

# Chemical diffusion in a cuboidal cell

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## 1 Overview

This article provides a short analysis of a chemical diffusion problem in a thin cuboidal cell filled with fluid. The base of the cell is divided into two halves, with the chemical initially uniformly distributed on one side. We are interested in how the chemical diffuses throughout the cell, and pay particular attention to the chemical concentration gradient between the two halves.

In section 2, we introduce the exact dimensions of the problem, and the mathematical notation used. Due to the structure of the cell, several analytical approximations can be found, which are discussed in section 3, and compared to numerical simulation in section 4. The chemical concentration gradient between the two halves of the cell is shown in figure 5, and it closely matches analytic approximations.

## 2 Mathematical setup

We consider a cuboidal cell with base length  $L = 0.9$  cm and width  $W = 0.45$  cm, filled with fluid to height of  $H = 150$   $\mu\text{m}$ . We make use of a coordinate system  $(x, y, z)$ , with the cell covering the region  $0 < x < L$ ,  $0 < y < W$ ,  $0 < z < H$ . Let the chemical concentration in the cell be  $\rho(x, y, z, t)$ , and let the chemical diffusion coefficient be  $b = 5 \times 10^{-5}$   $\text{cm}^2 \text{s}^{-1}$ . We postulate that the concentration obeys the diffusion equation

$$\frac{\partial \rho}{\partial t} = b \nabla^2 \rho.$$

At each wall, we use the boundary conditions

$$\hat{n} \cdot \nabla \rho = 0$$

where  $\hat{n}$  is a normal vector at the surface; this corresponds to no chemical flux across the wall. Since the problem is symmetric in the  $y$  direction, we make the simplification  $\rho(x, y, z, t) = \rho(x, z, t)$ . Initially, the chemical is concentrated in a thin layer on the base of the cell in the region  $x < L/2$  with density  $\eta = 1$   $\mu\text{g cm}^{-2}$ . We therefore use the initial condition

$$\rho(x, z, 0) = \begin{cases} \eta/\delta & \text{if } x < L/2 \text{ and } z < \delta \\ 0 & \text{otherwise} \end{cases}$$

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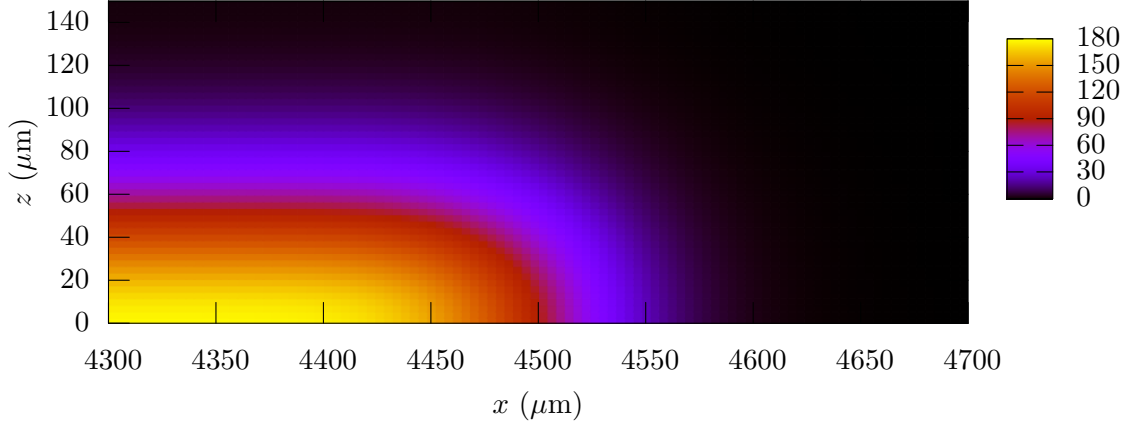


Figure 1: A two dimensional plot of the concentration of  $\rho(x, z)$  after 0.2 s, in units of  $\mu\text{g cm}^{-3}$ .

where  $\delta$  is a small value, corresponding to the width of strip. After finding the evolution of  $\rho$  as a function of time, we are interested in the horizontal concentration gradient  $\partial\rho/\partial x$  in the region  $4400 \mu\text{m} < x < 4600 \mu\text{m}$ ,  $0 < z < 10 \mu\text{m}$ .

### 3 Approximating formulae

In general, the only way to solve a two dimensional diffusion problem is to use a numerical method. However, in this case, we can derive several approximating formulae to describe the chemical's diffusion, by exploiting the fact that  $H \ll L$ . By dimensional analysis, the characteristic time for chemical to diffuse is proportional to the characteristic length squared. We therefore expect the chemical will equilibrate in the vertical direction a factor of  $L^2/H^2 = 45^2$  times faster than in the horizontal direction.

This separation of time scales allows us to find several analytical approximations, by examining the vertical and horizontal diffusion separately. In the appendix, the derivations of three useful analytic approximations are provided, making use of Fourier series and Green's functions, two standard techniques for solving the diffusion equation. We begin by considering diffusion in the vertical direction: in appendix A.1, it is shown that the chemical concentration near the surface where it originates from is approximately given by

$$\rho(x, 0, t) \sim \frac{\eta}{H} + \frac{2\eta}{H} e^{-b\pi^2 t/H^2}. \quad (1)$$

Thus the chemical equilibrates in the vertical direction to a concentration of  $\eta/H$  in a time proportional to  $H^2/b$ .

In appendix A.2, it is shown that after the chemical is equally distributed in  $z$ , the concentration

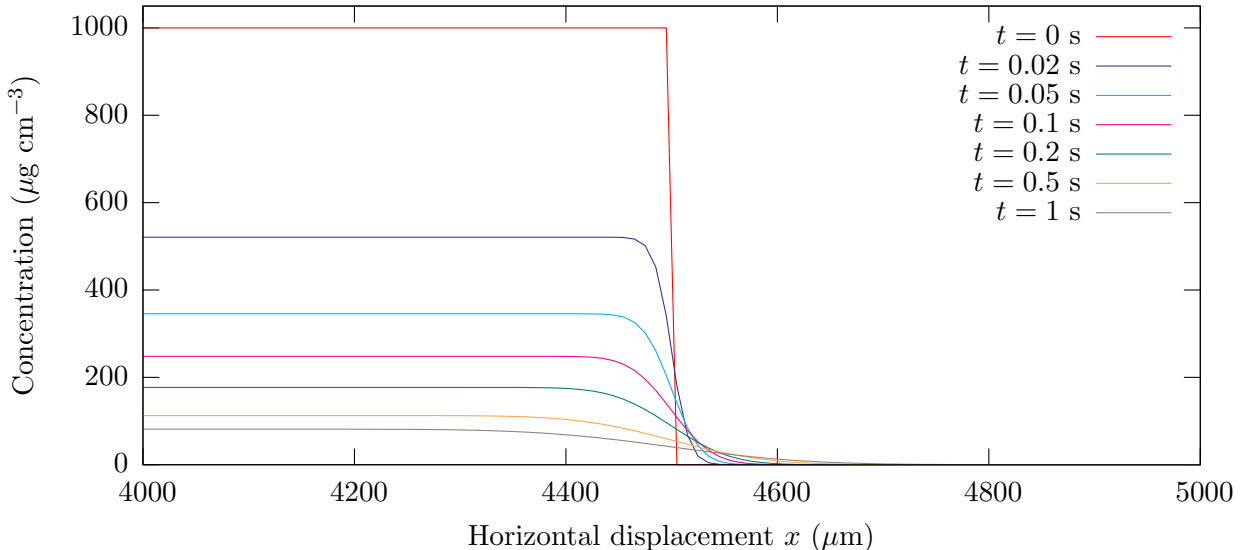


Figure 2: Plots of the diffusion profile in the range  $0 < z < 10 \mu\text{m}$  for short times. The plots show that the chemical rapidly reaches equilibrium in the vertical direction.

gradient in the center of the cell is given by

$$\frac{\partial \rho}{\partial x}(L/2, 0, t) \sim -\frac{\eta}{H\sqrt{4\pi bt}};$$

this is derived by approximating the concentration by an error function, and we expect this to be valid until  $t \sim L^2/16b$ . Eventually, a cosine approximation becomes more appropriate, and in appendix A.3, we show that for late times,

$$\frac{\partial \rho}{\partial x}(L/2, 0, t) \sim -\frac{2\eta}{HL} \exp\left(\frac{-\pi^2 bt}{L^2}\right).$$

## 4 Numerical simulation

To obtain accurate results for the two-dimensional problem, a numerical integration of the diffusion equation was carried out in C++. The integration was performed on a  $900 \times 45$  lattice, with spacings of  $\Delta x = 10 \mu\text{m}$ ,  $\Delta y = 10/3 \mu\text{m}$ , and  $\Delta t = 0.001$  s, using the ADI Crank–Nicolson method. The method provides an accurate description of the full 2D problem, and figure 1 shows how the chemical diffuses away from the initial surface, a behavior which is not separable and is not described by any of the approximating formulae.

Figure 2 shows a plot of the average concentration in the strip  $0 < z < 10 \mu\text{m}$  for several different small times, to illustrate the diffusion in the vertical direction. We see that the concentration decays rapidly, as the chemical diffuses away from the glass surface to fill the entire height of fluid. After only 1 s, the chemical concentration in the left half of the cell is close to its equilibrium value of  $\eta/H = 66.7 \mu\text{g cm}^{-3}$ . Figure 3 shows a semi-log plot of the difference in chemical concentration at the initial surface, compared to the equilibrium value. We see that the difference decays

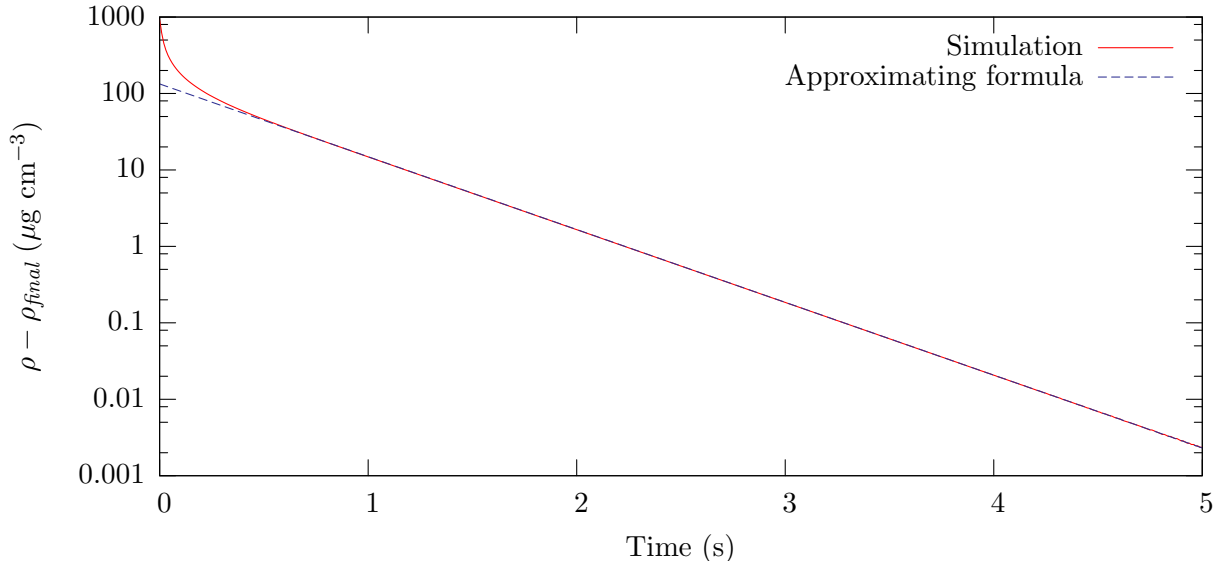


Figure 3: Semi-log plot of the equilibration of the concentration in the vertical direction. We see that the approximation derived in appendix A.1 is very accurate for large times.

exponentially, and very closely matches the approximation given in equation 1 after 0.5 s. The timescales for vertical diffusion are so small that they may be experimentally insignificant.

Figure 4 shows several plots of the horizontal diffusion profile. For  $t < 360$  s, before the sloped section of the profile reaches the ends of the box, the concentration closely matches an error-function curve, used in the approximation derived in appendix A.2. After  $t = 1$  h, the curves begin to be well-described by a cosine, as used in appendix A.3.

Figure 5 shows a semi-log plot of the concentration gradient in the center of the cell, and compares it to the two different approximations. By using the error function approximation for short times, and the cosine approximation for long times, almost the entire curve from simulation can be described. Since we are particularly interested in the diffusion after several hours, the cosine approximation formula may be the most useful.

## A Derivation of approximating formulae

### A.1 Vertical equilibration

Initially, the chemical forms a layer from  $0 < z < \delta$ ; this density can be written as a Fourier series

$$\rho(z, 0) = \eta/H + \frac{2\eta}{\pi\delta} \sum_{n=0}^{\infty} \sin\left(\frac{n\pi\delta}{H}\right) \cos\left(\frac{n\pi z}{H}\right).$$

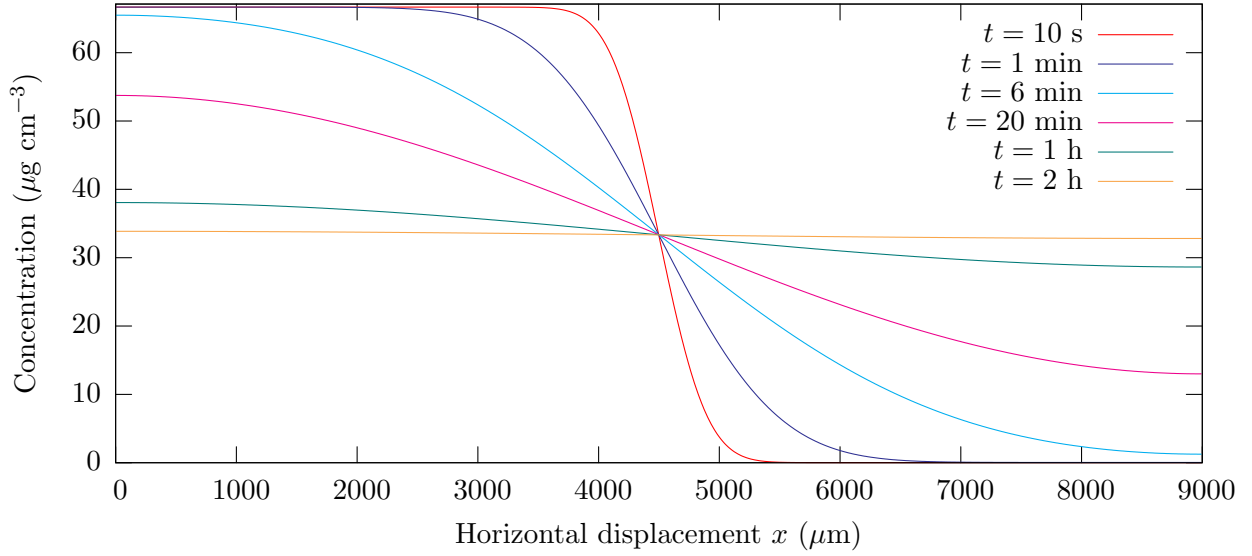


Figure 4: Plots of the diffusion profile in the range  $0 < z < 10 \mu\text{m}$  for long times. For  $t < 360 \text{ s}$ , the curves are well-matched by the error function approximation. For  $t > 1 \text{ h}$ , the curves match the decaying cosine approximation.

Consider a separable solution of the form  $\rho(z, t) = T(t) \cos(n\pi z/H)$ . By substituting into the diffusion equation, we see that

$$\begin{aligned} \frac{dT}{dt} \cos\left(\frac{n\pi z}{H}\right) &= -bT(t) \left(\frac{n\pi}{H}\right)^2 \cos\left(\frac{n\pi z}{H}\right) \\ \frac{dT}{dt} &= -bT(t) \left(\frac{n\pi}{H}\right)^2 \\ T(t) &= T(0) \exp\left(-\frac{bn^2\pi^2 t}{H^2}\right). \end{aligned}$$

This shows that a cosine initial condition will decay exponentially, with decay constant  $-bn^2\pi^2/H^2$ . Hence the general solution is

$$\rho(z, t) = \frac{\eta}{H} + \frac{2\eta}{\pi\delta} \sum_{n=1}^{\infty} \sin\left(\frac{n\pi\delta}{H}\right) \cos\left(\frac{n\pi z}{H}\right) e^{-bn^2\pi^2 t/H^2}.$$

The coefficients in the exponents increase as  $n$  gets large. Hence for large  $t$  we can obtain an approximating formula by taking the first few terms in this sum. To first order, we have

$$\rho(z, t) \sim \frac{\eta}{H} + \frac{2\eta}{\pi\delta} \sin\left(\frac{\pi\delta}{H}\right) \cos\left(\frac{\pi z}{H}\right) e^{-b\pi^2 t/H^2}.$$

Near the initial surface,

$$\begin{aligned} \rho(0, t) &\sim \frac{\eta}{H} + \frac{2\eta}{\pi\delta} \sin\left(\frac{\pi\delta}{H}\right) e^{-b\pi^2 t/H^2} \\ &\sim \frac{\eta}{H} + \frac{2\eta}{H} e^{-b\pi^2 t/H^2} \end{aligned}$$

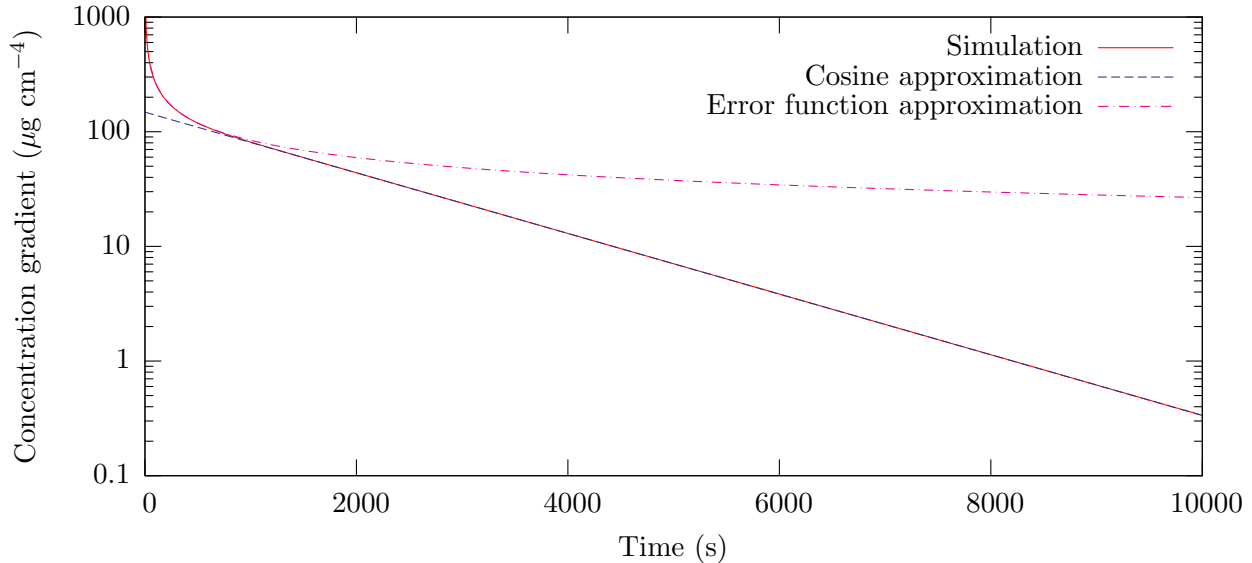


Figure 5: Semi-log plot of the concentration gradient in the center of the cell, based on the region  $4400 \mu\text{m} < x < 4600 \mu\text{m}$ ,  $0 < z < 10 \mu\text{m}$ .

and thus the chemical reaches an approximate equilibrium when  $t \sim H^2/b\pi^2$ .

## A.2 Horizontal diffusion: short times

Since the vertical diffusion happens much faster than that in the horizontal direction. assume that the chemical starts evenly distributed. This corresponds to the initial condition

$$\rho(x, 0) = \begin{cases} \eta/H & \text{if } x < L/2 \text{ and } z < \delta \\ 0 & \text{otherwise.} \end{cases} \quad (2)$$

We first consider finding an approximation when  $t$  is small. In this limit, we can neglect the effects of the end walls, and approximate the problem as an infinite cell. For this situation, we can write down the solution in terms of the error function,

$$\rho(x, t) = \frac{\eta}{2H} \left( 1 - \operatorname{erf} \left( \frac{2x - L}{4\sqrt{bt}} \right) \right).$$

Hence,

$$\frac{\partial \rho}{\partial x}(x, t) = -\frac{\eta}{H\sqrt{4\pi bt}} \exp \left( -\frac{(x - L/2)^2}{4bt} \right) \quad (3)$$

and thus

$$\frac{\partial \rho}{\partial x}(L/2, t) = -\frac{\eta}{H\sqrt{4\pi bt}}.$$

We expect this to be valid until the spreading Gaussian in equation 3 reaches the ends of the cell, which happens when  $L^2 \sim 16bt$ .

### A.3 Horizontal diffusion: late times

The initial condition given in 2 has Fourier series

$$\rho(x, 0) = \frac{\eta}{2H} + \frac{2\eta}{\pi H} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \cos\left(\frac{(2n+1)\pi x}{L}\right),$$

and hence

$$\rho(x, t) = \frac{\eta}{2H} + \frac{2\eta}{\pi H} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \cos\left(\frac{(2n+1)\pi x}{L}\right) \exp\left(\frac{-(2n+1)^2 \pi^2 b t}{L^2}\right).$$

The concentration gradient is given by

$$\frac{\partial \rho}{\partial x}(x, t) = -\frac{2\eta}{HL} \sum_{n=0}^{\infty} (-1)^n \sin\left(\frac{(2n+1)\pi x}{L}\right) \exp\left(\frac{-(2n+1)^2 \pi^2 b t}{L^2}\right)$$

and in the middle of the cell, this is given by

$$\frac{\partial \rho}{\partial x}(L/2, t) = -\frac{2\eta}{HL} \sum_{n=0}^{\infty} \exp\left(\frac{-(2n+1)^2 \pi^2 b t}{L^2}\right).$$

This sum is difficult to evaluate exactly, but for late times, the first term in the expression will dominate, as the others will be exponentially smaller. We can therefore write

$$\frac{\partial \rho}{\partial x}(L/2, t) \sim -\frac{2\eta}{HL} \exp\left(\frac{-\pi^2 b t}{L^2}\right)$$

as  $t \rightarrow \infty$ .