6.5: Kinetic Theory of Gases- Pressure

There will be more about *macroscopic PVT* relations for gases when we go further into thermodynamics. In this section, we deal with *microscopic* properties, and how pressure and temperature are related to the number density of molecules and their speed.

We shall consider an ideal gas, containing n molecules per unit volume, each of mass m, held in a cubical box of side l. The velocity of a particular molecule is to be denoted by $\mathbf{c} = u\mathbf{i} + v\mathbf{j} + w\mathbf{k}$. Here u, v, w are the components of the velocity parallel to the sides of the box. As ever, I shall use the word *velocity* to mean "velocity" and the word *speed* to mean "speed". Thus the velocity of the molecule is $\mathbf{c}$ and its speed is c. We are going to start by calculating the pressure on the walls, assumed to be caused by the collisions of millions of molecules repeatedly colliding with the walls.

("Why do you keep banging your head against the wall?" "Because it feels so good when I stop.")

Consider the x-motion. Assuming that collisions are elastic, we note that the change of the x-component of momentum when a molecule bounces off a yz-wall is $2mu$. The time taken to cross to the other side of the cube and back again is $2l/u$. The number of collisions that this molecule makes with one yz-wall per unit time is $u/(2l)$. The rate of change of momentum of that molecule at that wall is therefore $2mu$ x $u/(2l) = mu^2/l$. The rate of change of the x-component of the momentum at that wall of all the nl^3 molecules in the box is $nl^3 \times m\overline{u^2}/l = nml^2\overline{u^2}$. That is, the force on that wall is $nml^2\overline{u^2}$, and so the pressure on the wall is $nm\overline{u^2}$. But $\overline{u^2} = \overline{v^2} = \overline{w^2}$ (that's assuming that the velocities are isotropic and there's no wind) and $\overline{u^2} + \overline{v^2} + \overline{w^2} = \overline{c^2}$ (that's Pythagoras's theorem), and therefore $\overline{u^2} = \frac{1}{3}\overline{c^2}$. So the pressure is

$$P = \frac{1}{3}nm\overline{c^2} = \frac{1}{3}\rho\overline{c^2}. \tag{6.5.1}$$

Here ρ is the density = mass ÷ volume = molar mass ÷ molar volume = μ/V, (here V = molar volume) and therefore

$$PV = \frac{1}{3}\mu\overline{c^2}. \tag{6.5.2}$$

But $\frac{1}{3}\mu\overline{c^2}$ is $\frac{2}{3}$ of the translational kinetic energy of a mole of gas, and we already know that $PV = RT$, so that we deduce that the *translational kinetic energy of the molecules in a* <u>*mole*</u> *of gas* is equal to $\frac{3}{2}RT$. That is to say the <u>mean</u> translational kinetic energy per <u>molecule</u> is $\frac{3}{2}kT$, where k is Boltzmann's constant (see Section 6.1).