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# Udai Pratap (Autonomous) College, Varanasi

## E-learning Material

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| **Module/ Lecture** | **01** |
| **Topic** | **Maxwell's Law of Distribution of Molecular Speed** |
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# Maxwell's Law of Distribution of Molecular Speed

The number of molecules in a given speed range at any temperature T is given by Maxwell's law of distribution of molecular speed, which can be deduced under following assumptions:

1. The gas consists of molecules with all speed between 0 and $\infty$.
2. When the gas is in steady state, its everage molecular density remains constant everywhere in the volume of the gas.
3. Though the speed of individual molecules are changing, a definite number of molecules are present between definite ranges.

**Derivation:** Let $n_v$ be the number of molecules (of all velocities) per unit volume.

Let $n_v$ $f(C_x)$ $dC_x$ represents the number of molecules per unit volume with velocity between $C_x$ and $C_x + dC_x$ i.e. in the velocity range $dC_x$.

Thus the probability that any molecule selected at random will have velocity component lying between $C_x$ and $C_x + dC_x$ will be $\frac{n_v f(C_x) dC_x}{n_v} = f(C_x) dC_x$ .

Similarly the probability for molecule having velocity component lying between $C_y$ and $C_y + dC_y$ will be $f(C_y) dC_y$ and that for velocity component lying between $C_z$ and $C_z + dC_z$ will be $f(C_z) dC_z$.

Maxwell assumed that the velocity components $C_x$, $C_y$ and $C_z$ are of a molecule are independent.

From the theorem of probability for independent events, "the probability of composite event is equal to the product of the probabilities of individual events."

Thus the probability that a molecule selected at random will have velocity components between $C_x$ & $C_x + dC_x$, $C_y$ & $C_y + dC_y$ and $C_z$ & $C_z + dC_z$ will be

$f(C_x)f(C_y)f(C_z)dC_x dC_y dC_z$ and hence number of such molecules per unit volume will be

$$n_v f(C_x)f(C_y)f(C_z)dC_x dC_y dC_z. \tag{1}$$

Let we assume a velocity space with $C_x$, $C_y$ and $C_z$ as axis. All the molecules whose component lie in the range $C_x$ & $C_x + dC_x$, $C_y$ & $C_y + dC_y$ and $C_z$ & $C_z + dC_z$ will be contained in a cuboid of volume $dC_x dC_y dC_z$.

Hence the number of molecules per unit volume with velocity lying between $\vec{C}$ and $\vec{C} + d\vec{C}$ (component $C_x$ & $C_x + dC_x$, $C_y$ & $C_y + dC_y$ and $C_z$ & $C_z + dC_z$) can also be written as

$$n_v F(C)dC_x dC_y dC_z \tag{2}$$

Where F(C) is an isotropic function. Also,

$$F(C) = f(C_x)f(C_y)f(C_z) \tag{3}$$

The function F(C) is constant at all points at same radial distance $C = \sqrt{C_x^2 + C_y^2 + C_z^2}$. Thus for constant value of C,

$$dF(C) = \frac{\partial F(C)}{\partial C_x}dC_x + \frac{\partial F(C)}{\partial C_y}dC_y + \frac{\partial F(C)}{\partial C_z}dC_z = 0$$

i.e. $$f'(C_x)f(C_y)f(C_z)dC_x + f(C_x)f'(C_y)f(C_z)dC_y + f(C_x)f(C_y)f'(C_z)\,dC_z = 0$$

i.e. $$\frac{f'(C_x)}{f(C_x)}dC_x + \frac{f'(C_y)}{f(C_y)}dC_y + \frac{f'(C_z)}{f(C_z)}dC_z = 0 \tag{4}$$

where $f'(C_x) = \frac{\partial f(C_x)}{\partial C_x}, f'(C_y) = \frac{\partial f(C_y)}{\partial C_y}, f'(C_z) = \frac{\partial f(C_z)}{\partial Cz}$ .

Also for constant value of C from $C^2 = C_x^2 + C_y^2 + C_z^2$ we have

$$C_x dC_x + C_y dC_y + C_z dC_z = 0 \tag{5}$$

To solve Equations (4 & 5) we multiply Eq. (5) by an arbitrary constant $\lambda$ (undetermined multiplier) and add the result to Eq. (4) , we get

$$\left(\frac{f'(C_x)}{f(C_x)} + \lambda C_x\right)dC_x + \left(\frac{f'(C_y)}{f(C_y)} + \lambda C_y\right)dC_y + \left(\frac{f'(C_z)}{f(C_z)} + \lambda C_z\right)dC_z = 0 \qquad (6)$$

Since each term is independent , so each term must be equal to zero separately. Also since $dC_x, dC_y$ and $dC_z$ are not themselves zero, we have

$$\frac{f'(C_x)}{f(C_x)} + \lambda C_x = 0 \qquad (7a)$$

$$\frac{f'(C_y)}{f(C_y)} + \lambda C_y = 0 \qquad (7b)$$

$$\frac{f'(C_z)}{f(C_z)} + \lambda C_z = 0 \qquad (7c)$$

On integration to Eq. (7a) we get

$$\log_e f(C_x) = -\frac{1}{2}\lambda C_x^2 + \log_e a$$

or

$$f(C_x) = ae^{-bC_x^2} \qquad (8)$$

where a=constant of integration and $b = \frac{1}{2}\lambda$ is a constant. Maxwell pointed out that if $\lambda$ were negative, the number of molecule would be infinite, so $\lambda \rangle 0$.

Similarly we can find the values of $f(C_y)$ and $f(C_z)$ and hence

$$F(C) = f(C_x)f(C_y)f(C_z) = a^3 e^{-b(C_x^2+C_y^2+C_z^2)} dC_x dC_y dC_z \qquad (9)$$

Hence from relation (2) the number of molecules per unit volume with velocity lying between $\vec{C}$ and $\vec{C} + d\vec{C}$ (component $C_x$ & $C_x$+ $dC_x$, $C_y$ & $C_y$+ $dC_y$ and $C_z$ & $C_z$+ $dC_z$) are

$$dn_v = n_v\, a^3 e^{-b(C_x^2+C_y^2+C_z^2)} dC_x dC_y dC_z \qquad (10)$$

where a and b are constant to determine.

**Value of constant a:** Since the number of molecules (of all velocities) per unit volume is $n_v$ i.e. form Eq. (10);

$$n_v \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} a^3 e^{-b(C_x^2+C_y^2+C_z^2)} dC_x dC_y dC_z = n_v \tag{11}$$

Since $\int_{-\infty}^{\infty} e^{-px^2} dx = \sqrt{\frac{\pi}{p}}$ , thus above equation (11) gives

$$a^3 \left(\frac{\pi}{b}\right)^{3/2} = 1$$

$$a = \sqrt{\frac{b}{\pi}} \tag{12}$$

**Value of constant b:** We can calculate $\overline{c^2} = \frac{3}{2b} = \frac{3}{2a^2\pi}$ and substituting the value of $\overline{c^2}$ in the relation $\frac{1}{2}\mu\overline{c^2} = \frac{3}{2}kT$ we get

$$b = \frac{\mu}{2kT} \tag{13}$$

Thus

$$a = \sqrt{\frac{\mu}{2\pi kT}} \tag{14}$$

Substituting these values of a and b in the Eq. (10) we get the number of molecules per unit volume with velocity component lying between $C_x$ & $C_x + dC_x$, $C_y$ & $C_y + dC_y$ and $C_z$ & $C_z + dC_z$ as

$$dn_v = n_v \left(\frac{\mu}{2\pi kT}\right)^{3/2} e^{-\frac{\mu(C_x^2+C_y^2+C_z^2)}{2kT}} dC_x dC_y dC_z \tag{15}$$

Equation (15) is the Maxwell's distribution law of molecular velocities.

Often we are interested only on the range of between C and C+dC and not on the direction of molecular velocity. Therefore we should replace the volume $dC_x dC_y dC_z$ of cuboid in velocity space by the volume $4\pi C^2 dC$ of a spherical shell lying between two concentric spheres of radii C and C+dC and the distribution law can be written as

$$dn_v(C) = 4\pi n_v \left(\frac{\mu}{2\pi kT}\right)^{3/2} e^{-\frac{\mu C^2}{2kT}} C^2 dC \qquad (16)$$

Equation (16) is known as Maxwell's law of distribution of molecular speed. For N molecules contained in a box of volume V, $n_v = \frac{N}{V}$ and writing $Vdn_v(c) = dN(c)$ we have Maxwell's law of distribution of molecular speed. In familiar form, thus

$$dN(C) = 4\pi N \left(\frac{\mu}{2\pi kT}\right)^{3/2} e^{-\frac{\mu C^2}{2kT}} C^2 dC \qquad (17)$$

Which gives total number of molecules having speed between C and C+dC.

From Maxwell's law of distribution of molecular speed given by Eq. (17) we see that,

**1.** If C=0,

dN(C)=0

i.e. no molecule has zero speed i.e. no any molecule is at rest, all molecules ate moving.

**2.** For small value of C,

$\frac{\mu C^2}{2kT} \ll 1$, and $e^{-\frac{\mu C^2}{2kT}} \cong 1$

$dN(C) \propto C^2$

Thus the number of molecules increases parabolically with increasing value of C for small values of C and attains a maximum value for a particular value of C.

**3.** For large value of C,

$\frac{\mu C^2}{2kT} \gg 1$ and $e^{-\frac{\mu C^2}{2kT}}$ dominate over $C^2$ , hence

$$dN(C) \propto e^{-\frac{\mu C^2}{2kT}}$$

Hence number of molecules decreases exponentially with increase of value of C.