27.4: The Frequency of Collisions with a Wall

In the derivation of an expression for the pressure of a gas, it is useful to consider the frequency with which gas molecules collide with the walls of the container. To derive this expression, consider the expression for the "collision volume".

$$V_{col} = v_x \Delta t \cdot A$$

in which the product of the velocity v_x and a time interval Δt is multiplied by A, the area of the wall with which the molecules collide.

All of the molecules within this volume, and with a velocity such that the x-component exceeds v_x (and is positive) will collide with the wall. That fraction of molecules is given by

$$N_{col} = \frac{N}{V} \frac{\langle v_x \rangle \Delta t \cdot A}{2}$$

and the frequency of collisions with the wall per unit area per unit time is given by

$$z_w = \frac{N}{V} \frac{\langle v_x \rangle}{2}$$

In order to expand this model into a more useful form, one must consider motion in all three dimensions. Considering that

$$\langle v \rangle = \sqrt{\langle v_x \rangle + \langle v_y \rangle + \langle v_z \rangle}$$

and that

$$\langle v_x \rangle = \langle v_y \rangle = \langle v_z \rangle$$

it can be shown that

$$\langle v \rangle = 2 \langle v_x \rangle$$

or

$$\langle v_x \rangle = \frac{1}{2} \langle v \rangle$$

and so

$$z_w = \frac{1}{4} \frac{N}{V} \langle v \rangle$$

A different approach to determining z_w is to consider a collision cylinder that will enclose all of the molecules that will strike an area of the wall at an angle θ and with a speed v in the time interval dt. The volume of this collision cylinder is the product of its base area (A) times its vertical height ($v \cos\theta dt$), as shown in figure $27.4.1$.

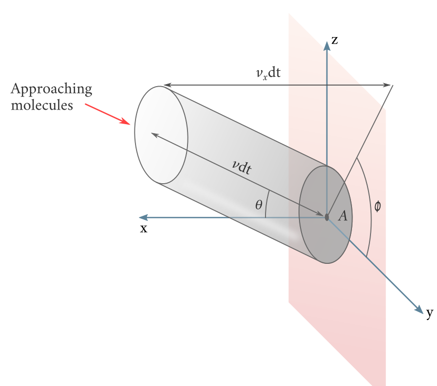

Figure 27.4.1: The collision cylinder for determining the number of collisions of gas molecules with a wall. (CC BY-NC; Ümit Kaya)

The number of molecules in this cylinder is $\rho \cdot A \cdot v \cdot \cos\theta dt$, where ρ is the number density $\frac{N}{V}$. The fraction of molecules that are traveling at a speed between v and $v+dv$ is $F(v)dv$. The fraction of molecules traveling within the solid angle bounded by θ and $\theta+d\theta$ and between ϕ and $\phi+d\phi$ is $\frac{\sin\theta d\theta d\phi}{4\pi}$. Multiplying these three terms together results in the number of molecules colliding with the area A from the specified direction during the time interval dt

$$dN_w = \rho \cdot A \cdot v \cdot \cos\theta\, dt \, \cdot \, F(v)dv \cdot \frac{\sin\theta d\theta d\phi}{4\pi}$$

This equation can be rearranged to obtain

$$\frac{1}{A}\frac{dN_w}{dt} = \frac{\rho}{4\pi} vF(v)dv \cdot \cos\theta \sin\theta \, d\theta d\phi = dz_w$$

Integrating this equation over all possible speeds and directions (on the front side of the wall only), we get

$$z_w = \frac{\rho}{4\pi} \int_0^\infty vF(v)dv \cdot \int_0^{\pi/2} \cos\theta \sin\theta \, d\theta \int_0^{2\pi} d\phi$$

The result is that

$$z_w = \frac{1}{A}\frac{dN_w}{dt} = \frac{1}{4}\frac{N}{V}\langle v\rangle = \rho \frac{\langle v\rangle}{4} \tag{27.4.1}$$

Example 27.4.1

Calculate the collision frequency per unit area (Z_w) for oxygen at 25.0°C and 1.00 bar using equation 27.4.1:

$$z_w = \frac{1}{4}\frac{N}{V}\langle v\rangle$$

Solution

N molecules = N_A x n, so that

$$\frac{N}{V} = \frac{(N_A)\cdot n}{V} = \frac{(N_A)\cdot P}{R\cdot T}$$

$$\frac{(6.022x10^{23}\, mole^{-1})(1.00\, bar)}{(0.08319\, L\cdot bar\cdot mole^{-1}\cdot K^{-1})(298\, K)} = 2.43\times 10^{22}\, L^{-1} = 2.43\times 10^{25}\, m^{-3}$$

and

$$\langle v\rangle = \left(\frac{8RT}{\pi M}\right)^{\frac{1}{2}} = \left(\frac{8(8.314J\cdot K^{-1}\cdot mol^{-1})(298K)}{\pi\cdot(0.031999\, kg)}\right)^{\frac{1}{2}} = 444\, m\cdot s^{-1}$$

Thus

$$z_w = \frac{1}{4}(2.43\times 10^{25}m^{-3})(444\, m\cdot s^{-1})\left(\frac{1\, m}{100\, cm}\right)^2 = 2.70\times 10^{23}s^{-1}\cdot cm^{-2}$$

The factor of N/V is often referred to as the “number density” as it gives the number of molecules per unit volume. At 1 atm pressure and 298 K, the number density for an ideal gas is approximately 2.43 x 10^{19} molecule/cm^3. (This value is easily calculated using the ideal gas law.) By comparison, the average number density for the universe is approximately 1 molecule/cm^3.

Exercise 27.4.1

Calculate the collision frequency per unit area (Z_w) for hydrogen at 25.0°C and 1.00 bar using equation 27.4.1:

$$z_w = \frac{1}{4}\frac{N}{V}\langle v\rangle$$

Answer

$$\langle v \rangle = 1770\, m \cdot s^{-1}$$

and

$$Z_w = 1.08 \times 10^{24} s^{-1} \cdot cm^{-2}$$

Contributors and Attributions

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