

Lecture 4-5

Kinetic Theory of Gas

Kinetic model of gas:

Daniel Bernoulli derives Boyle's law (1661) using Newton's laws of motion applied to molecules (1738)

Work ignored for 100 years

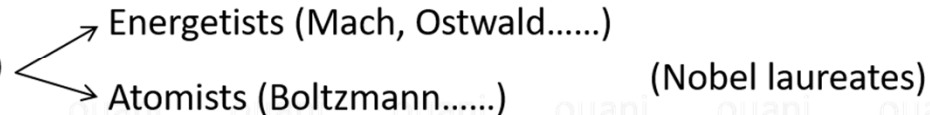
John Dalton's (1766-1844) atomic theory - 1805

John Waterston submits a paper to Royal Society of England correctly (1845) describing the concepts of kinetic model

Paper gets rejected as "non-sense"

Avogadro 1776-1856

From 1848 to 1898 kinetic model was developed by Joule, Clausius, Maxwell and Boltzmann

1870-1910 
Energetists (Mach, Ostwald.....)
Atomists (Boltzmann.....) (Nobel laureates)

1898: Boltzmann writes "I am conscious of being only an individual struggling weakly against the stream of time. But it still remains in my power to contribute in such a way that when theory of gas is again revised, not too much will leave to be rediscovered."[Lectures on Gas theory, University of California Press, 1964]

1905: Einstein applied kinetic model to Brownian motion of a tiny particle suspended in fluid (Theory)

1908: Perrin experimentally verifies Einstein's theory, thus energetists were convinced to the reality of atoms and molecules
But by then Boltzmann has already passed away (1906)

Kinetic model of a gas can be seen/viewed as a connection between classical mechanics, quantum mechanics and statistical mechanics.

How to relate macroscopic properties like pressure or volume with microscopic properties like mass of an atom/molecule, velocity of the molecule etc.? If it can be done then people might believe the atomistic view.

Basic assumptions/considerations of Kinetic Theory of Gases:

Observation \Rightarrow Hypothesis \Rightarrow Model \Rightarrow Theory \Rightarrow Law

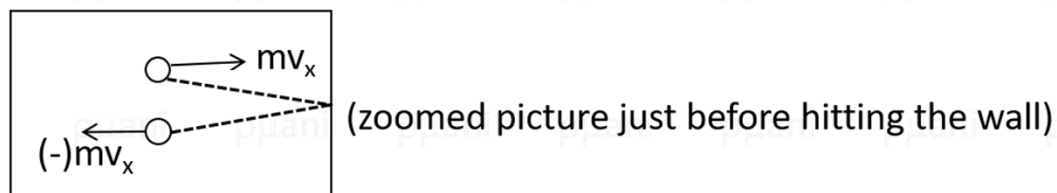
1. A gas consists of a large number of molecules, considered as perfectly elastic hard spheres.
2. The molecules are in a state of complete molecular chaos, i.e. they move erratically along all possible directions, with all possible speeds from zero to infinity.
3. The movement of the molecules are in straight lines (in the absence of any external force, like gravity), which are occasionally broken by collisions between themselves and, with the walls of the container.
4. The collisions that the molecules make are all perfectly elastic, in which the conservation of momentum as well as the kinetic energy hold.
5. In the steady state, the collisions between the molecules do not affect the molecular density, i.e., the number of molecules per unit volume is uniform everywhere and, remains the same with time.
6. The distance traversed by a molecule between two successive collisions is called the free path. It is assumed that the size of the molecules is negligible in comparison to the mean free path. The molecules are therefore regarded as a point masses.
7. The time during which a collision lasts is negligible in comparison to the time required by a molecule to traverse the mean free path.
8. The forces between the molecules are neglected entirely, so that the energy of a gas is totally kinetic.
9. During the bombardment of the molecules on the wall of the container, a certain momentum is transferred on the wall. The net momentum transferred normally-per unit area of the wall per second is defined as the pressure of the gas.
10. The molecules move with different speeds, and hence, with different translation kinetic energies. The average translational kinetic energy of the molecules of a sample of gas is directly proportional to the kelvin temperature of the gas.

The kinetic theory of gas:

1. The gas consists of molecules of mass 'm' in ceaseless random motion.
2. The size (diameter) of molecules is negligible in comparison to the average distance travelled between collisions (dilute gas).
3. The molecules do not interact except making perfectly elastic collisions when they are in contact.

This means P.E. contribution is negligible in comparison to K.E. contribution [Hence the name 'kinetic']

Elastic collision: no internal modes of motion is excited, i.e. translational energy of molecules is conserved in a collision



A particle (atomistic view) of mass 'm' (atomistic view) is travelling with a component of velocity (not avg. velocity) v_x (|| to x-axis) collides with the wall on the right and gets reflected.

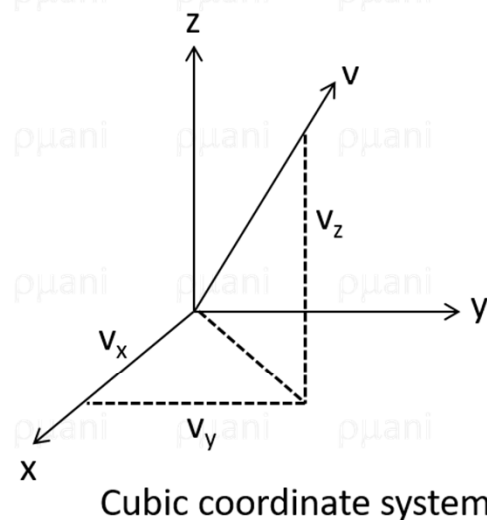
Therefore, its linear momentum changes from mv_x to $(-)mv_x$

So, change of momentum per collision = $2mv_x [mv_x - (-mv_x)]$ [Newton's third law]

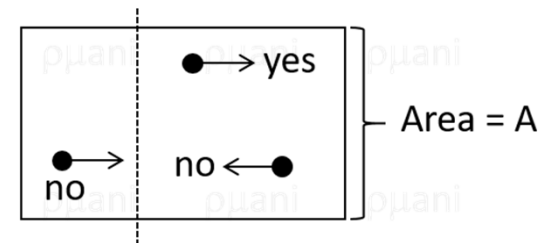
(this value is per molecule)

(-y, -z components are unchanged)

(Pressure will be generated because of collision of many molecules, but how many molecules? That depends on how much time)



Let us calculate the no. of molecules that will collide with the wall in a time interval of Δt . All molecules within the distance $(v_x \cdot \Delta t)$ will reach the wall and make collision provided it is travelling towards it. If the wall has area 'A' then all molecules within the volume $(A \cdot v_x \cdot \Delta t)$ will make collision.



Let, 'n' be total no. of moles in container of volume V and N_A be the Avogadro constant

So, the number of molecules in volume $(A \cdot v_x \cdot \Delta t)$ is

$$(A \cdot v_x \cdot \Delta t) \cdot \frac{(n \cdot N_A)}{V} \quad \left[\frac{(n \cdot N_A)}{V} \text{ is the number density of particle} \right]$$

Assuming, on the **average half of the molecule** (coming from the assumption of random motion) are travelling toward the wall and thereby making collision

So, Average no. of molecules making collision is

$$\frac{1}{2} \cdot \frac{(n \cdot N_A)}{V} \cdot (A \cdot v_x \cdot \Delta t)$$

So, total change of linear momentum (for all molecule) in a time interval of Δt is

$$\underbrace{\frac{1}{2} \cdot \frac{(n \cdot N_A)}{V} \cdot (A \cdot v_x \cdot \Delta t)}_{\text{Total no. of molecules}} \cdot \underbrace{2mv_x}_{\text{per molecule}} = \frac{n m N_A \cdot A \cdot v_x^2 \cdot \Delta t}{V} = \frac{n M A v_x^2 \cdot \Delta t}{V} \quad [m \cdot N_A = M \text{ (Molar mass)}]$$

So, **the rate of change of momentum** = $\frac{n M A v_x^2}{V} = \text{Force}$ (Newton's second law of motion)

Average force for all molecules

$$\frac{F}{N} = \frac{m \cdot (v_{x1}^2 + v_{x2}^2 + v_{x3}^2 + \dots + v_{xN}^2)}{L \cdot N} = \frac{m \cdot \langle v_x^2 \rangle}{L} \quad [N = \text{total no. of molecules and } \left\{ \frac{(v_{x1}^2 + v_{x2}^2 + v_{x3}^2 + \dots + v_{xN}^2)}{N} \right\} = \langle v_x^2 \rangle]$$

$$N = n \cdot N_A$$

$$L = \frac{L^3}{L^2} = \frac{V}{A} \quad \text{or,} \quad \frac{1}{L} = \frac{A}{V}$$

$$\text{So, } F = \frac{m \cdot N \cdot A \cdot \langle v_x^2 \rangle}{V} = \frac{m \cdot n \cdot N_A \cdot A \cdot \langle v_x^2 \rangle}{V} = \frac{n \cdot M \cdot A \cdot \langle v_x^2 \rangle}{V}$$

Rate of change of momentum = Force

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}}$$

Actually we need to take avg. pressure (macroscopic) i.e. we need to take avg. force (macroscopic)

$$\text{Pressure (p)} = \frac{n \cdot M \cdot v_x^2}{V}$$

All molecules do not travel with same velocity, so, the detected pressure will be an average one (Average denoted as $\langle \rangle$)

Question: $\langle v_x^2 \rangle$ or $(\langle v_x \rangle)^2$?

You take $\langle v_x \rangle$ when velocity changes. Velocity of one molecule does not change (elastic collision)

$$\text{Avg. force} = \frac{n \cdot M \cdot A \cdot \langle v_x^2 \rangle}{V} \quad \text{and not} \quad \frac{n \cdot M \cdot A \cdot (\langle v_x \rangle)^2}{V}$$

$$\text{So, Pressure (p)} = \frac{n \cdot M \cdot \langle v_x^2 \rangle}{V}$$

Equilibrium situation:

As the molecules are moving randomly and there is no net flow in a particular direction, so average speed (velocity) along x-direction is same as that in the y-direction and z-direction.

Thus, root mean square speed of molecules $\Rightarrow c = \sqrt{\langle v^2 \rangle} \Rightarrow c^2 = \langle v^2 \rangle$

$$c^2 = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle \quad \{\text{comes from Pythagoras theorem in 3 dimensions}\}$$

$$= 3 \langle v_x^2 \rangle$$

$$\text{So, } \langle v_x^2 \rangle = \frac{1}{3} c^2$$

$$\text{So, } pV = nM \cdot \frac{1}{3} c^2$$

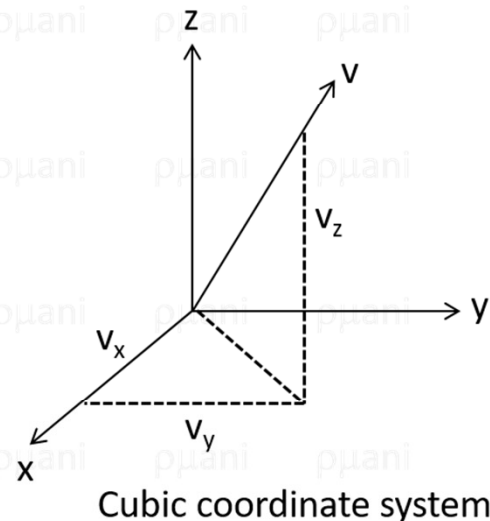
$$\Rightarrow \boxed{pV = \frac{1}{3} nM c^2} \quad \dots\dots\dots (A)$$

Similar to Boyle's law: $\boxed{pV = \text{constant}}$ at a constant temperature

Thus by using above equation we will be able to calculate the root mean square speed of molecules

$$\text{Now, } pV = \frac{1}{3} nM c^2 \quad \text{and} \quad pV = nRT$$

$$\Rightarrow \boxed{c = \sqrt{\frac{3RT}{M}}} \quad \text{So, root mean square speed of molecules is dependent on temperature and molar mass of the molecule}$$



Question:

Calculate root mean square speed of N_2 , O_2 , CO_2 at 298K. Compare the values with the speed of sound. (Similarity between c and speed of sound in air ?)

$$pV = \frac{1}{3} n M c^2 \quad (\text{For an ideal gas})$$

This equation expresses macroscopic property of pressure in terms of molecular properties like n , M , c^2

Average translational kinetic energy per molecule is

$$\langle \epsilon_{tr} \rangle = \frac{1}{2} m c^2$$

$$\Rightarrow c^2 = \frac{2 \langle \epsilon_{tr} \rangle}{m}$$

$$\text{Now, } pV = \frac{1}{3} n M c^2 = \frac{2}{3} n M \frac{\langle \epsilon_{tr} \rangle}{m}$$

$$\Rightarrow pV = \frac{2}{3} n N_A \langle \epsilon_{tr} \rangle \quad \left[\frac{M}{m} = N_A \right]$$

$$\Rightarrow pV = \frac{2}{3} \epsilon_{tr} \quad [\epsilon_{tr} = n \cdot N_A \cdot \langle \epsilon_{tr} \rangle ; n = \text{no. of moles, } N_A = \text{Avogadro constant, } n \cdot N_A = \text{Total no. of molecule}]$$

ϵ_{tr} is termed as total translational kinetic energy of (all) gas molecules

So, for an ideal gas

$$pV = \frac{2}{3} \epsilon_{tr} \quad \dots\dots\dots(B)$$

Question: How will the Dalton's law of partial pressure look like for a mixture of two different gases in terms of root mean square speed?

$$\begin{aligned}
 p &= p_i + p_j \\
 &= \frac{1}{3} \frac{n_i M_i c_i^2}{V} + \frac{1}{3} \frac{n_j M_j c_j^2}{V} \\
 \boxed{p} &= \frac{1}{3V} \sum_i (n_i M_i c_i^2)
 \end{aligned}$$

Question: Why don't we use the time of impact of collision (which is very short) to calculate rate of momentum change? Instead we use Δt that is a much longer time. What is the physical significance of Δt ?

⇒ Because we are calculating avg. force over time to get the pressure which is macroscopic w.r.t. time.

$$\begin{aligned}
 p &\propto \frac{1}{V} \quad \text{and} \quad p \propto T \\
 \Rightarrow p &\propto \frac{T}{V} \quad \text{or} \quad p = \frac{n R T}{V} \quad [R \text{ is a proportionality constant to match dimension of lit (vol.), atm (pressure); for } n \text{ moles of gas}] \\
 \Rightarrow \boxed{p V} &= n R T \quad [\text{Ideal gas equation for } n \text{ moles}]
 \end{aligned}$$

Recall : Pressure (p) = $\frac{1}{3} \frac{n \cdot M \cdot \langle c^2 \rangle}{V}$ and $c = \sqrt{\frac{3 R T}{M}}$