

1.5 An Introduction to Kinetic Theory of Gases

The kinetic theory of gases was developed in the late nineteenth century to explain the observed properties of gases in terms of random motion of molecules. One of the most important accomplishments of this theory is that it showed that temperature is proportional to the average kinetic energy of the molecules. Many quantities such as pressure, diffusion constant and the coefficient of viscosity could be related to the average velocities, mass and size of the molecules. In this section we shall deal with some elementary aspects of kinetic theory

Kinetic Theory of Pressure

Using the basic concepts of force and randomness, it is possible to relate the pressure of a gas to molecular properties such as average speed. Pressure is the average force per unit area exerted on the walls by colliding molecules.

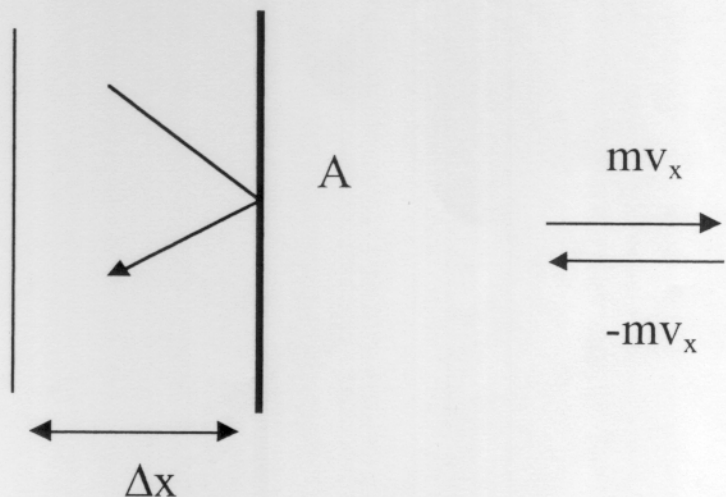


Fig. 1 Molecular collisions with the walls give rise to pressure. By computing the average momentum transferred to the wall by colliding molecules, pressure can be related to the average velocity of the molecules.

We begin by looking at some aspects of the random motion of molecules. First, all directions are equally probable: the properties of molecules moving in one direction will be the same as the properties of molecules moving in any other direction. Let us assume the average speed of the gas molecules is v_{avg} . We denote its x , y and z components of the by v_{xavg} , v_{yavg} , and v_{zavg} . Thus

$$v_{\text{avg}}^2 = v_{x\text{avg}}^2 + v_{y\text{avg}}^2 + v_{z\text{avg}}^2 \quad (1.5.1)$$

Because all directions are similar, we may expect,

$$v_{x\text{avg}}^2 = v_{y\text{avg}}^2 = v_{z\text{avg}}^2 = (v_{\text{avg}}^2 / 3) \quad (1.5.2)$$

Also:

$$\begin{aligned} N &= \text{total number of moles of the gas} \\ V &= \text{volume of the container} \\ M &= \text{Molar mass of the gas} \\ m &= \text{mass of the molecule} = M/N_A \\ n &= \text{number of molecules per unit volume} = NN_A/V \end{aligned} \quad (1.5.3)$$

Now we can calculate the pressure by considering the molecular collisions with the wall. Consider a layer of a gas, of thickness Δx , close to the wall of the container (see Fig. 1). When a molecule collides with the wall, the change in momentum of the molecule in the x-direction equals $2mv_x$. In the layer of thickness Δx and area A , about half the molecules will be moving towards the wall, while the other half will be moving away from the wall. In a time $\Delta t = (\Delta x/v_x)$ about half the molecules in the layer will collide with the wall.

The number of molecules in the layer = $(\Delta x A) n$

The number of molecules colliding with the walls = $(\Delta x A) n/2$

Since each collision imparts a momentum $2mv_x$, the total momentum imparted to the wall in a time $\Delta t = 2mv_{x\text{avg}} (\Delta x A) n/2$.

Thus the force F on the wall of area A is:

$$F = \frac{\text{Change in momentum}}{\Delta t} = \frac{2mv_{x\text{avg}} \Delta x A n}{\Delta t} = \frac{mv_{x\text{avg}} \Delta x A n}{(\Delta x / v_{x\text{avg}})} = mv_{x\text{avg}}^2 n A. \quad (1.5.4)$$

Since pressure p is the force F per unit area,

$$p = \frac{F}{A} = mv_{x\text{avg}}^2 n \quad (1.5.5)$$

Since the direction x is arbitrary it is better to write this expression in terms of the average velocity of the molecule rather than one component of the velocity. We can do this by using (1.5.2):

$$p = \frac{1}{3} mn v_{\text{avg}}^2 = \frac{1}{3} M \frac{N}{V} v_{\text{avg}}^2 \quad (1.5.6)$$

This expression relates the pressure to the average square of the molecular velocity.

Now according to the the ideal gas equation, $pV=NRT$. Comparing this with (1.5.6) we see that:

$$\boxed{RT = \frac{1}{3} M v_{\text{avg}}^2} \quad (1.5.7)$$

Using the Boltzmann constant $k_B=R/N_A=1.3807 \times 10^{-23} \text{ J/K}$ and (1.5.3), a useful way of rewriting this expression is:

$$\boxed{\frac{1}{2} m v_{\text{avg}}^2 = \frac{3}{2} k_B T} \quad (1.5.8)$$

It shows us that the average kinetic energy of a molecule is $3k_B T/2$. These two expressions enable us to calculate the average velocity of a molecule at a given temperature.

Maxwell-Boltzmann Velocity Distribution

Further development of kinetic theory led to a better understanding of the nature of the randomness of molecular motion. Surely molecules in gas move with different velocities. The expression (1.5.8) only tells us about the average of the square of the velocities. It does not tell us what fraction of molecules have velocities with a particular magnitude and direction. It is the **probability distribution** that specifies such details. We shall denote the probability distribution of the molecular velocity \mathbf{v} , by $P(\mathbf{v})$. The meaning of $P(\mathbf{v})$ is as follows:

$P(\mathbf{v})dv_x dv_y dv_z =$ the fraction of the total number of molecules whose velocity vectors have their components in the range $(v_x, v_x + d v_x)$, $(v_y, v_y + d v_y)$ and $(v_z, v_z + d v_z)$.

As shown in the figure below, this corresponds to all the velocity vectors being in a cube defined by the edges dv_x , dv_y and dv_z at the point $(v_x v_y v_z)$.

The mathematical form of $P(\mathbf{v})$ was initially obtained by James Clerk Maxwell (1831-1879) and later generalized by Ludwig Boltzmann (1844-1906). According to the principle discovered by Boltzmann, when a system reaches thermodynamic equilibrium, the probability that a molecule is in a state with energy E is proportional to $\text{Exp}(-E/k_B T)$. If $\rho(E)$ is the number of different states in which the molecule has energy E :

$$P(E) \propto \rho(E)e^{-E/k_B T} \quad (1.5.9)$$

The quantity $\rho(E)$ is called the **density of states**. For an ideal gas the energy of the molecules is entirely kinetic.

The probability that a molecule's velocity is in an elemental cube in velocity space, as shown in the figure below, can now be deduced from the above principle by using the corresponding kinetic energy, $mv^2/2$. Since the velocity is a continuous variable, we must define a probability density $P(\mathbf{v})$ so that the probability that a molecule's velocity is in an elemental cube of volume $dv_x dv_y dv_z$ located at the tip of the velocity vector \mathbf{v} is $P(\mathbf{v})dv_x dv_y dv_z$. According to the Boltzmann principle, this probability is:

$$P(\mathbf{v})dv_x dv_y dv_z = N e^{-mv^2/2k_B T} dv_x dv_y dv_z \quad (1.5.10)$$

in which:

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

Here N is the "normalization factor" chosen so that :

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} N e^{-mv^2/2k_B T} dv_x dv_y dv_z = 1 \quad (1.5.11)$$

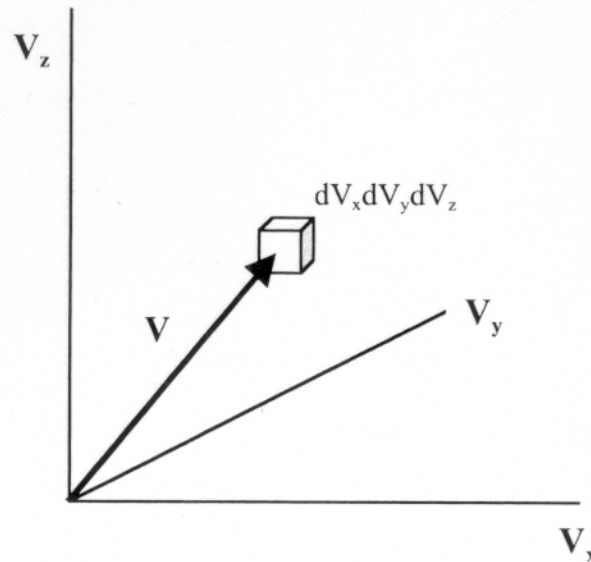


Fig. 2 The probability distribution for the velocity is defined in the velocity space. $P(\mathbf{v})dv_x dv_y dv_z$ is the probability that the velocity of a molecule is point with in the cube shown.

The normalization factor is obtained using the integral:

$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \left(\frac{\pi}{a}\right)^{1/2} \quad (1.5.12)$$

The condition (1.5.11) gives: $N = \left(\frac{m}{2\pi k_B T} \right)^{3/2}$. With the normalization factor thus determined, the probability distribution for the velocity can be written explicitly as:

$$P(\mathbf{v})dv_x dv_y dv_z = \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-mv^2/2k_B T} dv_x dv_y dv_z. \quad (1.5.13)$$

Maxwell Speed Distribution

From the above expression we can obtain the probability distribution for molecular speed, i.e., the probability that a molecule will have a speed in the range $(v, v+dv)$ regardless of direction. This can be done by summing or integrating $P(\mathbf{v})$ over all the directions in which the velocity can point. In spherical coordinates, since the volume element is $v^2 \sin\theta d\theta d\phi dv$, the probability is written as $P(\mathbf{v})v^2 \sin\theta d\theta d\phi dv$. The integral over all possible directions is:

$$\int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} P(\mathbf{v})v^2 \sin\theta d\theta d\phi dv = 4\pi P(\mathbf{v})v^2 dv \quad (1.5.14)$$

The quantity $4\pi P(\mathbf{v})v^2$ is the probability density for the speed. We shall denote it by $f(v)$. With this notation, the probability distribution for molecular speeds can be written explicitly as:

$$f(v)dv = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-\beta v^2} v^2 dv \quad (1.5.15)$$

$$\beta = \frac{m}{2k_B T}$$

Because the molar mass $M = mN_A$ and $R = k_B N_A$, the above expression can also be written as:

$$f(v)dv = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} e^{-\beta v^2} v^2 dv \quad \beta = \frac{M}{2RT} \quad (1.5.16)$$

The shape of the function $f(v)$ is shown in the Fig. 3 below. This graph shows that at a given T , there are a few molecules with low speeds and a few with large speeds. The speed v at which $f(v)$ reaches its maximum is the most probable speed.

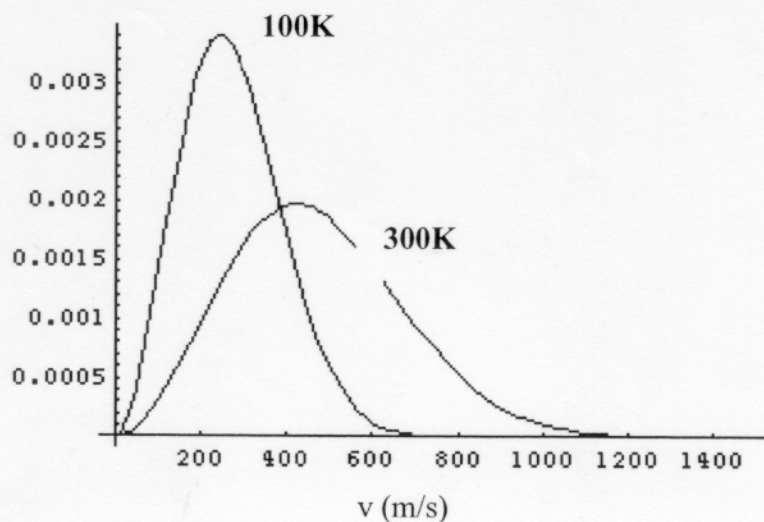


Fig. 3 $f(v)$ versus v (m/s) for nitrogen at $T= 100\text{K}$ and 300K .

We shall use the notation in which the average value of a quantity S is denoted by $\langle S \rangle$. The average speed is given by the integral:

$$\langle v \rangle = \int_0^{\infty} v f(v) dv \quad (1.5.17)$$

For the probability distribution (1.5.15), such integrals can be calculated using integral tables or Mathematica or Maple. While doing such calculations it is convenient to write the probability $f(v)$ as:

$$f(v)dv = 4\pi N e^{-\beta v^2} v^2 dv \quad (1.5.18)$$

$$\beta = \frac{M}{2RT}, \quad N = \left(\frac{M}{2\pi RT} \right)^{3/2}$$

The average speed can now be written as (using the integral (4) in the appendix):

$$\langle v \rangle = 4\pi N \int_0^{\infty} v^3 e^{-\beta v^2} dv = 4\pi N \frac{1}{2\beta^2} = \sqrt{\frac{8RT}{\pi M}} \quad (1.5.19)$$

Similarly, one can calculate the average energy of a single molecule (using m and k_B instead of M and R):

$$\left\langle \frac{1}{2}mv^2 \right\rangle = \frac{mN}{2} \int_0^{\infty} v^4 e^{-\beta v^2} dv = \frac{mN}{2} \frac{3\sqrt{\pi}}{8\beta^{5/2}} = \frac{3}{2}k_B T \quad (1.5.20)$$

The value of v at which $f(v)$ has a maximum is the most probable speed. This can easily be determined by setting $df/dv = 0$.

Add a paragraph/section energy of monatomic and diatomic gases.

Appendix: Some Useful Integrals

$$1. \quad \int_0^{\infty} e^{-ax^2} dx = \frac{1}{2} \left(\frac{\pi}{a} \right)^{1/2}$$

$$2. \quad \int_0^{\infty} x e^{-ax^2} dx = \frac{1}{a}$$

$$3. \quad \int_0^{\infty} x^2 e^{-ax^2} dx = \frac{1}{4a} \left(\frac{\pi}{a} \right)^{1/2}$$

$$4. \quad \int_0^{\infty} x^3 e^{-ax^2} dx = \frac{1}{2a^2}$$

More generally:

$$5. \quad \int_0^{\infty} x^{2n} e^{-ax^2} dx = \frac{1 \cdot 3 \cdot 5 \dots (2n-1)}{2^{n+1} a^n} \left(\frac{\pi}{a} \right)^{1/2}$$

$$6. \quad \int_0^{\infty} x^{2n+1} e^{-ax^2} dx = \frac{n!}{2} \left(\frac{1}{a^{n+1}} \right)$$

(* This program plots Maxwell-Boltzmann speed distribution for a gas of molar mass M at temp T*)

$M=28.0 \cdot 10^{-3}$; $R=8.314$; $b=M/(2 \cdot R)$;

$p[v, T_] := (4 \text{ Pi}) \cdot ((M/(2 \cdot \text{Pi} \cdot R \cdot T))^{3/2}) \cdot (v^2) \cdot \text{Exp}[-(b \cdot v^2)/T]$;

Plot[{p[v,300],p[v,100]},{v,0,1500}]

