A two-scale reaction-diffusion system with micro-cell reaction concentrated on a free boundary

Citation for published version (APA):

Meier, S. A., & Muntean, A. (2008). *A two-scale reaction-diffusion system with micro-cell reaction concentrated on a free boundary*. (CASA-report; Vol. 0801). Technische Universiteit Eindhoven.

Document status and date:

Published: 01/01/2008

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

A two-scale reaction-diffusion system with micro-cell reaction concentrated on a free boundary

Sebastian A. Meier ^a, Adrian Muntean ^b

^a *Centre for Industrial Mathematics (ZeTeM), FB3, University of Bremen, Postfach 330 440, 28334 Bremen, Germany*

^b *CASA-Centre for Analysis, Scientific computing and Applications, Department of Mathematics and Computer Science, Technical University of Eindhoven, PO Box 513, 5600 MB Eindhoven, The Netherlands*

Abstract

We discuss the fast-reaction limit of a two-scale reaction-diffusion model. We point out that if the reaction constant a explodes to infinity, then a two-scale PDEs system with free boundary at the micro cell is obtained. The aim of this note is to answer the question: Can the same two-scale free-boundary problem be obtained if we first pass to the fast-reaction limit $a \rightarrow \infty$ and then take the homogenization limit $\varepsilon \rightarrow 0$ that is behind the derivation of the two-scale model? Here ε is the typical height of a representative rectangular micro-cell. Using the method of asymptotic expansions, we show that it does not matter whether we first take $\varepsilon \rightarrow 0$ and then $a \rightarrow \infty$, or vice-versa. Finally, we illustrate numerically the solution behavior of the two-scale model in case of a fast reaction.

Résumé

Sur un système de réaction-diffusion avec une frontière libre de réaction pénétrant la micro-structure. On considère un modèle de réaction-diffusion à deux échelles, dont la micro-structure contient une réaction rapide. Lorsque la constante de réaction a explose vers l'infini, le modèle à deux échelles converge vers un modèle à frontière libre concentrée dans la micro-structure. Le but de cette Note est de montrer qu'en échangeant la limite d'homogénéisation $\varepsilon \rightarrow 0$ avec celle de la réaction rapide $a \rightarrow \infty$, on ne change pas le modèle limite. Des résultats numériques sont également présentés.

Key words: Porous media ; Two-scale model ; Homogenization ; Fast reaction ; Free-boundary problem

Mots-clés : Milieux poreux ; Modèle à deux échelles, Homogénéisation, Réaction rapide ; Frontière libre

Email addresses: sebam@math.uni-bremen.de (Sebastian A. Meier), a.muntean@tue.nl (Adrian Muntean).

1. Introduction. A two-scale reaction-diffusion model and its fast-reaction limit

We consider the following prototypical reaction-diffusion scenario: A gaseous species A penetrates a non-saturated porous medium via the air phase of its pore space, instantaneously dissolves in the pore water where A reacts very fast with a species B . The species B becomes available by a dissolution mechanism. See, for instance, [1,2,3] for fast reaction – slow diffusion settings playing an important role in pattern formation and corrosion of porous materials, and [4,5] for further conceptually related scenarios arising in the modeling of catalytic reactors and deformation in hydrophilic swelling porous media.

In this note, we present a coupled two-scale reaction-diffusion system whose distributed micro-structure hosts the fast reaction of A and B . Making use of singular-limit analysis we derive a non-standard free-boundary problem and its pseudo-steady state approximation (PSSA) as the fast-reaction limit $a \rightarrow \infty$ of the two-scale model. a stands for the corresponding reaction constant. The question that we answer here is: Is the *same* two-scale free-boundary problem obtained if we first pass to the fast-reaction limit $a \rightarrow \infty$ and then take the homogenization limit $\varepsilon \rightarrow 0$ (that is behind the derivation of the two-scale model)? Using the method of formal homogenization, we show that interchanging the limits $\varepsilon \rightarrow 0$ and $a \rightarrow \infty$ gives the same result.

We denote the macroscopic domain by $\Omega =]0, L[$ and the micro-cell by $Y =]0, R[$. Here we take $0 < R < 1$ and $0 < L < \infty$. C_1^A , C_2^A , and C^B are the active concentrations. By the upper indices A and B , we indicate the two reactants. The lower index concerns either the phase 1 and refers to the macro-scale, or the phase 2 and then it refers to the micro scale. The species A is present in both phases and it is active on both scales, while the species B only appears in phase 2 (i.e. on the micro-scale, which we also call pore scale). We denote by S_T the time interval $]0, T[$, where $T > 0$ is finite and arbitrarily fixed.

Figure 1. Geometry of the two-scale model (P_a).

We consider the following set of mass-balance equations motivated in [2] (see also fig. 1):

$$\partial_t C_1^A - D_1^A \partial_{xx} C_1^A = -(1 - R)^{-1} D_2^A \partial_y C_2^A(t, x, R), \quad x \in \Omega, \quad t \in S_T, \quad (1)$$

$$\partial_t C_2^A - D_2^A \partial_{yy} C_2^A = -a C_2^A C^B, \quad x \in \Omega, \quad y \in Y, \quad t \in S_T, \quad (2)$$

$$\partial_t C^B - D^B \partial_{yy} C^B = -a C_2^A C^B, \quad x \in \Omega, \quad y \in Y, \quad t \in S_T, \quad (3)$$

initial conditions

$$C_1^A(0, x) = 0, \quad C_2^A(0, x, y) = 0, \quad C^B(0, x, y) = C_B^0, \quad x \in \Omega, \quad y \in Y, \quad (4)$$

boundary conditions connecting the *micro* scale with the *macro* one

$$C_2^A(t, x, R) = C_1^A(t, x), \quad x \in \Omega, \quad t \in S_T, \quad (5)$$

boundary conditions at the micro scale

$$\partial_y C_2^A(t, x, 0) = 0, \quad \partial_y C^B(t, x, 0) = \partial_y C^B(t, x, R) = 0, \quad x \in \Omega, \quad t \in S_T \quad (6)$$

as well as of boundary conditions for the species living at the *macro* scale

$$C_1^A(t, 0) = C_1^{A, ext}(t), \quad (7)$$

$$\partial_x C_1^A(t, L) = 0, \quad t \in S_T. \quad (8)$$

The system (1)–(8) forms our *two-scale model*. We refer to this system as (P_a) .

Limiting behavior as $a \rightarrow \infty$. The first question that we address is: What happens in the limit $a \rightarrow \infty$ with the system (1)–(8)? Relying on arguments from [1,6,7], we deduce the structure of the system in the limit $a \rightarrow \infty$. Rigorous convergence proofs will be presented elsewhere [8]. We denote by c_1^A , c_2^B and c^B the active concentrations arising in the following limit problem

$$\partial_t c_1^A - D_1^A \partial_{xx} c_1^A = -(1-R)^{-1} D_2^A \partial_y c_2^A(t, x, R), \quad x \in \Omega, \quad t \in S_T, \quad (9)$$

$$\partial_t c_2^A - D_2^A \partial_{yy} c_2^A = 0, \quad x \in \Omega, \quad y \in (s(t), R), \quad t \in S_T, \quad (10)$$

$$\partial_t c^B - D^B \partial_{yy} c^B = 0, \quad x \in \Omega, \quad y \in (0, s(t)), \quad t \in S_T, \quad (11)$$

initial conditions

$$c_1^A(0, x) = 0, \quad c_2^A(0, x, y) = 0, \quad y \in (s_0, R), \quad c^B(0, x, y) = c_B^0, \quad y \in (0, s_0), \quad s(0, x) = s_0, \quad x \in \Omega, \quad (12)$$

where $0 < s_0 \leq R$ is the initial position of the interface s , one boundary condition matching the micro with the macro scale,

$$c_2^A(t, x, R) = c_1^A(t, x), \quad x \in \Omega, \quad t \in S_T, \quad (13)$$

and boundary conditions for the species living at the *macro* scale

$$c_1^A(t, 0) = c_1^{A, ext}(t), \quad t \in S_T, \quad (14)$$

$$\partial_x c_1^A(t, L) = 0, \quad t \in S_T. \quad (15)$$

Looking at the free-boundary conditions (particularly at the Stefan condition), we distinguish two cases:

(i) one-phase Stefan problem (for $D_B = 0$), and (ii) two-phase Stefan problem (for $D_B > 0$).

In case (i), we have $c^B = c_0^B$ on $[s(t, x), R]$, while the other interfacial conditions are

$$c_2^A(t, x, s(t, x)) = 0, \quad (16)$$

$$s'(t, x) c_0^B = -D_2^A \partial_y c_2^A(t, x, s(t, x)), \quad x \in \Omega, \quad t \in S_T, \quad (17)$$

as long as $s(t, x) > 0$. Otherwise, we have

$$s'(t, x) = 0 \quad \text{and} \quad D_2^A \partial_y c_2^A(t, x, s(t, x)) = 0. \quad (18)$$

(17) is the classical Stefan condition with c_0^B as "latent heat". In case (ii), the interfacial conditions look different:

$$\partial_y c^B(t, x, 0) = 0, \quad (19)$$

$$c_2^A(t, x, s(t, x)) = 0, \quad (20)$$

$$c^B(t, x, s(t, x)) = 0, \quad (21)$$

$$D^B \partial_y c^B(t, x, s(t, x)) = D_2^A \partial_y c_2^A(t, x, s(t, x)), \quad x \in \Omega, \quad t \in S_T. \quad (22)$$

as long as $s(t, x) > 0$. Otherwise, (18) holds also in this case. (22) represents the Stefan condition with zero latent heat. Here $y = s(t, x) \in Y$ represents the position of the free boundary at time $t \in S_T$ in the micro-cell associated to the point $x \in \Omega$. If we now assume

$$D^B = 0, \quad (H1)$$

then (9)–(18) is the free-boundary problem resulting in the *fast-reaction limit* of the two-scale model (P_a) . We refer to this problem as (P_∞) .

PSSA for the free-boundary problem (9)-(18). We consider the pseudo-steady state approximation (PSSA) for the concentration c_2^A ; it basically implies that

$$\partial_t c_2^A \text{ can be neglected in (10).} \quad (\text{H2})$$

This approximation is valid only if one can the characteristic time of the (fast) reaction in the reaction-diffusion scenario described by (P_a) is much smaller that the characteristic time of the diffusion of the species A . This is, for instance, the case of fast gas-liquid reactions in heterogeneous porous media, where the gaseous reactant dissolves infinitely fast in pore water; see e.g. the reaction-diffusion scenario described in [9]. By (H1), (H2), (10), (13), and (17), we obtain the relation

$$c_2^A(t, x, y) = \frac{c_1^A(t, x)}{R - s(t, x)}(y - s(t, x)) \quad \text{as long as } s(t, x) > 0. \quad (23)$$

Combining now (17) and (23), we get the following expression for the velocity s' of the free boundary

$$s'(t, x) = \begin{cases} \frac{-D_2^A c_1^A(t, x)}{c_0^B(R - s(t, x))} & \text{for } s(t, x) > 0 \\ 0, & \text{for } s(t, x) = 0. \end{cases} \quad (24)$$

for all $t \in S_T$ and $x \in \Omega$. In this way, the singular limit system (P_∞) is reduced to the scalar equation

$$\partial_t c_1^A - D_2^A \partial_{xx} c_2^A = (1 - R)^{-1} s'(t, x) c_0^B \quad \text{for } s(t, x) > 0, \quad (25)$$

coupled with (24) and with the boundary conditions (14) and (15) at the macro-scale. This result is an important gain at the practical level: one does not have to solve numerically a coupled system of PDEs with moving boundary but only a PDE coupled with an ODE acting like a memory term. Note however, that (23) and (25) are only valid up to the time where the front $s(t, x)$ becomes zero at some point $x \in (0, 1)$. Afterwards, some degeneracy in the model occurs, which needs to be further investigated.

The ODE (24) provides an explicit expression for the position of the free boundary. This can be obtained by integrating along $]0, t[$ the expression $-s'(t, x)(R - s(t, x)) = \mathcal{A}(t, x)$, where $\mathcal{A}(t, x) := \frac{D_2^A}{c_0^B} c_1^A(t, x)$. It yields

$$R - s(t, x) = \begin{cases} \sqrt{2 \int_0^t \mathcal{A}(\tau, x) d\tau} & s(t, x) > 0 \\ 0 & s(t, x) = 0. \end{cases} \quad (26)$$

By the uniform boundedness of c_1^A , the relation (26) indicates in case of $s(t, x) > 0$ the asymptotic behavior $R - s(t, x) = \mathcal{O}(\sqrt{t})$ for each $x \in \Omega$ as we actually expect from the behavior of the solution to the classical one-phase Stefan problem. Now, the whole process can be described by the single scalar equation (25) with s' computed by means of (26). Moreover, we can further exploit (26) in order to get a lower bound for the time at which the interface reaches a given spatial point $s_1 \geq 0$, say the *final time* of the motion of the free boundary $T_{\text{fin}}^{\text{PSSA}}$. Particularly, we obtain the estimate

$$0 < \frac{(R - s_1)^2 c_{0, \max}^B}{2D_2^A c_1^{A0}} \leq T_{\text{fin}}^{\text{PSSA}}.$$

2. Permuting the homogenization limit with the fast-reaction limit

It is well known (see [10] for the formal proof, and [11,12,13] for related work) that the two-scale model (1)–(8) can be obtained when taking the limit $\varepsilon \rightarrow 0$ in the reaction-diffusion system (27)–(34) defined

Figure 2. Left: Geometry of the model (P_a^ε) . Right: Possible position of the free boundary $\Sigma^\varepsilon(t)$ in the model (P^ε) .

at the pore level. We assume (H1) and let $\varepsilon > 0$ be a small parameter. The two-dimensional, ε -periodic micro geometry is depicted in fig. 2 (left). Let $R \in (0, 1)$ and $L > 0$. Furthermore, we define the sets $\Omega_1^\varepsilon := (0, L) \times (\varepsilon R, \varepsilon)$, $\Omega_2^\varepsilon := (0, L) \times (0, \varepsilon R)$ and $\Gamma^\varepsilon := \partial\Omega_1^\varepsilon \cap \partial\Omega_2^\varepsilon$. Then the unit normal at Γ^ε pointing towards Ω_1^ε is $\nu^\varepsilon = (0, 1)^T$. Moreover, let $\Gamma^{\varepsilon, \text{ext}} := \{0\} \times (\varepsilon R, \varepsilon)$ and $\Gamma_1^{N\varepsilon} := \partial\Omega_1^\varepsilon \setminus (\Gamma^\varepsilon \cup \Gamma^{\varepsilon, \text{ext}})$ and $\Gamma_2^{N\varepsilon} := \partial\Omega_2^\varepsilon \setminus \Gamma^\varepsilon$. The model equations are

$$\partial_t C_1^{A\varepsilon} - D_1^A \Delta C_1^{A\varepsilon} = 0, \quad x \in \Omega_1^\varepsilon, \quad t \in S_T, \quad (27)$$

$$\partial_t C_2^{A\varepsilon} - \varepsilon^2 D_2^A \Delta C_2^{A\varepsilon} = -a C_2^{A\varepsilon} C^{B\varepsilon}, \quad x \in \Omega_2^\varepsilon, \quad t \in S_T, \quad (28)$$

$$\partial_t C^{B\varepsilon} = -a C_2^{A\varepsilon} C^{B\varepsilon}, \quad x \in \Omega_2^\varepsilon, \quad t \in S_T, \quad (29)$$

with boundary conditions

$$D_1^A \partial_{x_2} C_1^{A\varepsilon} = \varepsilon^2 D_2^A \partial_{x_2} C_2^{A\varepsilon}, \quad x = (x_1, x_2) \in \Gamma^\varepsilon, \quad t \in S_T, \quad (30)$$

$$C_1^{A\varepsilon} = C_2^{A\varepsilon}, \quad x \in \Gamma^\varepsilon, \quad t \in S_T, \quad (31)$$

$$C_1^{A\varepsilon} = C_1^{A, \text{ext}}(t), \quad x \in \Gamma^{\varepsilon, \text{ext}}, \quad t \in S_T, \quad (32)$$

$$D_i^A \nabla C_i^{A\varepsilon} \cdot \nu = 0, \quad x \in \Gamma_i^{N\varepsilon}, \quad t \in S_T, \quad i = 1, 2, \quad (33)$$

and initial conditions

$$C_1^{A\varepsilon}(0, x) = 0, \quad x \in \Omega_1^\varepsilon, \quad C_2^{A\varepsilon}(0, x) = 0, \quad x \in \Omega_2^\varepsilon, \quad C^{B\varepsilon}(0, x) = C_B^0, \quad x \in \Omega_2^\varepsilon. \quad (34)$$

The system (27)–(34) is referred to as (P_a^ε) . To obtain the two-scale model (P_a) in the limit $\varepsilon \rightarrow 0$ (see [14, 10], e.g.), we need the special scaling $\varepsilon^2 D_2^A$ of the diffusivity of the slowest species C_2^A . We have seen in section 1 that if we consider firstly $\varepsilon \rightarrow 0$ and then $a \rightarrow \infty$, we obtain the free-boundary problem (9)–(17). The question, which we address now, is: Do we obtain the same PDE system as homogenized singular limit if we permute the two limits? In other words, what happens if we first take $a \rightarrow \infty$ and then $\varepsilon \rightarrow 0$?

Let Ω_2^ε be separated by the interface $\Sigma^\varepsilon(t)$ evolving in time (cf. fig. 2, right). We assume that the surface $\Sigma^\varepsilon(t)$ can be represented via

$$(x_1, x_2) \in \Sigma^\varepsilon(t) \iff x_2 = s^\varepsilon(t, x_1), \quad t \in S_T, \quad x_1 \in (0, L),$$

and select $s^\varepsilon(0, x_1) = s_0 \in (0, R]$. We define $\Omega_2^\varepsilon(t) := (0, L) \times (s^\varepsilon(t), \varepsilon R)$ and denote by $w^\varepsilon(t, x)$ the normal velocity of $\Sigma^\varepsilon(t)$ pointing outwards from $\Omega_2^\varepsilon(t)$. By passing to the limit $a \rightarrow \infty$ in (27)–(34), we obtain the one-phase Stefan problem (35)–(42), viz.

$$\partial_t c_1^{A\varepsilon} - D_1^A \Delta c_1^{A\varepsilon} = 0, \quad x \in \Omega_1^\varepsilon, \quad t \in S_T, \quad (35)$$

$$\partial_t c_2^{A\varepsilon} - \varepsilon^2 D_2^A \Delta c_2^{A\varepsilon} = 0, \quad x \in \Omega_2^\varepsilon(t), \quad t \in S_T, \quad (36)$$

with boundary conditions

$$D_1^A \partial_{x_2} c_1^{A\varepsilon} = \varepsilon^2 D_2^A \partial_{x_2} c_2^{A\varepsilon}, \quad x = (x_1, x_2) \in \Gamma^\varepsilon, \quad t \in S_T, \quad (37)$$

$$c_1^{A\varepsilon} = c_2^{A\varepsilon}, \quad x \in \Gamma^\varepsilon, \quad t \in S_T, \quad (38)$$

$$c_1^{A\varepsilon} = c_1^{A,ext}(t), \quad x \in \Gamma^{\varepsilon,ext}, \quad t \in S_T, \quad (39)$$

$$D_1^A \nabla C_1^{A\varepsilon} \cdot \nu = 0, \quad x \in \Gamma_1^{N\varepsilon}, \quad t \in S_T, \quad (40)$$

and initial conditions

$$c_1^{A\varepsilon}(0, x) = 0 \quad x \in \Omega_1^\varepsilon, \quad c_2^{A\varepsilon}(0, x) = 0, \quad x \in \Omega_2^\varepsilon(0), \quad s^\varepsilon(0, x_1) = s_0, \quad x_1 \in (0, L). \quad (41)$$

The free boundary $\Sigma^\varepsilon(t)$ completely separates the support of the species A from the species B . The limit problem is closed by the following interface conditions:

$$w^\varepsilon(t, x) c_0^B = -\varepsilon^2 D_2^A \nabla c_2^{A\varepsilon}(t, x) \cdot \nu^\varepsilon(t, x), \quad c_2^{A\varepsilon}(t, x) = 0, \quad t \in S_T, \quad x \in \Sigma^\varepsilon(t), \quad (42)$$

as long as $s(t, x) > 0$, and otherwise

$$w^\varepsilon(t, x) = 0 \quad \text{and} \quad -\varepsilon^2 D_2^A \nabla c_2^{A\varepsilon}(t, x) \cdot \nu^\varepsilon(t, x) = 0, \quad t \in S_T, \quad x \in \Sigma^\varepsilon(t), \quad (43)$$

cf. the discussion above.

We carry out now the homogenization procedure by the method of asymptotic expansions; see [15,16], e.g. To this aim, we omit the upper index “ A ” in the following calculations and assume that the functions c_1^ε and c_2^ε admit the asymptotic representations

$$c_1^\varepsilon(t, x) = c_1^0(t, x_1, \frac{x_2}{\varepsilon}) + \varepsilon c_1^1(t, x_1, \frac{x_2}{\varepsilon}) + \dots, \quad x_1 \in (0, L), \quad x_2 \in (R\varepsilon, \varepsilon),$$

$$c_2^\varepsilon(t, x) = c_2^0(t, x_1, \frac{x_2}{\varepsilon}) + \varepsilon c_2^1(t, x_1, \frac{x_2}{\varepsilon}) + \dots, \quad x_1 \in (0, L), \quad x_2 \in (0, R\varepsilon),$$

valid for small ε , where all coefficients are Y -periodic functions w.r.t. their third coordinate. Moreover, we rescale

$$s^\varepsilon(t, x_1) =: \varepsilon s^0(t, x_1), \quad t \in S_T, \quad x_1 \in (0, L). \quad (44)$$

By (44), we obtain the important geometrical relations

$$\begin{aligned} \nu^\varepsilon(t, x) &= \frac{1}{\sqrt{1 + |\partial_{x_1} s^\varepsilon|^2}} \begin{pmatrix} \partial_{x_1} s^\varepsilon \\ -1 \end{pmatrix} \\ &= \frac{1}{\sqrt{1 + \varepsilon^2 |\partial_{x_1} s^0|^2}} \begin{pmatrix} \varepsilon \partial_{x_1} s^0 \\ -1 \end{pmatrix} \\ &\approx \begin{pmatrix} 0 \\ -1 \end{pmatrix} + \mathcal{O}(\varepsilon), \quad t \in S_T, \quad x \in \Sigma^\varepsilon(t) \end{aligned} \quad (45)$$

and

$$\begin{aligned} w^\varepsilon(t, x) &= \begin{pmatrix} 0 \\ \partial_t s^\varepsilon \end{pmatrix} \cdot \nu^\varepsilon(t, x) \\ &= \frac{-\partial_t s^\varepsilon}{\sqrt{1 + |\partial_{x_1} s^\varepsilon|^2}} \\ &\approx -\varepsilon \partial_t s^0(t, x_1) + \mathcal{O}(\varepsilon^2), \quad t \in S_T, \quad x \in \Sigma^\varepsilon(t). \end{aligned} \quad (46)$$

Now we calculate the limit equations by plugging into (35)-(42) the asymptotic expansions introduced above and capture the model (P_∞) collecting zeroth order (in ε) terms. Note that

$$\nabla_x c \left(x_1, \frac{x_2}{\varepsilon} \right) = \begin{pmatrix} \partial_{x_1} c \\ \varepsilon^{-1} \partial_{x_2} c \end{pmatrix}.$$

In what follows, the variables x_1 and x_2 will be denoted by x and y . The problem of order zero is:

$$-\partial_y(D_1\partial_y c_1^0) = 0, \quad y \in (R, 1), \quad (47)$$

$$\partial_y c_1^0 = 0, \quad y = R \text{ or } y = 1. \quad (48)$$

It follows that $c_1^0 = c_1^0(t, x)$ is independent of y .

The problem of order 1 is:

$$-\partial_y(D_1\partial_y c_1^1) = 0, \quad y \in (R, 1), \quad (49)$$

$$\left(\frac{\partial_x c_1^0}{\partial_y c_1^1}\right) \cdot \nu = 0, \quad y = R \text{ or } y = 1. \quad (50)$$

Since the normal ν at $y = R$ and $y = 1$ is plus or minus $(0, 1)^T$, the problem (49)–(50) for c_1^1 reduces to the same problem as (47)–(48) for c_1^0 . Hence, also $c_1^1 = c_1^1(t, x)$. The problem of second order, for $t \in S_T$ and $x \in (0, 1)$, (using (46) and (45)) consists of

$$\partial_t c_1^0 - \partial_x(D_1\partial_x c_1^0) = \partial_y(D_1\left(\frac{\partial_x c_1^1}{\partial_y c_1^2}\right)), \quad y \in (R, 1), \quad (51)$$

$$\partial_t c_2^0 - \partial_y(D_2\partial_y c_2^0) = 0, \quad y \in (s^0(t, x), R), \quad (52)$$

$$D_1\left(\frac{\partial_x c_1^1}{\partial_y c_1^2}\right) \cdot \begin{pmatrix} 0 \\ -1 \end{pmatrix} = D_2\left(\frac{0}{\partial_y c_2^0}\right) \cdot \begin{pmatrix} 0 \\ -1 \end{pmatrix}, \quad y = R, \quad (53)$$

$$c_2^0 = c_1^0, \quad y = R, \quad (54)$$

$$\partial_y c_2^0 = 0, \quad y = 1, \quad (55)$$

and the conditions on the moving interface

$$-\partial_t s^0 c_0^B = -D_2\left(\frac{0}{\partial_y c_2^0}\right) \cdot \begin{pmatrix} 0 \\ -1 \end{pmatrix}, \quad y = s^0(t, x) > 0, \quad (56)$$

$$c_2^0 = 0, \quad y = s^0(t, x) > 0 \quad (57)$$

and otherwise, if $s^0(t, x) = 0$,

$$-D_2\left(\frac{0}{\partial_y c_2^0}\right) \cdot \begin{pmatrix} 0 \\ -1 \end{pmatrix} = 0, \quad y = s^0(t, x) = 0. \quad (58)$$

Eq. (53) simplifies to

$$D_1\partial_y c_1^2 = D_2\partial_y c_2^0, \quad y = R, \quad (59)$$

(56) becomes

$$-\partial_t s^0 c_0^B = D_2\partial_y c_2^0, \quad y = s^0(t, x) > 0,$$

and (58) becomes

$$\partial_y c_2^0 = 0, \quad y = s^0(t, x) = 0,$$

We integrate (51) over $(R, 1)$ and use Green's theorem. This gives

$$\begin{aligned} (1-R)\partial_t c_1^0 - (1-R)D_1\Delta_x c_1^0 &= D_2\left(\frac{\partial_x c_1^1}{\partial_y c_1^2}\right) \cdot \begin{pmatrix} 0 \\ -1 \end{pmatrix} \Big|_R^1 \\ &= -D_2\partial_y c_2^0 \Big|_R^1 \\ &= -D_2\partial_y c_2^0(t, x, R), \end{aligned} \quad (60)$$

where we have used (59) and (55). It follows via dividing by $(1-R)$

$$\partial_t c_1^0 - D_1\Delta_x c_1^0 = -(1-R)^{-1}D_2\partial_y c_2^0(t, x, R), \quad t \in S_T, \quad x \in (0, 1).$$

Setting $c_1^A := c_1^0$, $c_2^A := c_2^0$ and $s := s^0$, we have captured the model (P_∞) in the homogenisation limit.

3. Numerical example

Fig. 3 contains typical solution profiles of (P_a) for parameters $L = 1$, $R = 0.6$, $D_1^A = 0.5$, $D_2^A = 5$, $c_0^B = 10$ and $a = 500$. Diffusion of c_1^A takes place at the macro scale (left figure). The value of c_1^A at $x = 0.14$ ranges from 0.1 at $t = 0.1$ to about 0.42. Due to coupling condition (5), these values are exactly the boundary values of c_2^A in the local cell profiles at $x = 0.15$ (right figure). From this plot, it can be seen that the reaction in fact concentrates on a narrow zone *and* that the PSSA is reasonable for this choice of parameters.

Figure 3. Solutions of the two-scale model (P_a) . Left: Profiles of C_1^A . Right: Profiles of C_2^A and C^B/C_0^B for fixed $x = 0.14$.

References

- [1] Y. Nishiura, Far-from-Equilibrium Dynamics, vol. 209, AMS, Providence, Rhode Island, 2002.
- [2] S. A. Meier, M. A. Peter, A. Muntean, M. Böhm, J. Kropp, A two-scale approach to concrete carbonation, in Proc. Int. RILEM Workshop on Integral Service Life Modeling of Concrete Structures, 2007, Guimares, Portugal, pp. 3-10.
- [3] T. L. van Noorden, I. S. Pop, A Stefan problem modelling crystal dissolution and precipitation, to appear in IMA J. Appl. Math.
- [4] A. Friedman, A. T. Tzavaras, A quasilinear parabolic system arising in modeling of catalytic reactors, J. Diff. Eqs., 70, 1987, 167-196.
- [5] M. A. Murad, J. H. Cushman, Multiscale flow and deformation in hydrophilic swelling porous media, Internat. J. Engrg. Sci., 34 (3) (1996), 313-338.
- [6] A. Fasano, M. Primicerio, R. Ricci, Limiting behaviour of some problems in diffusive penetration, Rendiconti di Matematica, Serie VII, 10 (1990) 39-57.
- [7] D. Hilhorst, R. van der Hout, L. A. Peletier, The fast reaction limit for a reaction-diffusion system, J. Math. Anal. Appl. 199 (1996) 349-373.
- [8] A. Muntean, S. A. Meier, Existence of weak solutions to a two-scale reaction-diffusion system with micro-cell reaction concentrated on a free boundary. in preparation.
- [9] M. A. Peter, Homogenisation of a chemical degradation mechanism inducing an evolving microstructure, C. R. Mécanique 335 (11) (2007) 679-684.
- [10] S. A. Meier, Two-scale models of reactive transport in porous media involving microstructural changes, PhD thesis, University of Bremen, Germany, to be submitted.
- [11] C. Eck, P. Knabner, S. Korotov, A two-scale method for the computation of solid-liquid phase transitions with dendritic microstructure, J. Comput. Physics 178 (2002) 58-80.

- [12] C. Eck, H. Emmerich, Models for liquid phase epitaxy, Preprint No. 146, DFG-SPP 1095 Analysis, Modellbildung und Simulation von Mehrskalenproblemen, 2004.
- [13] S. A. Meier, M. Böhm, A note on the construction of function spaces for distributed-microstructure models with spatially varying cell geometry, to appear in *Electr. J. Diff. Eqs.*
- [14] T. Arbogast, J. Douglas Jr., U. Hornung, Derivation of the double porosity model of single phase flow via homogenization theory, *SIAM J. Math. Anal.* 21 (4) (1990) 823-836.
- [15] D. Ciorănescu, P. Donato, *An Introduction to Homogenization*, Oxford University Press, 1999.
- [16] E. Sanchez-Palencia, *Non-Homogeneous Media and Vibration Theory*, Springer Verlag, Berlin, 1980.