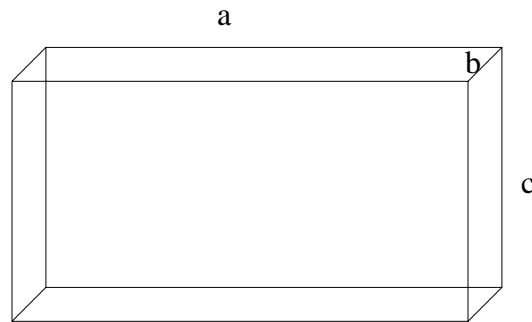


In Isaac Asimov's *Understanding Physics* Volume I, George Allen and Win, London (1966), there is a simple derivation of the relationship between temperature and kinetic energy. Here is my slightly extended version of it, and if you compare Asimov's approach to that found in a typical first year university physical chemistry textbook, you appreciate how good a teacher the late Asimov was.



Consider a box of dimensions  $a$ ,  $b$ , and  $c$  filled with  $N$  particles, each with a mass  $m$ , moving with a velocity  $v$ . The particles are free to move in any direction, but any motion can be decomposed into three components,  $x$ ,  $y$  and  $z$ , perpendicular to one another. That means that  $1/3$  of all particles will have a component moving along one edge, say  $a$ . (Collisions between particles can be ignored because they are perfectly elastic and because the direction-change caused by a collision will be cancelled by another collision causing a change in the opposite direction.)

If a particle hits the wall represented by edge  $bc$ , it will experience a change in momentum  $2mv$ . [=  $mv - (-mv)$ , since the particle will bounce off  $bc$  in the opposite direction ]

To get the total force exerted on the wall  $bc$ , we need to know how many collisions occur on that wall per unit time. (Recall that impulse(Force\*time) equal momentum). Before the next collision with wall  $bc$ , the particle must travel a distance of  $2a$ . Since it moves with velocity  $v$ , by dividing  $v$  by  $2a$ , we get the frequency or the number of collision per second. Confusing? Suppose that  $a = 10$  m, for a total length of  $2a = 20$  m. If the particle moved at  $5$  m/s, it would have a collision frequency of  $v/2a = 5/20 = 0.25/s$  equivalent to 1 collision every 4 seconds.

The total force exerted on the wall by one particle in one second equals the change in momentum in one bounce times the collision frequency:

$2mv(v/[2a]) = mv^2/a$ . To get the force exerted by all N particles, remember that only one third of the particles are moving that way, so  $F = Nm v^2/(3a)$ . To get an expression for pressure, which is force per unit area, we simply divide F by the area of the wall in question, yielding

$$P = \frac{F}{bc} = \frac{Nm v^2}{3abc}$$

Since  $abc =$  volume of the box,

$$P = \frac{Nm v^2}{3V}$$

Multiplying both the numerator and denominator by 2:

$$P = \frac{2(Nm v^2)}{2(3V)} = \frac{2NE_k}{3V}$$

, since kinetic energy,  $E_k = mv^2/2$ .

Rearranging  $PV = (2/3)N E_k$ . For one mole of particles,  $N = n$ , (correspondingly, we would have m becoming the molar mass)so

$$PV = (2/3)n E_k$$

$$\text{Since } PV = nRT,$$

Equating the two above equations:

$$RT = (2/3) E_k$$

$$T = (2/3R) E_k, \text{ or}$$

$$E_k = (3/2)RT.$$

$$\text{Or } mv^2/2 = (3/2)RT.$$

$$v = \sqrt{\frac{3RT}{m}}$$

where m = molar mass in kg

Example: At 273 K, what is the average velocity of oxygen molecules?

$$v =$$

$$\sqrt{\frac{3(8.31)273}{0.032}} = 461 \text{ m/s}$$

A dimensional analysis for the above problem( to check the units):

$$1000 \text{ L} = 1 \text{ m}^3$$

$$1000 \text{ N/m}^2$$

$$1 \text{ kPa} =$$

$$R = 8.31 \text{ L} \cdot \text{kPa} / (\text{K} \cdot \text{mole})$$

$$1 \text{ N} = 1$$

$$v = \sqrt{\frac{3 \left( 8.31 \frac{\text{m}^3 \text{ N}}{\text{K mole}} \right) (273 \text{ K})}{0.032 \text{ kg / mole}}} = \sqrt{212684.0625 \frac{\text{Nm}}{\text{kg}}} = \sqrt{212684.0625 \frac{\text{kg} (\text{m/s}^2) \text{m}}{\text{kg}}} = 461 \text{ m/s}$$