Teacher notes Topic B

About rms speed.

In section B3 of the IB Guide it is stated that in the formula for pressure $P = \frac{1}{3}\rho v^2$ where v is described as the "average translational speed of molecules".

This is wrong on two counts.

It is not an average speed, and it is not a translational speed. The word "translational" should have been replaced by random. The speed that appears in the formula above is best denoted by *c* (no connection to the speed of light!) and is defined as the square root of the average (mean) of the squares of the speeds, i.e. r.m.s. (root mean square) speed.

In other words, if we have *N* molecules of an ideal monatomic gas, the internal energy of the gas consists of just the random kinetic energy of the molecules. The total random kinetic energy is

$$K = \frac{1}{2}mv_1^2 + \frac{1}{2}mv_2^2 + \dots + \frac{1}{2}mv_N^2$$

If we wanted to find the average random kinetic energy we would write

$$\overline{K} = \frac{\frac{1}{2}mv_1^2 + \frac{1}{2}mv_2^2 + \dots + \frac{1}{2}mv_N^2}{N}$$
$$= \frac{1}{2}m\frac{v_1^2 + v_2^2 + \dots + v_N^2}{N}$$

We see the quantity $\frac{v_1^2 + v_2^2 + \dots + v_N^2}{N}$ appearing here. It is the average of the squares of the speeds. It has dimensions of speed². To get a quantity with units of speed we take the square root:

$$c = \sqrt{\frac{v_1^2 + v_2^2 + \dots + v_N^2}{N}}$$

This is the root of the mean of the squares of the speeds, the r.m.s. speed. Hence the **average** random kinetic energy of the molecules is

$$\overline{K} = \frac{1}{2}mc^2$$

The r.m.s. speed *c* is **not** the same as the average speed of the molecules which is $\overline{v} = \frac{v_1 + v_2 + \dots + v_N}{N}$.

(Note that the average velocity of the molecules is zero.)

As a trivial example consider the 10 random speeds (in m s⁻¹) which have been generated randomly by a computer in the range 0 to 300 m s⁻¹:

142, 136, 251, 166, 215, 167, 24, 247, 202, 169

The average speed is

$$\overline{v} = \frac{v_1 + v_2 + \dots + v_N}{N} = \frac{142 + 136 + 251 + 166 + 215 + 167 + 24 + 247 + 202 + 169}{10} = 172 \text{ m s}^{-1}$$

The r.m.s. speed is

$$c = \sqrt{\frac{v_1^2 + v_2^2 + \dots + v_N^2}{N}} = \sqrt{\frac{142^2 + 136^2 + 251^2 + 166^2 + 215^2 + 167^2 + 24^2 + 247^2 + 202^2 + 169^2}{10}} = 175 \,\mathrm{m \, s^{-1}}$$

It is very close to the average speed but is different from it.

We can make progress by recalling the Maxwell-Boltzmann distribution $f(v) = 4\pi v^2 \sqrt{\frac{m}{2\pi kT}} e^{-\frac{mv^2}{2kT}}$. The quantity f(v)dv gives the fraction of molecules whose speeds are in the range (v, v + dv).



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We can use this distribution to find the most probable speed v_p of a molecule (the speed at the peak of the curve) the mean speed, \overline{v} , and the r.m.s. speed *c*.

Most probable speed: we find this by finding the speed that maximizes f.

$$\frac{d}{dv}f(v) = 0$$

$$8\pi v e^{-\frac{mv^2}{2kT}} - 4\pi v^2 \frac{mv}{kT} e^{-\frac{mv^2}{2kT}} = 0$$

$$4\pi v e^{-\frac{mv^2}{2kT}} (2 - v \frac{mv}{kT}) = 0$$

$$v_p = \sqrt{\frac{2kT}{m}}$$

Average speed:
$$\bar{v} = \int_{0}^{\infty} vf(v) dv = \int_{0}^{0} 4\pi v^{3} \sqrt{\frac{m}{2\pi kT}} e^{-\frac{2kT}{2kT}} dv = \sqrt{\frac{3kT}{\pi m}} = \frac{2}{\sqrt{\pi}} v_{p}$$

R.m.s. speed: $c = \sqrt{\int_{0}^{\infty} v^{2} f(v) dv} = \sqrt{\int_{0}^{\infty} 4\pi v^{4} \sqrt{\frac{m}{2\pi kT}}} e^{-\frac{mv^{2}}{2kT}} dv = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3}{2}} v_{p}$

(The integrals are standard.)

So we see that $v_p < \overline{v} < c$ but numerically these three speeds are approximately equal.

To summarize: the IB guide is not correct in its definition of the speed in the formula $P = \frac{1}{3}\rho v^2$ but in view of the fact that the three speeds v_p , \overline{v} , c are numerically close to each other, the IB can be excused despite their serious conceptual error.