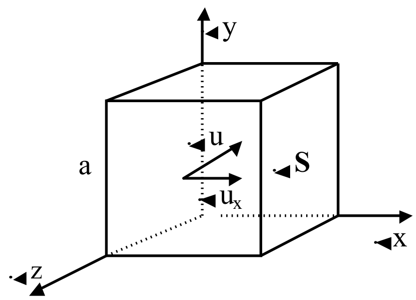
Derivation: Pressure of an ideal gas and root mean square speed

Recall from physics: $\text{pressure} = \dfrac{\text{force}}{\text{area}}$ or $P = \dfrac{F}{A}$

Also:

$$F = m\,a$$
$$= m\frac{du}{dt} = \frac{d(mu)}{dt} = \frac{\Delta(\text{momentum})}{\Delta t}$$
$$= \text{change in momentum per second}$$

Therefore: F = (change in momentum per collision) x (number of collisions per second)



Consider a cube of length a, that contains N identical molecules, each of mass m.

<u>What is the change of momentum per collision?</u>

Now consider <u>one</u> of those molecules. It has speed u, and its speed in the x direction is u_x. After it collides at wall **S**, its new speed in the x direction is $-u_x$.

∴ Change in momentum of the molecule, per collision $= -mu_x - (mu_x) = -2mu_x$

∴ Change in momentum of the wall, per collision $= +2mu_x$

<u>How many collisions are there per second for one molecule?</u>

Speed in the x direction is u_x cm per second.

The molecule travels 2a cm in the x direction between collisions at **S**.

∴ Number of collisions per second $= \dfrac{u_x \text{ cm s}^{-1}}{2a \text{ cm coll}^{-1}} = \dfrac{u_x}{2a} \text{ coll s}^{-1}$

<u>Pressure due to one molecule, on side **S**, is:</u>

$$P_x = \frac{F_x}{\text{area}} = \frac{2mu_x \cdot \frac{u_x}{2a}}{a^2} = \frac{mu_x^2}{a^3} = \frac{m}{V}u_x^2 \qquad | \text{ since } a^3 = V$$

<u>Pressure due to all N molecules:</u>

$$P_x = \frac{m}{V}u_{x(1)}^2 + \frac{m}{V}u_{x(2)}^2 + \ldots\ldots\ldots$$

$$= \frac{m}{V}(u_{x(1)}^2 + u_{x(2)}^2 + \ldots\ldots)$$

$$\therefore \quad P_x = \frac{m}{V}\sum_{1}^{N} u_{x(i)}^2 \qquad \text{(Eq. 1)}$$

But the average of u_x^2 values is, by definition:

$$\langle u_x^2 \rangle = \frac{1}{N}\left(u_{x(1)}^2 + u_{x(2)}^2 + \ldots\ldots\right) = \frac{1}{N}\sum_{1}^{N} u_{x(i)}^2$$

Multiplying by N gives: $N \langle u_x^2 \rangle = \sum_{1}^{N} u_{x(i)}^2$

Therefore, eq. 1 becomes: $P_x = \frac{m}{V} N \langle u_x^2 \rangle$ (Eq. 2)

<u>Now relate u_x to u, the total velocity.</u>

By Pythagoras, for molecule 1: $u_1^2 = u_{x(1)}^2 + u_{y(1)}^2 + u_{z(1)}^2$

for molecule 2: $u_2^2 = u_{x(2)}^2 + u_{y(2)}^2 + u_{z(2)}^2$

and so on …………..

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for molecule N: $u_N^2 = u_{x(N)}^2 + u_{y(N)}^2 + u_{z(N)}^2$

Adding: $\sum_{1}^{N} u_i^2 = \sum_{1}^{N} u_{x(i)}^2 + \sum_{1}^{N} u_{y(i)}^2 + \sum_{1}^{N} u_{z(i)}^2$

Dividing by N gives: $\frac{1}{N}\sum_{1}^{N} u_i^2 = \frac{1}{N}\left(\sum_{1}^{N} u_{x(i)}^2 + \sum_{1}^{N} u_{y(i)}^2 + \sum_{1}^{N} u_{z(i)}^2\right)$ (Eq. 3)

But, the LHS of eq. 3 is the average speed. Therefore, eq. 3 becomes:

$$\langle u^2 \rangle = \langle u_x^2 \rangle + \langle u_y^2 \rangle + \langle u_z^2 \rangle$$

But, in a box at rest, the average speed in each direction is the same, i.e., $\langle u_x^2 \rangle = \langle u_y^2 \rangle = \langle u_z^2 \rangle$

Therefore, $\langle u^2 \rangle = 3 \langle u_x^2 \rangle$ or $\langle u_x^2 \rangle = \frac{1}{3} \langle u^2 \rangle$

Logically, the pressure, P_x, on wall S is the same as the pressure, P, on any wall.

Therefore, eq. 2 becomes: $P = \frac{1}{3}\frac{Nm}{V} \langle u^2 \rangle$ (Eq. 4)

What is the <u>root-mean-square speed</u> u_{rms}, or $\langle u^2 \rangle^{1/2}$?

For one mole of a gas: $N = N_A$ and $N_A m = M$ □ N_A - the Avogadro constant

□ M - molar mass

Also, for one mole, experimentally: $PV = RT$

Replacing P above by the expression in eq. 4 gives: $\frac{1}{3}(N_A m) \langle u^2 \rangle = RT$

Therefore: $\langle u^2 \rangle = \frac{3RT}{M}$ or $\langle u^2 \rangle^{1/2} = \sqrt{\frac{3RT}{M}} = u_{rms}$ (Eq. 5)