Engineering Physics 1
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Module-05
Lecture-04
Maxwellian Distribution Law of Velocity – Part 02

So, we have already told to experiment first one is Stern experiment second one is Zartmann and KO, Zartmann and KO. For third experiment just I want to tell which the Stern improved experiment is okay. Actually in this experiment Stern has improved his earlier experiment so that is the reason it is known as turns improved experiment.

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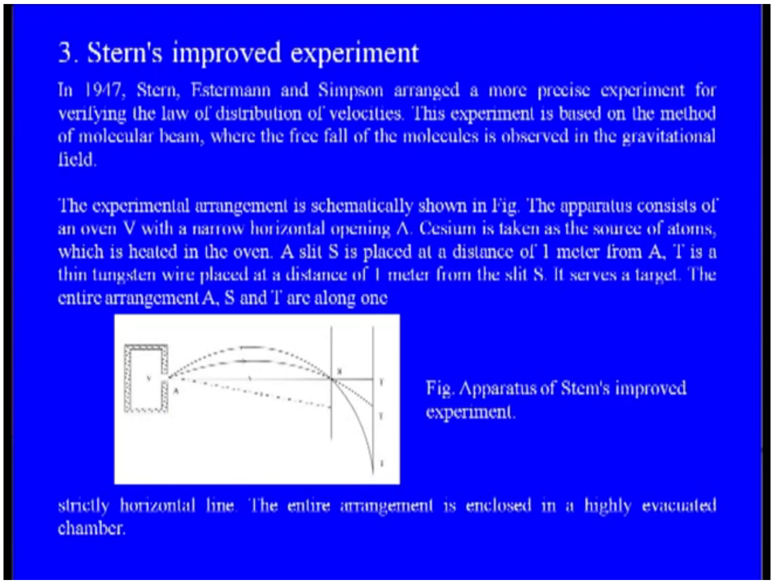

3. Stern's improved experiment

In 1947, Stern, Fstermann and Simpson arranged a more precise experiment for verifying the law of distribution of velocities. This experiment is based on the method of molecular beam, where the free fall of the molecules is observed in the gravitational field.

The experimental arrangement is schematically shown in Fig. The apparatus consists of an oven V with a narrow horizontal opening A. Cesium is taken as the source of atoms, which is heated in the oven. A slit S is placed at a distance of 1 meter from A, T is a thin tungsten wire placed at a distance of 1 meter from the slit S. It serves a target. The entire arrangement A, S and T are along one strictly horizontal line. The entire arrangement is enclosed in a highly evacuated chamber.

Fig. Apparatus of Stem's improved experiment.

So, in 1947 so, Stern, Estermann and Simpson have arranged a more precise experiment for verifying the law of distribution of velocities. This experiment is based on the method of molecular beam where the free fall of the molecules is observed in the gravitational field. Actually there they have exploited the free fall of molecular beam in the presence of gravitational field okay.

The experimental arrangement is schematically shown in figure I will also explain it. The apparatus consists of an oven just like Zartmann and KO with a narrow horizontal opening A here the working substance they have taken cesium okay. Cesium is taken as the source of atoms which is heated in the oven B. A slit S is placed at a distance of one meter from A; T is thin tungsten were placed at a distance one meter from this slit S.

Basically it serves as a target itself. The entire arrangement A, S and T are all along strictly horizontal line. The entire arrangement is enclosed in a highly evacuated chamber. So, obviously you understand it when Stern has done his first experiment that time and whatever the vacuum he has maintained. This time he has maintained higher degree of vacuum, so that is the reason it is known as improved experiment. Main thing is the vacuum of this cymbal that is the main idea actually.

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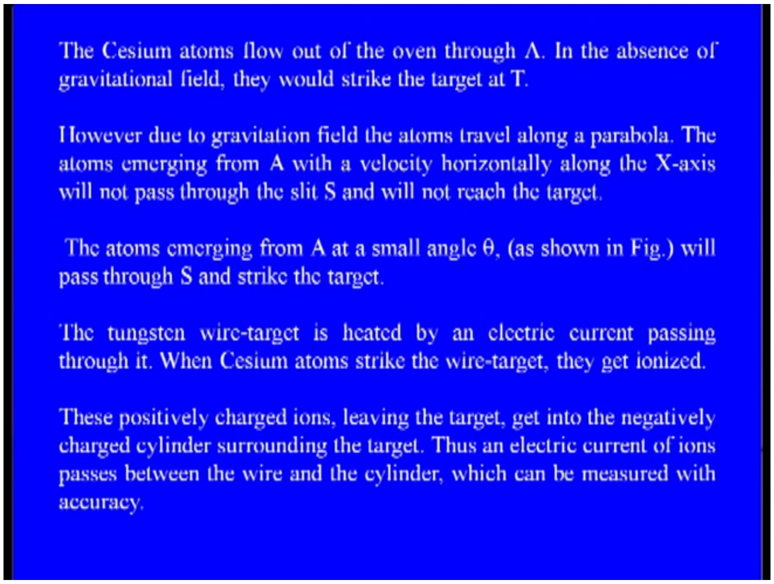

The Cesium atoms flow out of the oven through A. In the absence of gravitational field, they would strike the target at T.

However due to gravitation field the atoms travel along a parabola. The atoms emerging from A with a velocity horizontally along the X-axis will not pass through the slit S and will not reach the target.

The atoms emerging from A at a small angle θ, (as shown in Fig.) will pass through S and strike the target.

The tungsten wire-target is heated by an electric current passing through it. When Cesium atoms strike the wire-target, they get ionized.

These positively charged ions, leaving the target, get into the negatively charged cylinder surrounding the target. Thus an electric current of ions passes between the wire and the cylinder, which can be measured with accuracy.

So, the cesium atoms flow out of the oven through A, A is the narrow opening in the absence of gravitational field they will strike the target at T directly this is obvious. If there is no gravitational field so it will heat directly to the target T okay. However due to gravitational field the atoms travel along a parabola that we know the trajectory of the particle in the presence of a gravitational field is a parabola.

So, obviously so in the presence of gravitational field the atom travel along a parabola. The atom emerging from a with a velocity horizontal along the X axis will not pass through the slit S and we will not reach the target okay. The atom emerging from A at small angle theta will pass through it S and the strike the target. The tungsten were target is heated by an electric current passing through it.

When cesium atom strikes the wire target they get ionized ok. These positively charged ions leaving the target get into the negatively charged cylinder surrounding the target. Thus an electric current of ion passes through the earth and the cylinder which can be measured with accuracy.

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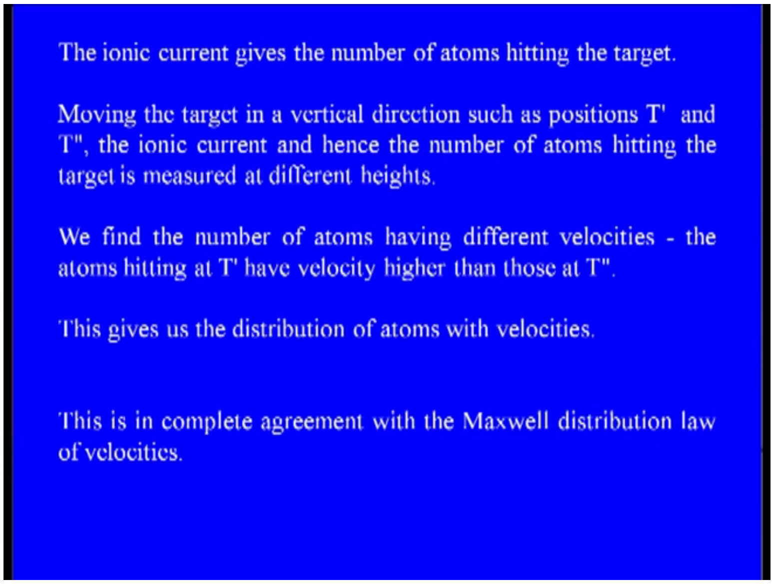

The ionic current gives the number of atoms hitting the target.

Moving the target in a vertical direction such as positions T' and T", the ionic current and hence the number of atoms hitting the target is measured at different heights.

We find the number of atoms having different velocities - the atoms hitting at T' have velocity higher than those at T".

This gives us the distribution of atoms with velocities.

This is in complete agreement with the Maxwell distribution law of velocities.

The ionic current gives the number of atoms hitting the target this is the definition of current. Moving the target in a vertical direction such as position T prime and T double prime. The ionic current and hence the number of atoms hitting the target is measured at different heights. We find the number of atoms having different velocities. The atom hitting at T prime have velocity higher than those at T double prime.

This gives us the distribution of atoms with velocities these observation experimental observation whose is in complete agreement complete agreement with Maxwell's law of distribution of velocity. So, this is the experiment which proves very accurately Maxwell's law of distribution of velocities okay. So, now next couple of minutes we will try to we will try to deduce some equations of some law from Maxwell's distribution law.

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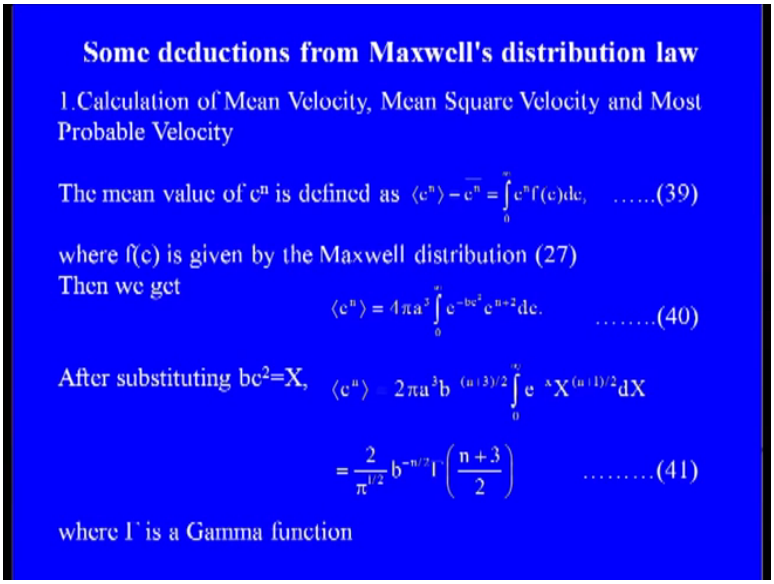

Some deductions from Maxwell's distribution law

1.Calculation of Mean Velocity, Mean Square Velocity and Most Probable Velocity

The mean value of c^n is defined as $\langle c^n\rangle = \overline{c^n} = \int_0^\infty c^n f(c)dc,$ ……(39)

where f(c) is given by the Maxwell distribution (27)
Then we get

$$\langle c^n\rangle = 4\pi a^3\int_0^\infty e^{-bc^2}c^{n+2}dc. \qquad \text{……..(40)}$$

After substituting $bc^2=X$,

$$\langle c^n\rangle = 2\pi a^3 b^{-(n+3)/2}\int_0^\infty e^{-X}X^{(n+1)/2}dX$$

$$= \frac{2}{\pi^{1/2}}b^{-n/2}\Gamma\left(\frac{n+3}{2}\right) \qquad \text{………(41)}$$

where Γ is a Gamma function

First calculation of mean velocity, mean square velocity and most probable velocity. The mean value of cn is defined as in general average values of c to the power n is 0 to infinity c to the power n f of c dc; f of c dc is the probability of finding c well variable c and c + dc where f of c is given by the Maxwell distribution. Then we get c to the power n is 4 Pi a cube, 0 to infinity if you will substitute f of c, c to the power of -bc square c to the power n plus half 2 dc.

So, if you will substitute bc square = X then average values of c to the power n is 2 Pi a cube times b to the power n + 3 by 2, 0 to infinity e to the power –X, X to the power n +1 by 2 dX. This is just you substitute the variable bc square =X and if you do a little bit mathematics you will get this expression. This is a standard integration and this standard integration can be written in terms of this gamma function.

So, it is given in any mathematical physics book. So, this value is 2 by Pi to the power half b to the - n by 2 gamma of n + 3 by 2. This gamma is nothing but the gamma function its value is tabulated in any mathematical physics.

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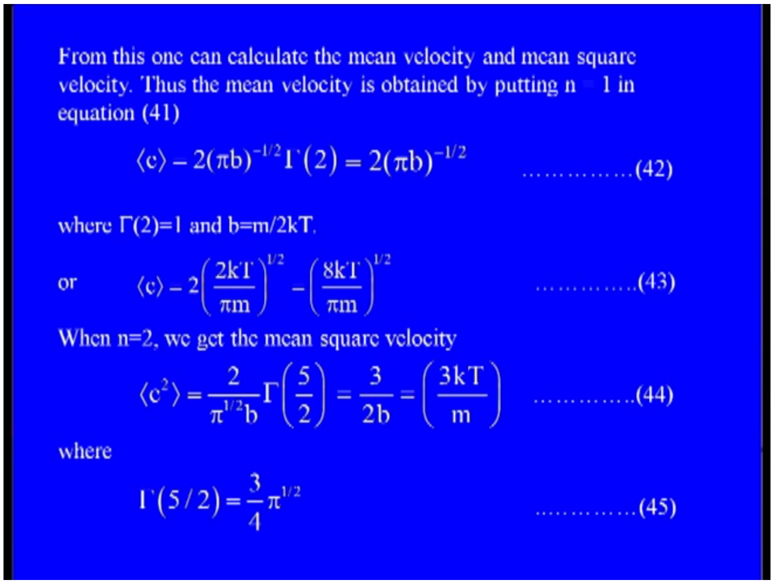

From this one can calculate the mean velocity and mean square velocity. Thus the mean velocity is obtained by putting n = 1 in equation (41)

$$\langle c\rangle = 2(\pi b)^{-1/2}\Gamma(2) = 2(\pi b)^{-1/2} \qquad \ldots\ldots\ldots\ldots\ldots(42)$$

where Γ(2)=1 and b=m/2kT.

or

$$\langle c\rangle = 2\left(\frac{2kT}{\pi m}\right)^{1/2} = \left(\frac{8kT}{\pi m}\right)^{1/2} \qquad \ldots\ldots\ldots\ldots\ldots(43)$$

When n=2, we get the mean square velocity

$$\langle c^2\rangle = \frac{2}{\pi^{1/2}b}\Gamma\left(\frac{5}{2}\right) = \frac{3}{2b} = \left(\frac{3kT}{m}\right) \qquad \ldots\ldots\ldots\ldots\ldots(44)$$

where

$$\Gamma(5/2) = \frac{3}{4}\pi^{1/2} \qquad \ldots\ldots\ldots\ldots\ldots(45)$$

From this one can calculate the mean velocity, mean square velocities etcetera. So, let me first calculate mean velocity, then mean square velocity and then we will calculate some other velocity and try to see a relation among them. So, firstly we want to calculate the mean velocity that means the mean of the velocity c ok. So, in that case in the in our general expression we just put n =1 that means c to the power 1 which is c in the equation.

What we will get it average values of c we will get 2Pi b to the power minus of gamma of 2, gamma of 2 means gamma function having argument 2. If you will put the value of gamma 2 which is nothing but the 1 as we know so which is nothing but the 2 into Pi b to the power minus half? So, we know b is m by 2 KT. So, if you will put again the values of b in the above expression what we will get.

The average values of the mean velocity is 8 by 8 KT by Pi m to the half this is the mean value of a velocity c which is obviously proportional to the temperature and the more the temperature the average values of velocity of will be more and it is inversely proportional to the mass of these atoms or molecules. So, if the mass will be large then the average values mean velocity will be small, if the mass is small then the mean velocity will be large.

And that happens in the in our atmosphere also. If I want to calculate the mean of the square velocity then I have to take the mean of c square then in that case I have to put n = 2, so if I put n

= 2 then I will get the mean of c square is just I will substitute values of n = 2, I will get 2 by Pi to the power half b gamma of 5 by 2. Just we will we know what is a gamma of 5 by 2, so which is nothing but the 3 y 4 square root of Pi that we know.

Gamma of n = in gamma of n – 1, so these values are tabulated in a mathematical physics book if I will see it then I will get the value which is nothing but the 3 by 2 b. If I put the values of b; which is m by 2 KT which is 3 KT by m, so, this is the mean of this square which is c square which is square root of 3 KT by m sorry 3 KT by n, if I want to calculate the RMS velocity which is the square root of the mean of the square velocity.

In that case it will be square root of 3 KT by n, so in both cases the mean velocity as well as the RMS velocity in both cases velocities proportional to the temperature which is physically looks which looks feasible. And which is a always universally proportional to the mass of this molecule or atom. Which is also physically it looks physically feasible.

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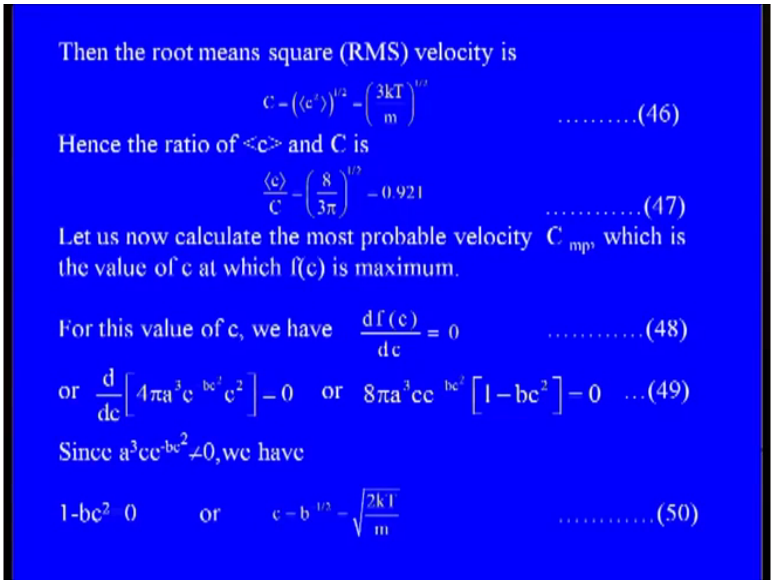

Then the root means square (RMS) velocity is

$$C = (\langle c^2 \rangle)^{1/2} = \left(\frac{3kT}{m}\right)^{1/2} \qquad \ldots\ldots\ldots(46)$$

Hence the ratio of <c> and C is

$$\frac{\langle c \rangle}{C} = \left(\frac{8}{3\pi}\right)^{1/2} = 0.921 \qquad \ldots\ldots\ldots\ldots(47)$$

Let us now calculate the most probable velocity C_{mp}, which is the value of c at which f(c) is maximum.

For this value of c, we have $\frac{df(c)}{dc} = 0$ ………..(48)

or $\frac{d}{dc}\left[4\pi a^3 e^{-bc^2} c^2\right] = 0$ or $8\pi a^3 c e^{-bc^2}\left[1 - bc^2\right] = 0$ …(49)

Since $a^3 c e^{-bc^2} \neq 0$, we have

$1 - bc^2 = 0$ or $c = b^{-1/2} = \sqrt{\frac{2kT}{m}}$ ………..(50)

So, then I will see the ratio of mean of the velocity and the RMS velocity which I will get it so 8 by 3 Pi to the power 1 by half which is 0.921. So, that means the so that means velocity is smaller than the ah me as RMS velocity by the amount .921%. So, now let us calculate some other velocity which is very useful quantity in these areas which is known as the most probable velocity which is the values of c at which f of c is maximum, I have already shown you when we have disc discussed the figure f of X versus X.

Where I have shown you when f of c will be when the probability is 1 at what values of the variable it is 1, so that this is known as the most probable velocity. That time we have already calculated okay. So, the other way to calculate it if the f of c is maximum then df by dc should be the 0. You know what is f of c is 4 Pi a cube e to the power –bc square into c square this is the probability.

So, if you this flow if you demand that probability is maximum then d dc of this d of d of c should be the 0, if I will differentiate it I will get the equation 8 Pi a cube ce to the power - bc square into 1 - bc square = 0. Since a is a constant, since a cube c to the minus bc square not equal to 0 then we have 1 - bc square = 0 or c = b to the power - half, so which is nothing but the if you will inverse it then which is 2 KT by m.

So, this is the most probable velocity so, till now we have calculated the three velocities. First one is the mean velocity, second one is the square root of the mean of the square velocity which is nothing but the root mean square velocity, and third one is the most probable velocity. Let us see what is the relation among these three velocities?

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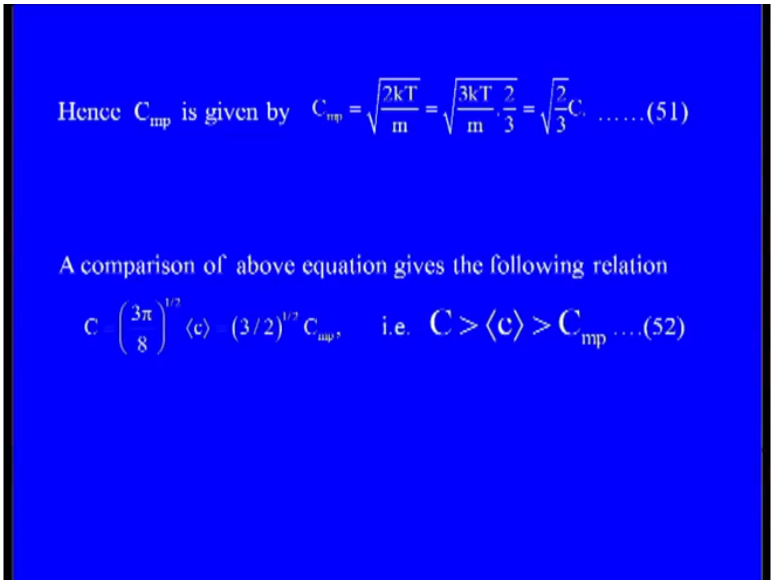

Hence C_{mp} is given by $C_{mp} = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{3kT}{m} \cdot \frac{2}{3}} = \sqrt{\frac{2}{3}} C$ ……(51)

A comparison of above equation gives the following relation

$C = \left(\frac{3\pi}{8}\right)^{1/2} \langle c \rangle = (3/2)^{1/2} C_{mp}$, i.e. $C > \langle c \rangle > C_{mp}$ ….(52)

So if you write it most well velocity in terms of the root mean square velocity then it will come out Cmp = root over 2 KT by m then just multiply two third inside and 3 so we will get 3 KT by m into two third. So, which is nothing but the square root 2 by 3 times root mean square velocity. Same square root 2 by 3 is less than 1, so obviously most well velocity is less than the root mean square velocity.

So, now if you compare the above three velocities we get a beautiful relations which is nothing but the root mean square velocity is just greater than the means mean velocity which is greater than the most probable velocity. So, this is the beautiful relation among the three velocities. These three velocities sometimes depending on the situation, these three velocities play an important role.

So, one must know the form of these three velocities okay. So, now I will calculate different quantities using the Maxwell law of distribution of velocities. First I want to calculate what is the mean kinetic energy? Okay. We have already calculated the mean kinetic energy in my earlier lectures on kinetic theory of gases but there I have done in some empirical way because there I have taken; there is no concept of temperature as such.

The concept of temperature was a foreign element in the kinetic theory of gases where we have we had brought the temperature through the experimental equation of state. If you remember my earlier lectures there temperature was in foreign element. But here just let me see how the temperature has come here temperature will come automatically.

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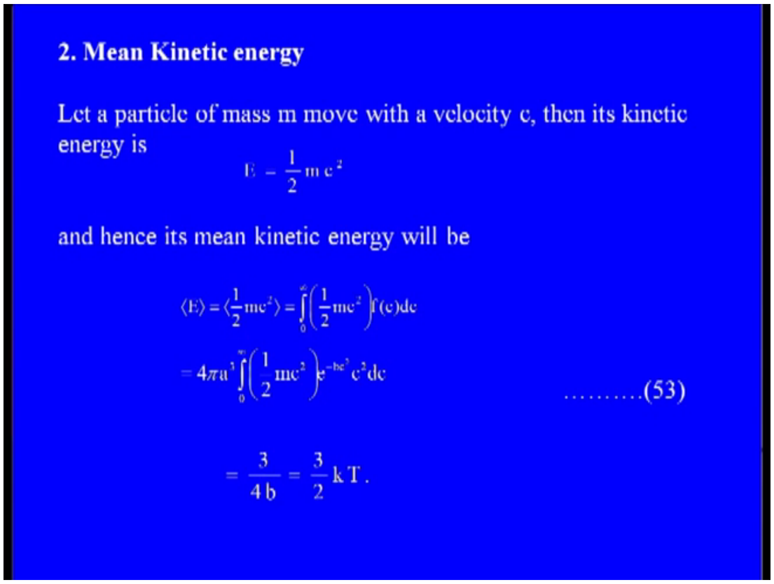

2. Mean Kinetic energy

Let a particle of mass m move with a velocity c, then its kinetic energy is

$$E = \frac{1}{2} m c^2$$

and hence its mean kinetic energy will be

$$\langle E \rangle = \langle \frac{1}{2} mc^2 \rangle = \int_0^\infty \left(\frac{1}{2} mc^2 \right) f(c) dc$$

$$= 4\pi a^3 \int_0^\infty \left(\frac{1}{2} mc^2 \right) e^{-bc^2} c^2 dc \qquad \text{..........(53)}$$

$$= \frac{3}{4b} = \frac{3}{2} kT.$$

So, let us see later particle of mass m move with a velocity c then its kinetic energy is E = half mc square. But anyway let me say some few words here we are talking and the Maxwell distribution of velocities for the mono atomic gases. So, obviously here the kinetic energy although it is not; I have told you but it is implicit here kinetic energy is nothing but the translation kinetic energy.

So, so hence the it is mean we will be E average of half mc square then we know the definition of average definition of average of any quantity is integration that quantity we have already told you average values of cn is integral cn f of c bc 0 to infinity. So, same thing is here also 0 to infinity half of mc square f of c dc, half of m, m by 2i will come out of this integration. So, what I will get it once I will substitute f of c, f of c is the it will come from the Maxwell law of distribution of velocity.

So, if you will substitute values of f of c, so what we will get 4 Pi aq 0 to infinity half mc square e to the power - bc square c square dc. So, half of m will come out, so finally we will get 0 to infinity e to the power - bc square c to the power 4 dc. Then if you integrate that equation that integration this is a way the standard integration. If you will integrate that equation what you will get? You will come 3 by 4b which is 3 by 2 KT.

Here it will come automatically now you understand the difference of my earlier lecture to these lectures. In my earlier two lectures if you remember correctly their temperature was a purely foreign concept. The concept of temperature has come from the experimental equation of state. From there we have made a statement that the average kinetic energy is a interpretation of the average kinetic energy as a temperature. But here the average values of kinetic energy will come automatically the temperature has come that is the beauty of it.

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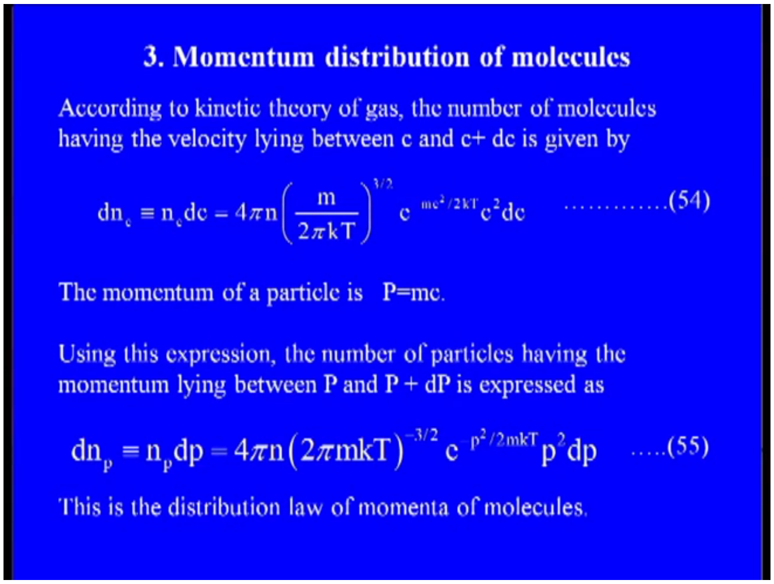

3. Momentum distribution of molecules

According to kinetic theory of gas, the number of molecules having the velocity lying between c and c+ dc is given by

$$dn_c \equiv n_c dc = 4\pi n\left(\frac{m}{2\pi kT}\right)^{3/2} c^{mc^2/2kT} c^2 dc \quad \text{............(54)}$$

The momentum of a particle is P=mc.

Using this expression, the number of particles having the momentum lying between P and P + dP is expressed as

$$dn_p \equiv n_p dp = 4\pi n\left(2\pi mkT\right)^{-3/2} c^{-p^2/2mkT} p^2 dp \quad \text{.....(55)}$$

This is the distribution law of momenta of molecules.

Third thing we want to calculate what is the momentum distribution of particles of molecules? Suppose somebody could ask what is the probability of finding the molecule having momentum P and P + dP. So, answer is very straightforward if you know from the distribution of velocities that means Maxwell's law of distribution of velocities tells that velocity of molecules having velocity V and V + dV.

So, just you know velocity and momentum at least for non relativistic particle II you know the relation between momentum and velocity P mass times velocity just you rewrite the Maxwell distribution of velocity in terms of the coordinate in terms of the vehicle momentum. So, you will get the Maxwell distribution of the moment of the particle. So, that is what we are going to do it.

So, according to kinetic theory of gases the number of molecules having the velocity lying between c and c + dc is given as dN c = nc time dc which is 4 Pi n m by 2 Pi KT to the power 3 by 2 e to the - mc square by 2 KT dc c square dc. The momentum of a particle is mass times velocity here mass times velocity c, please do not confuse this c with the velocity of light in free space, since we have no other options left, so we are forced to use the velocity c.

These velocities completely the velocity which is nothing to receive velocity of light in free space, so be careful. So, otherwise you cannot write P = m times c as you know this is the purely non relativistic expression. Using this expression the number of particles having the momentum line between P and + dP is expressed as np dnp = np dp is 4 Pi n 2 Pi mKT to the power - 3 by 2 e to the power - p square by 2 mKT into p square dp. This is the distribution law of momenta of molecules.

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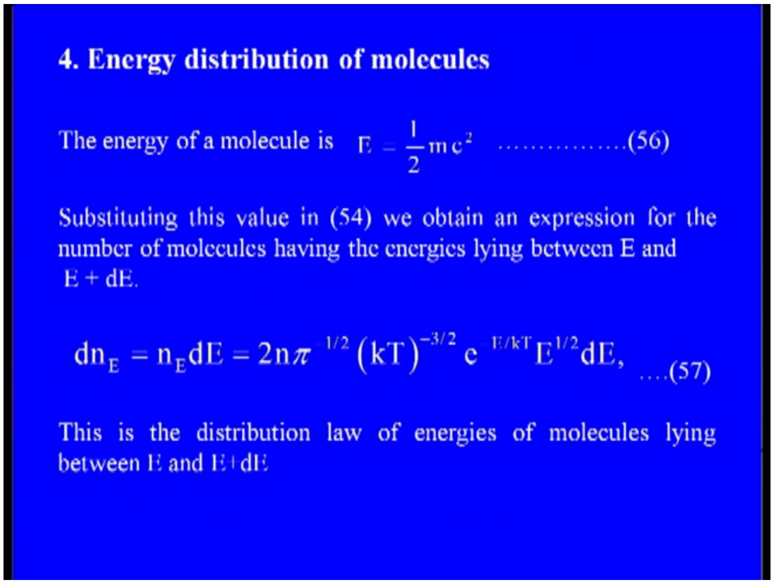

4. Energy distribution of molecules

The energy of a molecule is $E = \frac{1}{2} m c^2$ ……………(56)

Substituting this value in (54) we obtain an expression for the number of molecules having the energies lying between E and E + dE.

$$dn_E = n_E dE = 2n\pi^{-1/2} (kT)^{-3/2} e^{-E/kT} E^{1/2} dE, \quad \ldots(57)$$

This is the distribution law of energies of molecules lying between E and E+dE

Fourth, Energy distribution of molecules, now somebody could ask no I am not interested the velocity distribution of molecules, I have not interested the momentum distribution of molecules, I know the energy you tell me what are the number of particles having energy E and E + dE ok. So, let me so energy of a molecule obviously in that case we assume that they are non interacting in the sense and that there are no interactions among them.

So, that means E energy is nothing but the kinetic energy however we can incorporate the potential energy also means we can incorporate the interaction among them also. So, we will do it in the next couple of minutes. The energy of a molecule is half E = half mc square and the interaction among them I have not been incorporated. So, if you will substitute this E = half mc square in the velocity in the Maxwell distribution of velocities.

We obtain an expression, so if you will substitute in the equation 54 we will get; so, number of molecules having the energies between E and E + dE is dnE = nE dE = 2n Pi to the power - half KT to the power -3 by 2 E to the power - e by KT it is your half dE. This is the distribution law of energies or molecules lying between E and E + dE. So, finally we have got Maxwell distribution of velocities, Maxwell distribution of momentum and Maxwell distribution of energy.

So, depending on the situation we can use the Maxwell distribution law. If I needed the Maxwell distribution of velocity then I will use that. If I need Maxwell distribution of energy then I will use that expression. So, depending on the situation I will use the Maxwell distribution law, for velocities, for momentum, for energy okay. So, now I will ask a very fundamental; I would like to address a very fundamental question is suppose if the available energy of the system is E.

So, then may I address a question how this energy is distributed among its different degrees of freedom. This is a very fundamental question which can be asked to somebody. So, if the available energy of the system, if the system as a thermal equilibrium or at commonly at equilibrium then how this available energy of the system which is maintained at equilibrium is distributed among its different degrees of freedom.

So, let me start; let me first discuss what are the degrees of freedom for the different system, so let me understand what are the different degrees of freedom for the different systems okay.

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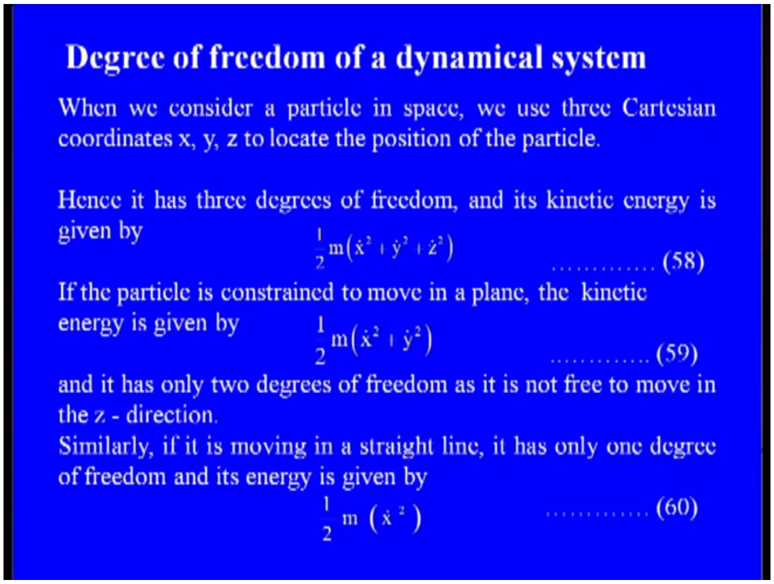

Degree of freedom of a dynamical system

When we consider a particle in space, we use three Cartesian coordinates x, y, z to locate the position of the particle.

Hence it has three degrees of freedom, and its kinetic energy is given by

$$\frac{1}{2}m\left(\dot{x}^2+\dot{y}^2+\dot{z}^2\right) \quad \text{............ (58)}$$

If the particle is constrained to move in a plane, the kinetic energy is given by

$$\frac{1}{2}m\left(\dot{x}^2+\dot{y}^2\right) \quad \text{............ (59)}$$

and it has only two degrees of freedom as it is not free to move in the z - direction.

Similarly, if it is moving in a straight line, it has only one degree of freedom and its energy is given by

$$\frac{1}{2}m\left(\dot{x}^2\right) \quad \text{............ (60)}$$

When we consider a particle in space we use three Cartesian coordinates x, y, z to locate the position of the particle hence it has three degrees of freedom. So, it is kinetic energy is given as half m x dot square + y dot square + z dot square which is nothing but the summed over the kinetic energy in the x direction, y direction and z direction respectively half mx dot square is the kinetic energy in the x direction, half my dot square is the kinetic energy in the y direction etcetera.

Suppose if the particle is constant to move in a flame the kinetic energy is given by half mx dot square + y dot square. So, it has only two degrees of freedom as it is not free to move in all direction in this case not in the z direction. So, it has only two degrees of freedom. So, similarly if it is moving in a straight line it has only one degree of freedom and its energy is given by the kinetic energy in the x direction itself.

So, degrees of freedom of a dynamical system will be given by the motion of the particular system in which in dimension. Suppose if its motion is a three dimensional then its degrees of freedom is 3, if the motion is constrained to move in a plane then its degrees of freedom is 2, if the particle is moving in a straight line then the degrees of freedom is 1.

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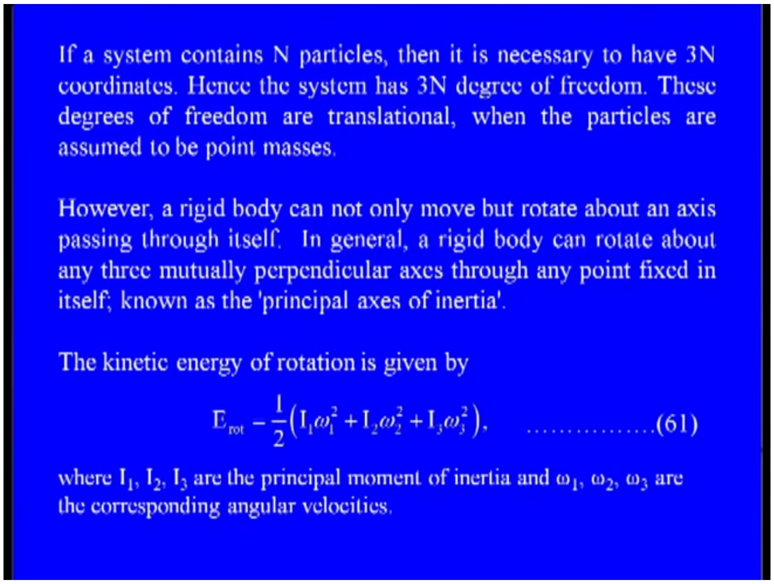

If a system contains N particles, then it is necessary to have 3N coordinates. Hence the system has 3N degree of freedom. These degrees of freedom are translational, when the particles are assumed to be point masses.

However, a rigid body can not only move but rotate about an axis passing through itself. In general, a rigid body can rotate about any three mutually perpendicular axes through any point fixed in itself; known as the 'principal axes of inertia'.

The kinetic energy of rotation is given by

$$E_{rot} = \frac{1}{2}\left(I_1\omega_1^2 + I_2\omega_2^2 + I_3\omega_3^2\right), \qquad \ldots\ldots\ldots\ldots\ldots(61)$$

where I_1, I_2, I_3 are the principal moment of inertia and ω_1, ω_2, ω_3 are the corresponding angular velocities.

If this system contains N particles then it is necessary to have 3N coordinates hence this system has 3N degrees of freedom these degrees of freedom are translational when the particles are assumed to be point masses okay. So, suppose a for a monatomic gas; so if it consists of N number of monatomic N number of molecules or atoms are there so all these are I have these are only translational degrees of freedom.

Since each atoms of molecules has three degrees of freedom so there are N molecule, so there will be 3N degrees of freedom will be there. However a rigid body cannot, can not only move but rotate about an axis passing through itself. In general a rigid body can rotate about any three mutually perpendicular axis through any point fixed in itself known as the principal axis of inertia.

So, the kinetic energy of rotation is given as E rot = half I1 Omega 1 square + I2 Omega 2 square + I3 Omega 3 square where I1, I2, I3 are the principal moment of inertia and Omega 1, Omega 2, Omega 3 are the corresponding angular velocity. Obviously means that Omega 1 is the angular velocity in the direction x axis keeping y and z direction fixed. Similarly Omega 2, Omega 3 represents the angular velocities 1 and 2 axis fixed respectively.

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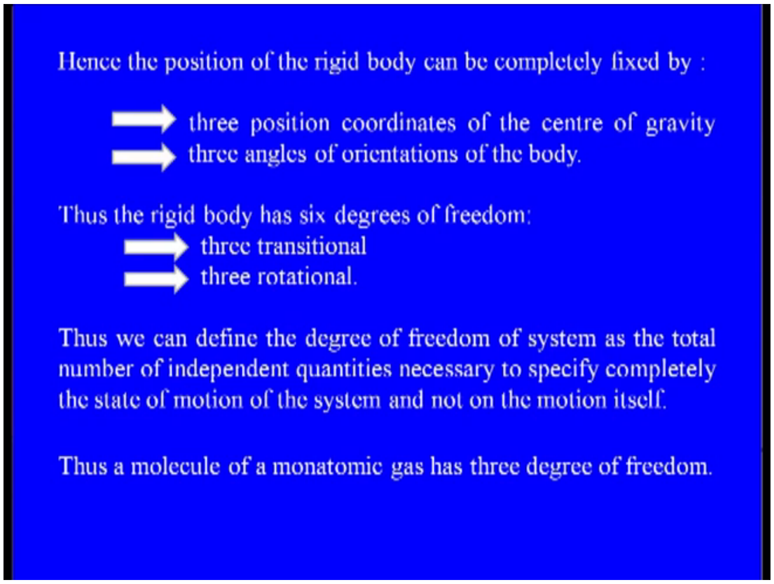

Hence the position of the rigid body can be completely fixed by :

→ three position coordinates of the centre of gravity
→ three angles of orientations of the body.

Thus the rigid body has six degrees of freedom:

→ three transitional
→ three rotational.

Thus we can define the degree of freedom of system as the total number of independent quantities necessary to specify completely the state of motion of the system and not on the motion itself.

Thus a molecule of a monatomic gas has three degree of freedom.

Hence the position of the rigid body can be completely fixed by three position coordinates of the center of gravity three angles of orientation of the body thus the rigid body has 6 degrees of freedom in which there are 3 translational degrees of freedom 3 rotational degrees of freedom. So, there will be 2 energy, 1 energy will be associated with the translational degrees of freedom. Other energy will be associated with the rotational degrees of freedom.

Thus we can define the degrees of freedom of the system as the total number of independent quantities necessary to specify completely the state of motion of the system and not on the motion itself. Thus a molecule of a monatomic gas has 3 degrees of freedom only and which are translational in character.

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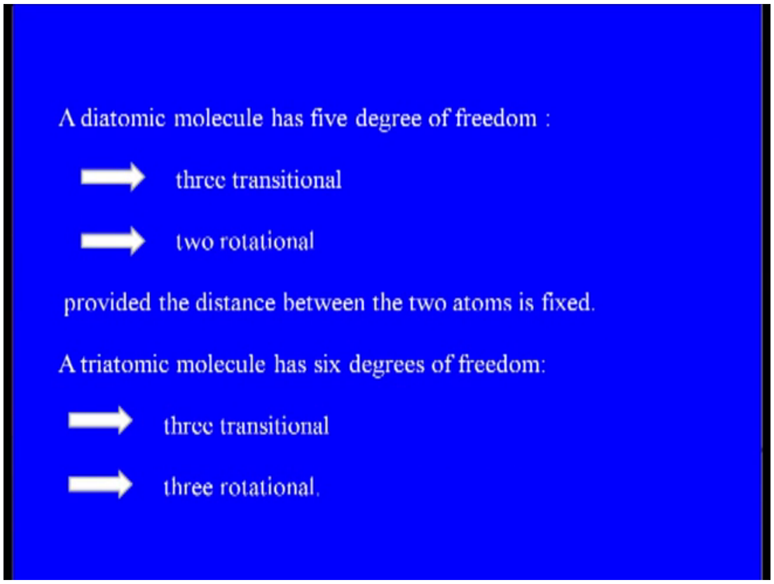

A diatomic molecule has five degree of freedom :

- three transitional
- two rotational

provided the distance between the two atoms is fixed.

A triatomic molecule has six degrees of freedom:

- three transitional
- three rotational.

Diatomic molecules have 5 degrees of freedom where there will be 3 translational and 2 rotational provided the relative separation between the two atoms which forms a diatomic gas are kept constant. A tri atomic molecule has 6 degrees of freedom where 3 translational and 3 rotational. So, let me summarize once again a monatomic gas has three degrees of freedom which are only translational.

A diatomic gas has 5 degrees of freedom where 3 translational and 2 rotational and tri atomic gas has 6 degrees of freedom where 3 are translational and another 3 are rotational. Extension of Maxwell distribution law as we have already told you that whatever we have derived Maxwell distribution law of velocities momentum and energy. It is only for the translational motion but now for a rigid body suppose for a diatomic gas tri-atomic gas or in general for any polyatomic gas.

It has all energy is translational as well as kinetic energy. So, let me derive Maxwell's distribution law for any diatomic or any polyatomic gases okay.

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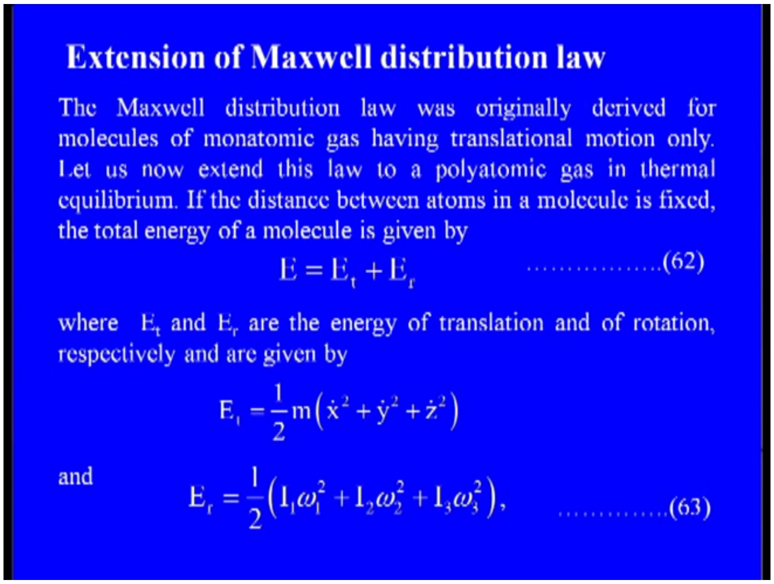

Extension of Maxwell distribution law

The Maxwell distribution law was originally derived for molecules of monatomic gas having translational motion only. Let us now extend this law to a polyatomic gas in thermal equilibrium. If the distance between atoms in a molecule is fixed, the total energy of a molecule is given by

$$E = E_t + E_r \qquad \text{.................}(62)$$

where E_t and E_r are the energy of translation and of rotation, respectively and are given by

$$E_t = \frac{1}{2}m\left(\dot{x}^2 + \dot{y}^2 + \dot{z}^2\right)$$

and

$$E_r = \frac{1}{2}\left(I_1\omega_1^2 + I_2\omega_2^2 + I_3\omega_3^2\right), \qquad \text{..............}(63)$$

The Maxwell distribution law was originally derived for molecules of monatomic gas having translational motion only. Let us now extend this law to a polyatomic gas in thermal equilibrium. If the distance between atoms in a molecule is fixed the total energy of a molecule is given by E = Et + Ef. So, in principle for any polyatomic gas the total energy consists of two parts. One is due to the translational motion another is due to the rotational motion.

Where the energy of the translational and rotational are given as follows Et = half mx dot square + y dot square + z dot square and Er is 1/2 I1 Omega 1 square + I2 Omega 2 square + I3 Omega 3 square. So, these are the 2 energies rotational and translational motion.

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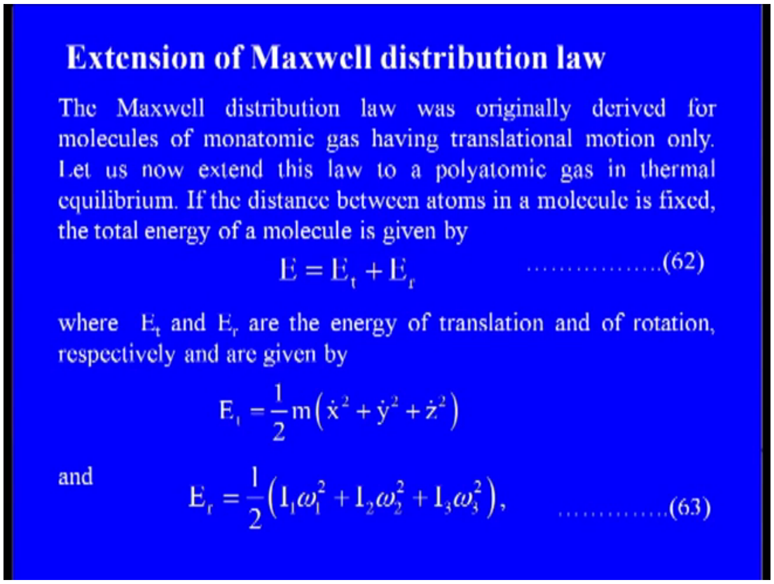

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and

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The molecules of the gas will collide with one another and the energy corresponding to any degree of freedom for a molecule will vary from 0 to infinity. So, therefore we can extend the distribution to include the other modes of motion. So, in case of polyatomic gas the probability distribution for velocity can be modified as follows dW = at into ar exponents E to the power - Et + Er by KT dx dy dz d Omega1 d Omega2 d Omega3.

It is actually product of 2 terms one is due to the translational motion another is due to the rotational motion okay where at as we know already which is m by 2 Pi KT to the power half, ar is nothing but I1 by 2Pi KT to the power half I2 by 2 Pi KT to the power half I3 by 2 Pi KT to the power half. As we know that moment of inertia I is the equivalent of mass in the translational motion. So, that is there is an at consists of product of 3 terms I1 by 2 Pi KT to the power I2 by 2 Pi KT to the power half I3 by 2 Pi KT to the power of half.

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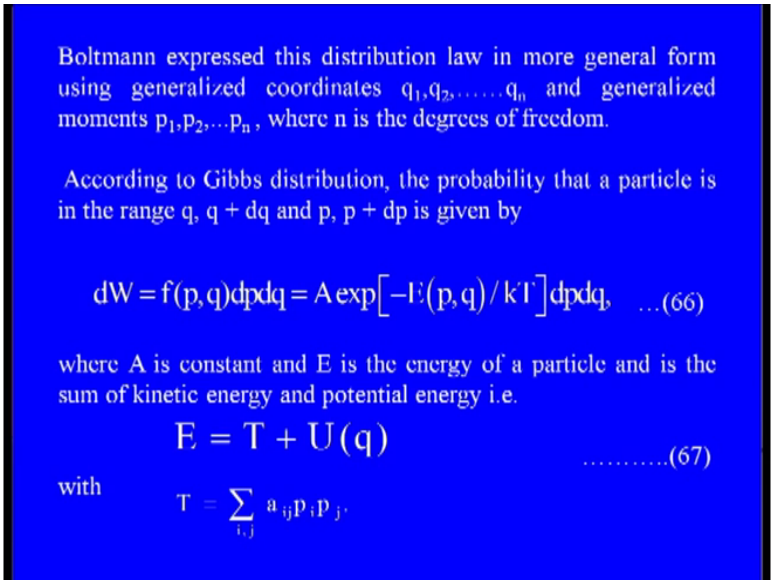

Boltzmann expressed this distribution law in more general form using generalized coordinates $q_1, q_2, \ldots\ldots q_n$ and generalized moments $p_1, p_2, \ldots p_n$, where n is the degrees of freedom.

According to Gibbs distribution, the probability that a particle is in the range q, q + dq and p, p + dp is given by

$$dW = f(p,q)dpdq = A\exp\left[-E(p,q)/kT\right]dpdq, \quad \ldots(66)$$

where A is constant and E is the energy of a particle and is the sum of kinetic energy and potential energy i.e.

$$E = T + U(q) \quad \ldots\ldots\ldots\ldots(67)$$

with

$$T = \sum_{i,j} a_{ij} p_i p_j.$$

Boltzmann expressed this distribution law in more general form using generalized coordinates q1, q2, q3, qn and generalized momenta p1, p2, p3, pn where n is the number of degrees of freedom. According to Gibbs distribution the probability that a particle in the range q and q + dq, p and p + dp is given as dW is f of pq dp dq which is nothing but the ae to the power of - E as a function of pq by KT dp dq where A constant and E is the energy of a particle.

And is the sum of kinetic energy and potential energy that is E = T + U of q with T is nothing or T is summed over I,j a ij, pi, into pj.

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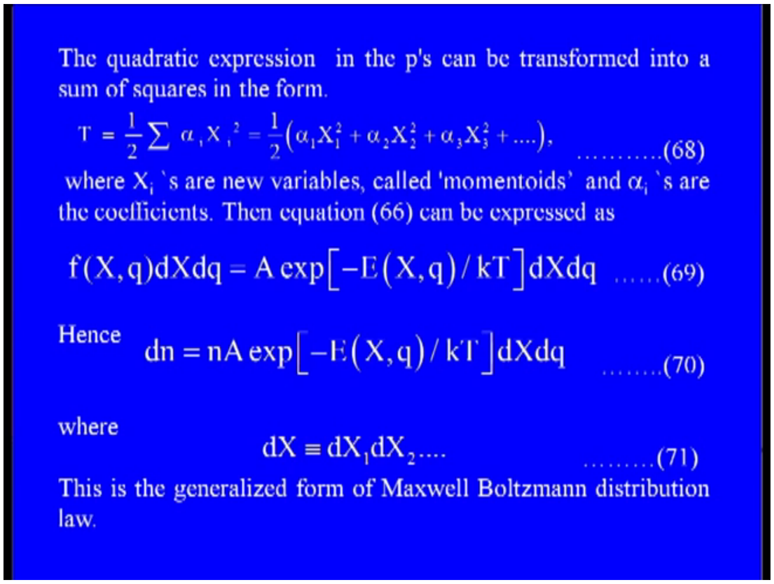

The quadratic expression in the p's can be transformed into a sum of squares in the form.

$$T = \frac{1}{2}\sum \alpha_i X_i^2 = \frac{1}{2}\left(\alpha_1 X_1^2 + \alpha_2 X_2^2 + \alpha_3 X_3^2 + ...\right), \qquad ....(68)$$

where X_i `s are new variables, called 'momentoids' and $\alpha_i$ `s are the coefficients. Then equation (66) can be expressed as

$$f(X,q)dXdq = A\exp\left[-E(X,q)/kT\right]dXdq \qquad ......(69)$$

Hence

$$dn = nA\exp\left[-E(X,q)/kT\right]dXdq \qquad ....(70)$$

where

$$dX \equiv dX_1 dX_2.... \qquad ....(71)$$

This is the generalized form of Maxwell Boltzmann distribution law.

The quadratic expression in the piece can be transformed into a sum of squares in the form which can be written as T = half summed over alpha Xi square, if you split the summer sum then it is half alpha 1 X1 square + alpha 2 X2 square + alpha 3 X3 square where Xi’s are the new variables called the momentiod and alpha I are the coefficient. So, that is the beauty in terms of coding is written as summed over aij is a product of pi pj.

Which can be written as a square of some term, so that it can be easily handled, so, in terms of new variables f of Xq, Xq dX dq is A exponential - E of Xq by KT dX dq where dn is nA exponential - E by KT dX dq where dX is dX1 dX2 dX3 dXn. This is the generalized form of Maxwell distribution law. Now let us see what will happen in case of some ordinary Cartesian coordinates.

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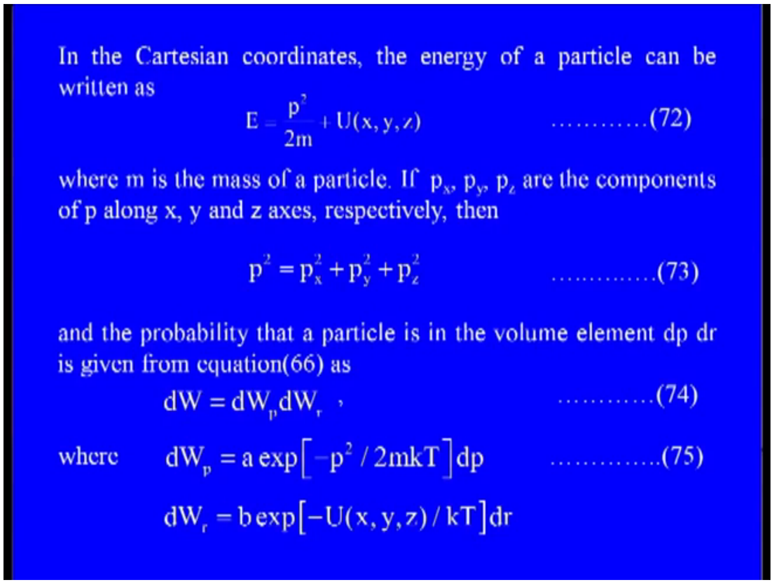

In the Cartesian coordinates, the energy of a particle can be written as

$$E = \frac{p^2}{2m} + U(x, y, z) \qquad \text{...........(72)}$$

where m is the mass of a particle. If p_x, p_y, p_z are the components of p along x, y and z axes, respectively, then

$$p^2 = p_x^2 + p_y^2 + p_z^2 \qquad \text{.............(73)}$$

and the probability that a particle is in the volume element dp dr is given from equation(66) as

$$dW = dW_p dW_r \qquad \text{...........(74)}$$

where

$$dW_p = a\exp\left[-p^2 / 2mkT\right]dp \qquad \text{.............(75)}$$

$$dW_r = b\exp\left[-U(x, y, z)/kT\right]dr$$

In the Cartesian coordinates the inertia of a particle can be written as E = p square by 2m + U of x, y, z for p square by 2m is the kinetic energy. U of x, y, z dz measure of interaction or potential energy, if px, py, pz are the components of p along x, y, z direction and then p square is px square + py square + pz square and the probability that a particle is in the volume element dp into dr, dp means in the volume element in the momentum space.

dr is the volume element in the coordinate space is given by dW = dWp into dWr, dWp in the momentum space dWr in the coordinate space where dWp is a e to the power of -p square by 2 mKT dp where dwr is be to the power of –U by KT dr.

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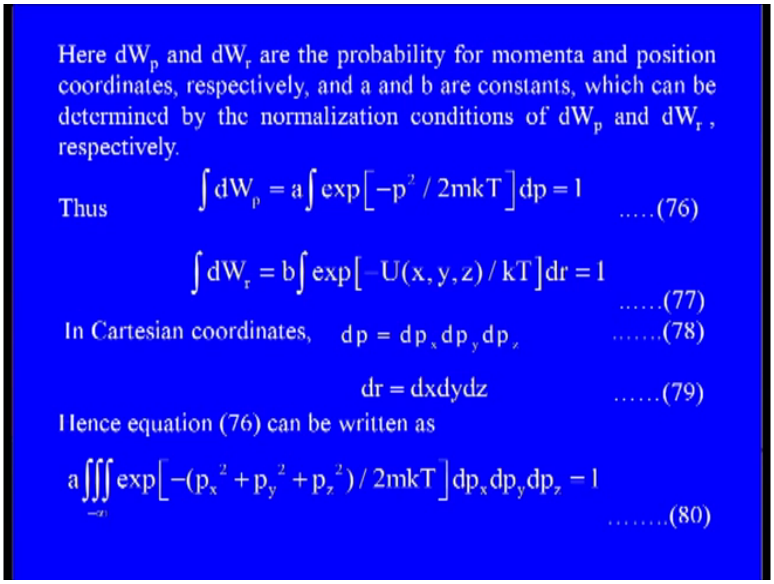

Here dW_p and dW_r are the probability for momenta and position coordinates, respectively, and a and b are constants, which can be determined by the normalization conditions of dW_p and dW_r, respectively.

Thus

$$\int dW_p = a\int \exp\left[-p^2 / 2mkT\right]dp = 1 \qquad \text{.....(76)}$$

$$\int dW_r = b\int \exp\left[-U(x, y, z)/kT\right]dr = 1 \qquad \text{......(77)}$$

In Cartesian coordinates,

$$dp = dp_x dp_y dp_z \qquad \text{.......(78)}$$

$$dr = dxdydz \qquad \text{......(79)}$$

Hence equation (76) can be written as

$$a\iiint_{-\infty} \exp\left[-(p_x^{\,2} + p_y^{\,2} + p_z^{\,2})/2mkT\right]dp_x dp_y dp_z = 1 \qquad \text{........(80)}$$

Here dWp and dWr are the probability of moment and position coordinates respectively and a and b are the constant which can be determined by the normalization conditions of dWp and dWr respectively. First normalization condition is integral dWp = 1, if we will substitute values of dWp then it will come a to the power -p square by 2mKT dP = 1, second normalization condition is integral dWr =1 if you will put the values of dWr then it will come b e to the power –U byKT dr = 1.

So, the in Cartesian coordinate dp is dpx, dpy, dpz, dr is nothing but the dx, dy, dz. So, if you will substitute these values. So, first equation, equation number is 76 in integral dWp will come out a integral - infinity to + infinity e to the power of -px square + py square + pz square by 2 mKT dpx, dpy, dpz integrating over all momentum values = 1.

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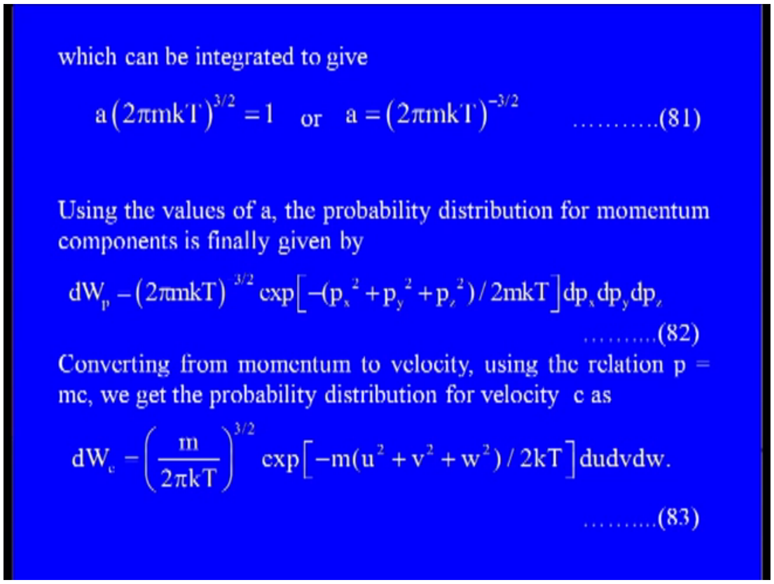

which can be integrated to give

$$a(2\pi mkT)^{3/2} = 1 \quad \text{or} \quad a = (2\pi mkT)^{-3/2} \qquad \ldots\ldots\ldots\ldots(81)$$

Using the values of a, the probability distribution for momentum components is finally given by

$$dW_p = (2\pi mkT)^{-3/2} \exp\left[-(p_x^2 + p_y^2 + p_z^2)/2mkT\right] dp_x dp_y dp_z \qquad \ldots\ldots\ldots\ldots(82)$$

Converting from momentum to velocity, using the relation p = mc, we get the probability distribution for velocity c as

$$dW_c = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left[-m(u^2 + v^2 + w^2)/2kT\right] dudvdw. \qquad \ldots\ldots\ldots\ldots(83)$$

This will give the values of a, a is nothing but the 2 Pi mKT to the power of - half which is understandable. Because in one dimension a is 1 by 2 Pi mKT in three dimension obviously it is a product of three quantities so a is 1 by 2 Pi mKT to the power 3 by 2. Using the values of a the product distribution for momentum components is finally given as dWp is 2 Pi mKT to the power 3 by 2 e to the power - px square + py square + pz square by 2 mKT dpx dpy dpz.

So, this is the probability distribution for momentum component. So, converting momentum to velocity using the relation momentum equal to mass times velocity. We get the fall distribution for velocity as dWc means probability of Miller's having the velocity c is dWc is m by 2 Pi KT to the 3 by 2 exponential e to the power of -m u square + v square + w square by 2 KT du dv dw where u, v, w as we have already told earlier is the velocity component in the along x, y, z direction. So, px is nothing but the m times u, py is nothing but the m times v, pz is nothing but the m times w.

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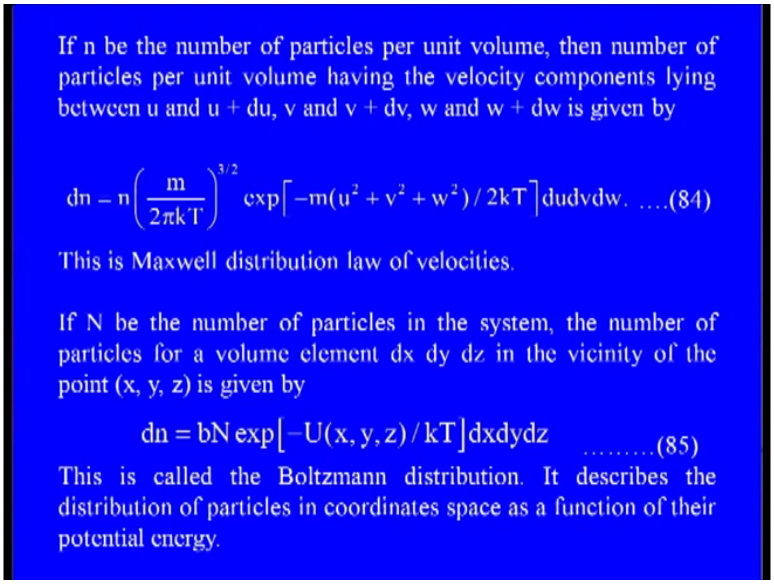

If n be the number of particles per unit volume, then number of particles per unit volume having the velocity components lying between u and u + du, v and v + dv, w and w + dw is given by

$$dn = n\left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left[-m(u^2+v^2+w^2)/2kT\right]dudvdw. \quad \ldots.(84)$$

This is Maxwell distribution law of velocities.

If N be the number of particles in the system, the number of particles for a volume element dx dy dz in the vicinity of the point (x, y, z) is given by

$$dn = bN\exp\left[-U(x,y,z)/kT\right]dxdydz \quad \ldots\ldots\ldots(85)$$

This is called the Boltzmann distribution. It describes the distribution of particles in coordinates space as a function of their potential energy.

If the; now n be the number of particles per unit volume then number of particles per unit volume having the velocity components lying between u and u + du, v and v +dv, w and w + dw is given as dn is n times m by 2 Pi KT to the power 3 by 2 e to the power of -m u square + v square + w square by 2 KT du dv dw this is the Maxwell distribution law of velocities. Now let me calculate what is the probability in the coordinate space? Okay.

When dWr we have to calculate, if N be the number of particles in the system, the number of particles for a volume element dx, dy, dz in the vicinity of the point xyz is given as dn = b times Ne to the power of - e of x y z by KT dx dy dz this is called the Boltzmann distribution. It describes the distribution of particles in the coordinate space as a function of their potential energy.

Basically whenever we have extended the Maxwell's law so we have got two kinds of Maxwell distribution want one tells the Maxwell distribution of velocities or momentum in the momentum space or velocity space which are almost same. So, another distribution Maxwell distribution which is in the coordinate space, what is the fault of finding particle between x and x + dx, y and y + dy, z and z + dz okay, which will be driven by its potential energy okay.

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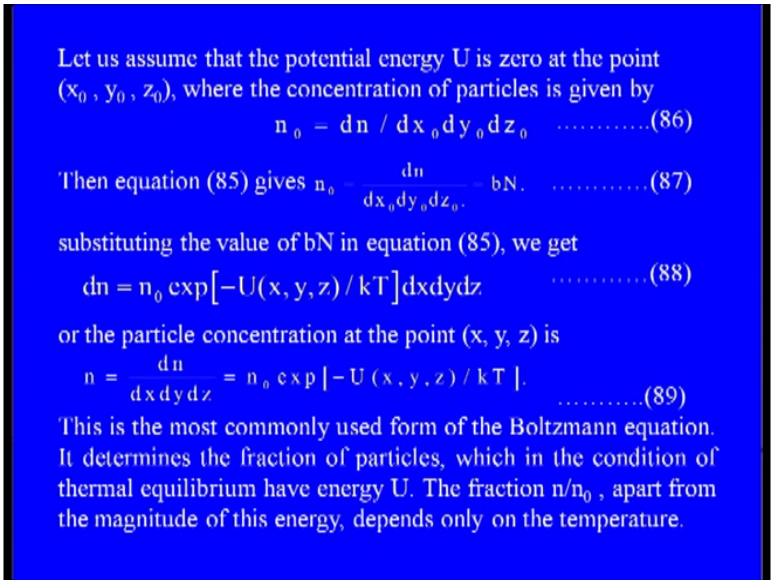

Let us assume that the potential energy U is zero at the point (x_0, y_0, z_0), where the concentration of particles is given by

$$n_0 = dn / dx_0 dy_0 dz_0 \quad \text{...........(86)}$$

Then equation (85) gives $n_0 = \frac{dn}{dx_0 dy_0 dz_0} = bN.$ ....(87)

substituting the value of bN in equation (85), we get

$$dn = n_0 \exp\left[-U(x, y, z) / kT\right] dxdydz \quad \text{...........(88)}$$

or the particle concentration at the point (x, y, z) is

$$n = \frac{dn}{dxdydz} = n_0 \exp\left[-U(x, y, z) / kT\right]. \quad \text{...........(89)}$$

This is the most commonly used form of the Boltzmann equation. It determines the fraction of particles, which in the condition of thermal equilibrium have energy U. The fraction n/n_0, apart from the magnitude of this energy, depends only on the temperature.

Let us assume that the potential energy U is 0 at the point some reference point which is x naught, y naught, z naught. What the concentration of the particle is given by n naught is dn by dx naught dy naught dz naught which is the volume element around that point x naught y naught z naught. Then from this above equation dn = bn e to the - of U by K T dx dy dz then n naught will be given as dn by dx naught, dy naught, dz naught which is nothing but the bn.

Then or other way around b naught b into n is nothing but the n naught then you substitute the values of bn in equation number 85 what you will get is dn is n naught e to the power of -U by KT dx dy dz or the particle concentration at the point x y z is nothing but n is dn by dx dy dz = n naught e to the power of -U by KT where n naught is the particle concentration at some reference point where potential energy was zero.

So, if some point potential energy 0, if the particle concentration is n then one can ask what is the concentration of particle at some arbitrary point xyz where the potential energy U is as a function of xyz then Maxwell distribution tells that n is n naught e to the power of -U by KT. So, that means the concentration of particle at some particular point will be driven by its potential energy at that particular point.

So, finally the particle concentration of a system having at having at equilibrium at the point xyz is n = n naught e to the minus of –U by KT this is the most commonly used form of Boltzmann equation. It determines the fraction of particles who is in the condition of thermal equilibrium have energy U. The fraction n by n naught apart from the magnitude of this energy depends only on the temperature that is the beauty ok.