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2. Heat and Thermodynamics

Principle of temperature measurements: platinum resistance thermometer, thermoelectric thermometer, pyrometer; Kinetic theory of gases: Maxwell's distribution of molecular speeds, mean free path, equipartition of energy, Brownian motion, Van der Waal's equation of state, review of the First Law of thermodynamics and its application, reversible and irreversible processes, Second Law of thermodynamics, Carnot cycle; Efficiency of heat engines, Carnot's Theorem, entropy and disorder, thermodynamic functions, Maxwell relations, Clausius-Clapeyron Equation, Gibbs Phase Rule, Third Law of thermodynamics.

8 Lectures



Chapter 2

Heat and Thermodynamics



Brownian Motion (Robert Brown in 1827)

You might well have studied Brownian Motion before. It is unlikely that you fully appreciated or understood it!!!

One of the first pieces of evidence for how gases move was discovered by Robert Brown a botanist who noticed that pollen grains in water moved about randomly.

Robert Brown noticed that small grains of pollen (clarkia) suspended in water, moved in a haphazard or random fashion.



Brownian Motion

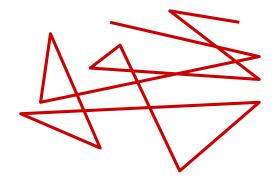
It was only visible under a microscope (he used fairly low magnification).

Being a botanist he logically thought that the grains of pollen were alive.

He then tried various other small particles such as carbon (in ink) and realized that the motion was not truly due to life.



Brownian Motion

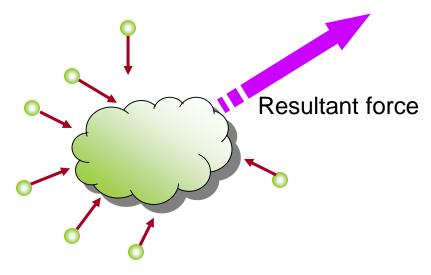


Remember

- There is no appreciable displacement of the particle
- The particle travels more or less in straight lines
- The motion is RANDOM



Brownian Motion



At any point of time the forces on the particles are uneven causing a net force and therefore acceleration in that direction.

Their light mass means they change direction quickly and easily.

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Brownian Motion

The non-stop, random, perpetual, spontaneous, and haphazard motion of a colloidal solution is called the Brownian motion.



Essential Features of Brownian Motion

- 1. The motion of each particle is completely irregular, and random. No two particles are found to execute the same motion.
- 2. The motion is continuous and takes place for ever.
- 3. The smaller particles appear to be more agitated than the longer ones.
- 4. The motion is independent of the nature of the suspended articles. Two particles of the same weight and size move equally fast at the same temperature.



- 5. The motion becomes more vigorous when the temperature is increased.
- 6. The motion is more conspicuous in a liquid of lower viscosity.
- 7. The motion is not modified due to the shaking of the containing vessel.



Basis of Brownian Motion

Brownian motion is due to the bombardment of the dispersed particles by molecules of the medium which are themselves in a state of continuous haphazard motion. When the particles are sufficiently large, the forces due to molecular impact is nearly balanced. This is why Brownian motion cannot be observed with particles of large size. But when the size of the particles is very small each particle will be acted upon by a resultant unbalanced force and will consequently move in a haphazard manner in response to the magnitude and direction of this force.

In other words, the particles move in response to the molecules of the liquid in a completely haphazard manner. The motion of the molecules of a gas is similar to Brownian movement if suspended particles in colloidal solution. Thus, the laws of kinetic theory of gases are applicable to Brownian motion.



Question

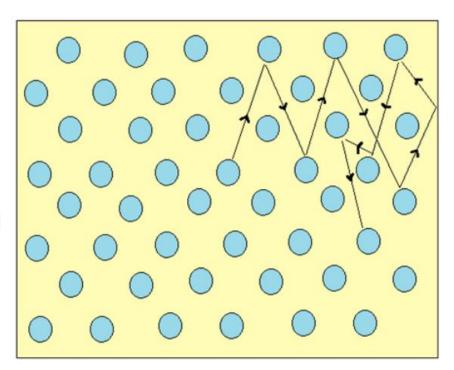
Q. Define Brownian motion with its essential features. Explain the basis of Brownian motion.



Mean Free Path of Gases

The mean free path λ of a gas molecule is its average path length between collisions.

The random path followed by a gas molecule.

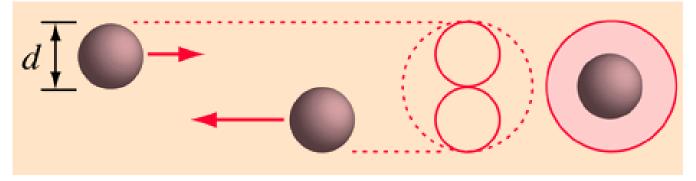




- •On the basis of kinetic theory of gases, it is assumed that the molecules of a gas are continuously colliding against each other.
- •Molecules move in straight line with constant speeds between two successive collisions.
- •Thus path of a single molecule is a series of zig-zag paths of different lengths as shown in figure.

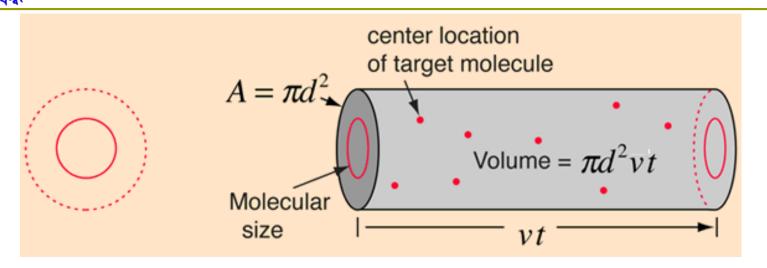
These paths of different lengths are called free paths of the molecule. Mean free path is the average distance traversed by molecule between two successive collisions.

If the molecules have diameter d, then the effective cross-section for collision can be defined by,



The effective cross-section for collision, $A = \pi d^2$.

Using a circle of diameter 2d to represent a molecule's effective collision area while treating the 'target' molecules as point masses. In time t, the circle would sweep out the volume shown and the number of collisions can be estimated from the number of gas molecules available in that volume.



The mean free path could then be taken as the length of the path divided by the number of collisions. Mathematically,

$$\lambda = \frac{Distance\ traveled\ in\ time\ t}{No\ of\ collisions\ suffered\ in\ time\ t}$$



The mean free path,

$$\lambda = \frac{vt}{\pi d^2 vt \cdot \frac{N}{V}}$$
$$= \frac{1}{\pi d^2 n}$$

This is the expression for the mean free path of a gas molecule.

This equation was deduced by Clausius.

$$\lambda \propto \frac{1}{d^2}$$

The mean free path is inversely proportional to the square of the diameter of the molecules.

Here, we have assumed that all the particles are stationary with respect to the particle we are studying, but in reality all the molecules are moving relative to each other, we have cancelled two velocities in the equation but actually the v in the numerator is the average velocity and v in the denominator is relative velocity hence they both differ from each other with a factor $\sqrt{2}$ therefore the final expression of the mean free path would be,

$$\lambda = \frac{1}{\sqrt{2}\pi d^2 n}$$

This is known as the Maxwell's mean free path based on the law of equipartition of energy.



Let m be the mass of each molecule.

Then,

$$m \times n = \rho$$

$$\lambda = \frac{m}{\pi d^2 \rho}$$

The mean free path is inversely proportional to the density of the gas.

The expression for the mean path according to Boltzmann is

$$\lambda = \frac{3}{4\pi d^2 n}$$

He assumed that all molecules have the same average speed.



Law of Equipartition of Energy

A molecule in a gas can move along any of the three co-ordinate axes. It has three degrees of freedom. Degrees of freedom mean the number of independent variables that must be known to describe the state or the position of the body completely. A monoatomic gas molecule has three degrees of freedom. A diatomic gas molecule has three degrees of freedom of translation and two degrees of freedom of rotation. It has in all five degrees of freedom.

According to kinetic theory of gases, the mean kinetic energy of a molecule at a temperature T is given by

$$\frac{1}{2}mC^2 = \frac{3}{2}kT \qquad ...(i)$$

But

$$C^2 = u^2 + v^2 + w^2$$

As x, y and z are all equivalent, mean square velocities along the three axes are equal

or
$$u^{2} = v^{2} = w^{3}$$

$$\frac{1}{2} m(u^{2}) = \frac{1}{2} m(v^{2}) = \frac{1}{2} m(w^{2})$$

$$\frac{1}{2} mC^{2} = 3 \left[\frac{1}{2} m(u^{3})\right] = 3 \left[\frac{1}{2} m(v^{2})\right]$$

$$= 3 \left[\frac{1}{2} m(w^{2})\right]$$

$$= \frac{3}{2} kT$$

$$\frac{1}{2} mu^{3} = \frac{1}{2} kT$$

$$\frac{1}{2} mv^{2} = \frac{1}{2} kT$$

$$\frac{1}{2} mv^{2} = \frac{1}{2} kT$$
...(iii)
$$\frac{1}{2} mv^{2} = \frac{1}{2} kT$$
...(iv)

Therefore, the average kinetic energy associated with each degree of freedom $= \frac{1}{2}kT$



Thus the energy associated with each degree of freedom (whether translatory or rotatory) is ½ kT.

This represents the theorem of equipartition of energy.

(i) Mono-atomic gas. A mono-atomic gas molecule has one atom. Each molecule has three degrees of freedom due to translatory motion only.

Energy associated with each degree of freedom = $\frac{1}{2}kT$

Energy associated with three degrees of freedom

$$=\frac{3}{2}kT$$

Consider one gram molecule of a gas.

Energy associated with one gram molecule of a gas

$$= N \times \frac{3}{2} kT$$

$$=\frac{3}{2} (N \times k) T$$

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Heat & Thermodynamics

[But,
$$N \times k = R$$
]
$$\therefore U = \frac{3}{2} RT$$

This energy of the gas is due to the energy of its molecules. It is called internal energy U. For an ideal gas, it depends upon temperature only.

$$C_v = \frac{dU}{dT} = \frac{3}{2} R$$

 $\left(\frac{dU}{dT}\right)$ is the increase in internal energy per unit degree rise of

temperature)

But
$$C_{\mathbf{P}}-C_{\mathbf{V}}=R$$
 $C_{\mathbf{P}}=C_{\mathbf{V}}+R$
 $=\frac{3}{2}R+k=\frac{5}{2}R$



For a mono-atomic gas
$$\gamma = \frac{C_{\mathbf{P}}}{C_{\mathbf{V}}}$$

$$= \frac{\frac{5}{2}R}{\frac{3}{2}R} = 1.67$$

The value of γ is found to be true experimentally for mono-atomic gases like argon and helium.



(ii) Diatomic gas. A diatomic gas molecule has two atoms. Such a molecule has three degrees of freedom of translation and two degrees of freedom of rotation.

Energy associated with each degree of freedom

$$=\frac{1}{2}kT$$

Energy associated with 5 degrees of freedom = $\frac{5}{2} kT$

Consider one gram molecule of gas.

Energy associated with ! gram molecule of a diatomic gas

$$= N \times \frac{5}{2} kT = \frac{5}{2} RT$$

$$U = \frac{5}{2} RT$$

$$C_{V} = \frac{dU}{dT}$$

$$5 = \frac{1}{2} RT$$



But
$$C_P - C_V = R$$

$$C_P = C_V + R$$

$$= \frac{5}{2}R + R = 7/2R$$

$$\gamma = \frac{C_P}{C_V}$$

$$= \frac{\frac{7}{2}R}{\frac{5}{2}R} = 1.40$$
The value of $\gamma = 1.40$ has been found to be

The value of $\gamma = 1.40$ has been found to be true experimentally for diatomic gases like hydrogen, oxygen, nitrogen etc.



(iii) Triatomic gas. (a) A triatomic gas having 6 degrees of freedom has an energy associated with 1 gram molecule

$$= N \times \frac{6}{2} kT = 3RT$$

$$U = 3RT$$

$$C_{V} = \frac{dU}{dT} = 3R$$

But

$$C_{P}-C_{V} = R$$
 $C_{P} = C_{V}+R$
 $= 3R+R = 4R$

(b) A triatomic gas having 7 degrees of freedom has an energy associated with 1 gram molecule = $N \times \frac{7}{2} kT = \frac{7}{2} R$

$$U = \frac{7}{2} RT$$

$$C_{V} = \frac{dU}{dT} = \frac{7}{2} R$$
But
$$C_{P} - C_{V} = R$$

$$C_{P} = C_{V} + R$$

$$= \frac{7}{2} R + R = \frac{9}{2} R$$

$$Y = \frac{C_{P}}{C_{V}}$$

$$= \frac{9/2 R}{7/2 R} = 1.28$$

Thus the value of γ , C_P and C_V can be calculated depending upon the degrees of freedom of a gas molecule.



Home Work

Solve a few problems related to the theory we have studied in this chapter



chank You for Listening

