

Numerical results for the Codiffusion of Isotopes

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Abstract

Numerical simulations have been performed for a model for the distribution of radionuclides in the ground water around a deep repository for used nuclear fuel, based on the assumption that different isotopes of the same chemical element A contribute jointly to the chemical potential of A , through two different components of the flux. The corresponding problem consists in a parabolic system strongly coupled, that, in the physically relevant assumption that one of these components is negligible, reduces to a parabolic equation for the total concentration of the element A , possibly coupled with hyperbolic equations for the concentrations of the single isotopes. These simulations evidenciate the qualitative behaviour of the solution in dependence of the diffusion coefficients, showing striking effects that can be observed when one of the component of the flux is much smaller than the other.

key words: isotopes; diffusion; numerical simulations.

1. Introduction

We consider the Pescatore's model proposed in [8], see also [3], for the diffusion of n species of isotopes of the same element in a medium and based on the assumption that the flux of the i component J_i is given by

$$(1) \quad J_i = - \left(\tilde{D}_i \nabla c_i + D_i \frac{c_i}{c} \nabla c \right), \quad i = 1, \dots, n, \quad c = \sum_{i=1}^n c_i.$$

In the above constitutive law, the coefficients \tilde{D}_i are the usual parabolic diffusion coefficients, which account for the interaction of the i -component

with the surrounding medium, while the coefficients D_i are related to the interaction among the isotopes.

In the case of radioactive isotopes, we have to take into account the radioactive decay law, which for spatially homogeneous distributions is a linear ODE system

$$(2) \quad \frac{d\underline{C}}{dt} = \Lambda \underline{C}, \quad \underline{C} \in \mathbb{R}^N, \quad \Lambda \text{ suitable } N \times N \text{ constant matrix.}$$

The main idea of Pescatore's model is that each component feels the gradient of the total element concentration in a relative percentage $\frac{c_i}{c}$, because the isotopes are chemically indistinguishable.

For n species, in the general case of positive diffusion coefficients, possibly all different, the resulting problem consists in a parabolic system strongly coupled:

$$(3) \quad \frac{\partial c_i}{\partial t} = -\operatorname{div} J_i + \sum_{j=1}^n \lambda_{ij} c_j,$$

The mathematical analysis of the above system in a bounded domain, with Dirichlet boundary conditions was the object of paper [4], in the physically relevant assumption that the total concentration of the element is positive and bounded.

As relation (1) reduces to Fick's law in the case of a single isotope solute (where the diffusion coefficient is $\tilde{D}_i + D_i$), it is not clear at present whether the diffusion coefficient that is measured classically is dominated by the term \tilde{D}_i or D_i . If the latter is the case, then there might be important non-linear effects, especially in the field of radioactive waste repository, where the diffusion regime is created and elemental concentrations are highest.

In [2] we have studied some qualitative properties of the solution in the assumption that the diffusion coefficients \tilde{D}_i are negligible with respect to the D_i , thus showing the appearance of a "hyperbolic" behaviour for the c_i , quite interesting for the applications. Assuming that all diffusion coefficient D_i are equal and $\tilde{D}_i = 0$, the system reduces to a parabolic equation for the total concentration c (possibly coupled with hyperbolic linear equations for the ratios $r_i = \frac{c_i}{c}$, in the case with decay). The solutions of such a problem, which we denote as "hyperbolic problem", show the possibility of the onset of regions depleted of a component c_i and of strong oscillations also asymptotically (say a "asymptotic localization property").

There are examples of discordance between predictions and experiments in the co-diffusion of isotopic molecules (see [5], [6]): many studies often assume that the isotopes ratios are constant, at the so called "secular equilibrium", however the analysis of isotopes in long-term experiments in bedrock

and buffer materials (see [7]) evidentiates changes in the original isotope composition, called “fractionations”.

This phenomenon can be observed e.g. in the field of Uranium mobilization in geological media the existence, next to fractures surfaces, of a narrow zone where the U^{234} , U^{238} activity ratio (the ratio of the concentrations of the two isotopes) are significantly different from unity, i.e. from secular equilibrium. In some sense, the activity ratio does not seem to support a simple classical diffusion mechanism: there are jagged areas of enrichment and depletion of one isotope over the other, not as expected from classical diffusion theory, even if the profile of the total Uranium is diffusion-like.

In this paper we deal with this striking effects, comparing the solution of the parabolic problem with the solution of the hyperbolic one, varying the parameters of the problem. That is done by means of numerical simulations, and some explicit examples have been tested. These simulations evidentiates the qualitative behaviour of the solution in dependence of the diffusion coefficients D_i and \tilde{D}_i , both in the presence of radioactivity and for stable isotopes.

2. Statement of the problem

Let us consider n species, in the one-dimensional case, assuming that the diffusion coefficients D_i and \tilde{D}_i are constants. System (3), with Dirichlet boundary conditions, becomes

$$(4) \quad \begin{cases} \frac{\partial c_i}{\partial t} = \tilde{D}_i \frac{\partial^2 c_i}{\partial x^2} + D_i \frac{\partial}{\partial x} \left[\frac{c_i}{c} \frac{\partial c}{\partial x} \right] + \sum_{j=1}^n \Lambda_{ij} c_j, & \text{in } (a, b) \times (0, T), \\ c_i(a, t) = f_i^a, \text{ for } & c_i(b, t) = f_i^b, & \text{for } t \in (0, T), \\ c_i(x, 0) = c_{i0}(x), & i = 1, \dots, n, & \text{in } [a, b]. \end{cases}$$

In order to make clearer the situation, we will refer to the case of a couple of isotopes. An important example is the couple U^{238} , U^{234} isotopes of Uranium for which the decay law is

$$\begin{cases} \frac{dc_1}{dt} = -\lambda_1 c_1, \\ \frac{dc_2}{dt} = \lambda_1 c_1 - \lambda_2 c_2, \end{cases}$$

with c_1 concentration of U^{238} , c_2 concentration of U^{234} , $\lambda_2 \simeq \frac{1000}{7} \lambda_1$.

An example of stable isotopes is the couple (Cl^{37} , Cl^{35}), Chlorine, for which $\lambda_2 = \lambda_1 \equiv 0$.

The Dirichlet problem for 2 species becomes

$$(5) \quad \begin{cases} \frac{\partial c_1}{\partial t} = \tilde{D}_1 \frac{\partial^2 c_1}{\partial x^2} + D_1 \frac{\partial}{\partial x} \left[\frac{c_1}{c} \frac{\partial c}{\partial x} \right] - \lambda_1 c_1, & \text{in } (a, b) \times (0, T), \\ \frac{\partial c_2}{\partial t} = \tilde{D}_2 \frac{\partial^2 c_2}{\partial x^2} + D_2 \frac{\partial}{\partial x} \left[\frac{c_2}{c} \frac{\partial c}{\partial x} \right] + \lambda_1 c_1 - \lambda_2 c_2, & \text{in } (a, b) \times (0, T), \\ c_i(a, t) = f_i^a, \text{ for } c_i(b, t) = f_i^b, & \text{for } t \in (0, T), \\ c_i(x, 0) = c_{i0}(x), \quad i = 1, 2 & \text{in } [a, b], \end{cases}$$

Homogeneous Neumann B.C. have been considered too: in this case we have to substitute boundary conditions on c_{i0} with

$$\frac{\partial c_i}{\partial x}(a, t) = \frac{\partial c_i}{\partial x}(b, t) = 0.$$

We denote the above written problem "parabolic" if all the \tilde{D}_i, D_i are positive, and "hyperbolic" if all the $\tilde{D}_i = 0$.

As a matter of fact, in this last case we deal with the ratios $r_i = \frac{c_i}{c}$, that satisfy hyperbolic equations (see [2]): for two isotopes, we have

$$(6) \quad r_{1t} = r_{1x} \frac{c_x}{c} + \lambda_2 r_1 (r_E - r_1), \quad r_E = \frac{\lambda_2 - \lambda_1}{\lambda_2}, \quad r_2 = 1 - r_1.$$

Each r_i evolves along the characteristics $X(t)$ with the same law as the spatially homogeneous solutions, which is known a priori, and then

$$(7) \quad \begin{cases} r_1(0) = 0 \quad \rightarrow \quad r_1(t) \equiv 0, \quad t > 0 \\ 0 < r_1(0) \leq 1 \quad \rightarrow \quad r_1(t) = \frac{r_E r_1(0) \exp(\lambda_2 - \lambda_1)t}{r_E - r_1(0) + r_1(0) \exp(\lambda_2 - \lambda_1)t}, \\ r_1(t) \rightarrow r_E \quad \text{as } t \rightarrow \infty, \end{cases}$$

in accordance with the physical fact that the couple (U^{238}, U^{234}) has a "secular equilibrium" positive and attractive (i.e. normally the two isotopes are found in a precise positive ratio).

3. Numerical Experiments - B-spline collocation

Recalling the results obtained by the hyperbolic approach, also from a numerical point of view, a "hyperbolic-solver" may be the right choice to deal with this problem. However here we are interested in the parabolic behaviour, with the aim of showing how this behaviour is related to the parameters of the problem. Thus in the choice of a numerical approach we are targeted to solving a system of partial differential equations of parabolic

type “near” the hyperbolic limit i.e. where solutions exhibit sharp gradients (approximating actual discontinuities in the hyperbolic limit).

Our choice was finally to use `Bacolr`, code for B-spline collocation with error control. This code, which has been published very recently (see [9]), uses the classical MOL (*method of lines*) to discretize the system of p.d.e.’s in space allowing the imposition of boundary condition in a straightforward way. The space discretization is done via *B-spline collocation* with error control (i.e. two approximations - with different order - are used in space for error estimation and, if a given error-constraint is not satisfied, a new mesh is *adaptively* computed). The solution of the system of o.d.e’s (in the time variable) obtained after the spatial discretization is finally approximated using the implicit Runge-Kutta `RADAU5` code which provides error control in time [10]. In our experience the coupling of B-spline collocation in space and Radau in time results in a very fast and robust numerical scheme that adapts very well to our equations. On the other hand we should remark that this approach forced us to work only on parabolic problems (i.e. $\tilde{D}_i \neq 0$), as expected, and to *smooth* the eventually discontinuous initial data, because discontinuities prevent convergence of the initial approximation in the numerical scheme.

Actually we remark that our “quasi”-hyperbolic approach is justified in the problem of codiffusion, because in the physical problem the coefficients \tilde{D}_i are very small but not null and by the following result:

if the total concentration is strictly positive^a, the solution constructed along the characteristics is the “viscosity solution” obtained as the limit of the complete physical model, with $\tilde{D}_i = \tilde{D} \neq 0$, $D_i = D = 1$ as $\tilde{D} \rightarrow 0$ (see [2], [1]).

The order of magnitude to get a “hyperbolic” problem in the numerical simulations has been found to be $\tilde{D}_i/D_i \simeq 10^{-4}$.

Finally we observe that the smoothing^b of the initial data is negligible by comparison with the explicit solutions of Sect.4, however let us stress that no theoretical result on continuous dependence on the data has been proved.

4. Simulations

A complete review of numerical simulations can be found in the web site: <http://web.math.unifi.it/users/mancini/Codiffusion/>.

We give here a list of explicit solutions of the “hyperbolic” problem, in

^a We note that the numerical simulations all confirm the convergence also if c_0 is allowed to become zero. In the limit, boundary layers will appear (see again [1]).

^bpresent in all our simulations but actually unnoticeable being really small

order to test the numerical simulations. The agreement between theoretical and numerical results appears very good.

Example A1 Dirichlet Problem (without decay) in $[-L, L] \times \{t \geq 0\}$:

$$\begin{cases} c(-L, t) = c_L = \text{constant} \geq 0, & c(L, t) = c_R = \text{constant} \geq c_L, \\ c(x, 0) = c_L + \frac{c_R - c_L}{2L}(x + L), \end{cases}$$

$c(x, t)$ is the stationary solution of the heat equation, i.e. $c(x, t) \equiv c(x, 0)$, the characteristics (see [3], (3.1), (3.2)) are a family of parabolas

$$t = t_0 - \frac{(X(t) - x_0)(X(t) + x_0 + 2\mu L)}{2}, \quad \mu = \frac{c_R + c_L}{c_R - c_L}, \quad x_0 \in \Omega, \quad t_0 \geq 0.$$

Denoting by $\Gamma = (t, X^*(t))$ the characteristic starting at $(0, L)$, and by $T = 2\mu L^2$ the time such that $X^*(T) = 0$, then Γ separates the domain in two zones, $R_1 = \{-L < x < X^*(t), t < T\}$ influenced by the initial datum, and $R_2 = \{X^*(t) < x < L, t \geq 0\}$ influenced by the datum on $x = L$, and $c_i(x, t) = r_i(x, t)c(x, t) = r_i(x, t)c(x, 0)$, where

$$r_i(x, t) = \begin{cases} r_{0i} \left(\sqrt{(x + \mu L)^2 + 2t} - L\mu \right), & (x, t) \in R_1, \\ r_i^+ \left[t - \frac{1}{2} \left(L^2(1 + \mu)^2 - (x + L\mu)^2 \right) \right], & (x, t) \in R_2 \end{cases}$$

$$r_{0i} = \frac{c_i(x, 0)}{c(x, 0)}, \quad r_i^+ = \frac{c_i(L, t)}{c(L, t)} = \frac{c_i(L, t)}{c_R}.$$

Example A2 Dirichlet Problem (without decay) in $[-L, L] \times \{t \geq 0\}$. Let $c = c(x, t) = h(x)g(t)$ be a separated variable solution then the characteristic $X(t; x_0, t_0)$ is the solution of

$$\frac{dX}{dt} = -\frac{h'(X)}{h(X)}, \quad X(t_0) = x_0,$$

Let us consider $h(x) = a \cos(\omega x + \gamma)$, $g(t) = e^{-\omega^2 t}$, with a, ω, γ constants. Then we obtain

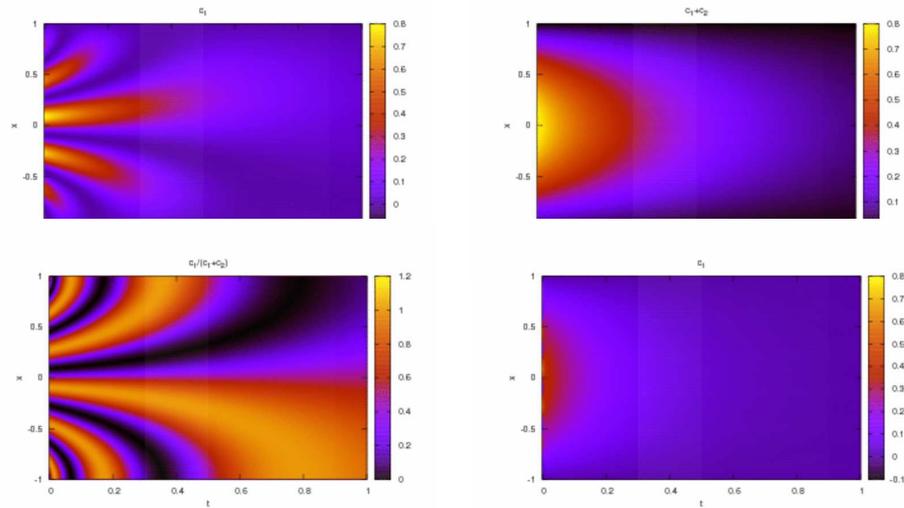
$$t - t_0 = \ln \{ [\sin(\omega X + \gamma)] [\sin(\omega x_0 + \gamma)]^{-1} \} / \omega^2.$$

If e.g. $\gamma = 0$, $\omega = \frac{\pi}{2L}$, we have $c(x, t) = a \exp\{-\frac{\pi^2}{4L^2}t\} \cos \frac{\pi}{2L}x$, $X \equiv 0$ is a characteristic, and the other characteristics are given by

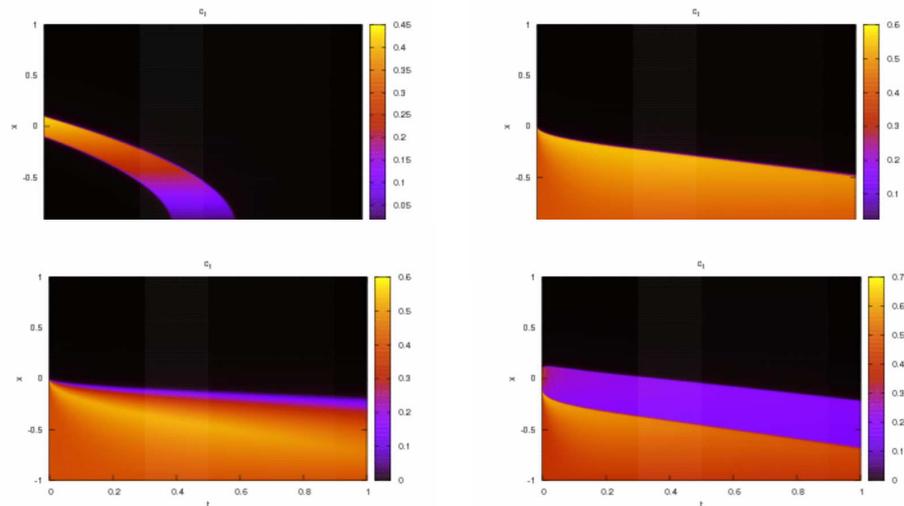
$$t = \frac{4L^2}{\pi^2} \ln \left\{ \left[\sin \left(\frac{\pi}{2L} X \right) \right] \left[\sin \left(\frac{\pi}{2L} x_0 \right) \right]^{-1} \right\}, \quad x_0 \neq 0.$$

Codiffusion

The following figures show the behaviour of c_1 (upper-left), c (upper-right), $r_1 = \frac{c_1}{c}$ (lower-left) when $D_1 = D_2 = 1$ and $\tilde{D}_1 = \tilde{D}_2 = 10^{-4}$ and c_1 with large “diffusivity” $\tilde{D}_1 = \tilde{D}_2 = 1$ (lower-right).



In the following we are going to show some simulations where the behaviour of the solution in corrispondance to "holes" of c_i is evidentiated: separated initial data with a bump (upper-left); appearance of a free boundary: separated initial data with $\tilde{D}_1 = \tilde{D}_2 \ll D_i$ $D_1 = D_2$ (upper-right) and $D_1 \neq D_2$ (lower-left); appearance of two free boundaries (lower-right)



4.1. – E_4 - Holes of c

Finally the behaviour of the solution in corrispondance to the "holes" of c : we consider different kinds of initial data and we show the corresponding behaviour of c , c_1 and r_1 . All the simulation, if not specified, have been done imposing (constant) Dirichlet boundary conditions.

In figure 1 a simulation with c_1, c_2 null inside the interval $[-l, l]$, $l < L$, and constant outside (see plot upper-left) is presented; the evolution of each component (plot upper-right) is qualitatively identical to the evolution of the parabolic total concentration c (plot lower-left) and, as trivially following by the identical initial condition $c_1/(c_1 + c_2)$ is constant (plot lower-right)

In figure 2 the initial distribution of isotopes is chosen so that the total concentration is identical to the one in figure 1 but the c_i are unmixed. Here the evolution of c_i and of r_i dramatically differs from the one of the parabolic total concentration (that has an evolution identical to the "mixed components" case).

Figures 3 and 4 depict a numerical experiment where c is non zero just in a thin region at the center of the computational domain. Figure 3 shows the evolution when c_1 and c_2 are fully mixed and exhibits, as in 1, a behavior identical to the parabolic total concentration. On the other hand, in figure 4 whereas the total concentration is identical to the one in previous plots, the hyperbolic nature of the evolution of c_i is evident and we can note that the isotopes, unmixed at the beginning of the simulation, remains unmixed (the same behavior can be observed, of course, in figure 2). Note that the simulations in the unmixed case are incomplete probably due to the appearance of very sharp gradients when the boundaries separating $c_i = 0$ and $c_i \neq 0$ reach the boundary where zero Dirichlet boundary conditions are imposed. The same behavior is exhibited in figure 5 but the homogeneous Neumann boundary conditions let our numerical scheme proceed without problems. As shown in figure 6 the "unmixing" property and the persistence of sharp boundary characterize all the simulations where the isotopes are initially unmixed despite the parabolicity of the evolution of the total concentration.

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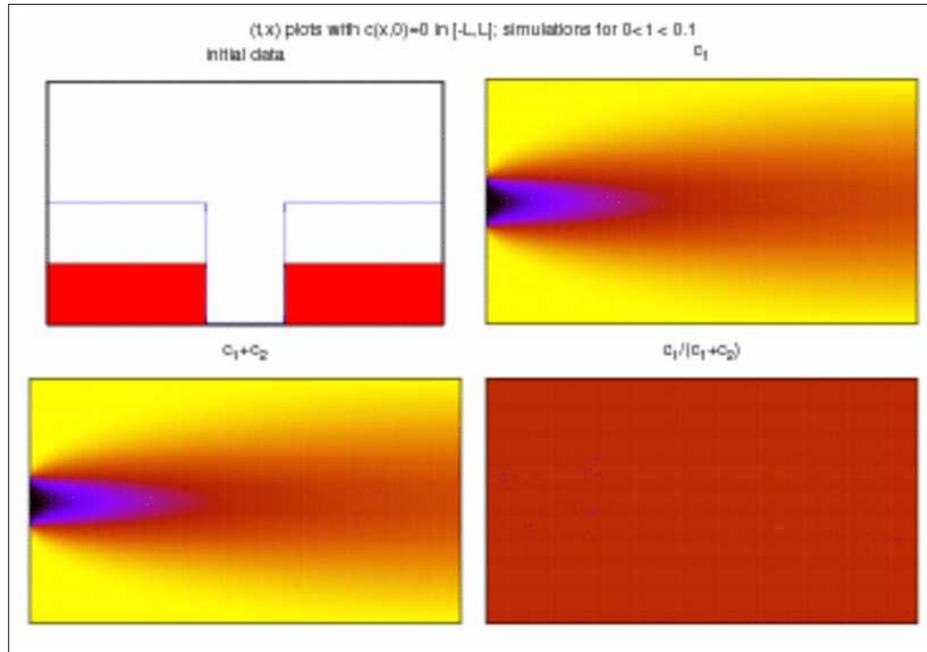


Fig. 1. hole in the center, mixed components

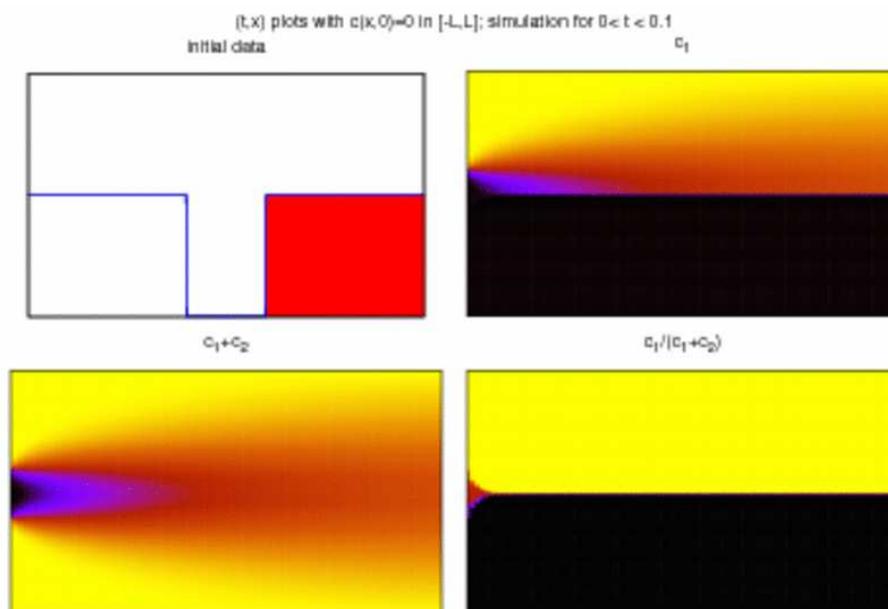


Fig. 2. hole in the center, un-mixed components

Codiffusion

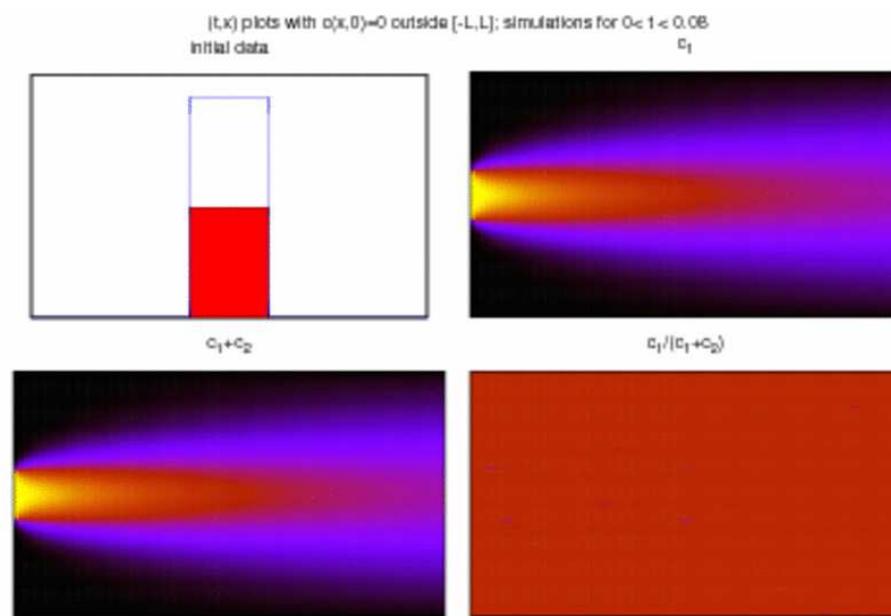


Fig. 3. hole at the boundary, mixed components

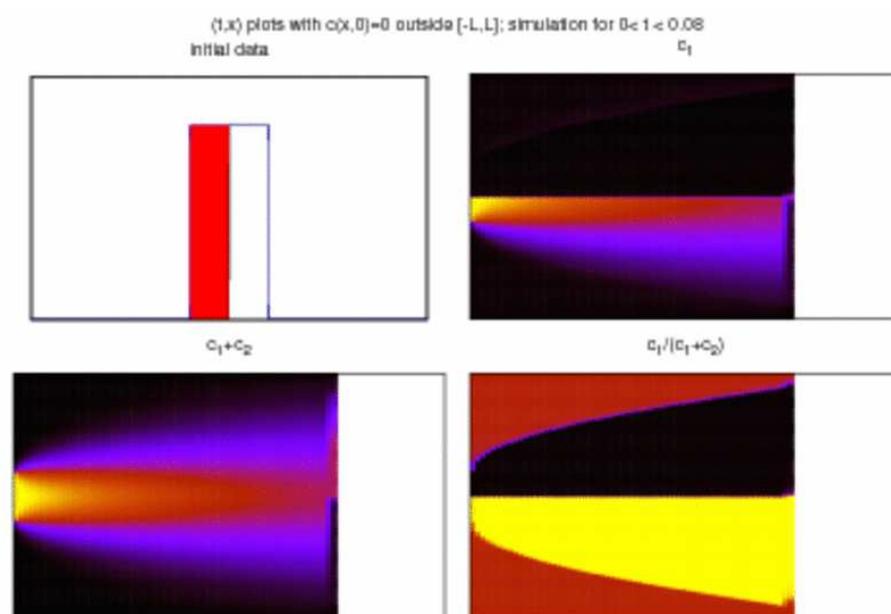


Fig. 4. hole at the boundary, un-mixed components

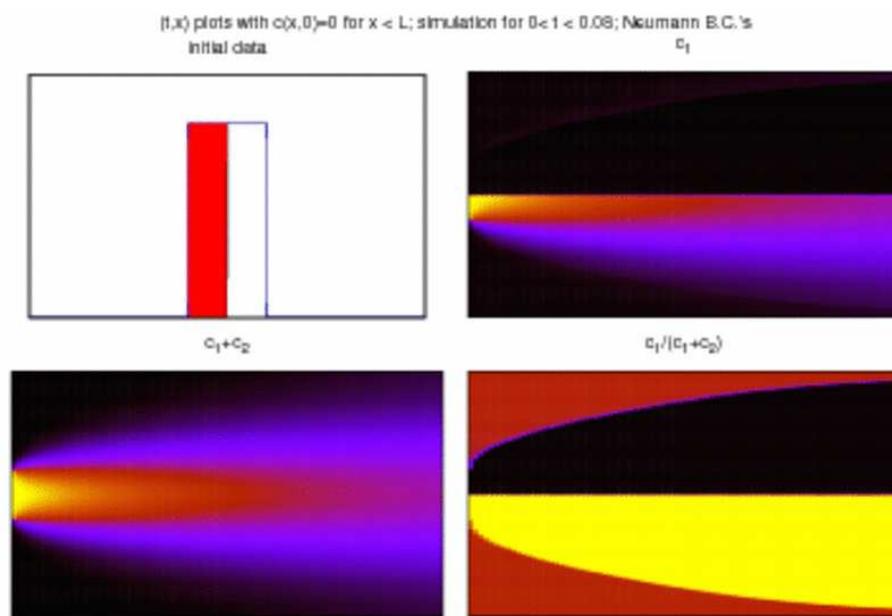


Fig. 5. Neumann boundary conditions, un-mixed components

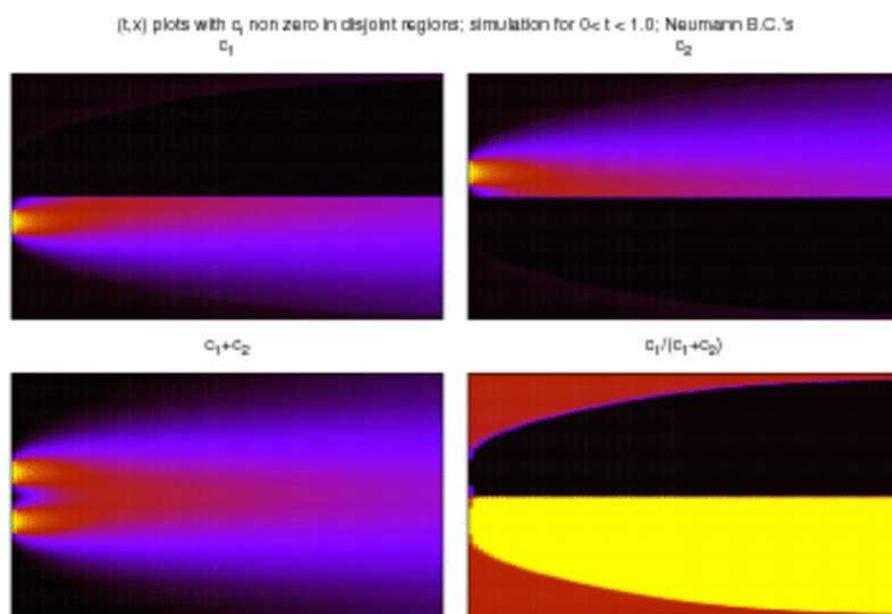


Fig. 6. Neumann boundary conditions, un-mixed components, disjoint support