

## 1.5: 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  $\Delta t$  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

$$\langle v \rangle = \sqrt{\langle v_x \rangle^2 + \langle v_y \rangle^2 + \langle v_z \rangle^2}$$

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  $\theta$  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 1.5.1.

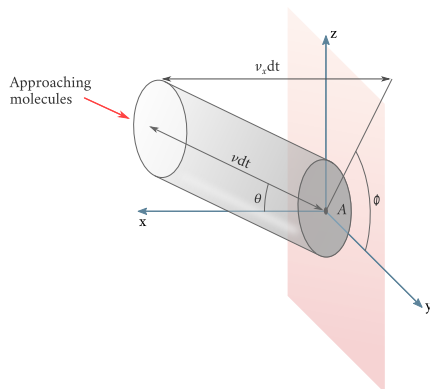


Figure 1.5.1: The collision cylinder for determining the number of collisions of gas molecules with a wall. (CC BY-NC; Ümit Kaya)

The number of molecules in this cylinder is  $\rho \cdot A \cdot v \cdot \cos\theta dt$ , where  $\rho$  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  $\theta$  and  $\theta + d\theta$  and between  $\phi$  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

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

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

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

The result is that

$$z_w = \frac{1}{A} \frac{dN_w}{dt} = \frac{1}{4} \frac{N}{V} \langle v \rangle = \rho \frac{\langle v \rangle}{4} \quad (1.5.1)$$

#### 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 1.5.1:

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

#### Solution

$N$  molecules =  $N_A \times n$ , so that

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

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

and

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

Thus

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

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  $2.43 \times 10^{19}$  molecule/cm<sup>3</sup>. (This value is easily calculated using the ideal gas law.) By comparison, the average number density for the universe is approximately 1 molecule/cm<sup>3</sup>.

#### 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 1.5.1:

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

Answer

and

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

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

### Contributors and Attributions

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