Molecules in motion

- Transport processes
  - Diffusion: transport of matter
  - Thermal conductivity: transport of energy
  - Viscosity: transport of momentum
  - **Ionic conduction: transport of ions/charge**
- Interpretation of transport processes with the kinetic theory of gases
- Effusion
- Barometric formula

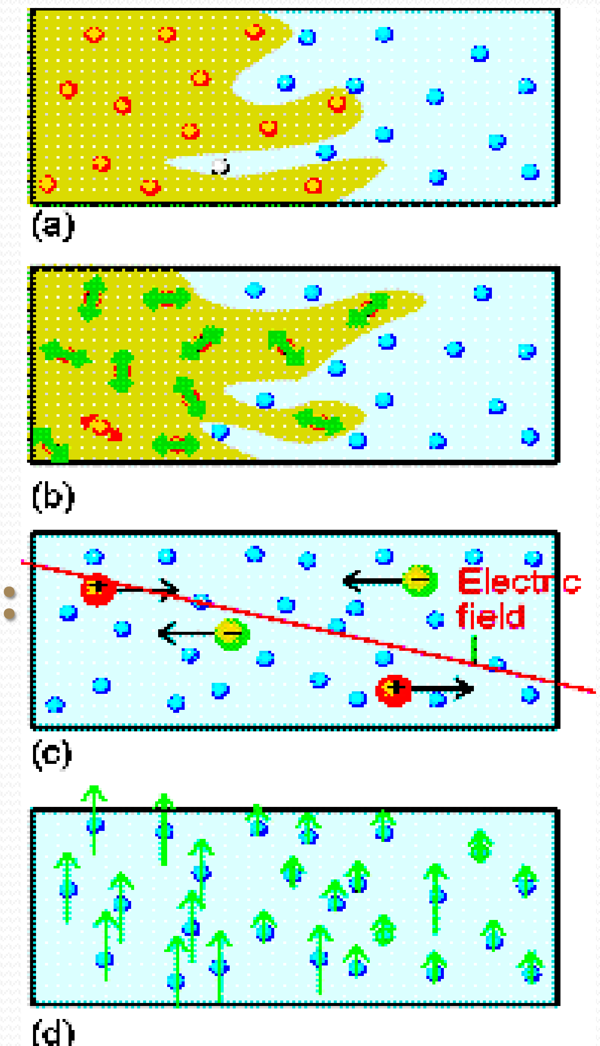
Transport phenomena

Phenomenon	gradient	transport
Diffusion	concentration	matter
Thermal conduction	temperature	energy
Viscosity	velocity	momentum
Ionic conduction	electronic potential	charge

- Transport processes can be found in all three phases (with some exceptions.
- In transport processes, only the molecules are in motion, the system and its macroscopic parts are not.
- There is no convection or mixing.

Transport phenomena

- Diffusion:
  - particle transport
- Thermal conduction:
  - energy transport
- Electrolytic conduction:
  - charge transport
- Viscosity:
  - momentum transport



Transport phenomena

Common concepts in transport phenomena:

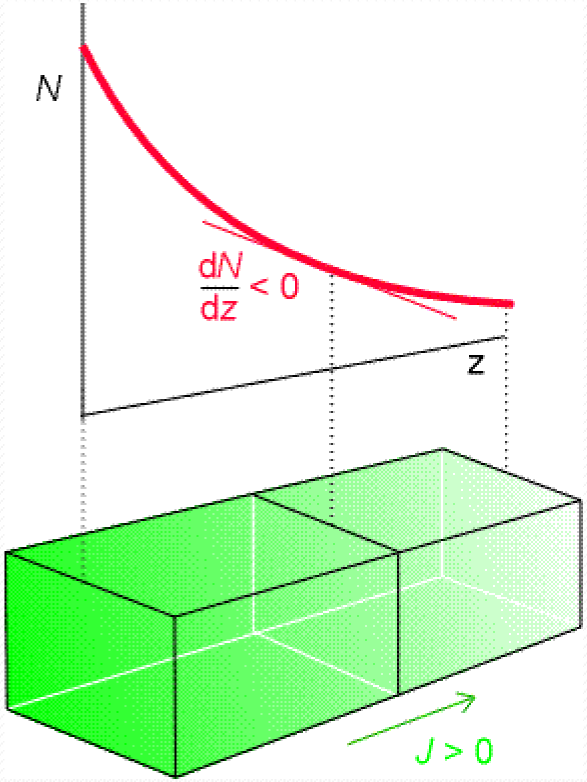
- **Gradient**: one of the parameters (T, c, E ...) is inhomogeneously distributed in space, at least in one direction.
- **Flux**: the quantity of a given property (m, v ...) passing through a given area in a given time interval divided by the area and the duration of the interval.
  - Symbol: J(matter, charge ...).
  - $J(\text{matter}) \propto \frac{\mathrm{d}N}{\mathrm{d}z}$
  - N: number density of particles with units number per cubic meter

Diffusion: transport of matter (molecular level)

$$J(\text{matter}) = -D\frac{\mathrm{d}N}{\mathrm{d}z}$$

[J]: $m^{-2}\,s^{-1}$ flux of matter
[D]: $m^{2}\,s^{-1}$ diffusion coefficient
$\mathrm{d}N/\mathrm{d}z$: m^{-4} concentration gradient

- **Fick's first law of diffusion**: diffusion will be faster when the concentration varies steeply with position than when the concentration is nearly uniform.
- Different concentrations mean different chemical potentials (since μ depends on c),
- Practical importance: motion of matter in soils.



Thermal conduction: transport of energy

$$J(\text{energy}) = -\kappa \frac{\mathrm{d}T}{\mathrm{d}z}$$

$[J]$:	$\mathrm{J\,m^{-2}\,s^{-1}}$	flux of energy
$[\kappa]$:	$\mathrm{J\,K^{-1}\,m^{-1}\,s^{-1}}$	coefficient of thermal conductivity
$\mathrm{d}T/\mathrm{d}z$:	$\mathrm{K\,m^{-1}}$	temperature gradient

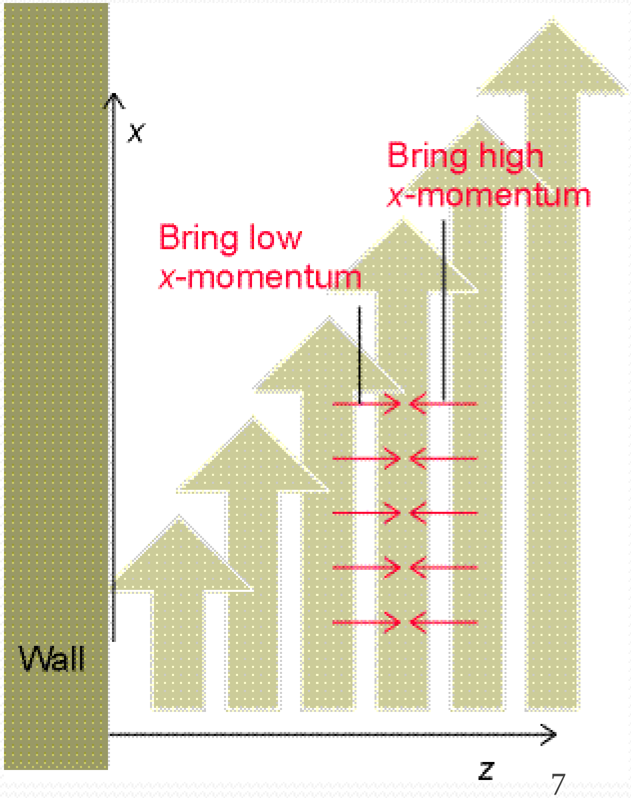
- Energy migrates down a temperature gradient.
- The connection between flux and gradient is similar to **Fick's first law of diffusion**.
- Good thermal conductors: metals (Ag, Cu, Au, Al), marble, diamond
- Good thermal insulators: vacuum, CO_2, plastic, wood
- Practical importance: thermal insulation of houses.
- There is **molecular heat conduction**, **macroscopic (convective) heat flow** and **heat radiation**.

Viscosity: transport of momentum

$$J(\text{momentum})_z = -\eta \frac{dv_x}{dz}$$

$[J]$:	kg m^{-1} s^{-2}	flux of momentum
$[\eta]$:	kg m^{-1} s^{-1}	coefficient of viscosity (or simply 'the viscosity')
dv_x/dz:	s^{-1}	velocity gradient

- Because the retarding effect depends on the transfer of the ***x***-component of linear momentum into the layer of interest,
- the viscosity depends on the flux of this ***x***-component in the ***z***-direction.



Data for gases:

- diffusion coefficients: 10^{-4} m^2 s^{-1}
- coefficients of thermal conductivity: 0.01-0.1 J K^{-1} m^{-1} s^{-1}
- coefficients of viscosity: 1-2×10^{-5} kg m^{-1} s^{-1}

	Density (g cm^{-3})	Diffusion (cm^2 s^{-1})	Viscosity (g cm^{-1} s^{-1})
Gas	10^{-3}	10^{-1}	10^{-4}
Supercritical fluid	10^{-1} – 1 *Liquid-like*	10^{-4} – 10^{-3} *Liquid-like*	10^{-4} – 10^{-3} *Gas-like*
Liquid	1	< 10^{-5}	10^{-2}

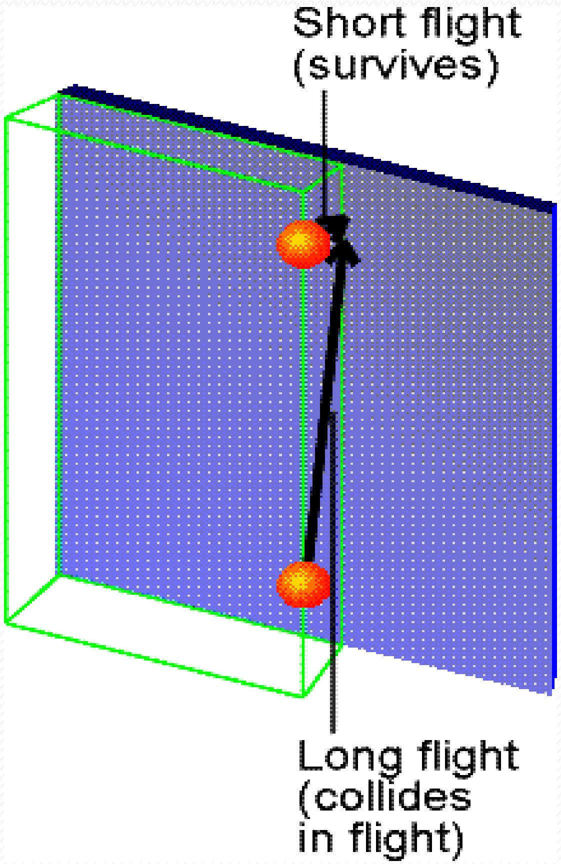
Kinetic theory of gases:

- Molecules in the gaseous phase (macroscopic equilibrium).
  - The gas particles (with *m* mass) move continuously in a straight line with constant speed and
  - they collide. The collisions are perfectly elastic (there is no change in the shape of the molecule).
- The gas molecules have „only” *m* mass and *v* velocity, so, **momentum** (mv) and **kinetic energy** ($\frac{1}{2} mv^2$).

Kinetic theory of gases - results:

- **Mean free path**: $$\lambda = \frac{k_B T}{\sqrt{2}\sigma p}$$
  - σ: collision cross-section
  - p and T have opposite effects on λ.
- **Mean speed** of a particle with m mass (*i.e.* $M = N_A \cdot m$ molar mass): $$\bar{c} = \left(\frac{8 k_B T}{\pi m}\right)^{1/2} = \left(\frac{8RT}{\pi M}\right)^{1/2}$$
  - The mean speed is directly proportional with $T^{1/2}$ and
  - inversely proportional to $M^{1/2}$.
- **Collision frequency**: $$Z_w = \frac{p}{\left(2\pi m k_B T\right)^{1/2}}$$
  - Z_w: the number of collisions made by one molecule divided by the time interval during which the collisions are counted

The **transport constants** from the **kinetic theory of gases:**



diffusion coefficient:	$D = \frac{1}{3}\lambda\bar{c}$
coefficient of thermal conductivity:	$\kappa = \frac{1}{3}\lambda\bar{c}C_{V,m}[\mathrm{A}]$
coefficient of viscosity:	$\eta = \frac{1}{3}\lambda\bar{c}mN$

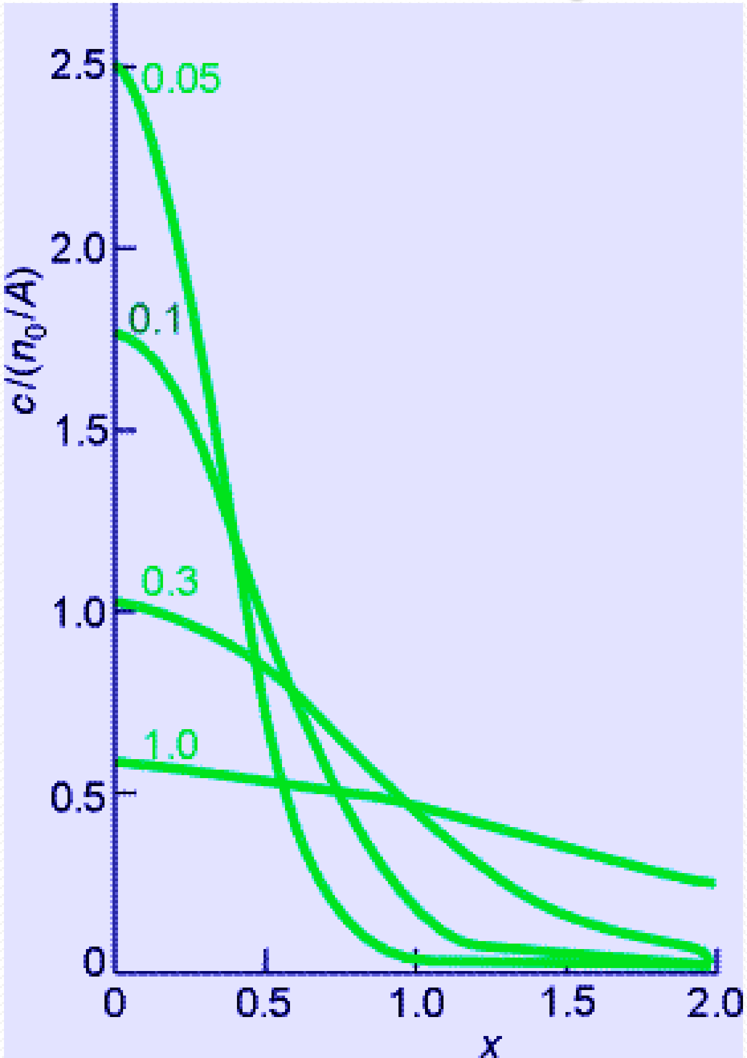
Time and diffusion: **the diffusion equation (Fick's 2nd law)**

- At a given position *x*, the concentrations change is given as:

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

- Some solutions of the diffusion equation:
- An initial value and two boundary conditions are needed:
  - At $t = 0$, the concentration is N_0 in the *x*, *y* plane
  - No reactions in the system
  - Concentration are always finite.
  - *Sugar at the bottom of the tea cup: diffusion in space*

Time and diffusion: **the diffusion equation (Fick's 2nd law)**



- A solution of the diffusion equation:

$$c = \frac{n_0 e^{-\frac{x^2}{4Dt}}}{A(\pi Dt)^{1/2}}$$

Effusion:

- Effusion: gas slowly escapes through a small hole into an external vacuum (a tire becomes flat slowly if the hole is small *[Vacuum is relative: the essence is the unidirectional diffusion.]*
- **Graham's law of effusion**: the rate of effusion is inversely proportional to the square root of the molar mass (an old determination method for molar mass):

$$\text{rate of effusion} \propto \frac{1}{\sqrt{M}}$$

Inhomogeneity in gas pressure in an external force field:

- In a force field (e.g. **gravity field of Earth**), the pressure is not uniform (e.g. atmosphere): there is an exponential decrease in pressure with the elevation. This is described by the barometric formula:

$$p = p_0 e^{-\frac{Mgh}{RT}}$$

- The phenomenon can be observed in an artificial „gravity" field (centrifuge) as well, and the distribution (which depend on the molar mass) can be used in separating different isotopes.