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*KINETIC THEORY, MEAN FREE PATH*

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# PHS-G-CC-3-3-TH

# 3. KINETIC THEORY OF GASES

# Maxwell's Velocity Distribution Law

If we were to plot the number of molecules whose velocities fall within a series of narrow ranges, we would obtain a slightly asymmetric curve known as a *velocity distribution*. The peak of this curve would correspond to the *most probable* velocity. This velocity distribution curve is known as the *Maxwell-Boltzmann distribution*, but is frequently referred to only by Boltzmann's name. The **Maxwell-Boltzmann distribution law** was first worked out around 1850 by the great Scottish physicist, **James Clerk Maxwell** (left, 1831-1879), who is better known for discovering the laws of electromagnetic radiation. Later, the Austrian physicist **Ludwig Boltzmann** (1844-1906) put the relation on a sounder theoretical basis and simplified the mathematics somewhat.

The Maxwell-Boltzmann distribution is used to determine how many molecules are moving between velocities $v$ and $v + dv$. Assuming that the one-dimensional distributions are independent of one another, that the velocity in the $y$ and $z$ directions does not affect the $x$ velocity, for example, the Maxwell-Boltzmann distribution is given by

$$\frac{dN}{N} = \left(\frac{m}{2\pi k_b T}\right)^{1/2} exp\left[\frac{-mv^2}{2k_b T}\right] dv$$

where

- $dN/N$ is the fraction of molecules moving at velocity $v$ to $v + dv$,
- $m$ is the mass of the molecule,
- $k_b$ is the Boltzmann constant, and
- $T$ is the absolute temperature.[1]

Additionally, the function can be written in terms of the scalar quantity speed $v$ instead of the vector quantity velocity. This form of the function defines the distribution of the gas molecules moving at different speeds, between $v_1$ and $v_2$, thus

$$f(v) = 4\pi v^2 \left(\frac{m}{2\pi k_b T}\right)^{3/2} exp\left[\frac{-mv^2}{2k_b T}\right] \quad (1.7.6$$

## Kinetic Theory

The thermodynamic approach does not allow a calculation of the quantities involved, based on the first principles e.g., to calculate $U$, we must know the mechanism that contributes to $U$. The microscopic description of molecular motion, as given in the pioneering work of Maxwell, really solves these problems. Maxwell's work in this area provided a breakthrough by demonstrating the real importance of molecular motion (which still had its sceptics) in understanding thermal phenomena and the importance of statistics. Maxwell deduced the law of distribution of velocities from considerations of probabilities "far in advance of anything previously attempted on the subject" His ideas, though simplified, did hit upon some of the essentials, as are elaborated below.

(a) The gas molecules are point masses. The system is considered to be in equilibrium, external disturbances being totally absent. (In fact, the equilibrium follows from the elastic collisions between molecules which are in continual motion, as was pointed out by L Boltzmann, another great player in this field who was almost contemporary to Maxwell).

(b) To meet the requirements of statistical considerations, the system must be assumed to be made up of a very large number of molecules; there should be an equal number of molecules in any given volume $\delta V$ within the system. In other words, the system should be homoge-

(c) The motion of the molecules is totally random such that the molecules have the same velocities in all directions. As a consequence of this isotropy the components of velocities along any system of coordinates are equal and it is immaterial which coordinate system the results are expressed in.

(d) The velocity components $(u, v, w)$ along any three coordinates $(x, y, z)$ are uncorrelated to each other. The quantities $(u, v, w)$ being uncorrelated, their probabilities are also independent of each other.

(e) The probability function describing the molecules with a particular velocity component $v$ in the interval $v$ to $v + dv$ is dependent only on $v$ and the element $dv$.

All these assumptions were obviously consistent with the observed facts about the randomness of molecular motion leading to uniform bulk properties like density, temperature, etc. throughout the entire volume of the gaseous system in equilibrium. Now, with $O$ as the origin of a rectangular Cartesian system of coordiantes $(x, y, z)$ and $(u, v, w)$ as the corresponding triad of velocity components, the resultant velocity $c$ is related to $(u, v, w)$ by

$$c^2 = u^2 + v^2 + w^2. \tag{1}$$

To calculate the probability of a molecule to have a velocity between $c$ and $c + dc$, the same can be calculated component-wise. If $dn_u$ be the number of molecules per unit volume which have the x-component of velocity between $u$ and $u + du$, then the corresponding probability function

$$P(u, du) = dn_u/n = f(u)\, du, \tag{2}$$

where $n$ is the total number of molecules per unit volume. On similar considerations, the corresponding probabilities for a molecule to have the y-component of velocity between $v$ and $v + dv$ and the z-component of velocity

between $w$ and $w + dw$ may be written respectively as

$$P(v, dv) = dn_v/n = f(v)\, dv$$

and

$$P(w, dw) = dn_w/n = f(w)\, dw. \tag{2a}$$

The functional form has been taken the same for all three velocity components by virtue of assumption (c). So, the effective probability of a molecule having its velocity components between $u$ and $u + du$, $v$ and $v + dv$ and $w$ and $w + dw$ simultaneously, is given by

$$P(u, v, w, du, dv, dw) = dn_{u,v,w}/n =$$

$$f(u)\, f(v)\, f(w)\, du\, dv\, dw \tag{3}$$

so that the number of molecules within the specified velocity ranges will be

$$dn_{u,v,w} = n\, f(u)\, f(v)\, f(w)\, du\, dv\, dw. \tag{4}$$

The same set of velocity components make a single resultant velocity vector $\vec{c}$. All the velocity vectors start from a common origin $O$. The lengths of these vectors give the magnitudes and their directions are the directions of motion of the molecules at any given time. If spheres of radii $c$ and $c + dc$ are drawn centred at $O$, the origin, the vectors ending between these two concentric spheres would represent all the velocities present that have values between $c$ and $c + dc$. The chance that this single velocity vector $\vec{c}$ ends in the volume element $du\, dv\, dw$ is, by assumption (e), $\phi(c)\, du\, dv\, dw$, which may be alternatively written as

$$F(c^2)du\, dv\, dw = f(u)\, f(v)\, f(w)\, du\, dv\, dw \tag{5}$$

valid for any arbitrary range of values of $du, dv, dw$, i.e.

$$F(c^2) = F(u^2 + v^2 + w^2) = f(u)\, f(v)\, f(w). \tag{6}$$

Thus we get a remarkable result that the product of a set of functions of some variables is equal to a function of the sum of the squares of the variables, which at once indicates a logarithmic relationship between the variables. Maxwell immediately took this relationship as the form of the probability function or the distribution law. To deduce the distribution law we need to identify the functional forms for $F(c^2)$ and $f(u)$. This is achieved by choosing a particular value of $c$ keeping $c$ constant and hence $F(c^2) =$ a constant.

We must have

$$d[F(c^2)] = 0 = d[f(u)\, f(v)\, f(w)]. \tag{7}$$

Since $c^2 = u^2 + v^2 + w^2 =$ a constant, we must also have

$$dc^2 = 0 = udu + vdv + wdw. \tag{8}$$

Using the method of undetermined multiplier in the form of a constant $\lambda$, (7) and (8) yield

$$[f'(u)/f(u) + \lambda u]du + [f'(v)/f(v) +$$

$$\lambda v]dv + [f'(w)/f(w) + \lambda w]dw = 0. \tag{9}$$

It is to be borne in mind that the velocity components are independent of each other and that $du, dv, dw$ are totally arbitrary. The coefficients of $du, dv, dw$ in (9) must be zero separately and we have

$$f'(u)/f(u) = -\lambda u$$

$$f'(v)/f(v) = -\lambda v$$

$$f'(w)/f(w) = -\lambda w \tag{10}$$

which, on integration, yield

$$f(u) = A\exp(-\lambda u^2/2) = A\exp(-u^2/\alpha^2), \tag{11}$$

where $\alpha^2 = 2/\lambda$.

Equation (11) has two unknown constants $A$ and $\alpha$. The constant $A$ can be determined from the normalisation condition that the probability of finding a molecule within the velocity range $-\infty < u(\text{or } v, w) < +\infty$ must be equal to one. This gives

$$\int_{-\infty}^{+\infty} f(u)du = A\alpha\sqrt{\pi} = 1,$$

or,

$$A = \frac{1}{\alpha\sqrt{\pi}}. \qquad (12)$$

From the above we see

$$\begin{aligned}
f(u) &= (1/\alpha\sqrt{\pi})\exp(-u^2/\alpha^2) = (1/\alpha\sqrt{\pi})f_g(u), \\
f(v) &= (1/\alpha\sqrt{\pi})\exp(-v^2/\alpha^2) = (1/\alpha\sqrt{\pi})f_g(v), \\
f(w) &= (1/\alpha\sqrt{\pi})\exp(-w^2/\alpha^2) = (1/\alpha\sqrt{\pi})f_g(w),
\end{aligned} \qquad (13)$$

where $f_g(x) = \exp(-x^2/\alpha^2)$, the suffix $g$ expresses the Gaussian nature. From the definition of probability it is clear that the probability of finding molecules in the range of velocities $u, u + du$, $v, v + dv$ and $w, w + dw$ is

$$\begin{aligned}
&f(u)\ f(v)\ f(w)\ du\ dv\ dw \\
&= (1/\alpha\sqrt{\pi})^3\ f_g(u)\ f_g(v)\ f_g(w)\ du\ dv\ dw \\
&= (1/\alpha\sqrt{\pi})^3 f_g(\sqrt{u^2 + v^2 + w^2})du\ dv\ dw \\
&= (1/\alpha\sqrt{\pi})^3\ f_g(c)du\ dv\ dw \qquad (14)
\end{aligned}$$

in conformity with (6), so that $F(c^2)$ of (6) is simply $(1/\alpha\sqrt{\pi})^3\ f_g(c)$.

Further defining an element of the type shown in *Figure 1*, we find that the volume element $du\ dv\ dw = c^2\ dc\ d\Omega_c$, where $d\Omega_c$ is the solid angle subtended at the origin in the velocity space by the surface element $dS_c$. Suppose we want to know the probability of finding a molecule in the velocity range $c$ and $c + dc$. This can be calculated by integrating over $d\Omega_c$.

**Figure 1.**
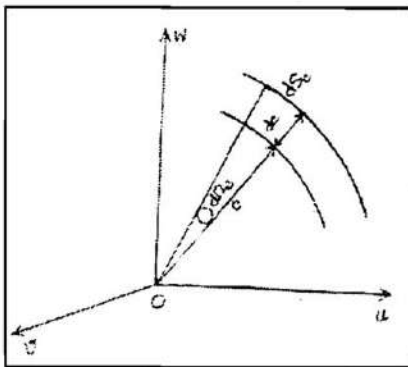


Since $\int d\Omega_c = 4\pi$, we find this probability to be

$$p(c)dc = (1/\alpha\sqrt{\pi})^3\ f_g(c)4\pi\ c^2\ dc. \qquad (15)$$

**Significance of $\alpha$**

In the Gaussian distributions $f(u), f(v), f(w)$ given above, the quantity $\alpha$ cannot be found independently. These functions help us calculate the average of any $\chi(u, v, w)$ as

$$\langle \chi \rangle = \int \chi(u, v, w)\ f(u)\ f(v)\ f(w)du\ dv\ dw.$$

We thus find the following averages:

$$\langle |u^{2n+1}| \rangle = \int_{-\infty}^{+\infty} |u^{2n+1}|f(u)\ du =$$

$$2\int_0^{\infty} u^{2n+1}f(u)\ du = n!\alpha^{2n+1}/\sqrt{\pi}\langle u^{2n+1} \rangle = 0;$$

$$\langle u^{2n} \rangle = \alpha^{2n}\Gamma(n + \tfrac{1}{2})/\sqrt{\pi}. \qquad (16)$$

These results show that $\alpha$ describes the moments of $u$ and hence to know $f(u)$, one of the moments of the distribution must be known. By putting $n = 1$, we find $\langle u^2 \rangle = \alpha^2/2$ so that the average kinetic energy per molecule must be

$$\langle E \rangle = \frac{1}{2}m(\langle u^2 \rangle + \langle v^2 \rangle + \langle w^2 \rangle) =$$

$$\frac{3}{2}\ m(\alpha^2/2) = \frac{3}{2}\ k_B\ T, \qquad (17)$$

where $k$ is the Boltzmann constant and $T$ the absolute temperature. For this identification of the average kinetic energy with temperature, the reader may look up the *Feynman Lectures*, Volume 1, pp.491-495. Thus

$$\alpha^2 = 2k_B\ T/m. \qquad (18)$$

It is thus seen (*Figure 2*) that as $T$ increases, the width of the curve broadens while the height shrinks. This implies
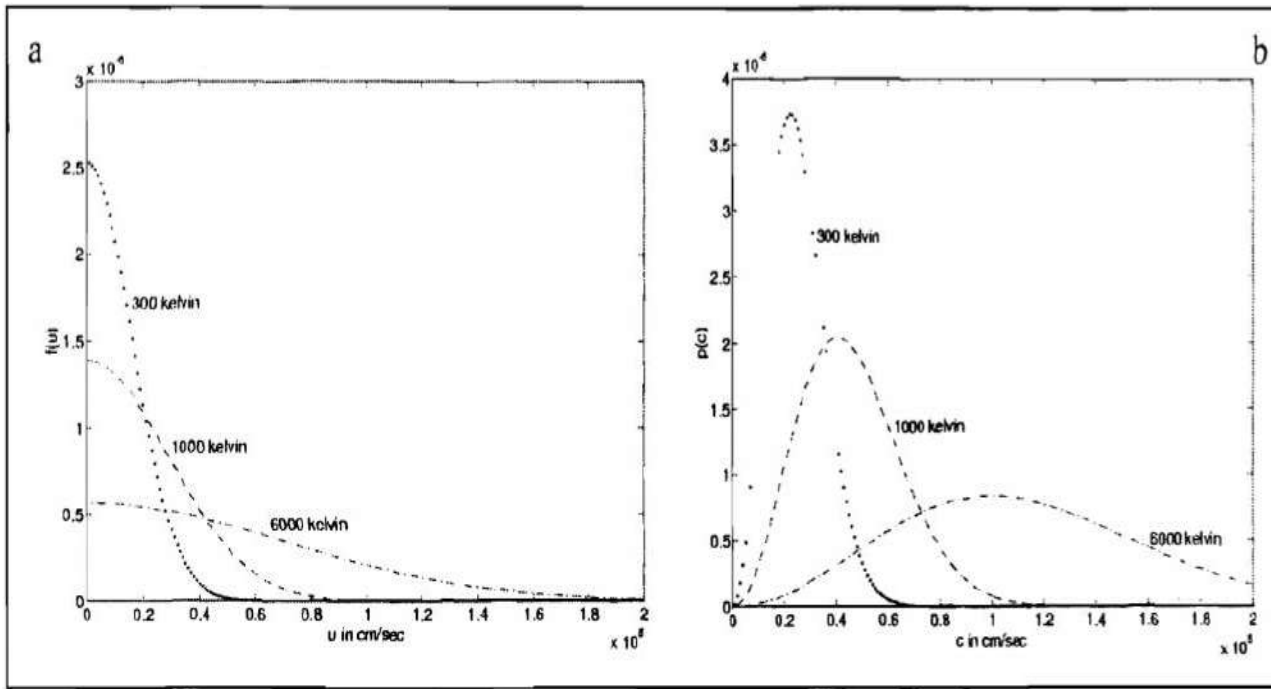
**Figure 2.**

implies that an increase in the temperature randomizes the system. Its role vis-a-vis the entropy of a system can be pondered over and a student may also try as an exercise as to what happens when $T = 0$ (suppose we reach it). While (16) and (17) give us the averages, we may ask – what is the most probable velocity? Note any study of the velocity distribution actually involves constructing a histogram $np(c)dc$. The most probable velocity occurs at $c = c_*$ where $p(c)$ has a maximum. From (16) we find that $c_* = \alpha$. Thus for a Maxwellian distribution we must have

$$c_* : \langle c \rangle : \langle c^2 \rangle^{\frac{1}{2}} = 1 : (2/\sqrt{\pi}) : (\sqrt{3}/2). \qquad (19)$$

These have been checked experimentally by various means, e.g., rotating sector velocity discriminations or shapes of spectral lines and show excellent agreement with Maxwell's distribution.
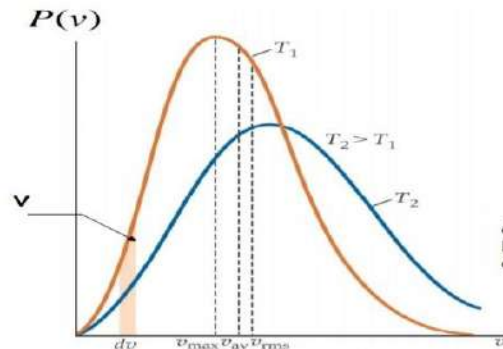
# Maxwell's Velocity Distribution curve and consequences

## The Distribution of Molecular Speeds in a Gas
### first derived by J.C. Maxwell in 1852

$$P(v)dv = \frac{4}{\sqrt{\pi}}\left(\frac{m}{2k_BT}\right)^{3/2} v^2 \, e^{-mv^2/2k_BT} \, dv = \frac{n(v)}{N}dv$$

- Normalized
- $v \equiv \sqrt{v_x^2 + v_y^2 + v_z^2}$
- Probability that molecule has speed $v \propto e^{-mv^2/2k_BT}$
- Number of molecules with speed $v \propto v^2$
- Note that P(v) is a continuous probability distribution function
- Note that only $v^2$ appears, not the components of velocity
- Connects macroscopic Thermodynamic properties with microscopic models

## Maxwell Speed Distribution Function



$P(v)$, $T_1$, $T_2 > T_1$, $T_2$, $v$, $dv$, $v_{max} v_{av} v_{rms}$

Shaded area represents probability that molecule will have a speed $v \pm dv/2$

Note asymmetry – there are more ways to get a large speed than a small one.

The inherent asymmetry gives rise to different values for $v_{max}$, $v_{av}$, and $v_{rms}$.

Check out:
http://www.chm.davidson.edu/ChemistryAppl
ets/KineticMolecularTheory/Maxwell.html

## The Average Speed

$$v_{avg} \equiv \int_0^{\infty} v\, P(v)dv = \frac{4}{\sqrt{\pi}}\left(\frac{m}{2k_BT}\right)^{3/2}\int_0^{\infty} v^3 e^{-mv^2/2k_BT}dv$$

$$\int_0^{\infty} x^{2n+1}e^{-ax^2}dx = \frac{n!}{2a^{n+1}}; \quad n=1; \; a=\frac{m}{2k_BT}$$

$$v_{avg} = \sqrt{\frac{8k_BT}{\pi m}} \quad \text{(mean speed)}$$

On earth, T=300K, atmosphere is mostly $N_2$. Mass of $N_2$ molecule is $4.7\times10^{-26}$ kg. What is $v_{avg}$?

$$v_{avg} = \sqrt{\frac{8k_BT}{\pi m}} = \sqrt{\frac{8(1.38\times10^{-23})(300)}{3.14(4.7\times10^{-26})}} = 474\, m/s$$

## Most Probable Speed

$$v_{most\,probable} \Rightarrow \frac{dP(v)}{dv} = 0$$

$$2ve^{-mv^2/2k_BT} + v^2(-\frac{2mv}{2k_BT})e^{-mv^2/2k_BT} = 0$$

$$v^2 = \frac{2k_BT}{m}$$

$$v_{most\,probable} = \sqrt{\frac{2k_BT}{m}}$$

## Square Root of the Mean Squared Speed

$$(v_{avg})^2 \equiv \int_0^{\infty} v^2\, P(v)dv = \frac{4}{\sqrt{\pi}}\left(\frac{m}{2k_BT}\right)^{3/2}\int_0^{\infty} v^4 e^{-mv^2/2k_BT}dv$$

$$\int_0^{\infty} x^{2n}e^{-ax^2}dx = \frac{1\cdot3\cdot5\cdots(2n-1)}{2^{n+1}a^n}\sqrt{\frac{\pi}{a}}; \quad n=2; \, a=\frac{m}{2k_BT}$$

$$(v_{avg})^2 = \frac{3k_BT}{m}$$

$$v_{rms} = \sqrt{(v_{avg})^2} = \sqrt{\frac{3k_BT}{m}}$$

$$\frac{1}{2}mv_{rms}^2 = \frac{1}{2}m\cdot\frac{3k_BT}{m} = \frac{3}{2}k_BT \quad \text{(equipartition theorem)}$$

# Mean Free Path

- On the basis of kinetic theory of gases, it is assumed that the molecules of a gas are continuously colliding against each other. Mean Free Path is the average distance traversed by molecule between two successive collisions.

- If s is the Total path travelled in $N_{coll}$ collisions, then mean free path $\lambda = s/N_{coll}$
  Expression for mean free path :

- Consider a gas containing n molecules per unit volume.

- We assume that only one molecule which is under consideration is in motion while all others are at rest.

- If $\sigma$ is the diameter of each molecule then the moving molecule will collide with all these molecules where centers lie within a distance from its centre .

- If v is the velocity of the moving molecule then in one second it will collide with all molecules with in a distance σ between the centres.

- In one second it sweeps a volume $\pi\sigma^2 v$ where any other molecule will collide with it.

- If n is the total number of molecules per unit volume, then $n\pi\sigma^2 v$ is number of [collisions](collisions) a molecule suffers in one second.

- If v is the distance traversed by molecule in one second then mean free path is given by
  λ = total distance traversed in one second /no. of collision suffered by the molecules
  $= v/\pi\sigma^2 vn$
  $= 1/\pi\sigma^2 n$

- This expression was derived with the assumption that all the molecules are at rest except the one which is colliding with the others.

- However this assumption does not represent actual state of affair.

- More exact statement can be derived considering that all molecules are moving with all possible velocities in all possible directions.

- More exact relation found using distribution law of molecular speeds is
  $\lambda = 1/(\sqrt{2})\pi\sigma^2 n$
  its derivation is beyond our scope.

# Some Important Links:

- 1. https://youtu.be/UlWBZOtV72E
- 2. https://youtu.be/RZPWtJrqR4I
- 3. https://youtu.be/aC9tZeWHFjc