

Transport processes II: 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 continuous 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.

Earlier we learned the average kinetic energy of a single particle in thermal equilibrium (model of the ideal gas):

$$\bar{\varepsilon}_{\text{kin}} = \frac{1}{2} m \overline{v^2} = \frac{3}{2} kT .$$

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

$$l = v\tau .$$

When an **external field** is applied, 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 the **drift speed**

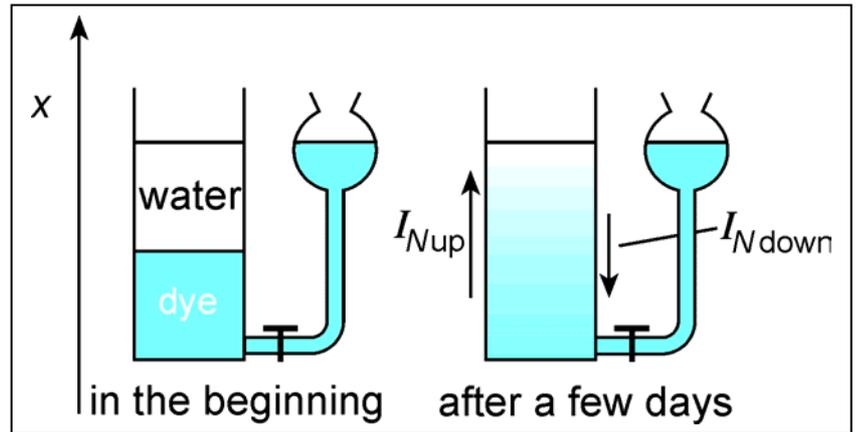
$$v_{\text{drift}} = \frac{F}{m} \tau ,$$

and the **mobility**

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

Diffusion phenomena, Fick's first law

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.



Diffusion takes place in two-component systems most of the time: for example let A denote **the diffusing component**, and B **the medium, in which it diffuses**. "A" can be the dye, and "B" is the water.

The **particle-flux** is:

$$I_N = \frac{\Delta N}{\Delta t},$$

where ΔN is the number of particles travelling through a certain surface A in a time-interval Δt . For experimental use, it is more convenient to use the **matter flow rate**. (In this case, the amount of substance is expressed in moles.)

Since $\Delta v = \Delta N/N_A$, where N_A is the Avogadro's number, the matter flow rate (I_v) through the surface A is:

$$I_v = \frac{\Delta v}{\Delta t}.$$

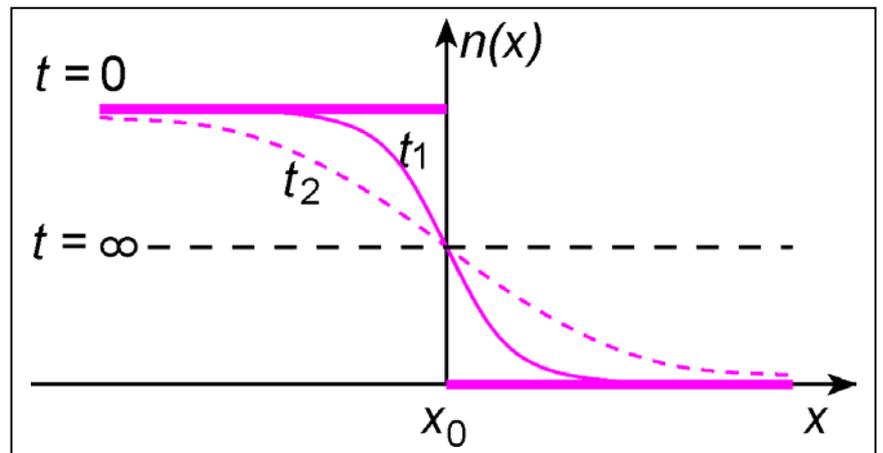
The unit of the matter flow rate is mol/s. For the following calculations, it is practical to introduce the **matter flow density**:

$$J_v = \frac{\Delta I_v}{\Delta A}.$$

Fick interpreted diffusion along the concept of Brownian motion, which was known by that time.

Each dye molecule undergoes random thermal motion, and the molecules can travel in any direction with equal probability. In this situation, if x denotes the direction parallel to the longitudinal axis of the container, then two particle fluxes form, one upwards (denoted by I_{Nup}) and another one downwards (denoted by I_{Ndown}). Since the number of dye molecules is higher at the bottom of the container than in the upper regions in the beginning of the process, $I_{Nup} > I_{Ndown}$, thus the net particle-flux (or net substance transport) proceeds upwards, its value equals $I_{Nup} - I_{Ndown}$.

What does the diffusion rate depend on and what will be the size of the flux-density (J_v) of the blue particles?



$$J_v = -D \frac{\Delta c}{\Delta x}$$

This is **Fick's first law**. The meaning of $\Delta c/\Delta x$ 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 .

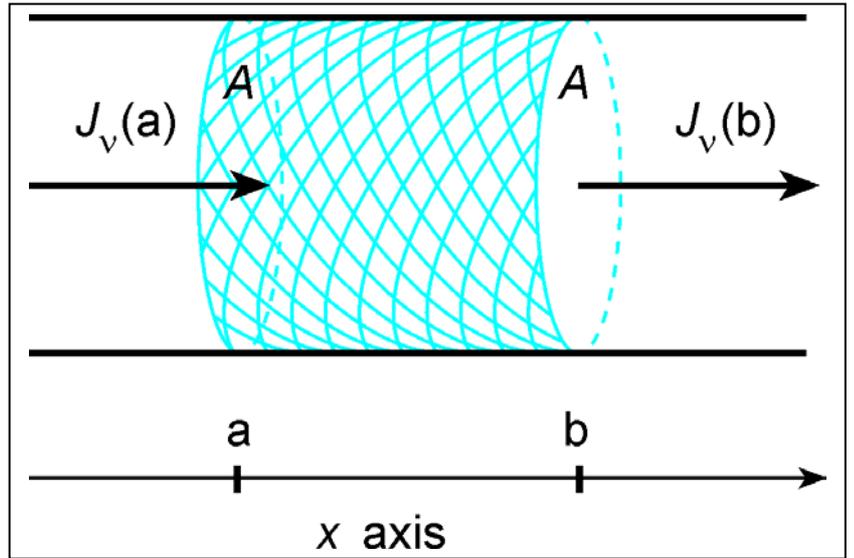
$$D = \frac{kT}{6\pi\eta r}$$

This is the **Stokes-Einstein equation**.

Fick's second law

(describes the concentration's spatial and temporal variation)

The equation can be derived quite simply from Fick's first law, if we generalize the equation of continuity.



$$J_v(a)A - J_v(b)A = 0$$

Which expresses the fact: the amount of substance that fluxed in through a surface of A equals the amount of substance effluxed.

If there is a net substance influx into the space enclosed by a and b , then this amount of substance has to appear in the given volume. Thus the concentration of the substance (c) will grow there during net influx.

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

$$[J_v(x)A - J_v(x + \Delta x)A]\Delta t = [c(t + \Delta t) - c(t)]A\Delta x$$

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

This is the **generalized continuity-equation**. Let's replace (J_v) from Fick's first law:

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

This is **Fick's second law**. (See in the manuel: DIFFUSION)

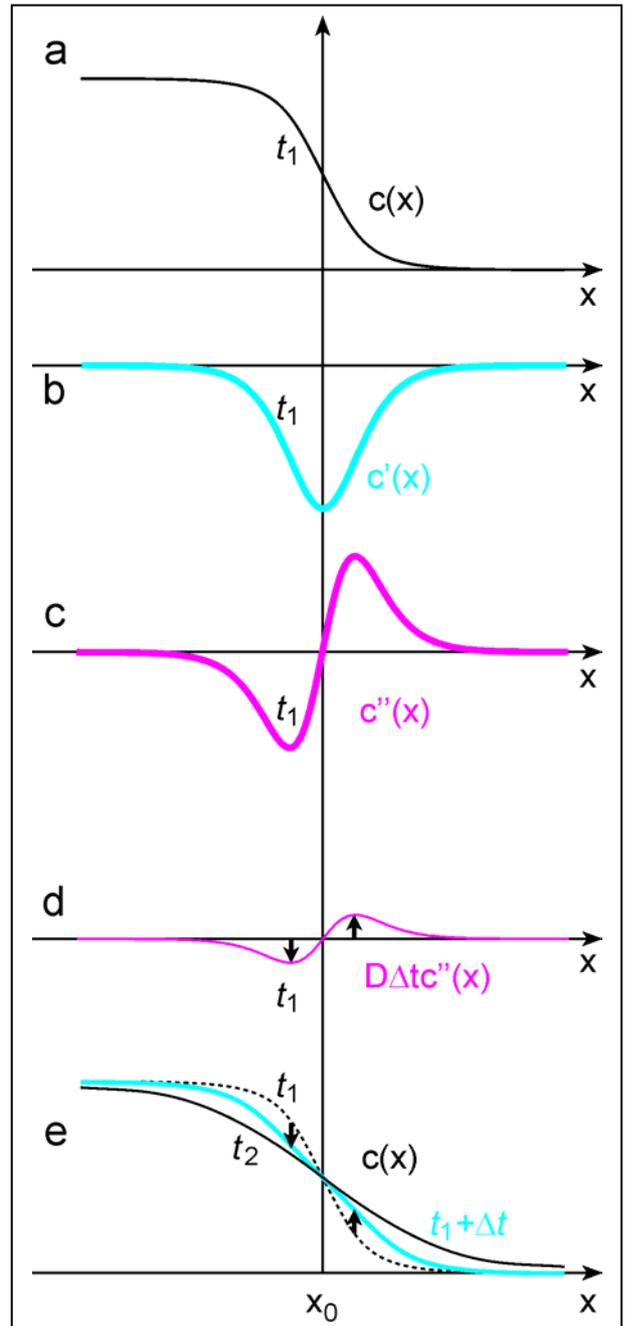
Meaning of Fick's second law

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.

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

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

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



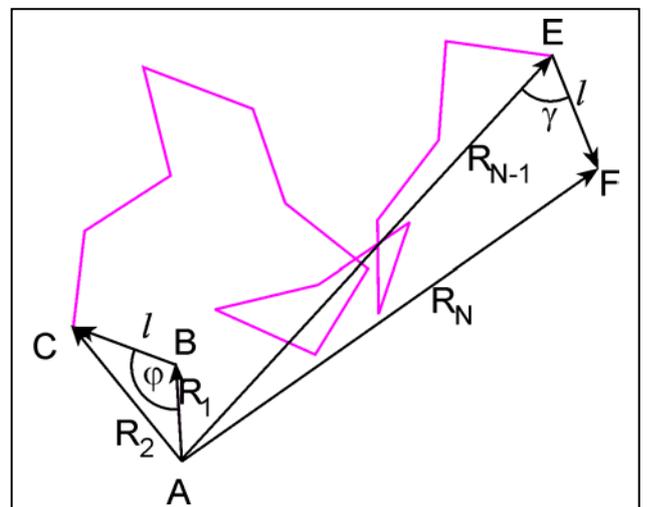
Random-walk problem

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

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

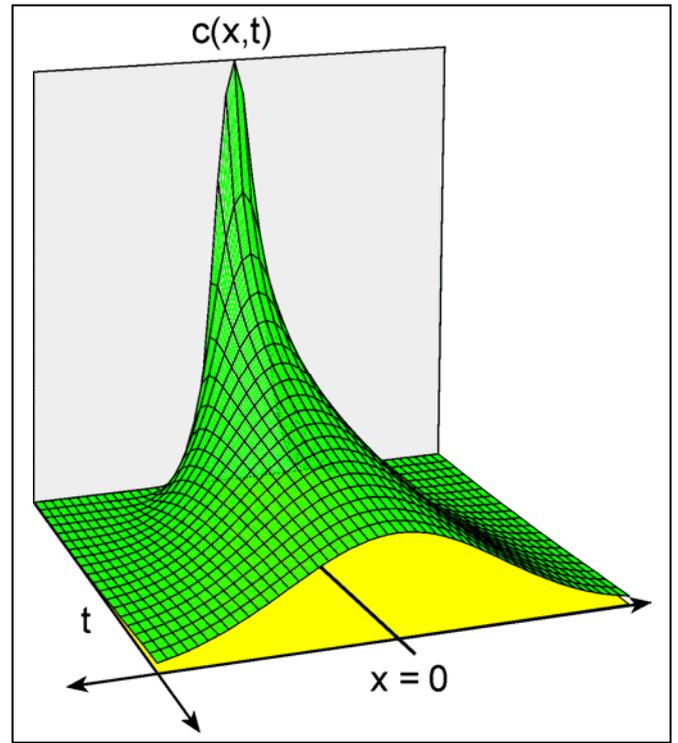
$$\overline{R_N^2} = \overline{R_{N-1}^2} + l^2 = Nl^2$$

$$\overline{R(t)} = \sqrt{3Dt}$$



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

(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 not know exactly, because it is not determinable, but we can calculate the average distance the sailor takes if the incident is repeated daily.)



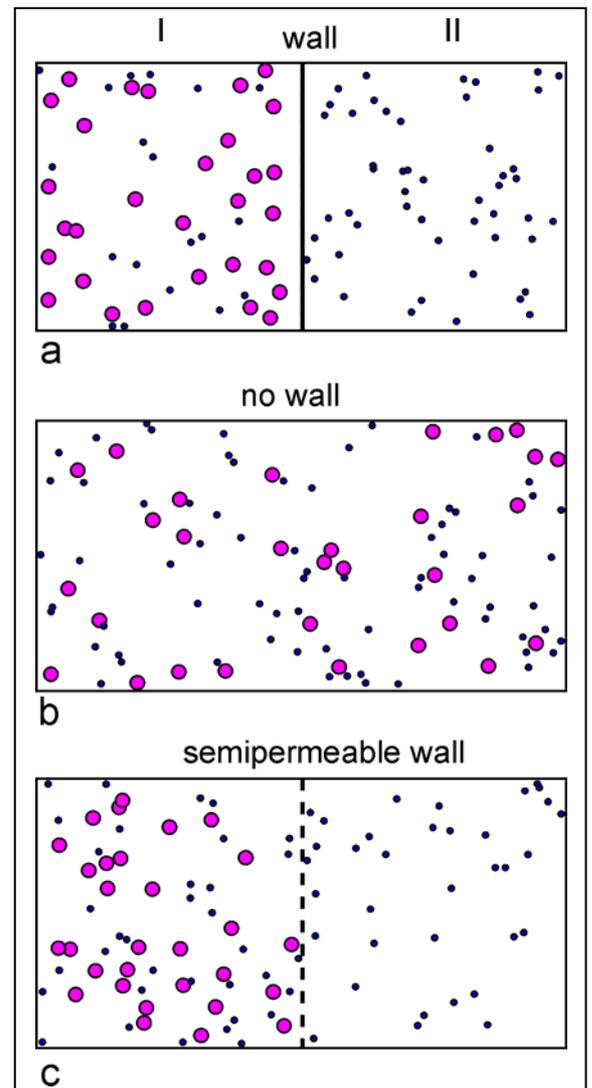
Osmotic phenomenon

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 outside 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.**

van t'Hoff law: $P_{\text{osmotic}} = cRT$.

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



Thermodiffusion:

one end of a U-shaped pipe with Na_2SO_4 -salt solution was heated with hot steam, and the other end was cooled with ice. Due to the temperature difference, dissolved salt migrated from the warmer section of the pipe to the colder section. (Ludwig–Soret-effect)

The law that describes this phenomenon is:

$$J_v = -L_T \frac{\Delta T}{\Delta x} .$$

We can see that this equation is very similar to Fick's first law, so the coefficient L_T corresponds in some sense to the diffusion coefficient.

Heat conduction

If the net particle flux is zero, means the same number of particles cross the wall from left to right as right to left, but the temperature-difference between the two sides is maintained, we are faced with another phenomenon (Fourier).

$$J_E = -\lambda \frac{\Delta T}{\Delta x} .$$