4. Mass conservation law part II-diffusion

To fully understand "what's it all about" we will have to look back both to mass conservation law and constitutive equations, since diffusion equation is simply mass conservation law written for diffusion process. We will start with differential form of mass conservation law, from equation (1.26):

$$\nabla \cdot (\rho \vec{u}) + \frac{\partial \rho}{\partial t} = r \tag{4.1}$$

In exercise 2.5. we already introduced idea of superposition of mass velocities (velocity of the river + diffusion velocity). Now we will use that idea but in more general form. Let's formulate equation for a mass flux in a multi-component system:

$$\vec{J}_i = \rho_i \vec{u}_i^{diff} + \rho_i \vec{u}^{drift} \tag{4.2}$$

Where:

$\vec{u}_i^{diff}$ – velocity of mass resulting from diffusion processes

$\vec{u}^{drift}$ – velocity of mass resulting from other processes like convection, stress etc.

After inserting (4.2) into (4.1):

$$\nabla \cdot (\rho_i \vec{u}_i^{diff} + \rho_i \vec{u}^{drift}) + \frac{\partial \rho_i}{\partial t} = r_i \tag{4.3}$$

As a final result we obtain:

$$\overbrace{\frac{\partial \rho_i}{\partial t}}^{\text{accumulation}} + \underbrace{\nabla \cdot \rho_i \vec{u}_i^{diff}}_{\text{diffusion term}} + \overbrace{\nabla \cdot \rho_i \vec{u}^{drift}}^{\text{convection term}} = \underbrace{r_i}_{\text{source/sink}} \tag{4.4}$$

Now we will formulate diffusion equation for the most basic system. Following assumptions are made:

- $\vec{u}^{drift} = 0$
- $r_i = 0$
- $\vec{u}_i^{diff} = -D_i \frac{1}{\rho_i} \nabla \rho_i \quad while \quad J_i^{diff} = \rho_i \vec{u}_i^{diff} \quad \Longrightarrow \quad J_i^{diff} = -D_i \nabla \rho_i \quad Fick's\ 1st\ law$
- $D_i = const$

After taking under consideration this assumptions, equation (4.4) can be expressed as:

$$\frac{\partial \rho_i}{\partial t} = -\nabla \cdot D_i \nabla \rho_i \quad \Rightarrow \quad \frac{\partial \rho_i}{\partial t} = D_i \Delta \rho_i \tag{4.5}$$

Equation (4.5) is well known as **Fick's 2nd law.**

In the previous paper, analogy between heat flux and mass flux were shown. This analogy is still true for this case:

$$\frac{\partial T}{\partial t} = k \Delta T \tag{4.6}$$

(4.6) is so called “heat equation”, and it’s full analogy to Fick’s 2nd law is clearly visible. In fact from the modeling point of view this equations are exactly the same.

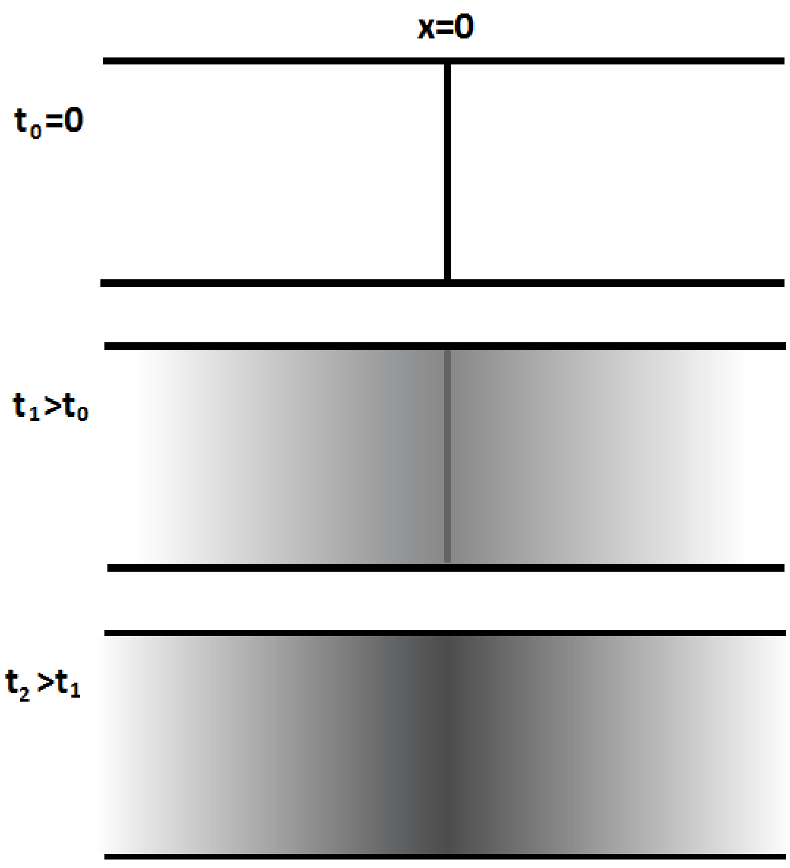
Although (4.5) was derived for the most basic diffusion process, analytical solutions are known only for specific cases and they require extensive mathematical knowledge. One of such cases is presented in Example 4.1. (**remember, it’s just to show how it looks like!**)During our classes we will focus on solving (4.5) for steady-state situations which are much easier, what is presented in Example 4.2.

To solve any differential equation, boundary and initial conditions are needed. The most common ones are:

- Neumann boundary condition (NBC)– it specifies the values that the derivative of our function takes on the boundary of the domain. In our case NBC define fluxes through boundary
- Dirichlet boundary conditions (DBC) – it specifies the values of our function on the boundary of the domain. In our case DBC defines value of concentration (or temperature for heat transport) on the boundary of the system.

Example 4.1.

Calculate solution for instantaneous planar diffusion source in an infinite medium. If you can’t stand mathematics, just skip to the final conclusion (**written in bold**) because it will be useful later.



Solution

We are solving equation:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \tag{4.7}$$

which is a Fick's 2nd law for one dimensional case. This equation is a second order partial differential equation. To obtain a unique solution, we will need two different conditions. In our case we release a quantity of diffusant M at the plane *x*=0 and *t*=0 into surrounding space (see the picture). The diffusant will spread into two adjacent material bodies occupying the half-spaces 0< x <∞ and −∞< x<0. Because of that, our conditions will be:

- Initial condition

$$at\ t = 0, c(x,0) = 0\ \ for\ all\ x \neq 0$$

- Boundary condition

$$c(\pm\infty, t) = 0$$

From all those assumptions, following conclusion can be drawn:

$$\int_{-\infty}^{\infty} c(x,t) = M$$

To solve our equation, we will use Laplace transforms. Laplace transform of a function *f(t)* is given by:

$$\mathcal{L}[f(t)] = \int_0^\infty f(t)e^{-st}dt = \overline{f(s)}$$

Now we will apply Laplace transform to both sides of (4.7):

$$Right\ side: \mathcal{L}[f(t)] = D\int_0^\infty \frac{\partial^2 c}{\partial x^2}e^{-st}dt = D\frac{\partial^2}{\partial x^2}\int_0^\infty ce^{-st}dt = D\frac{d^2\bar{C}}{dx^2}$$

Where:

$$\bar{C} = \int_0^\infty ce^{-st}dt$$

For the second side:

$$Left\ side: \mathcal{L}[f(t)] = \int_0^\infty \frac{\partial c}{\partial t}e^{-st}dt = ce^{-st}|_0^\infty - s\int_0^\infty -ce^{-st}dt = -c(x,0) + s\bar{C}$$

Now, after combining both sides we will get:

$$\frac{s}{D}\bar{C}(x,s) - \frac{d^2\bar{C}(x,s)}{dx^2} = \frac{c(x,0)}{D}$$

Thanks to our initial condition it can be reduced to:

$$\frac{s}{D}\bar{C}(x,s)-\frac{d^2\bar{C}(x,s)}{dx^2}=0$$

Our problem became now an ordinary differential equation which is much easier to solve. As a result we obtain:

$$\bar{C}=Ae^{x\sqrt{s/D}}+Be^{-x\sqrt{s/D}}$$

Now we can separate this solution for two cases: mass going left (x<0) and mass going right (x>0). To fulfill our boundary conditions ($c(\pm\infty,t)=0$) , we have to assume that:

- $For\ right\ side\colon \bar{C}=Be^{-x\sqrt{s/D}}\ and\ A=0$
- $For\ right\ side\colon \bar{C}=Ae^{x\sqrt{s/D}}\ and\ B=0$

Because mass is spreading symmetrically, we can say, that:

$$\int_0^\infty c(x,t)dx=\frac{M}{2}$$

After applying Laplace transforms to both sides of this equation we get:

$$\int_0^\infty \bar{C}(x,s)dx=\frac{M}{2s}$$

What is equal to:

$$\int_0^\infty Be^{-x\sqrt{s/D}}\,dx=\frac{M}{2s}$$

As a result:

$$B=\frac{M}{2\sqrt{sD}}$$

So:

$$\bar{C}(x,s)=\frac{M}{2\sqrt{sD}}e^{-x\sqrt{s/D}}=\frac{M}{2\sqrt{D}}\frac{e^{-\left(\frac{x}{\sqrt{D}}\right)\sqrt{s}}}{\sqrt{s}}$$

Now we have to transform our solution back to time domain. To do this, we will use tables for inverse Laplace transforms:

$$\mathcal{L}^{-1}[\bar{C}(x,s)]=c(x,t)=\frac{M}{2\sqrt{D}}\mathcal{L}^{-1}\left[\frac{e^{-\left(\frac{x}{\sqrt{D}}\right)\sqrt{s}}}{\sqrt{s}}\right]$$

For this type of equations:

$$\mathcal{L}^{-1}\left[\frac{e^{-a\sqrt{s}}}{\sqrt{s}}\right] = \frac{M}{\sqrt{\pi t}} e^{-x^2/4t}$$

So finally:

$$\boldsymbol{c(x,t) = \frac{M}{2\sqrt{D\pi t}} e^{-x^2/4Dt}} \tag{4.8}$$

Because mass is spreading symmetrically, this solution is symmetrical to the x=0 plane. For some, this form of solution may look familiar. Let's take a look at Gaussian distribution:

$$\boldsymbol{N(\mu, \sigma^2) = \frac{1}{\sigma\sqrt{2\pi}} e^{\frac{-(x-\mu)^2}{2\sigma^2}}}$$

It is clear that our concentration is given by normal distribution with mean μ=0 and variance σ^2=2Dt. As a result we can say that standard deviation σ:

$$\boldsymbol{\sigma = \sqrt{2Dt}} \tag{4.9}$$

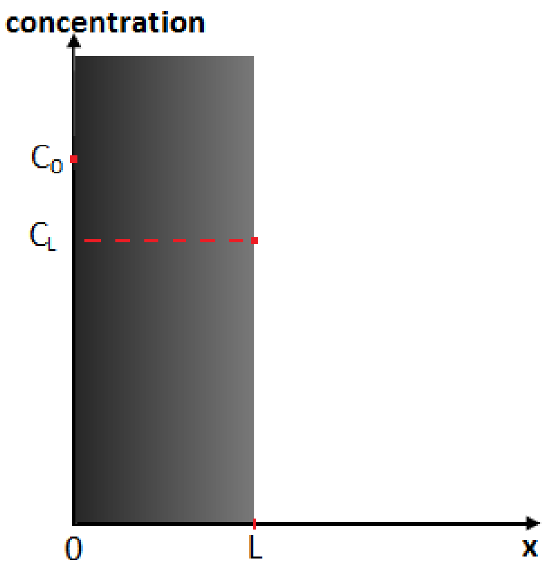
That means that after time t over 68% of mass going in given direction will be placed between x=0 and x=$\sqrt{2Dt}$. This value is called a penetration depth.

Example 4.2.

Consider a system which is in steady state. Following Dirichlet boundary conditions are applied to the concentration function:

$$\begin{cases} c(0,t) = c_0 \\ c(L,t) = c_L \end{cases}$$

Calculate function c(x)



Solution

Our starting point is equation (4.5):

$$\frac{\partial c_i}{\partial t} = D_i \frac{d^2 c_i}{dx^2}$$

For steady-state case:

$$0 = D_i \frac{d^2 c_i}{dx^2} \implies 0 = \frac{d^2 c_i}{dx^2}$$

First integral:

$$\int \frac{d^2 c_i}{dx^2} dx = \int 0 = k_1 \quad \Rightarrow \quad \frac{\partial c}{\partial x} = k_1$$

Second integral:

$$\int \frac{\partial c}{\partial x} dx = \int k_1 \, dx = k_1 x + k_2 \quad \Rightarrow \quad c(x) = k_1 x + k_2$$

From the first boundary condition:

$$c(0) = c_0 \quad \Rightarrow \quad c_0 = k_1 \cdot 0 + k_2 \quad \Rightarrow \quad c_0 = k_2$$

From the second boundary condition:

$$c(L) = c_L \quad \Rightarrow \quad c_L = k_1 \cdot L + c_0 \quad \Rightarrow \quad k_1 = \frac{c_L - c_0}{L}$$

As a result:

$$c(x) = \frac{c_L - c_0}{L} x + c_0$$

As it was already said, it is hard to define one "diffusion equation". In fact there are as many diffusion equations as constitutive equations. Let's take another look on equations (4.5) and (4.2). It is clear, that for general case diffusion equation can be written as:

$$\frac{\partial \rho_i}{\partial t} = -\nabla \cdot \vec{J}_i \tag{4.10}$$

Fick's second law is derived for Fick's diffusion flux. Now we will try to use a different flux equation.

Example 4.4.

Write a diffusion equation for Nernst-Planck flux.

Solution

Nernst-Planck flux equation has a form:

$$\vec{J}_i^{diff} = -B_i c_i \nabla \mu_i$$

For this case we will assume, there isn't any additional velocities which we should take into account (see 4.2), so:

$$\vec{J}_i = \vec{J}_i^{diff}$$

On the basis of (4.10):

$$\frac{\partial \rho_i}{\partial t} = B_i c_i \Delta \mu_i$$