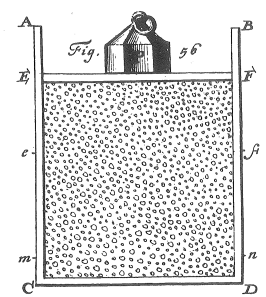
Module 6

Kinetic gas theory & Statistical mechanics



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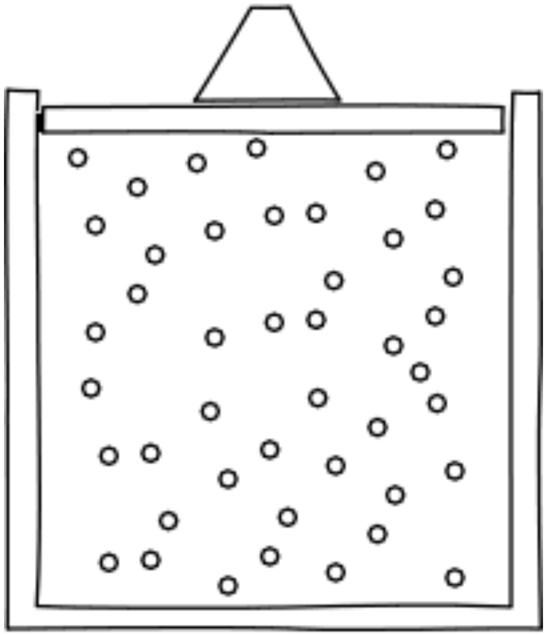
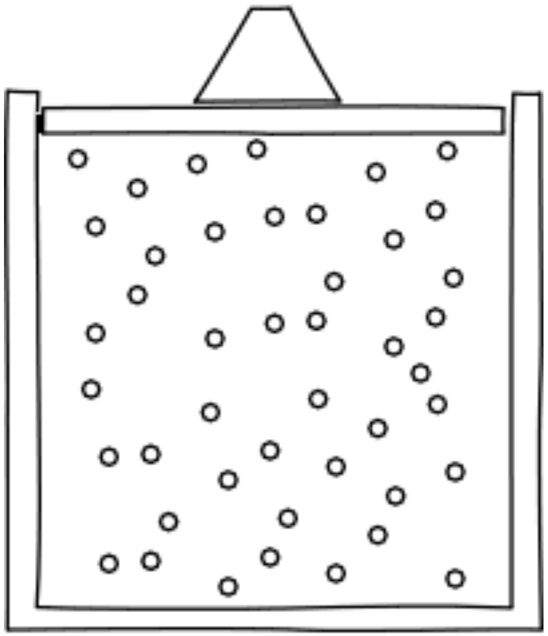
Kinetic gas theory (hypothesis)

The properties of elastics fluids (i.e. gases) depend especially on the facts that: (1) they posses weight; (2) they expand in all directions unless restrained; and (3) they allow themselves to be more and more compressed as the force of compression increases. These properties can be explained if we assume a fluid to consist of a very large number of small particles in rapid motion. (D. Bernoulli, 1738)



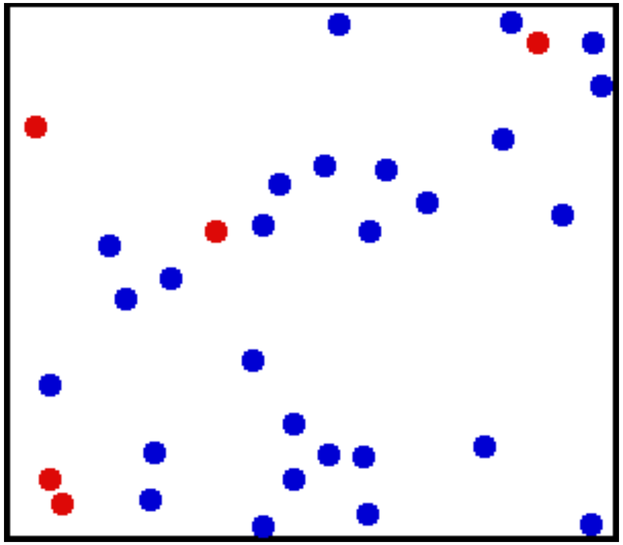
Kinetic gas theory (hypothesis)

Die Gase bestehen aus Atomen, welche sich verhalten wie feste, vollkommen elastische, mit gewissen Geschwindigkeiten innerhalb eines leeren Raumes sich bewegende Kugeln. (Krönig, 1856)

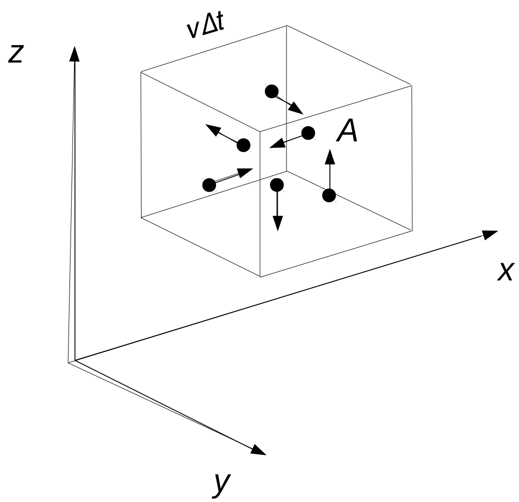


Kinetic gas theory (hypothesis)

I shall demonstrate the laws of motion of an indefinite number of small, hard and perfectly elastic spheres acting on one another only during impact. If the properties of such a system are found to correspond to those of gases, an important physical analogy will be established, which may lead to more accurate knowledge of the properties of matter. If experiments on gases are inconsistent with the hypothesis, then our theory, though consistent with itself, is proved to be incapable of explaining the phenomena of gases. (Maxwell, 1860)



Krönig (1852) and Clausius (1857)



Number of particles moving in the +x direction

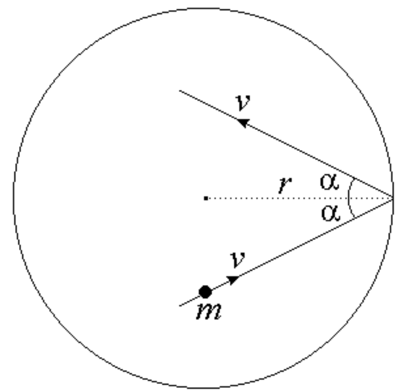
$$\frac{1}{6}\,\frac{N}{V}\,A\,\overline{v}\,\Delta t$$

Momentum transferred per (elastic) collision

$$2\,m\,\overline{v}$$

Total momentum transferred in Δt

$$\frac{1}{6}\,\frac{N}{V}\,A\,\overline{v}\,\Delta t\,2\,m\,\overline{v}$$



$$\vec{F} = \frac{\Delta\vec{p}}{\Delta t}$$

Wall pressure

$$PV = \frac{1}{3}Nm\overline{v}^2 \qquad PV = \tfrac{2}{3}N\overline{E}_{kin}$$

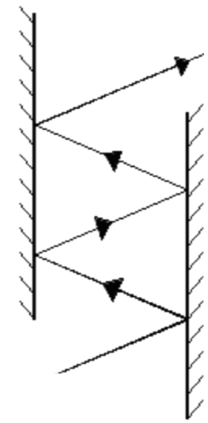
Ideal Gas Law (empirical)

$\frac{PV}{T} = a$ = gas = m

$\frac{PV}{T} \propto m$ = gas ≠ m

$\frac{PV}{T} \propto \frac{1}{M}$ ≠ gas = m

$$PV = nRT$$



Clausius (1857)
How he obtains the same result?
- Rotational and vibrational motions?

Thus, temperature ∝ average translational *vis viva*

$$\overline{E}_{kin} = \frac{3}{2}\,kT$$

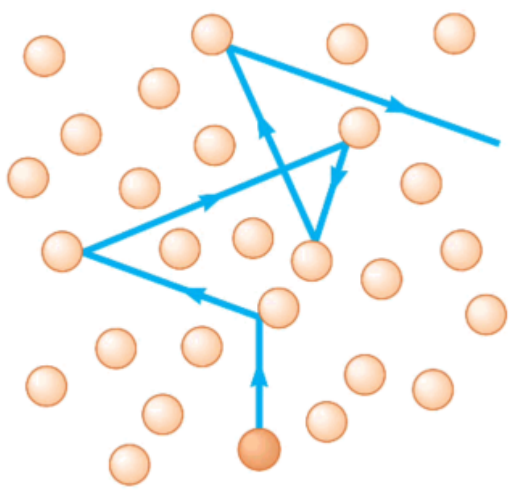
For each degree of freedom

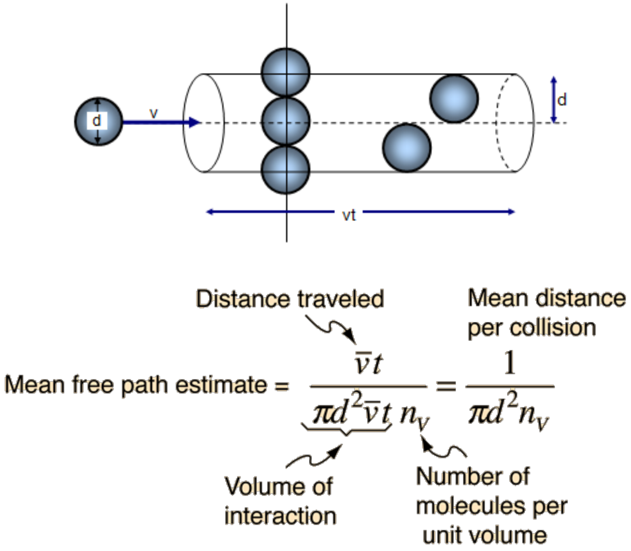
$$\overline{E}_{kin} = \tfrac{1}{2}kT$$

Mean free path – Clausius (1858)

Ballot's "dining room rebuttal"

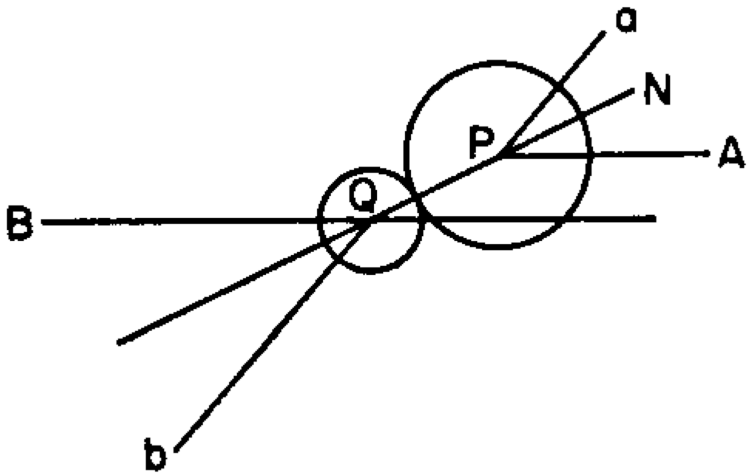
- Average distance travelled by a gas molecule or other particle between "collisions" with other particles

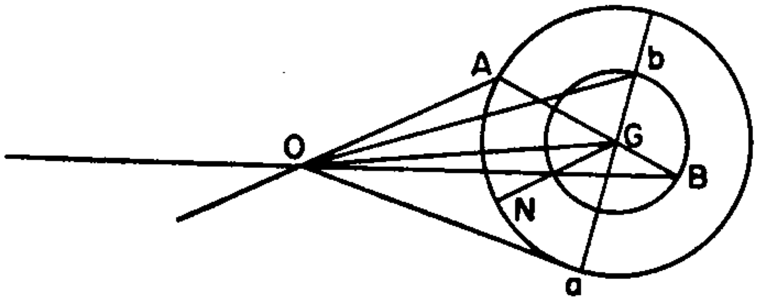




- First (non-trivial) statistical concept of Kinetic gas theory: It is **not** a property of an individual particle **nor** a macroscopic property of gas (Darrigol & Renn)

Velocity distribution – Maxwell (1860)





Velocity distribution – Maxwell (1860)

Now the existence of the velocity x does not in any way affect that of the velocities y or z, since these are all at right angles to each other and independent, so that the number of particles whose velocity lies between x and $x+dx$ and also between y and $y+dy$ and also between z and $z+dz$ is

$$Nf(x)f(y)f(z)dxdydz.$$

If we suppose the N particles to start from the origin at the same instant, then this will be the number in the element of volume $(dxdydz)$ after unit of time, and the number referred to unit of volume will be

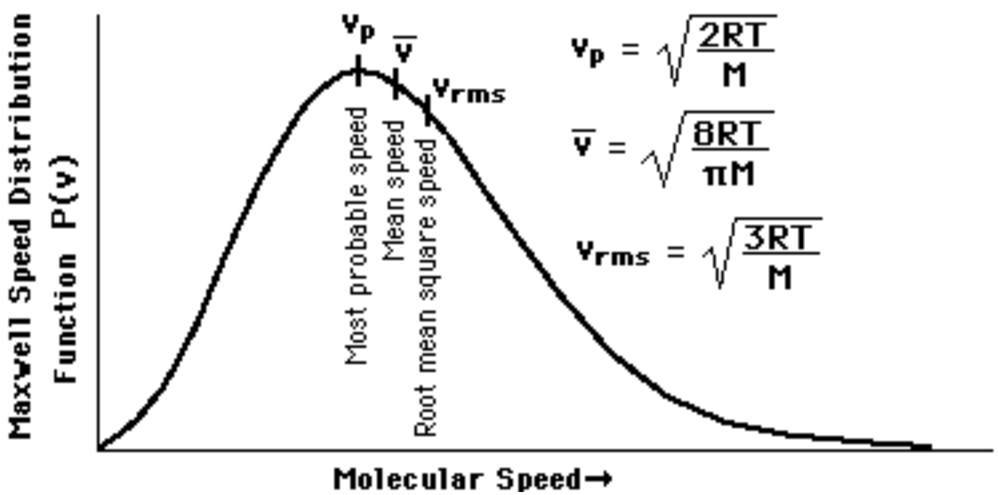
$$Nf(x)f(y)f(z)$$

But the directions of the coordinates are perfectly arbitrary, and therefore this number must depend on the distance from the origin alone, that is

$$f(x)f(y)f(z)=\phi(x^2+y^2+z^2).$$

Velocity distribution – Maxwell (1860)

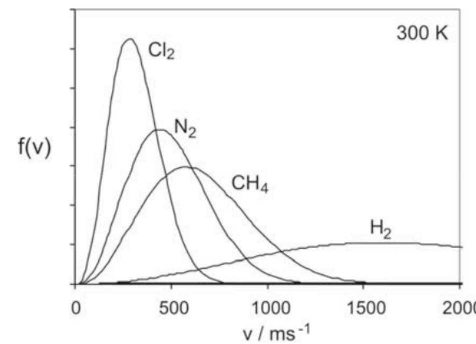
$$P(v) = 4\pi \left[\frac{M}{2\pi RT}\right]^{\frac{3}{2}} v^2 \exp\left[\frac{-Mv^2}{2RT}\right]$$



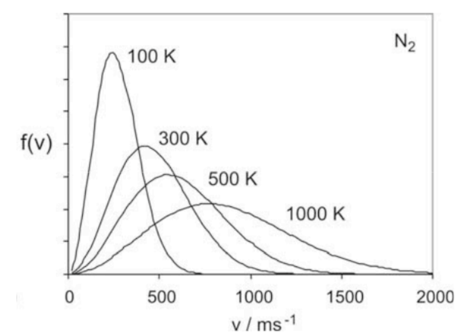
$$v_p = \sqrt{\frac{2RT}{M}}$$

$$\bar{v} = \sqrt{\frac{8RT}{\pi M}}$$

$$v_{rms} = \sqrt{\frac{3RT}{M}}$$



Mass dependence



Temperature dependence

$S = k \ln W$

Physics' [2nd] most famous equation

- Where does it come from?
- What does it mean?
- How/Why was it proposed?

Discussion session 1: Boltzmann (1872)

2

Further Studies on the Thermal Equilibrium of Gas Molecules *

LUDWIG BOLTZMANN

Discussion session 2: Boltzmann (1877)

4

On the Relation of a General Mechanical Theorem to the Second Law of Thermodynamics *

LUDWIG BOLTZMANN

$S = k \ln W$

Physics' [2nd] most famous equation

W microstates from a macrostate

N cells in phase space

$$W = \frac{N!}{n_0!\, n_1!\, n_2! \cdots n_i!}$$

n_0, n_1, n_2, … n_i molecules in each cell

Assuming same energy to each cell

W is maximum at $n_0 = n_1 = n_2 \ldots = \ldots = n_i$

But energy are "probabilistic weights"

And $\Sigma n_i . E_i = E$

Thus, the solution with greatest probability is

$$n_i = A e^{-E_i / kT}$$

Boltzmann distribution

Large numbers! Stirling approximation

$$N! \sim \sqrt{2\pi N}\left(\frac{N}{e}\right)^N$$

End of module feedback

- Please go to b.socrative.com (student login)
- Enter the HISPHYSKU room
- Fill out the short (anonymous) survey
- Tak skal du have!