

# Kinetic theory

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**Kinetic theory** (or **kinetic theory of gases**) attempts to explain macroscopic properties of gases, such as pressure, temperature, or volume, by considering their molecular composition and motion. Essentially, the theory posits that pressure is due not to static repulsion between molecules, as was Isaac Newton's conjecture, but due to collisions between molecules moving at different velocities. Kinetic theory is also known as the **Kinetic-Molecular Theory** or the **Collision Theory** or the **Kinetic-Molecular Theory of Gases**.

## Postulates

The theory for ideal gases makes the following assumptions:

- The gas consists of very small particles, each of which has a mass or weight in SI units, kilograms.
- The number of molecules is large such that statistical treatment can be applied.
- These molecules are in constant, random motion. The rapidly moving particles constantly collide with the walls of the container.
- The collisions of gas particles with the walls of the container holding them are perfectly elastic.
- The interactions among molecules are negligible. They exert no forces on one another except during collisions.
- The total volume of the individual gas molecules added up is negligible compared to the volume of the container. This is equivalent to stating that the average distance separating the gas particles is relatively large compared to their size.
- The molecules are perfectly spherical in shape, and elastic in nature.
- The average kinetic energy of the gas particles depends only on the temperature of the system.
- The time during collision of molecule with the container's wall is negligible as comparable to the time between successive collisions.
- The equations of motion of the molecules are time-reversible.

In addition, if the gas is in a container, the collisions with the walls are assumed to be instantaneous and elastic.

## Pressure

Pressure is explained by kinetic theory as arising from the force exerted by gas molecules impacting on the walls of the container. Consider a gas of  $N$  molecules, each of mass  $m$ , enclosed in a cuboidal container of volume  $V$ . When a gas molecule collides with the wall of the container perpendicular to the  $x$  coordinate axis and bounces off in the opposite

direction with the same speed (an elastic collision), then the momentum lost by the particle and gained by the wall is:

$$\Delta p_x = p_i - p_f = 2mv_x$$

where  $v_x$  is the  $x$ -component of the initial velocity of the particle.

The particle impacts the wall once every  $2l/v_x$  time units (where  $l$  is the length of the container). Although the particle impacts a side wall once every  $l/v_x$  time units, only the momentum change on one wall is considered so that the particle produces a momentum change on a particular wall once every  $2l/v_x$  time units.

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

The force due to this particle is:

$$F = \frac{\Delta p}{\Delta t} = \frac{2mv_x}{\frac{2l}{v_x}} = \frac{mv_x^2}{l}$$

The total force acting on the wall is:

$$F = \frac{m \sum_j v_{jx}^2}{l}$$

where the summation is over all the gas molecules in the container.

The magnitude of the velocity for each particle will follow:

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

Now considering the total force acting on all six walls, adding the contributions from each direction we have:

$$\text{Total Force} = 2 \cdot \frac{m}{l} (\sum_j v_{jx}^2 + \sum_j v_{jy}^2 + \sum_j v_{jz}^2) = 2 \cdot \frac{m}{l} \sum_j (v_{jx}^2 + v_{jy}^2 + v_{jz}^2) = 2 \cdot \frac{m \sum_j v_j^2}{l}$$

where the factor of two arises from now considering both walls in a given direction.

Assuming there are a large number of particles moving sufficiently randomly, the force on each of the walls will be approximately the same and now considering the force on only one wall we have:

$$F = \frac{1}{6} \left( 2 \cdot \frac{m \sum_j v_j^2}{l} \right) = \frac{m \sum_j v_j^2}{3l}$$

The quantity  $\sum_j v_j^2$  can be written as  $N\overline{v^2}$ , where the bar denotes an average, in this case an average over all particles. This quantity is also denoted by  $v_{rms}^2$  where  $v_{rms}$  is the root-mean-square velocity of the collection of particles.

Thus the force can be written as:

$$F = \frac{Nm v_{rms}^2}{3l}$$

Pressure, which is force per unit area, of the gas can then be written as:

$$P = \frac{F}{A} = \frac{Nm v_{rms}^2}{3Al}$$

where  $A$  is the area of the wall of which the force exerted on is considered.

Thus, as cross-sectional area multiplied by length is equal to volume, we have the following expression for the pressure

$$P = \frac{Nm v_{rms}^2}{3V}$$

where  $V$  is the volume. Also, as  $Nm$  is the total mass of the gas, and mass divided by volume is density

$$P = \frac{1}{3} \rho v_{rms}^2$$

where  $\rho$  is the density of the gas.

This result is interesting and significant, because it relates pressure, a macroscopic property, to the average (translational) kinetic energy per molecule ( $1/2mv_{rms}^2$ ), which is a microscopic property. Note that the product of pressure and volume is simply two thirds of the total kinetic energy.

## Temperature and kinetic energy

From the ideal gas law,

$$PV = Nk_B T \quad (1)$$

where  $k_B$  is the Boltzmann constant, and  $T$  the absolute temperature, it follows from the above result that the temperature  $T$  takes the form

$$PV = Nk_B T = \frac{Nmv_{rms}^2}{3} \implies T = \frac{mv_{rms}^2}{3k_B} \quad (2)$$

and the kinetic energy  $K$  of the system can now be written as

$$K = \frac{1}{2}Nmv_{rms}^2 = \frac{3}{2}Nk_B T \text{ and } T = \frac{2}{3} \frac{K}{Nk_B} \quad (3)$$

Eq.(3)<sub>1</sub> is one important result of the kinetic theory: *The average molecular kinetic energy is proportional to the absolute temperature.*

From Eq.(1) and Eq.(3)<sub>1</sub>, we have

$$PV = \frac{2}{3}K \quad (4)$$

Thus, the product of pressure and volume per mole is proportional to the average (translational) molecular kinetic energy.