Derivation of the ideal gas law

Derek W. Harrison

February 24, 2021

Introduction

The ideal gas law is derived based on the assumptions of kinetic theory. These are that the particles are small with respect to the domain in which they travel, the particles have the same mass and that collisions with walls and with other particles are fully elastic.

Derivation

In addition to the assumptions of kinetic theory the domain of the system is assumed to be cubic. Based on these assumptions it is possible to deduce a relation between pressure, volume and total kinetic energy of the system.

The time it takes Δt_i for some particle to travel a distance $2L$ in the x-direction, with L the length of one of the sides of the domain, is:

$$\Delta t_i = \frac{2L}{|v_{x,i}|} \tag{1}$$

Where $v_{x,i}$ is the x-component of the velocity of particle i. The frequency f_i with which particle i collides with the west and east boundary is:

$$f_i = \frac{1}{\Delta t_i} \tag{2}$$

The momentum particle i imparts on the west or east boundary is:

$$\Delta p_i = 2m|v_{x,i}| \tag{3}$$

Where m is the mass of the particle. The momentum imparted by particle i on the west or east boundary per unit time is:

$$\frac{\Delta p_i}{\Delta t_i} = f_i \Delta p_i = \frac{m v_{x,i}^2}{L} \tag{4}$$

Note the absolute signs have been dropped since the square of a real number is always greater or equal to zero. The total momentum imparted on the west or east boundary by all particles per unit time is equal to the average force exerted on the boundary:

$$F = \sum_i^N \frac{\Delta p_i}{\Delta t_i} = \sum_i^N \frac{m v_{x,i}^2}{L} \tag{5}$$

With F the force exerted on the boundary by the particles and N the number of particles. The pressure at the boundary is therefore:

$$p = \frac{F}{L^2} = \frac{1}{L^2} \sum_i^N \frac{m v_{x,i}^2}{L} \tag{6}$$

Equation (6) can be rewritten as:

$$p = \frac{F}{L^2} = \frac{Nm}{L^3}\frac{\sum_i^N v_{x,i}^2}{N} \tag{7}$$

Where the factor containing the summation is:

$$\frac{\sum_i^N v_{x,i}^2}{N} = \langle v_x^2 \rangle \tag{8}$$

Where $\langle v_x^2 \rangle$ is the average squared velocity. And so equation (7) becomes:

$$p = \frac{Nm}{L^3}\langle v_x^2 \rangle \tag{9}$$

Since velocities are random it holds that:

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle \tag{10}$$

The speed v_i of particle i is:

$$v_i^2 = v_{x,i}^2 + v_{y,i}^2 + v_{z,i}^2 \tag{11}$$

And therefore the average squared speed of all particles $\langle v^2 \rangle$ is:

$$\langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle \tag{12}$$

Since the average squared velocity is the same along each coordinate equation (9) can be reformulated as:

$$p = \frac{Nm}{3L^3}\langle v^2 \rangle \tag{13}$$

With L^3 the volume V of the domain equation (13) becomes:

$$pV = \frac{Nm}{3}\langle v^2 \rangle \tag{14}$$

Which concludes the derivation.

Discussion

Equation (14) shows that the product pV is proportional with the total kinetic energy of the particles.

Experimentally it has been shown that the product pV is equal to:

$$pV = NkT \tag{15}$$

Where k is the Boltzmann constant. It therefore follows that the temperature T is proportional with the kinetic energy of the system, which can be shown by combining (14) and (15):

$$\frac{3}{2}kT = \frac{1}{2}m\langle v^2 \rangle \tag{16}$$

Conclusion

The ideal gas law is derived based on the assumptions of kinetic theory. The derived equation is then compared with the gas law derived from experimental results. Comparison of the derived relation with the experimentally determined relation shows that kinetic energy of the system is proportional with temperature.