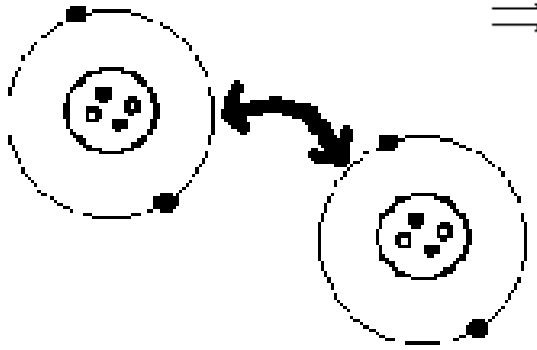
5.1. Kinetic theory of gases

Matter consists out of a great many atoms:

e.g.: He-Gas : $3 \cdot 10^{19}$ Atoms/cm^3

those interact via electric forces:

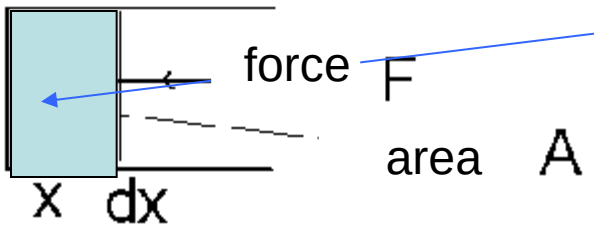


$\Rightarrow$ obey the laws of mechanics

Goal: Understanding of various states of matter (Gas, liquid, solid state)

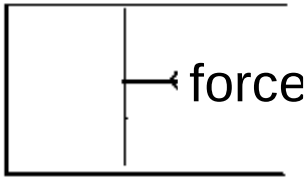
Here: Discussion of properties of gases starting from the mechanics of Newton.

Pressure of gases:



Piston without friction, atoms of gases in volume V

How large is F on the piston?



Keeps the balance

Atoms hit the piston, get reflected!

Pressure: $P = \frac{F}{A}\left(\frac{force}{area}\right)$

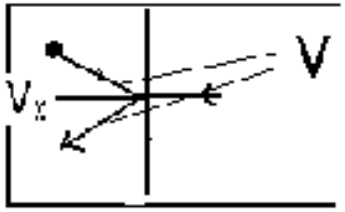
Pressure on gas → leads to work ΔW !

$$dW = F(-dx) = -P \cdot A \cdot dx = -P \cdot dV$$

How much force does one need, the ',knocking" of molecules to balance?

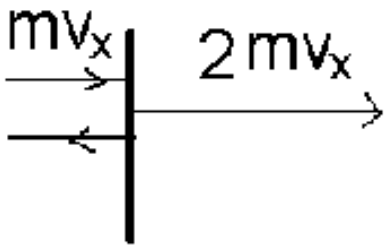
$F = \frac{dp}{dt}$ with p momentum

Ass.: Piston is a ideal reflector, i.e. molecules bounce elastically



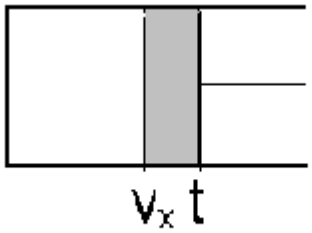
Laws of collisions:
Reflexion on a wall

Momentum transfer: $2mv_x$



Number of bounces: How many atoms kick against the piston in time t ?

Be N atoms in V or n= N/V in a unity volume



only molecules (Atoms) up to a distance $v_x \cdot t$

hit the piston. The volume hitting the piston:

$$v_x \cdot t \cdot A \Rightarrow n \cdot v_x \cdot t \cdot A$$

n as number of the knocking molecules

per unit time $\Rightarrow n \cdot v_x \cdot A$

$$F = n \cdot v_x \cdot A \cdot 2 \cdot m \cdot v_x =$$ number/time ·momentum transfer

$$\Rightarrow \text{pressure} : P = 2n \cdot m \cdot v_x^2$$

Not all atoms have the same velocity!

average: $P = n \cdot m \cdot \langle v_x^2 \rangle; \langle v_x^2 \rangle$ Average in ±x - direction

Factor of 2 is missing, because half fly into + x-direction!

Movements are isotropical:

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle \Rightarrow$$

$$\langle v_x^2 \rangle = \frac{1}{3}\langle v_x^2 + v_y^2 + v_z^2 \rangle = \frac{1}{3}\langle v^2 \rangle \Rightarrow$$

Basic equations of kinetic theory of gases

$$P = n \cdot m \cdot \langle v^2 \rangle / 3$$

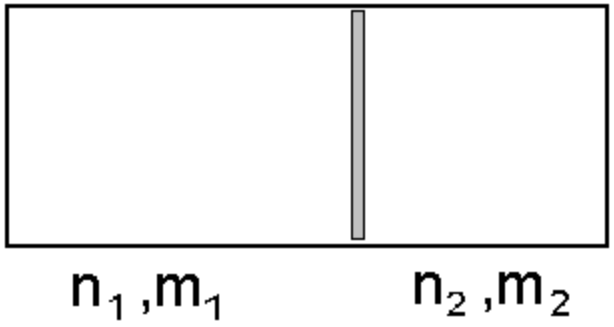
$$P = \frac{2}{3} \cdot n \cdot \left\langle m \cdot \frac{v^2}{2} \right\rangle$$

$$\Rightarrow P \cdot V = N \cdot \left(\frac{2}{3}\right) \cdot \left\langle m \cdot \frac{v^2}{2} \right\rangle$$

Be U the total energy: $U = N\left\langle m \cdot \frac{v^2}{2} \right\rangle \Rightarrow P \cdot V = \frac{2}{3}U$

5.2. Connection between temperature and kinetic energy

Two gases



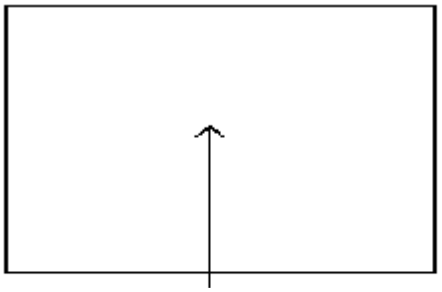
movable piston

equilibrium: pressure on pistons from both sides equal

$$\Rightarrow n_1 \left\langle m_1 \frac{v_1^2}{2} \right\rangle = n_2 \left\langle m_2 \frac{v_2^2}{2} \right\rangle$$

Question: Are large n and small v equivalent to small n and large v?

Special example



two gases in
one volume

m_1, m_2, v_1, v_2

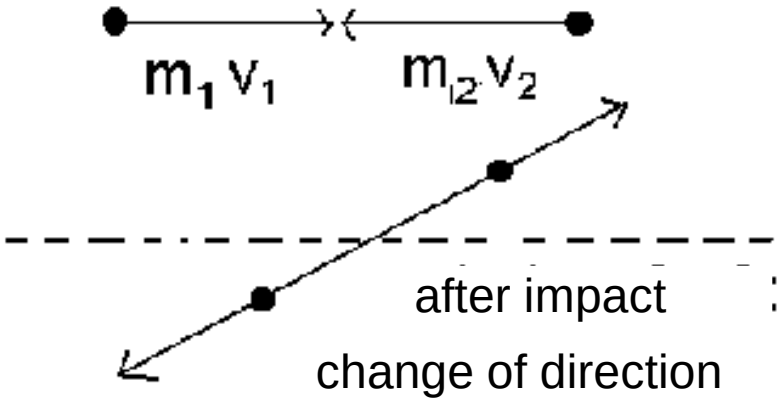
Starting point:

$$v_2 = 0$$

Not a long time!

Impact in center of mass system (c.m.):

After time t, independent of the starting situation



Probability for all directions is equal.
not only in c.m.

$$\vec{v}_1, \vec{v}_2; \vec{v}_{sp} = \frac{m_1 \cdot \vec{v}_1 + m_2 \cdot \vec{v}_2}{m_1 + m_2}$$

Relative velocity:

$$\vec{w} = \vec{v}_1 - \vec{v}_2$$

After impact: No change in c.m. movement

In equilibrium:

All directions of $\vec{w}$

are equal probable towards direction of movement of c.m.

Mathematical:

$$\langle \vec{w} \cdot \vec{v}_{sp} \rangle = 0$$

$$\vec{w} \cdot \vec{v}_{sp} = \frac{(\vec{v}_1 - \vec{v}_2) \cdot (m_1 \cdot \vec{v}_1 + m_2 \cdot \vec{v}_2)}{m_1 + m_2} = \frac{(m_1 \cdot v_1^2 - m_2 \cdot v_2^2) + (m_2 - m_1) \cdot (\vec{v}_1 \cdot \vec{v}_2)}{m_1 + m_2}$$

Average of $\vec{v}_1 \cdot \vec{v}_2$ *=0, because the average of* $\vec{v}_1, \vec{v}_2$ *=0*

$$\langle m_1 \cdot v_1^2 \rangle = \langle m_2 \cdot v_2^2 \rangle \quad \text{or} \quad \left\langle m_1 \frac{v_1^2}{2} \right\rangle = \left\langle m_2 \frac{v_2^2}{2} \right\rangle \Rightarrow$$

The averages kinetic energies must be equal!

The average kinetic energy depends only from temperature.

and is independent from nature of gases

The average kinetic energy can be used to define temperature.

Or: •**Temperature is** average kinetic energy

Out of historic reasons T is defined via relations which are discussed further below.

One uses therefore a conversion factor k

Joule for 1 Kelvin (absolute scale of temperature)
or the mean atomic kinetic energy : $\frac{3}{2}kT,$

$$k = 1.38 \cdot 10^{-23} \ \frac{Joule}{one \text{ degree } Kelvin}$$

i.e.: each single direction (v_x, v_y, v_z) has $\frac{1}{2}kT$

Ideal gas

From above: $P \cdot V = N \cdot \left(\frac{2}{3}\right) \cdot \left\langle m \ \frac{v^2}{2} \right\rangle \Rightarrow$ $P \cdot V = N \cdot k \cdot T$

At equal temperature:
Pressure and volume fix
the number of atoms (molecules)!

Macroscopically chemist
Introduced:

$$P \cdot V = N \cdot R \cdot T$$

One mole (molecular weight in gram) contains:

N :number of moles, $R = N_0 \cdot k$

$$N_0 = 6.02 \cdot 10^{23} \text{ molecules}$$

View so far: Monoatomic molecule. How is it for polyatomic molecules? e.g.: a diatomic molecule:

For each atom
Spring constant=0:

$$\left\langle m_A \frac{v_A^2}{2} \right\rangle = \left\langle m_B \frac{v_B^2}{2} \right\rangle = \frac{3}{2} k \cdot T$$

A and B can oscillate!

How do they act together in a bound state?

Movement of center of mass: $M = m_A + m_B$

$$\left\langle \frac{1}{2} M \cdot v_{cm}^2 \right\rangle = \frac{3}{2} k \cdot T$$

More energy can go into vibration and rotation !

Real spring constant: Binding

Ca rotate!

Generally can be stated that 1/2kT can go into each degree of freedom

The number of degrees of freedom results from the number of possibilities of energy to bring into a system! e.g:

Ideal gas: each direction of velocity represents a degree of freedom.

$$\Rightarrow \frac{3}{2}kT$$

Having molecules there are besides c.m.-movement oscillation degrees of freedom and rotation degrees of freedom!

5.3. Specific degrees of freedom: Thermal energies

$$PV = N \cdot \left(\frac{2}{3}\right) \cdot \left\langle m \frac{v^2}{2} \right\rangle = N \cdot k \cdot T = (\gamma - 1) \cdot U; (\gamma - 1) = \frac{2}{3}$$

for atomic gas

With complicated molecules:

Rotation, Vibration

The total energy contains not only contributions of kin. energy!

$\Rightarrow \gamma$ depends on the structure of the molecule!

Basic equation of kinetic theory of gases, s.a.

Molar heat

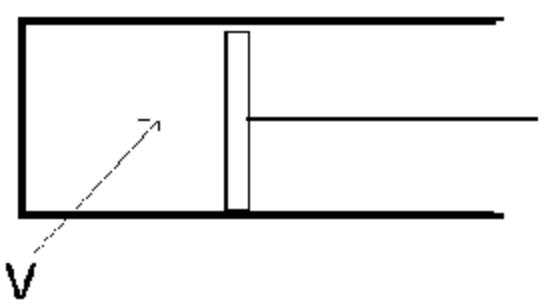
a) At constant volume:

$$N_A \cdot \overline{E}_{kin} = \frac{3}{2} N_A \cdot k \cdot T$$

$$\overline{E}_{kin}^{Mol} = \frac{3}{2} R \cdot T$$

At increase of energy, i.e. addition of heat

in case , if



V remains constant .

$$\Delta \overline{E}_{kin}^{Mol} = \frac{3}{2} R \cdot \Delta T \quad \text{with} \quad \frac{3}{2} R = c_V$$

Generally: Addition of heat ΔQ ~ leads to increase of temperature

$$\Delta Q \sim \Delta T$$

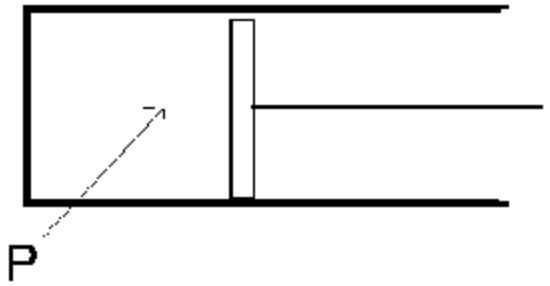
$$\Delta Q = c_V \Delta T$$

State variables
up to now: P, V, T, Q

c_V Specific heat depends on properties of matter!

b) Molar heat at constant pressure

P= constant



More energy (ΔQ) is necessary, in order to heat up the gas, compared to V= constant .

Reason: More work goes in $\Delta W = P \cdot \Delta V$

→Two shares of energy: $P \cdot \Delta V = R \cdot \Delta T$

and $\Delta \overline{E}_{kin}^{Mol} = c_V \cdot \Delta T$

or $\Delta E_{total} = (c_V + R) \cdot \Delta T$ $\quad (c_V + R) = c_P$: Specific heat at constant pressure

with $c_V = \frac{3}{2} R \Rightarrow c_P = \frac{5}{2} R$

$\gamma = \frac{c_P}{c_V}$ Examples of measured : γ

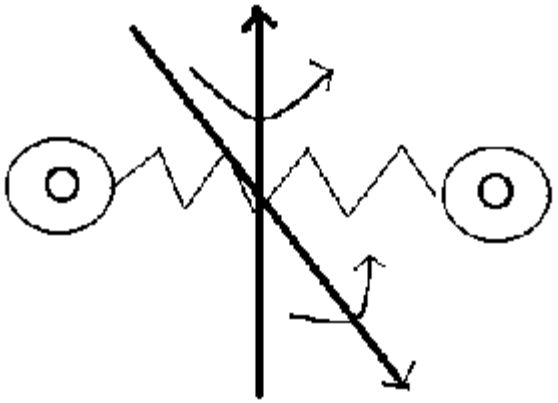
Well fullfilled at monoatomar gases!

γ	
1.66	He,Ar
1.4	O_2,N_2
1.3	CO_2,N_2O

Not so at , e.g.: O_2

How large is the total energy of that molecule at temperature T?

c.m. -energy (3/2kT) + rotation +oscillation
the molecule can rotate in two directions



i.e.: in addition there are 1kT+oscilation

Important: Here one can see what makes a degree of freedom

Addition of energy by oscillating can go into kinetic , but also into potential energy !

$$\overline{E}_{pot} = \overline{E}_{kin}$$

i.e.: + 2 more degrees of freedom

$$\Rightarrow 1 \cdot k \cdot T$$

Total energiy $U = \frac{7}{2}kT$ From above $N \cdot k \cdot T = (\gamma - 1) \cdot U$

or $kT = \frac{2}{7}U$ per molecule with $\frac{2}{7} = (\gamma - 1)$

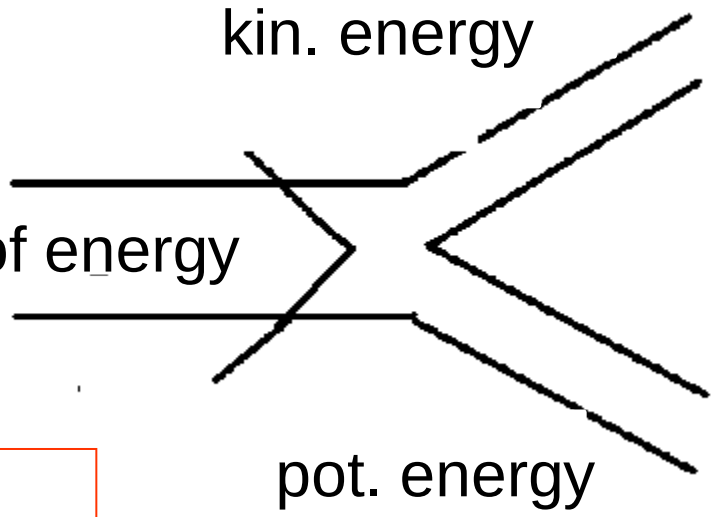
$$\gamma = \frac{kT+U}{U} = \frac{\frac{9}{2}}{\frac{7}{2}} = 1.29$$ s.a. CO_2

for N molecules:

$$N \cdot kT = (\gamma - 1) \cdot U_{total}$$

The average kinetic energy makes up
a fraction of total energy!

Equal input of energy leads to a different
temperature rise
at a different materials



Limit of a classical description:
Not all degrees of freedom take up energy!
It depends on temperature!
Adequate description needs quantenmechanics!

Examples: H_2, O_2, N_2

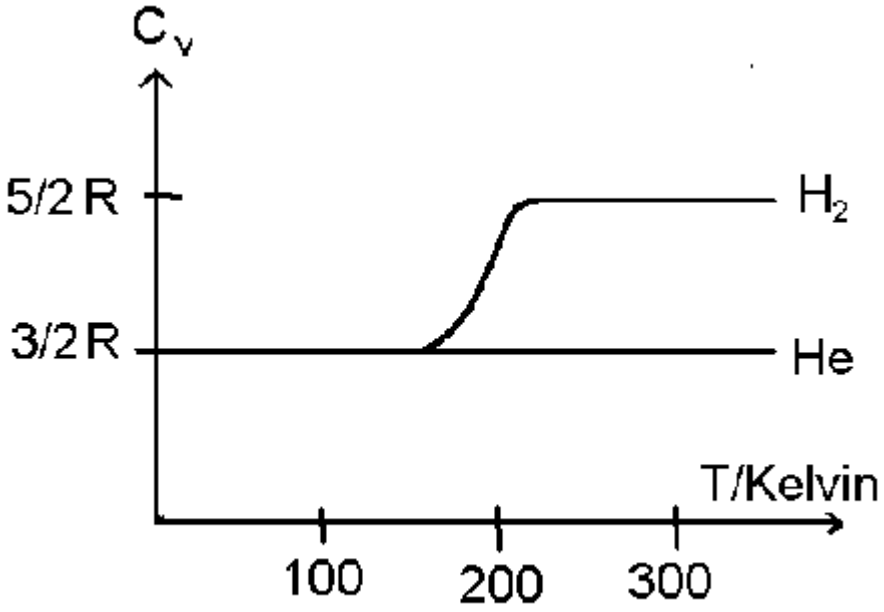
Ass.: Those molecules do not vibrate!

U=7/2kT reduces to 5/2kT

i.e.: not 7 degrees of freedom, but 5

$$\gamma = \frac{kT + \frac{5}{2}kT}{\frac{5}{2}} = \frac{\frac{7}{2}}{\frac{5}{2}} = 1.4 \Rightarrow$$

agrees with experiment !



At certain temperatures are degrees of freedom frozen.
i.e. : No energy is absorbed!