

Theory of Diffusion

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1 Introduction

According to thermodynamics, any isolated system tends to evolve towards an equilibrium state by maximizing its entropy. As the equilibrium state is usually characterized by homogeneity, matter in an out-of-equilibrium system will move to eliminate variances in its concentration [1]. This behaviour is called diffusion and occurs in all forms of matter at non-zero temperature. Every flow of mass, that is not due to external forces or bulk flow, falls under this category.

In this handout, we will first explore the mechanisms connected to diffusion. In the second half, we will investigate how diffusion fits into the picture of a general continuum description of fluids, leading to us to the Navier-Stokes equations.

2 Diffusion

The term *diffusion* might most commonly be associated with the spreading of a liquid in another in order to reduce the gradient in concentration, like a drop of paint dissipating in a glass of water. However, even in this simple system, several different mechanisms cause movement in the liquid. The paint molecules, moving along their own concentration gradient, will interact with each other and the surrounding water, but even every single water molecule will move throughout the glass due to its thermal motion. As none of these effects are caused by a bulk motion, like a current in the water, they all fall under the umbrella term *diffusion*.

In the following sections, we will discuss the differences and analogies between these processes, starting from the well-known concentration equalisation and ending at the atomic level with the stochastic motion of single particles.

2.1 Transport diffusion

Following the work of Thomas Graham, who recognized, that the diffusiveness of gases must depend on their density, Adolf Fick saw the analogy of the process to heat conduction. He found, that the flow \mathbf{j} of a substance is proportional to the gradient of its concentration ρ and formulated his *Fick's first law of diffusion* [1]:

$$\mathbf{j} = -D_t \nabla \rho. \quad (1)$$

This first law is nothing more or less than the definition of the diffusion coefficient D in a continuum.

It should be noted, that we use the mass flow and density here, instead of the common formulation with the particle flow and concentration c . This does not change any derivation, but will later allow us to insert our results directly into the general fluid mechanics. The index t denotes, that the force in form of the gradient produces a net flux of mass,

hence the name *transport diffusion*.

While Fick's description is certainly the most common for this effect, the flow have other causes, like gradients in chemical potential, pressure or temperature.

Especially the concept of the chemical potential gradient should be remembered, as a concentration gradient doesn't have to result in a diffusive mass flow. A simple example would be the interface between two immiscible fluids, like oil and water, where no transport diffusion occurs, despite the massive gradient in concentration for each liquid. The formulation of Fick's law using the chemical potential μ : $\mathbf{j} = -L\nabla\mu$, can therefore be considered more general. The transport coefficient L is in this case named after Lars Onsager [2], who is famous for his Onsager theory of the interactions of just these transport coefficients.

But - while the conversion between both descriptions is possible - Fick's law is definitely more prominent, so we will also stick with the diffusion coefficient $D_{(t)}$.

To describe, how the density in equation (1) will change due to the flow, we combine it with the conservation of mass. In the continuum, mass is given as the integral of the density over a volume V : $\int_V \rho dV'$. For the mass in the volume to change, density needs to flow over the surface ∂V of the volume. This means, that the flow velocity \mathbf{u} has to have a component perpendicular to said surface. The change rate of mass in V is therefore given by

$$\frac{\partial}{\partial t} \int_V \rho dV' = - \int_{\partial V} \rho \mathbf{u} \cdot \mathbf{n} dS = - \int_V \nabla \cdot (\rho \mathbf{u}) dV', \quad (2)$$

where we used Gauss's theorem in the second equality. Left and right side can be combined into

$$\int_V \left[\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) \right] dV' = 0, \quad (3)$$

which has to hold for any volume V . Therefore, the integrand is itself 0:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = \frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{j} = 0. \quad (4)$$

Here we used the of flow and flow velocity $\mathbf{j} = \rho \mathbf{u}$ and arrived at the conservation law of mass.

Now we can insert Fick's first law (Eq. (1)) and obtain Fick's second law [4], also known as the *diffusion equation*:

$$\frac{\partial \rho}{\partial t} = \nabla \cdot (D_t \nabla \rho). \quad (5)$$

Most of the time, the diffusion coefficient is assumed to be constant, giving us the Laplacian of ρ on the right:

$$\frac{\partial \rho}{\partial t} = D_t \nabla \cdot (\nabla \rho) = D_t \Delta \rho. \quad (6)$$

The similarity to the heat equation is now obvious, and we can find a fundamental solution of the diffusion equation of a form similar to the heat kernel:

$$\frac{\rho}{M} = \frac{1}{(4\pi D_t)^{\frac{3}{2}}} e^{-\mathbf{r}^2/4D_t t} \quad (7)$$

The fundamental solution gives the density at a certain place \mathbf{r} and time t , if a point of mass M is introduced at the origin at time $t = 0$.

2.2 Self-diffusion

The motion due to thermodynamic gradients is certainly of the most interest in larger-scale systems, where the dimensions of the system are large compared to the size and movement of single particles, and we can describe the fluid as a continuum. In porous media however, we also have confined spaces so small, that any macroscopic gradients can be neglected and the thermal motion of the molecules dominate their behaviour. But also in larger systems at thermal equilibrium, when all gradients have vanished, is the thermal motion the last form of diffusion, that has to be considered.

The self-diffusion is a measure for the mobility of a single particle in a bulk of otherwise identical particles. As the notion of a particle diffusion in vacuum makes no sense, since the thermal motion is created by the interaction with the other molecules in the bulk, the idea is to imagine a single marked particle performing its Brownian motion. As self-diffusion is deeply connected to Brownian motion, it can also be modelled with a random walk. An important quantity for characterizing a random walk model is the mean square displacement

$$\langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle = \frac{1}{N} \sum_{i=1}^N |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2. \quad (8)$$

Here, $\mathbf{r}(t)$ denotes the location of a particle at time t and we averaged over an ensemble of N particles. Using the diffusion equation (Eq. (6)), it is possible to assign a diffusion coefficient even to the mean square displacement. Apart from the spread of a certain amount of mass starting at a single point, the fundamental solution (Eq. (7)) of Fick's second law can also be interpreted as the probability to find a single molecule, that started at the origin at time 0, at another place \mathbf{r} at time t . Calculating the mean square displacement of this distribution yields

$$\langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle = 6D_s t, \quad (9)$$

thus defining a self-diffusion coefficient D_s .

It is important to emphasize, that D_t and D_s describe fundamentally different processes, as the transport diffusivity refers to a system with driving forces (gradients) resulting

in net mass flux, while self-diffusion does not. The two coefficients are not the same, equation (9) is an independent definition from Fick's first law.

A completely synonymous definition to the mean square displacement uses the fact, that a displacement can be written as an integral over the velocity \mathbf{v} :

$$\mathbf{r}(t) - \mathbf{r}(0) = \int_0^t \mathbf{v}(t') dt'. \quad (10)$$

Inserted into equation (9), we get a so-called Green-Kubo relation

$$D_s = \frac{1}{6} \langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle = \frac{1}{3} \int_0^\infty \left\langle \frac{1}{N} \sum_{i=1}^N \mathbf{v}_i(t) \cdot \mathbf{v}_i(0) \right\rangle dt, \quad (11)$$

that relates the transport coefficient to the velocity autocorrelation function (the last bracket).

As in the example of ink in water, we might have more than one kind of particle diffusing within each other. A marked particle in a mixture of different particles is called a tracer. The *tracer diffusion coefficient* is equal to the self-diffusion coefficient in the limit of an infinitely diluted mixture.

2.3 Collective diffusion

The fact, that tracer diffusion and self-diffusion generally don't have to match, means that the motion of a particle doesn't only depend on its own velocity, but is correlated with every other particle as well. This means, that particles diffuse as a collective. Analogous to equation (11), we can define a collective diffusion coefficient by taking into account the interaction with every particle:

$$D_c = \frac{1}{3} \int_0^\infty \left\langle \frac{1}{N} \sum_{i=1}^N \mathbf{v}_i(t) \cdot \sum_{j=1}^N \mathbf{v}_j(0) \right\rangle dt. \quad (12)$$

The term inside the brackets is the complete velocity correlation function. As the velocity autocorrelation function is part of the correlation function, the collective diffusion coefficient is constituted of the self-diffusion and a cross-correlation term D_ξ :

$$D_c = D_s + D_\xi. \quad (13)$$

For low-density fluids, the cross-correlation term becomes neglectable and the collective diffusion approaches the self-diffusion.

When talking about the collective behaviour of particles under thermal fluctuation, the fluctuation-dissipation theorem [11] should be mentioned. Used by Einstein to describe

the connection of Brownian motion and drag, it builds a bridge between the microscopic world and the macroscopic continuum description of fluids. In a general form, it states that any process that dissipates heat is connected to a reverse process with origins in thermal fluctuations. In the case of Brownian motion, the thermal fluctuations of the fluid surrounding the Brownian particle transfer kinetic energy. On the other hand, if the Brownian particle has kinetic energy and moves through the fluid, the thermal fluctuations cause the drag, that turns the particles kinetic energy into dissipating heat. From this concept, it is possible to derive the Stokes-Einstein equation [5]

$$D = \frac{k_{\text{B}}T}{6\pi\eta R} \quad (14)$$

for a spherical particle with radius R . Here, k_{B} is the Boltzmann constant and T the temperature and η the dynamic viscosity of the fluid surrounding the particle. Therefore, this equation connects the macroscopic fluid viscosity with the microscopic diffusion coefficient.

3 Continuum mechanics

We will now try to make the connection from microscopic diffusion to macroscopic fluid mechanics on an even broader scale and derive fundamental equations governing the dynamics of any fluid substance. For this purpose, two principles have to be translated into the continuum description. The mass conservation (continuity equation) and momentum conservation (Newton's second law).

3.1 Reaction-diffusion-advection equation

We did already derive the conservation law of mass

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{j} = 0 \quad (15)$$

in the first section to be able to talk about mass transport. We then replaced the flow by the density gradient using Fick's law. However, in a more general case, especially in a mixture of different fluids, both effects can occur. Here, flow can emerge both from a concentration gradient of the substance of interest, as well as a bulk motion in the solution. Transport due to bulk motion of a fluid is called advection, while any other form of transport, as noted in the introduction, is called diffusion. The combination of both effects is the total transport called convection. In the most general case, we even consider, that the different substances might react with each other, creating or removing the substance of interest in the equation. As this contribution can depend on the density or any other parameter, we simply denote it with a reaction term R [10]. This results in

the full reaction-diffusion-advection equation. This most general of mass conservation equations is therefore given by

$$\frac{\partial \rho}{\partial t} = \nabla \cdot (D \nabla \rho) - \nabla \cdot (\rho \mathbf{u}) + R \quad (16)$$

The interaction of the two contributions of flow might again be best imagined using the drop of paint, this time dropping it into a water current. For small times, it will be carried along with the flow, still visible as a point of colour. But shortly after, the diffusion part will make it dissolve out of sight.

3.2 Navier-Stokes equations

Next, we want to obtain an equation for the general momentum of a fluid. In classical mechanics, this is given by Newton's second law

$$\mathbf{F} = m \cdot \mathbf{a} = m \cdot \dot{\mathbf{v}}. \quad (17)$$

It governs the dynamics of mass points with mass m at a point \mathbf{r} with a velocity \mathbf{v} . Now let's take a look at the continuum side. Just like in the discrete case, we expect a force to change our liquid's velocity. Therefore we take the time derivative of the flow velocity

$$\frac{D}{Dt} \mathbf{u}(\mathbf{r}, t) = \frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{u}, \quad (18)$$

where $\frac{D}{Dt}$ denotes the total derivative with respect to time, also called the material derivative.

We subdivide the forces, that cause this change in velocity, into two categories:

External forces, like gravity, that can be written as a force per unit mass \mathbf{f} , which acts on a volume V according to $\int_V \rho \mathbf{f} dV$.

Internal forces, that act on the volume through its bounding surface, because the volume of liquid is itself surrounded by liquid, for example pressure. These forces act according to $\int_{\partial V} \mathbf{n} T dS$, with \mathbf{n} being the normal vector to the surface element dS and the stress tensor $T = \{T_{ij}\}$. Again, we can change this integral to one over the volume, this time using Green's theorem: $\int_V \nabla \cdot T dV$.

Like when we derived the mass conservation equation, the integral can be neglected due to the integration volume again being arbitrary:

$$\int_V \rho \frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{u} dV = \int_V (\rho \mathbf{f} + \nabla \cdot T) dV \Rightarrow \rho \frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{u} = \rho \mathbf{f} + \nabla \cdot T \quad (19)$$

We have now arrived at a set of general equations (Eq. (16) and Eq. (19)), that describe the dynamics of all fluids. Because of this generality, they are however unsolvable for arbitrary systems. For the rest of this handout, we will deal with common assumption, that allow us to solve these equations for our model systems.

First, we still need to specify the stress tensor. Most fluids can be described as Stokesian, meaning that they are homogeneous and isotropic [3]. Commonly, they are also Newtonian, so their stress tensor depends linearly on the deformation. Inserting the Newtonian stress tensor into equation (19) yields

$$\rho \frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{u} = -\nabla p + (\lambda + \eta) \nabla(\nabla \cdot \mathbf{u}) + \eta \Delta \mathbf{u} + \rho \mathbf{f}. \quad (20)$$

This is called the Navier-Stokes equation.

Let's look at the different terms. The total change in the flow velocity on the left side can be caused by four different contributions: A pressure gradient ∇p , a deformation term $\propto \nabla(\nabla \cdot \mathbf{u})$ with the dampening factors λ and η , a diffusive term $\propto \Delta \mathbf{u}$, reduced by the dynamic viscosity η and an external force \mathbf{f} .

3.3 Characterizing the flow

Now that we know the Navier-Stokes equation, we can see it in its full partial differential equation glory. To this day, we do not even understand its potential and challenges. It is a millennium problem, to prove (or disprove), that a solution even exists for any problem in three dimension. Let me adjust that: We still have to make two simplifications to get to the form, that the millennium problem is formulated for.

To understand, which simplifications we can justify, we need to characterize our system. This is done using dimensionless numbers that give the ratios of certain flow parameters.

Péclet number

$$\text{Pe} = \frac{Lu}{D} \hat{=} \frac{\text{advective transport}}{\text{diffusive transport}} \quad (21)$$

The Péclet number gives the ratio of the advective and diffusive transport rates in the reaction-diffusion-advection equation (Eq. (16)) [12]. L describes a characteristic length of the system, e.g. the diameter of a pore in a porous medium. For high Péclet numbers (and without sinks or sources due to reactions), the reaction-diffusion-advection equation can again be approximated by the simple mass conservation equation (Eq. (15)), while low Péclet numbers give us the diffusion equation (Eq. (6)).

Mach number

$$\text{Ma} = \frac{u}{c} \hat{=} \frac{\text{flow velocity}}{\text{speed of sound}} \quad (22)$$

The Mach number is the ratio of the flow velocity to the fluid's speed of sound [13]. In the standard case of dynamics far under the speed of sound, the Mach number is therefore

small. This allows the important simplification to treat the fluid as incompressible. As the density is constant, the continuity equation (Eq. (15)) now only demands the flow velocity to be divergence-free. Also, the deformation term in the Newtonian Navier-Stokes equation (Eq. (20)) vanishes. This results in the system of equations

$$\begin{aligned}\nabla \cdot \mathbf{u} &= 0 \\ \frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{u} &= -\nabla p + \eta \Delta \mathbf{u} + \rho \mathbf{f}.\end{aligned}\tag{23}$$

Proving the existence of a solution in three dimensions to these equations is worth a prize of one million US\$ [9]!

Reynolds number

$$\text{Re} = \frac{\rho u L}{\eta} \hat{=} \frac{\text{inertial forces}}{\text{viscous forces}}\tag{24}$$

The Reynolds number is defined as the ratio of the inertial and the viscous forces [8]. A high Reynolds number is often understood as a criterion for turbulent flow. In porous media, however, we are on the other side of the spectrum. Flow is here often so slow, that inertial forces can be neglected. The inertial contributions can be found on the left side of the Navier-Stokes equation, so that in the case of very small Reynolds numbers, it converts into the simple Stokes equation

$$0 = -\nabla p + \eta \Delta \mathbf{u} + \rho \mathbf{f}.\tag{25}$$

Knudsen number

$$\text{Kn} = \frac{l}{L} \hat{=} \frac{\text{mean free path}}{\text{system size}}\tag{26}$$

The Knudsen number is the ratio of the mean free path of the particles to the characteristic length L of the system [7]. Higher Knudsen numbers mean, that the particles collide more often with the system boundaries than other particles, making surface properties and interactions more important. For small Knudsen numbers, these effects can be neglected. However, for very high Knudsen numbers, the Navier-Stokes description can even break down, since the particles interact to rarely with each other to consider them a collective continuum.

Capillary number

$$\text{Ca} = \frac{\eta u}{\gamma} \hat{=} \frac{\text{viscous drag forces}}{\text{surface tension}}\tag{27}$$

The Capillary number relates the viscous forces to a surface tension γ [6]. For porous media, the small velocities already discussed for the Reynolds number mean, that interfacial forces often dominate the system.

4 Summary

In this handout, we investigated the different processes underlying diffusion. We saw, that this includes driven macroscopic transport due to thermodynamic gradients as well as force-free random-walk-like behaviour on the microscale. Still, for all these mechanisms, it is possible to define a diffusion coefficient D according to Fick's laws. For the macroscopic transport diffusion, this coefficient is linked to a concentration gradient, while for the microscopic self- and collective diffusion, it can be defined using velocity correlation functions.

The idea, that microscopic fluctuations lead to macroscopic properties like viscosity led us to look into a general description of fluid mechanics including diffusion using the mass conservation and Navier-Stokes equations. As the full equations are almost unsolvable, we analysed, what simplifications we could justify, knowing the properties of our system. The Péclet number allows us to prioritize or neglect diffusion. At low Mach numbers we can treat our fluid as incompressible. For the small Reynolds numbers in porous media, inertial forces can be neglected, resulting in the Stokes equation. Knudsen and Capillary number give us an idea, how much surface interactions and capillary effects affect our system.

Using these common assumptions, we are able to calculate the dynamics of our fluid systems despite the immense complexity diffusion and fluid mechanics have to offer.

5 Sources

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