Lecture 33 - Kinetic theory of gases

What's important:

· kinetic theory of gases

Demonstrations:

· marbles in a box

Text: Walker, Secs. 17.1, 17.2

Problems:

Gas Laws

In chemistry, we learn that two laws govern the behaviour of dilute gases:

· Boyle's law: V $1/P$

· Charles' law: V T

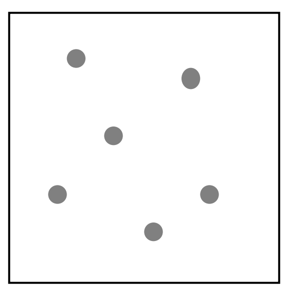
These can be combined to read

PV/T = constant (ideal gas law)

In this lecture, we derive the ideal gas law assuming that the molecules of the gas are point particles moving randomly within a confining box of volume V. The gas pressure results from the molecules colliding elastically with the walls of the container.

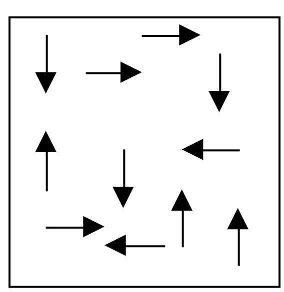
Kinetic model

We confine N molecules within a cube of volume V



All molecules have the same mass m and move with the same speed v.

Suppose for now that each molecule can move along only one of the Cartesian directions x, y, or z.



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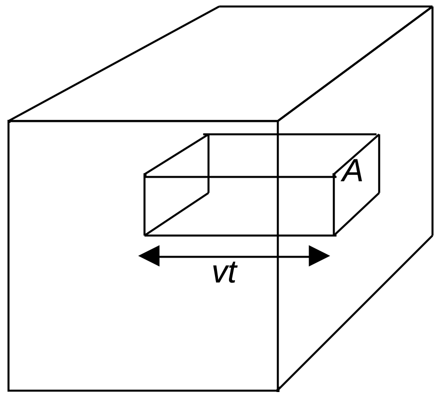
Then, on average:
N / 3 molecules move along a given axis
N / 6 molecules move towards each wall

When a molecule collides elastically with a wall, the wall is given an impulse $2mv$.

How many molecules collide with a wall in time t?



All molecules within a distance vt moving towards the wall will collide with it in time t.

Further, all molecules within the volume Avt will collide with area A on the wall.

This number of molecules equals the density of molecules travelling in the right direction, times the volume of the box Avt:

$[density] = (N/6)/V$
$[number] = [density] \bullet [volume\ of\ box] = Avt \bullet (N/6)/V$
or
$[number] = NAvt / 6V$.

These molecules give the area A an impulse
$[impulse] = 2mv \bullet [number]$
$= 2mv\, NAvt / 6V$
$= mv^2\, NAt / 3V$.

Now, the force experienced by A is equal to the impulse divided by the time interval:
$[force] = [impulse] / [time]$
$= (mv^2\, NAt / 3V) / t$
$= mv^2\, NA / 3V$.

The pressure P experienced by the area A is just the force divided by the area, or

$$P = (mv^2\, NA / 3V) / A = mv^2\, N / 3V$$

This equation is starting to look like the ideal gas law. Let's transpose the volume, to write

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$PV = (2/3)\ (mv^2/2)\ N.$

The term inside the bracket is the kinetic energy of a single molecule. Thus, the PV term is equal to 2/3 of the total kinetic energy of the gas molecules.

Now, to make this expression look like the ideal gas result, we have to take a result from statistical mechanics relating the average kinetic energy of a particle to the temperature T of the system. The result is that

$mv_x^2 / 2 = k_B T /2$ for each direction x, y or z.

where k_B is Boltzmann's constant: $k_B = 1.38 \times 10^{-23}$ J/K.

This result applies to the average value of v_x^2 of particles in thermal equilibrium. For particles moving in three dimensions,

$$mv^2 /2 = m(v_x^2 + v_y^2 + v_z^2) / 2 = 3k_B T/2.$$

Thus:

$$PV = (2/3)\ (3k_B T/2)\ N$$

or

$$PV = Nk_B T.$$

This is the ideal gas law, although some students will be more familiar with the version commonly used in chemistry:

$$PV = nRT$$

where n = number of moles and R is the universal gas constant.

Moles etc.

A mole is defined as a specific number of atoms or molecules, namely

$$N_o \equiv \text{Avogadro's number} = 6.023 \times 10^{23}.$$

To find the number of moles in an sample, just divide the total number of atoms N by N_o, to yield

$$n = N / N_o.$$

Thus,

$$PV = (N / N_o) \bullet (N_o k_B)\ T$$
$$= n\ (N_o k_B)\ T.$$

But the product $N_o k_B$ is a constant, and is equal to the universal gas constant R ,which can be verified by direct substitution:

$$R = N_o k_B = 8.31 \text{ J/ K} \bullet \text{mole}$$

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Example

Just to familiarize ourselves with the chemist's version of the gas law, we calculate the volume occupied by a mole of gas at 1 atmosphere pressure and $T = 0\ ^oC = 273.15$ K.

$P = 1.01 \times 10^5$ N/m^2 $T = 273$ K

$$PV = nRT$$

reads

$$V = nRT / P$$
$$= 1 \bullet 8.31 \bullet 273 / 1.01 \times 10^5$$
$$= 0.0225 \text{ m}^3 \qquad (\text{J / N/m}^2 = \text{m}^3)$$
$$= 22.5 \text{ litres}$$

Note that the volume does not depend upon the structure of the gas molecules - we assumed that they are point particles.

Example

Estimate the average speed of the nitrogen molecules in the air under standard conditions

$T = 273$ K

$m = 2 \bullet 14 \bullet 1.66 \times 10^{-27}$ kg

Then

$$mv^2 / 2 = 3k_B T / 2$$

implies

$$v^2 = 3k_B T / m$$
$$= 3 \times 1.38 \times 10^{-23} \times 273 / (28 \times 1.66 \times 10^{-27}) = 2.43 \times 10^5 \text{ m}^2/\text{s}^2.$$

Taking the square root gives

$v = 493$ m/s.

Lighter molecules, like hydrogen, are even faster.

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