

2_Flows_Transport

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1 Flows and Transport in Liquids

1.1 Diffusion and Brownian Motion

```
[14]: import numpy as np
import matplotlib.pyplot as plt
import scipy.special as sp
import json
from ipywidgets import interact

%config InlineBackend.figure_format = 'retina'

with open('style.json', 'r') as fp:
    style = json.load(fp)

plt.rcParams.update(style)
```

For describing the transport and the dynamics of objects we need to write down some basic relations that will later govern our analysis. One is of course the continuity equation essentially stating that in the absence of sources or sinks, material flowing into a system has to move out of it as well. The flow is characterized by a current density \mathbf{j} . The flow through a surface is then governed by the normal components of the flow with respect to the surface having a normal \mathbf{n} .

The total flow through a surface is then

$$\int_S \mathbf{j} \cdot \mathbf{n} dS$$

If f is now some quantity (a density, probability density or other) that can be transported through a surface or exist inside a volume surrounded by an area, the total amount inside the volume is given by

$$\int_V f \cdot dV$$

The change of the total content inside the volume with time is then

$$\frac{d}{dt} \int_V f \cdot dV = \int_V \frac{df}{dt} \cdot dV$$

This then yields the continuity equation

$$\frac{df}{dt} + \nabla \mathbf{j} = 0 \quad (\text{Continuity Equation})$$

If we specifically consider the number density n and insert this as f

$$\frac{dn}{dt} + \nabla(n\mathbf{v}) = 0 \quad (\text{Continuity Equation for } n)$$

The continuity equation states that the amount of the quantity (such as mass, charge, or energy) within a defined system can only change if there is a flow of that quantity into or out of the system. More generally, the continuity equation may have a source term on the right side instead of the 0 when there is a production or destruction of the quantity in the volume.

As the next step, we would like to obtain an equation, which tells us about the flow of the density of objects, due to their Brownian motion. We consider a vertical wall of area A , which separates two regions. There are $N(x)$ on the left and $N(x + \Delta x)$ on the right of area A .

We can calculate the number of particles that goes through the area from the difference of the number of particles on the left and on the right side and divided by the area where the particles go through and the time τ they need to go through that this is the current density j

$$j = -\frac{1}{2} \frac{N(x + \Delta x) - N(x)}{A\tau}$$

The fact, the one half makes sure that we consider only 50% of the particles on the left side going through the area while the other 50% go further to the left.

We can also rewrite the number of particles in terms of the density n

$$n(x) \equiv \frac{N(x)}{A\Delta x}$$

where Δx spans a volume from which the particles travel through the area A . With the help of the density, we can replace the number of particles in the equation before and obtain an equation, which only contains the density of the particles.

$$j = -\frac{1}{2} \frac{n(x + \Delta x)A\Delta x - n(x)A\Delta x}{A\tau}$$

$$j = -\frac{1}{2} \frac{\Delta x^2}{\tau} \frac{n(x + \Delta x) - n(x)}{\Delta x}$$

You can see that the area A drops out of the equation and we can summarise the term with Δx^2 and τ into a new coefficient, which is the diffusion coefficient D . We just arrived at the Fick's first law, which is fixed first law, which tells us that the current density is proportional to the diffusion coefficient times the negative gradient of the density.

$$j = -D \frac{dn}{dx}$$

with

$$D = \frac{\Delta x^2}{2\tau}$$

In 3 dimensions this yields

$$\mathbf{j} = -D \nabla n \quad (1. \text{ Ficks Law})$$

which we can also combine with the continuity equation to give

$$\frac{dn}{dt} = D \nabla^2 n \quad (2. \text{ Ficks Law})$$

which describes the time evolution of the density n . This type of diffusion equation is found for many transport problems. We just have to exchange the density n by other densities:

flux	transport property	gradient
particles	diffusivity	particle density
charge	conductivity	potential
liquid	permeability	pressure
momentum	viscosity	momentum density
energy	heat conductivity	temperature

1.2 Diffusion in External Potential - Smoluchowski Equation

And some of the cases we may need to describe the diffusion in the presence of an external force field like we did already for the sedimentation problems we studied at the beginning of the course. The force is given by a potential gradient.

$$F = -\frac{dU}{dx}$$

If the force, for example, acts on a colloid in a liquid, a steady speed of the colloid will appear after a while, when the force is balanced by the frictional force in the liquid, which amounts to $F_s = -6\pi\eta Rv$, where R is the radius of the colloid, η is the viscosity of the liquid. The steady speed of the colloid in the liquid under a force F is therefore given as

$$v = -\frac{1}{\xi} \frac{dU}{dx}$$

where $\xi = 6\pi\eta R$ is the friction coefficient for a sphere. Therefore we have an additional current density due to the external force, which is given by $j = nv$ and therefore the total current density is given by

$$j = -D \frac{dn}{dx} - \frac{n}{\xi} \frac{dU}{dx}$$

As we will see later, the diffusion coefficient can be also written as $D = k_B T / \xi$, which results in

$$j = -\frac{1}{\xi} \left(k_B T \frac{dn}{dx} + n \frac{dU}{dx} \right)$$

using

$$\frac{d}{dx} \ln(n(x)) = \frac{1}{n(x)} \frac{dn}{dx}$$

we find

$$j = -\frac{1}{\xi} n \frac{d}{dx} \left(\underbrace{k_B T \ln(x) + U}_{\text{chemical potential}} \right) = -\frac{1}{\xi} n \frac{d\mu}{dx}$$

where we recognize the term in the bracket as chemical potential. In general, an inhomogeneous chemical potential drives currents in a system. This is the general version of Fick's first law, while Fick's second law results in

$$\frac{dn}{dt} = -\frac{dj}{dx} = \frac{1}{\xi} \frac{d}{dx} \left(k_B T \frac{dn}{dx} + n \frac{dU}{dx} \right)$$

or

$$\frac{dn}{dt} = \nabla \cdot \left(D \nabla n + n \frac{\mathbf{F}}{\xi} \right) \quad (\text{Smoluchowski equation})$$

This may be even further generalized and leads to the Fokker-Planck-Equation, which we leave out here in the discussion.

The time dependent diffusion equation

$$\frac{\partial}{\partial t} n(\vec{r}, t | \vec{r}_0, t_0) = D \nabla^2 n(\vec{r}, t | \vec{r}_0, t_0)$$

can be solved for given boundary and initial conditions. For the following

$$n(\vec{r}, t \rightarrow t_0 | \vec{r}_0, t_0) = \delta(\vec{r} - \vec{r}_0) \quad (\text{initial condition})$$

$$n(|\vec{r}| \rightarrow \infty, t | \vec{r}_0, t_0) = 0 \quad (\text{boundary condition})$$

we obtain the Greens function

$$n(\vec{r}, t | \vec{r}_0, t_0) = \frac{1}{(4\pi D(t - t_0))^{3/2}} e^{-\frac{(\vec{r} - \vec{r}_0)^2}{4D(t - t_0)}} \quad (\text{Greens function})$$

for the diffusion equation and the corresponding boundary conditions. The Greens function is the impulse response. With the help of it, new solutions for any initial condition can be constructed. Lets assume we have an initial condition given by

$$n(\vec{r}, t \rightarrow 0) = f(\vec{r}_0)$$

then the time dependent solution is a superposition of the Greens function solutions

$$n(\vec{r}, t) = \int n(\vec{r}, t | \vec{r}_0, t_0) f(\vec{r}_0) d\vec{r}_0$$

Let is quickly consider the solution in 1 dimension and derive some simple properties of it. The first is the mean position of the density. The mean position is calculated by

$$\langle x \rangle = \int_{-\infty}^{+\infty} x \frac{\Delta}{\sqrt{4\pi D(t - t_0)}} \cdot e^{-\frac{(x - x_0)^2}{4D(t - t_0)}} dx$$

and the result states

$$\langle x \rangle = x_0$$

that it is constant, i.e. the initial position is stationary even though the particles spread in space. This is of course expected as there is no drift in the system to one or the other direction. As the particles still spread in space, the change is in the second moment of the distribution, which is the variance calculated by

$$\langle (x - x_0)^2 \rangle = \int_{-\infty}^{+\infty} (x - x_0)^2 n(x, t) dx = 2Dt$$

The result of this is corresponds to the mean squared displacement of a single particle. The variance of the distribution grows linearly in time and the coefficient characterizing the spread of the particles is the diffusion coefficient D . The law obtained here, can be generalized to $d = 3$ dimensions by

$$\langle (\mathbf{r} - \mathbf{r}_0)^2 \rangle = 2dDt = 6Dt$$

A mean distance travelled is therefore related to the square root of time. This diffusion processes are rapid at short distances but very slow for largedistance as can be seen from the table below.

Times for one-dimensional diffusion in aqueous solution

Object	Length	Diffusion coefficient	Time
H^+	0.20 nm	$2.5 \times 10^9 \text{ s}^{-1}$	$2.5 \times 10^{-10} \text{ s}$
Protein	1 nm	$10 \times 10^8 \text{ s}^{-1}$	10^{-8} s
Organelle	1 μm	10^7 s^{-1}	10^{-7} s

Note: H^+ : Radius = 0.1 nm, $T = 25^\circ\text{C}$, $D = 1000 \mu\text{m}^2/\text{s}$
Protein: Radius = 1 nm, viscosity = 0.001 Pa·s, $T = 25^\circ\text{C}$, $D = 100 \mu\text{m}^2/\text{s}$

1.2.1 Application: Fluorescence Recovery after Photobleaching

One application of our Greens function approach that is frequently used in studying biological materials is Fluorescence Recovery after Photobleaching or short **FRAP**.

Initial condition:

$$n(x, t_0) = \Theta(-a - x) + \Theta(x - a)$$

Boundary Condition

$$\lim_{|x| \rightarrow \infty} n(x, t) = 0$$

Greens Function

$$n(x, t | x_0, t_0) = \frac{1}{\sqrt{4\pi D(t - t_0)}} e^{-\frac{(x - x_0)^2}{4D(t - t_0)}}$$

Therefore the total solution

$$n(x, t) = \int_{-\infty}^{+\infty} dx_0 n(x, t | x_0, t_0) \cdot [\Theta(-a - x) + \Theta(x - a)] \quad (1)$$

$$= \int_{-\infty}^{-a} dx_0 \frac{1}{\sqrt{4\pi D(t - t_0)}} e^{-\frac{(x - x_0)^2}{4D(t - t_0)}} \quad (2)$$

$$= \int_a^{\infty} dx_0 \frac{1}{\sqrt{4\pi D(t - t_0)}} e^{-\frac{(x - x_0)^2}{4D(t - t_0)}} \quad (3)$$

The solution of the integration is

$$n(x, t) = 1 - \frac{1}{2} \left(\operatorname{erf} \left[\frac{x + a}{2\sqrt{D(t - t_0)}} \right] - \operatorname{erf} \left[\frac{x - a}{2\sqrt{D(t - t_0)}} \right] \right)$$

with erf being the error function

$$\operatorname{erf}(x) = \frac{1}{\sqrt{\pi}} \int_{-x}^x e^{-t^2} dt = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt$$

```
[15]: ## Example of a FRAP density profile
def heaviside(x):
    return np.where(x >= 0, 1, 0)

def n_step(x, a):
    return heaviside(-a - x) + heaviside(x - a)
```

```

def n_solution(x, a, D, t, t0):
    term1 = sp.erf((x + a) / (2 * np.sqrt(D * (t - t0))))
    term2 = sp.erf((x - a) / (2 * np.sqrt(D * (t - t0))))
    return 1 - 0.5 * (term1 - term2)

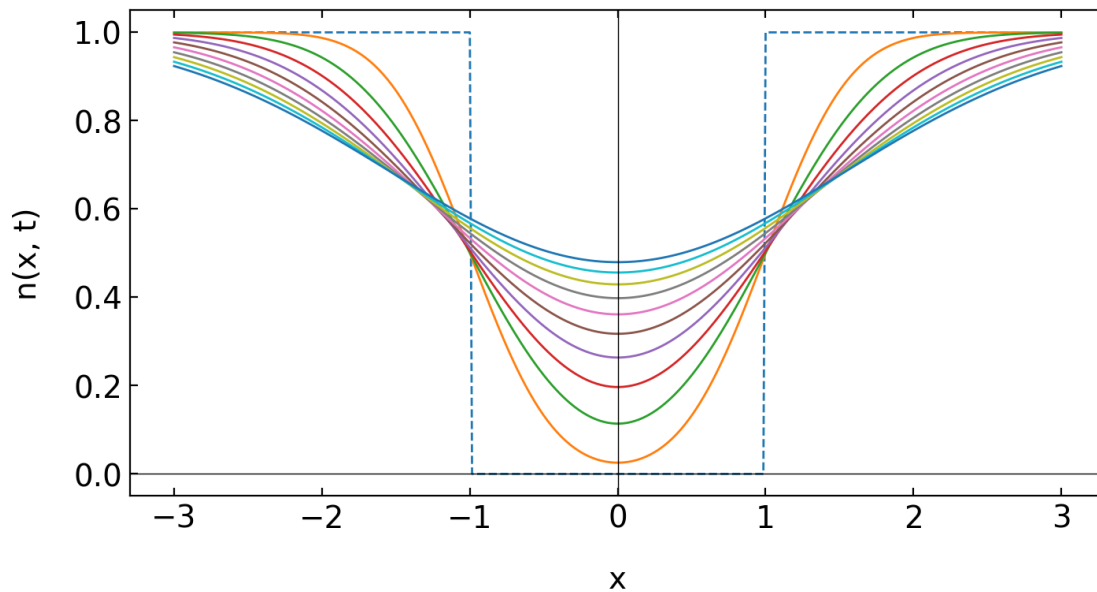
# Parameters
a = 1 # size of the bleached region
D = 0.1 # diffusion coefficient
t0 = 0 # initial time
times = np.arange(1, 11) # times from 1 to 10 seconds
x = np.linspace(-3, 3, 400) # range of x values

plt.figure(figsize=(8, 4))
plt.plot(x, n_step(x, a), label='n(x, t0)', linestyle='--')

for t in times:
    plt.plot(x, n_solution(x, a, D, t, t0), label=f'n(x, t={t}s)')

plt.xlabel('x')
plt.ylabel('n(x, t)')
plt.axhline(0, color='black', linewidth=0.5)
plt.axvline(0, color='black', linewidth=0.5)
plt.show()

```



We can also characterize the amount of density in the bleached region as a function of time. This gives a single time trace, which we can analyze to obtain the diffusion coefficient

$$N(t, t_0) = \int_{-a}^{+a} n(x, t) dx$$

The integration of the previously obtained density then results in

$$N(t, t_0) = \frac{\sqrt{D(t-t_0)}}{a\sqrt{\pi}} \left(1 - \exp \left[-\frac{a^2}{D(t-t_0)} \right] \right) + 1 - \operatorname{erf} \left[\frac{a}{\sqrt{D(t-t_0)}} \right]$$

which is plotted below.

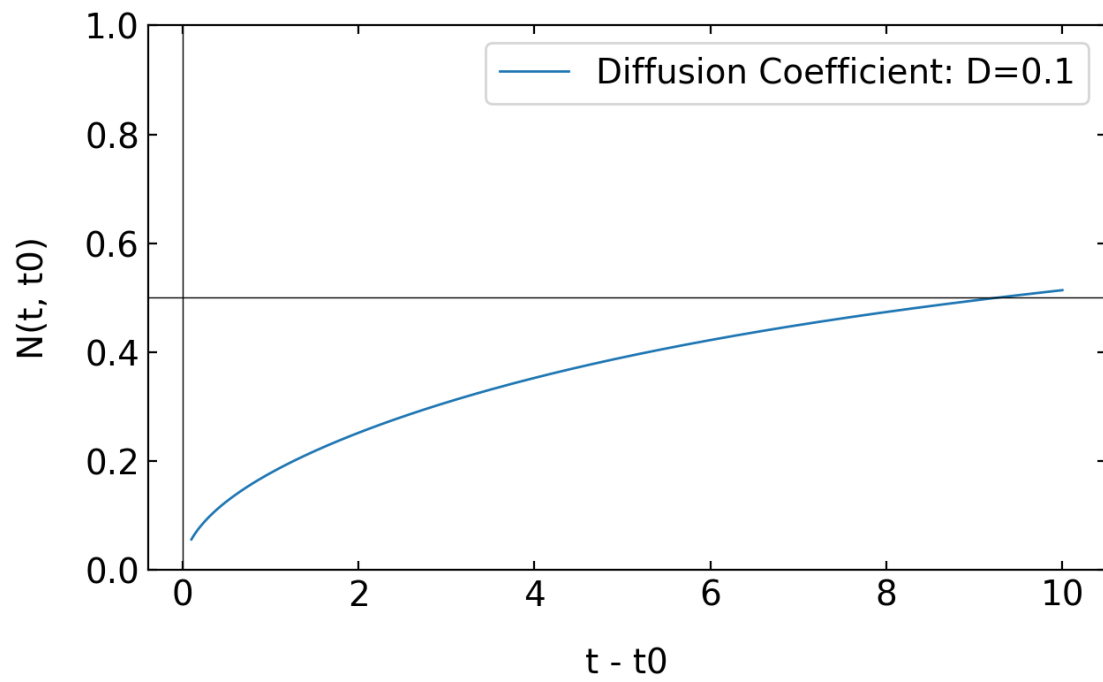
```
[26]: def N(t, t0, D, a):
    term1 = (np.sqrt(D * (t - t0)) / (a * np.sqrt(np.pi))) * (1 - np.exp(-a**2 / (D * (t - t0))))
    term2 = 1 - sp.erf(a / np.sqrt(D * (t - t0)))
    return (term1 + term2)

# Interactive plotting function
def plot_function(D):
    a = 1 # constant a
    t0 = 0 # initial time t0
    t = np.linspace(0.1, 10, 400) # time range from 0.1 to 10

    plt.figure(figsize=(7, 4))
    plt.plot(t, N(t, t0, D, a), label=f'Diffusion Coefficient: D={D}')
    plt.xlabel('t - t0')
    plt.ylabel('N(t, t0)')
    plt.axhline(0.5, color='black', linewidth=0.5)
    plt.axvline(0, color='black', linewidth=0.5)
    plt.ylim(0, 1)
    plt.legend()
    plt.show()

# Create the widget
#interact(plot_function, D=(0.01, 1.0, 0.01));

plot_function(0.1)
```

[]: