

Lecture 3

Ideal gas model
Equipartition of energy

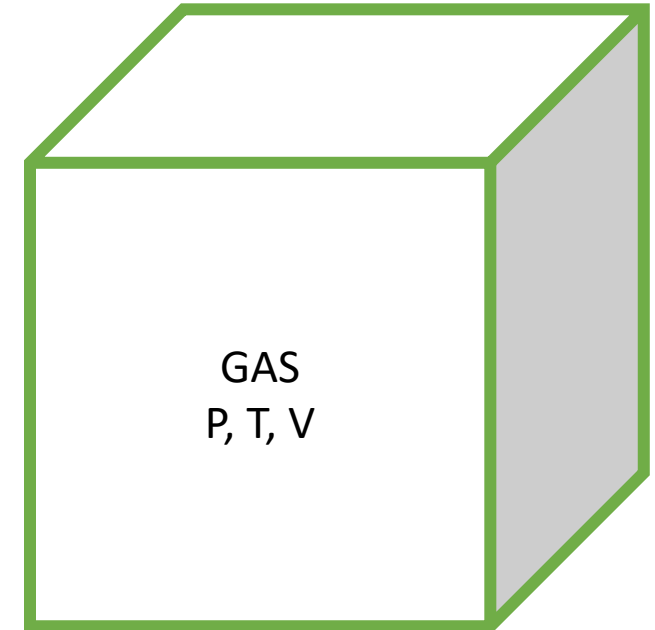
27.08.2018

Ideal gas in a box at equilibrium

Equation of state: $PV = nRT$

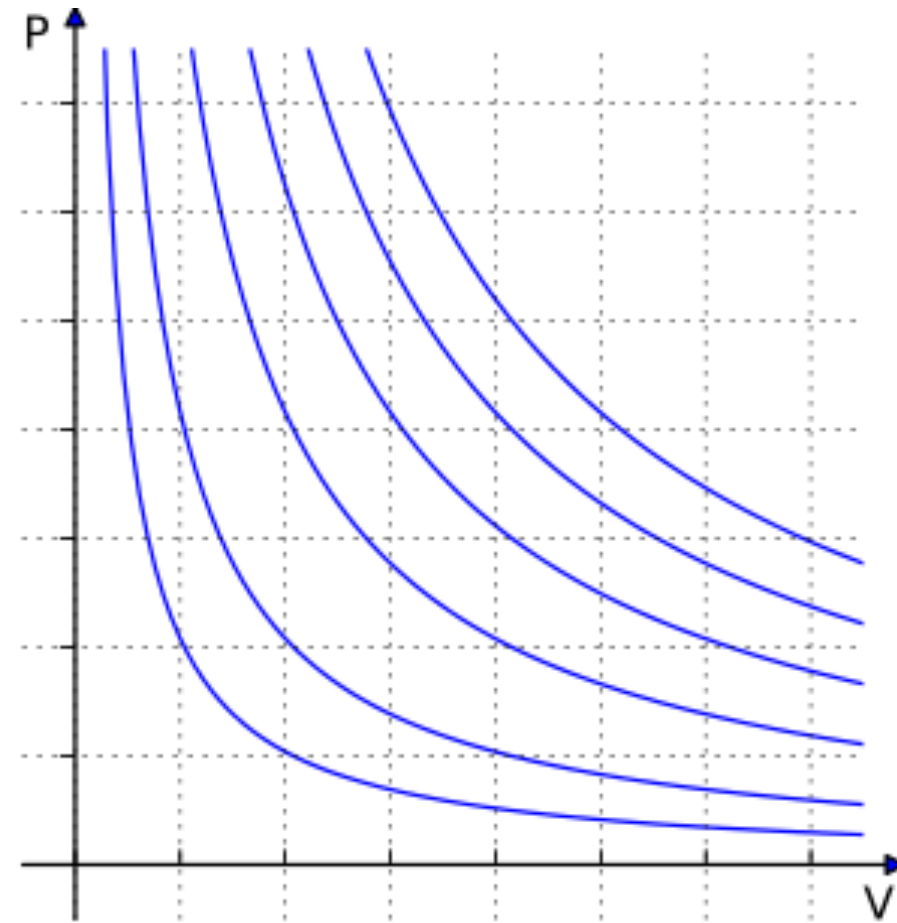
Experimental fact

- Pressure $[P] = 1 \text{ atm} = 1.013 \times 10^5 \text{ Pa}$
- Volume $[V] = 1 \text{ liter} = 10^{-3} \text{ m}^3$
- Temperature $[T] = 1 \text{ K}$
- Gas constant $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$
- Number of moles $n = \frac{N}{N_A}$
- Avogadro's number $N_A = 6.02 \times 10^{23}$ of molecules in 1 mole



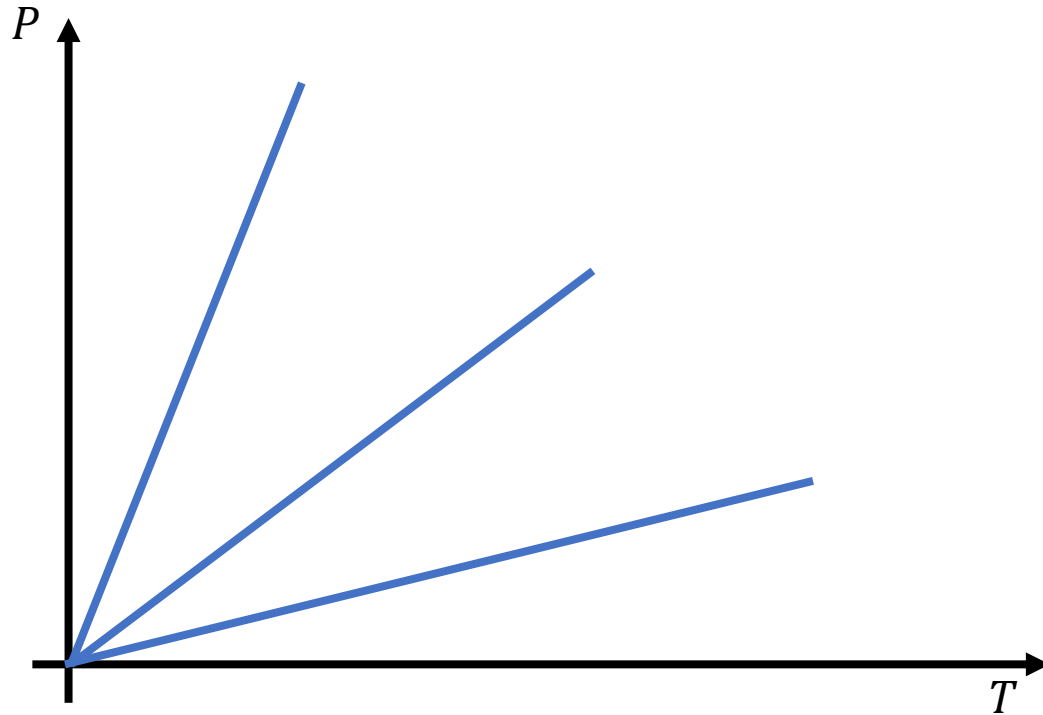
Isotherms

$$P = nRT \frac{1}{V}$$



P-T diagram: isocores

$$P = \frac{nR}{V} T$$



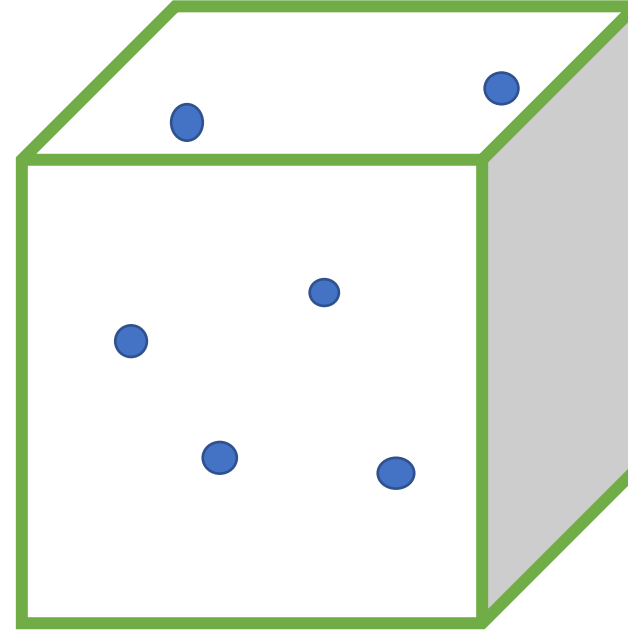
Ideal gas: Microscopic (statistical) model

Equation of state: $PV = NkT$

- Number of gas molecules N
- Boltzmann's constant

$$k = \frac{R}{N_A} = 1.381 \times 10^{-23} \text{ J K}^{-1}$$

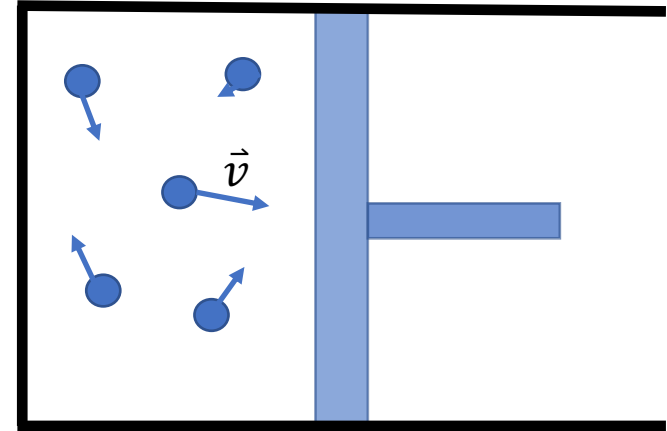
(conversion factor between energy and temperature?)



Ideal gas model: Pressure

Newtonian gas particle:

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

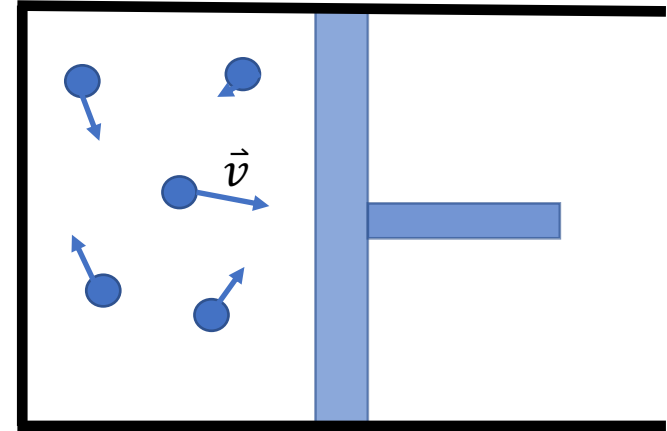


Q: What is the pressure in the ideal gas model?

Ideal gas model: Pressure

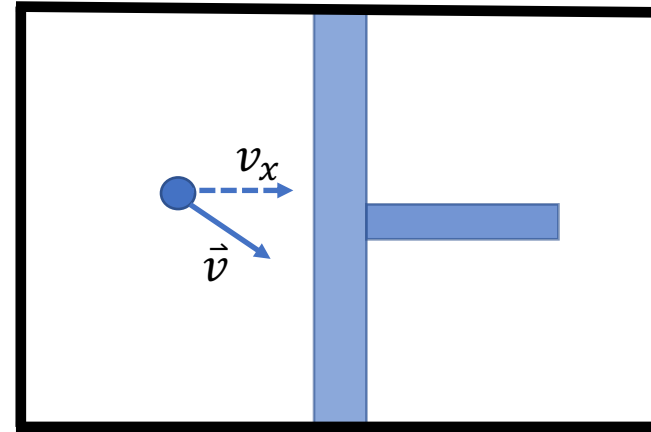
Q: What is the pressure in the ideal gas model?

- 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

$$\Delta v_x = v_{x,after} - v_{x,before} = -2v_x$$

Ideal gas model: Pressure

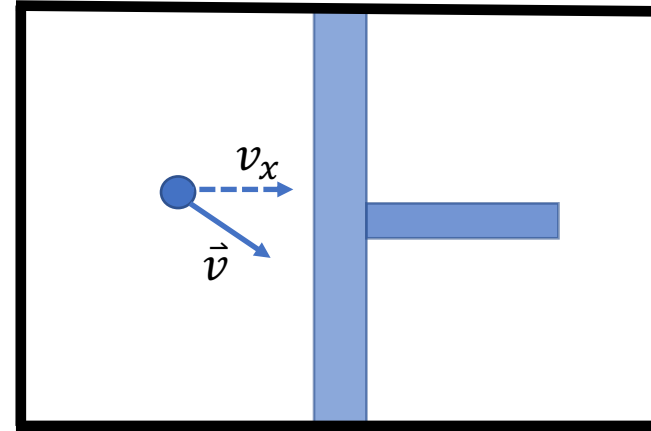
What is the average pressure exerted on the piston by the gas particles?

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

using

$$\circ \Delta t = \frac{2L}{v_x}$$

$$\circ \Delta v_x = v_{x,after} - v_{x,before} = -2v_x$$



Ideal gas model: Pressure

What is the average pressure exerted by the gas particles?

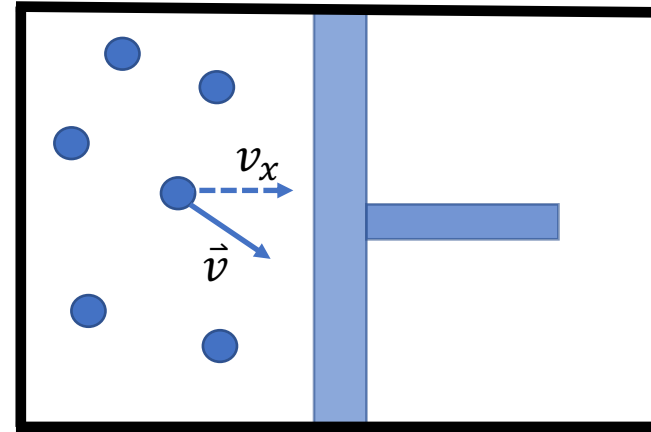
Pressure is the long-time average of v_x^2

$$P = \frac{\overline{mv_x^2}}{V}$$

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

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

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



Ideal gas model: Temperature

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

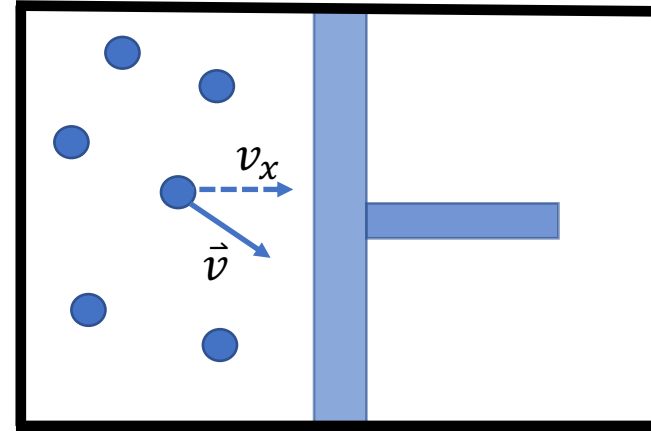
$$PV = NkT$$

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

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

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

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



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

Ideal gas model: Equipartition

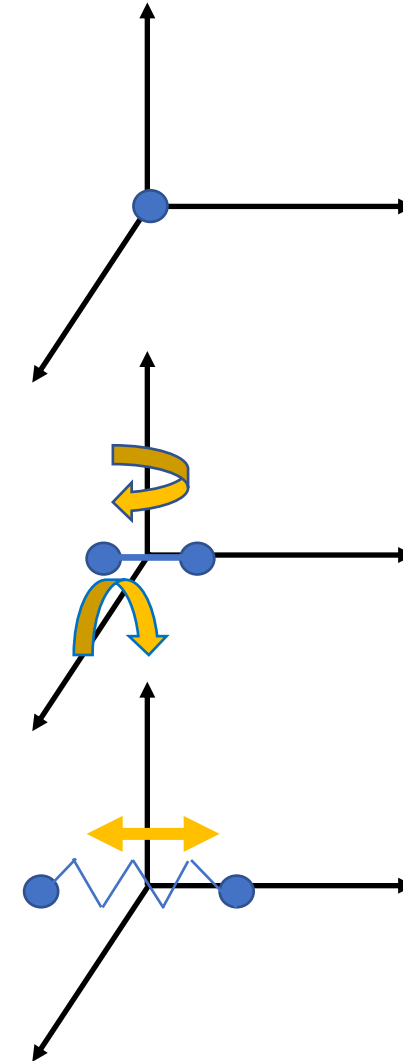
Equipartition of energy (theorem):

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*?

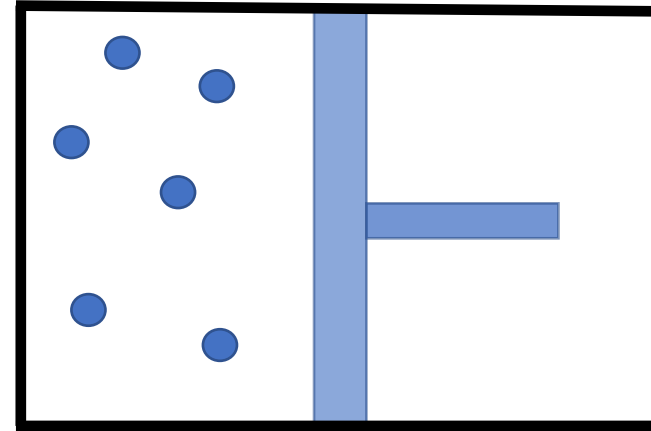
- Translation $K_{trans} = \frac{1}{2}mv^2$
- Rotation $K_{rot} = \frac{1}{2}I\omega^2$
- Vibration/oscillation $U_{harm} = -\frac{1}{2}k(\Delta x)^2$



Ideal gas model: Equipartition

Equipartition of energy (theorem):

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

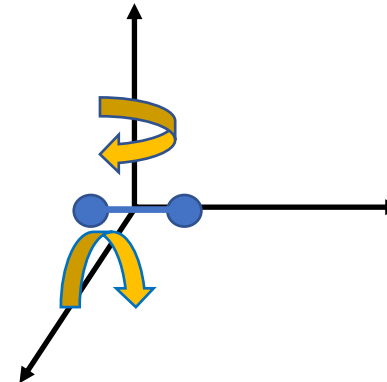


Example:

What is the internal energy of a diatomic gas:

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

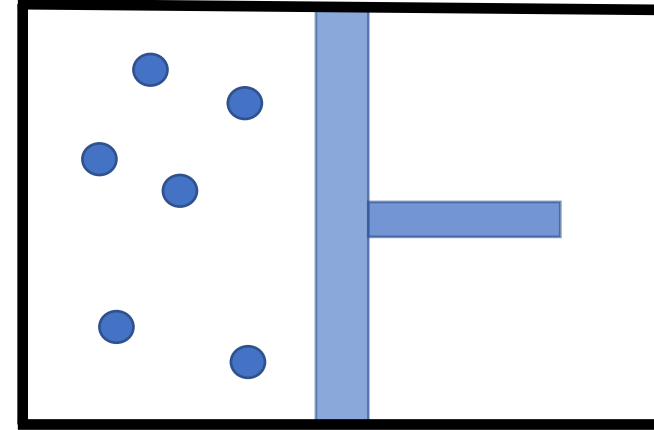
$$U = \frac{5}{2}NkT$$



Ideal gas model: Equipartition

Equipartition of energy (theorem):

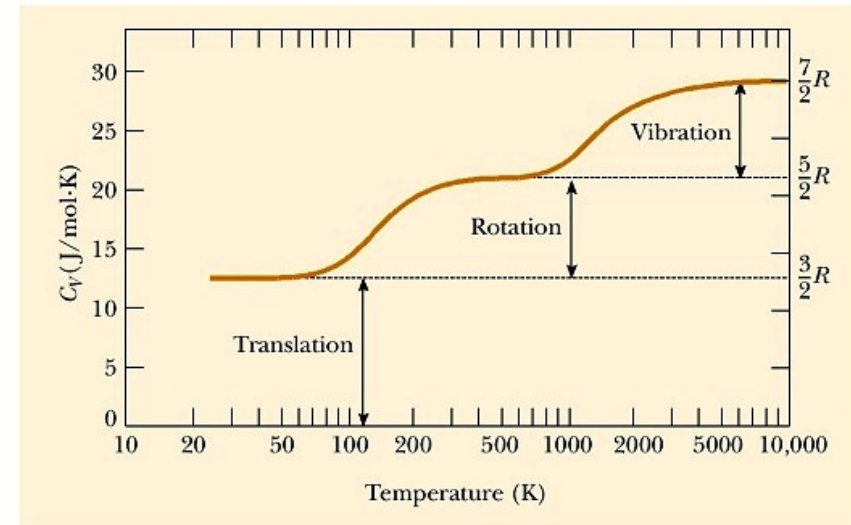
$$U = \frac{f}{2} NkT$$



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.

Mean free-path

Free path between collisions

Number of molecules per unit volume (density):

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

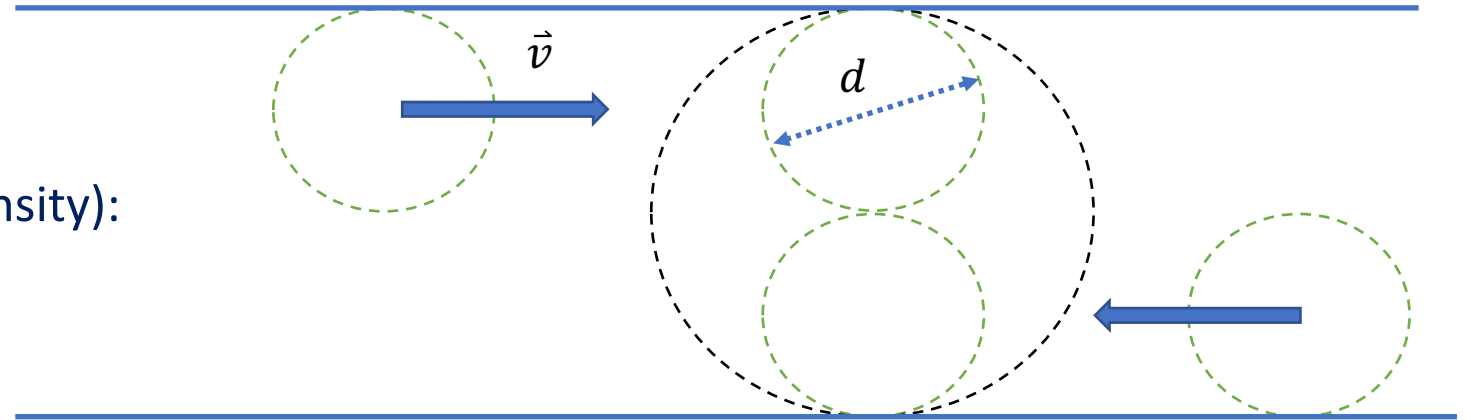
Effective collision area: $\sigma = \pi d^2$

Effective collision volume:

$$V_c = \bar{v}t\sigma = \pi d^2 \bar{v}t$$

Mean free path: $\lambda = \frac{\bar{v}t}{n_V V_c}$

$$\lambda = \frac{1}{\pi d^2 n_V}$$



Mean free path

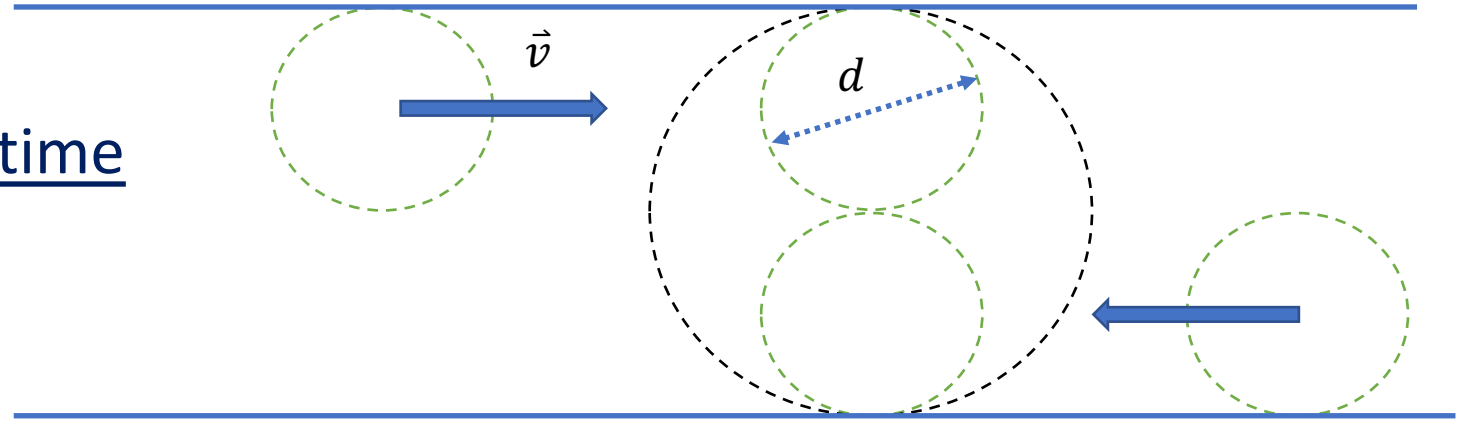
Gas particles spend most of their time between collisions

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

Average time between collisions:

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

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



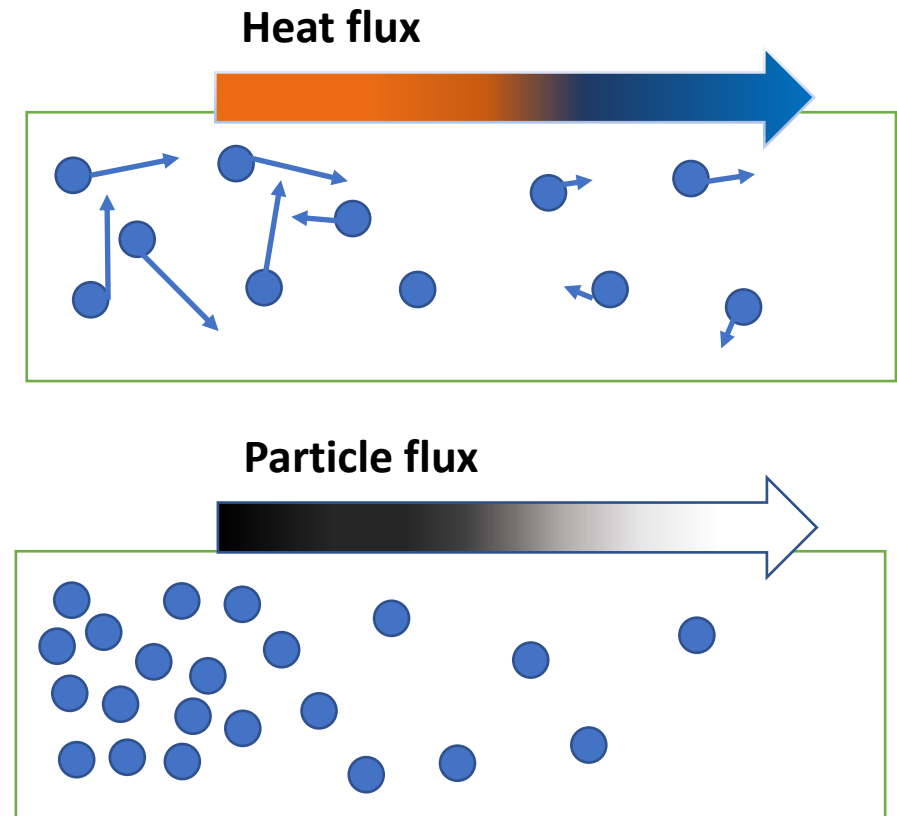
The mean-free path λ and mean lag time τ dictate the *kinetics* of the gas
(**diffusion and heat conduction properties**)

Relaxation to equilibrium by diffusion

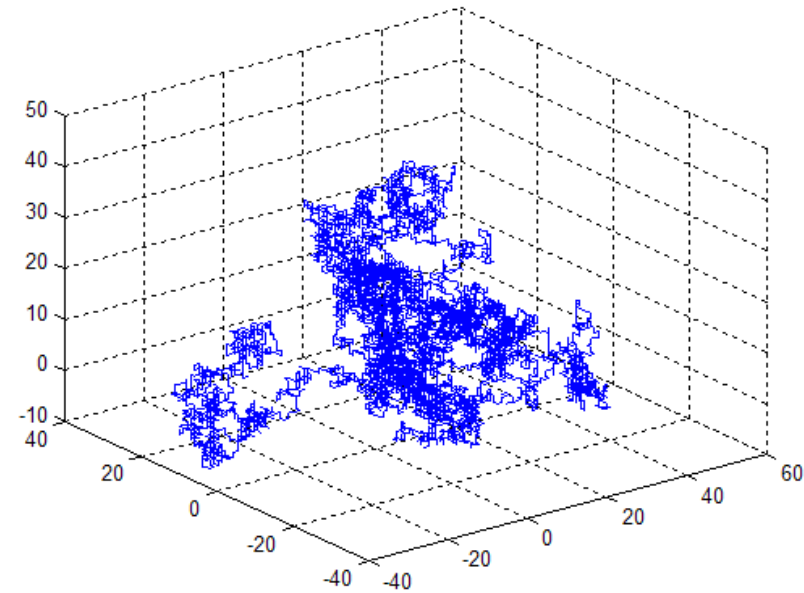
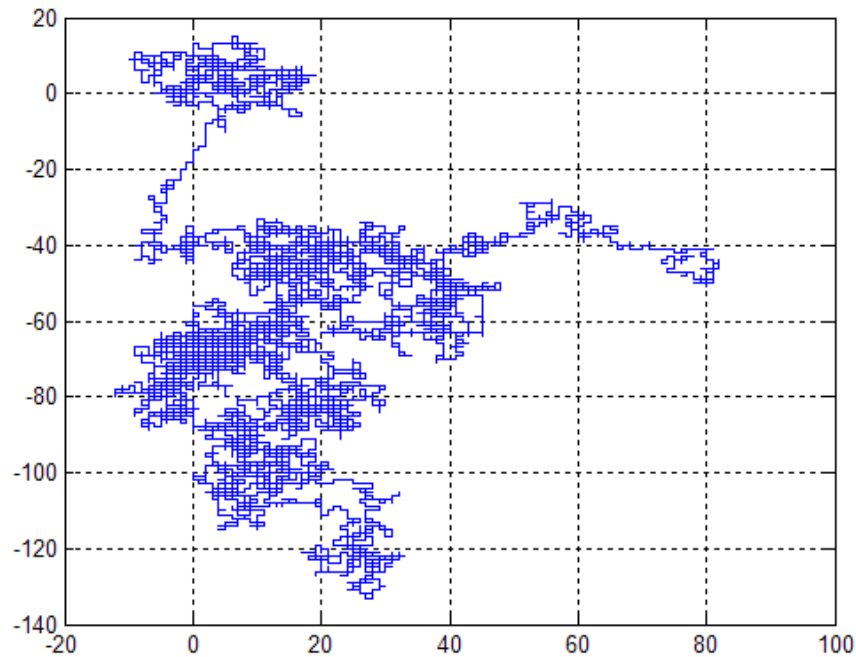
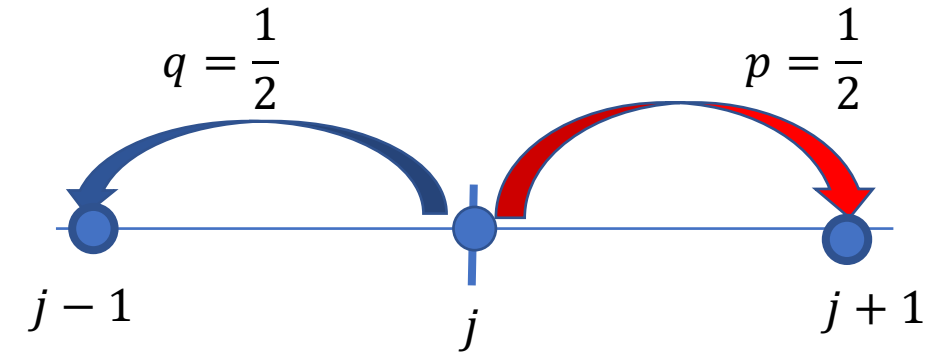
Diffusion:

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

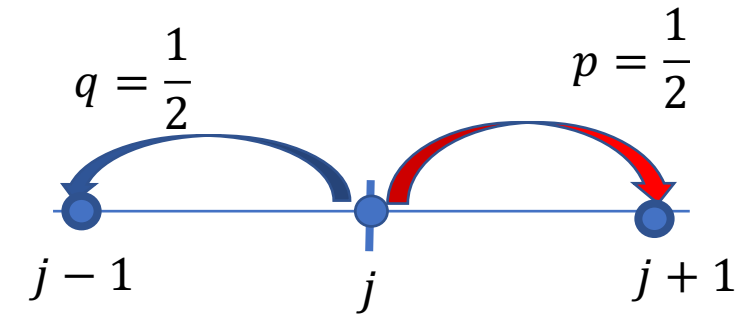
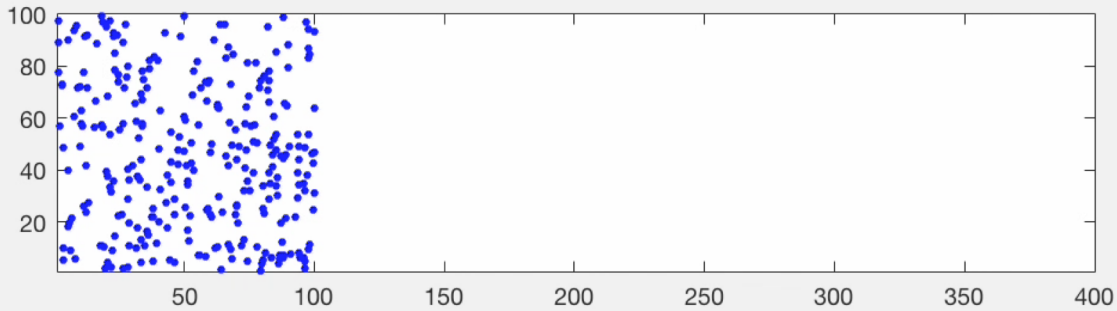
- At any $T > 0\text{K}$, particles are in *thermal motion*
- Collisions between particles \rightarrow particle trajectory is a zigzag -- random (*diffusive particle*)



Particle diffusion: Random walk (RW)



Random walk and diffusion



Fick's first law:

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

$$J = -D \nabla C$$

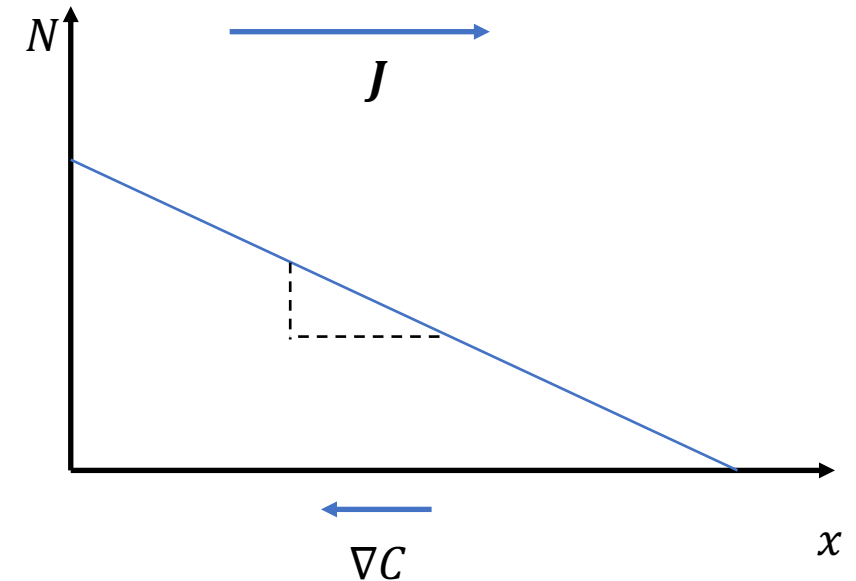
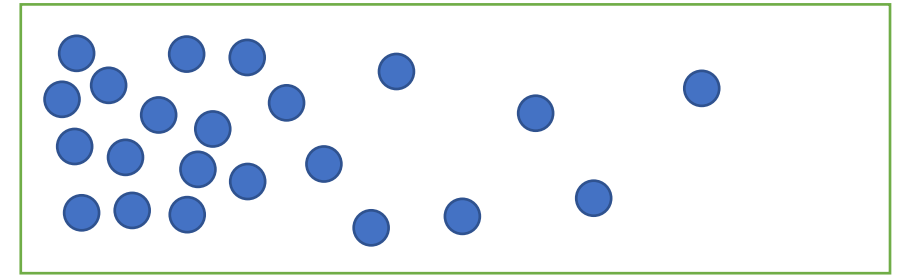
- Diffusivity D :** mobility of the diffusing particles

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

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

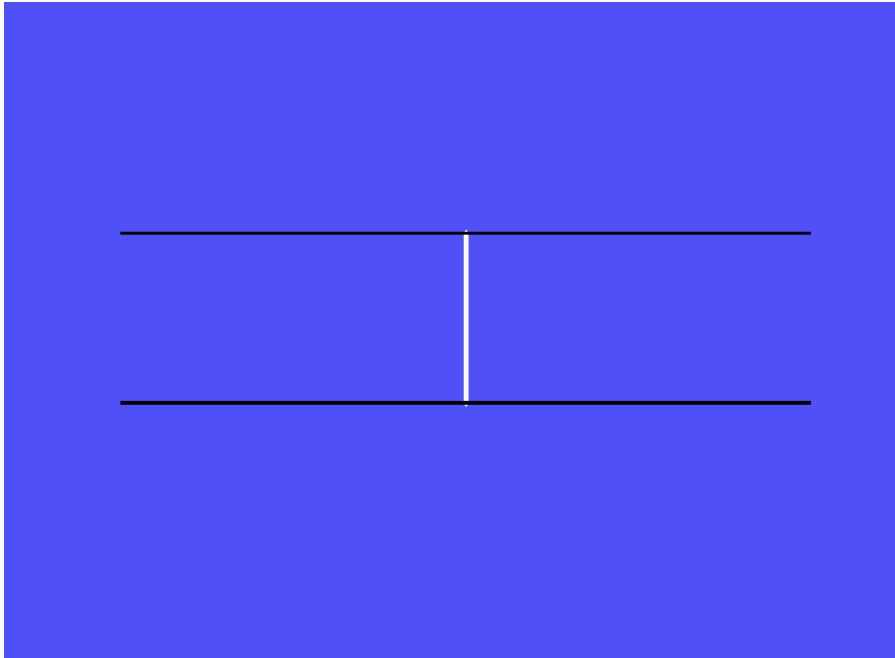
$$[D] = \frac{\text{m}^2}{\text{s}}$$

- $D_{C0} = 0.2 \frac{\text{cm}^2}{\text{s}}$ in *air*
- $D_{C0} = 2 \times 10^{-5} \frac{\text{cm}^2}{\text{s}}$ in *water*

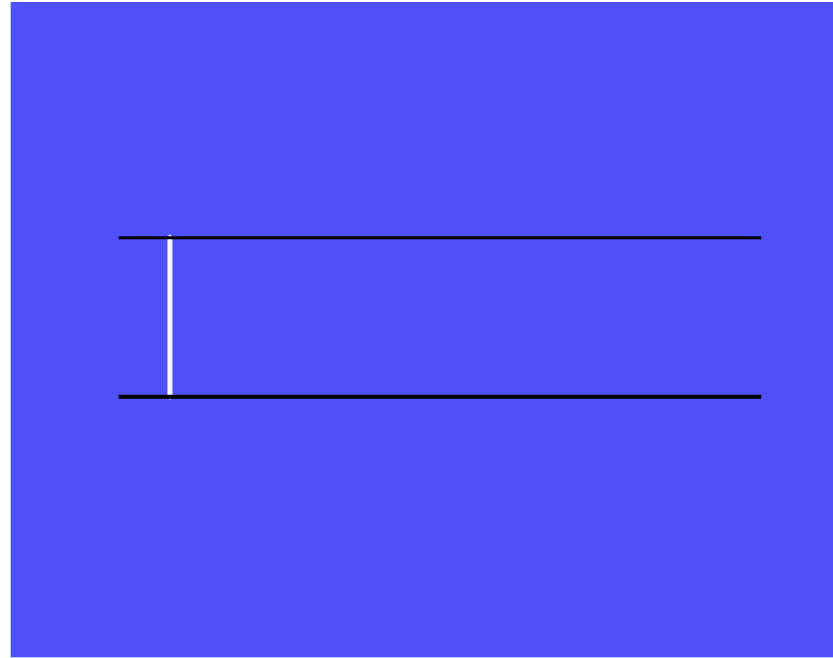


Flow and dispersion

Molecular dispersion (Diffusion)



Dispersion by flow



Molecular Diffusivity: gas kinetics

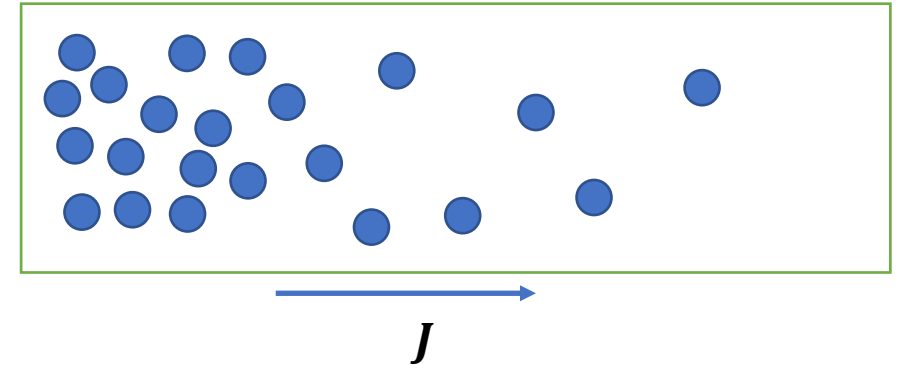
- Flux across a surface in a average time interval between collisions τ

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

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

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

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



Heat conduction

Fourier's law:

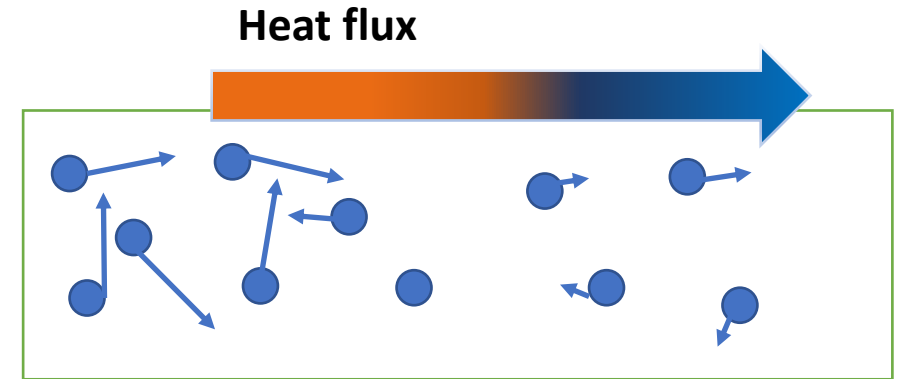
Rate of heat conduction is proportional to the temperature difference

$$J_Q = \frac{Q}{A\Delta t} = -k_t \nabla T$$

- Isocoric heat conduction $Q = \Delta U = C_V \Delta T$

$$\frac{C_V \Delta T}{A\tau} \approx k_t \frac{\Delta T}{\lambda} \rightarrow k_t \approx \frac{C_V}{V} \lambda \bar{v}, \quad C_V = \frac{f}{2} \frac{PV}{T}$$

$$k_t \approx \frac{P}{T} D \rightarrow \mathbf{k_t \sim \sqrt{T}}$$



Fick's second law:

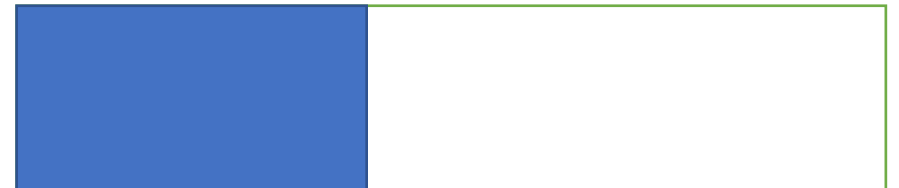
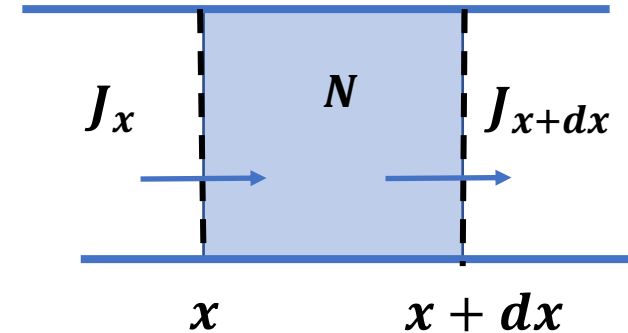
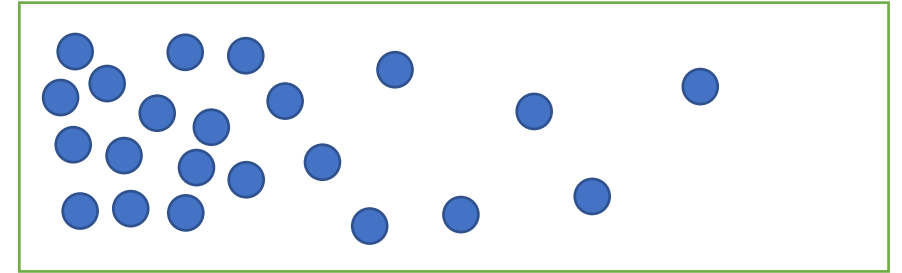
- *Rate of change in the number of particles = net flux times the cross-section area*

$$\frac{dN}{dt} = J_{net} \times A$$

$$\frac{dN}{dt} = (J_x - J_{x+dx}) \times A$$

$$\frac{d(N/A)}{dt} = -\frac{dJ_x}{dx} dx$$

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



Summary

- Equipartition of energy

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

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

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

$$k_t \approx \frac{C_V}{V} \lambda \bar{v} \sim \frac{\sqrt{T}}{P}$$