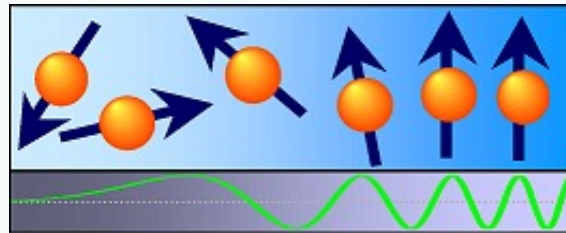# Experimental Physics EP2
Thermodynamics
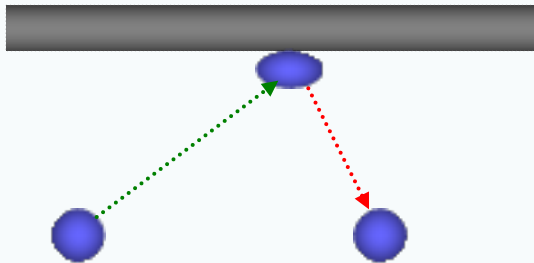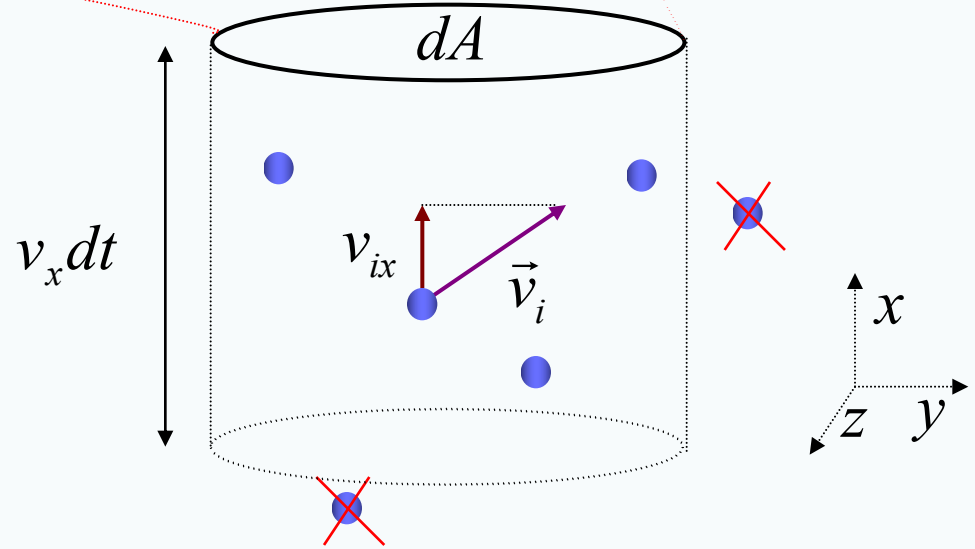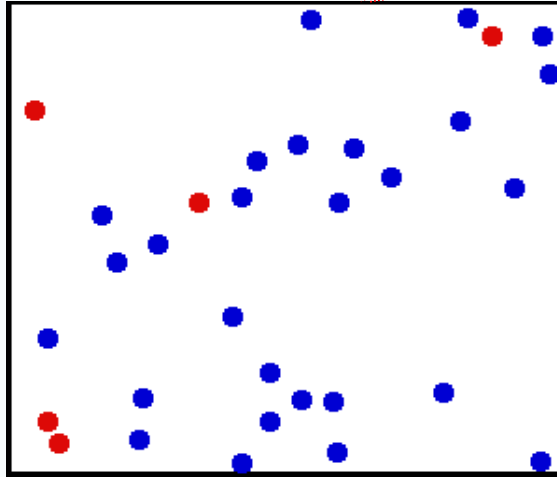
— Kinetic theory of gases —

Gas pressure

https://bloch.physgeo.uni-leipzig.de/amr/

Gas pressure

$v_x dt$

dA

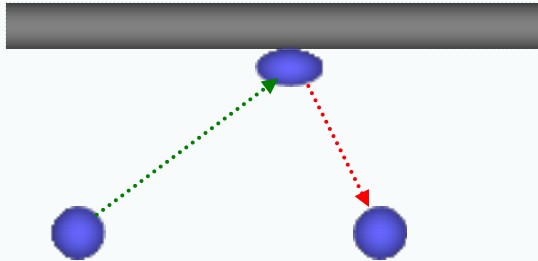v_{ix}

$\vec{v}_i$

x

z y

$\Delta \vec{p}_{i,1} = -m\vec{v}_i$

$$\Delta \vec{p}_{i,\text{total}} = -\vec{p}_i \frac{N_i}{V} A v_{ix} dt \quad = \vec{F}_{w \to i} dt$$

Force acting upon the wall in the first part of collision:

$$\vec{F}_1 = \sum_{v_{ix}>0} \frac{N_i A}{V} \vec{p}_i \, v_{ix}$$

Gas pressure

$$\Delta \vec{p}_{i,1} = -m\vec{v}_i$$

Force acting upon the wall in the second part of collision:

$$\vec{F}_2 = \sum_{v_{ix}<0} \frac{N_i A}{V} \vec{p}_i v_{ix}$$

$$\vec{F} = \vec{F}_1 + \vec{F}_2 = \sum \frac{N_i A}{V} \left(p_{ix} v_{ix} \hat{i} + p_{iy} v_{ix} \hat{j} + p_{iz} v_{ix} \hat{k} \right)$$

$$P = \frac{F_x}{A} = \frac{1}{V} \sum_i N_i p_{ix} v_{ix} \qquad N = \sum_i N_i \qquad P = \frac{N}{V} \langle p_x v_x \rangle$$

$$\langle \vec{p}\vec{v} \rangle = \langle p_x v_x + p_y v_y + p_z v_z \rangle = \langle p_x v_x \rangle + \langle p_y v_y \rangle + \langle p_z v_z \rangle = 3 \langle p_x v_x \rangle$$

$$PV = \frac{1}{3} N \langle \vec{p}\vec{v} \rangle \qquad PV = \frac{1}{3} m N \langle v^2 \rangle \qquad PV = \frac{2}{3} \langle E_{k,total} \rangle$$

Molecular speeds in gases

$$PV = \frac{1}{3} mN \langle v^2 \rangle \qquad \rho = \frac{mN}{V} \qquad v_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3P}{\rho}} =$$

Components in Dry Air	Volume Ratio compared to Dry Air	Molecular Mass M (kg/kmol)	Molecular Mass in Air
Oxygen	0.2095	32.00	6.704
Nitrogen	0.7809	28.02	21.88
Carbon Dioxide	0.0003	44.01	0.013
Hydrogen	0.0000005	2.02	0
Argon	0.00933	39.94	0.373
Neon	0.000018	20.18	0
Helium	0.000005	4.00	0
Krypton	0.000001	83.8	0
Xenon	0.09 10^{-6}	131.29	0
Total Molecular Mass of Air			28.97

T = 300 K

**~ 480 m/s**

~ 1930 m/s

~ 238 m/s

To remember!

➢ **Molecules in gases have relatively high speeds.**

➢ **Pressure of the gas is due to molecular collisions.**

➢ **In revealing the kinetic origin of pressure,**

it is worse remembering not only the

role of momentum transfer, but also

number of collision per unit time.

➢ **The joint effect makes the pressure**

being proportional to the average

kinetic energy of the molecules.

Experimental Physics EP2
Thermodynamics

— Kinetic theory of gases —
Kinetic interpretation of temperature
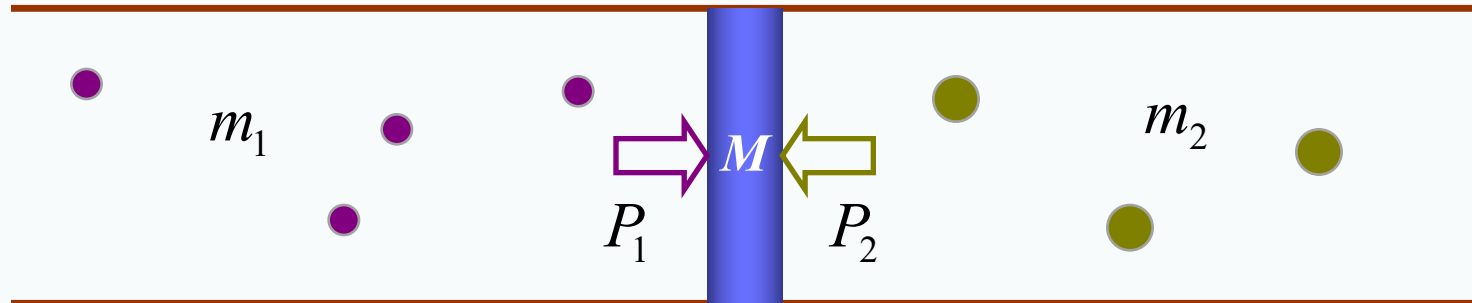

https://bloch.physgeo.uni-leipzig.de/amr/
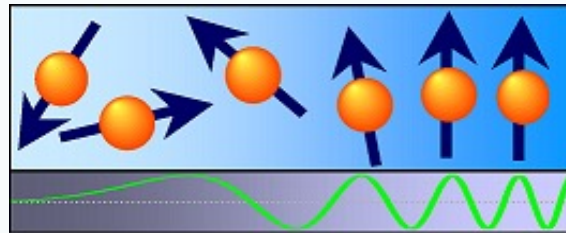
Kinetic interpretation of temperature

$$PV = \frac{1}{3}mN\langle v^2 \rangle \quad \boxed{= N k T}$$

We cannot use the ideal gas law because we intend to derive it from the microscopic principles!

T

T

m_1

$\Rightarrow$ **M** $\Leftarrow$

P_1 P_2

m_2

Mechanical equilibrium: $\qquad P_1 = P_2 \qquad m_1 N_1 \langle v_1^2 \rangle = m_2 N_2 \langle v_2^2 \rangle$

However, the condition above is not sufficient. The temperatures as well must be identical to provide equilibrium! Otherwise, the process of temperature equilibration will result in changing pressures, therefore in piston movement.

Kinetic interpretation of temperature
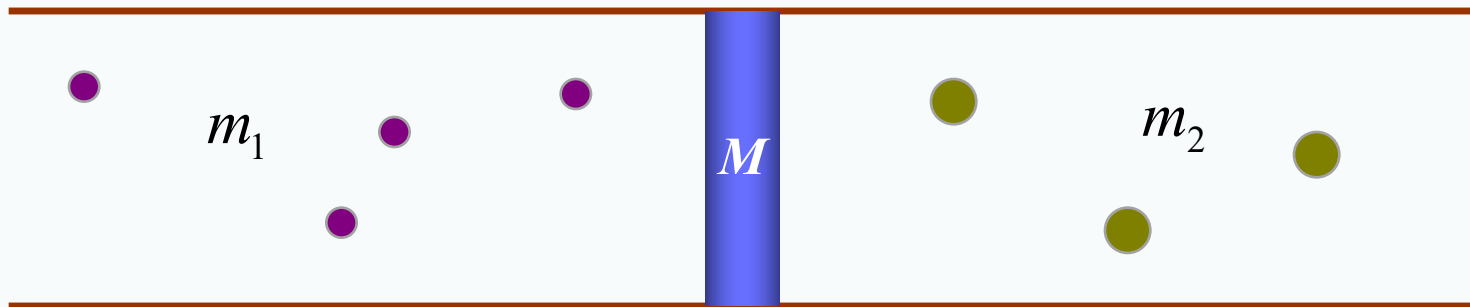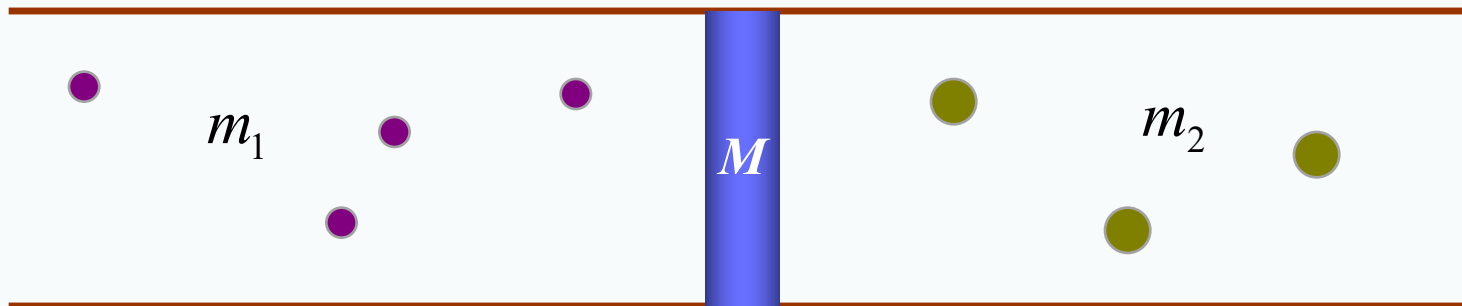

$$m_1 v_{1x} + Mu = m_1 v'_{1x} + Mu'$$

$$\tfrac{1}{2} m_1 v_{1x}^2 + \tfrac{1}{2} Mu^2 = \tfrac{1}{2} m_1 v'^2_{1x} + \tfrac{1}{2} Mu'^2$$

$$v'_{1x} = \frac{2Mu + (m_1 - M)v_{1x}}{m_1 + M}$$

$$v'^2_{1x} = \frac{4M^2 u^2 + 4M(m_{1m})uv_{1x} + (m_1 - M)^2 v_{1x}^2}{(m_1 + M)^2}$$

$$\left\langle v'^2_{1x} \right\rangle = \frac{4M^2 \left\langle u^2 \right\rangle + (m_1 - M)^2 \left\langle v_{1x}^2 \right\rangle}{(m_1 + M)^2}$$

if it is equilibrium then it must be $= \left\langle v_{1x}^2 \right\rangle$

Kinetic interpretation of temperature

$$\left\langle v_{1x}^2 \right\rangle = \frac{4M^2 \left\langle u^2 \right\rangle + (m_1 - M)^2 \left\langle v_{1x}^2 \right\rangle}{(m_1 + M)^2}$$

$$\frac{m_1}{2} \left\langle v_{1x}^2 \right\rangle = \frac{M}{2} \left\langle u^2 \right\rangle$$

$$\frac{m_2}{2} \left\langle v_{2x}^2 \right\rangle = \frac{M}{2} \left\langle u^2 \right\rangle$$

In the same spirit, it is valid for the second gas:

$$\frac{m_1}{2} \left\langle v_{1x}^2 \right\rangle = \frac{m_2}{2} \left\langle v_{2x}^2 \right\rangle$$

Motion is chaotic!

$$\left\langle v_{1x}^2 \right\rangle = \left\langle v_{1y}^2 \right\rangle = \left\langle v_{1z}^2 \right\rangle$$

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

Kinetic interpretation of temperature
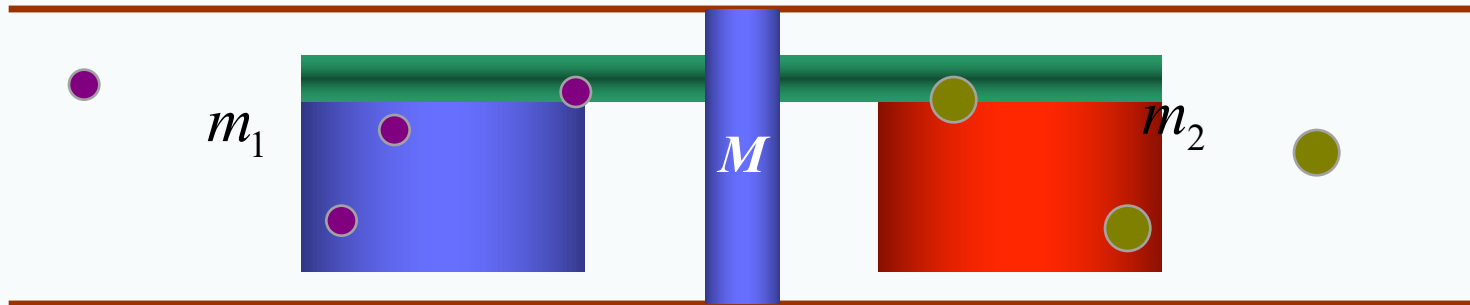
$$\frac{m_1}{2}\left\langle v_1^2 \right\rangle = \frac{m_2}{2}\left\langle v_2^2 \right\rangle$$

$$\Theta = \frac{2}{3}\left\langle E_k \right\rangle$$

$$PV = \frac{2}{3}\left\langle E_{k,total} \right\rangle$$

kinetic or energetic temperature

$$PV = N\Theta$$

Temperature can be defined as any monotonic function of the kinetic temperature. The introduction of a special unit T, which is measured in degrees of Celsius or K, is mostly due to historical reasons:

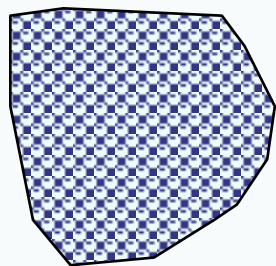$$\Theta = kT$$ **thermodynamic temperature**

The equipartition theorem

$$\frac{m_1}{2}\left\langle v_{1x}^2\right\rangle = \frac{M}{2}\left\langle u^2\right\rangle \qquad \left\langle v_{1x}^2\right\rangle = \left\langle v_{1y}^2\right\rangle = \left\langle v_{1z}^2\right\rangle \qquad \Theta = \frac{2}{3}\left\langle E_k\right\rangle \qquad \Theta = kT \qquad \left\langle E_k\right\rangle = \frac{3}{2}kT = 3\left(\frac{1}{2}kT\right)$$

In thermodynamic equilibrium there is an average energy of kT/2 per molecule (or per object) associated with each degree of freedom.

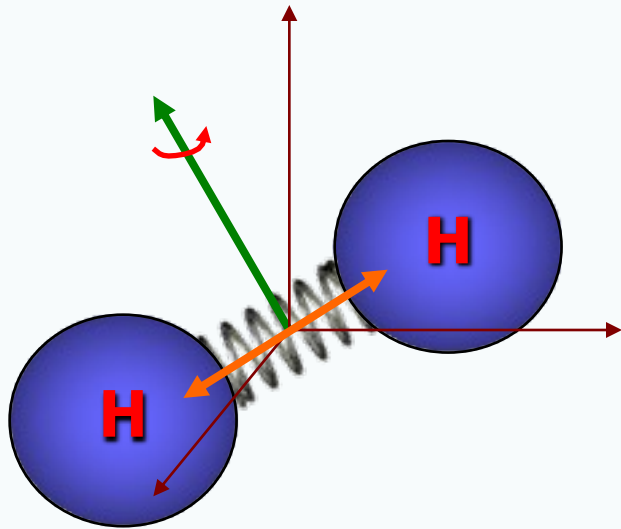$$u = \tfrac{1}{M}\sum_k m_k u_k \qquad\qquad \tfrac{1}{2}Mu^2 = \tfrac{1}{2M}\sum_{k,j} m_k m_j u_k u_j$$

$$\tfrac{1}{2}M\left\langle u^2\right\rangle = \tfrac{1}{2M}\sum_k m_k^2\left\langle u_k^2\right\rangle \qquad = \tfrac{1}{2}kT \qquad = \tfrac{1}{2}m_k\left\langle u_k^2\right\rangle$$

$$\tfrac{1}{2}M\left\langle V^2\right\rangle = \tfrac{1}{2M}\sum_k m_k^2\left\langle u_k^2\right\rangle = \tfrac{3}{2}kT$$

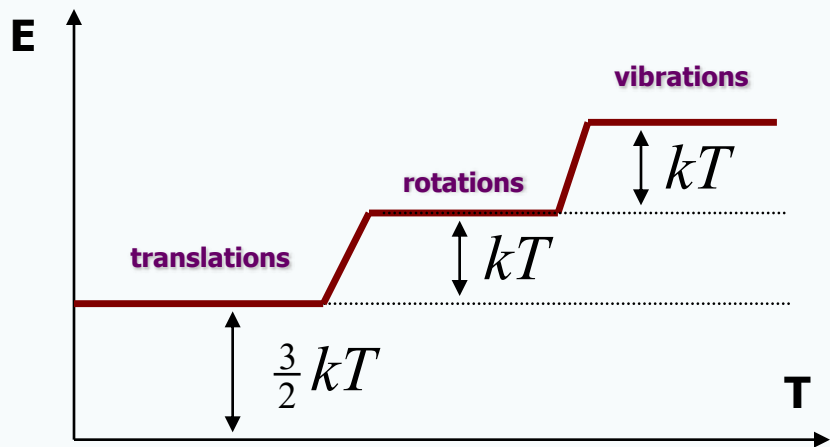**The equipartion theorem is valid for any degree of freedom.**

Energy of polyatomic molecules

$$\left\langle E_{translational} \right\rangle = \frac{1}{2}kT + \frac{1}{2}kT + \frac{1}{2}kT$$

$$\left\langle E_{rotational} \right\rangle = \frac{1}{2}kT + \frac{1}{2}kT$$

$$\left\langle E_{vibrational} \right\rangle = \frac{1}{2}kT + \frac{1}{2}kT$$

$$x = A\cos(\omega t + \delta)$$

$$E_p = \tfrac{1}{2}kx^2 = \tfrac{1}{2}kA^2 \cos^2(\omega t + \delta)$$

$$E_k = \tfrac{1}{2}m\left(\tfrac{dx}{dt}\right)^2 = \tfrac{1}{2}kA^2 \sin^2(\omega t + \delta)$$

$$\overline{E_k} = \overline{E_p} = \tfrac{1}{4}kA^2 = \tfrac{1}{2}kT$$

To remember!

➢ **Based solely on molecular kinetics in gases we were able to show that the average kinetic energy of molecules obeys the properties stated for temperature in the zero[th] law of thermodynamics.**

➢ **This allows us to introduce kinetic temperature.**

➢ **Kinetic and thermodynamic temperatures simply related to each other via $\Theta = kT$.**

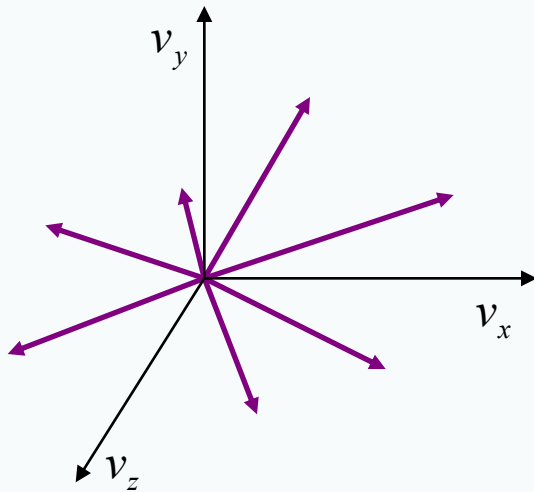➢ **In thermodynamic equilibrium there is kinetic energy $kT/2$ associated with each degree of freedom.**
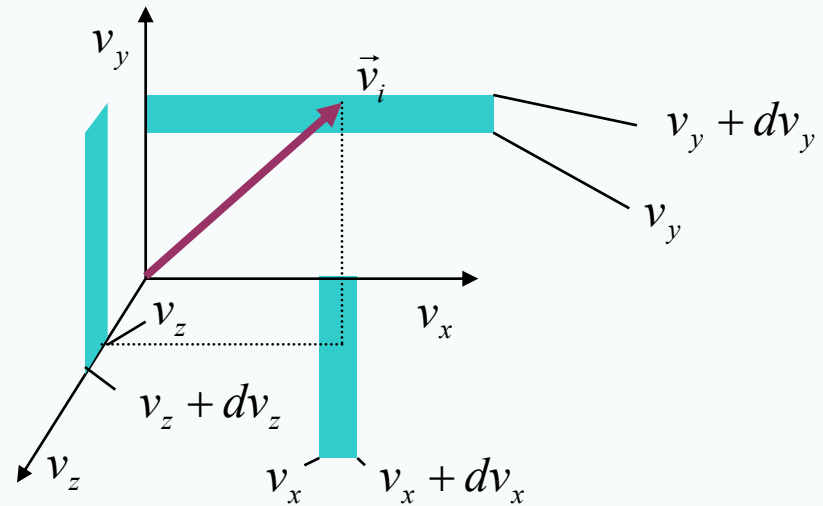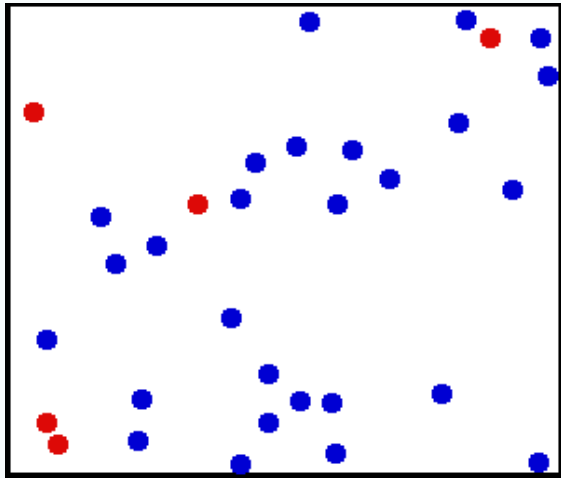
Experimental Physics EP2
Thermodynamics

— Kinetic theory of gases —
Maxwell and Boltzmann distributions

https://bloch.physgeo.uni-leipzig.de/amr/
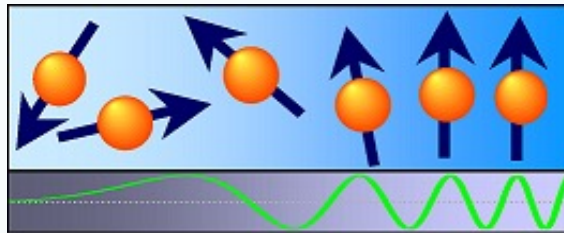
The Maxwell distribution of velocities

$$\varphi(v_x)dv_x \qquad \varphi(v_y)dv_y \qquad \varphi(v_z)dv_z$$

$$f(\vec{v}) = \varphi(v_x)\varphi(v_y)\varphi(v_z)$$

$$\varphi(v_x) = \varphi(-v_x) \quad \Rightarrow \quad \varphi(v_x) = F(E_{kx})$$

$$\boxed{\varphi(v_{x,y,z}) = A_1 \exp\{-\alpha E_{k(x,y,z)}\}}$$

The Maxwell distribution of velocities

$$\int_{-\infty}^{\infty} \varphi(v_x)\,dv_x = 1 = A_1 \int_{-\infty}^{\infty} \exp\left\{-\tfrac{1}{2}\alpha m v_x^2\right\} dv_x$$

$$\int_{-\infty}^{\infty} \tfrac{1}{2} m v_x^2 \varphi(v_x)\,dv_x = \langle E_{kx} \rangle = A_1 \int_{-\infty}^{\infty} \tfrac{1}{2} m v_x^2 \exp\left\{-\tfrac{1}{2}\alpha m v_x^2\right\} dv_x$$
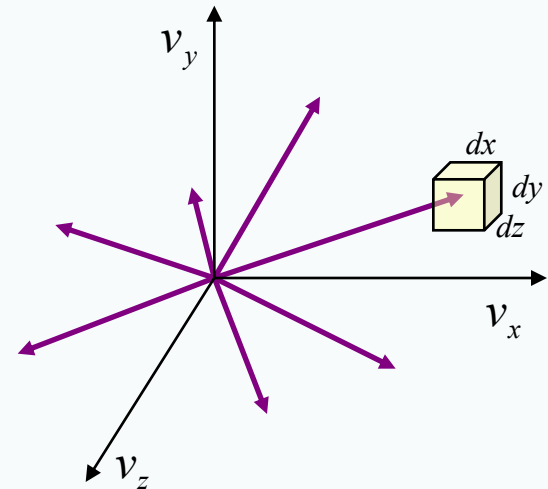
$$A_1 \sqrt{\frac{2}{m}} \int_{-\infty}^{\infty} \xi^2 \exp\left\{-\alpha \xi^2\right\} d\xi = A_1 \sqrt{\frac{2\pi}{m\alpha}} \frac{1}{2\alpha} = \frac{1}{2} kT$$

$$\varphi(v_x) = A_1 \exp\{-\alpha E_{kx}\}$$

$$\int_{-\infty}^{\infty} e^{-\xi^2}\,d\xi = \sqrt{\pi}$$

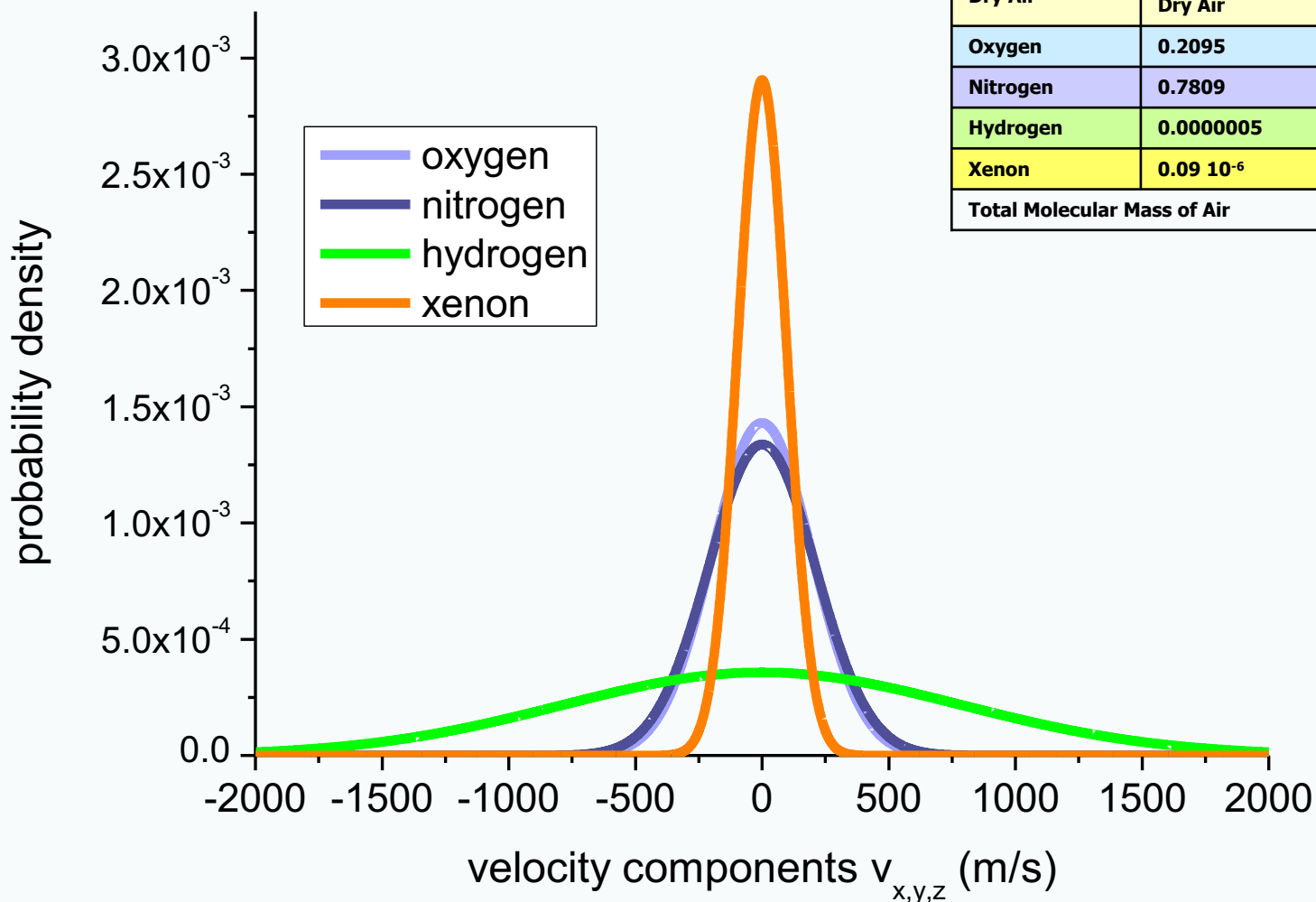$$A_1 = \sqrt{\frac{m\alpha}{2\pi}}$$

$$\alpha = \frac{1}{kT}$$

$$\varphi(v_{x,y,z}) = \sqrt{\frac{m}{2\pi kT}} \exp\left\{-\frac{m v_{x,y,z}^2}{2kT}\right\}$$

$$f(\vec{v}) = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left\{-\frac{m v^2}{2kT}\right\}$$
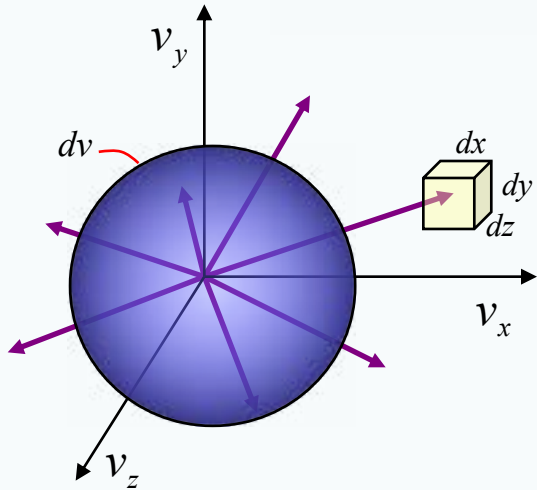
Distributions for air components

Components in Dry Air	Volume Ratio compared to Dry Air	Molecular Mass M (kg/kmol)	Molecular Mass in Air
Oxygen	0.2095	32.00	6.704
Nitrogen	0.7809	28.02	21.88
Hydrogen	0.0000005	2.02	0
Xenon	0.09 10^{-6}	131.29	0
Total Molecular Mass of Air			28.97

The Maxwell distribution of speeds

$$F(v) = f(\vec{v}) \cdot 4\pi v^2$$

$$F(v) = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 \exp\left\{ -\frac{mv^2}{2kT} \right\}$$

The most probable speed:

$$\frac{dF(v)}{dv} = 0$$

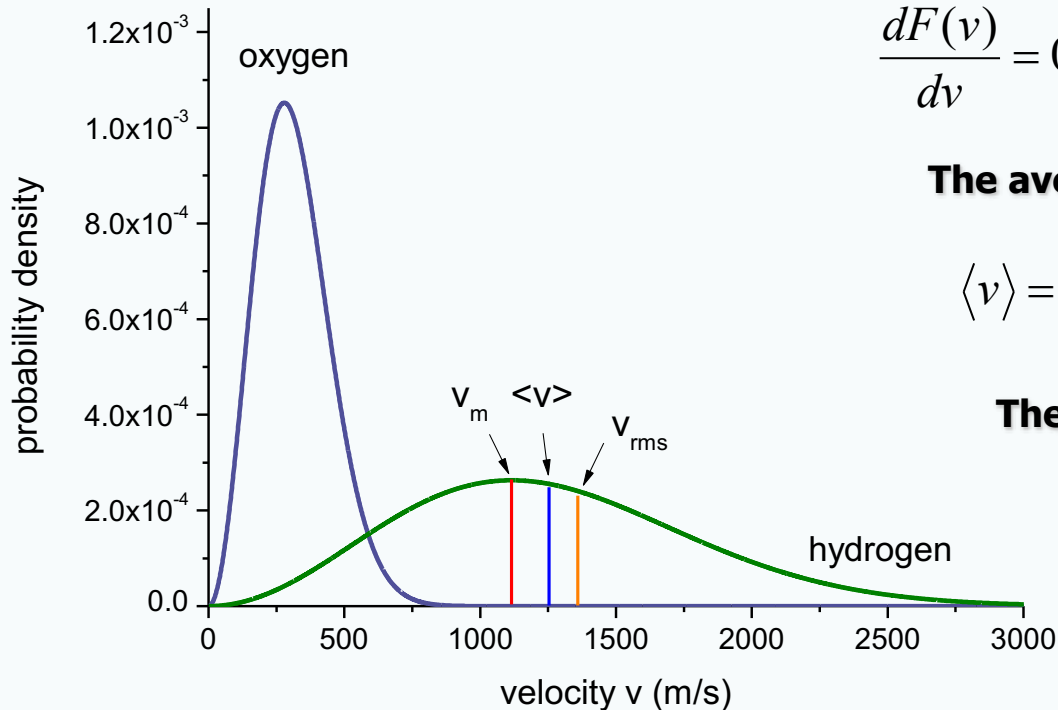$$v_m = \sqrt{\frac{2kT}{m}}$$

The average speed:

$$\langle v \rangle = \int vF(v)dv$$
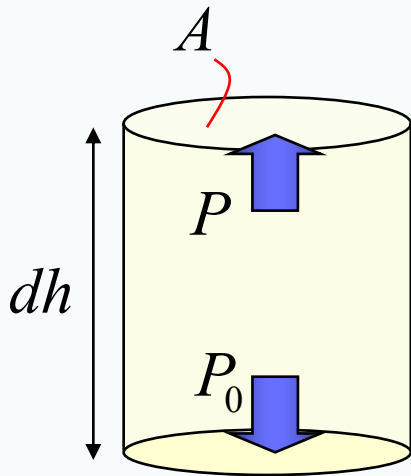
$$\langle v \rangle = \sqrt{\frac{8kT}{\pi m}}$$

The rms speed:

$$\tfrac{1}{2} m \langle v^2 \rangle = \tfrac{3}{2} kT$$

$$v_{rms} = \sqrt{\frac{3kT}{m}}$$

Boltzmann distribution

$$P = \frac{1}{3} mn \langle v^2 \rangle \qquad P_0 = \frac{1}{3} mn_0 \langle v_0^2 \rangle \qquad \boxed{m \langle v_0^2 \rangle = m \langle v^2 \rangle = 3kT}$$

$$M(h)g = \big(P(h) - P(h + dh)\big) \cdot A$$

$$= \big(n(h) - n(h + dh)\big)kTA = -kTA \frac{dn(h)}{dh} dh$$

$$M(h) \approx n(h)mAdh \qquad \boxed{n(h + dh) \approx n(h) + \frac{dn(h)}{dh} dh}$$

$$\frac{dn}{n} = -\frac{mgdh}{kT} \qquad \int_{n_0}^{n_1} \frac{dn}{n} = -\int_{h_0}^{h_1} \frac{mgdh}{kT} \qquad \boxed{n_1 = n_0 \exp\left\{ -\frac{mg\Delta h}{kT} \right\}}$$

Boltzmann distribution

$$\boxed{n_1 = n_0 \exp\left\{ -\frac{E_{potential}}{kT} \right\}}$$

Maxwell-Boltzmann distribution

$$\boxed{dn = n_0 \exp\left\{ -\frac{E_{total}}{kT} \right\} d^3 v}$$
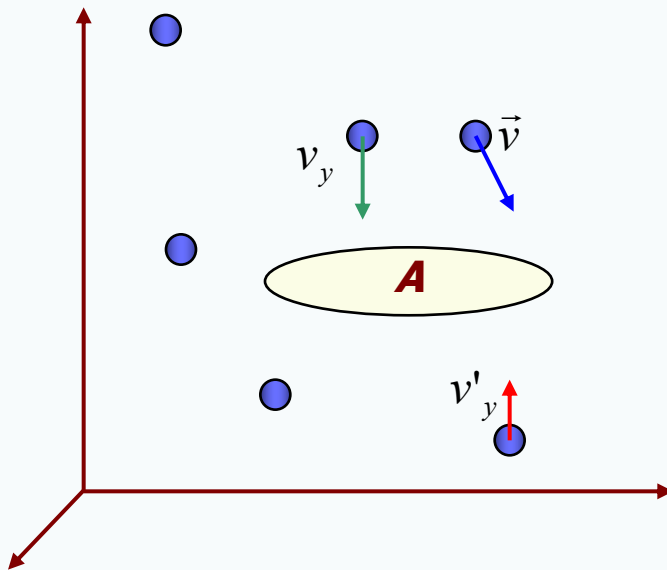
Boltzmann distribution: detailed balance

At equilibrium, each elementary process should be equilibrated by its reverse process.

$$dj_{y\downarrow} = Av_y \, dn_{\downarrow}(v_x, v_y, v_z) \; = Av_y n_u \, f(v_x, v_y, v_z) dv_x dv_y dv_z$$

$$\boxed{dj_{y\uparrow} = dj_{y\downarrow}} \qquad = Av_y n_u \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left\{-\frac{m(v_x^2 + v_y^2 + v_z^2)}{2kT}\right\} dv_x dv_y dv_z$$

$$dj_{y\uparrow} = Av_y' n_l \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left\{-\frac{m(v_x^2 + v_y'^2 + v_z^2)}{2kT}\right\} dv_x dv_y' dv_z$$

Two ensembles with equal total energies:
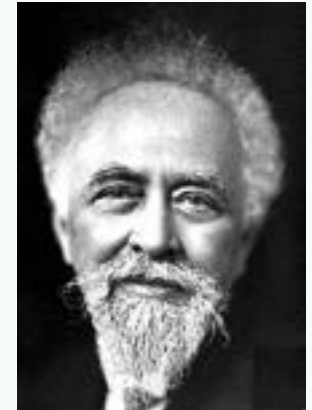
$$\frac{mv_y^2}{2} + U_u = \frac{mv_y'^2}{2} + U_l$$

$$n_u \exp\left\{-\frac{mv_y^2}{2kT}\right\} = n_l \exp\left\{-\frac{mv_y^2}{2kT} - \frac{U_u - U_l}{kT}\right\}$$

$$\frac{n_u}{n_l} = \exp\left\{-\frac{U_u - U_l}{kT}\right\}$$

Avogadro's number

The *gamboge*, which is used for a water-colour, comes from the desiccation of the latex secreted by *Garcinia morella* (*guttier* of Indo-China).

The mean radius of the granules of the emulsion employed was found equal to 0.212 μm, by counting 11,000 granules of a titrated emulsion, and to 0.213 μm by application of the law of Stokes. The difference of density between the material of the granules and the inter-granular water was 0.2067 at 20°, the temperature to which the measurements refer.

Some thousands of readings are required if some degree of accuracy is aimed at. To take an example, I have copied below the numbers given by 50 consecutive readings at two levels 30 μ apart in one of the emulsions I have used:

Jean Baptiste Perrin

Lower end									
3	2	0	3	2	2	5	3	1	2
3	1	1	0	3	3	4	3	4	4
0	3	1	3	1	4	2	2	1	3
1	1	2	2	3	0	1	3	4	3
0	2	2	1	0	2	1	3	2	4

Upper end									
2	1	0	0	1	1	3	1	0	0
0	2	0	0	0	0	1	2	2	0
2	1	3	3	1	0	0	0	3	0
1	0	2	1	0	0	1	0	1	0
1	1	0	2	4	1	0	1	0	1

30 μm
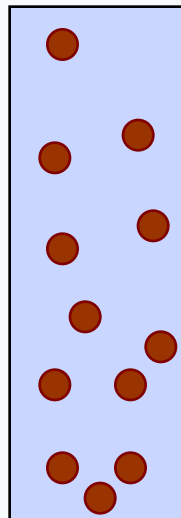
$$n = n_0 \exp\left\{ -\frac{(m_c - m_l)gz}{kT} \right\}$$

R = 0.212 μm
ρ_c = 1.207 g/cm³
ρ_l = 1.0 g/cm³
T = 20°C
n_1/n_2 = 2.08

$$k = -\frac{4\pi R^3(\rho_c - \rho_l)(z_2 - z_1)g}{3T \ln(n_1/n_2)} = 1.13 \times 10^{-23} \text{ J/K}$$

To remember!

➢ **The Maxwell velocity distribution gives the fraction of molecules having certain velocities.**

➢ **There are distributions for velocity components, for velocities and for molecular speeds.**

➢ **Due to occurrence of such distributions, one may introduce different average quantities.**

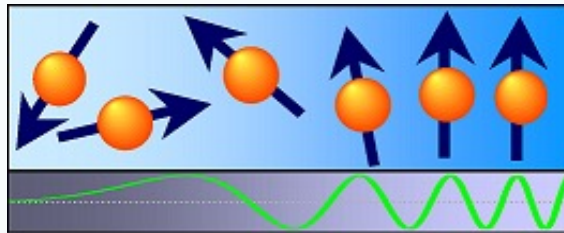➢**The Boltzmann distribution describes variation of particle densities in an external conservative potential field.**

Experimental Physics EP2
Thermodynamics

— Kinetic theory of gases —
Collisions

https://bloch.physgeo.uni-leipzig.de/amr/

Collision frequency

$$N_i = n_i \cdot A \cdot v_{iy}\Delta t$$

$$z \equiv \frac{N}{\Delta t} = A\sum_i n_i v_i = A\int_0^\infty v_y f(v_y)dv_y$$

v_y

$\vec{v}$

v_y

A
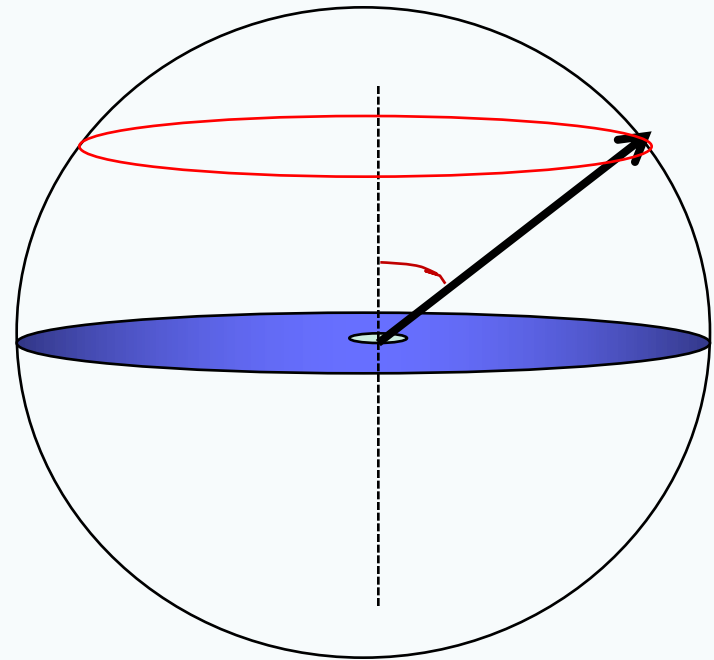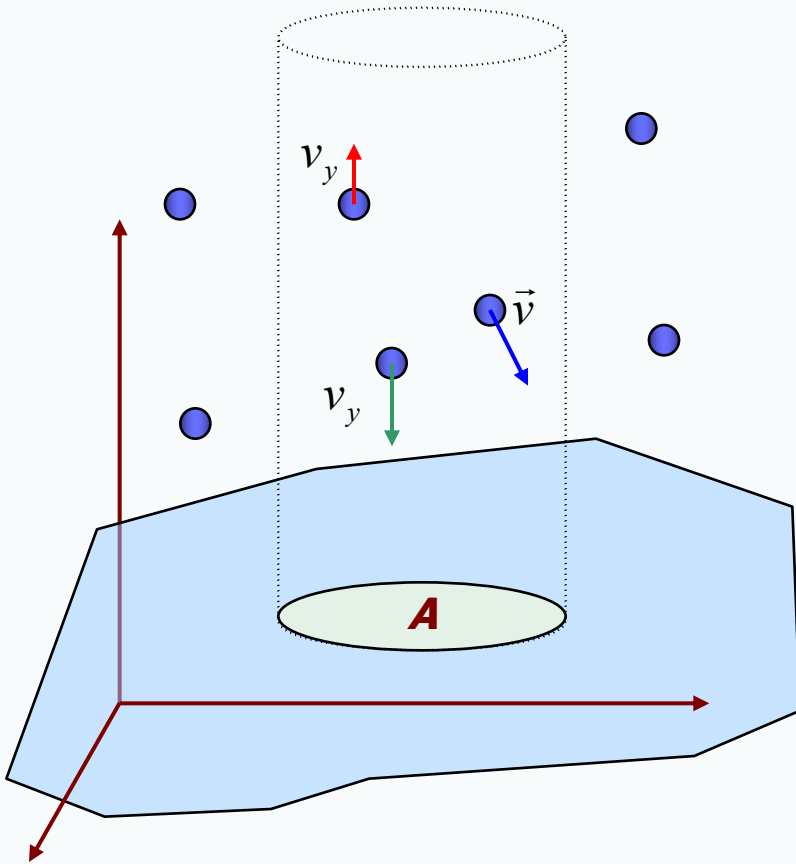
Collision frequency

$$N_i = n_i \cdot A \cdot v_{iy} \Delta t$$

$$z \equiv \frac{N}{\Delta t} = A \sum_i n_i v_i = A \int_0^\infty v_y f(v_y) dv_y$$

$$z = nA \sqrt{\frac{m}{2\pi kT}} \int_0^\infty v_y \exp\left\{-\frac{mv_y^2}{2kT}\right\} dv_y$$

$$\langle v \rangle = \sqrt{\frac{8kT}{\pi m}}$$

$$\int_0^\infty \xi \exp\left\{-\xi^2\right\} d\xi = \frac{1}{2}$$

$$z = nA \sqrt{\frac{m}{2\pi kT}} \frac{2kT}{m} \frac{1}{2} = nA \sqrt{\frac{kT}{2\pi m}}$$

$$z = \frac{1}{4} nA \langle v \rangle$$

Compare to what you will get without distribution of velocities.
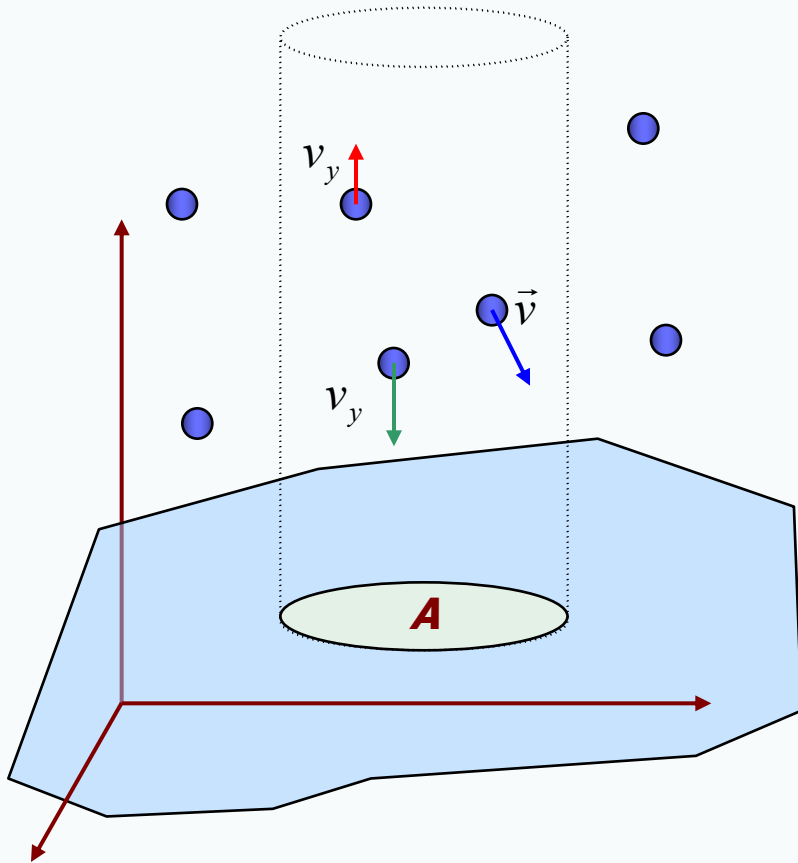
Reservoir with a hole

T

S

V

n_0

v_0
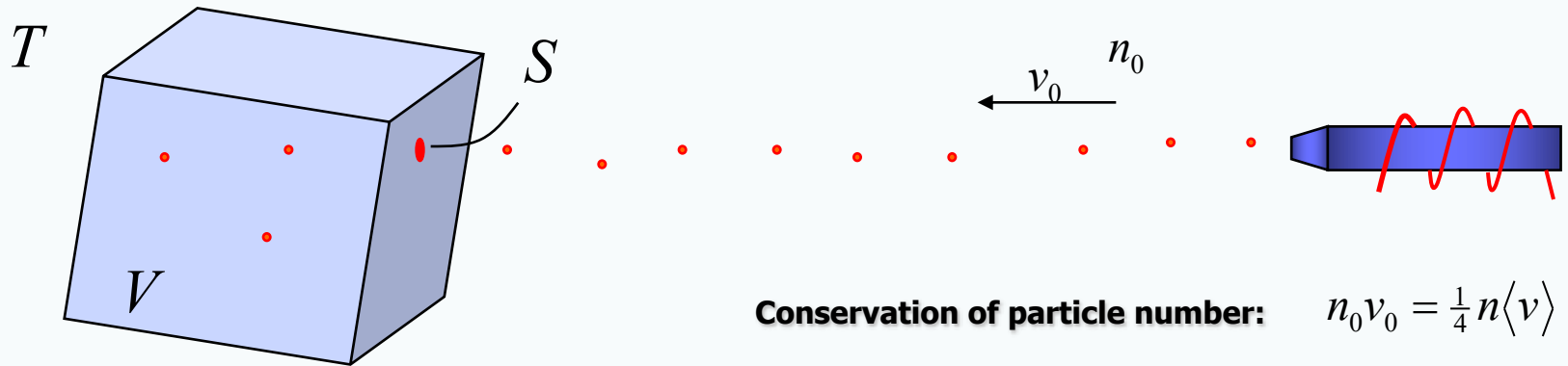
$$dN = -zSdt$$

$$dN = -\frac{1}{4}n\langle v\rangle Sdt$$

$$\frac{dn}{n} = -\frac{1}{4}\langle v\rangle\frac{S}{V}dt$$

$$n = n_0 e^{-\frac{t}{\tau}} \qquad \tau = \frac{4V}{\langle v\rangle S}$$

Conservation of particle number: $\quad n_0 v_0 = \frac{1}{4}n\langle v\rangle$

Conservation of energy: $\quad n_0 v_0 \cdot \frac{1}{2}mv_0^2 = \langle E_k\rangle_{\rightarrow}$

The average kinetic energy of a particle escaping a small hole in the reservoir

$$\boxed{\langle\varepsilon\rangle = 2kT}$$

$$\langle E_k\rangle_{\rightarrow} = n\sqrt{\frac{2(kT)^3}{m\pi}} \qquad \langle E_k\rangle_{\rightarrow} = \frac{1}{16}nm\pi\langle v\rangle^3$$

$$\langle v\rangle = \sqrt{\frac{2}{\pi}}v_0 \qquad n = n_0\sqrt{8\pi} \qquad T = \frac{mv_0^2}{4k}$$

Molecular collisions

$$\sigma = \pi d^2$$

$$2d$$
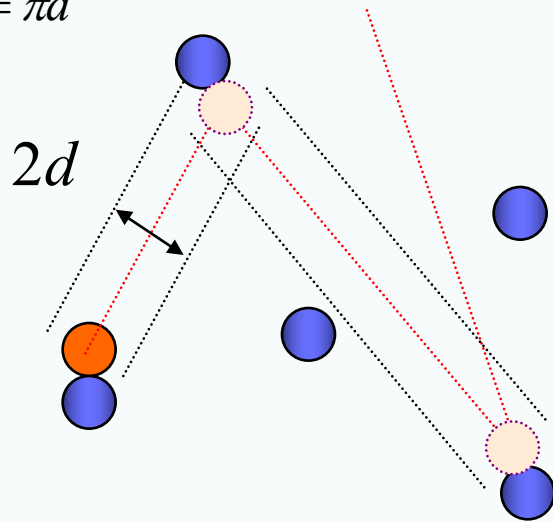
Volume explored by a molecule
$$V = \sigma \cdot \langle v \rangle t$$

Number of molecules collided with
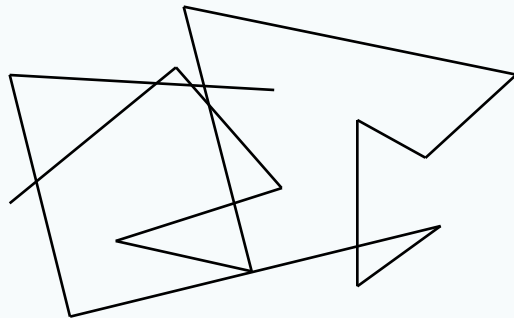$$N = nV = n\sigma \langle v \rangle t$$

Collision frequency
$$z = N/t = n\sigma \langle v \rangle$$

'Maxwellian' correction
$$z = \sqrt{2} n\sigma \langle v \rangle$$

Mean free-path- length

$$\lambda = \frac{L}{N} = \frac{\langle v \rangle t}{\sqrt{2} n\sigma \langle v \rangle t} = \frac{1}{\sqrt{2} n\sigma}$$

$$\lambda_n = \frac{1.38 \times 10^{-23} \cdot 300}{1.01 \cdot 10^5 \cdot 3.14 \cdot (0.3 \times 10^{-9})^2} \approx 145 \text{ nm}$$

Crooks radiometer

Kinetic interpretation of temperature

$$m_1 v_{1x} + Mu = m_1 v'_{1x} + Mu'$$

$$v'_{1x} = \frac{2Mu + (m_1 - M)v_{1x}}{m_1 + M}$$

$$\tfrac{1}{2} m_1 v_{1x}^2 + \tfrac{1}{2} Mu^2 = \tfrac{1}{2} m_1 v'^2_{1x} + \tfrac{1}{2} Mu'^2$$

$$v'^2_{1x} = \frac{4M^2 u^2 + M(m_1 - M)uv_{1x} + (m_1 - M)^2 v_{1x}^2}{(m_1 + M)^2}$$

$$\langle v'^2_{1x}\rangle = \frac{4M^2\langle u^2\rangle + (m_1 - M)^2\langle v_{1x}^2\rangle}{(m_1 + M)^2}$$

if it is equilibrium then it must be $= \langle v_{1x}^2 \rangle$

Very low pressures (~P)

Higher, but still low pressures (~1/P)

Momentum conservation in stationary state:

$$\langle v_x\rangle(x + \langle \lambda_x\rangle) - u = \langle v_x\rangle(x - \langle \lambda_x\rangle) + u$$

$$u = \langle \lambda_x\rangle \frac{d\langle v_x\rangle}{dx} \qquad \langle \lambda_x\rangle \approx \langle \lambda\rangle/\sqrt{3}$$
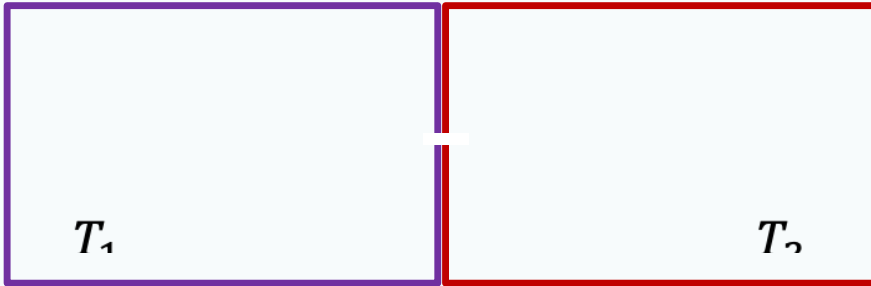
$$m\langle v_x^2\rangle = kT$$

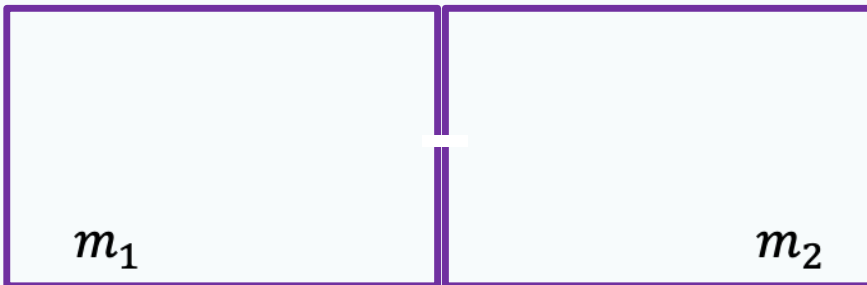$$u \approx \frac{\lambda}{3}\sqrt{\frac{k}{mT}\frac{dT}{dx}}$$

Thermal creep

u

$\langle \lambda_x\rangle$ $\langle \lambda_x\rangle$
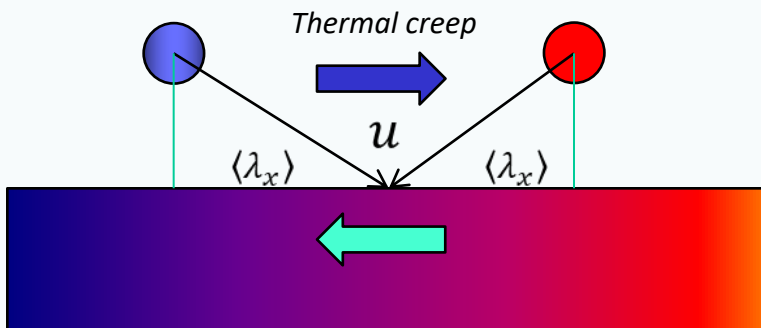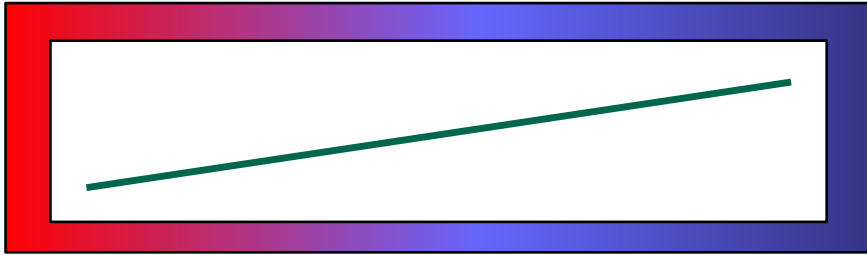
$$n_1 T_1 = n_2 T_2$$

$$n_1 \sqrt{T_1} = n_2 \sqrt{T_2}$$

$$n_1 \sqrt{\frac{T_1}{m_1}} = n_2 \sqrt{\frac{T_2}{m_2}}$$

T_1

T_2

m_1

m_2

To remember!

➢ **The Boltzmann distribution describes variation of particle densities in external potential fields.**

➢ **The Boltzmann and Maxwell distributions are intimately related and follow from each other.**

➢ **Molecular collisions play important role in establishing distribution of molecular velocities.**

➢ **Viscosity is related to momentum transfer, heat conduction – energy transfer, diffusion – mass transfer.**
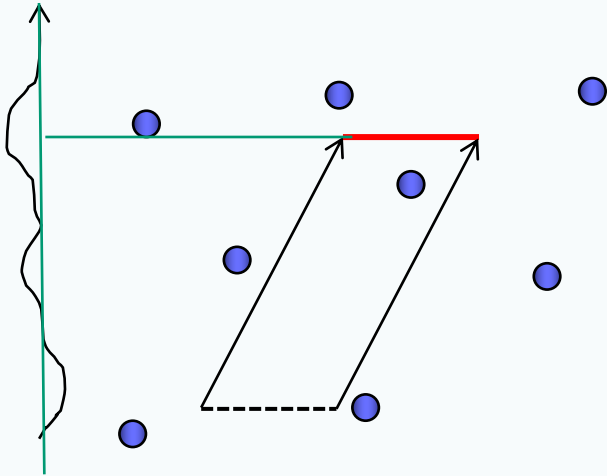
Experimental Physics EP2
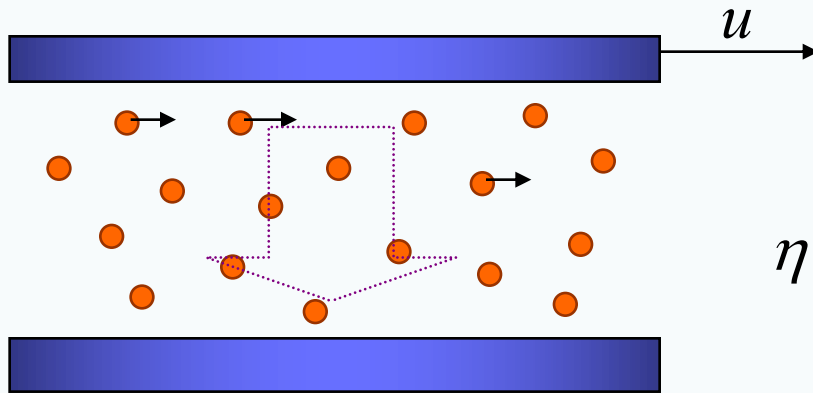# Thermodynamics

– Kinetic theory of gases –
Diffusion

https://bloch.physgeo.uni-leipzig.de/amr/
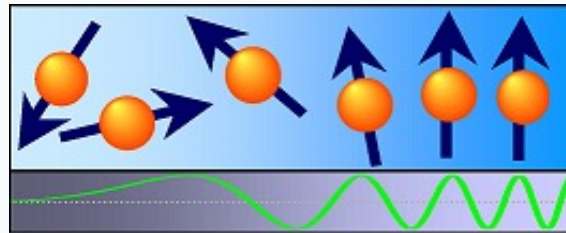
Self-diffusion

Viscosity and heat conduction

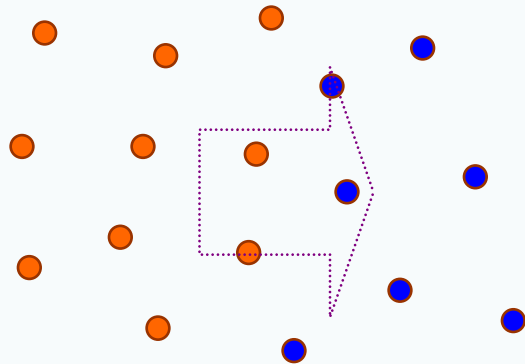$$J = \frac{dN}{t\,dS} = -D_s \frac{dn}{dx} \qquad D_s = \frac{1}{3}\lambda\langle v \rangle$$

u →

Momentum transfer

$$\eta = \frac{1}{3}\lambda\langle v \rangle \cdot nm \qquad \tau = \frac{dp}{t\,dS} = -\eta\frac{du}{dx}$$

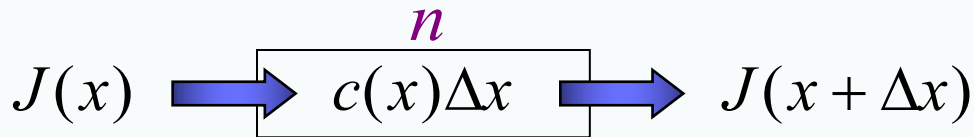$$\lambda = \frac{1}{\sqrt{2}\,n\sigma}$$

Energy transfer

$$\kappa = \frac{1}{3}\lambda\langle v \rangle \cdot nc_{particle} \qquad Q = \frac{dE}{t\,dS} = -\kappa\frac{dT}{dx}$$

The Fick's laws

$$J_{diffusion} = -D \frac{\partial c}{\partial x}$$

Fick's first law

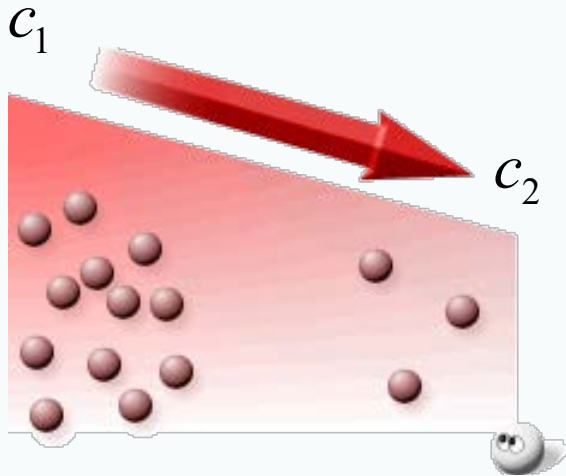$$\frac{\partial \rho(x,t)}{\partial t} = D \frac{\partial^2 \rho(x,t)}{\partial x^2}$$

n

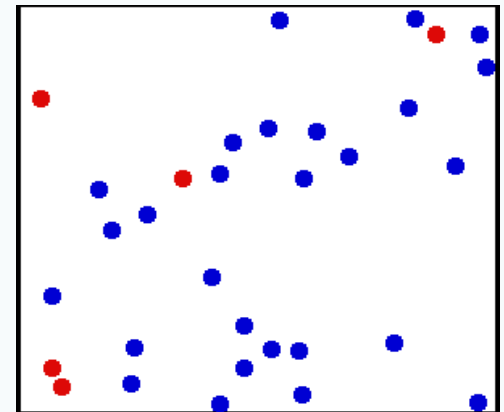$$J(x) \implies \boxed{c(x)\Delta x} \implies J(x + \Delta x)$$

conservation of matter

$$\frac{\partial n}{\partial t} = \frac{\partial c}{\partial t} \Delta x = J(x) - J(x + \Delta x)$$

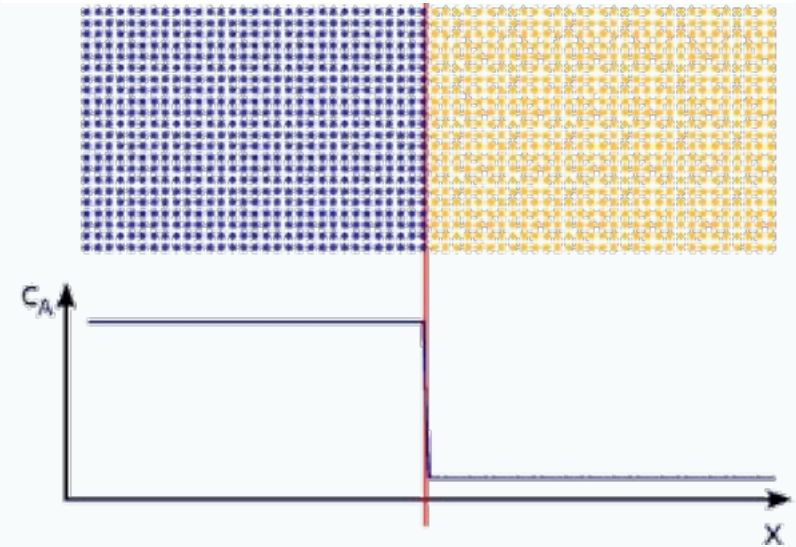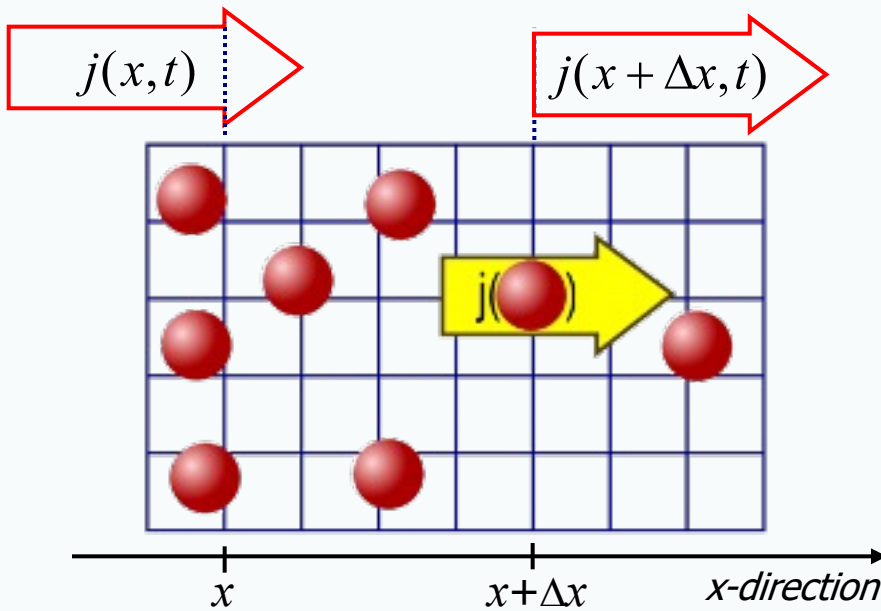$$\frac{\partial c}{\partial t} = -\frac{J(x) - J(x + \Delta x)}{\Delta x} = -\frac{\partial J}{\partial x}$$

c_1

c_2

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$

Fick's second law

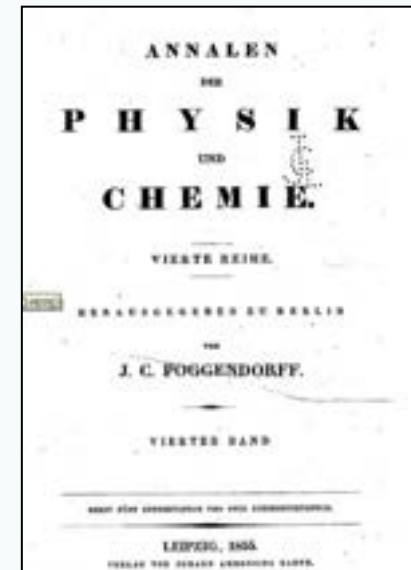# Diffusion flux under concentration gradient

1st Fick's law ➕ **Mass conservation**

$$j = -D \frac{\partial c}{\partial x} \qquad \frac{\partial c}{\partial t} = \frac{j_x(x) - j_x(x + \Delta x)}{\Delta x} \approx -\frac{\partial j}{\partial x}$$

2nd Fick's law
Diffusion equation

$$\frac{\partial c(x,t)}{\partial t} = D \frac{\partial^2 c(x,t)}{\partial x^2}$$

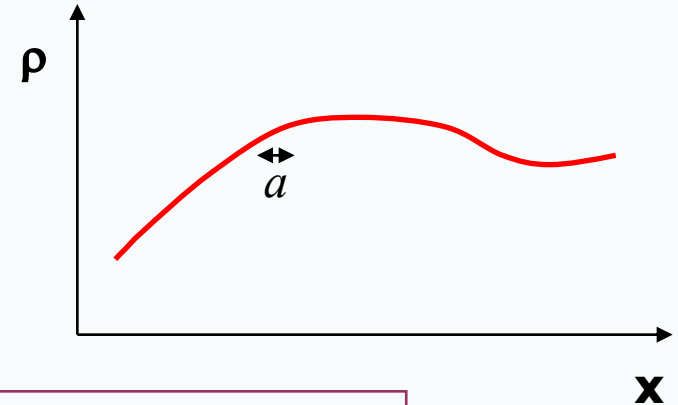A. Fick, Über Diffusion. Ann. Phys. Chem., 1855, 94, 59

The diffusion equation

$$x(t + \Delta t) = x(t) + l(t)$$

$\chi(l)$ - probability distribution for each step

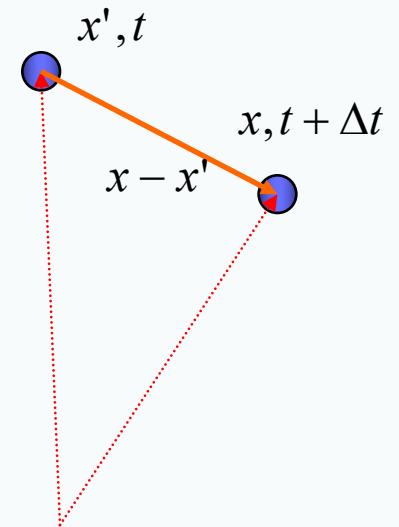$$\int \chi(z)dz = 1 \qquad \int z\chi(z)dz = 0 \qquad \int z^2 \chi(z)dz = a^2$$

ρ(x,t) - density of particles or probability density to find a particle at x and at time instant t

$$\rho(x, t + \Delta t) = \int_{-\infty}^{\infty} \rho(x', t)\chi(x - x')dx' \qquad z = x - x'; \; dz = -dx'$$

$$\rho(x, t + \Delta t) = \int_{-\infty}^{\infty} \rho(x - z, t)\chi(z)dz \approx \int_{-\infty}^{\infty} \left[\rho(x,t) - \frac{\partial \rho}{\partial x} z + \frac{\partial^2 \rho}{\partial x^2} \frac{z^2}{2} \right] \chi(z)dz$$

$$= \rho(x,t) \int_{-\infty}^{\infty} \chi(z)dz - \frac{\partial \rho}{\partial x} \int_{-\infty}^{\infty} z\chi(z)dz + \frac{1}{2} \frac{\partial^2 \rho}{\partial x^2} \int_{-\infty}^{\infty} z^2 \chi(z)dz$$

$$\frac{\rho(x, t + \Delta t) - \rho(x,t)}{\Delta t} = \frac{\partial \rho(x,t)}{\partial t} = \frac{a^2}{2\Delta t} \frac{\partial^2 \rho(x,t)}{\partial x^2} = D \frac{\partial^2 \rho(x,t)}{\partial x^2}$$

Solution of the diffusion equation

$$P(x,t;x_0) = \frac{1}{(4\pi Dt)^{1/2}} \exp\left\{-\frac{|x-x_0|^2}{4Dt}\right\}$$

$$\boxed{\frac{\partial \rho(x,t)}{\partial t} = D\frac{\partial^2 \rho(x,t)}{\partial x^2}}$$

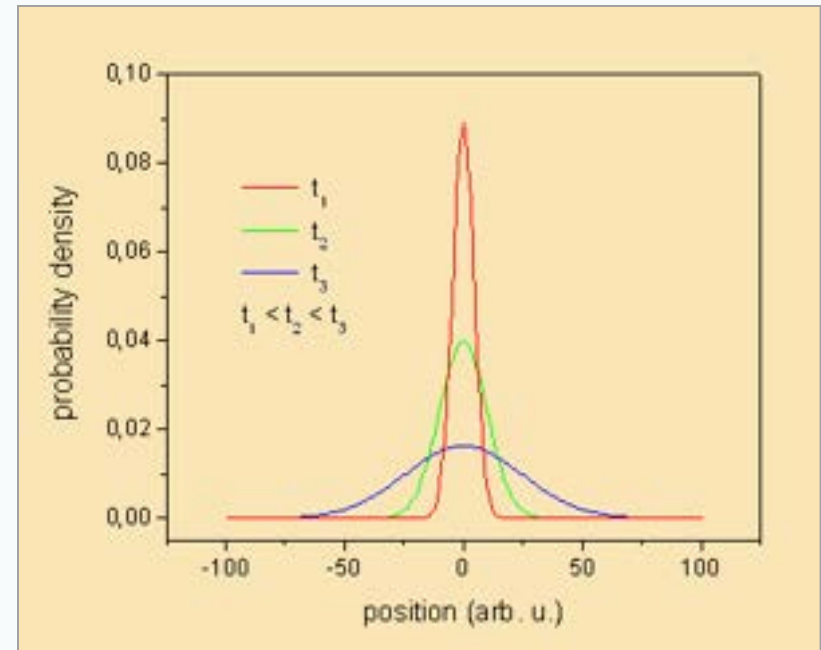$$P(\vec{r},t;\vec{r}_0) = \frac{1}{(4\pi Dt)^{d/2}} \exp\left\{-\frac{|\vec{r}-\vec{r}_0|^2}{4Dt}\right\}$$ ← in space with dimension d
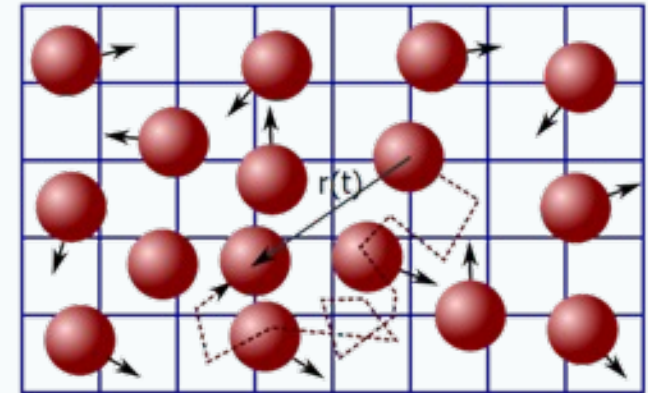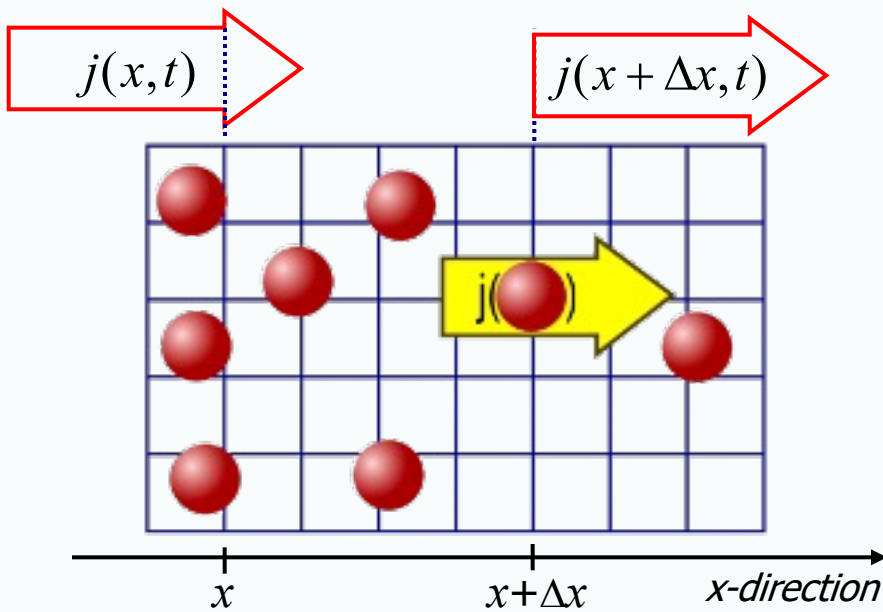
Central limit theorem:
The sum of many independent random variables has a probability distribution that converges to Gaussian.

$$\langle x^0 \rangle = \int_{-\infty}^{\infty} P(x,t;0)dx \qquad \langle x^1 \rangle = \int_{-\infty}^{\infty} xP(x,t;0)dx$$

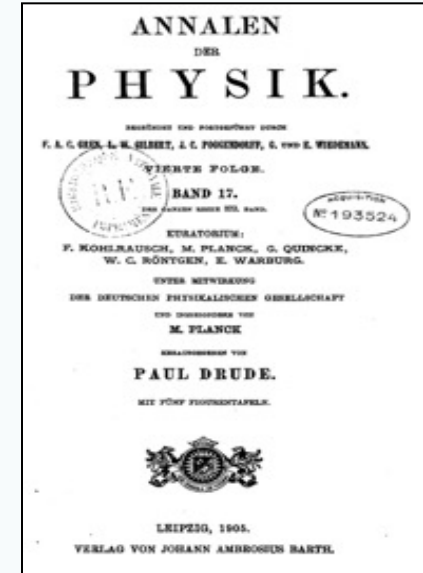$$\langle x^2 \rangle = \int_{-\infty}^{\infty} x^2 P(x,t;0)dx = 2Dt$$

$$\langle x^2(t) \rangle = 2Dt$$

2nd Fick's law
Diffusion equation

$$\frac{\partial c(x,t)}{\partial t} = D \frac{\partial^2 c(x,t)}{\partial x^2}$$

A. Einstein, Ann. Phys., 1905, 17, 54

Coin flips

s = +1

s = -1

$$s_N = \sum_{i=1}^{N} s_i$$

$$\langle s_N \rangle - ?$$

$$s_N = \sum_{i=1}^{N^+} s_i + \sum_{i=1}^{N^-} s_i$$

$$s_N = N^+ - N^-$$

$$\boxed{\langle s_N \rangle = \langle N^+ \rangle - \langle N^- \rangle = 0}$$

$$\langle s_1^2 \rangle_K = \frac{1}{K}\left(K^+(+1)^2 + K^-(-1)^2\right)$$

$$\langle s_1^2 \rangle = p^+(+1)^2 + p^-(-1)^2 = \tfrac{1}{2} + \tfrac{1}{2} = 1$$

$$\langle s_2^2 \rangle = \tfrac{1}{4}(+2)^2 + \tfrac{1}{2}(0) + \tfrac{1}{4}(-2)^2 = 2$$

$$\langle s_N^2 \rangle = \langle (s_{N-1} + s)^2 \rangle = \langle s_{N-1}^2 \rangle + \langle s_{N-1} s \rangle + \langle s^2 \rangle = \langle s_{N-1}^2 \rangle + 1$$

$$\boxed{\langle s_N^2 \rangle - ?}$$

$$\boxed{\langle s_N^2 \rangle = N} \qquad \boxed{1 \rightarrow l \implies \langle s_N^2 \rangle = Nl^2}$$

To remember!

➢ **The linear response thery - a concentration gradient results in a flux proportional to the gradient.**

➢ **The proprtionality coefficient is called "diffusivity".**

➢ **Combined with the mass conservation law it results in the differential diffusion equation.**

➢ **The random walk model can be analyzed to obtain mean-square-displacements.**

➢ **The m.s.d. grow linearly with time with the proportionality coefficient the same diffusivity as in the diffusion equation.**