

CHAPTER

12

Kinetic Theory

Molecular Nature of Matter • Gas Laws • Kinetic Theory of an Ideal Gas
• Equipartition of Energy and Mean Free Path

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READING KEY

DEFINITION

NOTE

REMEMBER

DERIVATION

STRATEGY

Formulas sit on graph paper • coloured words are the key terms

The **kinetic theory of gases** explains how a gas behaves. It pictures a gas as a huge number of tiny **atoms or molecules** that move **very fast**. The forces between atoms act only over **short distances**. In a gas the molecules are far apart, so these forces can be neglected. That is why gas molecules move so quickly and freely.

1.1 Molecular Nature of Matter

Richard Feynman was a great physicist of the 20th century. He rated one idea among the most important discoveries of science. The idea is that **matter is made up of atoms**.

The modern atomic theory comes from **John Dalton (1766–1844)**, an English chemist. He used it to explain two laws that elements obey when they join to form compounds:

i Law of Definite Proportions

A given compound always contains its elements in a **fixed ratio by mass**.

ii Law of Multiple Proportions

Two elements may join to form **more than one compound**. Take a fixed mass of the first element. The masses of the second element that join with it are then in a **ratio of small whole numbers**.

CONCEPT

Dalton's Atomic Theory

About **200 years ago**, Dalton said that the **smallest parts of an element are atoms**. All atoms of one element are **identical**. They differ from the atoms of every other element. A few atoms of each element join together to make a **molecule** of a compound.

Atoms join to form molecules. So this theory is also called the **molecular theory of matter**.

Gay Lussac's Law (19th century)

Gases may react and form another gas. Then the **volumes** of the gases are in a **ratio of small whole numbers**.

Avogadro's Law

Given by **Amedeo Avogadro (1776–1856)**. **Equal volumes** of all gases at the **same temperature and pressure** contain the **same number of molecules**.

NOTE

Avogadro's law, used together with **Dalton's theory**, explains **Gay Lussac's law**. Avogadro's idea made it easy to understand how different gases combine.

1.2 Atomic Hypothesis and States of Matter

CONCEPT

Atomic Hypothesis

The **atomic hypothesis** says that **everything is made of atoms**. Atoms are tiny particles that are always moving (**perpetual motion**). They **attract** each other when they are a little distance apart. They **repel** each other when they are pressed into one another.

Today we can actually **see molecules**. The **electron microscope** and the **scanning tunnelling microscope** make this possible.

Size of an atom (order of magnitude)

$$10^{-10} \text{ m}$$

This length is **one angstrom**

$$1 \text{ \AA} = 10^{-10} \text{ m}$$

• STATES OF MATTER

Solids

Have a **definite shape, size and volume**.

Spacing between atoms is the **smallest** (about $2 \text{ \AA}$).

Attraction between atoms is the **strongest**.

Liquids

Have a **definite volume** but **no definite shape or size**.

Spacing is **more than in solids** and **less than in gases**.

Attraction is **weaker than in solids**. So a liquid can **flow**.

Gases

Have **no fixed shape, size or volume**.

Spacing between molecules is the **largest** (about $20 \text{ \AA}$).

Attraction is the **weakest** of the three states.

1.3 Motion of Molecules in a Gas

DEFINITION

The **mean free path** is the **average distance** a molecule travels **without a collision**, that is, between two successive collisions. Topic 4.10 covers it in detail.

Mean free path of molecules in a gas (order)

Thousands of $\text{\AA}$

So gas molecules are **quite free** to move. They can travel **long distances** before they hit another molecule. This is why a gas **spreads out** (disperses) when it is not kept in a closed container.

• ATOMS ARE NOT ELEMENTARY

Modern theories show that atoms are **not indivisible**. They are made of still smaller particles:

Atom → Nucleus + Electrons → Protons + Neutrons → Quarks

NOTE

In future, **quarks** may also turn out to be made of some still smaller **elementary particles**.

1.4 Behaviour of Gases

Gases are the **easiest** state of matter to understand. Their molecules are **far from each other**. So the forces between them are **negligible**, except when two molecules collide.

Take a gas at **low pressure** and **high temperature**. The temperature must be far above the point where the gas liquefies (or solidifies). Such a gas obeys this relation:

$$pV = KT \quad \dots (i)$$

Here p = **pressure**, V = **volume** and T = **absolute temperature** (in kelvin). K is constant for a given sample. Its value depends on the size of the sample, that is, on the **number of molecules** N in it:

$$K = Nk \quad \dots (ii)$$

Experiments show that k has the **same value for all gases**. This universal constant is written as k_B . So Eq. (ii) becomes:

$$K = Nk_B \quad \dots (iii)$$

k_B = **Boltzmann constant** (SI value)

$$1.38 \times 10^{-23} \text{ J K}^{-1}$$

Putting Eq. (iii) in Eq. (i) gives:

GAS EQUATION WITH BOLTZMANN CONSTANT

$$pV = Nk_B T \quad \text{or} \quad \frac{pV}{NT} = k_B = \text{constant}$$

where, N = number of molecules in the sample, k_B = Boltzmann constant

So for different gases, we can write:

$$\frac{p_1 V_1}{N_1 T_1} = \frac{p_2 V_2}{N_2 T_2} = \frac{p_3 V_3}{N_3 T_3} = \dots = k_B = \text{constant}$$

LAW

Avogadro's Hypothesis

Equal volumes of all gases at the **same temperature and pressure** contain an **equal number of molecules**.

It follows from the relation above. If p , V and T are the same for two gases, then N must also be the same.

22.4 L of any gas at **STP** (273 K and 1 atm) has the same number of molecules

$$N_A$$

1.5 Perfect Gas Equation

The gas equation can also be written with the **number of moles**. This form is called the **perfect gas equation** (or **ideal gas equation**).

PERFECT GAS EQUATION

$$pV = \mu RT$$

where, μ = number of moles, $R = N_A k_B$ = universal gas constant, T = absolute temperature (in kelvin)

The number of moles of a gas is:

$$\mu = \frac{M}{M_0} = \frac{N}{N_A}$$

Here M = **mass of the gas**, M_0 = **molar mass** of the gas and N = number of molecules.

Universal gas constant

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

• PERFECT GAS EQUATION IN TERMS OF DENSITY

Put $\mu = \frac{M}{M_0}$ in $pV = \mu RT$ and divide by V . The mass per unit volume $\frac{M}{V}$ is the **density** ρ . So:

GAS EQUATION WITH DENSITY

$$p = \frac{\rho RT}{M_0}$$

where, ρ = mass density of the gas, M_0 = molar mass (mass of one mole of the gas)

NOTE

- ◆ Take **22.4 L** of any gas at STP. Its mass in grams is equal to its **molecular weight**. This amount of gas is **one mole**.
- ◆ **One mole** of any substance has 6.022×10^{23} atoms or molecules.
- ◆ So 22.4 L of any gas at STP holds **1 mole** of atoms or molecules.

02 PART 2 Gas Laws

An **ideal gas** obeys a few simple laws. This part covers these laws, how **real gases** differ from them, and the **work done** when a gas is compressed or expanded.

2.1 Real Gas and Ideal Gas

DEFINITION

An **ideal gas** is a **theoretical model** of a gas. **No real gas is perfectly ideal.** A real gas behaves most like an ideal gas at **low pressure** and **high temperature**.

The reason is simple. At low pressure and high temperature, the molecules are **far apart**. So the **attraction** between them becomes **negligible**.

For an ideal gas, $pV = \mu RT$. Here μ is the number of moles and $R = N_A k_B$ is the universal constant. It is called the **gas constant for one gram mole**. So:

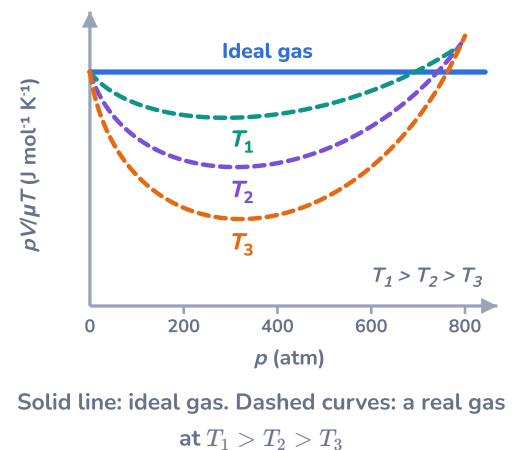
IDEAL GAS

$$\therefore \frac{pV}{\mu T} = R = \text{constant}$$

Plot $\frac{pV}{\mu T}$ against p . For an **ideal gas** the graph is a **horizontal straight line** (solid line).

Now plot the same graph for a **real gas** at three temperatures $T_1 > T_2 > T_3$. We get the **dashed curves**.

Every real-gas curve comes close to the ideal line at **low pressure**. The curve for the highest temperature T_1 stays closest to it. So a real gas behaves like an ideal gas at **low pressure and high temperature**.



2.2 Boyle's Law

LAW

Boyle's Law

For a **given mass of a gas** kept at **constant temperature**, the **volume** of the gas is **inversely proportional** to its **pressure**.

$$V \propto \frac{1}{p}$$

The ideal gas equation is $pV = \mu RT$. If the temperature T does not change, the right side stays constant. So $pV = \text{constant}$. This is **Boyle's law**:

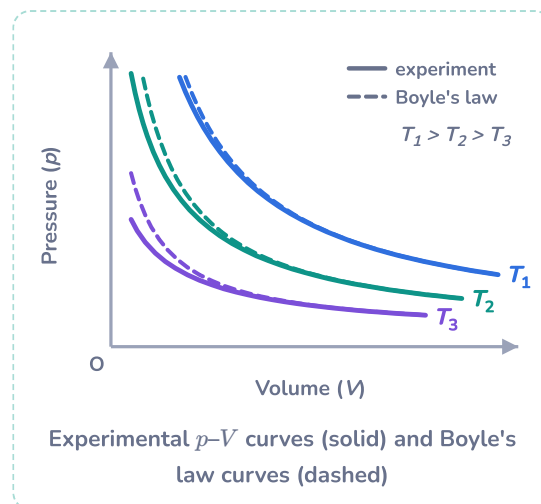
BOYLE'S LAW

$$p_1 V_1 = p_2 V_2 = p_3 V_3 = \dots = \text{constant}$$

The figure compares two sets of p - V curves at three temperatures $T_1 > T_2 > T_3$:

- ◆ **Solid lines:** curves found by **experiment** for a real gas.
- ◆ **Dashed lines:** curves **predicted by Boyle's law**.

At **low pressure** (large volume) the two sets agree. At **high pressure** the real gas moves away from Boyle's law.



2.3 Charles' Law

LAW

Charles' Law

For a **given mass of an ideal gas** kept at **constant pressure**, the **volume** V of the gas is **directly proportional** to its **absolute temperature** T .

$$V \propto T$$

Rearrange the ideal gas equation:

$$\frac{V}{T} = \frac{\mu R}{p}$$

If the pressure does not change, the right side is constant. So $\frac{V}{T} = \text{constant}$. This is **Charles' law**:

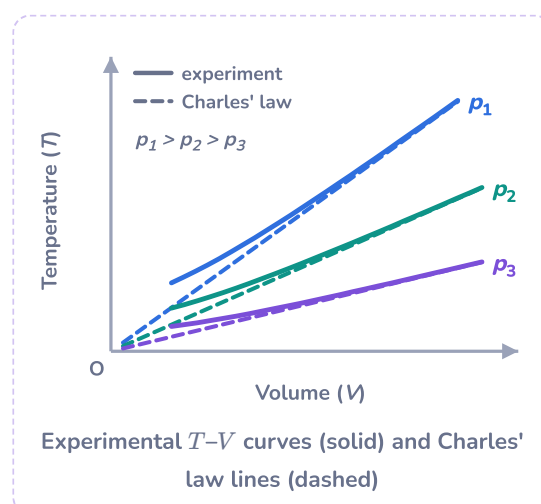
CHARLES' LAW

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} = \frac{V_3}{T_3} = \dots = \text{constant}$$

The figure compares two sets of T - V curves at three pressures $p_1 > p_2 > p_3$:

- ◆ **Solid lines:** curves found by **experiment** for a real gas.
- ◆ **Dashed lines:** straight lines **predicted by Charles' law**.

At **high temperature** the two sets agree. At **low temperature** the real gas moves away from Charles' law.



2.4 Dalton's Law of Partial Pressures

LAW

Dalton's Law of Partial Pressures

In a mixture of **non-interacting ideal gases**, the **total pressure** equals the **sum of the partial pressures** of all the gases present.

$$p = p_1 + p_2 + p_3 + \dots$$

SETUP – GIVEN INFORMATION

- ◆ A vessel holds a **mixture of non-interacting ideal gases**.
- ◆ Gas 1 has μ_1 moles, gas 2 has μ_2 moles, and so on.
- ◆ Volume of the mixture = V , temperature = T , pressure = p .

DERIVATION

- 1 Write the **equation of state** for the whole mixture:

$$pV = (\mu_1 + \mu_2 + \dots)RT$$

- 2 Divide both sides by V . The pressure splits into one part for each gas:

$$p = \frac{\mu_1 RT}{V} + \frac{\mu_2 RT}{V} + \dots$$

- 3 Each term is the partial pressure of one gas. So:

$$p = p_1 + p_2 + p_3 + \dots$$

NOTE

Here $p_1 = \frac{\mu_1 RT}{V}$ is the **partial pressure** of gas 1. It is the pressure that gas 1 would exert if it **alone** filled the same volume at the same temperature.

2.5 Graham's Law of Diffusion

LAW

Graham's Law of Diffusion

The **rate of diffusion** r of a gas varies **inversely** as the **square root of its density** ρ .

$$r \propto \frac{1}{\sqrt{\rho}} \quad \dots (i)$$

SETUP – GIVEN INFORMATION

- ◆ Ideal gas equation: $pV = \mu RT = \frac{M}{M_0} RT$
- ◆ M = mass of the gas, M_0 = molecular (molar) mass of the gas.

DERIVATION

- 1 Rearrange the ideal gas equation to get $\frac{M}{V}$:

$$\frac{M}{V} = \frac{pM_0}{RT} \quad \dots (ii)$$

- 2 Mass per unit volume is the density, $\rho = \frac{M}{V}$. So Eq. (ii) gives:

$$\rho = \frac{pM_0}{RT} \quad \dots (iii)$$

- 3 At the same p and T , density is proportional to molecular mass. Put this in Eq. (i):

$$r \propto \frac{1}{\sqrt{M_0}}$$

GRAHAM'S LAW FOR TWO GASES

$$\frac{r_1}{r_2} = \sqrt{\frac{\rho_2}{\rho_1}} = \sqrt{\frac{M_{02}}{M_{01}}}$$

where, r_1, r_2 = rates of diffusion, ρ_1, ρ_2 = densities and M_{01}, M_{02} = molecular masses of gas 1 and gas 2

2.6 Work Done on Compressing a Gas

When an ideal gas expands or is compressed, it follows relation (i) below. Here n is a **constant for the process**, called the **polytropic index**. The gas also obeys the **combined gas law** (ii):

$$pV^n = \text{constant} \quad \dots (i) \qquad \frac{pV}{T} = \text{constant} \quad \dots (ii)$$

• RELATIONS BETWEEN T , V AND P

DERIVATION

- 1 Divide Eq. (i) by Eq. (ii):

$$pV^n \div \frac{pV}{T} = pV^n \cdot \frac{T}{pV} = \text{constant}$$

2 Simplify. This is the **temperature–volume relation**:

$$TV^{n-1} = \text{constant} \quad \dots (iii)$$

3 From Eq. (ii), $V = \text{constant} \times \frac{T}{p}$. Put this value in Eq. (i):

$$p \left(\frac{T}{p} \right)^n = \frac{pT^n}{p^n} = \text{constant}$$

4 Take the n^{th} root. This is the **temperature–pressure relation**:

$$\frac{T}{p^{\frac{n-1}{n}}} = \text{constant} \quad \dots (iv)$$

• WORK DONE IN COMPRESSION

Let the gas be compressed from **state 1** to **state 2**. The work done **on the gas** is:

$$W = - \int_1^2 p dV \quad \dots (v)$$

DERIVATION

1 From Eq. (i), write p in terms of V . Here $C = pV^n$ is the constant:

$$p = \frac{C}{V^n}$$

2 Put this value in Eq. (v):

$$W = -C \int_1^2 V^{-n} dV$$

3 Integrate:

$$W = -C \left[\frac{V^{-n+1}}{-n+1} \right]_1^2$$

4 Put back $C = pV^n$ and simplify:

$$W = - \left[pV^n \frac{V^{1-n}}{1-n} \right]_1^2 = - \left[\frac{pV}{1-n} \right]_1^2$$

5 So the work done in compression is:

$$W = - \frac{p_2 V_2 - p_1 V_1}{1 - n} \quad \dots (vi)$$

6 For an ideal gas, $p_1 V_1 = \mu R T_1$ and $p_2 V_2 = \mu R T_2$. Put these in Eq. (vi):

$$W = - \frac{\mu R (T_2 - T_1)}{1 - n}$$

WORK DONE ON A GAS IN COMPRESSION

$$W = - \frac{p_2 V_2 - p_1 V_1}{1 - n} = - \frac{\mu R (T_2 - T_1)}{1 - n}$$

NOTE

Work Done in Expansion

For **expansion**, start from the work done **by the gas**, $W = \int_1^2 p dV$. The same steps give:

$$W = \frac{p_1 V_1 - p_2 V_2}{n - 1} \quad \text{and} \quad W = \frac{\mu R (T_1 - T_2)}{n - 1}$$

PART 3 03 Kinetic Theory of an Ideal Gas

The **kinetic theory of gases** explains the gas laws from the **motion of molecules**. It links what we measure, such as **pressure** and **temperature**, with how fast the molecules move.

3.1 Assumptions of Kinetic Theory

The kinetic theory of gases was built mainly by two scientists:

James Clerk Maxwell

(1831–1879), a **Scottish** physicist.

Ludwig Boltzmann

(1844–1906), a physicist from **Austria**.

Kinetic theory rests on the **molecular picture of matter**. It connects two kinds of properties of a gas:

Macroscopic: pressure, temperature ↔ **Microscopic: molecular speed, kinetic energy**

• POSTULATES (ASSUMPTIONS) OF KINETIC THEORY OF GASES

1 Large number of identical molecules.

Any amount of gas contains a **huge number of molecules**, about 10^{23} (the order of Avogadro's number). All the molecules are **identical in every way**.

2 Random motion.

The molecules move **randomly and non-stop** in all directions with different speeds. Between collisions, each molecule moves freely in a straight line, as **Newton's first law** says.

3 Negligible size.

A molecule is **much smaller** than the average distance between molecules. At ordinary pressure and temperature, a molecule is about **2 Å** in size. The average distance between molecules is about **20 Å**.

4 No intermolecular forces.

Molecules exert **no force on each other**, except during a collision.

5 Elastic collisions.

Collisions between molecules, and between molecules and the walls, are **perfectly elastic**. The total momentum and the total kinetic energy are **conserved**. Only the velocities of the molecules change.

6 Instantaneous collisions.

A collision lasts a **negligible time** compared with the time between two successive collisions.

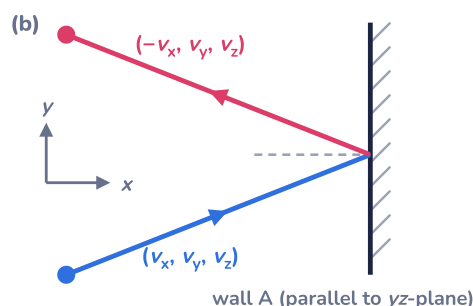
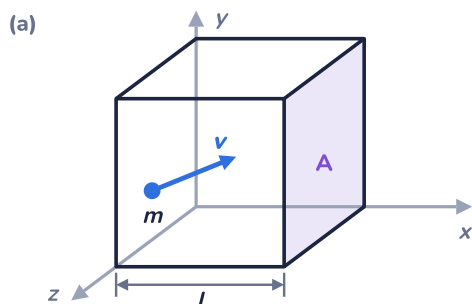
7 Uniform distribution.

The **density** of the gas and the spread of its molecules are **uniform** throughout the container.

3.2 Pressure of an Ideal Gas

SETUP – GIVEN INFORMATION

- ◆ An ideal gas has N molecules in a **cube of edge l** . So its volume is $V = l^3$.
- ◆ One molecule has **mass m** and **velocity (v_x, v_y, v_z)** .



(a) A molecule in a cube of edge l moves towards face A . (b) In an elastic hit on wall A , only v_x reverses

1 The molecule hits wall A (parallel to the yz -plane) **elastically**. Its x -component of velocity **reverses**. Its y - and z -components **do not change**. So the velocity changes from (v_x, v_y, v_z) to $(-v_x, v_y, v_z)$ in the collision.

2 Change in momentum of the molecule along the x -direction:

$$\Delta p_x = (p_x)_{\text{final}} - (p_x)_{\text{initial}} = (-mv_x) - (mv_x) = -2mv_x$$

3 Impulse = change in momentum. Let F be the **average force on the molecule by the wall**:

$$F \Delta t = \Delta p_x = -2mv_x \quad \dots (i)$$

4 To hit the **same wall again**, the molecule must go to the opposite wall and come back. This is a distance $2l$ along x . So the time between two hits on the same wall is:

$$\Delta t = \frac{2l}{v_x}$$

5 So the average force on the molecule by the wall, for each collision, is:

$$F = \frac{-2mv_x}{\Delta t} = \frac{-2mv_x}{(2l/v_x)} = \frac{-mv_x^2}{l}$$

6 By **Newton's third law**, the molecule pushes the wall with a force $\frac{mv_x^2}{l}$. For all N molecules, the total force on the wall is:

$$F_{\text{wall}} = \frac{m}{l} (v_{x1}^2 + v_{x2}^2 + \dots + v_{xN}^2) = \frac{Nm}{l} \overline{v_x^2} \quad \dots (ii)$$

Here $\overline{v_x^2} = \frac{v_{x1}^2 + v_{x2}^2 + \dots + v_{xN}^2}{N}$ is the average value of v_x^2 .

7 Velocity has three components, so $\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}$. The motion is **completely random**, so the three averages are equal:

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} \Rightarrow \overline{v^2} = 3\overline{v_x^2} \quad \text{or} \quad \overline{v_x^2} = \frac{1}{3} \overline{v^2} \quad \dots (iii)$$

8 From Eqs. (ii) and (iii), the **normal force** on the wall is:

$$F_{\text{wall}} = \frac{N}{3} \left(\frac{m}{l} \overline{v^2} \right) \quad \dots (iv)$$

9 Pressure = force $\div$ area. The wall's area is l^2 and the volume is $V = l^3$:

$$p = \frac{F_{\text{wall}}}{l^2} = \frac{1}{l^2} \left(\frac{N}{3} \frac{m \overline{v^2}}{l} \right) = \frac{1}{l^3} \left(\frac{Nm \overline{v^2}}{3} \right) = \frac{1}{V} \left(\frac{Nm \overline{v^2}}{3} \right)$$

- 10 Write $n = \frac{N}{V}$, the number of molecules per unit volume:

$$p = \frac{1}{3} \left(\frac{N}{V} \right) m \overline{v^2} = \frac{1}{3} n m \overline{v^2} \quad \dots (v)$$

KINETIC GAS EQUATION (PRESSURE OF AN IDEAL GAS)

$$p = \frac{1}{3} n m \overline{v^2}$$

where, p = pressure on the wall, n = **number density** (number of molecules per unit volume), m = mass of one molecule, $\overline{v^2}$ = **mean square speed**

CONCLUSIONS FROM THE DERIVATION

- ◆ The **shape of the vessel does not matter**. The area A and the time Δt are absent from the final answer. For a vessel of any shape, take a tiny flat area of its wall and repeat the same steps.
- ◆ By **Pascal's law**, a gas in equilibrium has the **same pressure** in every part of the container.
- ◆ We **ignored collisions between molecules**. Such collisions do not change the result if they are not too frequent and if each lasts a negligible time compared with the time between collisions.

3.3 Relation between Pressure and Density

SETUP – GIVEN INFORMATION

- ◆ A vessel holds an ideal gas.
- ◆ Total mass of all the molecules = M , volume = V , density = ρ .

DERIVATION

- 1 Multiply the **number density** n by the **mass of one molecule** m . The product is the total mass of the molecules in a unit volume:

$$n \times m = \frac{M}{V}$$

- 2 Mass per unit volume is the **density** of the gas $\left[\because \rho = \frac{\text{Mass}}{\text{Volume}} \right]$. So:

$$n \times m = \rho \quad \dots (vi)$$

- 3 Put Eq. (vi) in the kinetic gas equation (v):

$$p = \frac{1}{3} \rho \overline{v^2}$$

$$p = \frac{1}{3} \rho \overline{v^2}$$

where, ρ = density of the gas, $\overline{v^2}$ = mean square speed of its molecules

3.4 Kinetic Interpretation of Temperature

CONCEPT

The **average kinetic energy** of a gas molecule depends only on the **absolute temperature** of the gas. This idea is called the **kinetic interpretation of temperature**.

SETUP – GIVEN INFORMATION

- ◆ A sample of an ideal gas has N molecules.
- ◆ Volume = V , pressure = p , temperature = T .

DERIVATION

- 1 Start with the pressure of an ideal gas:

$$p = \frac{1}{3} nm\overline{v^2} \quad \dots (i)$$

- 2 Multiply both sides by V . Here $nV = N$, the number of molecules in the sample:

$$pV = \frac{1}{3}(nV)m\overline{v^2} = \frac{2}{3}N\left(\frac{1}{2}m\overline{v^2}\right) \quad \dots (ii)$$

- 3 $\frac{1}{2}m\overline{v^2}$ is the **average kinetic energy** of one molecule. So the total energy (internal energy) of the gas is:

$$E = N\left(\frac{1}{2}m\overline{v^2}\right) \quad \dots (iii)$$

- 4 From Eqs. (ii) and (iii):

$$pV = \frac{2}{3}E \quad \dots (iv)$$

- 5 For an ideal gas, $pV = \mu RT = \mu k_B N_A T = k_B(\mu N_A)T$. Here $\mu N_A = N$, the total number of molecules. So:

$$pV = k_B N T \quad \dots (v)$$

6 Compare Eqs. (iv) and (v):

$$\frac{2}{3}E = k_B NT \Rightarrow \frac{E}{N} = \frac{3}{2}k_B T \quad \dots (vi)$$

7 $\frac{E}{N}$ is the average kinetic energy of one molecule. So:

$$\frac{1}{2}m\overline{v^2} = \frac{3}{2}k_B T \quad \dots (vii)$$

AVERAGE KINETIC ENERGY OF A MOLECULE

$$\frac{1}{2}m\overline{v^2} = \frac{3}{2}k_B T \Rightarrow \frac{1}{2}m\overline{v^2} \propto T$$

IMPORTANT

A Basic Result

A molecule's average kinetic energy is **directly proportional** to the **absolute temperature** T . It does **not depend** on the pressure, the volume or the kind of ideal gas. This result links the **temperature** of a gas with the **average kinetic energy** of its molecules.

DEFINITION

Absolute Zero

Put $T = 0$ in Eq. (vii). Then $\frac{1}{2}m\overline{v^2} = 0$. Since $m \neq 0$, we get $\overline{v^2} = 0$.

Absolute zero is the temperature at which the **mean square speed of gas molecules becomes zero**.

3.5 Root Mean Square Speed

DEFINITION

The **root mean square (rms) speed** of gas molecules is the **square root of the mean square speed** $\overline{v^2}$. That is, $v_{\text{rms}} = \sqrt{\overline{v^2}}$.

DERIVATION

1 From the kinetic interpretation of temperature:

$$\frac{1}{2}m\overline{v^2} = \frac{3}{2}k_B T$$

2 So the **mean square speed** is:

$$\overline{v^2} = \frac{3k_B T}{m}$$

3 Take the **square root** of both sides:

$$\sqrt{\overline{v^2}} = \sqrt{\frac{3k_B T}{m}}$$

ROOT MEAN SQUARE SPEED

$$v_{\text{rms}} = \sqrt{\frac{3k_B T}{m}}$$

where, m = mass of one molecule, k_B = Boltzmann constant, T = absolute temperature

3.6 Maxwell's Speed Distribution

In a gas, the molecules do **not all have the same speed**. Their motion is random, in all directions. Still, the way the speeds are shared among the molecules (the **distribution of speeds**) stays **fixed**. **Maxwell** was the first to study this. He derived an equation for the speed distribution of molecules.

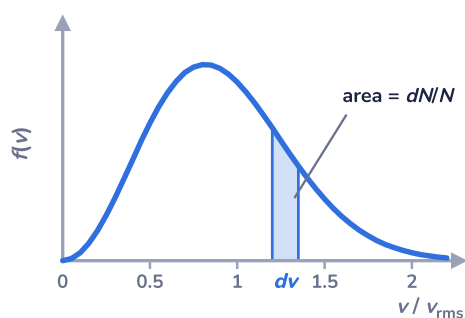
Let dN be the number of molecules with speeds between v and $v + dv$. Then:

MAXWELL'S SPEED DISTRIBUTION

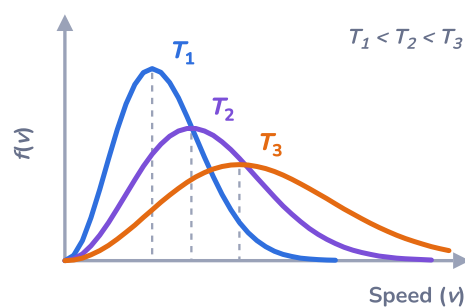
$$dN = 4\pi N \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-\frac{mv^2}{2k_B T}} dv$$

where, v = speed of a molecule, m = mass of one molecule, T = temperature (in kelvin), N = total number of molecules, k_B = Boltzmann constant

i Area Under the Curve



ii Effect of Temperature



In figure (i), the fraction of molecules with speeds between v and $v + dv$ is the **area of the thin strip**:

$$\frac{dN}{N} = f(v) dv = \text{area of the strip}$$

The **total area** under the curve is **1 (unity)**, because it covers all the molecules.

Figure (ii) shows $f(v)$ for a gas at **three temperatures**. Each curve has a **peak**. The peak shows the speed that the **largest fraction of molecules** have. This speed $v_{\max}$ is called the **most probable speed**.

NOTE

As the **temperature rises**, the curve becomes **flatter** and its peak **shifts towards higher speed**.

Most Probable Speed

The **most probable speed** is the speed that the **largest number of molecules** of a gas have at a given temperature.

$$v_{\text{mp}} = \sqrt{\frac{2k_B T}{m}}$$

Mean (Average) Speed

The **mean speed** is the **arithmetic mean** of the speeds of all the molecules of a gas at a given temperature.

$$v_{\text{av}} = \sqrt{\frac{8k_B T}{\pi m}}$$

04 PART 4 Equipartition of Energy and Mean Free Path

Energy is **shared equally** among the ways a molecule can move. This gives the **specific heats** of gases, solids and water.

4.1 Degrees of Freedom

DEFINITION

The **number of degrees of freedom** of a system is the total number of **independent coordinates** (or quantities) needed to describe its **position and configuration completely**. It is written as f .

DEGREES OF FREEDOM

$$f = 3N - K$$

where, N = number of particles in the system, K = number of independent relations (constraints) between the particles

Monoatomic Gas

e.g. Helium, neon, argon.
Only **translational** motion is possible.

Here $N = 1$ and $K = 0$. So
 $f = 3 \times 1 - 0$.

$$f = 3$$

Diatomic Gas

e.g. Oxygen, hydrogen, nitrogen. Each molecule has **3 translational** and **2 rotational** degrees of freedom.

$$f = 5$$

Triatomic Gas

e.g. SO_2 , H_2S . Each molecule has **three atoms**.

$$f = 7 \text{ (linear molecule)}$$

$$f = 6 \text{ (non-linear molecule)}$$

4.2 Law of Equipartition of Energy

LAW

Law of Equipartition of Energy

For a system in **thermal equilibrium**, the total energy is **shared equally** among all its degrees of freedom. The average energy of a molecule for **each degree of freedom** is $\frac{1}{2}k_B T$.

Here k_B = Boltzmann constant = $1.38 \times 10^{-23} \text{ J K}^{-1}$ and T = absolute temperature (kelvin scale).

• TRANSLATIONAL ENERGY

Take a **monoatomic gas** in thermal equilibrium at temperature T . The average translational energy of one molecule is:

$$\langle E_t \rangle = \langle \frac{1}{2}mv_x^2 \rangle + \langle \frac{1}{2}mv_y^2 \rangle + \langle \frac{1}{2}mv_z^2 \rangle = \frac{3}{2}k_B T$$

No direction is special. So each of the three terms gets an **equal share**:

$$\langle \frac{1}{2}mv_x^2 \rangle = \langle \frac{1}{2}mv_y^2 \rangle = \langle \frac{1}{2}mv_z^2 \rangle = \frac{1}{2}k_B T$$

KEY

Each molecule has an energy of $\frac{1}{2}k_B T$ per degree of freedom. This is the law of equipartition of energy.

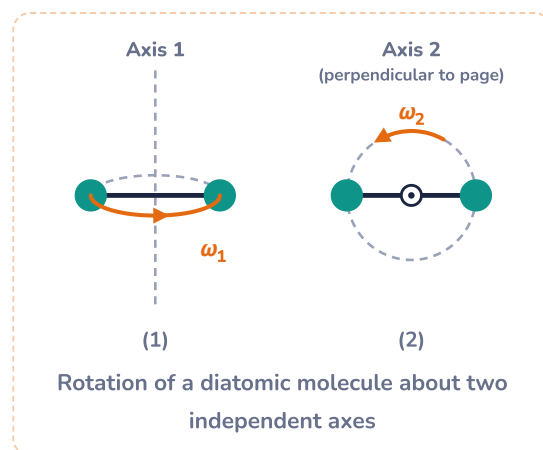
• ROTATIONAL ENERGY OF A DIATOMIC MOLECULE

A **diatomic molecule** can also rotate. So its total energy is the sum of the translational energy E_t and the rotational energy E_r :

$$E_t + E_r = \left(\frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 \right) + \left(\frac{1}{2}I_1\omega_1^2 + \frac{1}{2}I_2\omega_2^2 \right)$$

The molecule can rotate about **two independent axes**, called axis 1 and axis 2. Both axes pass through its centre and are **perpendicular** to the line joining the two atoms.

Here ω_1 and ω_2 are the **angular speeds** about axes 1 and 2. I_1 and I_2 are the **moments of inertia** about these axes.



• VIBRATIONAL ENERGY

A diatomic or polyatomic molecule is not always a **rigid rotator**. Its atoms may also **vibrate**. For example, the **CO** molecule vibrates even at moderate temperatures. This adds a **vibrational energy** E_v to the total energy:

$$E_v = \frac{1}{2}m \left(\frac{dy}{dt} \right)^2 + \frac{1}{2}ky^2$$

Here k = **force constant** of the oscillator and y = **vibrational coordinate**.

TOTAL ENERGY OF A MOLECULE

$$E = E_t + E_r + E_v$$

translational energy + rotational energy + vibrational energy

4.3 Specific Heat Capacity of Monoatomic Gases

The **law of equipartition of energy** lets us find the **specific heat capacity** of gases with different degrees of freedom.

A monoatomic molecule has **3 translational degrees of freedom**. Each one has an average energy of $\frac{1}{2}k_B T$:

$$3 \text{ degrees of freedom} \times \frac{1}{2}k_B T \text{ each} = \frac{3}{2}k_B T \text{ per molecule}$$

DERIVATION

- 1 One mole has N_A molecules. Using $R = N_A k_B$, the **internal energy of one mole** is:

$$U = \frac{3}{2}k_B T \times N_A = \frac{3}{2}RT \quad \dots (i)$$

- 2 Let dU be the heat needed to raise the temperature of **1 mole** of the gas by dT at **constant volume**. Then the **molar specific heat at constant volume** is:

$$C_V = \frac{dU}{dT} \quad \dots (ii)$$

3 Put $U = \frac{3}{2}RT$ in Eq. (ii):

$$C_V = \frac{d}{dT} \left(\frac{3}{2}RT \right) = \frac{3}{2}R$$

4 Use **Mayer's relation**, $C_p - C_V = R$, for the molar specific heat at **constant pressure**:

$$C_p = \frac{3}{2}R + R = \frac{5}{2}R$$

5 The **ratio of specific heats** is:

$$\gamma = \frac{C_p}{C_V} = \frac{(5/2)R}{(3/2)R} = \frac{5}{3} = 1.67$$

C_V

$$C_V = \frac{3}{2}R$$

C_p

$$C_p = \frac{5}{2}R$$

γ

$$\gamma = \frac{5}{3} = 1.67$$

4.4 Specific Heat Capacity of Diatomic Gases

Ignore the **vibrational mode**. At room temperature, a diatomic molecule then has:

3 translational + 2 rotational = 5 degrees of freedom ($f = 5$)

DERIVATION

1 By the law of equipartition, the **internal energy of one mole** is [$\because R = k_B N_A$]:

$$U = 5 \times \left(\frac{1}{2} k_B T \right) \times N_A = \frac{5}{2} RT$$

2 The molar specific heat at constant volume is:

$$C_V = \frac{dU}{dT} = \frac{d}{dT} \left(\frac{5}{2} RT \right) = \frac{5}{2} R$$

3 Use Mayer's relation, $C_p = C_V + R$:

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

- 4 The ratio of specific heats is:

$$\gamma = \frac{C_p}{C_V} = \frac{(7/2)R}{(5/2)R} = \frac{7}{5} = 1.40$$

C_V

$$C_V = \frac{5}{2}R$$

C_P

$$C_p = \frac{7}{2}R$$

γ

$$\gamma = \frac{7}{5} = 1.40$$

4.5 Specific Heat Capacity of Triatomic Gases

A **linear triatomic** molecule has **seven degrees of freedom** ($f = 7$).

DERIVATION

- 1 By the law of equipartition, the **internal energy of one mole** is [$\because R = k_B N_A$]:

$$U = 7 \times \left(\frac{1}{2} k_B T \right) \times N_A = \frac{7}{2} RT$$

- 2 The molar specific heat at constant volume is:

$$C_V = \frac{dU}{dT} = \frac{d}{dT} \left(\frac{7}{2} RT \right) = \frac{7}{2} R$$

- 3 Use Mayer's relation, $C_p = C_V + R$:

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

- 4 The ratio of specific heats is:

$$\gamma = \frac{C_p}{C_V} = \frac{(9/2)R}{(7/2)R} = \frac{9}{7} \approx 1.29$$

C_V

$$C_V = \frac{7}{2}R$$

C_P

$$C_p = \frac{9}{2}R$$

γ

$$\gamma = \frac{9}{7} \approx 1.29$$

4.6 Specific Heat Capacity of Polyatomic Gases

In general, a **polyatomic molecule** has:

3 translational + 3 rotational + f vibrational modes

Here f is the number of vibrational modes. Each mode has kinetic and potential energy, so it gets $2 \times \frac{1}{2}k_B T = k_B T$.

DERIVATION

- 1 By the law of equipartition, the **internal energy of one mole** is:

$$U = \left[\frac{3}{2}k_B T + \frac{3}{2}k_B T + f k_B T \right] \times N_A \Rightarrow U = (3 + f) RT$$

- 2 The molar specific heat at constant volume is:

$$C_V = \frac{dU}{dT} = \frac{d[(3 + f)RT]}{dT} = (3 + f) R$$

- 3 Use Mayer's relation, $C_p = C_V + R = (3 + f)R + R$:

$$C_p = (4 + f) R$$

- 4 The ratio of specific heats is:

$$\gamma = \frac{C_p}{C_V} = \frac{4 + f}{3 + f}$$

Taking $f = 6$: $\gamma = \frac{4 + 6}{3 + 6} = \frac{10}{9}$

$\gamma = 1.11$

4.7 Determination of γ from Degrees of Freedom

DERIVATION

- 1 Let a gas molecule have f **degrees of freedom**. The internal energy of **one mole** of the gas is:

$$U = f \times \left(\frac{1}{2}k_B T \right) \times N_A = \frac{f}{2} RT$$

- 2 The molar specific heat at constant volume is:

$$C_V = \frac{dU}{dT} = \frac{d}{dT} \left(\frac{f}{2} RT \right) = \frac{f}{2} R$$

- 3 Use Mayer's relation, $C_p = C_V + R = \frac{f}{2} R + R$:

$$C_p = \left(\frac{f}{2} + 1 \right) R$$

4 So the ratio of specific heats is:

$$\gamma = \frac{C_p}{C_V} = \frac{\left(\frac{f}{2} + 1\right) R}{\frac{f}{2} R} \Rightarrow \gamma = 1 + \frac{2}{f}$$

RELATION BETWEEN γ AND f

$$\gamma = 1 + \frac{2}{f}$$

where, f = degrees of freedom of one molecule

SUMMARY FOR GASES

GAS	f	C_V	C_p	$\gamma = C_p/C_V$
Monoatomic	3	$\frac{3}{2}R$	$\frac{5}{2}R$	$\frac{5}{3} = 1.67$
Diatomic	5	$\frac{5}{2}R$	$\frac{7}{2}R$	$\frac{7}{5} = 1.40$
Linear triatomic	7	$\frac{7}{2}R$	$\frac{9}{2}R$	$\frac{9}{7} \approx 1.29$

4.8 Specific Heat Capacity of Solids

SETUP – GIVEN INFORMATION

- ◆ In a solid, each atom **vibrates about its mean position**.
- ◆ One mole of a solid has N_A **atoms**.
- ◆ Each atom oscillates in **3 dimensions**.

DERIVATION

- 1 An oscillation in one dimension has kinetic and potential energy. By the law of equipartition, the **average energy per atom** for one dimension is:

$$2 \times \left(\frac{1}{2}k_B T\right) = k_B T$$

- 2 So in **three dimensions**, the average energy per atom is:

$$3k_B T$$

3 The **total energy of one mole** of the solid is:

$$U = (3k_B T) \times N_A = 3RT \quad [\because k_B N_A = R]$$

4 By the **first law of thermodynamics**, $\Delta Q = \Delta U + \Delta W = \Delta U + p \Delta V$. For a solid, ΔV is **negligible**. So:

$$\Delta Q \approx \Delta U$$

5 So the **molar specific heat** of a solid is:

$$C = \frac{\Delta Q}{\Delta T} = \frac{\Delta U}{\Delta T} = 3R$$

MOLAR SPECIFIC HEAT OF A SOLID

$$C = 3R = 3 \times 8.314 \approx 24.94 \text{ J mol}^{-1} \text{ K}^{-1}$$

using $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

• SPECIFIC HEAT CAPACITIES OF SOME SOLIDS

SUBSTANCE	SPECIFIC HEAT (J KG ⁻¹ K ⁻¹)	MOLAR SPECIFIC HEAT (J MOL ⁻¹ K ⁻¹)
Aluminium	900.0	24.4
Carbon	506.5	6.1
Copper	386.4	24.5
Lead	127.7	26.5
Silver	236.1	25.5
Tungsten	134.4	24.9

Values at room temperature and atmospheric pressure.

The table shows that the predicted value $3R$ **generally agrees** with experiment at ordinary temperatures.

Carbon is an exception.

NOTE

Each solid has a characteristic temperature called its **Debye temperature**. Above this temperature, the molar specific heat C_V of the solid becomes **nearly constant** (close to $3R$).

4.9 Specific Heat Capacity of Water

SETUP – GIVEN INFORMATION

- ◆ Treat a water molecule like a solid of **3 atoms** (2 hydrogen + 1 oxygen). Each atom can **vibrate in 3 dimensions** about its mean position.

DERIVATION

- 1 By the law of equipartition, the **average energy per atom** for one dimension is:

$$2 \times \left(\frac{1}{2} k_B T \right) = k_B T$$

- 2 In **three dimensions**, the average energy per atom is:

$$3k_B T$$

- 3 A water molecule has 3 atoms. So the **total energy of one molecule** is:

$$3 \times (3k_B T) = 9k_B T$$

- 4 The **total energy of 1 mole** of water is:

$$U = 3 \times 3k_B T \times N_A = 9RT$$

- 5 So the **molar specific heat** of water is:

$$C = \frac{\Delta Q}{\Delta T} = \frac{\Delta U}{\Delta T} = 9R$$

MOLAR SPECIFIC HEAT OF WATER

$$C = 9R = 9 \times 8.314 \approx 74.83 \text{ J mol}^{-1} \text{K}^{-1}$$

using $R = 8.314 \text{ J mol}^{-1} \text{K}^{-1}$

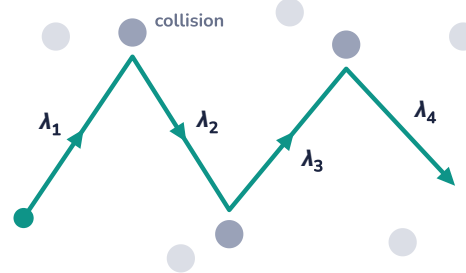
4.10 Mean Free Path

A gas has a huge number of molecules that **collide very often**. So a molecule **cannot travel straight** for long. The molecules are always in **continuous random motion**. Their collisions with each other are **perfectly elastic**.

DEFINITION

The **mean free path** (λ) of a gas molecule is the **average distance** it travels between **two successive collisions**.

Each straight piece of the path between two collisions is one **free path**. The mean free path is the average of these free paths.

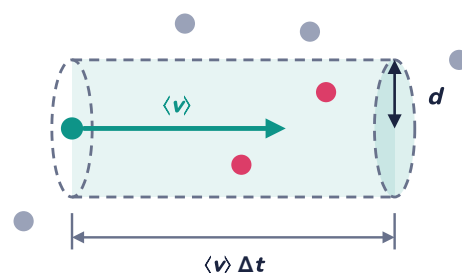


Free paths $\lambda_1, \lambda_2, \lambda_3, \lambda_4$ of one molecule between collisions

• EXPRESSION FOR MEAN FREE PATH

SETUP – GIVEN INFORMATION

- ◆ Let d be the **diameter** of each molecule.
- ◆ A molecule collides with every molecule whose centre comes within a **distance** d of its own centre.
- ◆ $\langle v \rangle$ = average speed of the molecule, n = number of molecules per unit volume.



Cylinder of radius d swept in time Δt . Red molecules lie inside it and collide

DERIVATION

- 1 In a small time Δt , the molecule sweeps a cylinder of radius d and length $\langle v \rangle \Delta t$. It collides with every molecule whose centre lies in this volume:

$$\text{Volume swept} = \pi d^2 \langle v \rangle \Delta t$$

- 2 There are n molecules per unit volume. So the number of collisions in time Δt is:

$$\pi d^2 \langle v \rangle \Delta t \times n$$

- 3 So the **number of collisions per second** is:

$$\frac{\pi d^2 \langle v \rangle \Delta t \times n}{\Delta t} = n \pi d^2 \langle v \rangle$$

- 4 The **average time between two successive collisions** is:

$$\tau = \frac{1}{n \pi d^2 \langle v \rangle}$$

- 5 The mean free path is the average distance covered between two successive collisions:

$$\lambda = \langle v \rangle \tau = \frac{\langle v \rangle}{n\pi d^2 \langle v \rangle} = \frac{1}{n\pi d^2}$$

MEAN FREE PATH

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

where, d = diameter of each molecule, n = number of molecules per unit volume

4.11 Assumptions and Accurate Value of Mean Free Path

The derivation in topic 4.10 rests on these **assumptions**:

- 1 The gas molecules are **hard spheres**, each of diameter d .
- 2 Collisions between gas molecules are **perfectly elastic**.
- 3 All the molecules are **at rest**, except the one being studied.
- 4 The chosen molecule collides with every molecule whose centre is at a **distance d** from its own centre.

In the derivation we took the other molecules to be at rest. In reality, **all the molecules are moving**. Including this gives a **more accurate value**:

MEAN FREE PATH (ACCURATE VALUE)

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

where, n = number of molecules per unit volume, d = diameter of a molecule, λ = mean free path

From $pV = Nk_B T$, we get $p = nk_B T$, that is, $n = \frac{p}{k_B T}$. Put this in the formula above:

MEAN FREE PATH IN TERMS OF T AND P

$$\lambda = \frac{k_B T}{\sqrt{2} \pi d^2 p}$$

where, T = absolute temperature (in kelvin), p = pressure of the gas

At Constant Pressure

λ is **directly proportional** to the absolute temperature.

$$\lambda \propto T$$

At Constant Temperature

λ is **inversely proportional** to the pressure.

$$\lambda \propto \frac{1}{p}$$

NOTE

Kinetic theory easily links **bulk properties** that we can measure, like **viscosity**, **heat conductivity** and the **rate of diffusion**, with **microscopic quantities** such as the size of a molecule.

4.12 Brownian Motion

In **1827**, the Scottish botanist **Robert Brown** was looking at the pollen grains of a flower under a microscope. He saw the grains moving all the time in a **zig-zag, random way**.

DEFINITION

Brownian motion is the **continuous zig-zag motion** of microscopic particles suspended in water, air or any other fluid. Kinetic theory explains this motion.

A tiny particle (size about 10^{-5} m) in a fluid is **hit from all sides** by the fluid molecules, all the time. The impulses and torques from these hits **do not add up exactly to zero**. So at every moment there is a **net impulse or torque** in some direction. This keeps the particle moving randomly.

BROWNIAN MOTION DEPENDS ON**i Size**

Size of the **suspended particle**.

ii Density

Density of the **fluid**.

iii Temperature

Temperature of the **medium**.

iv Viscosity

Viscosity of the **medium**.

NOTE

In **1987**, the Egyptian scientist **Ahmed Zewail** observed the detailed interactions of molecules. He lit them with very short flashes of **laser light**, each lasting about **10 femtoseconds** (1 femtosecond = 10^{-15} s).