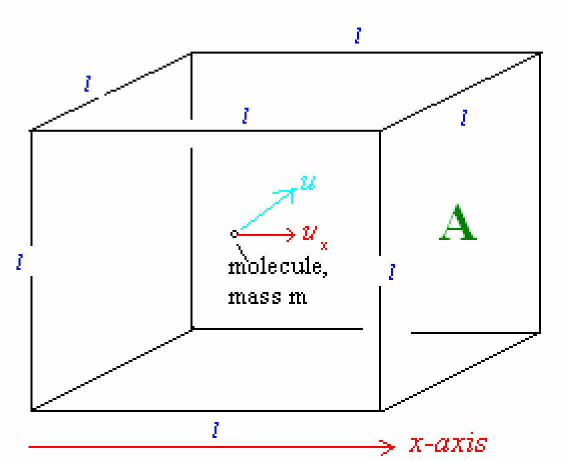
The Kinetic Molecular Theory Equation

For some interesting animations, and other useful material, see
http://www.chm.davidson.edu/vce/KineticMolecularTheory/BasicConcepts.html

The kinetic-molecular theory equation may be stated $PV = \frac{1}{3}Nm\overline{u^2}$ or $PV = \frac{1}{3}nM\overline{u^2}$, where

P is the pressure of the gas,
V its volume (i.e. the capacity of the container),
N the number of molecules present (a very large number),
m the mass of a single molecule of the gas (for a pure gas all the molecules will have the same mass),
u the velocity of a single molecule,
$\overline{u^2}$ (pronounced "you-square-bar") the average of the squared velocities of the molecules.

We consider a sample of gas in a cubical box of side l and focus our attention on just one molecule:



At any instant the molecule is moving with velocity u. Velocity is a vector and can be resolved into three components. Each of these components is parallel to one of the three coordinate axes (x, y and z) in 3-dimensional space: u_x, u_y, and u_z. We only need to consider the component of velocity along the x-axis, u_x, for the moment. (The small x is just a label: it is not a quantity in itself.) We can disregard the components of velocity along the other axes at this stage.

If the velocity of the molecule along the x-axis is u_x m/s, then in 1 second, the molecule will move a distance u_x m. To be sure of hitting the wall wherever it starts, and in whatever direction it is moving to start with, the molecule must move a distance l in one direction parallel to the x-axis, and then l back again, a total distance of $2l$, twice the length of the box. (We ignore the possibility of collisions with other molecules, which actually make no difference to the result.) If u_x happens to be the same as $2l$, the molecule will collide with wall **A** once every second. If u_x happens to be greater than $2l$, then the molecule will collide with wall **A** more than once per second. The number of collisions per second will be given by $\frac{u_x}{2l}$.

In order to determine the force that the molecule exerts on wall **A**, we have to consider the true nature of force. According to Newton, the force acting on a body is given by how fast it changes the momentum of the body, i.e.

$$\text{Force, } F = \text{rate of change of momentum} = \frac{\text{change of momentum}}{\text{time taken for the change}}$$

Since $\text{momentum} = \text{mass} \times \text{velocity} = mu_x$ and during the collision with wall **A** the velocity changes from $+u_x$ to

$-u_x$ so the momentum changes from $+mu_x$ to $-mu_x$, giving an overall change[1] of $2mu_x$. Since there are $\frac{u_x}{2l}$ such changes every second,

$$F = \frac{u_x}{2l} \times 2mu_x = \frac{mu_x^2}{l}$$

What we really need is the pressure exerted on wall **A,** which is also called simply "the pressure of the gas". Pressure is given by $\frac{\text{force}}{\text{area}} = \frac{F}{l^2}$ and so we have

$$P = \frac{F}{l^2} = \left(\frac{mu_x^2}{l^2}\right) \Big/ l^2 = \frac{mu_x^2}{l^3}$$

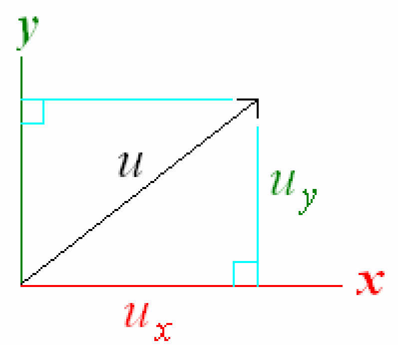
but $l^3 = V$, the volume of the container, and so

$P = \frac{mu_x^2}{V}$. This is the pressure of the gas produced by just one molecule.

Now let us consider all the molecules in the container. This is a large number, N. Since all the molecules are moving with different velocities u_x^2 is replaced with its average value, $\overline{u_x^2}$ and so we have:

$$P = N\frac{m\overline{u_x^2}}{V}$$

The component of the velocity along the x-axis (u_x) is next related to the actual velocity of the molecules, u. In two dimensions we would have



and it is clear from Pythagoras that $u^2 = u_x^2 + u_y^2$

In three dimensions the equation becomes $u^2 = u_x^2 + u_y^2 + u_z^2$.

This also applies to the average velocity and its components, and so:

$$\overline{u^2} = \overline{u_x^2} + \overline{u_y^2} + \overline{u_z^2}$$

For *average* velocities, it is clear that the components in the three dimensions must be the same (a gas is the same in all directions – it is *isotropic*), and so

$$\overline{u_x^2} = \overline{u_y^2} = \overline{u_z^2}$$

$\therefore \overline{u^2} = 3\overline{u_x^2}$ and

$$\overline{u_x^2} = \frac{1}{3}\overline{u^2}$$

Overall, we have:

[1] Strictly, change is given by "*final – initial",* which leads to $-2mu_x$, but the sign merely indicates that the force experienced by the molecule is in the negative x-direction (to the left). We want the force experienced by the wall, which is in the positive x-direction, to the right, hence the change of sign to positive.

$$P = N\frac{m\overline{u_x^2}}{V} = N\frac{m}{V}\times\frac{1}{3}\overline{u^2} = \frac{1}{3}\frac{Nm\overline{u^2}}{V} \text{ or}$$

$$PV = \frac{1}{3}Nm\overline{u^2}$$

This is not quite the final step, since the number of molecules (N), and the mass of a molecule (m), are difficult to measure. However, Nm represents the total mass of the gas, which can also be represented as nM (the number of moles × the mass of one mole). This gives, finally,

$$PV = \frac{1}{3}nM\overline{u^2}$$

This is one form of the "Kinetic Theory Equation".