MEAN FREE PATH OF GAS MOLECULES

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The behaviour of atoms and molecules in a gas is important for understanding the structure of stars. Here we'll have a look at the average distance a molecule can travel in a gas between collisions. For this purpose we'll use the root-mean-square speed v_{rms} of a gas molecule. This speed is defined in terms of the temperature T of the gas and the mass m of a gas molecule:

$$v_{rms} = \sqrt{\frac{3kT}{m}} \tag{1}$$

where k is Boltzmann's constant.

To get an estimate of the mean free path, we consider a gas with a density of ρ and whose molecules each have mass m. The number density of molecules n is then

$$n = \frac{\rho}{m} \tag{2}$$

Suppose each molecule is a sphere with radius r. This is an approximation since many molecules are not spheres (for example, the nitrogen molecule N_2), and even for those that are, they aren't hard spheres with rigid boundaries; the quantum description of a molecule is of a nucleus surrounded by an electron cloud with a fuzzy edge.

One way of estimating the mean free path is to consider one molecule with a radius of $2r$ moving through a gas where all the other molecules are mathematical points with no physical size. In a time t, this molecule travels a distance vt. Since its cross-sectional area is $\pi(2r)^2$, the molecule will sweep out a cylindrical volume

$$V = \pi(2r)^2 vt \tag{3}$$

The cylinder may be bent at several points due to collisions with some of the point molecules. The number n_c of collisions is the volume V multiplied by the number density 2, so we have

$$n_c = \frac{4\pi r^2 vt\rho}{m} \tag{4}$$

The average distance between successive collisions, which is the mean free path ℓ, is the distance travelled, which is vt, divided by the number of collisions, so we have

$$\ell = \frac{vt}{n_c} = \frac{mvt}{4\pi r^2 vt\rho} = \frac{m}{4\pi r^2\rho} \tag{5}$$

We see that ℓ depends only on the density of the gas (and on the properties of the gas molecules), and not on the speed, so ℓ is independent of the temperature.

However, the mean time between collisions *does* depend on the speed, and hence on the temperature. This time t_ℓ is

$$t_\ell = \frac{\ell}{v} \tag{6}$$

If we use v_{rms} from 1, we have

$$t_\ell = \frac{m}{4\pi r^2\rho}\sqrt{\frac{m}{3kT}} \tag{7}$$

We can do a few qualitative checks to see if this result makes sense. The average time decreases as any of the molecular size r, density ρ or temperature T increase, which does appear to make sense. A larger molecule would encounter more targets and thus have more collisions. A larger density means the molecules are more tightly packed, also resulting in more collisions. A higher temperature means the molecules are moving faster, also reducing the time between collisions. Finally, a larger mass m means that the molecules are moving more slowly at a given temperature, since a heavier molecule requires less speed to have a given amount of kinetic energy. Thus a larger mass results in a larger time between collisions.

Example. We'll consider the case of a nitrogen (N_2) atmosphere at room temperature (around 20°C = 293 K) and pressure, giving a density of around 1.2 kg m^{-3}. Taking the radius to be 10^{-10} m and the mass of a nitrogen molecule to be 28 times the mass of a proton, we have

$$m_N = 28 \times 1.67 \times 10^{-27}\text{ kg} \tag{8}$$

$$= 4.68 \times 10^{-26}\text{ kg} \tag{9}$$

The mean free path from 5 is

$$\ell = \frac{4.68 \times 10^{-26}}{4\pi\left(10^{-10}\right)^2(1.2)} = 3.11 \times 10^{-7}\text{ m} \tag{10}$$

The average time between collisions is, from 7

$$t_{\ell} = \frac{\left(4.68\times10^{-26}\right)^{3/2}}{4\pi\left(10^{-10}\right)^{2}(1.2)\sqrt{3\left(1.38\times10^{-23}\right)(293)}} \tag{11}$$

$$= 6.1\times10^{-10}\text{ s} \tag{12}$$

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