Transport processes (opposite of equilibrium)

(**matter**, heat, momentum, charge)

There are two distinct mechanisms.
The first is when particles of the quantity in question are translocated collectively and this is observable macroscopically, such as in a fluid flow. The other mechanism is where the detected macroscopic translocation is the result of individual motions of particles (**thermal motion**), which are not observable even microscopically. Diffusion is an example of the latter mechanism.

Diffusion

Molecular motions can only be observed indirectly.
Brownian motion, is the term used to describe the random motion of the pollens in a suspension, and is the result of continous collisions with otherwise invisible water molecules.

Characteristics of molecular motion

The description of molecular motion is much more complicated in fluid phase than in gases, thus we present the basic diffusion laws for gases, but the results are applicable under certain conditions to fluids too.

According to the model of the ideal gas the average kinetic energy of a single particle:

$$\bar{\varepsilon}_{\mathrm{kin}} = \frac{1}{2} m \overline{\upsilon^2} = \frac{3}{2} kT \, .$$

The **average time between collisions** is denoted by τ,
and the average distance travelled between two collisions, or the so-called **mean free path** is denoted by l.
Thus

$$l = \upsilon\tau .$$

When an **external field** is appiled, some of the particles' path is still zig-zagged, but a unidirectional drift is added to the random motion. (For example a portion of gas-particles are ionized and the applied external field is electric.)
Using Newton's second law ($F = ma$, Force = mass*acceleration) and that $\upsilon = at$, (velocity = acceleration*time)
the **drift speed**

$$\upsilon_{\text{drift}} = \frac{F}{m}\tau ,$$

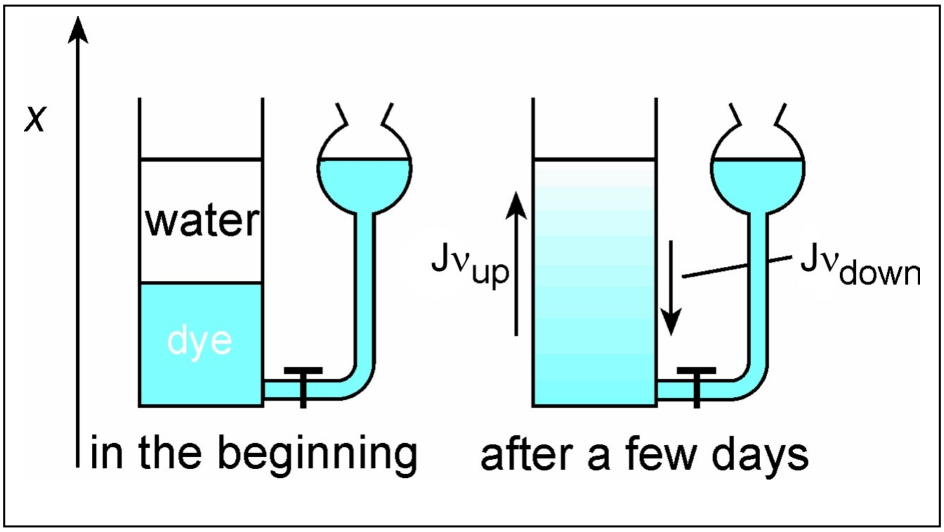
and a new quantity is the **mobility** u

$$u = \frac{\upsilon_{\text{drift}}}{F} = \frac{\tau}{m} .$$

which is the value of the velocity resulting from a unity of force.

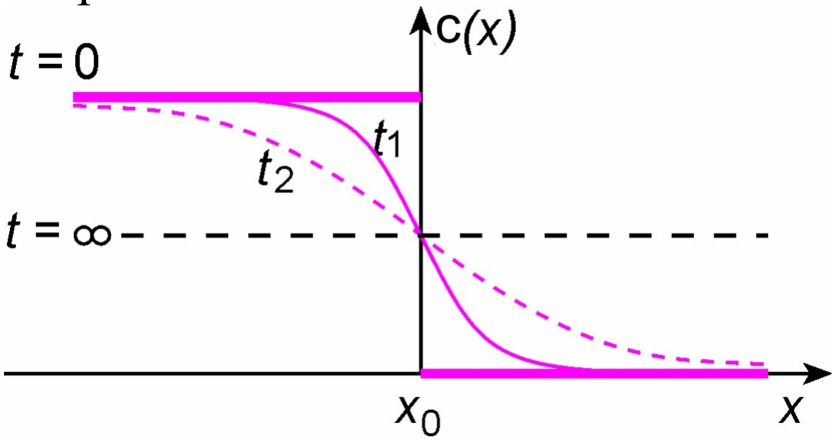
Diffusion phenomena, Fick's experiment

Spreading of particles because of the random thermal motion called **diffusion.** It continues until the distribution of the particles is uniform throughout the entire volume.

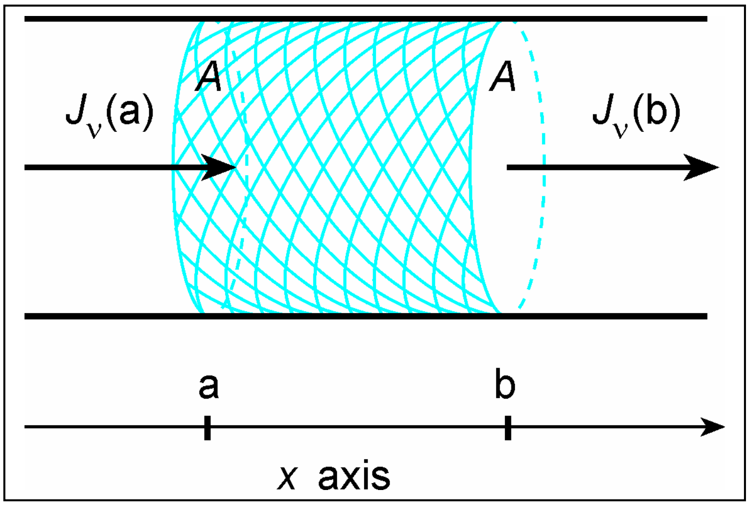


Fick interpreted diffusion along the concept of Brownian motion.

Qualitative description:



1. Law of continuity (in the simplest case)



particle-flux:

$$I_N = \frac{\Delta N}{\Delta t} = \text{constant}$$

N number of particles (pieces)
t time

matter flow rate:

$$I_\nu = \frac{\Delta \nu}{\Delta t}$$

$\nu = N/N_A$ amount of particles (mol) **(be careful υ standing for velocity)**
N_A (Avogadro number)

matter flow density:

$$J_\nu = \frac{\Delta I_\nu}{\Delta A} = \frac{\Delta \nu}{\Delta t \Delta A}$$

$$\Delta \nu = J_\nu(\mathrm{a}) A \Delta t = J_\nu(\mathrm{b}) A \Delta t$$

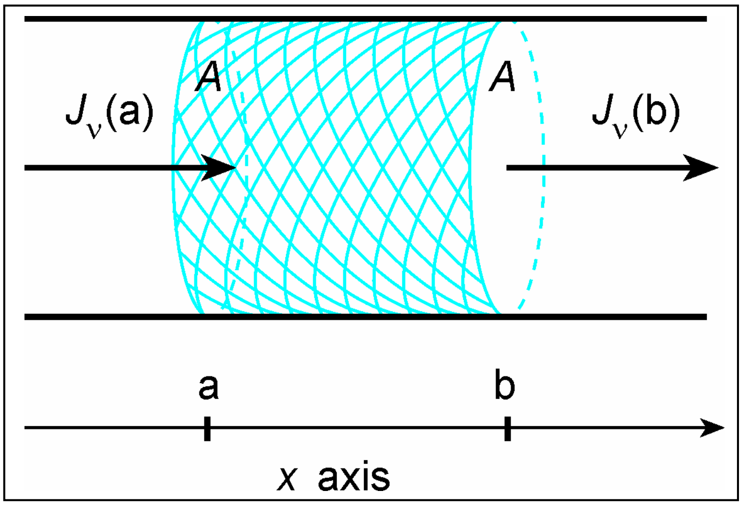
2. Law of continuity (in generalized form)

In the previous case:

$$J_\nu(\mathrm{a})A\Delta t - J_\nu(\mathrm{b})A\Delta t = 0$$

If J_ν(a) > J_ν(b)
there is a net substance influx into the space enclosed by a and b

This amount of substance has to appear in the given volume (V), thus the concentration of the substance (c) will grow.



$$c = \frac{\Delta \nu}{\Delta V}$$

and $c(t+\Delta t) > c(t)$

Let a = x and b = $x + \Delta x$ be very close to each other.

$$\left[J_\nu(x) - J_\nu(x+\Delta x)\right]A\Delta t = \left[c(t+\Delta t) - c(t)\right]A\Delta x$$

where $A\Delta x = \Delta V$

$$-\frac{\Delta J_\nu}{\Delta x} = \frac{\Delta c}{\Delta t}$$

3. Fick's first law

What does the diffusion rate depend on and
what will be the size of the matter flow density (J_ν)?

$$\frac{1}{6}(c_{\text{down}} - c_{\text{up}})\upsilon \Delta t A = \Delta \nu$$

$$-\frac{1}{6} 2l \frac{\Delta c}{\Delta x}\upsilon = -\frac{1}{3} l\upsilon \frac{\Delta c}{\Delta x} = -D\frac{\Delta c}{\Delta x} = J_\nu$$

$$J_\nu = -D\frac{\Delta c}{\Delta x}$$

This is Fick's first law. The meaning of Δc/Δx is the concentration drop of a unit-length, or concentration-gradient.
The most important message of the law is that the matter flow which characterizes the "strength" of diffusion is proportional to the drop in concentration. The proportionality coefficient is the called **diffusion coefficient.**

$$D = ukT$$

its dimension is: m^2/s.

4. Fick's second law

(describes the concentration's spatial and temporal variation)

We use the generalized continuity-equation

$$-\frac{\Delta J_v}{\Delta x} = \frac{\Delta c}{\Delta t} \qquad \left(J_v = -D\frac{\Delta c}{\Delta x} \right)$$

Let's replace (J_v) from Fick's first law:

$$D\frac{\Delta\left(\dfrac{\Delta c}{\Delta x}\right)}{\Delta x} = \frac{\Delta c}{\Delta t}, \qquad \left(D\frac{\partial^2 c}{\partial x^2} = \frac{\partial c}{\partial t} \right)$$

This is Fick's second law. (See also in the manual: DIFFUSION)

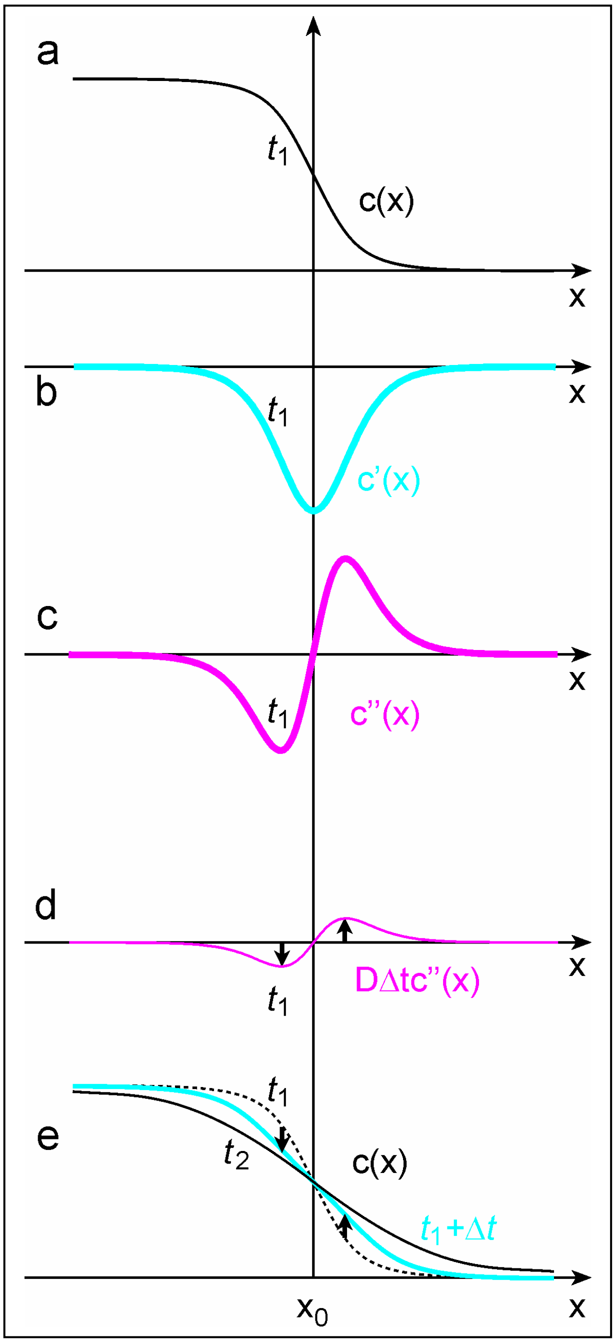
Meaning of Fick's second law

With the aid of numeric methods, and the knowledge of all initial conditions, the concentration's temporal and spatial alteration can be determined with good accuracy.

$$D\frac{\Delta\left(\dfrac{\Delta c}{\Delta x}\right)}{\Delta x}\Delta t + c(t) = c(t+\Delta t)$$

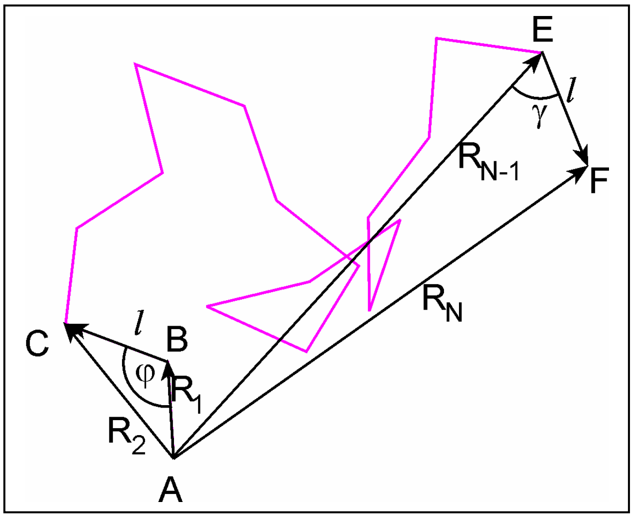
This expression give us the concentration a little later (t + Δt) time-point,
if its (spatial) distribution at a time point (t) was known.

$$c(t) + c''D\Delta t = c(t+\Delta t)$$



Random-walk problem

How far does the particle get from its initial position, because of the thermal motion?

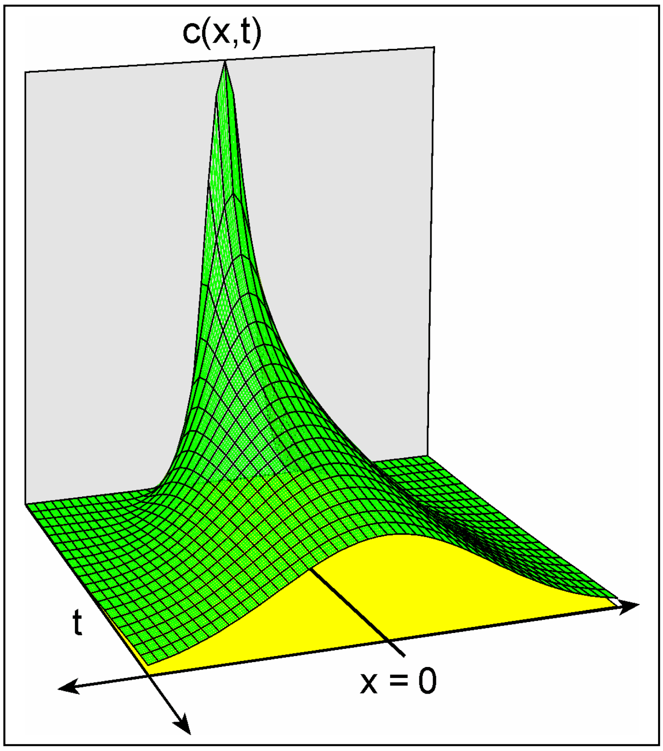


$$R_2^2 = l^2 + l^2 - 2l^2 \cos\varphi$$

$$\overline{R_N^2} = \overline{R_{N-1}^2} + l^2 = Nl^2$$

$$\overline{R(t)} = \sqrt{Nl^2} = \sqrt{\frac{t}{\tau} l^2} = \sqrt{t\upsilon l} = \sqrt{3Dt}$$

$$\sigma_x \sim \overline{R(t)} \sim \sqrt{Dt}$$

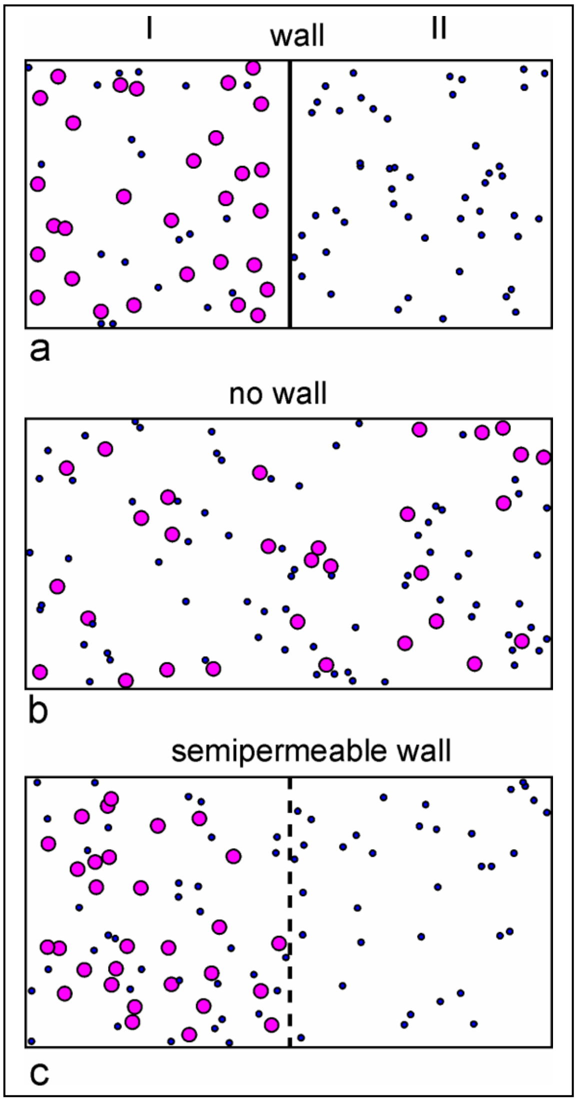


(The random-walk problem is sometimes called the problem of the ”drunk sailor”. The sailor comes out from the pub and sets off somewhere, but since his legs do not always obey his will, his steps are random. Every step is randomly angled to that of the previous one. Given these circumstances how far does the sailor get after a set amount of time? Naturally, we do know exactly, because it is not determinable, but we can calculate the average distance the sailor takes if the incident is repeated daily.)

Application from textbook (page 240)

Osmotic phenomenon

A small-sized, semi-permeable bag, filled with sugar dissolved in water is placed in a container filled with pure water. After a certain time, we can observe the bag swelling, and that ouside of it in the container the water remains pure, while the solution in the bag has been diluted.



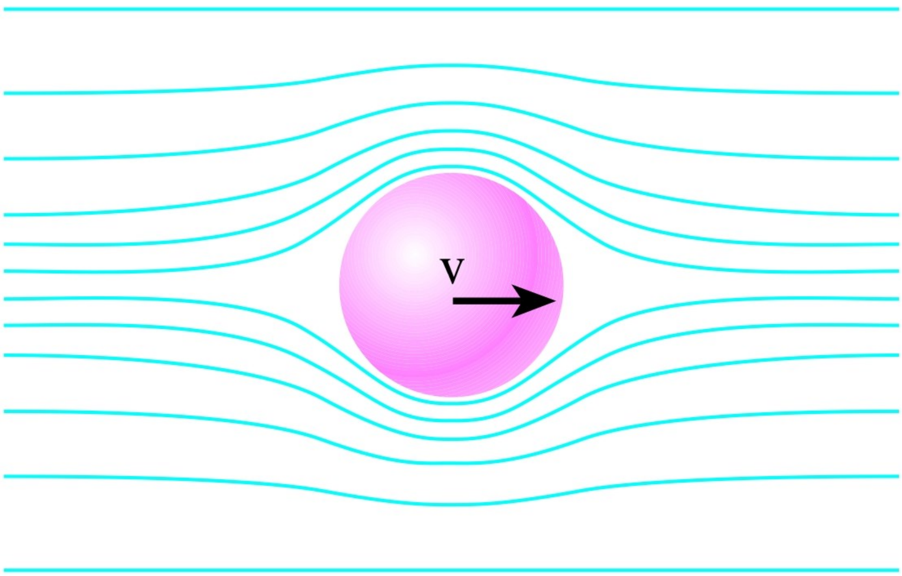
This **unidirectional matter flow, which takes place by means of diffusion, is called osmosis**.

5. van t'Hoff law: $p_{\mathrm{osmotic}} = cRT$.

If osmotic pressure is equal in two different solutions, we call them isotonic solutions.

Spherical body moving in a viscous medium

What frictional force acts on a spherical body moving in a fluid?



$$F_s = 6\pi\eta r \upsilon$$

η is the coefficient of viscosity or internal friction coefficient (unit: Pa·s).

This is Stokes' law. ($F \sim \upsilon$)
The coefficient that relates the two parameters is introduced in the following way:

$$u = \frac{\upsilon}{F} \quad , \quad u = \frac{1}{6\pi\eta r} \cdot$$

u is the mobility of the sphere.