



**Discipline Course-I
Semester-II**

Paper No: Thermal Physics : Physics-IIA

Lesson: Maxwell law of Distribution of velocities

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Maxwell Law of Distribution of velocities

Learning Objectives

After reading the lesson, you should be able to

- 1) understand the basis of kinetic theory of gases.
- 2) develop the concept of nature of molecules of a gas.
- 3) understand the phenomena of distribution of velocities.
- 4) answer the questions of interest to physicists and engineers.
- 5) apply your knowledge to the practical life.



Chapter: Title Maxwell Law of Distribution of velocities

1.1 Introduction Three states of matter are well known: solid, liquid and gas. Out of these three states, gaseous state is the simplest state. This state is governed by various definite laws. A gas has certain properties such as temperature, pressure, energy etc. These properties are characteristic of the gas as a whole rather than of its individual molecules. Bernoulli in 1738 explained kinetic theory. This theory takes into account various assumptions which explain the reasons gases act the way they do.

1.2 Kinetic theory of gases The kinetic theory of gases are based on two fundamental hypotheses: a) molecular constitution of matter b) the movement of molecules correlating with the term heat.

According to kinetic theory:

1. Pure gases are made up of a large number of identical molecules, all of the same mass.
2. During the motion, molecules collide with each other and also with the walls of the container. The collisions are perfectly elastic so that kinetic energy is not lost in the collisions.
3. The bombardment of the container walls by the molecules will lead to pressure i.e. the rate of change of momentum per unit surface area of the walls.
4. The molecules in their motion collide with each other and with the walls of the container and thus their speeds and directions will vary continuously.
5. The molecules exert no forces on each other except when they collide which means that the energy of the gas is wholly kinetic.
6. Lighter gas molecules move faster than heavier molecules.
7. The molecules are continuously colliding with each other. The distance between any two consecutive collisions is called free path and the average distance travelled by a molecule between two successive collisions is called mean free path.
8. The duration of collision is negligible compared with the time taken to traverse the free path. Thus the collisions are instantaneous.
9. Particles are point masses with no volume. Since the size of the molecules is small compared with the distances between them, their volumes may be considered to be negligible compared with the total volume of the gas.

1.3 Maxwell's law of Distribution of Velocities

According to Maxwell law of distribution of velocities, there is a steady state in which a certain number of molecules maintain their original velocity within a narrow range of values inspite of collision.

First of all, the gas molecules are assumed to obey some conditions which are as follows:

- a) According to kinetic theory, a gas consists of a large number of molecules so that the number of molecules in each area is the same.

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- b) The molecules have same velocities in all possible directions.
- c) The probability that any molecule selected at random have velocities lying between certain limits depend on the velocity and the limits considered.
- d) The velocities along the three perpendicular coordinate axes are not dependent on each other.

In Fig 1.1 we have shown a velocity diagram where O is the origin and OX , OY , OZ are the coordinate axes. Consider a velocity vector, say u , split into components u_x, u_y, u_z along X , Y and Z axes respectively and

$$u^2 = u_x^2 + u_y^2 + u_z^2 \quad (1)$$

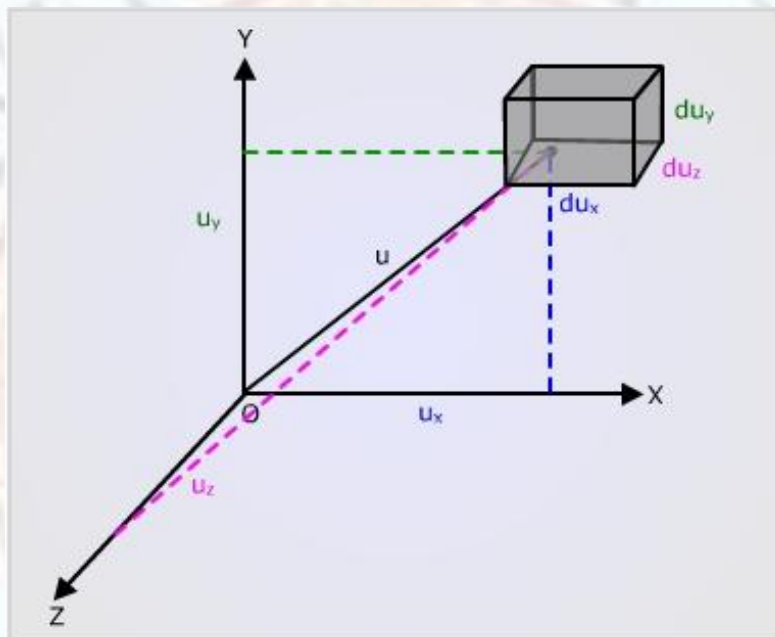


Fig 1.1

$f(u_x) du_x$ is the probability that a given molecule will have its velocity lying between u_x and $u_x + du_x$. We know that the probability of a composite event is equal to the product of the probabilities of individual and independent events, so probability that a molecule may have its velocity components lying between u_x and du_x , u_y and du_y , u_z and du_z simultaneously is given by

$$f(u_x) f(u_y) f(u_z) du_x du_y du_z$$

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The probability that single velocity of value u lies in the element of volume $du_x du_y du_z$ is $F(u) du_x du_y du_z$. Considering into account isotropy of the gas, we may write

$$f(u_x) f(u_y) f(u_z) du_x du_y du_z = \sigma(u^2) du_x du_y du_z \quad (2)$$

where σ denotes some function.

$$\text{Using eq(1), } f(u_x) f(u_y) f(u_z) = \sigma(u_x^2 + u_y^2 + u_z^2) \quad (3)$$

Solution of this equation is to be found. For a single value of u selected, $\sigma(u^2)$ is a constant or we get zero after differentiation $d[\sigma(u^2)] = 0$

Differentiating eq(3),

$$f'(u_x) du_x f(u_y) f(u_z) + f'(u_y) du_y f(u_x) f(u_z) + f'(u_z) du_z f(u_x) f(u_y) = 0 \quad (4)$$

Dividing eq(4) by $f(u_x) f(u_y) f(u_z)$, we get

$$\frac{f'(u_x)}{f(u_x)} du_x + \frac{f'(u_y)}{f(u_y)} du_y + \frac{f'(u_z)}{f(u_z)} du_z = 0 \quad (5)$$

Since $u^2 = u_x^2 + u_y^2 + u_z^2$, we can write on differentiation for a fixed value of u as

$$u_x du_x + u_y du_y + u_z du_z = 0 \quad (6)$$

Multiplying eq(6) by an arbitrary constant β and adding the product to eq(5)

$$\left(\frac{f'(u_x)}{f(u_x)} + \beta u_x \right) du_x + \left(\frac{f'(u_y)}{f(u_y)} + \beta u_y \right) du_y + \left(\frac{f'(u_z)}{f(u_z)} + \beta u_z \right) du_z = 0 \quad (7)$$

Since the velocity components u_x, u_y, u_z are assumed to be independent of each other, eq(7) can be satisfied only if each of the term is separately equal to zero.

$$\text{So, } \frac{f'(u_x)}{f(u_x)} du_x = -\beta u_x du_x \quad (8a)$$

$$\frac{f'(u_y)}{f(u_y)} du_y = -\beta u_y du_y \quad (8b)$$

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$$\frac{f'(u_z)}{f(u_z)} du_z = -\beta u_z du_z \quad (8c)$$

Integrating the eq(8a) with respect to u_x , we get

$$\log f(u_x) = -\frac{\beta u_x^2}{2} + \log a \quad (9)$$

where a is constant or $\log \frac{f(u_x)}{a} = -\frac{\beta u_x^2}{2}$

$$f(u_x) = a e^{-\frac{\beta u_x^2}{2}} = a e^{-b u_x^2} \quad (10a)$$

where $b = \frac{\beta}{2}$ is a constant. Similarly, $f(u_y)$ and $f(u_z)$ becomes

$$f(u_y) = a e^{-b u_y^2} \quad (10b)$$

$$f(u_z) = a e^{-b u_z^2} \quad (10c)$$

From eq (10a), (10b) and (10c), we can write

$$f(u_x) f(u_y) f(u_z) = a^3 e^{-b(u_x^2 + u_y^2 + u_z^2)} \quad (11)$$

Probability that a molecule has the velocity between u_x and $u_x + du_x$ is given by

$$f(u_x) du_x = a e^{-b u_x^2} du_x \quad (12)$$

This distribution law expressed is represented graphically in Fig 1.2. In this Fig, we have plotted e^{-x^2} against x .

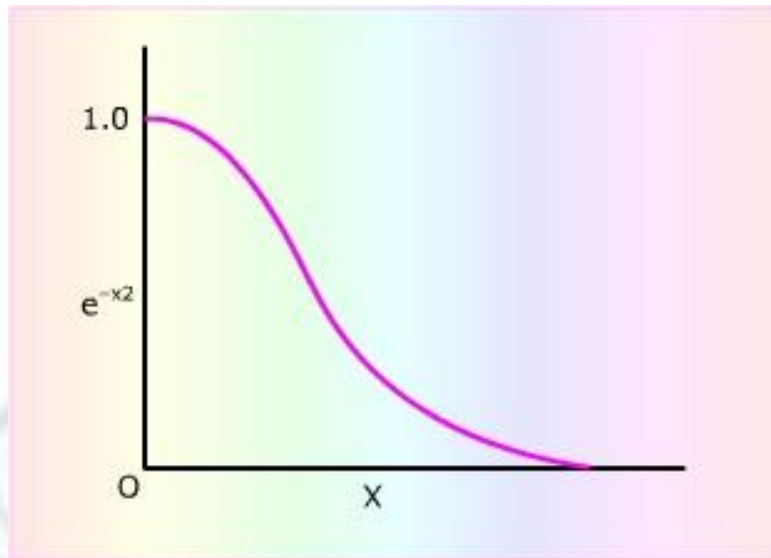


Fig 1.2

1.4 Determination of constants a and b

Consider a gas having n number of molecules per c.c. of the gas with all possible velocities from $-\infty$ to $+\infty$. Then the number of molecules per c.c. with velocity components between u_x and $u_x + du_x$, u_y and $u_y + du_y$, u_z and $u_z + du_z$ is given by $n f(u_x) f(u_y) f(u_z) du_x du_y du_z$. Thus, in limits from $-\infty$ to $+\infty$:

$$\iiint n f(u_x) f(u_y) f(u_z) du_x du_y du_z = n \quad (13)$$

Using eq(11), we can write

$$\iiint a^3 e^{-b(u_x^2 + u_y^2 + u_z^2)} du_x du_y du_z = 1 \quad (14)$$

The value of the definite integral of the form $\int_{-\infty}^{+\infty} e^{-bu_x^2} du_x$ is $\left(\frac{\pi}{b}\right)^{1/2}$.

Put this value in eq (14), value of a comes out to be:

$$a^3 = \left(\frac{b}{\pi}\right)^{3/2}$$

$$a = \left(\frac{b}{\pi}\right)^{1/2} \quad (15)$$

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Consider a vessel having perfect gas and assume the X-axis to be perpendicular to one surface of the enclosure. Here molecule having the velocity component u_x will collide with this surface and get reflected with a velocity $-u_x$ after collision. So, the change in momentum suffered by the molecule during collision is $2mu_x$. The other two components u_y and u_z do not get effected, hence they contribute nothing to the pressure and we can neglect these two.

Now pressure is equal to the change in momentum suffered by the molecule striking per unit area of the wall per second and hence it is equal to $2mu_x$ multiplied by the number of collisions on the surface in unit time. If n_{u_x} is the number of molecules per unit volume having the velocity u_x the number of impacts on area δA in time δt must be equal to $n_{u_x} u_x \delta t \delta A$. Hence the pressure P on the wall, averaged through the time interval δt is given by multiplying change in momentum with these number of impacts.

$$P \delta t \delta A = \sum_{u_x=0}^{\infty} 2mu_x \times n_{u_x} u_x \delta t \delta A \quad (16)$$

$$P = 2m \sum_0^{\infty} n_{u_x} u_x^2 \quad (17)$$

The number of molecules per c.c. having the velocity component lying between u_x and $u_x + du_x$ is given by

$$n_{u_x} = n f(u_x) = na e^{-bu_x^2}$$

Substituting value of a from eq (15), n_{u_x} becomes:

$$n_{u_x} = n \left(\frac{b}{\pi} \right)^{1/2} e^{-bu_x^2} \quad (18)$$

So, pressure given by eq(17) now gets modified to

$$\begin{aligned} P &= 2m \int_0^{\infty} n \left(\frac{b}{\pi} \right)^{1/2} e^{-bu_x^2} u_x^2 du_x \\ &= 2mn \left(\frac{b}{\pi} \right)^{1/2} \int_0^{\infty} e^{-bu_x^2} u_x^2 du_x \end{aligned}$$

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$$P = 2mn \left(\frac{b}{\pi} \right)^{1/2} \frac{1}{4} \left(\frac{\pi}{b^3} \right)^{1/2} = \frac{1}{2} \frac{mn}{b} \quad (19)$$

$$\text{since } \int_0^{\infty} e^{-bu_x^2} u_x^2 du_x = \frac{1}{4} \left(\frac{\pi}{b^3} \right)^{1/2}$$

Pressure given by eq(19) can also be written in terms of k_B as $P = nk_B T$ where k_B is the Boltzmann constant. Therefore,

$$nk_B T = \frac{1}{2} \frac{mn}{b} \quad (20)$$

$$b = \frac{m}{2k_B T}$$

Substituting this value of b in eq (15), we get

$$a = \left(\frac{b}{\pi} \right)^{1/2} = \left(\frac{m}{2\pi k_B T} \right)^{1/2} \quad (21)$$

Thus, the number dn of molecules having velocity components lying between u_x and $u_x + du_x$, u_y and $u_y + du_y$, u_z and $u_z + du_z$ is given by

$$dn = n f(u_x) f(u_y) f(u_z) du_x du_y du_z$$

$$dn = n a^3 e^{-b(u_x^2 + u_y^2 + u_z^2)} du_x du_y du_z$$

$$dn = n \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{m(u_x^2 + u_y^2 + u_z^2)}{2k_B T}} du_x du_y du_z \quad (22)$$

This is Maxwell's distribution law.

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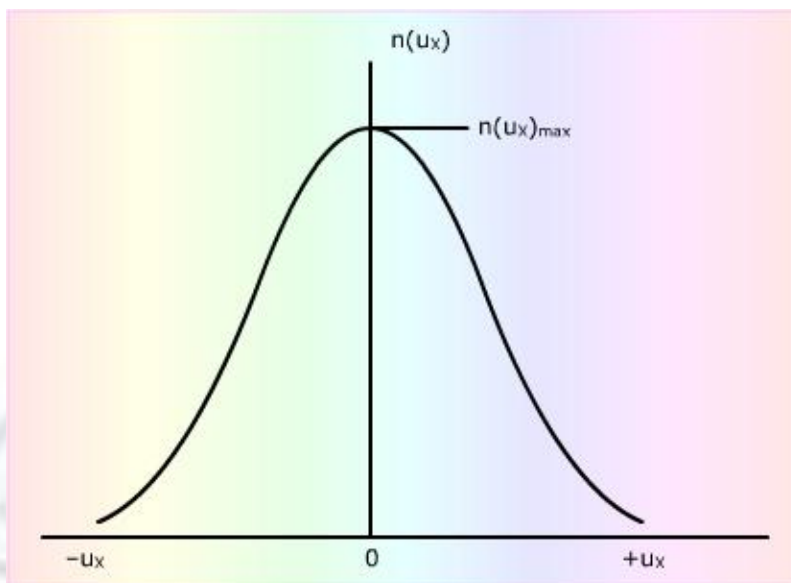


Fig 1.3

1.5 Experimental verification of velocity distribution

Using different methods, measurements of the distribution of velocities in a molecular beam have been done in a direct way. In 1920, Stern developed a technique to measure the velocity distribution, later on in 1930-34, Zartman and Ko described it in a more precise way.

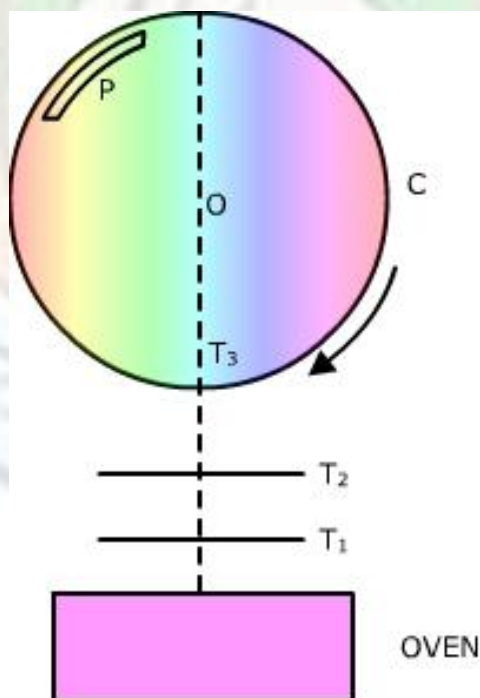


Fig 1.4

Maxwell Law of Distribution of velocities

Consider T_1 and T_2 as slits which are defining a molecular beam. Cylinder C can be rotated (shown clockwise) at approximately 6000 rpm about the axis O . If the cylinder is at rest, the molecular beam enters the cylinder through a slit T_3 and strikes a curved glass plate P . The molecules attach to this plate. The number of molecules reached at any section can be obtained by detaching the plate and the darkening that is achieved is measured with a microphotometer. Then cylinder is made to rotate. Slit T_3 crosses the molecular beam and during this time interval, molecules can enter the cylinder. The glass plate P moves in the right direction while the molecules cross the diameter of the cylinder. The molecules therefore strike the plate at the left of the point of impact when the cylinder is at rest, and the more slowly they travel, the farther to the left is this point of impact. The blackening of the plate is an indication of the 'velocity spectrum' of the molecular beam.

Value Addition:



- ChemWiki BioWiki GeoWiki StatWiki PhysWiki MathWiki SolarWiki
- **Periodic Table of the Elements Reference Tables Physical Constants Units & Conversions Lab Techniques**

Physical Chemistry
Kinetics
Rate Laws
Gas Phase Kinetics
Maxwell-Boltzmann Distributions

ChemWiki: The Dynamic Chemistry E-textbook > Physical Chemistry > Kinetics > Rate Laws > Gas Phase Kinetics > Maxwell-Boltzmann Distributions

Maxwell-Boltzmann Distributions

For more details please click on the link below:

http://chemwiki.ucdavis.edu/Physical_Chemistry/Kinetics/Rate_Laws/Gas_Phase_Kinetics/Maxwell-Boltzmann_Distributions

Maxwell Law of Distribution of velocities

Summary

1. All collision between molecules and with the walls are perfectly elastic so that kinetic energy is not lost in the collisions.
2. The intermolecular distance in a gas is much larger compared to case of solid or liquid and the molecules of a gas are free to move in the entire space available to them.
3. Probability that a molecule has the velocity between u_x and $u_x + du_x$ is given by

$$f(u_x)du_x = ae^{-bu_x^2} du_x$$

4. Maxwell's distribution law is given by $dn = n \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{m}{2k_B T} (u_x^2 + u_y^2 + u_z^2)} du_x du_y du_z$

5. Maxwell-Boltzmann Distribution Law for molecular velocities: This law can be used to calculate the number of molecules having velocity lying between u_x and $u_x + du_x$. It can be expressed as:

$$\frac{dn_u}{n} = 4\pi n a^3 e^{-bu^2} u^2 du$$

Solved Example

Q1 Making use of Maxwell-Boltzmann law, deduce the fraction of molecules within momentum range p and $p+dp$.

Sol. According to Maxwell Boltzmann Law,

$$dn_u = 4\pi n a^3 e^{-bu^2} u^2 du \quad (1)$$

$$\frac{dn_u}{n} = f(u) du = 4\pi a^3 e^{-bu^2} u^2 du \quad (2)$$

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We know momentum is the product of mass and velocity i.e. $p = mu$. Using this eq(2) gets modified to

$$f(p) dp = 4\pi \frac{a^3}{m^3} e^{-\frac{b p^2}{m^2}} p^2 dp \quad (3)$$

Since constants a and b are given by $a = \sqrt{\frac{m}{2\pi k_B T}}$ and $b = \frac{m}{2k_B T}$, we have

$$f(p) dp = 4\pi \frac{1}{m^3} \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{m p^2}{2k_B T m^2}} p^2 dp$$
$$\Rightarrow f(p) dp = 4\pi \left(\frac{1}{2\pi m k_B T} \right)^{3/2} e^{-\frac{p^2}{2m k_B T}} p^2 dp$$

i.e. the fraction of molecules within the momentum range p and $p+dp$.

Fill in the blanks.

1. The kinetic theory of gases is also known as _____.
2. The duration of collision of molecules is _____ compared with the time taken to traverse the free path.
3. Kinetic theory explains how the different sizes of the particles in a gas can give them _____ speeds.
4. The average kinetic energy of a gas particle is _____ proportional to temperature.
5. While deriving Maxwell derivation of speeds, it is assumed that the molecules have _____ velocities in all possible directions.
6. The root mean square velocity C_{rms} remains the _____ at a fixed value of temperature.
7. The mean kinetic energy of all the molecules remains _____ at a given temperature.
8. Kinetic theory was the first theory to describe gas pressure in terms of _____ with the walls of the container, rather than from static forces that push the molecules apart.
9. According to kinetic theory, all collision between molecules and with the walls are perfectly _____ so that kinetic energy is not lost in the collisions.
10. The kinetic theory of gases is based on identification of _____ with the motion of molecules.

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Answers

1. Kinetic molecular theory 2. negligible 3. different 4. directly 5. same 6. same 7. constant 8. collisions 9. elastic 10. heat

MCQ

Q1 The average translational kinetic energy of the molecules of a gas will be doubled if

- a) At constant volume, its pressure is reduced to half.
- b) At constant temperature, its pressure is doubled.
- c) At constant volume, its pressure is made twice.
- d) At constant temperature, its pressure is made thrice.

Q2 The mean translational kinetic energy per molecule of an ideal gas is

- a) $k_B T$
- b) $3k_B T$
- c) $\frac{1}{2} k_B T$
- d) $\frac{3}{2} k_B T$

Q3 At the same temperature and pressure, a mole of oxygen molecules and a mole of carbon dioxide molecules will have

- a) the same number of molecules.
- b) different volumes.
- c) different average kinetic energy per molecule.
- d) the same number of atoms.

Q4 When an ideal gas increases in volume at constant pressure, the average kinetic energy of the gas molecules

- a) constant
- b) decreases

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c) increases

d) changes irregularly

5. Pressure which determines the rate of change of _____ per unit surface area of the walls.

a) momentum

b) energy

c) velocity

d) mass

Answers

1. c 2. d 3. a 4. c 5. a

References/ Bibliography/ Further Reading References

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