Lecture 3

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Models
Ideal gas model
Equipartion of energy

27.08.2019

What is a model in physics?

- Talk to your neighbour 2 min

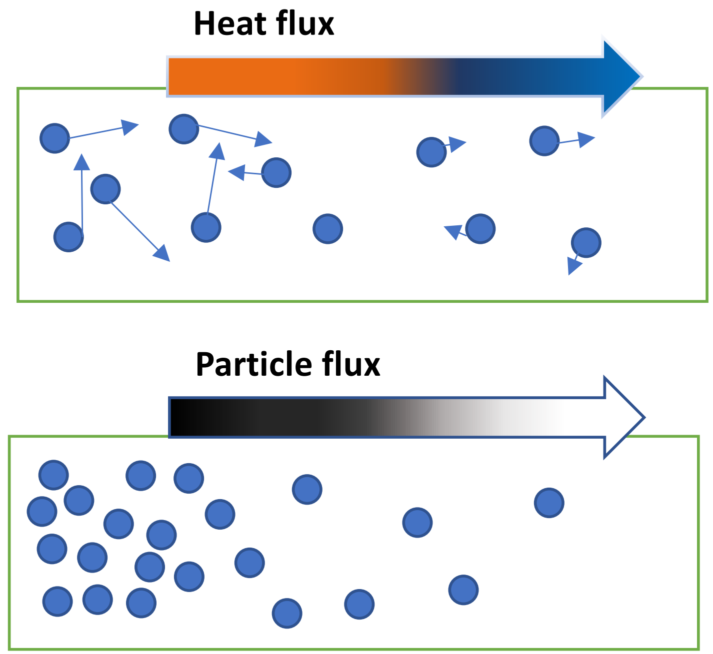

ASUME A
SPHERICAL
COW
IN A VACUUM

Phenomena:
Relaxation to equilibrium by diffusion

Diffusion:

Net transport of *energy*, *momentum* or *particles* through random thermal motion and particle collisions until thermodynamic equilibrium is reached

- At any $T > 0\mathrm{K}$, particles are in *thermal motion*
- Collisions between particles -> particle trajectory is a zigzag -- random *(diffusive particle)*

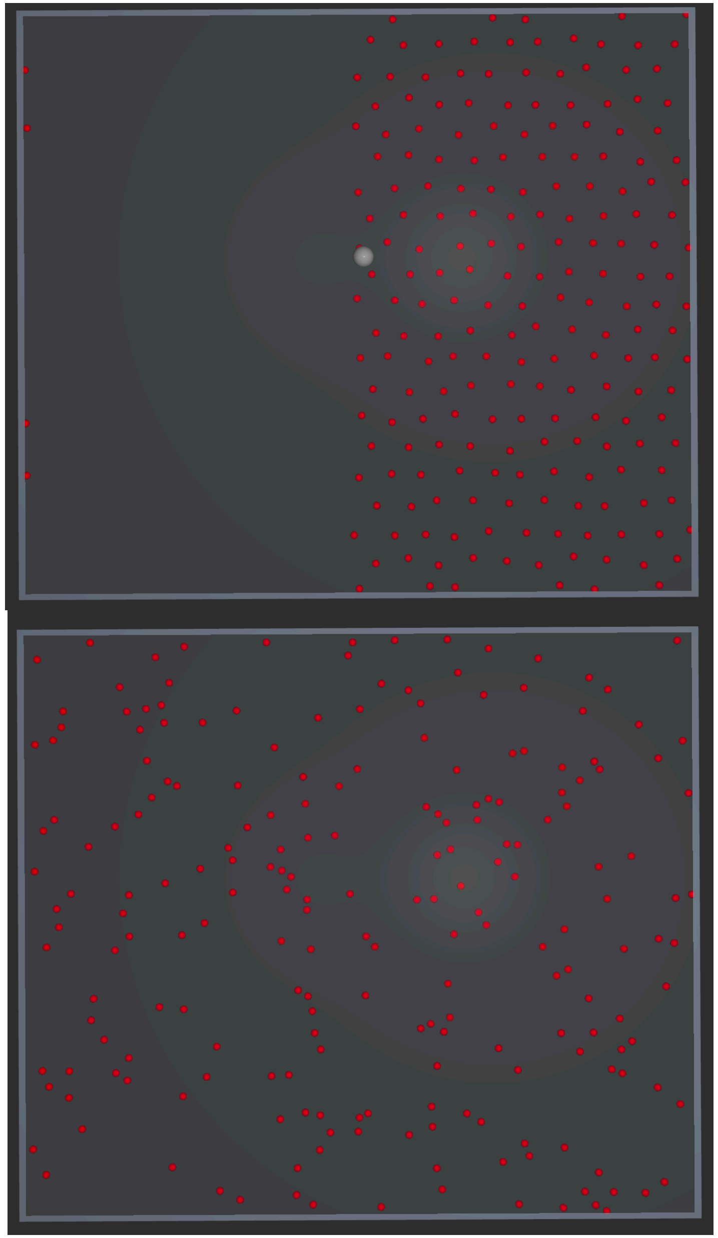


Models

- Molecular dynamics
- Random walk
- Algorithmic
- Ideal gas

- Reversible laws of motion
- Irreversible development: arrow of time
- Measure average property: distribution in box

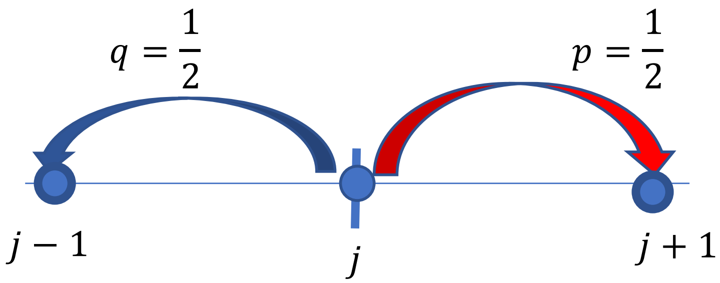
Gas particles moving randomly starting at one side.

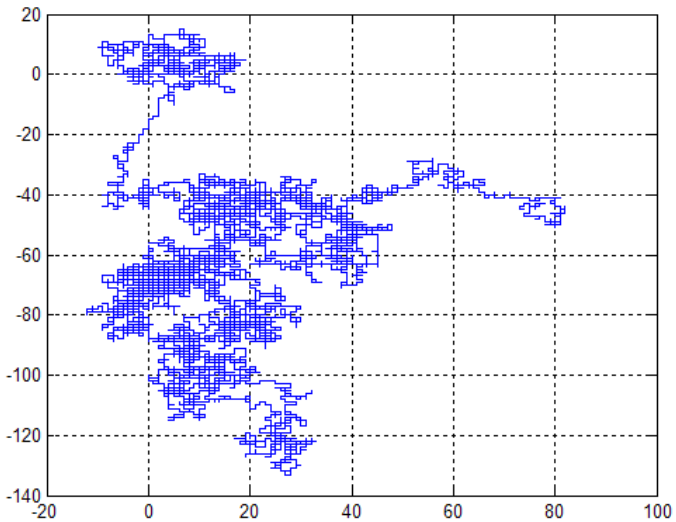


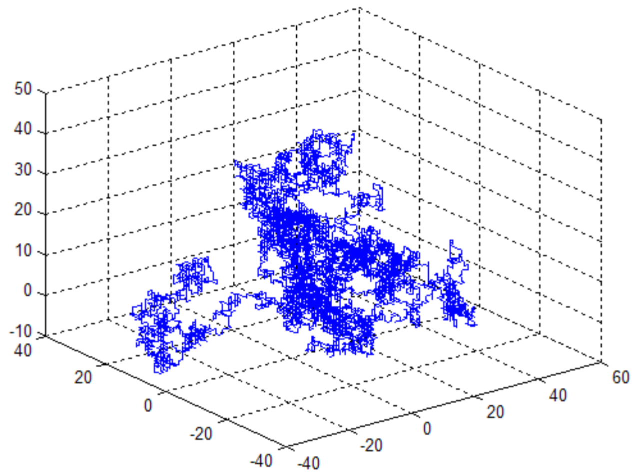
Molecular dynamics

- Atoms interacting by pairwise potential $U(r_{ij})$
- Forces $F_i = \sum_j \frac{d}{dr_{ij}} U(r_{ij})$
- Give atoms some initial positions r_i and velocity v_i
- Solve Newtons equations of motion
  - $r_i(t+dt)=r_i(t)+dt\ v_i$
  - $v_i(t+dt)=F_i(t+dt)dt/m_i$
- Record r_i, v_i, F_i to compute statistical averages and thermodynamical properties
- Atomify: Package made by Anders Hafreager & Sven Arne Dragly

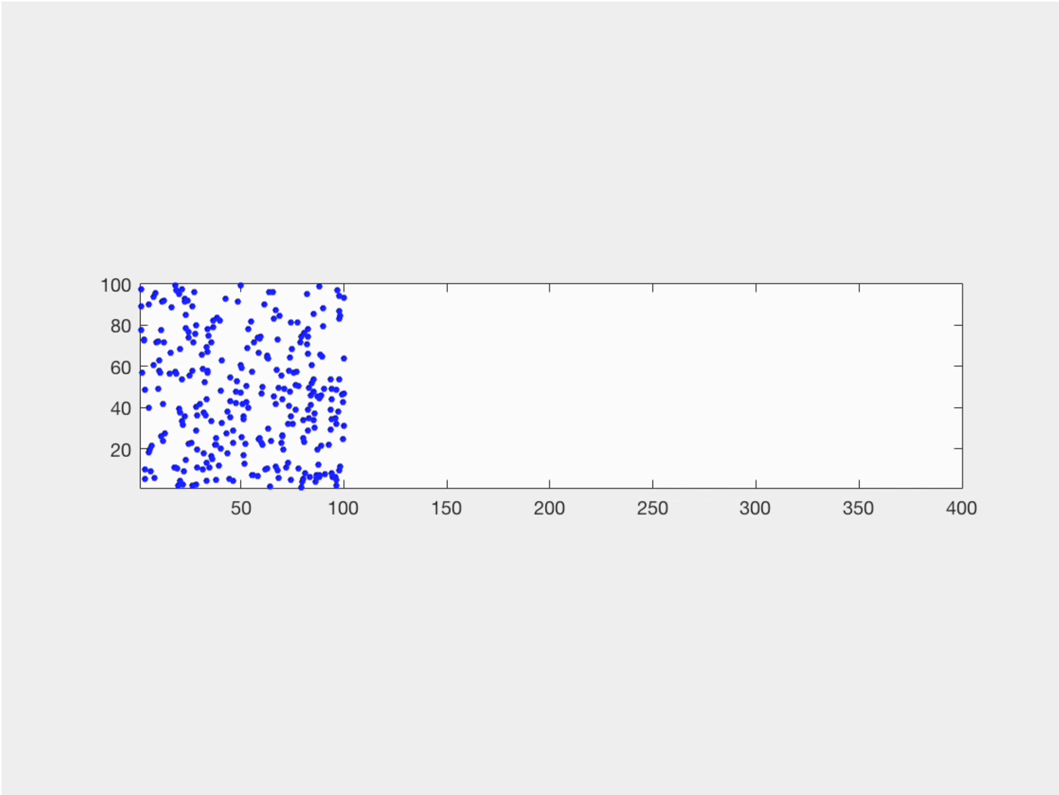
Random walk (RW)

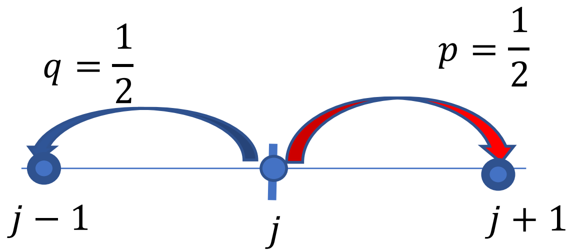




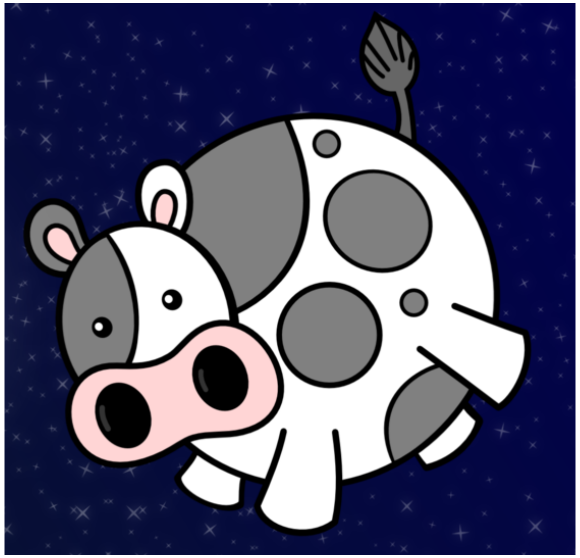


Random walk and diffusion





Algorithmic model

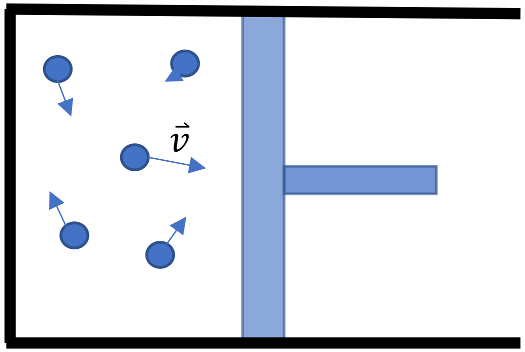


- How can we simplify?
- Positions: only left and right
- All start at left
- Every timestep: randomly (P=1/2) move 1 particle from left to right or right to left.
- measure fraction of particles on left side

Ideal gas model: Pressure

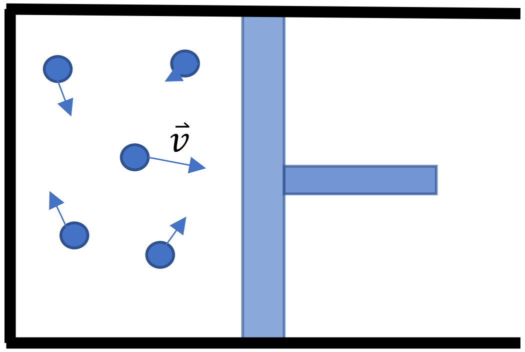
Newtonian gas particle:

- $m\frac{d\vec{v}}{dt} = \vec{F}(= 0)$
- Independent, identical particles



Q: What is the pressure in the ideal gas model?

Ideal gas model: Pressure



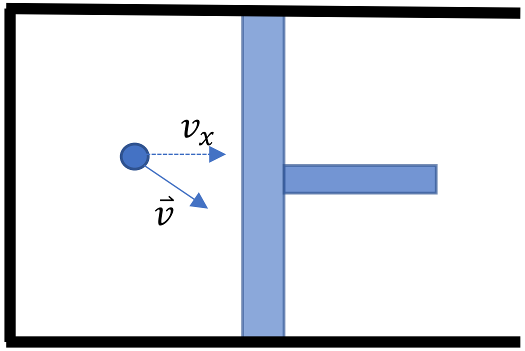
Q: What is the pressure in the ideal gas model?

- **pressure is isotropic and the same on all walls**

- **compute the pressure on the piston**

Ideal gas model: Pressure

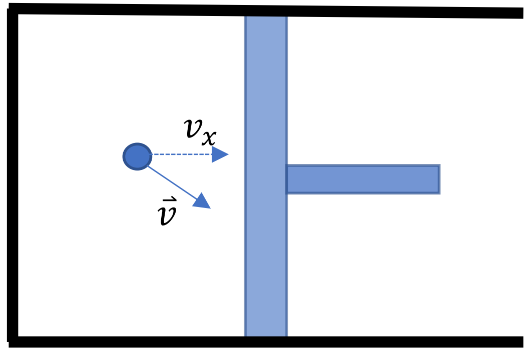
What is the long-time averaged pressure exerted on the piston by one particle?



- $$P = \frac{\overline{F}_{x,piston}}{A} = -\frac{\overline{F}_x}{A} = -\frac{m}{A}\overline{\left(\frac{\Delta v_x}{\Delta t}\right)}$$
  - Time it takes to go round-trip across the box
    $$\Delta t = \frac{2L}{v_x}$$
  - Change in velocity after one perfect collision with the piston
    $$\Delta \mathrm{v}_x = v_{x,after} - v_{x,before} = -2v_x$$

Ideal gas model: Pressure

What is the average pressure exerted on the piston by the gas particles?

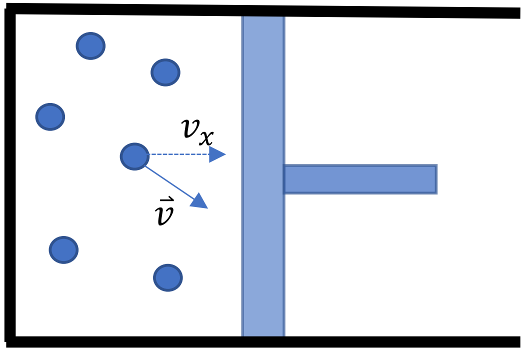


- $P = -\frac{m}{A}\overline{\left(\frac{\Delta v_x}{\Delta t}\right)} = \frac{m\overline{\mathrm{v}_\mathrm{x}^2}}{AL} = \frac{m\overline{\mathrm{v}_\mathrm{x}^2}}{V}$

  using
  - $\Delta t = \frac{2L}{v_x}$
  - $\Delta \mathrm{v}_x = v_{x,after} - v_{x,before} = -2v_x$

Ideal gas model: **Pressure**

What is the average pressure exerted by the gas particles?



Pressure is the long-time average of v_x^2

$$P = \frac{m\overline{\mathrm{v}_\mathrm{x}^2}}{V}$$

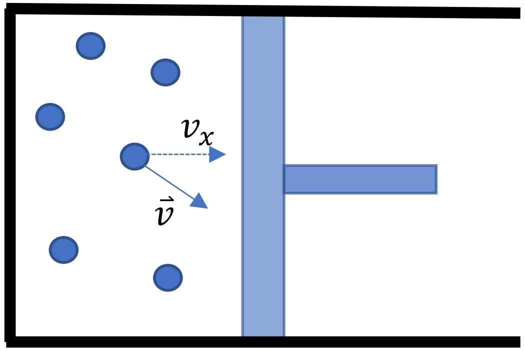
Consider **ALL** N particles at a given time and average over their velocities (**ensemble average**)

$$PV = Nm\langle \mathrm{v}_\mathrm{x}^2 \rangle = \frac{N}{3} m \langle v^2 \rangle$$

$$PV = \frac{2N}{3}\langle K_{trans} \rangle, \qquad \langle K_{trans} \rangle = \frac{1}{2} m \langle v^2 \rangle$$

Ideal gas model: **Temperature**

$$PV = \frac{2N}{3}\langle K_{trans}\rangle$$



$$PV = NkT$$

Average kinetic energy of a particle gives a measure of the gas temperature

$$\langle K_{trans}\rangle = \frac{3}{2}kT$$

In 1-D: $\langle K_{trans}\rangle = \frac{1}{2}kT$

In d-D: $\langle K_{trans}\rangle = \frac{d}{2}kT$

$$\langle |v| \rangle \approx \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3kT}{m}}$$

Ideal gas model: Equipartition

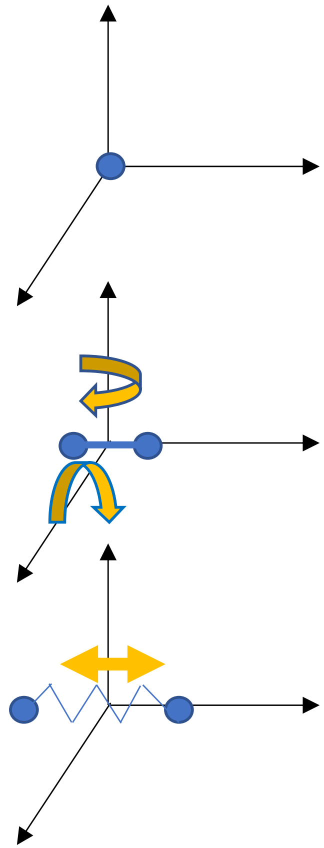
Equipartion of energy (theorem):

At equilibrium with temperature T, any quadratic form of the internal energy equal $\frac{1}{2}kT$ per degree of freedom

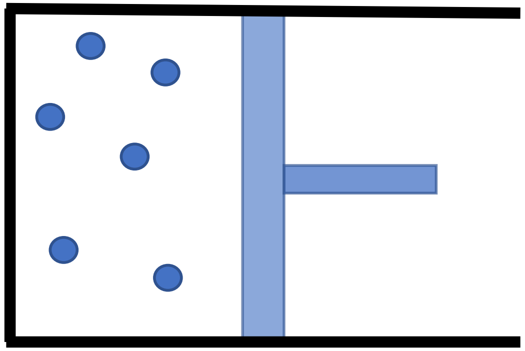
$$U = K + U_{potential} = \frac{f}{2}NkT$$

What is a *degree of freedom*?

- Translation $K_{trans} = \frac{1}{2}mv^2$
- Rotation $K_{rot} = \frac{1}{2}I\omega^2$
- Vibration/oscillation $U_{harm} = -\frac{1}{2}\mathrm{k}(\Delta x)^2$



Ideal gas model: Equipartition

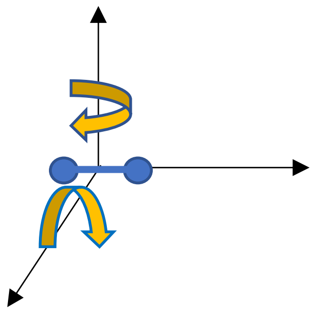


Equipartion of energy (theorem):

At equilibrium with temperature T, any quadratic form of the internal energy is $\frac{1}{2}kT$ per degree of freedom

Example:

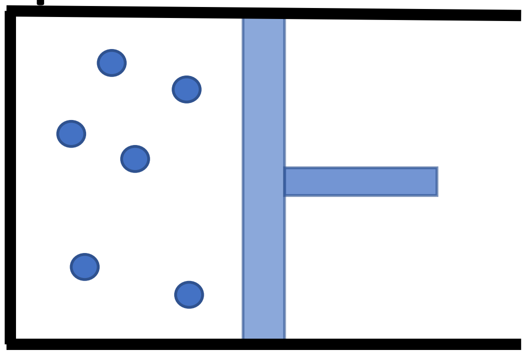
What is the internal energy of a diatomic gas:



$$U = K + U_{potential}$$

$$U = \frac{5}{2}NkT$$

Ideal gas model: Equipartition



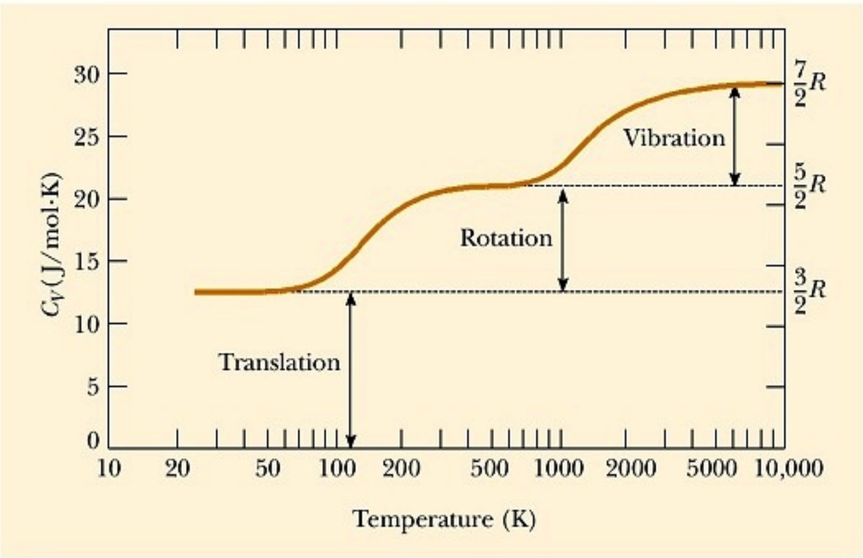
Equipartion of energy (theorem):

$$U = \frac{f}{2} NkT$$

What are the heat capacities C_V, C_P?

$$C_V = \frac{dU}{dT} = \frac{f}{2} Nk$$

$$C_P = C_V + P\left(\frac{\partial V}{\partial T}\right)_P = \frac{f+2}{2} Nk$$

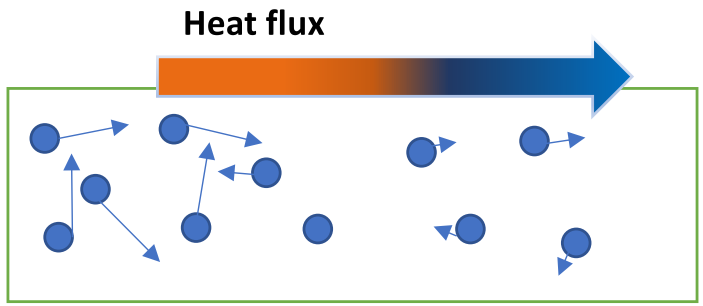


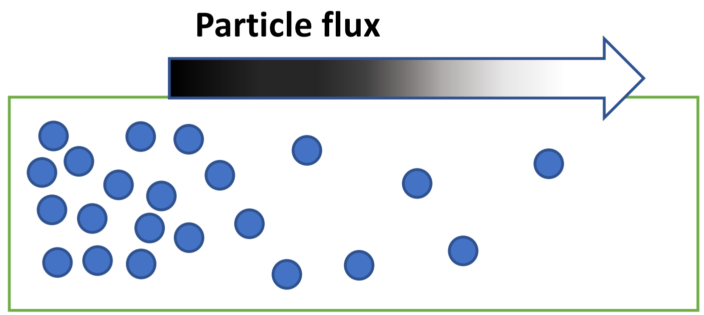
The molar specific heat of hydrogen as a function of temperature. The horizontal scale is logarithmic. Note that hydrogen liquefies at 20 K.

Phenomena:
Relaxation to equilibrium by diffusion

Diffusion:

Net transport of *energy*, *momentum* or *particles* through random thermal motion and particle collisions until thermodynamic equilibrium is reached

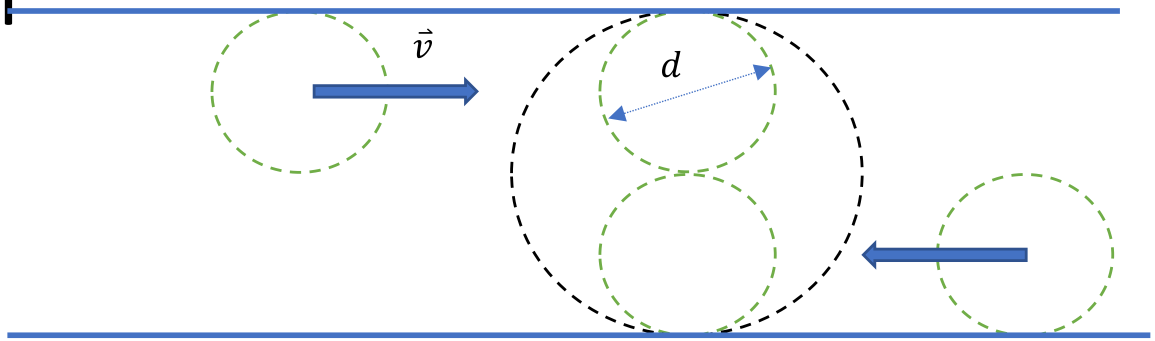




- At any $T > 0$K, particles are in *thermal motion*
- Collisions between particles -> particle trajectory is a zigzag -- random *(diffusive particle)*

We have shown that many models displays this irreversibility, but how fast does it happen?

Mean free-path



Free path between collisions

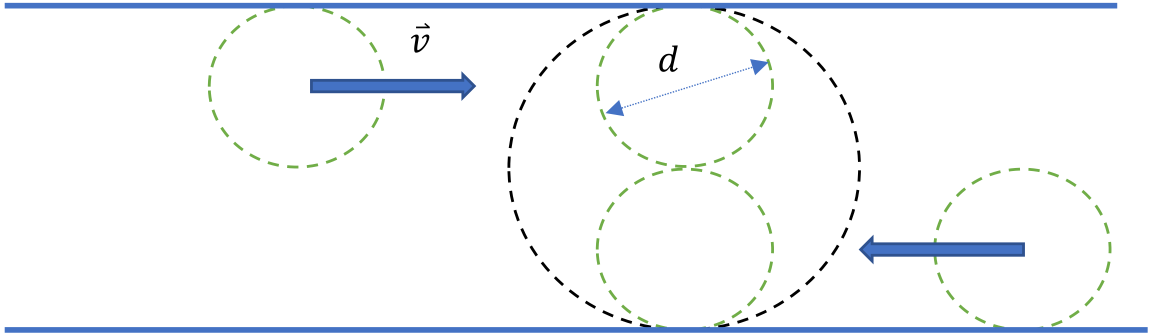
Number of molecules per unit volume (density):

$$n = \frac{N}{V}$$

Effective collision area: $\sigma = \pi d^2$

Mean free path: $\lambda = \frac{1}{n\sigma} = \frac{1}{\pi d^2 n_V}$

Mean free path



Gas particles spend most of their time between collisions

Mean free path: $\lambda = \frac{1}{\pi d^2 n_V}$

Average time between collisions:

$$\tau = \frac{\lambda}{\bar{v}}, \qquad \bar{v} \approx \frac{\sqrt{kT}}{\sqrt{m}}$$

$$\tau = \frac{\lambda}{\bar{v}} \approx \frac{1}{\pi d^2 n_V} \frac{\sqrt{m}}{\sqrt{kT}}$$

The mean-free path λ and mean lag time τ dictate the *kinetics* of the gas (***diffusion and heat conduction properties***)

Mean square displacement $r^2(t) = \frac{1}{\pi n d^2} \sqrt{\frac{3kT}{m}}\, t$

Relaxation to equilibrium by diffusion

Diffusion:

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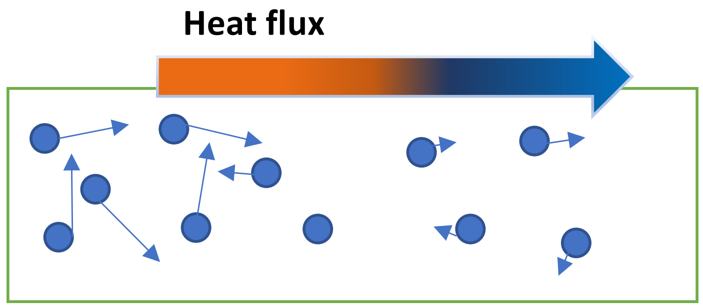
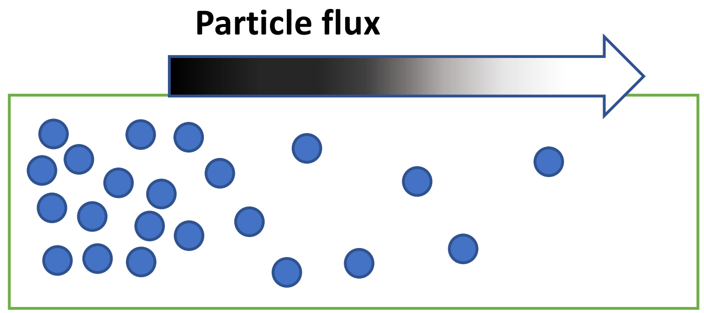




Fick's first law:

- Diffusive particle drift *from high to low* concentration $C = \frac{N}{V}$ of particles

$$\boldsymbol{J = -D\nabla C}$$

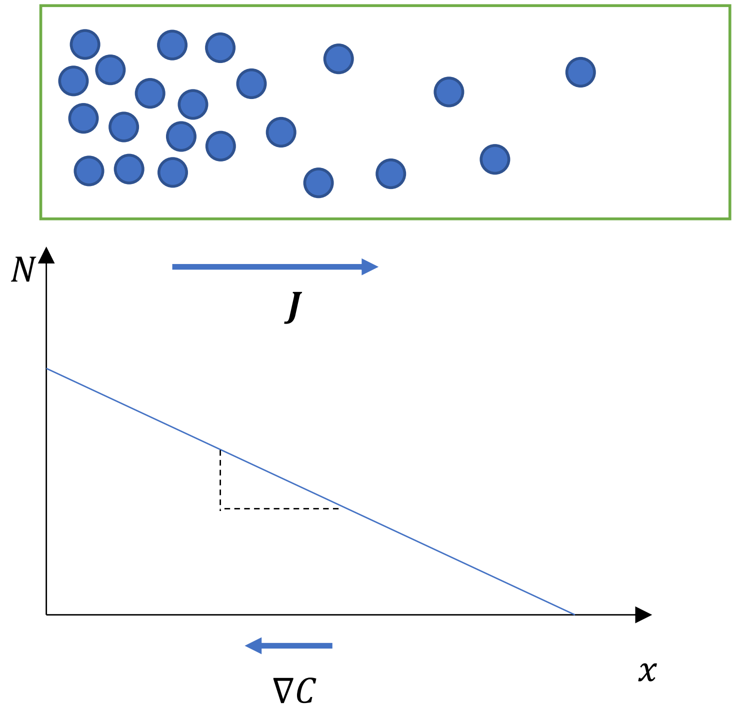
- **Diffusivity $\boldsymbol{D}$:** mobility of the diffusing particles

$$\frac{N}{A\Delta t} \approx D\frac{\Delta(N\,V^{-1})}{\Delta x}$$

$$\frac{moles}{m^2 s} = [D]\frac{moles \cdot m^{-3}}{m}$$

$$[D] = \frac{m^2}{s}$$

- $D_{CO} = 0.2\ \frac{cm^2}{s}$ in *air*
- $D_{CO} = 2\times10^{-5}\ \frac{cm^2}{s}$ in *water*



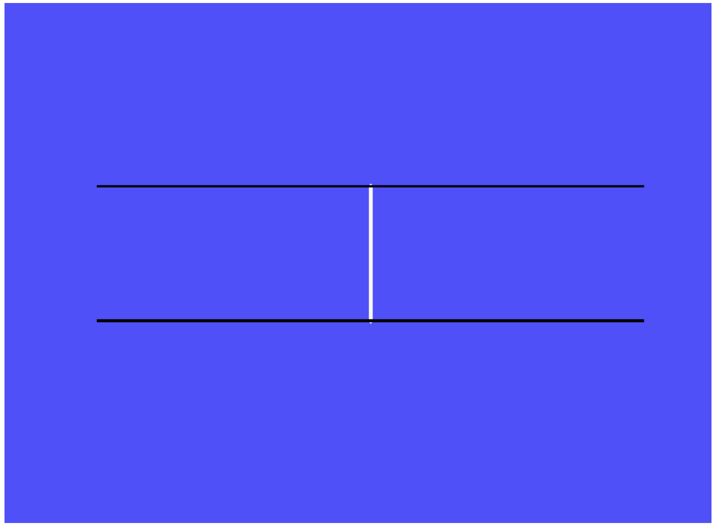
Atomify

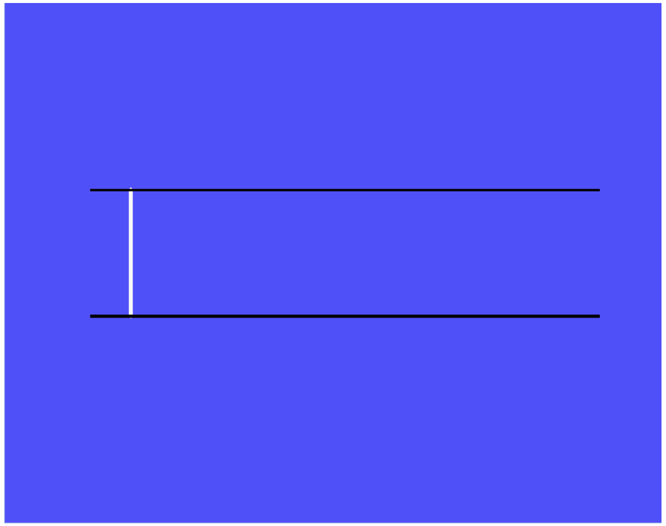
Flow and dispersion

Molecular dispersion

(Diffusion)

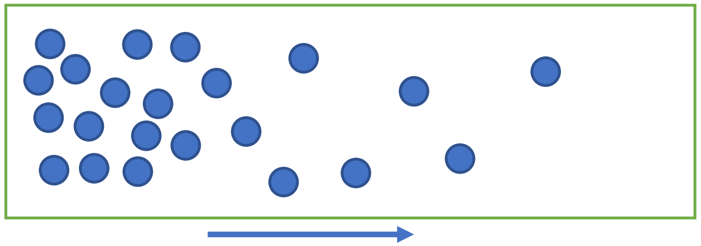
Dispersion by flow





Molecular Diffusivity: gas kinetics

- Flux across a surface in a average time interval between collisions τ



$$\boldsymbol{J \approx \frac{N}{A\tau} = \frac{N}{A\,\lambda}\bar{v} \sim c\bar{v}}$$

$$\boldsymbol{J = -D\frac{dc}{\mathrm{dx}} \approx D\frac{c}{\lambda}}$$

$$\boldsymbol{D \approx \lambda\bar{v}}$$

$$\boldsymbol{D \approx \frac{1}{\pi d^2}\frac{kT}{P} \times \frac{\sqrt{kT}}{\sqrt{m}} \sim \frac{T^{\frac{3}{2}}}{P}}$$

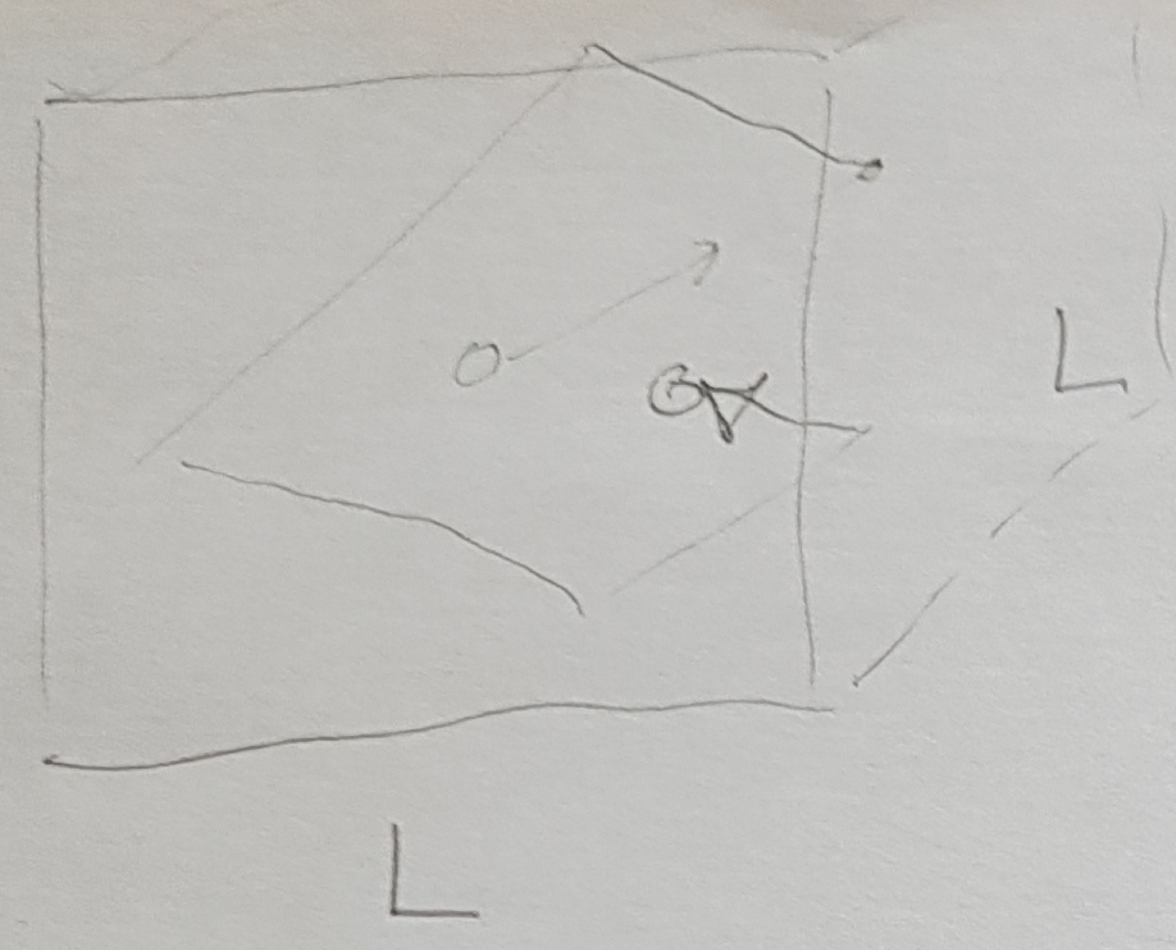
Summary

- **Irreversibility and models**
- **Model predictions**
- **Equipartition of energy**

$$U = \frac{f}{2}kT,\ f \text{ quadratic degrees of freedom}$$

- **Kinetic properties of gas depend on the mean-free path and mean velocity of the gas particles**

$$D \approx \lambda\bar{v} \sim \frac{T^{\frac{3}{2}}}{P},$$

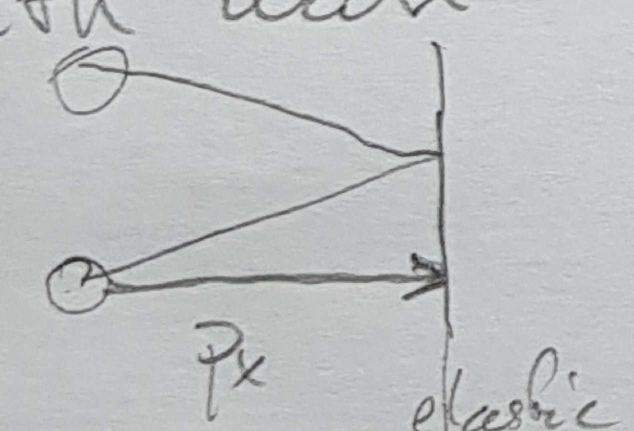


- N particles (identical, monatomic,)
- no interaction
- $V = L^3$
- momentum $\vec{p}_i = m_i \vec{v}_i$
- kinetic energy $E_{k,i} = \frac{\vec{p}_i^2}{2m} = \frac{1}{2} m \vec{v}_i^2 = \frac{1}{2} m (v_{xi}^2 + v_{yi}^2 + v_{zi}^2)$

- Total kinetic energy $E_{k,tot} = \sum_{i=1}^{N} E_{k,i} = \frac{1}{2} m \sum_i \vec{v}_i^2 = \frac{1}{2} Nm \langle \vec{v}_i^2 \rangle$ $\quad \langle \vec{v}_i^2 \rangle = \frac{\sum v_i^2}{N}$

- Pressure $P = \frac{F}{A} = \frac{1}{A} \sum_i \frac{\Delta p_i}{\Delta t_i} = \frac{1}{A} N \frac{\overline{\Delta p_i}}{\overline{\Delta t}}$ $\quad \langle \vec{v}_i \rangle = 0$

- collision with wall $\overline{\Delta p_x} = 2 m \bar{v}_x$ $\quad \bar{v}_x = \sqrt{\langle v_x^2 \rangle}$ RMS velocity



- Time between collisions with right wall $\overline{\Delta t} = \frac{2L}{\bar{v}_x}$

$$\Rightarrow P_x = \frac{1}{L^2} N \frac{2 m \bar{v}_x \cdot \bar{v}_x}{2L} = \frac{N}{V} m \bar{v}_x^2$$

$$PV = Nm \langle v_x^2 \rangle = 2N\bar{E}_{k,x}$$

Equipartition principle

At temperature T, the average energy of any quadratic degree of freedom is kT

= Definition of T in our model.

$$\overline{E}_{k,x} = \frac{1}{2} m \overline{v_x} = \frac{1}{2} kT$$

$$PV = N m \langle v_x^2 \rangle = NkT$$

Ideal gas "law" $PV = NkT$