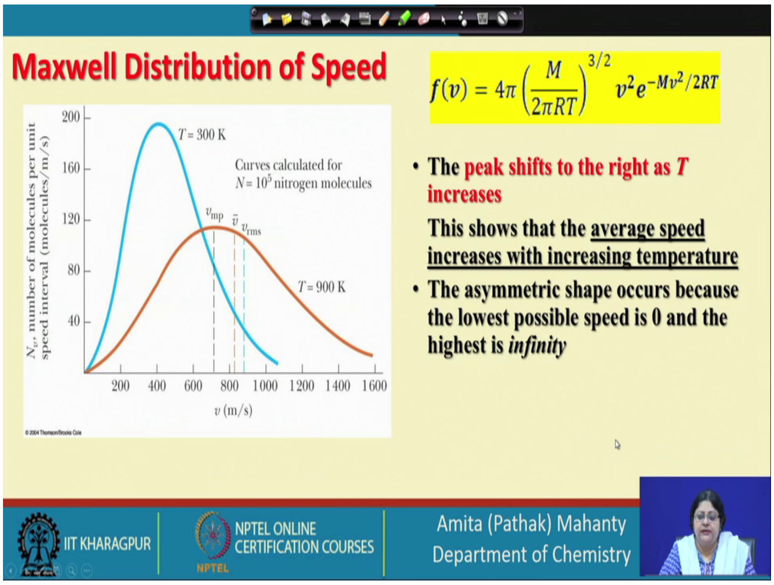

Maxwell Distribution of Speed

$$f(v) = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-Mv^2/2RT}$$

- The peak shifts to the right as *T* increases

This shows that the average speed increases with increasing temperature

- The asymmetric shape occurs because the lowest possible speed is 0 and the highest is *infinity*

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Now, the let us see how the peak shifts. As you increase the temperature, this is the temp peak here the peak shifts towards higher temperature as we increase the speed temperature of the system. The peak shifts as the to the right side as the temperature is and right side means you towards higher speed, this is the speed which we are like having this shows the average speed increases with increase in temperature. Asymmetric curve occurs because the lowest pass possible speed is 0 and the highest is infinity. So, this is a Gaussian error type graph and it is asymmetric graph this will extend to infinity and starts from 0.

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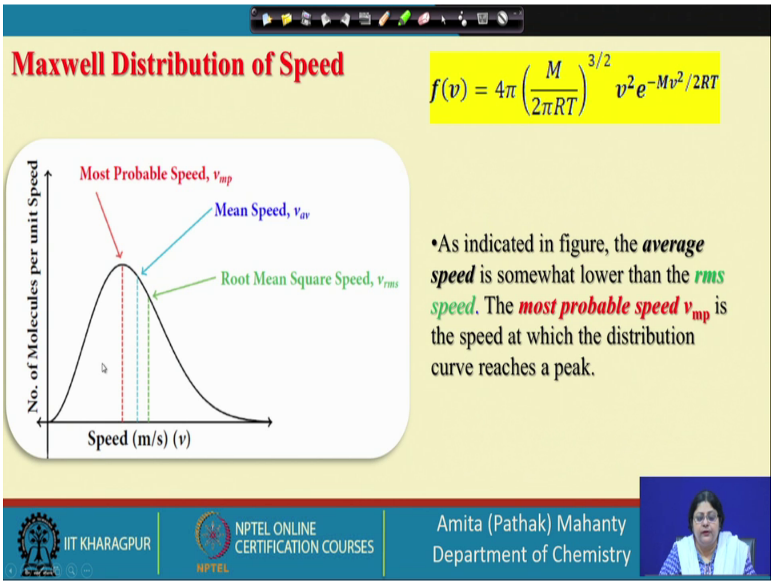

Maxwell Distribution of Speed

$$f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-Mv^2/2RT}$$

- As indicated in figure, the ***average speed*** is somewhat lower than the ***rms speed***. The ***most probable speed*** v_{mp} is the speed at which the distribution curve reaches a peak.

Now, there are two or three important factors which we need to look into. What is the most probable speed, what is the mean speed and what is the root means? What is root mean square speed, which we have already discussed, how we have evaluated we have taken into account. But, what is the in this figure you will see there we can numerically evaluate this expressions for average speed and the rms speed, as well as the most probable speed. I have given you one slide in the previous class where it from where you can evaluate, but I think I will give us give it that as miss right now.

The most probable speed is represented by this. As you see when you have a distribution this is the highest maximum possibility. So, this is the maximum possibility of the gas the molecules will have the speed as, but that is not the speed of the entire that is not the highest speed as you see. If you take the mean speed you the mean speed is in between the most probable speed and the rms speed. rms speed value is the highest value.

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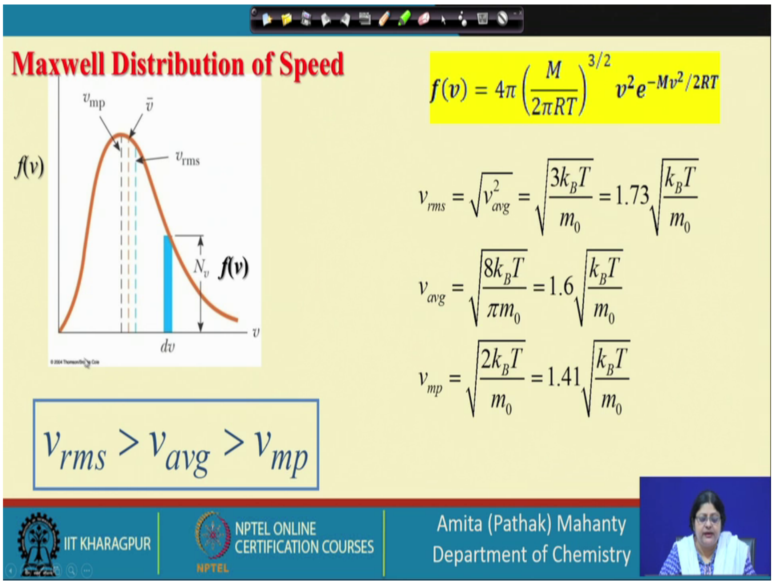

Maxwell Distribution of Speed

$$f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-Mv^2/2RT}$$

$$v_{rms} = \sqrt{v_{avg}^2} = \sqrt{\frac{3k_BT}{m_0}} = 1.73\sqrt{\frac{k_BT}{m_0}}$$

$$v_{avg} = \sqrt{\frac{8k_BT}{\pi m_0}} = 1.6\sqrt{\frac{k_BT}{m_0}}$$

$$v_{mp} = \sqrt{\frac{2k_BT}{m_0}} = 1.41\sqrt{\frac{k_BT}{m_0}}$$

$$v_{rms} > v_{avg} > v_{mp}$$

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As you can see from the expression I have not derived the expression, but we can easily we can numerically derive from the integration of this using the standard integrals. What we have derived is the rms speed we have already derived the rms speed, but we can numerically using a standard integral values we can evaluate this. We can find out what the average velocity is what is the most probable velocity. If you arrange them you will see this is how it is going to look like.

The rms speed is the highest value in speed and the average is in between the rms and the most probable. Most probable is the speed which is the most of them all gas molecules are likely to have the highest number of molecules are likely to have, but that is not the maximum speed of the distribution function.

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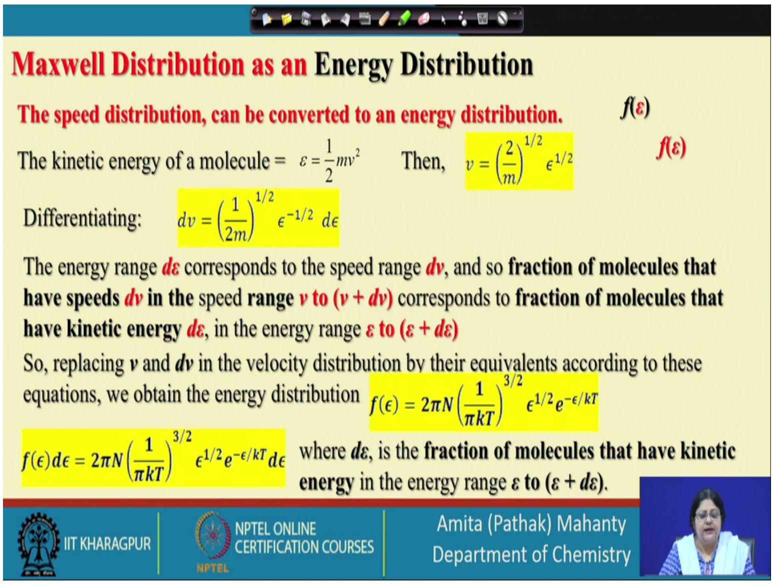

Maxwell Distribution as an Energy Distribution

The speed distribution, can be converted to an energy distribution.

$f(\varepsilon)$

The kinetic energy of a molecule = $\varepsilon = \frac{1}{2}mv^2$ Then, $v = \left(\frac{2}{m}\right)^{1/2} \epsilon^{1/2}$

$f(\varepsilon)$

Differentiating: $dv = \left(\frac{1}{2m}\right)^{1/2} \epsilon^{-1/2}\, d\epsilon$

The energy range $d\varepsilon$ corresponds to the speed range dv, and so **fraction of molecules that have speeds dv in the** speed **range v to $(v + dv)$** corresponds to **fraction of molecules that have kinetic energy** $d\varepsilon$, in the energy range **ε to $(\varepsilon + d\varepsilon)$**

So, replacing v and dv in the velocity distribution by their equivalents according to these equations, we obtain the energy distribution $f(\epsilon) = 2\pi N \left(\frac{1}{\pi kT}\right)^{3/2} \epsilon^{1/2} e^{-\epsilon/kT}$

$f(\epsilon)d\epsilon = 2\pi N \left(\frac{1}{\pi kT}\right)^{3/2} \epsilon^{1/2} e^{-\epsilon/kT} d\epsilon$ where $d\varepsilon$, is the **fraction of molecules that have kinetic energy** in the energy range **ε to $(\varepsilon + d\varepsilon)$**.

Similarly, as we have for the velocity this can be extended to the energy because Boltzmann distribution and Boltzmann Maxwell's distribution is actually was derived for the energy distribution. So, if you have the speed if you have the speed then you can easily derive the expression for energy, right in. In fact, we it is the other way round from the energy we have derived the speed, but here again we are going to go back and see how the speed distribution can be converted to energy distribution.

The kinetic energy of a molecule as you know is epsilon a half mv square. So, this mv square we are if we are looking into the root mean square velocity which we have derived for the distribution function, please ignore these are typographical errors do not ignore these two points.

So, what we have we are going to find out what is v, from this expression from the velocity equal the half mv square equal to the energy. From this expression we will find out what is the velocity and we what we are looking into? We are looking into a velocity interval dv. So, if we want to find out what is the dv in terms of the energy what you want you can we can write, you have this expression for v differentiate what you have dv 1 by m to the power half e to the power minus half because this is you have e to the power half here and dE.

So, this is the ene this represents the energy range dE corresponds to the speed range corresponding to the speed range dv. So, the fraction of molecules that have the speeds dv in the range in the speed range v plus dv corresponds to the fraction of molecules that have the kinetic energy in the range de and dE plus e plus dE.

So, the energy, what I am trying to say the energy range we have for dE corresponds to the same velocity range which we are looking into. We are not taking any separate thing we are looking into the same velocity range in which we are looking into this energy of the molecules. So, we are looking into the same dE corresponding to the same value coming out from the value which we have for the dv the interval of velocity.

The fraction of molecules within this dv is the speed that is in the speed range v plus dv will be the fraction of molecules which will be having in the same velocity range, but with the energy will be having e and e plus dE. I am not going to do go into the details of the derivation, but you can have this distribution function represented as this. You can do it if you want to, but the distribution function is something like this when dE is the fraction of molecules that have the kinetic energy in the energy range e d and d plus delta d dE.

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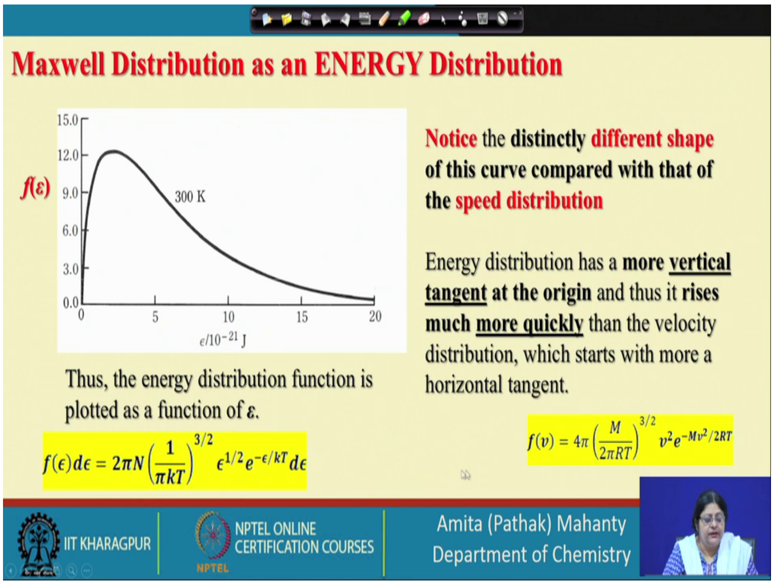

Maxwell Distribution as an ENERGY Distribution

Thus, the energy distribution function is plotted as a function of ε.

$$f(\epsilon)d\epsilon = 2\pi N\left(\frac{1}{\pi kT}\right)^{3/2}\epsilon^{1/2}e^{-\epsilon/kT}d\epsilon$$

Notice the **distinctly different shape of this curve compared with that of the speed distribution**

Energy distribution has a **more vertical tangent at the origin** and thus it **rises much more quickly** than the velocity distribution, which starts with more a horizontal tangent.

$$f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}v^2e^{-Mv^2/2RT}$$

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So, if you look into the graph if you this is the velocity distribution, this is the energy distribution which we have got. You just see the function this is here you have the energy this is this is the distribution function in energy. So, notice the distinct difference. If you look into the previous distribution you will see how the distribution is looking like. If you have a tangent drawn along the curve, what will you see; notice the different shape of the two curves. The energy distribution has a more vertical tangent this is a much more steeper than the velocity distribution.

The vertical tangent at the origin and thus it is rises much quicker. So, the energy distribution function rises very at a very higher rate as you v at the near the origin when that you have a vertical line instant which is otherwise for a velocity distribution it is a much more horizontal. It will it will be looking something like this the curve is like this. So, that this is the shape of the curve is not the same.

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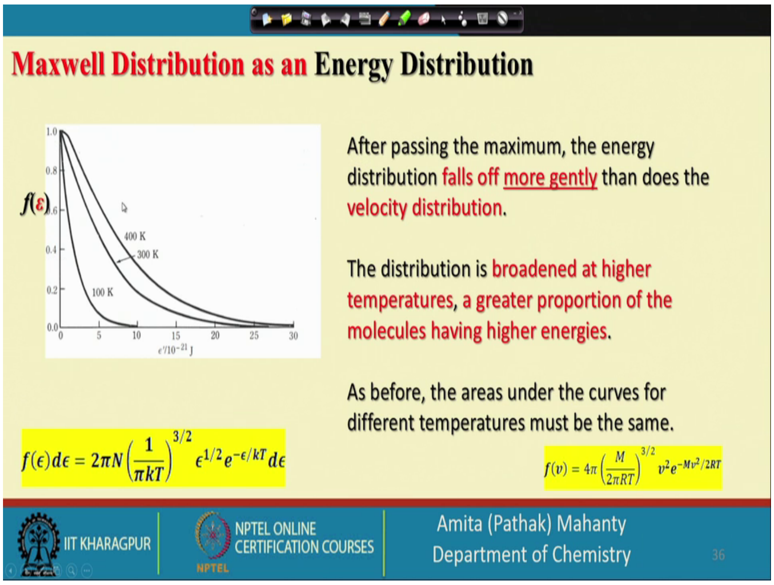

Maxwell Distribution as an Energy Distribution

After passing the maximum, the energy distribution falls off more gently than does the velocity distribution.

The distribution is broadened at higher temperatures, a greater proportion of the molecules having higher energies.

As before, the areas under the curves for different temperatures must be the same.

$$f(\epsilon)d\epsilon = 2\pi N\left(\frac{1}{\pi kT}\right)^{3/2} \epsilon^{1/2}e^{-\epsilon/kT}d\epsilon$$

$$f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-Mv^2/2RT}$$

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And, another one after passing through the maximum point suppose you are looking into this one you just see that you have this expression and this is the maximum peak which we have and when you are passing through the maximum the energy distribution falls more gently than the velocity distribution. See the distribution is broader at higher temperature you have three temperatures which we have the temperature as in velocity distribution. The temperature that curve is high much broader at higher temperature a greater proportion of the molecules will higher and have higher energy.

As before the area under the curve are different as temperatures must be the same. So, you can see how the energy distribution function falls the broadness at higher temperature than at higher proportion of the molecules having higher energies and the mostly the shape of the curve is different from that of the velocity distribution.

Thank you so much.