Kinetic Theory I

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1.3 Summary

- Kinetic theory
  predicts a few properties of gases from fundamental principles, but is approximate and fails completely to describe liquids and solids.

- Classical thermodynamics
  is rigorous and exact, but works with bulk properties such as pressure, work and heat, building a theory from elementary observations, without explaining the properties themselves.

- Statistical thermodynamics
  builds up many of the ideas of thermodynamics from a microscopic point of view, we will use it to introduce the concept of entropy which emerges rather mysteriously in classical thermodynamic.

1.1 The Assumptions of Kinetic theory

Kinetic theory is a microscopic model of gases which predicts macroscopic quantities such as pressure and heat capacity.
It is based on six assumptions:

1. A gas is composed of a large number of molecules.
2. The molecules are small compared to their separation.
3. The molecules are uniformly distributed and move randomly.
4. The molecules obey Newton's laws of motion.
5. The molecules feel no force except during collisions with other molecules or the walls of the container (hard spheres)
6. Molecules collide elastically, and the walls are smooth.

Limitations of these assumptions:

1. A gas is composed of a large number of molecules.
2. The molecules are small compared to their separation.
3. The molecules are uniformly distributed and move randomly.
4. The molecules obey Newton's laws of motion.
5. The molecules feel no force except during collisions with other molecules or the walls of the container (hard spheres)
6. Molecules collide elastically, and the walls are smooth.

ok not always wrong

2. The molecules are small compared to their separation.

5. The molecules feel no force except during collisions with other molecules or the walls of the container
(hard spheres)

These conditions are only met at low densities

4. The molecules obey Newton's laws of motion.

Quantum mechanics rules!

quantum predictions tend to those of classical physics
if the de Broglie wavelength of the molecules,
$\lambda = h/mv$, is much less than their mean separation.

This is true if the temperature is high so that
the speed v is large on average, and
at low density when the mean separation is large.

Main message:

kinetic theory is approximate

and applies best to gases at

low density
and
high temperature

1.2 Ideal Gases

An ideal gas obeys the assumptions of kinetic theory perfectly.

Real gases
approximate
ideal gases
in the limit of low density.

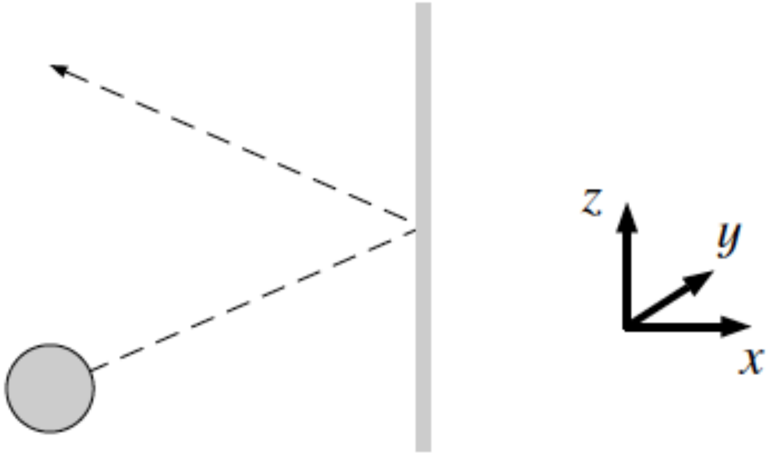
1.2.1 Pressure

Molecules in a gas collide with the walls of their container and transfer momentum to it.

Averaged over time, we have what is felt macroscopically as pressure.

Pressure is a force per unit area. [P] = [N m^{-2}] = [Pa]

Momentum variation = $-2mv_x$



In time Δt all atoms within a distance $v_x \Delta t$ of the wall can hit it, but only half are travelling towards the wall (by assumption 3), so the number of collisions per unit area in time Δt is

$$\frac{1}{2} n v_x \, \Delta t$$

where *n* is number of molecules per unit volume. The force exerted is the rate of momentum transfer, so the pressure, which is the force per unit area is

$$P = \frac{1}{2} n v_x \, \Delta t \times \frac{2 m v_x}{\Delta t} = n m v_x^2$$

This must be averaged because the molecules have a spread of v_x values

$$P = n m \overline{v_x^2} \qquad \overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}$$

The assumption that the molecules move randomly implies that they have no preferred direction, so

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} \quad \Rightarrow \quad \overline{v_x^2} = \overline{v^2}/3$$

$$\Downarrow$$

$$\boxed{P = \frac{1}{3} n m \overline{v^2}}$$

n is number of molecules per unit volume

$[P] = [N\ m^{-2}] = [Pa]$

Example:

standard temperature and pressure (STP)

T = 273 K
P = 1 atmosphere

For air:

P = 101 000 Nm^{-2}

density = 1.2 kg m^{-3} = density of molecules*mass = n*m = ρ

$$P = \frac{1}{3} n m \bar{v^2} \qquad v_{\mathrm{rms}} = \sqrt{\bar{v^2}} = \sqrt{\frac{3P}{\rho}} \approx 500\,\mathrm{m\,s^{-1}}$$

A light bulb of 10 cm in diameter will fill up in about
0.1 m/500 m s^{-1} = 0.2 ms

1.2.2 Internal Energy

If all the energy of a gas is kinetic energy, we can define the total energy of the molecules U, also called internal energy:

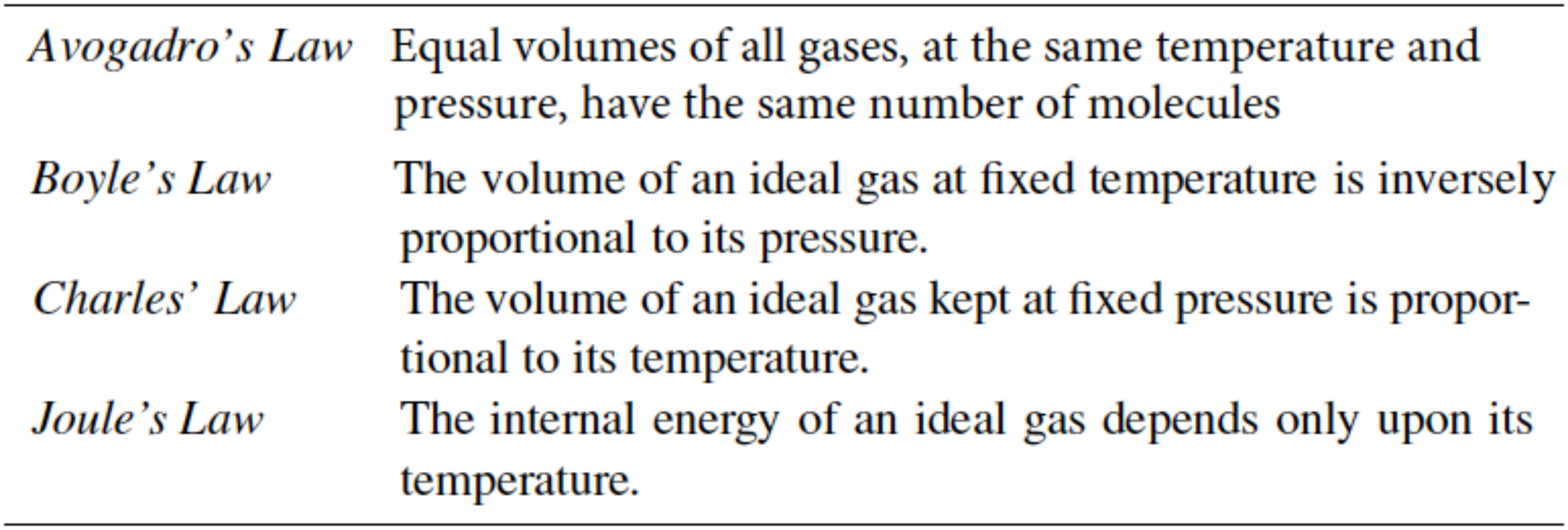
$$U = \frac{1}{2}(nV)m\overline{v^2}$$

n is number of molecules per unit volume and V is the volume occupied

Given that $$P = \frac{1}{3}nm\overline{v^2} \quad \Rightarrow \quad U = \frac{3}{2}PV$$

And we can define an energy density $U/V = 3P/2$

Ideal gas laws (empirical)



Avogadro's Law	Equal volumes of all gases, at the same temperature and pressure, have the same number of molecules
Boyle's Law	The volume of an ideal gas at fixed temperature is inversely proportional to its pressure.
Charles' Law	The volume of an ideal gas kept at fixed pressure is proportional to its temperature.
Joule's Law	The internal energy of an ideal gas depends only upon its temperature.

Boyle's law: at a fixed temperature T

$V \propto 1 / P$ → $PV = \text{constant}$

↓

$$U = \frac{3}{2}PV$$

Joule's law

the internal energy U of an *ideal gas* depends only upon its temperature, T_{I}, *not* on either P or V.

↓

$U_{\mathrm{I}} = U(T_{\mathrm{I}})$, where the subscript I stands for ideal

1.2.3 Equation of state of an ideal gas

Avogadro's Law Equal volumes of all gases, at the same temperature and pressure, have the same number of molecules

$V_1 = V_2$ and $T_1 = T_2$ and $P_1 = P_2$ $\Rightarrow$ $N_1 = N_2 = N$

Boyle's Law The volume of an ideal gas at fixed temperature is inversely proportional to its pressure.

T = fixed $V \propto 1 / P$ $\Rightarrow$ $PV = \text{constant}$

Charles' Law The volume of an ideal gas kept at fixed pressure is proportional to its temperature.

P = fixed $V \propto T$

$\Downarrow$

$$\boxed{PV = NkT_{\mathrm{I}}},$$

where

N is the number of molecules in volume V,
$k = 1.38 \times 10^{-23}\,\mathrm{J\,K^{-1}}$ is *Boltzmann's constant*,
T_{I} is the temperature in Kelvin.

$\boxed{PV = NkT_I}$ is an equation of state

one has only two degrees of freedom in fixing the state of a gas.

One can fix the temperature and pressure,
but not also the volume

One can set the temperature and volume,
but not also the pressure

because given the first two, the third is fixed by the equation of state.

Other ways of writing the equation of state $$\boxed{PV = NkT_{\mathrm{I}}}$$

We can define the number density (number of molecules per unit volume)

n = N/V

$$\boxed{P = nkT_{\mathrm{I}}}$$

We can define a mole as an Avogadro's number of molecules, where

$N_{\mathrm{A}} = 6.02 \times 10^{23}$ defined as the number of atoms in 12 g of ^{12}C

And we can thus write

where n_m is the number of moles

$$N = n_m N_{\mathrm{A}}$$

$$\Downarrow$$

$$PV = n_m N_{\mathrm{A}} k T_{\mathrm{I}}$$

$$PV = n_m N_A k T_I$$

We can define the gas constant, $R = N_A k = 8.314\ JK^{-1}\ mole^{-1}$

$$\boxed{PV = n_m R T_I}$$

We can define the molar volume $V_m = V/n_m$
which represents the volume occupied by one mole

$$PV_m = RT_I$$

1.2.4 Temperature and average kinetic energy

Combining $\boxed{PV = NkT_\mathrm{I}}$

and $\boxed{P = \frac{1}{3}nm\overline{v^2}}$

$$\Rightarrow \frac{1}{2}m\overline{v^2} = \frac{3}{2}kT_\mathrm{I}$$

temperature is a measure of the average molecular kinetic energy for the ideal gas.

Boltzmann's constant k is the conversion factor between units of temperature and energy.

Exercises

1. What is the volume of 1 mole of ideal gas at STP?

$$V_m = \frac{RT_\mathrm{I}}{P} = \frac{8.314 \times 273}{101,000} = 0.0225\,\mathrm{m}^3 = 22.5\,\mathrm{litre}$$

This result is independent on the gas, as long as it's ideal!

2. Intel manufactures Pentium chips in chambers where the pressure is equivalent to 1.0 10^{-10} mm of mercury.

2.1 What fraction is this of atmospheric pressure?

At atmospheric pressure, P_{atm}, air can support a column of mercury of height 760mm.

$$\frac{P}{P_\mathrm{atm}} = \frac{10^{-10}\,\mathrm{mm}}{760\,\mathrm{mm}} = 1.32 \times 10^{-13}$$

2.2 How many molecules are there in a chamber 40 cm in diameter and 30 cm tall at 20C?

$$\begin{aligned} N &= \frac{PV}{kT_\mathrm{I}} \\ &= \frac{13\,600\,\mathrm{kg\,m^{-3}} \times 9.81\,\mathrm{m\,s^{-2}} \times 10^{-13}\,\mathrm{m} \times \pi \times (40/2)^2 \times 30 \times 10^{-6}\,\mathrm{m^3}}{1.38 \times 10^{-23}\,\mathrm{J\,K^{-1}} \times 293\,\mathrm{K}} \\ &= 1.24 \times 10^{11}. \end{aligned}$$

1.3 Summary

- Kinetic theory is an approximate theory which can be expected to apply to low density gases
- Internal energy $U = \frac{3}{2}PV$
- Equations of state $\boxed{PV = NkT_{\mathrm{I}}}$ $\boxed{P = nkT_{\mathrm{I}}}$ $\boxed{PV = n_m RT_{\mathrm{I}}}$
- Relation between pressure and kinetic energy

$$\boxed{P = \frac{1}{3}nm\overline{v^2}} \qquad \frac{1}{2}m\overline{v^2} = \frac{3}{2}kT_{\mathrm{I}}$$