

**MULTICOMPONENT VOLUME DIFFUSION
WITH SELECTIVELY PERVIOUS BOUNDARY:
AN EXACTLY SOLVABLE MODEL**

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Abstract

We consider a diffusion model of two or more chemical components in a rectangular parallelepipedic domain. One component (solvent) is assumed to evaporate through the appropriate region of the boundary, while the other components (solutes) cannot cross the same boundary. Evaporation flow is modeled as proportional to solvent concentration at the boundary. The steady boundary value problem can be solved exactly. The analytical solution predicts that solute concentrations in the steady state can deplete or rise along the boundary where solvent evaporation occurs. The effect disappears if evaporation is prevented, for instance by covering the surface with an impervious wall. The latter prediction agrees with experimental observations on fine porous stones imbibed with protective polymer solutions.

1. Introduction.

Diffusion phenomena play an important role in many fields, from chemistry to physics, as also biology and engineering[1-5]. In some cases diffusion involves a unique, well-defined chemical component spreading through a stationary medium and the process can be described by means of the classical diffusion equation in terms of a constant diffusion coefficient or, for inhomogeneous media, by a Fokker-Plank equation[3,6] where the diffusion coefficient is regarded as a function of the position within the medium. In some other cases, diffusion involves more than one chemical component and appropriate cross diffusion coefficients, describing the reciprocal diffusive effect of one component upon each other, should be considered[7]. Nevertheless, the importance of cross-contributions in diffusion processes is often underestimated or even neglected. In this work we discuss a multicomponent diffusion model which accomplishes the following prescriptions: is simple to be understood and mathematically formulated; has a physical interest; shows the relevance of cross-diffusion effects; admits an explicit solution in an elementary form.

The model is as follows. Assume that at one of its faces a solid rectangular parallelepiped is put in contact with a solution consisting of a solvent and one or more solutes. The solution is at equilibrium in an infinite reservoir and it spreads within the solid domain through the face of contact. The remaining surface is in contact with an appropriate medium (air, for instance) where solvent, but not solutes, can evaporate. Solvent concentration in the surrounding medium is assumed to be constant (the excess of solvent is removed or, alternatively, evaporation is sufficiently slow and takes place in a wide environment able to take up the solvent without its concentration changes in an appreciable way). Solvent evaporation rate is proportional to the difference of solvent concentration at the surface of the solid sample and in the surrounding medium. Owing to the presence of one or more solutes, we have to take into account not only the diffusion coefficients of the solvent

and of each solute, but also the cross terms related to diffusion of each component in the concentration gradient of any other. Diffusivity is then described in terms of a suitable diffusion matrix D [7], which will be taken as a constant through the whole solid domain. The general setting of the system is shown in Figure 1 for the case of a unique solute — \hat{n} denotes the unit vector normal to the surface of the solid domain, oriented towards the exterior of it.

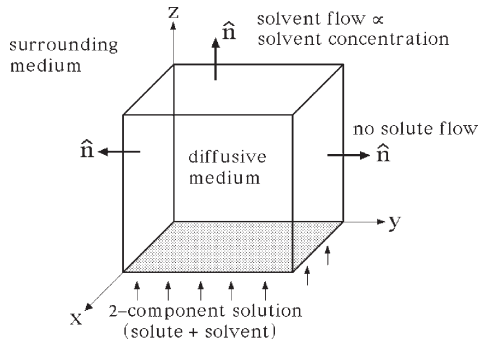


Figure 1: A sketch of the physical system.

We are particularly interested in the steady solutions of the problem. This kind of model, which is not described in the classical literature[2], can be useful in the analysis of multi-component diffusion processes taking place in a solid domain whose surface is selectively pervious to one component and not to the others. Incidentally, the model has been suggested by some experimental observations concerning solvent-polymer migration in fine porous stones[8]. As we will see, the model may qualitatively explain the enhancement of solute concentration at the surface of the solid sample which can be experimentally put into evidence when solvent can freely evaporate at the surface, and also correctly predicts

the suppression of the phenomenon whenever solvent evaporation is prevented[8]. Similar processes are supposed to play a role in the attempts of measuring the contact angle on porous materials by the Washburn approach[9,10]. The plan of the paper is as follows. In Section 2 the model is mathematically formulated in full generality as a boundary value (BV) problem, for a two-component system containing only one solvent and one solute. The steady BV problem is discussed in Section 3 and extended to the n -dimensional case in the subsequent Section 4, where further extension to domains of more general shape is discussed. The solution of the steady BV problem can be found in Section 5 along with a discussion of the general trend of the typical solutions, while Section 6 is devoted to conclusions.

2. The two-component diffusion model.

As illustrated in Figure 2, the diffusive domain will be described by the rectangular parallelepiped

$$\Omega = \{(x, y, z) \in [0, a] \times [0, b] \times [0, c]\} \subset \mathbb{R}^3$$

whose lower face is in contact with the solvent-solute solution reservoir and for brevity's sake will be denoted as

$$B = \{(x, y, 0) \in \mathbb{R}^3 : (x, y) \in [0, a] \times [0, b]\}.$$

$\partial\Omega$ symbolizes the positively-oriented boundary of Ω , with the normal unit vector \hat{n} directed outwards with respect to Ω . The real 2×2 diffusion matrix

$$D = \begin{pmatrix} D_{11} & D_{12} \\ D_{21} & D_{22} \end{pmatrix} \tag{2.1}$$

expresses the diffusive properties of the solvent-solute pair and is assumed to be constant throughout the domain Ω . Due to general inapplicability of Onsager reciprocity theorem to phenomenological diffusion coefficients[7], the matrix D is not necessarily symmetrical,

although in most cases it may be assumed to be. Solvent and solute concentrations will be written as

$$\ell(t, x, y, z) \quad s(t, x, y, z)$$

respectively; more precisely, ℓ stands for the difference between the solvent concentration at a given point and the constant value of the solvent concentration in the surrounding environment.

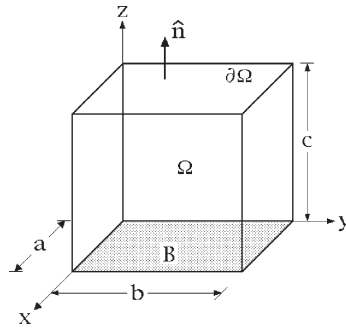


Figure 2: The mathematical description of the physical model. Ω is the diffusive medium (a rectangular parallelepiped of sides a , b and c), B denotes the lower rectangular face on which solvent and solute concentrations are kept constant and $\partial\Omega \setminus B$ is the residual surface of the rectangular parallelepiped, impervious to solute, where solvent evaporation takes place.

According to the definition (2.1) of the diffusion matrix, the current densities of solvent and solute can be given as:

$$J_{\text{solvent}} = -(D_{11}\nabla\ell + D_{12}\nabla s) \quad J_{\text{solute}} = -(D_{21}\nabla\ell + D_{22}\nabla s)$$

so that continuity equation implies the diffusion equations in the domain Ω :

$$\begin{cases} \frac{\partial\ell}{\partial t} = \nabla \cdot (D_{11}\nabla\ell + D_{12}\nabla s) \\ \frac{\partial s}{\partial t} = \nabla \cdot (D_{21}\nabla\ell + D_{22}\nabla s) \end{cases} \quad \forall (x, y, z) \in \Omega, t \geq 0. \quad (2.2)$$

The below boundary conditions must be satisfied:

- (i) on the lower face B the concentrations ℓ and s take their saturation values at any time, due to contact with the solution:

$$\begin{aligned}\ell(t, x, y, z) &= \ell_{\infty} & \forall (x, y, z) \in B, t \geq 0 \\ s(t, x, y, z) &= s_{\infty} & \forall (x, y, z) \in B, t \geq 0;\end{aligned}$$

- (ii) along all the other faces — $\partial\Omega \setminus B$ — the current density of the solvent is proportional to the concentration ℓ , because of evaporation into the surrounding medium

$$-\hat{n} \cdot (D_{11}\nabla\ell + D_{12}\nabla s) = \lambda\ell \quad \forall (x, y, z) \in \partial\Omega \setminus B, t \geq 0;$$

- (iii) in the same surface domain $\partial\Omega \setminus B$ the solute flow is negligible

$$-\hat{n} \cdot (D_{21}\nabla\ell + D_{22}\nabla s) = 0 \quad \forall (x, y, z) \in \partial\Omega \setminus B, t \geq 0.$$

Suitable initial conditions should be supplied for both concentrations ℓ and s in the domain Ω — for instance they could be zero at $t = 0$ — but, since we are mainly interested in steady solutions, they will be ignored in the present work.

For constant diffusion coefficients D_{ij} , $i, j = 1, 2$ we are lead to the boundary value problem

$$\left\{ \begin{array}{l} \frac{\partial\ell}{\partial t} = \nabla^2(D_{11}\ell + D_{12}s) \\ \frac{\partial s}{\partial t} = \nabla^2(D_{21}\ell + D_{22}s) \\ -\hat{n} \cdot \nabla(D_{11}\ell + D_{12}s) = \lambda\ell \\ -\hat{n} \cdot \nabla(D_{21}\ell + D_{22}s) = 0 \\ \ell = \ell_{\infty} \\ s = s_{\infty} \end{array} \right. \quad \begin{array}{l} \forall (x, y, z) \in \Omega, t \geq 0 \\ \forall (x, y, z) \in \partial\Omega \setminus B, t \geq 0 \\ \forall (x, y, z) \in B, t \geq 0 \end{array}$$

with the appropriate initial conditions, when needed.

3. The steady BV problem.

For the steady solution we pose $\ell = \ell(x, y, z)$, $s = s(x, y, z)$ and obtain the boundary value problem

$$\begin{cases} \nabla^2(D_{11}\ell + D_{12}s) = 0 \\ \nabla^2(D_{21}\ell + D_{22}s) = 0 & \forall (x, y, z) \in \Omega \\ -\hat{n} \cdot \nabla(D_{11}\ell + D_{12}s) = \lambda\ell \\ -\hat{n} \cdot \nabla(D_{21}\ell + D_{22}s) = 0 & \forall (x, y, z) \in \partial\Omega \setminus B \\ \ell = \ell_\infty \\ s = s_\infty & \forall (x, y, z) \in B \end{cases}$$

from which we deduce, in particular, the uncoupled BV problem in the field $D_{21}\ell + D_{22}s$

$$\begin{cases} \nabla^2(D_{21}\ell + D_{22}s) = 0 & \forall (x, y, z) \in \Omega \\ \hat{n} \cdot \nabla(D_{21}\ell + D_{22}s) = 0 & \forall (x, y, z) \in \partial\Omega \setminus B \\ D_{21}\ell + D_{22}s = D_{21}\ell_\infty + D_{22}s_\infty, & \forall (x, y, z) \in B \end{cases}$$

whose unique solution writes

$$D_{21}\ell + D_{22}s = D_{21}\ell_\infty + D_{22}s_\infty \quad \forall (x, y, z) \in \Omega.$$

As a consequence, there holds

$$s = \frac{D_{21}\ell_\infty + D_{22}s_\infty}{D_{22}} - \frac{D_{21}}{D_{22}}\ell \tag{3.1}$$

and equation $\nabla^2(D_{11}\ell + D_{12}s) = 0$ becomes

$$\nabla^2 \left[D_{11}\ell - \frac{D_{21}}{D_{22}}\ell D_{12} + D_{12} \frac{D_{21}\ell_\infty + D_{22}s_\infty}{D_{22}} \right] = 0$$

or equivalently

$$\frac{D_{11}D_{22} - D_{12}D_{21}}{D_{22}} \nabla^2 \ell = 0 \quad \forall (x, y, z) \in \Omega$$

with the boundary conditions

$$\begin{aligned} \ell &= \ell_\infty & \forall (x, y, z) \in B \\ -\hat{n} \cdot \nabla \ell \frac{D_{11}D_{22} - D_{12}D_{21}}{D_{22}} &= \lambda\ell & \forall (x, y, z) \in \partial\Omega \setminus B. \end{aligned}$$

The diffusion matrix is typically nonsingular, so that $D_{11}D_{22} - D_{12}D_{21} \neq 0$ and the steady solvent concentration is determined by the BV problem

$$\begin{cases} \nabla^2 \ell = 0 & \forall (x, y, z) \in \Omega \\ \ell = \ell_\infty & \forall (x, y, z) \in B \\ -\hat{n} \cdot \nabla \ell = \frac{\lambda D_{22}}{D_{11}D_{22} - D_{12}D_{21}} \ell & \forall (x, y, z) \in \partial\Omega \setminus B. \end{cases} \quad (3.2)$$

4. The multicomponent extension.

The previous model can be easily extended to the case of more than one solute. Let us denote with c_1 the solvent concentration — or actually the difference between the solvent concentration in the diffusive medium and that in the surrounding environment — and with c_2, \dots, c_n the concentration of the different solutes. Concentrations are maintained at the constant values c_i^∞ on the lower face of the domain Ω and lateral and upper faces are assumed to be impassable to the solutes, while solvent flow through the same surface is proportional to c_1 . By introducing the appropriate $n \times n$ diffusion matrix D , the time-dependent BV problem becomes

$$\begin{cases} \frac{\partial c_i}{\partial t} = \nabla \cdot \left(\sum_{j=1}^n D_{ij} \nabla c_j \right) & i = 1, \dots, n & \forall (x, y, z) \in \Omega, t \geq 0 \\ c_i = c_i^\infty & i = 1, \dots, n & \forall (x, y, z) \in B, t \geq 0 \\ -\hat{n} \cdot \left(\sum_{j=1}^n D_{1j} \nabla c_j \right) = \lambda c_1 & & \forall (x, y, z) \in \partial\Omega \setminus B, t \geq 0 \\ -\hat{n} \cdot \left(\sum_{j=1}^n D_{ij} \nabla c_j \right) = 0 & i = 2, \dots, n & \forall (x, y, z) \in \partial\Omega \setminus B, t \geq 0 \end{cases}$$

The steady solution satisfies the set of parabolic equations

$$0 = \nabla \cdot \left(\sum_{j=1}^n D_{ij} \nabla c_j \right) \quad i = 1, \dots, n \quad \forall (x, y, z) \in \Omega$$

with the same boundary conditions. For constant diffusion coefficients D_{ij} we have

$$0 = \nabla^2 \left(\sum_{j=1}^n D_{ij} c_j \right) \quad i = 1, \dots, n \quad \forall (x, y, z) \in \Omega.$$

In particular, $\forall i = 2, \dots, n$ we deduce the BV problem

$$\begin{cases} 0 = \nabla^2 \left(\sum_{j=1}^n D_{ij} c_j \right) & \forall (x, y, z) \in \Omega \\ \sum_{j=1}^n D_{ij} c_j = \sum_{j=1}^n D_{ij} c_j^\infty & \forall (x, y, z) \in B \\ -\hat{n} \cdot \nabla \left(\sum_{j=1}^n D_{ij} c_j \right) = 0 & \forall (x, y, z) \in \partial\Omega \setminus B \end{cases}$$

whose unique solution writes

$$\sum_{j=1}^n D_{ij} c_j = \sum_{j=1}^n D_{ij} c_j^\infty \quad i = 2, \dots, n \quad \forall (x, y, z) \in \Omega$$

By posing, for simplicity's sake,

$$\sum_{j=1}^n D_{ij} c_j^\infty = \alpha_i \quad \forall i = 2, \dots, n \quad , \quad D_{[2:n]} = \begin{pmatrix} D_{22} & \dots & D_{2n} \\ \vdots & \ddots & \vdots \\ D_{n2} & \dots & D_{nn} \end{pmatrix}$$

the latter relationships can be expressed in the matrix form

$$\begin{pmatrix} D_{21} c_1 \\ \vdots \\ D_{n1} c_1 \end{pmatrix} + D_{[2:n]} \begin{pmatrix} c_2 \\ \vdots \\ c_n \end{pmatrix} = \begin{pmatrix} \alpha_2 \\ \vdots \\ \alpha_n \end{pmatrix}$$

from which we deduce

$$D_{[2:n]} \begin{pmatrix} c_2 \\ \vdots \\ c_n \end{pmatrix} = \begin{pmatrix} \alpha_2 \\ \vdots \\ \alpha_n \end{pmatrix} - \begin{pmatrix} D_{21} \\ \vdots \\ D_{n1} \end{pmatrix} c_1 .$$

Under the hypothesis of nonsingular D the submatrix $D_{[2:n]}$ is also invertible, so that

$$\begin{pmatrix} c_2 \\ \vdots \\ c_n \end{pmatrix} = D_{[2:n]}^{-1} \begin{pmatrix} \alpha_2 \\ \vdots \\ \alpha_n \end{pmatrix} - D_{[2:n]}^{-1} \begin{pmatrix} D_{21} \\ \vdots \\ D_{n1} \end{pmatrix} c_1 . \tag{4.1}$$

As a consequence, a short algebraic manipulation provides

$$\begin{aligned} \sum_{j=1}^n D_{1j} c_j &= D_{11} c_1 + (D_{12} \dots D_{1n}) \begin{pmatrix} c_2 \\ \vdots \\ c_n \end{pmatrix} = \\ &= (D_{12} \dots D_{1n}) D_{[2:n]}^{-1} \begin{pmatrix} \alpha_2 \\ \vdots \\ \alpha_n \end{pmatrix} + D_{11} c_1 - (D_{12} \dots D_{1n}) D_{[2:n]}^{-1} \begin{pmatrix} D_{21} \\ \vdots \\ D_{n1} \end{pmatrix} c_1 \end{aligned}$$

and since the first matrix product on the right-handed side is a constant, we obtain

$$\begin{aligned}
 \sum_{j=1}^n D_{1j} c_j &= \text{constant} + D_{11} c_1 - \sum_{i,j=2}^n D_{1i} \left(D_{[2:n]}^{-1} \right)_{ij} D_{j1} c_1 = \\
 &= \text{constant} + c_1 \left[D_{11} - \sum_{i,j=2}^n D_{1i} \left(D_{[2:n]}^{-1} \right)_{ij} D_{j1} \right] = \\
 &= \text{constant} + c_1 \left[D_{11} - \sum_{i,j=2}^n D_{1i} \frac{(D_{[2:n]}^*)_{ji}}{D_{11}^*} D_{j1} \right] = \\
 &= \text{constant} + \frac{c_1}{D_{11}^*} \left\{ D_{11} D_{11}^* + \sum_{i=2}^n D_{1i} \left[- \sum_{j=2}^n (D_{[2:n]}^*)_{ji} D_{j1} \right] \right\} = \\
 &= \text{constant} + \frac{c_1}{D_{11}^*} \left[D_{11} D_{11}^* + \sum_{i=2}^n D_{1i} D_{1i}^* \right] = \\
 &= \text{constant} + \frac{c_1}{D_{11}^*} \sum_{i=1}^n D_{1i} D_{1i}^* = \\
 &= \text{constant} + c_1 \frac{\det D}{D_{11}^*}
 \end{aligned}$$

where:

- $(D_{[2:n]}^*)_{ji}$ denotes the classical adjoint of the entry D_{ji} in the matrix $D_{[2:n]}$;
- D_{ij}^* stands for the classical adjoint of the entry D_{ij} in the complete matrix D ;
- clearly $D_{11}^* = \det D_{[2:n]}$, so that

$$\left(D_{[2:n]} \right)_{ij}^{-1} = \frac{1}{\det D_{[2:n]}} (D_{[2:n]}^*)_{ji} = \frac{1}{D_{11}^*} (D_{[2:n]}^*)_{ji} ;$$

- the following identity has been applied

$$- \sum_{j=2}^n (D_{[2:n]}^*)_{ji} D_{j1} = D_{1i}^* \quad \forall i = 2, \dots, n.$$

Whence we derive, for $i = 1$, the BV problem

$$\begin{cases} \nabla^2 \left(\text{constant} + c_1 \frac{\det D}{D_{11}^*} \right) = 0 & \forall (x, y, z) \in \Omega \\ c_1 = c_1^\infty & \forall (x, y, z) \in B \\ -\hat{n} \cdot \nabla \left(\text{constant} + c_1 \frac{\det D}{D_{11}^*} \right) = \lambda c_1 & \forall (x, y, z) \in \partial\Omega \setminus B \end{cases}$$

or, equivalently,

$$\begin{cases} \nabla^2 c_1 = 0 & \forall (x, y, z) \in \Omega \\ c_1 = c_1^\infty & \forall (x, y, z) \in B \\ -\hat{n} \cdot \nabla c_1 = \lambda \frac{D_{11}^*}{\det D} c_1 & \forall (x, y, z) \in \partial\Omega \setminus B. \end{cases} \quad (4.2)$$

The concentrations c_2, \dots, c_n are uniquely determined in terms of the saturation values $c_1^\infty, \dots, c_n^\infty$ and of c_1 , by solving the linear set of equations

$$\sum_{j=2}^n D_{ij} c_j = \sum_{j=1}^n D_{ij} c_j^\infty - D_{i1} c_1 \quad i = 2, \dots, n$$

i.e. by using equation (4.1). Each $c_i, i = 2, \dots, n$, is of the form $a_i + b_i c_1$, for appropriate real coefficients a_i and $b_i, i = 2, \dots, n$, and therefore it may increase or decrease relatively to c_1 according to the sign of the slope b_i .

Remark

It is noticeable that the previous argument can be easily extended to domains much more general than the rectangular parallelepiped Ω and the square face B . We only need that the volume domain Ω and the surface $B \subset \partial\Omega$ are sufficiently nice in order that uniqueness of the solution of Laplace equation $\nabla^2 \rho = 0$ holds in Ω [11] for the concentration ρ of any solute, with the mixed BC

$$\begin{aligned} \rho(x) = \rho_\infty = \text{constant} & \quad \forall x \in B \\ -\hat{n} \cdot \nabla \rho(x) = 0 & \quad \forall x \in \Omega \setminus B; \end{aligned}$$

in that case, indeed, the only steady solution for solute concentration is the trivial one, $\rho(x) = \rho_\infty \forall x \in \Omega$. Of course, the solution of the equivalent Laplace boundary value problem for solvent concentration cannot be given in a closed form. But this is possible with the particular choice of Ω and B considered in Section 2.

5. Solution of the steady BV problem.

For simplicity of notation we pose

$$c_1(x, y, z) := \rho(x, y, z) \quad \lambda \frac{D\hat{1}_1}{\det D} := \mu$$

so that the stationary BV problem (4.2) becomes

$$\begin{cases} \nabla^2 \rho = 0 & \forall (x, y, z) \in \Omega \\ \rho = \rho^\infty & \forall (x, y, z) \in B \\ -\hat{n} \cdot \nabla \rho = \mu \rho & \forall (x, y, z) \in \partial\Omega \setminus B. \end{cases}$$

Tentative solutions can be found by separation of variables

$$\rho(x, y, z) = X(x)Y(y)Z(z).$$

The solution must be a harmonic function

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) X(x)Y(y)Z(z) = 0$$

a condition which can be accomplished by posing

$$X''(x) = -\alpha^2 X(x) \quad Y''(y) = -\beta^2 Y(y) \quad Z''(z) = (\alpha^2 + \beta^2) Z(z)$$

with appropriate constants α and β to be determined.

Dependence on x

In terms of arbitrary real constants a_1, a_2 , the solution for the function $X(x)$ is of the form

$$X(x) = a_1 \cos \alpha x + a_2 \sin \alpha x \quad x \in [0, a]$$

with first derivative

$$\frac{dX}{dx}(x) = -\alpha a_1 \sin \alpha x + \alpha a_2 \cos \alpha x$$

but it must also obey the boundary conditions on the faces $x = 0$ and $x = a$

$$\frac{dX}{dx}(0) = \mu X(0) \qquad \frac{dX}{dx}(a) = -\mu X(a)$$

which explicitly write as

$$\begin{cases} \alpha a_2 = \mu a_1 \\ \alpha a_1 \sin \alpha a - \alpha a_2 \cos \alpha a = \mu [a_1 \cos \alpha a + a_2 \sin \alpha a]. \end{cases}$$

The first equation gives

$$a_1 = \frac{\alpha}{\mu} a_2$$

which implies that $\alpha \neq 0$, otherwise $X(x)$ would be identically zero in $[0, a]$, a contradiction.

By replacing into the second BC we get

$$a_2 \left[\frac{\alpha^2}{\mu} \sin \alpha a - 2\alpha \cos \alpha a - \mu \sin \alpha a \right] = 0.$$

In order that $a_2 \neq 0$ — $X(x)$ not identically zero — there must hold

$$\left(\frac{\alpha^2}{\mu} - \mu \right) \sin \alpha a - 2\alpha \cos \alpha a = 0$$

or, being $\alpha \neq 0$,

$$\frac{1}{2} \left(\frac{\alpha}{\mu} - \frac{\mu}{\alpha} \right) \sin \alpha a - \cos \alpha a = 0$$

and since $\sin \alpha a$ cannot be zero because this would imply $\cos \alpha a = 0$ as well, we conclude that for the given $\mu > 0$ and $a > 0$ the allowed values of α are the positive roots of the equation

$$\frac{1}{2} \left(\frac{\alpha}{\mu} - \frac{\mu}{\alpha} \right) = \cot \alpha a. \tag{5.1}$$

Such roots constitute a countable subset of \mathbb{R}^+ whose elements can be ranked into an increasing sequence $(\alpha_n)_{n \in \mathbb{N}}$

$$\alpha_1 < \alpha_2 < \alpha_3 < \dots < \alpha_n < \alpha_{n+1} < \dots$$

and satisfy the conditions

$$\alpha_n \in \left(\frac{\pi}{a}(n-1), \frac{\pi}{a}n \right) \quad \forall n \in \mathbb{N}$$

$$\alpha_n \sim \frac{\pi}{a}(n-1) \quad (n \rightarrow +\infty)$$

as illustrated in Figure 3. The function $X(x)$ can then be any of the form

$$X_n(x) = \frac{\alpha_n}{\mu} \cos \alpha_n x + \sin \alpha_n x \quad \forall n \in \mathbb{N}.$$

They constitute a complete orthogonal set in the space of continuous functions on $[0, a]$:

$$\int_0^a X_n(x)X_m(x) dx = \frac{1}{2} \left(\frac{\alpha_n^2}{\mu^2} a + \frac{2}{\mu} + a \right) \delta_{nm} \quad \forall n, m \in \mathbb{N}$$

δ_{nm} being the usual Kronecker delta.

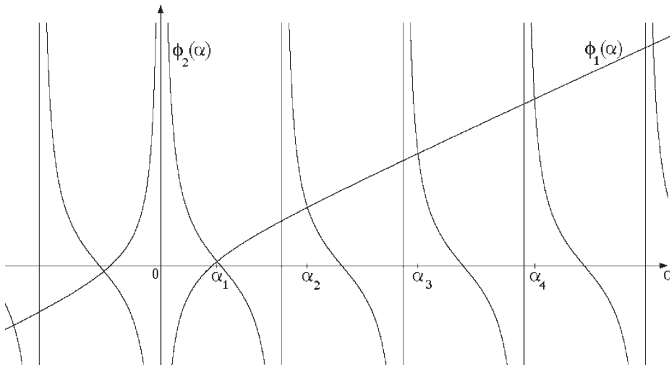


Figure 3: The coefficients $\alpha_n, n \in \mathbb{N}$, determined as the positive solutions of the equation $\Phi_1(\alpha) = \Phi_2(\alpha)$, with $\Phi_1(\alpha) = \frac{1}{2} \left(\frac{a}{\mu} - \frac{\mu}{\alpha} \right)$ and $\Phi_2(\alpha) = \cot \alpha a$.

Dependence on y

An analogous calculation holds for the function $Y(y)$, which takes the form

$$Y(y) = b_1 \cos \beta y + b_2 \sin \beta y$$

with derivative

$$\frac{dY}{dy}(y) = -\beta b_1 \sin \beta y + \beta b_2 \cos \beta y$$

and b_1, b_2 real constants. The boundary conditions on the faces $y = 0$ and $y = b$

$$\frac{dY}{dy}(0) = \mu Y(0) \quad - \frac{dY}{dy}(b) = \mu Y(b)$$

lead to the general solutions

$$Y_m(y) = \frac{\beta_m}{\mu} \cos \beta_m y + \sin \beta_m y \quad \forall m \in \mathbb{N}$$

where β_m s are the positive roots of the equation

$$\frac{1}{2} \left(\frac{\beta}{\mu} - \frac{\mu}{\beta} \right) = \cot \beta b \tag{5.2}$$

ranked in increasing order. The properties of coefficients β_m are essentially the same already illustrated for the α_n s. Functions $Y_m(y)$ define a complete orthogonal set in the space of continuous functions on $[0, b]$:

$$\int_0^b Y_m(y) Y_n(y) dy = \frac{1}{2} \left(\frac{\beta_m^2}{\mu^2} b + \frac{2}{\mu} + b \right) \delta_{mn} \quad \forall m, n \in \mathbb{N}.$$

Dependence on z

The solution for $Z(z)$ can be written as a linear combination of exponentials

$$Z(z) = c_1 e^{\sqrt{\alpha^2 + \beta^2} z} + c_2 e^{-\sqrt{\alpha^2 + \beta^2} z}$$

on which we do not impose, for the moment, any boundary condition.

Solution by separation of variables

The products $X_n(x)Y_m(y)$, $n, m \in \mathbb{N}$, constitute a complete orthogonal set in the space of continuous functions on the square $[0, a] \times [0, b]$. Consequently, we can write the steady solution as a double series

$$\rho(x, y, z) = \sum_{n,m=1}^{\infty} \left[c_{n,m}^{(1)} e^{\sqrt{\alpha_n^2 + \beta_m^2} z} + c_{n,m}^{(2)} e^{-\sqrt{\alpha_n^2 + \beta_m^2} z} \right] X_n(x) Y_m(y) \tag{5.3}$$

where the unknown coefficients $c_{n,m}^{(1)}$ and $c_{n,m}^{(2)}$ must be determined by applying boundary conditions. Actually, boundary conditions on the lateral surface of Ω are already satisfied because of the choice of $X_n(x)$ and $Y_m(y)$, so that we only have to impose BC at the lower and at the upper face.

In the lower face B — i.e. $z = 0$ — the steady solution takes the saturation value

$$\rho(x, y, 0) = \rho_\infty \quad \forall (x, y) \in [0, a] \times [0, b] \tag{5.4}$$

with

$$\rho(x, y, 0) = \sum_{n,m=1}^{\infty} [c_{n,m}^{(1)} + c_{n,m}^{(2)}] X_n(x) Y_m(y),$$

while at the upper face $z = c$ there holds

$$-\frac{\partial \rho}{\partial z}(x, y, c) = \mu \rho(x, y, c) \quad \forall (x, y) \in [0, a] \times [0, b] \tag{5.5}$$

with

$$\mu \rho(x, y, c) = \sum_{n,m=1}^{\infty} \left[\mu c_{n,m}^{(1)} e^{\sqrt{\alpha_n^2 + \beta_m^2} c} + \mu c_{n,m}^{(2)} e^{-\sqrt{\alpha_n^2 + \beta_m^2} c} \right] X_n(x) Y_m(y)$$

and

$$\frac{\partial \rho}{\partial z}(x, y, c) = \sum_{n,m=1}^{\infty} \left[c_{n,m}^{(1)} e^{\sqrt{\alpha_n^2 + \beta_m^2} c} - c_{n,m}^{(2)} e^{-\sqrt{\alpha_n^2 + \beta_m^2} c} \right] \sqrt{\alpha_n^2 + \beta_m^2} X_n(x) Y_m(y)$$

The boundary conditions (5.4) and (5.5) become then

$$\sum_{n,m=1}^{\infty} [c_{n,m}^{(1)} + c_{n,m}^{(2)}] X_n(x) Y_m(y) = \rho_\infty \tag{5.6.a}$$

$$\sum_{n,m=1}^{\infty} \left[\mu c_{n,m}^{(1)} e^{\sqrt{\alpha_n^2 + \beta_m^2} c} + \mu c_{n,m}^{(2)} e^{-\sqrt{\alpha_n^2 + \beta_m^2} c} + \right. \tag{5.6.b}$$

$$\left. + c_{n,m}^{(1)} \sqrt{\alpha_n^2 + \beta_m^2} e^{\sqrt{\alpha_n^2 + \beta_m^2} c} - c_{n,m}^{(2)} \sqrt{\alpha_n^2 + \beta_m^2} e^{-\sqrt{\alpha_n^2 + \beta_m^2} c} \right] X_n(x) Y_m(y) = 0$$

$$\forall (x, y) \in [0, a] \times [0, b].$$

By introducing the short-hand

$$K_{n,m}(\mu, a, b) = \frac{4\left(\frac{1}{\mu} \sin \alpha_n a + \frac{1 - \cos \alpha_n a}{\alpha_n}\right)\left(\frac{1}{\mu} \sin \beta_m b + \frac{1 - \cos \beta_m b}{\beta_m}\right)}{\left(\frac{\alpha_n^2}{\mu^2} a + \frac{2}{\mu} + a\right)\left(\frac{\beta_m^2}{\mu^2} b + \frac{2}{\mu} + b\right)},$$

equation (5.6.a) provides $\forall n, m \in \mathbb{N}$

$$\begin{aligned} c_{n,m}^{(1)} + c_{n,m}^{(2)} &= \frac{1}{\frac{1}{2}\left(\frac{\alpha_n^2}{\mu^2} a + \frac{2}{\mu} + a\right)} \frac{1}{\frac{1}{2}\left(\frac{\beta_m^2}{\mu^2} b + \frac{2}{\mu} + b\right)} \int_{[0,a] \times [0,b]} \rho_\infty X_n(x) Y_m(y) dx dy = \\ &= \rho_\infty K_{n,m}(\mu, a, b) \end{aligned}$$

while (5.6.b) implies

$$(\mu + \sqrt{\alpha_n^2 + \beta_m^2}) e^{\sqrt{\alpha_n^2 + \beta_m^2} c} c_{n,m}^{(1)} + (\mu - \sqrt{\alpha_n^2 + \beta_m^2}) e^{-\sqrt{\alpha_n^2 + \beta_m^2} c} c_{n,m}^{(2)} = 0.$$

The latter two equations provide an algebraic non-homogeneous linear set of equations in the variables $c_{n,m}^{(1)}$ and $c_{n,m}^{(2)}$ whose determinant writes

$$\begin{aligned} \Delta &= \begin{vmatrix} (\mu + \sqrt{\alpha_n^2 + \beta_m^2}) e^{\sqrt{\alpha_n^2 + \beta_m^2} c} & (\mu - \sqrt{\alpha_n^2 + \beta_m^2}) e^{-\sqrt{\alpha_n^2 + \beta_m^2} c} \\ 1 & 1 \end{vmatrix} = \\ &= \mu(e^{\sqrt{\alpha_n^2 + \beta_m^2} c} - e^{-\sqrt{\alpha_n^2 + \beta_m^2} c}) + \sqrt{\alpha_n^2 + \beta_m^2} (e^{\sqrt{\alpha_n^2 + \beta_m^2} c} + e^{-\sqrt{\alpha_n^2 + \beta_m^2} c}) = \\ &= 2\mu \sinh(c\sqrt{\alpha_n^2 + \beta_m^2}) + 2\sqrt{\alpha_n^2 + \beta_m^2} \cosh(c\sqrt{\alpha_n^2 + \beta_m^2}) \end{aligned}$$

so that the solution becomes, through Cramer's formula,

$$\begin{aligned} c_{n,m}^{(1)} &= \frac{1}{\Delta} \begin{vmatrix} 0 & (\mu - \sqrt{\alpha_n^2 + \beta_m^2}) e^{-\sqrt{\alpha_n^2 + \beta_m^2} c} \\ \rho_\infty K_{n,m}(\mu, a, b) & 1 \end{vmatrix} = \\ &= -\frac{\mu - \sqrt{\alpha_n^2 + \beta_m^2} e^{-\sqrt{\alpha_n^2 + \beta_m^2} c} \rho_\infty K_{n,m}(\mu, a, b)}{\Delta} \\ c_{n,m}^{(2)} &= \frac{1}{\Delta} \begin{vmatrix} (\mu + \sqrt{\alpha_n^2 + \beta_m^2}) e^{\sqrt{\alpha_n^2 + \beta_m^2} c} & 0 \\ 1 & \rho_\infty K_{n,m}(\mu, a, b) \end{vmatrix} = \\ &= \frac{\mu + \sqrt{\alpha_n^2 + \beta_m^2} e^{\sqrt{\alpha_n^2 + \beta_m^2} c} \rho_\infty K_{n,m}(\mu, a, b)}{\Delta} \end{aligned}$$

By inserting into equation (5.3) we finally obtain the steady solution

$$\rho(x, y, z) = \sum_{n,m=1}^{\infty} \frac{\rho_{\infty}}{2} \frac{K_{n,m}(\mu, a, b)}{\mu \sinh(c\sqrt{\alpha_n^2 + \beta_m^2}) + \sqrt{\alpha_n^2 + \beta_m^2} \cosh(c\sqrt{\alpha_n^2 + \beta_m^2})} \cdot \left[(-\mu + \sqrt{\alpha_n^2 + \beta_m^2})e^{(z-c)\sqrt{\alpha_n^2 + \beta_m^2}} + (\mu + \sqrt{\alpha_n^2 + \beta_m^2})e^{(c-z)\sqrt{\alpha_n^2 + \beta_m^2}} \right] \cdot \left[\frac{\alpha_n}{\mu} \cos \alpha_n x + \sin \alpha_n x \right] \left[\frac{\beta_m}{\mu} \cos \beta_m y + \sin \beta_m y \right]$$

which can also be put into the equivalent form

$$\rho(x, y, z) = \rho_{\infty} \sum_{n,m=1}^{\infty} \frac{K_{n,m}(\mu, a, b)}{\mu \sinh(c\sqrt{\alpha_n^2 + \beta_m^2}) + \sqrt{\alpha_n^2 + \beta_m^2} \cosh(c\sqrt{\alpha_n^2 + \beta_m^2})} \cdot \left\{ \mu \sinh \left[(c-z)\sqrt{\alpha_n^2 + \beta_m^2} \right] + \sqrt{\alpha_n^2 + \beta_m^2} \cosh \left[(c-z)\sqrt{\alpha_n^2 + \beta_m^2} \right] \right\} \cdot \left[\frac{\alpha_n}{\mu} \cos \alpha_n x + \sin \alpha_n x \right] \left[\frac{\beta_m}{\mu} \cos \beta_m y + \sin \beta_m y \right]$$

The typical trend of the stationary solution we have obtained is illustrated in Figures 4 and 5 for two different values of the coordinate z , one close to the bottom — $z \sim 0$ — and one close to the top — $z \sim c$.

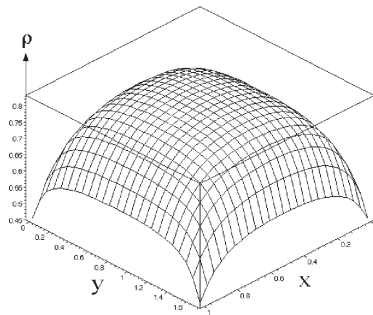


Figure 4: The steady solution ρ at $z=0.1c$ for edges $a=1.0$, $b=1.7$, $c=1.234$ and evaporation coefficient $\mu=2.567$.

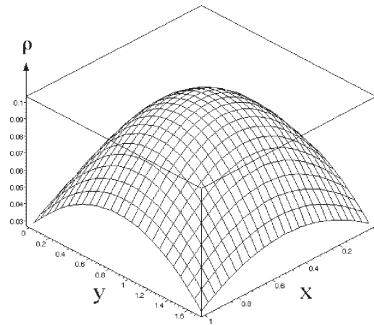


Figure 5: The steady solution ρ at $z=0.9c$ for edges $a=1.0$, $b=1.7$, $c=1.234$ and evaporation coefficient $\mu=2.567$.

If the diffusion matrix D is chosen in such a way that equation (3.1) takes, for instance, the explicit form $s = 0.96 - 1.20 \ell$, then the comparison of solvent and solute concentration in the steady state are shown in Figure 6 near the bottom of the sample, where the solution enters the solid sample ($z = 0.1c$), and in Figure 7 at a height close to the top of the sample ($z = 0.9c$).

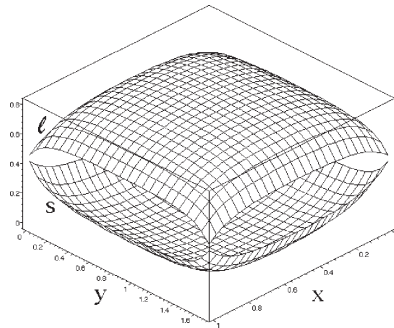


Figure 6: Comparison of solute (s) and solvent (ℓ) steady concentrations near the bottom of the diffusive domain ($z=0.1c$), for an appropriate choice of the diffusion matrix D , which is given in such a way that equation (3.1) reduces to $s=0.96-1.20 \ell$.

We notice that in this case solvent concentration is higher at the bottom of the sample, in the vicinity of the solution reservoir, while solute concentration reaches larger values in the top of the sample. Moreover, solute concentration increases near at the lateral faces of the rectangular parallelepiped, even in the lower portion of the sample. In both cases solute concentration enhancement is associated to an important evaporation rate of the solvent at the sample surface.

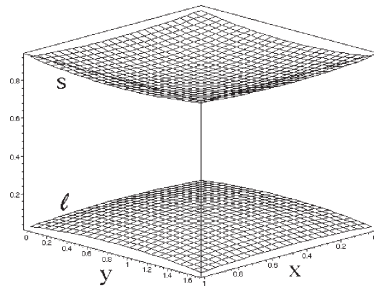


Figure 7: Comparison of solute (s) and solvent (l) steady concentrations near the top of the diffusive domain ($z=0.9c$), for an appropriate choice of the diffusion matrix D (the same of figure 6).

6. Conclusions

We have shown that a simple model of multicomponent diffusion can qualitatively explain the effects of solute accumulation/depletion at the surface of a sample where a solution spreads. Conditions for that are: (1) the existence of appropriate solute-solvent(s) cross diffusion coefficients and (2) the occurrence of solvent evaporation at the surface, modeled as proportional to solvent concentration at the same boundary. For a simple, but however realistic, choice of the diffusion domain the steady solution of the diffusion problem can be obtained analytically. The model predicts that the accumulation/depletion effect

disappears whenever solvent evaporation is prevented. The latter prediction agrees with experimental observations on porous stones imbibed with protective polymer solutions[8].

References

- [1] R.B. Bird, W.E. Stewart, E.N. Lightfoot, Transport phenomena, J. Wiley & Sons, New York (1960)
- [2] J. Crank, The Mathematics of Diffusion, Clarendon Press, Oxford (1975)
- [3] E.L. Cussler, Diffusion. Mass Transfer in Fluid Systems, Cambridge University Press (1997)
- [4] Diffusion in Polymers, P. Neogi Ed., Dekker, New York (1996)
- [5] R.L. Fournier, Basic Transport Phenomena in Biomedical Engineering, 2nd edition, Taylor & Francis, New York (2007)
- [6] H. Risken, The Fokker-Planck equation, Springer Verlag, Berlin (1981)
- [7] I. Prigogine, D. Kondepudi, Thermodynamique. Dès moteurs thermiques aux structures dissipatives, Éditions Odile Jacob, Paris (1999)
- [8] W. Domasłowski, The mechanism of polymer migration in porous stones, Wiener Berichte über Naturwissenschaft in der Kunst 4/5, 402-25 (1988)
- [9] M. Brugnara, E. Degasperì, C. Della Volpe, D. Maniglio, A. Penati, S. Siboni, Wettability of porous materials. II. Can we obtain the contact angle form the Washburn equation?, Contact Angle, Wettability and Adhesion, K.L. Mittal Ed., 143-164, Volume 4, VSP, Utrecht, (2006)

- [10] M. Brugnara, C. Della Volpe, D. Maniglio, S. Siboni, A critical approach to surface and porous stone analysis methods, *Fracture and Failure of Natural Building Stones - Applications in the Restoration of Ancient Monuments*, Stavros K. Kourkoulis Ed., 541-551, Springer-Verlag, Dordrecht (2006)
- [11] R. Courant, D. Hilbert, *Methods of Mathematical Physics*, Interscience Publishers - J. Wiley & Sons, New York, (1962) Vol. II