

Thermal Physics
(Maxwell Distribution Law)
Lecture - 5

Dr. Tarun Kumar Dey,
Associate professor
Department of Physics ,
L.S College; BRA Bihar University, Muzzaffarpur

Youtube channel – Tarun Kumar Dey

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Maxwell's distribution law : The gas molecules moves with different velocity in different direction due to collisions The RMS velocity remains the same at a fixed temperature .

Some molecules are moving with a velocity higher than RMS velocity but others are lower than RMS velocity .

But the mean kinetic energy of all the molecules remains constant at a given temperature .Why this so ?

This interesting question was first answered by Maxwell in 1859 .

These velocities are governed by a certain laws known as Maxwell distribution law .

Let n be the number of molecules per unit volume, if molecules move with a velocity c in an arbitrary direction, whose components are u, v and w along X, Y and Z direction respectively. Such that

$$c^2 = u^2 + v^2 + w^2 \quad (1)$$

The number of molecules per unit volume having the velocities lying between u and $u + du$ is given by

$$= n_u du$$

When n_u is some function of u i.e. ,

$$n_u = n f(u)du$$

and hence the probability that a molecule selected at random will have the velocities lying between u and $u+du$ is

$$= f(u)du$$

We assume that $f(u)$ is independent of v and w .Similarly , the probability for molecules with velocities lying between v and $v + dv$ is

$$= f(v)dv$$

and that with velocities lying between w and $w + dw$ is

$$= f(w)dw$$

Hence the total probability that a molecule have the velocity components lying between u and $u + du$, v and $v + dv$ and w and $w + dw$ is

$$= f(u)f(v)f(w)du dv dw , \quad (2)$$

Which is the product of the individual probabilities .

Then the number of such molecules per unit volume will be

$$= nf(u)f(v)f(w)dudvdw \quad (3)$$

If c be the resultant velocity , so the number of these molecules must be

$$= n F(c) du dv dw \quad (4)$$

Where $F(c)$ is the probability for molecules with velocity c

Equating Eq.(3) and (4) ,we get

$$f(u)f(v)f(w) = F(c) = \phi (c^2) \quad (5)$$

where $\phi(c^2)$ is a new function of c^2 , For a fixed value of c , $\phi(c^2)$ is constant, hence

$$d[f(u)f(v)f(w)] = d[\phi(c^2)] = 0$$

or

$$f'(u)du f(v) f(w) + f(u)f'(v) dv f(w) + f(u) f(v)f' dw = 0 \quad (6)$$

where $f' = \frac{df}{du}$, etc dividing by $f(u)f(v)f(w)$, we get

$$\frac{f'(u)}{f(u)} du + \frac{f'(v)}{f(v)} dv + \frac{f'(w)}{f(w)} dw = 0 \quad (7)$$

For fixed value of c , we have Eq. (1)

$$u du + v dv + w dw = 0 \quad (8)$$

Multiplying Eq. (8) by β and adding to Eq. (7) , which is known as Laplace's method of undetermined multiplier ,we get

$$\left[\left(\frac{f'(u)}{f(u)} + \beta u \right) du + \left(\frac{f'(v)}{f(v)} + \beta v \right) dv + \left(\frac{f'(w)}{f(w)} + \beta w \right) dw \right] = 0 \quad (9)$$

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$$\frac{f'(u)}{f(u)} = - \beta u \quad (10a)$$

$$\frac{f'(v)}{f(v)} = - \beta v \quad (10b)$$

$$\frac{f'(w)}{f(w)} = - \beta w \quad (10c)$$

From Eq. (10a)

$$\frac{df(u)}{f(u)} = - \beta u du$$

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$$\frac{df(u)}{f(u)} = \beta u du$$

On integration ,we have

$$\ln f(u) - \frac{1}{2} \beta u^2 + \ln a$$

or ,

$$f(u) = a e^{-\beta u^2 / 2} = a e^{-b u^2} , \quad (11)$$

a and b are constants . similarly Eq.(10b) and Eq.(10c) give

$$f(v) = a e^{-bv^2} , \quad (12)$$

$$f(w) = a e^{-bw^2} , \quad (13)$$

Hence the number of molecules having the velocity components lying between u and $u + du$, v and $v + dv$ and w and $w + dw$ is given by

$$dn = na^3 e^{-b(u^2+v^2+w^2)} du dv dw , \quad (14)$$

where a, b and c are constants . **This is called Maxwell's law for velocity components** . Here $du dv dw$ is volume element in the velocity space .