Engineering Physics 1

Dr. B. K. Patra
Department of Physics
Indian Institute of Technology-Roorkee

Module-05
Lecture-05
Maxwellian Distribution Law of Velocity – Part 03

Let me start the law of equipartition of energy, as I have already told you for a given available energy of the system, how the energy have been distributed among its different degrees of freedom. Since we have already come to know what are the different degrees of freedom for the various systems? Now let me see let me see how the energy is distributed among the different degrees of freedom this is known as the law of equipartition of energy okay.

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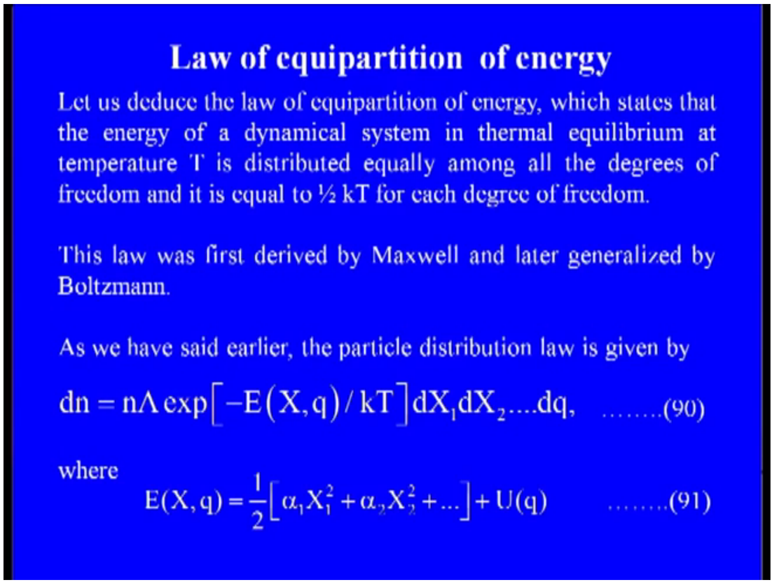

Law of equipartition of energy

Let us deduce the law of equipartition of energy, which states that the energy of a dynamical system in thermal equilibrium at temperature T is distributed equally among all the degrees of freedom and it is equal to ½ kT for each degree of freedom.

This law was first derived by Maxwell and later generalized by Boltzmann.

As we have said earlier, the particle distribution law is given by

$$dn = n\Lambda \exp\left[-E(X,q)/kT\right] dX_1 dX_2 \ldots dq, \qquad \ldots\ldots(90)$$

where

$$E(X,q) = \frac{1}{2}\left[\alpha_1 X_1^2 + \alpha_2 X_2^2 + \ldots\right] + U(q) \qquad \ldots\ldots(91)$$

Let us deduce the law of equipartition of energy which states that the energy of a dynamical system in thermal equilibrium at temperature T is distributed equally among all the degrees of freedom and it is equal to half KT for each degree of freedom. So, what does it mean by equipartition, equi means equal that means energy U will be distributed equally among all its degrees of freedom and it can be shown that energy for each degrees of freedom is half KT ok.

This law was first derived by Maxwell and later generalized by Boltzmann. As we have said earlier the particle distribution law is given by dn = n times A A e to the power - E by KT dX1 dX2 dX3 dq where E of Xq is nothing but it consists of kinetic energy plus potential energy. In terms of new coordinates half alpha 1 X1 square + half alpha2 X2 square + EU of KT.

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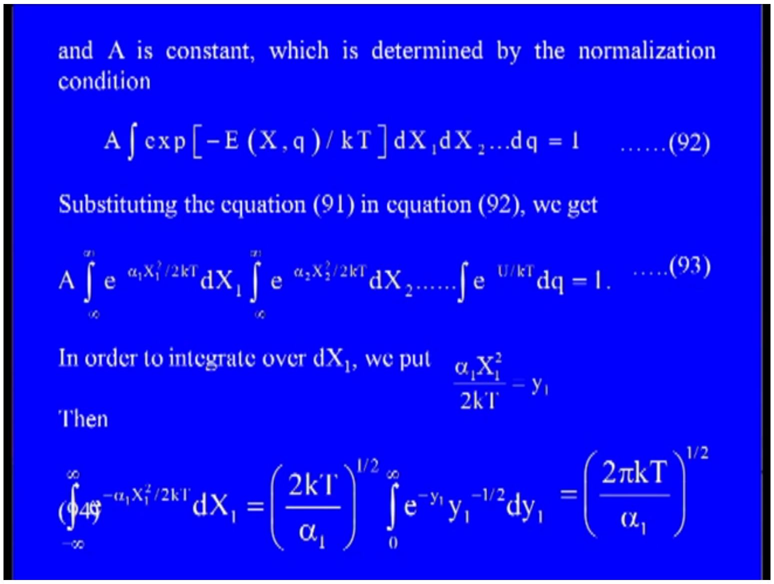

and A is constant, which is determined by the normalization condition

$$A\int \exp\left[-E\left(X,q\right)/kT\right]dX_1 dX_2 \ldots dq = 1 \qquad \ldots\ldots(92)$$

Substituting the equation (91) in equation (92), we get

$$A\int_{\infty}^{\infty} e^{\alpha_1 X_1^2/2kT}dX_1 \int_{\infty}^{\infty} e^{\alpha_2 X_2^2/2kT}dX_2 \ldots\ldots \int e^{U/kT}dq = 1. \qquad \ldots\ldots(93)$$

In order to integrate over dX_1, we put $\frac{\alpha_1 X_1^2}{2kT} = y_1$

Then

$$(94)\quad \int_{-\infty}^{\infty} e^{-\alpha_1 X_1^2/2kT}dX_1 = \left(\frac{2kT}{\alpha_1}\right)^{1/2}\int_0^{\infty} e^{-y_1}y_1^{-1/2}dy_1 = \left(\frac{2\pi kT}{\alpha_1}\right)^{1/2}$$

And A is a constant which is determined by the normalization condition A entry integral e to the power of -E by KT integrated over all coordinates dX1 dX2 dX3 and dq = to 1. If you will substitute these normalization condition then you will get A in the above equations in the above equation what you will get it you will get A - integrating from - infinity to + infinity e to the - alpha 1 X1 square by 2 KT dX1 - infinity to + infinity e to the - alpha2 X2 square by 2 KT dX2.

And up to nth term and last term is e to the power of -U by KT dq = 1 this is the normalization condition. So, we have got basically n + 1 integration X1, X2, X3, Xn and another integration over dq. So, in order to integrate our dX1, dX2, dX3 let us substitute alpha1 X1 square by 2 KT is y1 alpha2 X2 square by 2 KT is y2 etcetera. If I will substitute it then I can rewrite these equations as minus infinity to plus infinity e to the - alpha1 X1 square by 2 KT dX1.

After substitution it will look like 2 KT by alpha1 to the power of half 0 to infinity e to the power minus y1 y1 to the power minus of dy 1 which is nothing but the 2 Pi KT by alpha 1 to the power half. So, you will get in terms you will get terms of this type n number of terms you will get, so if you so because of the integration over X1, X2, X3, Xn.

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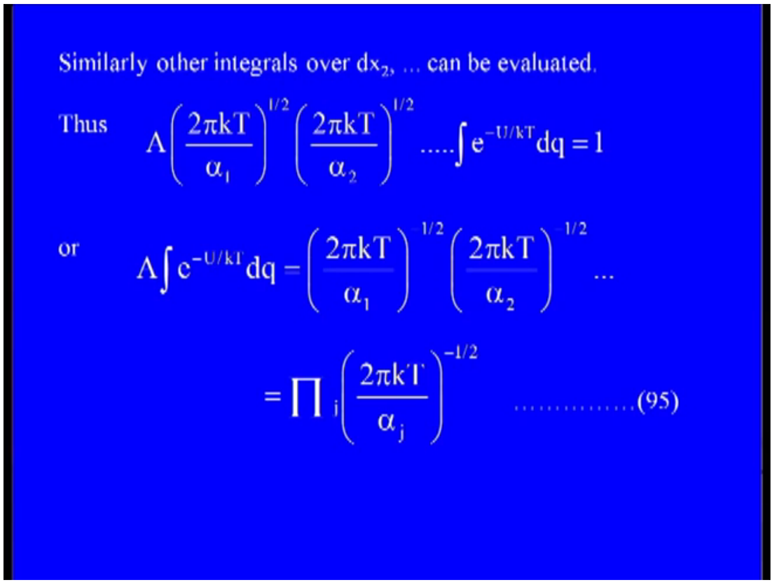

Similarly other integrals over dx_2, ... can be evaluated.

Thus $$A\left(\frac{2\pi kT}{\alpha_1}\right)^{1/2}\left(\frac{2\pi kT}{\alpha_2}\right)^{1/2}.....\int e^{-U/kT}dq = 1$$

or $$A\int e^{-U/kT}dq = \left(\frac{2\pi kT}{\alpha_1}\right)^{1/2}\left(\frac{2\pi kT}{\alpha_2}\right)^{-1/2}...$$

$$= \prod_j \left(\frac{2\pi kT}{\alpha_j}\right)^{-1/2} \quad ....(95)$$

So, finally what we will get A 2 Pi KT by alpha1 to the power of half 2 Pi KT by alpha2 to the power of half into last term e to the power -e U by KT dq = 1. So, finally we can get A e to the power of -e U by KT dq = 2 Pi kt by alpha1 to the power of half 2 Pi K T by alpha 2 to the power of half we will get we will be having n number of term. So, it is a product of 2 Pi KT by alpha j to the power - half where j runs from 1 to n ok.

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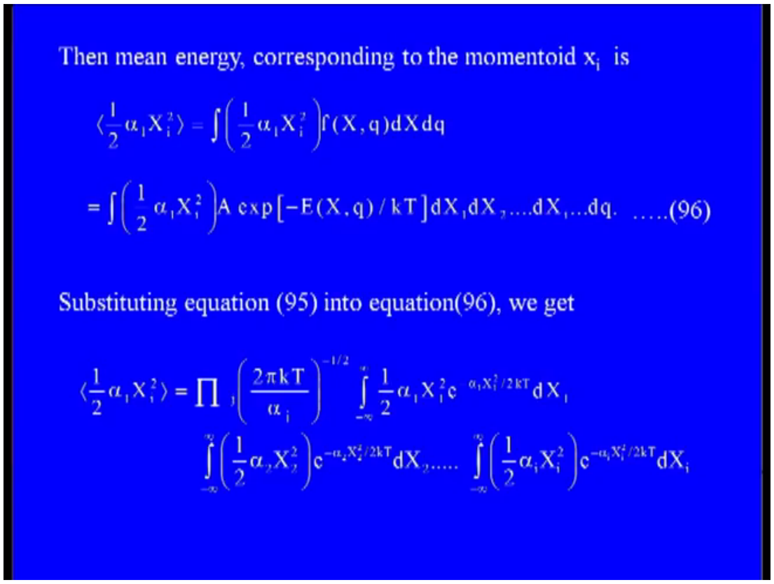

Then mean energy, corresponding to the momentoid x_i is

$$\langle\frac{1}{2}\alpha_1 X_i^2\rangle = \int\left(\frac{1}{2}\alpha_1 X_i^2\right)f(X,q)dX\,dq$$

$$= \int\left(\frac{1}{2}\alpha_1 X_i^2\right)A\exp[-E(X,q)/kT]dX_1 dX_2....dX_i...dq. \quad .....(96)$$

Substituting equation (95) into equation(96), we get

$$\langle\frac{1}{2}\alpha_1 X_i^2\rangle = \prod_j \left(\frac{2\pi kT}{\alpha_j}\right)^{-1/2}\int_{-\infty}^{\infty}\frac{1}{2}\alpha_1 X_1^2 e^{\alpha_1 X_i^2/2kT}dX_1$$
$$\int_{-\infty}^{\infty}\left(\frac{1}{2}\alpha_2 X_2^2\right)e^{-\alpha_2 X_2^2/2kT}dX_2..... \int_{-\infty}^{\infty}\left(\frac{1}{2}\alpha_i X_i^2\right)e^{-\alpha_i X_i^2/2kT}dX_i$$

So, then the mean energy now I will calculate different quantities then mean energy corresponding to the moment towards Xi is as we know energy is some half alpha Xi square. So, average mean of half alpha Xi square is interest integration half Alpha Xi square into probability f of Xq dX dq. So, then you will substitute f of Xq, so what we will get it half alpha Xi square A e to the power by KT dX1, dX2, dX3 dXi into dX cube. So, we know that average values of half alpha Xi square is we know it is a product of it is a;

So, it is product of 2 Pi KT by alpha J to the power – half. So, if you put the values of e = half of alpha Xi square summed over +U of KT, so that part we know what is it e to the power U by KT. Let me show you Ae to the power - e U by KT dq is is a product of n terms 2 Pi KT by alpha j to the power of half. So, just we have substituted that thing product of 2 Pi KT by alpha j to the power - half which is nothing but A integral e to the power - U by KT.

Now I have to do rest of the terms I have to integrate the race term which is minus infinity to plus infinity half alpha1 X1 square e to the power –alpha1 X1 square by 2 KT dX1 half alpha2 X2 square e to the power alpha2 X2 square by 2 KT dX 2. And finally half of alpha nth ith term is alpha Xi square e to the power of alpha Xi square by 2 KT dXi. So, this term we also know so apart from half KT.

So, finally what we will get the product of 2 Pi KT by alpha z to the power of minus half into product of n terms of inverse thing means 2 Ppi KT by alpha1 to the were + half apart from half KT. So, obviously this term will cancel except half KT. So, we will get the mean of, we will finally we will go we got the result the mean energy that means average values of half alpha Xi square is nothing but half KT.

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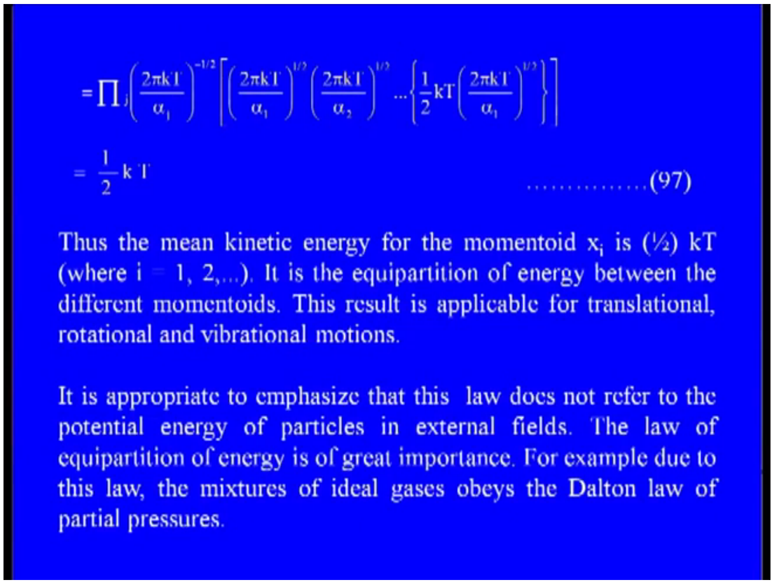

$$=\prod_j \left(\frac{2\pi kT}{\alpha_1}\right)^{-1/2} \left[\left(\frac{2\pi kT}{\alpha_1}\right)^{1/2} \left(\frac{2\pi kT}{\alpha_2}\right)^{1/2} \ldots \left\{\frac{1}{2}kT\left(\frac{2\pi kT}{\alpha_1}\right)^{1/2}\right\}\right]$$

$$= \frac{1}{2}kT \qquad \ldots\ldots\ldots\ldots\ldots(97)$$

Thus the mean kinetic energy for the momentoid x_i is (½) kT (where i = 1, 2,...). It is the equipartition of energy between the different momentoids. This result is applicable for translational, rotational and vibrational motions.

It is appropriate to emphasize that this law does not refer to the potential energy of particles in external fields. The law of equipartition of energy is of great importance. For example due to this law, the mixtures of ideal gases obeys the Dalton law of partial pressures.

So, thus the mean kinetic energy for the momentoid Xi is half KT who are i =1 to n, it is the equipartition of energy between the different momentoid. This result is applicable for translational, rotational and vibrational motions and it is appropriate to emphasize that these law does not refer to the potential energy of particles in the external field. The law of equipartition of energy is of great importance.

For example due to this law the mixture of ideal gases obeys the Dalton law of partial pressures okay. So, the microscopic origin of Dalton law partial pressure is nothing but the equipartition energy law of equipartition of energy and as a result we got the Dalton's law of partial pressure who are total if; that means if the system has n number of components the total pressure exerted by the system is the summed of partial pressures exerted by the individual components respectively.

So, next I will tell atomicity of gases. The law equipartition of energy atomicity, of gas means I will next couple of minutes I will tell the result of equipartition of energy law of equipartition of energy in predicting in predicting the ratio of the specific 8 CP CV etcetera okay.

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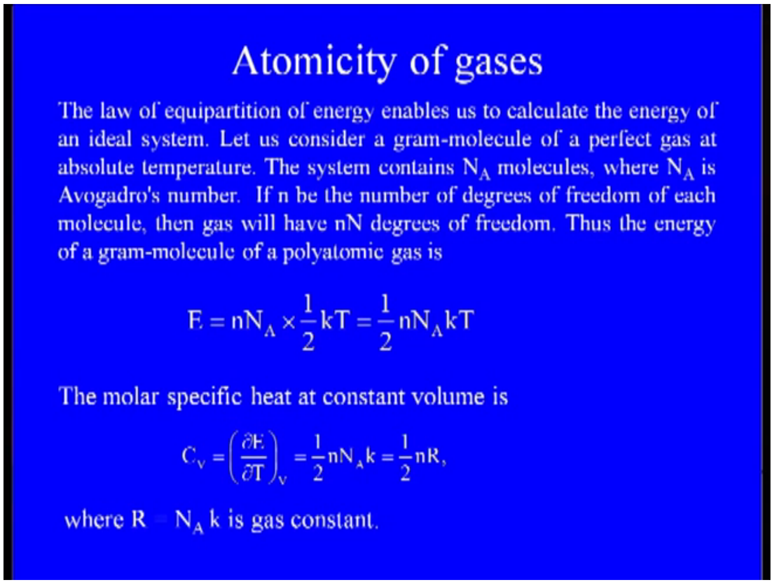

Atomicity of gases

The law of equipartition of energy enables us to calculate the energy of an ideal system. Let us consider a gram-molecule of a perfect gas at absolute temperature. The system contains N_A molecules, where N_A is Avogadro's number. If n be the number of degrees of freedom of each molecule, then gas will have nN degrees of freedom. Thus the energy of a gram-molecule of a polyatomic gas is

$$E = nN_A \times \frac{1}{2}kT = \frac{1}{2}nN_A kT$$

The molar specific heat at constant volume is

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{1}{2}nN_A k = \frac{1}{2}nR,$$

where R N_A k is gas constant.

So, the law of equipartition of energy enables us to calculate the energy of an ideal system. Obviously we will constraint ourselves to an ideal system. Let us consider a gram molecule of a perfect gas at absolute temperature. The system contains any molecules where NA is the Avogadro number. Because we have considered one gram molecule, so obviously it contains Avogadro number of molecules.

If N be the number of degrees of freedom of each molecule then gas will have small n times capital NA degrees of freedom. Thus the energy of a gram molecule of a polyatomic gas is number of degrees of freedom into half KT because per degree of freedom is half KT, total degrees of freedom n times capital NA, so, these times half KT. So, total energy is half small n is the number of degrees of freedom.

Total molecule is NA times KT, so the molar specific heat at constant volume is Cv is del E by Del T at constant v. So, half small n into capital NA into K which is nothing but the half times n into R where R is nothing but the universal gas constant which can be written as Avogadro number times the Boltzmann constant. So, finally the molar specific heat at constant volume we have got is NR by 2 and exactly which matches with the experiment.

That at room temperature a molar specific heat at constant volume is independent of the temperature.

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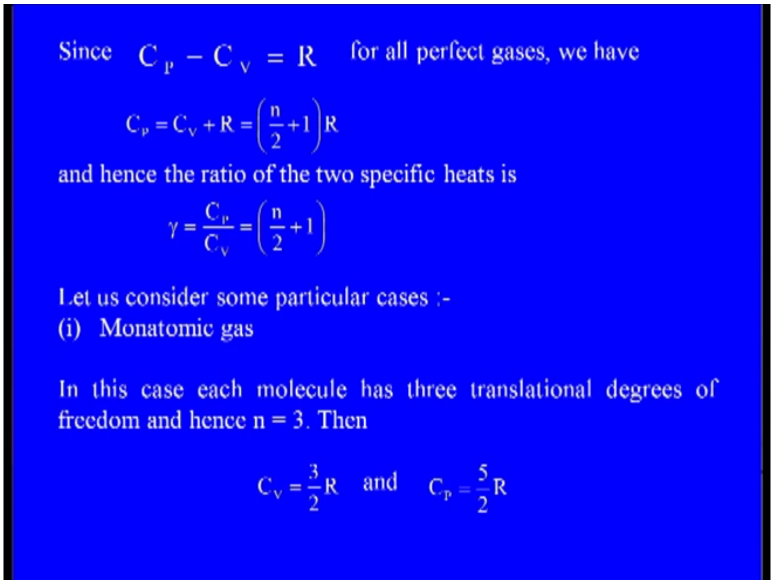

Since $C_p - C_V = R$ for all perfect gases, we have

$$C_p = C_V + R = \left(\frac{n}{2}+1\right)R$$

and hence the ratio of the two specific heats is

$$\gamma = \frac{C_p}{C_V} = \left(\frac{n}{2}+1\right)$$

Let us consider some particular cases :-

(i) Monatomic gas

In this case each molecule has three translational degrees of freedom and hence n = 3. Then

$$C_V = \frac{3}{2}R \quad \text{and} \quad C_p = \frac{5}{2}R$$

Since Cp by Cv = R for perfect all perfect gases we have Cp = Cv + R, since we have got Cv is n by 2 times R, so if you will put this value, so Cp is n by 2 + 1 into R and hence the ratio of two specific heat is gamma = Cp by Cv n by 2 + 1. So, let us consider some particular cases let us start for the mono atomic gas. In this case as you know let us try to derive this ratio gamma equal to Cp by Cc for three cases.

First one is the mono atomic gases, second one is the diatomic gases, third one is the triatomic gases. Because we know monatomic we know the degrees of freedom for monatomic, diatomic, triatomic gases and just we will put the degrees of freedom for three gases individually and calculate the ratio gamma and let us see whether it matches with the experiment or not. For the mono atomic gases each molecule has only three translational degrees of freedom and hence n = 3. So, Cv = 3 by 2 R and Cp = 5 by 2 R;

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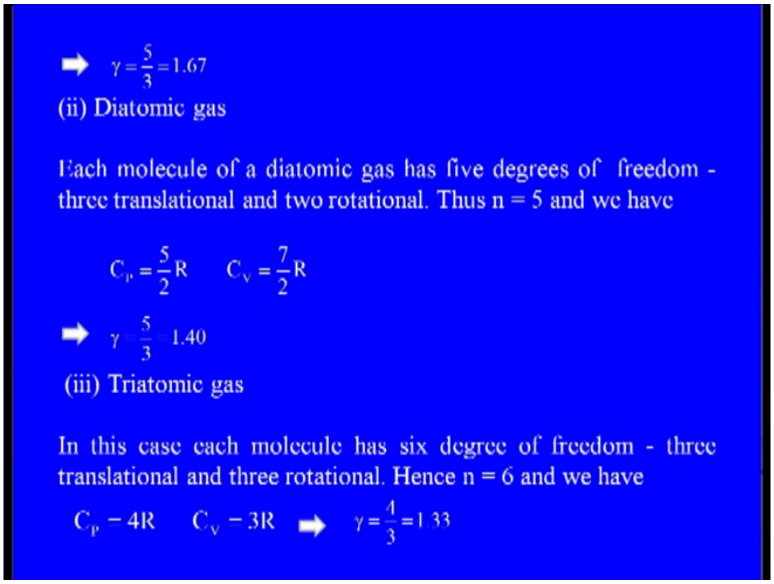

$\Rightarrow \quad \gamma = \frac{5}{3} = 1.67$

(ii) Diatomic gas

Each molecule of a diatomic gas has five degrees of freedom - three translational and two rotational. Thus n = 5 and we have

$$C_P = \frac{5}{2}R \qquad C_V = \frac{7}{2}R$$

$\Rightarrow \quad \gamma = \frac{5}{3} = 1.40$

(iii) Triatomic gas

In this case each molecule has six degree of freedom - three translational and three rotational. Hence n = 6 and we have

$$C_P = 4R \qquad C_V = 3R \quad \Rightarrow \quad \gamma = \frac{4}{3} = 1.33$$

So, the ratio = gamma 5 by 3 which is 1.67 which matches with the experiment beautifully. Now let us come to the diatomic gas we know for the diatomic gases it has 5 degrees of freedom where three are the translational degrees of freedom and two are the rotational degrees of freedom provided their inter particle separation are held constant. So, each molecule of a diatomic gas has 5 degrees of freedom where 3 translational and 2 rotational.

Thus n = 5, now if we will put gamma = 5 by 2 R, Cv = 7 by 2 R they our ratio is 7 by 5 which is which comes out to be 1.4 it also matches with the experiment beautifully, try to make gases. In this case each molecule has 6 degrees of freedom who are 3 are due to translational motion and 3 are due to rotational motion. So, we will put n = 6 we will get Cp = 4R where Cv = 3R where gamma equal to 4 by 3 = 1.33.

So, here I should say something suppose if you want to calculate the ratio for the polyatomic gases. So, they are the observed value from this derivation and did not match with the experimental result. So, that is there is in this form of derivation is not good for a multi for a polyatomic gas where you need to look for some new theory. May be statistical mechanics will be able to handle polyatomic cases much better than this kinetic theory of gases.

Atmosphere of planets, so, that is the one of the most beautiful example through this we will see how the density of molecules are distributed in our atmosphere.

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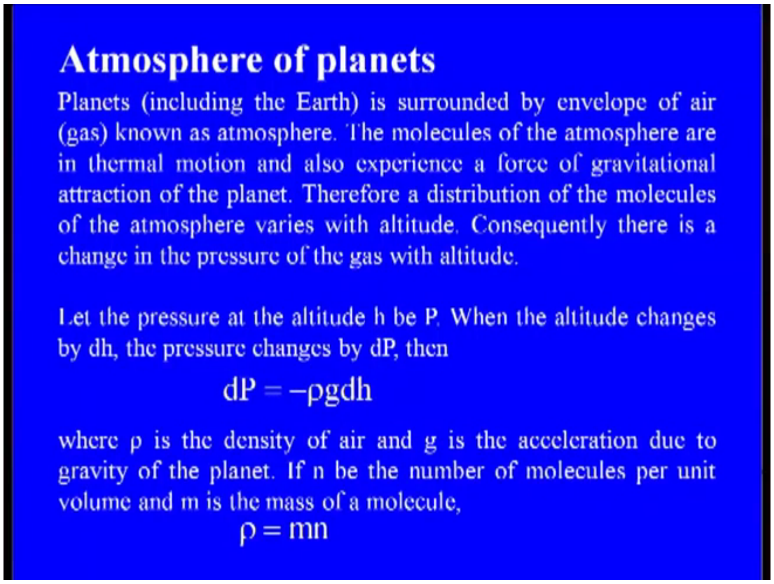

Atmosphere of planets

Planets (including the Earth) is surrounded by envelope of air (gas) known as atmosphere. The molecules of the atmosphere are in thermal motion and also experience a force of gravitational attraction of the planet. Therefore a distribution of the molecules of the atmosphere varies with altitude. Consequently there is a change in the pressure of the gas with altitude.

Let the pressure at the altitude h be P. When the altitude changes by dh, the pressure changes by dP, then

$$dP = -\rho g dh$$

where ρ is the density of air and g is the acceleration due to gravity of the planet. If n be the number of molecules per unit volume and m is the mass of a molecule,

$$\rho = mn$$

Planets, including the earth are surrounded by envelope of air known as atmosphere. The molecules of the atmospheres are in thermal motion and also experience a force of gravitational attraction of the planet. Therefore a distribution of the molecules of the atmosphere varies with altitude. Consequently there is a change in pressure of the gas with altitude. Let us derive how the pressure changes with the altitude okay.

Let the pressure at the altitude h be P on the altitude changes by dh the pressure changes by an amount dp where dp is related to dh by dP = -Rho g times dh where Rho is the density of the air and g is the acceleration due to gravity of the planet. If n be the number of molecules per unit volume and m is the mass of the molecule then Rho = m times n okay.

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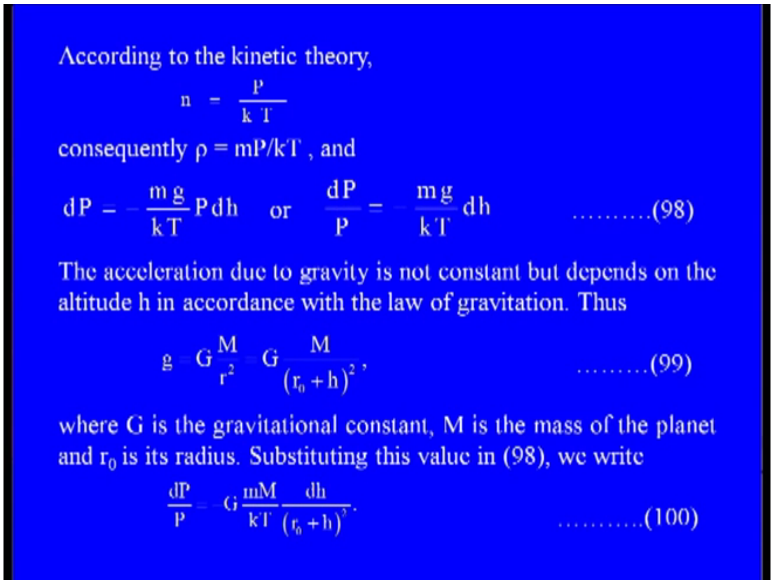

According to the kinetic theory,

$$n = \frac{P}{kT}$$

consequently $\rho = mP/kT$, and

$$dP = -\frac{mg}{kT} P dh \quad \text{or} \quad \frac{dP}{P} = -\frac{mg}{kT} dh \qquad \text{..........(98)}$$

The acceleration due to gravity is not constant but depends on the altitude h in accordance with the law of gravitation. Thus

$$g = G\frac{M}{r^2} = G\frac{M}{(r_0 + h)^2}, \qquad \text{.........(99)}$$

where G is the gravitational constant, M is the mass of the planet and r_0 is its radius. Substituting this value in (98), we write

$$\frac{dP}{P} = -G\frac{mM}{kT}\frac{dh}{(r_0 + h)^2}. \qquad \text{...........(100)}$$

So, according to the kinetic theory we know P = n KT, so, n = P by KT consequently Rho = small mP by KT and dP if you substitute values of Rho in the dP, so we will get dP = mg by KT into Pdh or dP by P = mg by KT into dh. So, so here the acceleration due to gravity g is not constant but depends on the altitude h in accordance with the law of gravitation. In our school level physics we know how to derive.

We feel go away from this surface if you go towards the center then how the acceleration changes with the distance. So, the g = Gm by r square where G is M by r naught + h whole square where G is the gravitational constant M is the mass of the planet r naught is its radius okay. So, that means if you will go away from the surface and that means you are away from; so r naught + h, if you will go towards the center by a distance h then it will be reduced r naught r naught - h should be.

So, substituting this value in the equation we will write dP by P is mg into small m into capital M by KT dh by r naught + h whole square.

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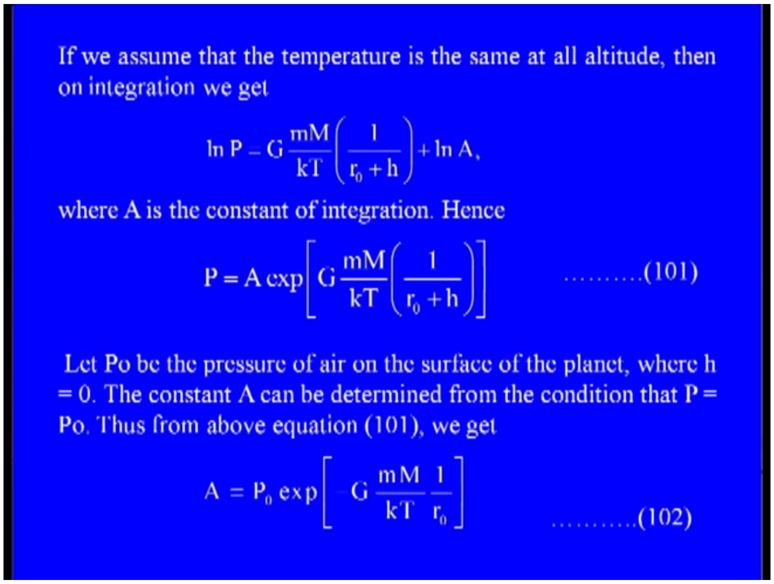

If we assume that the temperature is the same at all altitude, then on integration we get

$$\ln P - G\frac{mM}{kT}\left(\frac{1}{r_0 + h}\right) + \ln A,$$

where A is the constant of integration. Hence

$$P = A\exp\left[G\frac{mM}{kT}\left(\frac{1}{r_0 + h}\right)\right] \qquad \text{..........(101)}$$

Let Po be the pressure of air on the surface of the planet, where h = 0. The constant A can be determined from the condition that P = Po. Thus from above equation (101), we get

$$A = P_0\exp\left[-G\frac{mM}{kT}\frac{1}{r_0}\right] \qquad \text{..........(102)}$$

If we assume that temperature is the same at all altitude for the sake of simplicity then we can take outside T, we can take outside of this integration. Then on integration we get log of P =G small m capital M by KT 1 by r naught + h + log of A where log of A is a integration constant. Hence P if we rewrite this equation P = A times e to the power G small m capital M by KT 1 by r naught + h.

Let P naught be the pressure of the air on the surface of the planet where h = 0 just surface. So, then that means we want to say how the pressure changes with the altitude as you will be away from this surface okay. Let us say pressure is P = P naught at the surface that means h = 0. The constant A can be calculated from the condition that P = P naught. So, the constant is A = P naught e to the power – G small m capital M by KT into 1 by r naught.

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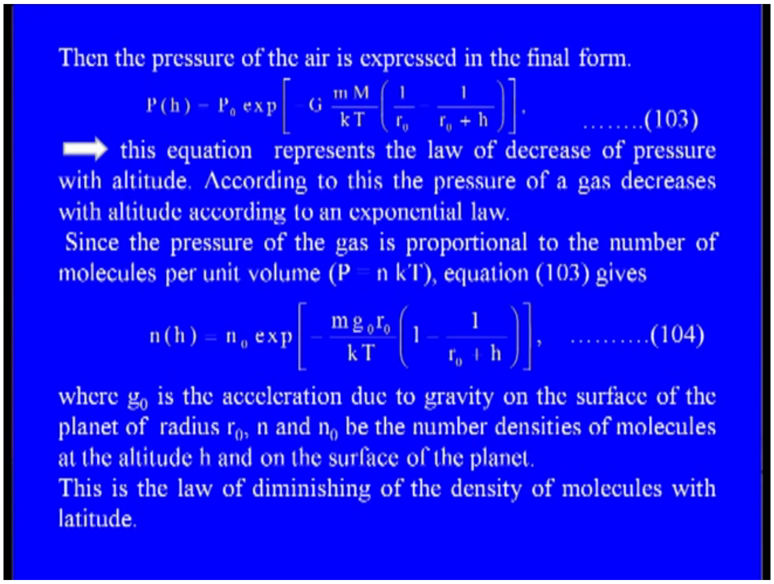

Then the pressure of the air is expressed in the final form.

$$P(h) = P_0 \exp\left[-G\frac{mM}{kT}\left(\frac{1}{r_0} - \frac{1}{r_0 + h}\right)\right]. \qquad \ldots\ldots\ldots(103)$$

➡ this equation represents the law of decrease of pressure with altitude. According to this the pressure of a gas decreases with altitude according to an exponential law.

Since the pressure of the gas is proportional to the number of molecules per unit volume ($P = n\,kT$), equation (103) gives

$$n(h) = n_0 \exp\left[-\frac{m g_0 r_0}{kT}\left(1 - \frac{1}{r_0 + h}\right)\right], \qquad \ldots\ldots\ldots\ldots(104)$$

where g_0 is the acceleration due to gravity on the surface of the planet of radius r_0, n and n_0 be the number densities of molecules at the altitude h and on the surface of the planet.

This is the law of diminishing of the density of molecules with latitude.

If we will put back the constant A so we will get P as a function of h is the pressure of the earth is P of h = P naught e to the power - G small m capital M by into 1 by r naught - 1 by r naught + h. So, this equation represents the law of decrease of pressure with altitude. According to this pressure of a gas decreases with altitude according to an exponential law and exactly it happens in our atmosphere.

If you will be away from the atmosphere, if you go above to our surface where we will feel less pressure and that is the reason we have seen less pressure in the air of atmosphere. Since the pressure of the gas is proportional to the number molecules per unit volume. So, the above equation pressure can be written in terms of number of molecules as a height. So, n of h = n naught, n naught means number of molecules per unit volume at the surface into e to the - m g naught r naught by KT into 1 - 1 by r naught + h.

Where g naught is the acceleration due to gravity on the surface of the planet of radius r naught, n and n naught be the number of number densities of molecules means number of molecules per unit volume at the altitude h. And on the surface of the planet for h assumed to be 0 respectively this is the law of diminishing of the density of the molecules with the latitude that means as we as we will go above to the surface the density of molecules will be decreasing. So, that is expected and that it happened in this expression also.

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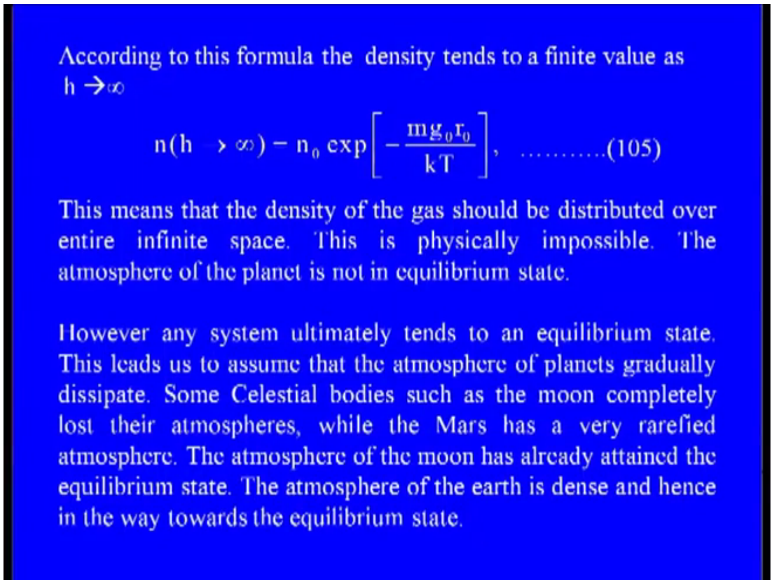

According to this formula the density tends to a finite value as $h \to \infty$

$$n(h \to \infty) = n_0 \exp\left[-\frac{mg_0r_0}{kT}\right], \quad ....(105)$$

This means that the density of the gas should be distributed over entire infinite space. This is physically impossible. The atmosphere of the planet is not in equilibrium state.

However any system ultimately tends to an equilibrium state. This leads us to assume that the atmosphere of planets gradually dissipate. Some Celestial bodies such as the moon completely lost their atmospheres, while the Mars has a very rarefied atmosphere. The atmosphere of the moon has already attained the equilibrium state. The atmosphere of the earth is dense and hence in the way towards the equilibrium state.

According to this formula the density tends to a finite value as h tends to infinity, which if you will substitute in the above equation h = infinity then we will get a n at h tends to infinity = n naught e to the -m naught g naught r naught by KT. This means that the density of gas should be distributed over the entire infinite space. This is physically impossible the atmosphere of the planet is not in equilibrium state.

However any system ultimately tends to an equilibrium state, so dependent for different systems suppose if we allow the system for to come to equilibrium different system will take different time to come to the equilibrium. But asymptotically any system will come to the equilibrium, so this leads us to assume that the atmosphere of the planets gradually dissipate. Some celestial bodies such as the moon completely lost they are atmospheres.

While the Mars have has a very rarefied atmosphere. The atmosphere of the moon has already attained the equilibrium state, the atmosphere of the earth is dense and hence in the way towards the equilibrium state thank you very much.