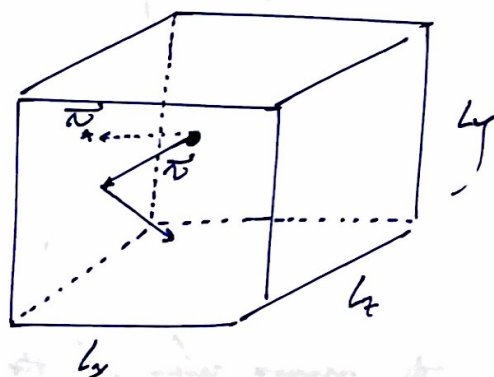


The Kinetic Theory of Gases

1. Temperature & microscopic kinetic energy

In this section we will ~~carefully~~ define the relationship between temperature, a macroscopic physical quantity, and the kinetic energy of microscopic particles. We will also see the role of the Boltzmann constant as fundamental constant that relates microscopic to macroscopic physics.

Consider a cubic container of dimension L_x, L_y, L_z filled w/ gas. The pressure on the container walls is due to collisions of particles on the surface.



Consider a particle colliding on the left wall of the cubic. Assuming the collision is elastic, the particle remains in the same velocity in the y & z direction after the collision, but the x component is flipped.

$$\vec{v}_{x,i} \rightarrow -\vec{v}_{x,i} \text{ ith particle.}$$

The magnitude of the change in momentum is then

$$|\Delta \vec{p}_i| = 2m v_{x,i}$$

After colliding w/ the left wall, the particle moves towards the right wall and bounces back again. The time it takes to travel from the left to right wall is

$$\Delta t = L_x / v_{x,i}$$

This particle thus strikes the left wall every $2\Delta t$.

The average force exerted on the i th particle by the left wall is then,

$$F_{\text{avg}, i} = \frac{|\Delta \vec{p}_i|}{\Delta t} = \frac{mv_{x,i}^2}{L_x}$$

By Newton's third law, the force on the wall by the i th particle is then also

$$F_{\text{avg}, i \text{ on wall}} = \frac{mv_{x,i}^2}{L_x}$$

Adding up contributions from N particles,

$$F_{\text{avg}} = \frac{m}{L_x} \sum_{i=1}^N v_{x,i}^2 \quad \text{Average force on the wall by all } N \text{ particles.}$$

Because there are so many particles F_{avg} is the same for any time interval, therefore,

$$F = F_{\text{avg}} = \frac{m}{L_x} \sum_{i=1}^N v_{x,i}^2$$

The average value of $v_{x,i}^2$ is defined as

$$\langle v_x^2 \rangle \equiv \frac{1}{N} \sum_{i=1}^N v_{x,i}^2 \quad \langle \dots \rangle \text{ denotes the average value of the } N \text{ particles of the quantity inside the brackets.}$$

Therefore, the force on the left wall is

$$F = \frac{mN \langle v_x^2 \rangle}{L_x}$$

The pressure on the left wall is then given by

$$P = \frac{F}{L_y L_z} = \frac{mN \langle v_x^2 \rangle}{L_x L_y L_z} = \frac{mN \langle v_x^2 \rangle}{V}$$

V volume of the container.

Although we focus on the left wall, the discussion is general & applies to all directions. Since $v_i^2 = v_{xi}^2 + v_{yi}^2 + v_{zi}^2$ the same relation holds for all average values $\langle v^2 \rangle$

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

Even though the container has different dimensions, the particles do not move the walls when traveling and so

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{1}{3} \langle v^2 \rangle$$

We can then express pressure on the walls as

$$P = \frac{mN \langle v^2 \rangle}{3V} = \frac{2N \langle K \rangle}{3V} \quad \left| \quad \langle K \rangle = \frac{1}{2} m \langle v^2 \rangle \right.$$

We see that we connect the pressure of the gas, a macroscopic property, with the average kinetic energy of the microscopic constituents. Furthermore, if we write the ideal gas law as

$$P = \frac{N k_B T}{V}$$

we see that

$$P = \frac{2N \langle K \rangle}{3V} = \frac{N k_B T}{V} \implies \langle K \rangle = \frac{3}{2} k_B T$$

↳ we now explicitly see that the higher kinetic energy particles have, the higher the temperature. The Boltzmann constant plays the role of the proportionality constant between microscopic & macroscopic physics.

The equation

$$\langle E \rangle = \frac{3}{2} k_B T$$

is actually a special case of the equipartition theorem, which states that if the energy of a degree of freedom has a quadratic form

$$\frac{1}{2}mv^2, \frac{1}{2}I\omega^2, \frac{1}{2}kx^2, \dots$$

and if the temperature is high enough to treat the allowed energy levels to be continuous, then for each degree of freedom, the average energy is

$$\langle E \rangle = \frac{1}{2} k_B T$$

And since the particles have 3 degrees of freedom v_x, v_y, v_z we get an additional factor of 3.