### Kinetic pressure of a gas

Here we relate the pressure of a gas to the collisions of the molecules on the walls of the container holding the gas.

Consider a container that is a rectangular parallelpiped. The dimension in the *x* direction is *L*. The area of the *yz* side is *A*. The volume is therefore *LA*. We focus on any molecule in the gas. Its *x* component of its velocity is v_x. Consider a time interval, *Δt*. What is the probability that a gas molecule will hit the right wall and bounce back? We choose *Δt* to be small enough that the molecule is very unlikely to hit any other molecule before it hits the wall. So $Δl = v_x Δt$ must be << the mean free path, *mfp*, of the molecules, that is, the average distance traveled by molecules between collisions.

So if the molecule is farther from the wall than *Δl*, then the molecule will not hit the wall within the time interval, *Δt*. Of the molecules that have an *x* component of velocity equal to v_x, half of them are moving toward the wall and half are moving away from the wall. So the probability of molecules hitting the wall is

$$f = \frac{1}{2}\frac{\Delta l}{L} = \frac{|v_x|\Delta t}{2L}$$

f is the probability that a randomly chosen molecule with a velocity, v_x, hits the wall and rebounds within a time interval, *Δt*.
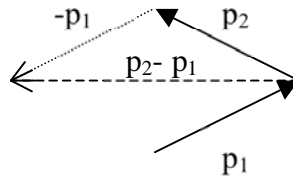
Momentum exchange

The figure above shows the momentum vectors of the molecule, before (p_1) and after (p_2) the collision with the wall. The change in the momentum of the **molecule** as a result of the collision with the wall is

$$\boldsymbol{p_2} - \boldsymbol{p_1} = -2\,p_x\,\mathbf{i} = -2\,m\,v_x\,\mathbf{i}$$

By Newton's 3rd law, the momentum impulse absorbed by the **wall** from the collision of the single molecule is equal and opposite to the change in momentum experienced by the molecule and is therefore

$$\boldsymbol{I_x} = \boldsymbol{p_1} - \boldsymbol{p_2} = +2\,p_x\,\mathbf{i} = +2\,m\,v_x\,\mathbf{i}$$

The *expected value* of the impulse, $\boldsymbol{I_1}$, is the probability of a collision by a molecule with the wall times the impulse associated with that collision.

$$I_1 = f\,I_x = \frac{|v_x|\Delta t}{2L}2mv_x = \frac{\Delta t}{L}mv_x^2$$

$\boldsymbol{I_1}$ is the average impulse delivered by a molecule collision in the time interval, *Δt*. Averaging over all molecules yields an average impulse per molecule of

$$\overline{I_1} = \frac{\Delta t}{L}m\overline{v_x^2}$$

The overbar designates an average over all molecules.

Multiplication by N_V, the total number of molecules in the container, gives the total impulse, $\mathbf{I}$, delivered to the right wall in time interval, Δt.

$$I\,\hat{x} = N_V\,\overline{I_1}\,\hat{x} = \frac{N_V}{L}\,m\overline{v_x^2}\,\Delta t\,\hat{x}$$

Since an impulse can be expressed as the average force over a time interval, Δt,

$$I = \overline{F}\,\Delta t$$

the average force on the wall of the container is

$$\overline{F} = \frac{N_V}{L}\,m\overline{v_x^2}$$

The pressure on the wall is $P = \overline{F}/A$ (force per unit area),

$$P = \frac{N_V}{LA}\,m\overline{v_x^2} = \frac{N_V}{V}\,m\overline{v_x^2} = N\,m\overline{v_x^2}$$

where V is the volume of the container.

The next step is to recognize that the mean-square velocity of the molecules, $\overline{v^2}$, can be written as

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}$$

Assuming no bulk motion of the gas, all directions are equally likely. Therefore, $\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}$ and $\overline{v^2} = 3\,\overline{v_x^2}$ so

$$\overline{v_x^2} = \frac{\overline{v^2}}{3}$$

So

$$P = \frac{N_V}{3V}\,m\overline{v^2}$$

$$PV = \frac{1}{3}N_V m\overline{v^2}$$

but

$$PV = n_V RT$$

$$PV = n_V k_B N_A T$$

$$\frac{1}{3}N_V m\overline{v^2} = N_V k_B T$$

$$\frac{1}{3}m\overline{v^2} = k_B T$$

$$\frac{1}{2}m\overline{v^2} = \overline{K} = \frac{3}{2}k_B T$$

So temperature is proportional to translational energy (and only the translational energy). We have successfully and quantitatively linked the macroscopic (temperature) and submicroscopic (kinetic energy) worlds.

As we will see, this is the first hint that energy is distributed such that each energy "degree of freedom" gets or stores $\frac{1}{2} k_B T$. This is a very important concept in understanding specific heat or heat capacity.

IMPLICATIONS

Let's consider at least a couple of implications of this relation. One basic point is the mean square of the velocity is proportional to T, the temperature, and inversely proportional to m, the mass of the molecules in the gas:

$$\overline{v^2} \sim \frac{T}{m}$$

This says that at the same temperature, heavier or more massive molecules move more slowly than lighter molecules. Let's think of some examples of this.

Diffusion

Diffusion is a process that we will discuss in more detail later in the class. Diffusion of a certain gas molecule in a gas depends on how fast the molecules of the diffusing gas move. Consider Helium which has a molar mass of 4 g and Sulfur Dioxide , SO_2, which has a molar mass of $32 + 16 + 16 = 64$ g. So, for a given temperature, the velocity should scale as $m^{-1/2}$. So SO_2 molecules should be moving about $(4/64)^{1/2} = 4$ times slower than the helium atoms and should diffuse through air about 4 times slower. Indeed Helium gas is observed to diffuse through air 4 times faster than Sulfur dioxide does.

Speed of sound

Sound involves collisions between molecules that carry the pressure (sound) wave forward through the gas. Therefore, the speed of sound in a gas must be close to the thermal kinetic velocity of the molecules in the gas. The speed of sound is

$$v_{sound} = \sqrt{\gamma \frac{kT}{m}} = \sqrt{\gamma \frac{\overline{v^2}}{3}} = \sqrt{\frac{\gamma}{3}} v_{rms}$$

γ is the ratio of the specific heat of the gas at constant pressure to the specific heat at constant volume. (We will go through specific heats momentarily.) The point at the moment is the speed of sound scales as the square root of temperature (hotter = faster sound speed) and inversely with the square root of molecular mass, both of which are indeed observed.

Escape velocity

The escape velocity is the velocity where the kinetic energy of an object just equals its gravitational potential energy (we'll go through this in more detail when we talk about gravity). This leads to the following relation

$$\frac{1}{2} m v_{esc}^2 = mgR$$

where R is the radius of the Earth. Solving for v_{esc} yields

$$v_{esc} = \sqrt{2gR}$$

Note that this has no mass dependence.

Now we can ask the question, at what temperature will a given molecule have a velocity equal to the escape velocity. We can set the square root of the mean square velocity equal to the escape velocity and solve for temperature:

$$\sqrt{\overline{v^2}} = \sqrt{\frac{3k_B T}{m}} = \sqrt{2gR}$$

So

$$T = \frac{2gRm}{3k_B}$$

Note that the temperature needed for molecular thermal velocities to be comparable to the escape velocity scales linearly with molecular mass. So heavier molecules must be hotter to escape than light molecules. Equivalently, at a given temperature, far more light molecules will escape from a planet's gravity field than heavier ones. This is why planets preferentially loose hydrogen.