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A spectral approach for homogenization of diffusion and heterogeneous reaction in porous media

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Abstract

Macroscopic models for diffusion and heterogeneous reversible reaction of two species in porous media are developed by using coupled homogenization technique and spectral approach. Three representative cases related to the order of magnitude of the macroscopic Damköhler number Da_L , namely predominating reaction, diffusion-reaction of the same order and dominating diffusion, are considered. The concentrations are developed as time series in an eigenfunctions basis associated with periodic spectral problems formulated in the unit-cell, thus forming a new microscopic problem to be homogenized. Such an approach represents a powerful tool to upscale diffusion-reaction microscopic problems, especially for high Damköhler number values where classical asymptotic development fails. It enables to capture the physics at very short times, when the characteristic time of reaction involved is much faster than the diffusion one. This work allows us to formulate the complex macroscopic laws describing the heterogeneous diffusion/reaction problem for two species in high Damköhler number regime.

Keywords: Diffusion-reaction, Damköhler number, Spectral problem, Homogenization

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1. Introduction

Reactive mass transport in porous media, which is the subject of many studies in scientific and engineering disciplines, is a coupled multiscale and multi-physics process. For example, convection-diffusion-reaction of multi-species in a poroelastic tissue, coupling mechanical and reactive mass transfer problem has been recently examined [1]. Slightly non-isothermal diffusion-reaction problem in a catalyst pellet was studied in [2].

To overcome the time and computational resources challenge of pore-scale modeling, the most suitable way is to upscale the local problem and to consider the porous medium as a continuous domain. Several approaches exist to perform such upscaling: method of moments [3, 4], periodic homogenization technique [5, 6], homogenization by two-scale convergence [7, 8], volume averaging technique [9]. In this work, the problem of diffusion in the fluid phase and heterogeneous first-order chemical reaction at the fluid/solid interface is investigated. In the literature, the convection and diffusion are frequently considered for the transport problem. However, the main challenge for the upscaling procedures stems from the heterogeneous reaction. Three cases (related to the order of magnitude of the macroscopic Damköhler number Da_L), namely predominating reaction, diffusion-reaction of the same order and dominating diffusion, can be distinguished. In the linear case with a small Damköhler number, all upscaling techniques give the standard result of a macroscopic diffusion-reaction equation characterized by a macroscopic diffusion tensor solely depending on the geometry and microscopic diffusion coefficients, and a reactive source term depending on the specific surface area, reaction rates and concentrations [9].

Specific applications of this problem can be found in many fields. For example, in electrochemical systems, the porous bio-electrode proceeds to reduce oxygen indirectly so that heterogeneous reaction and diffusion of the two dilute species O_2 and H_2O_2 are involved [10]. The reaction rates depend on the operating potential and can be very large for a low operating potential. The macroscopic equations developed in [10] form the basis of a numerical tool for optimizing porous micro-electrode thickness [11]. However, the authors considered only the low kinetic number regime for the sake of simplicity. The high Damköhler regime remains an open issue. Another field of application is agronomy with ion uptake (metals, ligands, ligand-complexed metals) by roots. Homogeneous and heterogeneous reactions combined with the diffusion mechanism take place in the soil with very variable orders of magnitude of the reaction rates [12]. There is a strong motivation to elucidate the upscaling procedure for diffusion-reaction problems especially

in the case of large Damköhler number.

Battiato and Tartakovsky have applied the asymptotic expansion method in the case of diffusion-advection coupled to a non linear chemical reaction for small values of Damköhler number considering one species [13] and multi-species [14]. However, the standard multiscale expansion fails to derive macroscopic mass conservation equations in the case of a large Damköhler number. In a previous work [15], we have examined theoretical models for the diffusion of two species coupled to a heterogeneous reaction by the classical periodic homogenization procedure. It has been emphasized that the homogenized models obtained for high Damköhler number fail to predict the physics at short times when the chemical equilibrium is not achieved.

For the more challenging case of predominating reaction, several attempts have been made to derive macroscopic laws for one species. The first one goes back to Shapiro and Brenner [16] using the method of moments. Mauri [17] has used the periodic homogenization method to upscale the diffusion-convection problem coupled with linear heterogeneous chemical reaction for different orders of magnitude of the Péclet and Damköhler numbers. The homogenized diffusion (or dispersion) tensor is affected by the local chemical reaction rate for high values of the Damköhler number. Its determination requires the resolution of a boundary value problem coupled to an auxiliary eigenvalue problem. With the help of the volume averaging approach, Valdés-Parada et al. [18, 19] have shown that the effective diffusion tensor depends on the reaction rate for high Damköhler number. Multi-species diffusion/heterogeneous reaction problem has also been studied by Qiu et al. [20] using the same approach. Effective diffusion and co-diffusion tensors depending on the reaction rates are introduced and the authors highlight the influence of the local variation of the reaction rate on the macroscopic response of the upscaled model.

A general framework to study the diffusion-advection-reaction problem in the case of large Damköhler number has been introduced by Allaire et al. [21, 22] combining the asymptotic expansion method with spectral problems at the unit cell level. The authors highlight the influence of the reaction on the diffusion-dispersion tensor. Recently, this technique has been used by Bourbatache et al. [23] to upscale a diffusion-reaction problem for a single species. Municchi and Icardi [24] have solved the same problem including advection.

The novel method proposed in this paper to upscale a two species diffusion/reaction problem makes use of a change of variable based on a spectral approach coupled with a homogenization procedure. The concentrations are developed in series in the basis of eigenfunctions associated with periodic spectral problems, thus

forming a new microscopic problem to be homogenized. The proposed approach leads to consistent homogenized models, even for large Damköhler number values. These models are capable of capturing the physics at very short times, when the characteristic time of reaction is much faster than the diffusion one.

2. Pore-scale model

2.1. Initial problem

Consider a porous medium occupying a macroscopic domain Ω^* of characteristic length L , composed of an immobile fluid phase Ω_f^* and of a rigid solid phase Ω_s^* ; the solid-fluid interface is denoted Γ_{fs}^* . We consider a diffusion problem of two species A and B in the fluid phase Ω_f^* . At the solid/fluid interface Γ_{fs}^* , a reversible chemical reaction occurs as follows



where k_1^* and k_2^* are the associated constant reaction rates. It should be noted that the dimensional quantities are indexed by the superscript $*$.

Let c_1^* and c_2^* be the concentrations of A and B respectively. Assuming that the transport is ruled by a Fickian process, the microscopic diffusion/reaction equations at the pore-scale are written as

$$\begin{cases} \frac{\partial c_1^*}{\partial t^*} - \nabla^* \cdot (\mathcal{D}_1^* \nabla^* c_1^*) = 0 & \text{in } \Omega_f^* \\ \frac{\partial c_2^*}{\partial t^*} - \nabla^* \cdot (\mathcal{D}_2^* \nabla^* c_2^*) = 0 & \text{in } \Omega_f^* \\ -\mathcal{D}_1^* \nabla^* c_1^* \cdot \mathbf{n}_{fs} = k_1^* c_1^* - k_2^* c_2^* & \text{at } \Gamma_{fs}^* \\ -\mathcal{D}_2^* \nabla^* c_2^* \cdot \mathbf{n}_{fs} = k_2^* c_2^* - k_1^* c_1^* & \text{at } \Gamma_{fs}^* \end{cases} \quad (2)$$

where \mathcal{D}_1^* and \mathcal{D}_2^* denote the diffusion coefficients of A and B respectively, \mathbf{n}_{fs} the normal unit vector at the solid/fluid interface pointing out of the fluid phase.

The microstructure of Ω^* is assumed to be constituted of the repetition of a periodic elementary cell Y^* of characteristic length l . The macroscopic and microscopic spatial coordinates are noted $\mathbf{x}^* = (x_1^*, x_2^*, x_3^*)$ and $\mathbf{y}^* = (y_1^*, y_2^*, y_3^*)$ respectively. The scale separation condition ($l \ll L$) allows introducing the small parameter $\varepsilon = l/L$, the micro-scale l to the macro-scale L ratio.

The elementary cell of the porous medium $Y^* = Y_f^* \cup Y_s^*$ is composed of the fluid phase Y_f^* and of the solid phase Y_s^* . The boundary of the fluid phase $\partial Y_f^* = \partial Y_{fs}^* \cup \partial Y_{fe}^*$ is constituted of the solid-fluid interface ∂Y_{fs}^* assumed to be impermeable and of the external interface ∂Y_{fe}^* (figure 1).

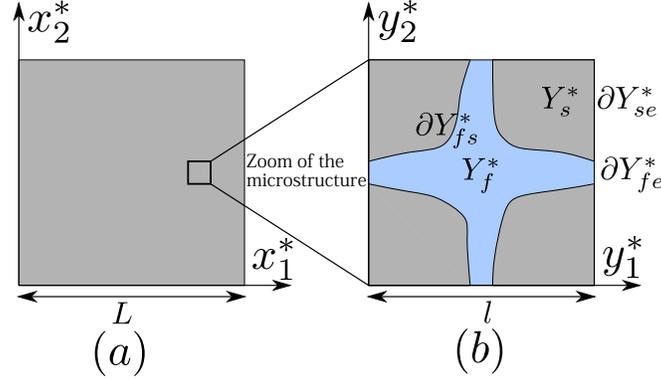


Figure 1: Schematic representation of a porous medium with periodic microstructure. a) Macroscopic scale. b) Elementary reference cell.

2.2. Associated spectral problem

The initial microscopic model will be transformed into a new problem associated with the following spectral problem defined in the periodic unit cell Y^*

$$\begin{cases} -\nabla^* \cdot (\mathcal{D}_1^* \nabla^* \psi_{1,n}^*) &= \lambda_n^* \psi_{1,n}^* & \text{in } Y_f^* \\ -\nabla^* \cdot (\mathcal{D}_2^* \nabla^* \psi_{2,n}^*) &= \lambda_n^* \psi_{2,n}^* & \text{in } Y_f^* \\ -\mathcal{D}_1^* \nabla^* \psi_{1,n}^* \cdot \mathbf{n}_{fs} &= k_1^* \psi_{1,n}^* - k_2^* \psi_{2,n}^* & \text{at } \partial Y_{fs}^* \\ -\mathcal{D}_2^* \nabla^* \psi_{2,n}^* \cdot \mathbf{n}_{fs} &= k_2^* \psi_{2,n}^* - k_1^* \psi_{1,n}^* & \text{at } \partial Y_{fs}^* \end{cases} \quad (3)$$

where $\psi_{1,n}^*(\mathbf{y}^*)$ and $\psi_{2,n}^*(\mathbf{y}^*)$ denote the Y -periodic eigenfunctions sharing the same eigenvalues λ_n^* , with $n \in \mathbb{N}$.

Three important points must be emphasized. First, the eigenfunctions $\psi_{1,n}^*$ and $\psi_{2,n}^*$ are defined to within a same multiplicative constant. Secondly, it should be noted that $\lambda_0^* = 0$ is also an eigenvalue associated with the constant eigenfunctions $\psi_{1,0}^*$ and $\psi_{2,0}^*$ satisfying the condition $k_1^* \psi_{1,0}^* - k_2^* \psi_{2,0}^* = 0$. Thirdly, the eigenfunctions $(\psi_{1,n}^*, \psi_{2,n}^*)$ for $n \geq 1$ obey a compatibility equation. Integrating Eqs. (3a) and (3b) over Y_f^* , using the divergence theorem yields

$$\langle \psi_{1,n}^* \rangle^f + \langle \psi_{2,n}^* \rangle^f = 0 \quad \text{for } n \geq 1 \quad (4)$$

where the operator $\langle \cdot \rangle^f$ denotes the intrinsic average in the fluid phase of the unit cell defined in (20).

The unknowns c_i^* ($i \in \{1, 2\}$) are sought in a series development related to the spectral problem as follows¹

$$c_i^*(t^*, \mathbf{x}^*, \mathbf{y}^*) = \sum_{n=0}^{\infty} \psi_{i,n}^*(\mathbf{y}^*) \exp(-\lambda_n^* t^*) v_{i,n}^*(t^*, \mathbf{x}^*, \mathbf{y}^*) \quad (5)$$

where $v_{i,n}^*$ are new variables depending also on time and position.

The decomposition (5) is based on the idea of a separation of variables in the unit cell Y . This choice is justified by the orthogonality condition (A.9) for the eigenfunctions $\psi_{i,n}^*$ (see Appendix A and reference [25]). Generally, the function $v_{i,n}^*$ should be constant in the unit cell, *i.e.* depending only on \mathbf{x}^* . However, the complex feature of local chemical non-equilibrium at short time requires that $v_{i,n}^*$ should depend also on y^* and t^* in order to describe two separated time scales: a short time related to the chemical reaction in the exponential term and a macroscopic time corresponding to the transport problem. As shown later, at the leading order $\mathcal{O}(\epsilon^0)$ corresponding to the macroscale, $v_{i,n}^*$ is only function of x^* and t^* (Eq. (24)).

Inserting (5) into the initial problem (2) written on Y_f^* yields

$$\left\{ \begin{array}{l} \sum_{n=0}^{\infty} \exp(-\lambda_n^* t^*) \left\{ \psi_{i,n}^* \left(\frac{\partial v_{i,n}^*}{\partial t^*} - \lambda_n^* v_{i,n}^* \right) \right. \\ \quad \left. - \nabla^* \cdot [D_i^* \nabla^* (\psi_{i,n}^* v_{i,n}^*)] \right\} = 0 \quad \text{in } Y_f^* \\ - \sum_{n=0}^{\infty} \exp(-\lambda_n^* t^*) D_1^* \nabla^* (\psi_{1,n}^* v_{1,n}^*) \cdot \mathbf{n}_{fs} \\ \quad = \sum_{n=0}^{\infty} \exp(-\lambda_n^* t^*) (k_1^* \psi_{1,n}^* v_{1,n}^* - k_2^* \psi_{2,n}^* v_{2,n}^*) \quad \text{at } \partial Y_{fs}^* \\ - \sum_{n=0}^{\infty} \exp(-\lambda_n^* t^*) D_2^* \nabla^* (\psi_{2,n}^* v_{2,n}^*) \cdot \mathbf{n}_{fs} \\ \quad = \sum_{n=0}^{\infty} \exp(-\lambda_n^* t^*) (k_2^* \psi_{2,n}^* v_{2,n}^* - k_1^* \psi_{1,n}^* v_{1,n}^*) \quad \text{at } \partial Y_{fs}^*. \end{array} \right. \quad (6)$$

When the eigenvalues are well separated, the problem (6) can be solved separately

¹A priori the unknowns c_i^* depend on the macroscopic and microscopic space variables x^* and y^* assumed to be independent.

for each value of n , leading to the n -systems of equations for $v_{i,n}^*$

$$\begin{cases} \psi_{i,n}^* \left(\frac{\partial^* v_{i,n}^*}{\partial t^*} - \lambda_n v_{i,n}^* \right) = \nabla^* \cdot [\mathcal{D}_i^* \nabla^* (\psi_{i,n}^* v_{i,n}^*)] & \text{in } Y_f^* \\ -\mathcal{D}_1^* \nabla^* (\psi_{1,n}^* v_{1,n}^*) \cdot \mathbf{n}_{fs} = k_1^* \psi_{1,n}^* v_{1,n}^* - k_2^* \psi_{2,n}^* v_{2,n}^* & \text{at } \partial Y_{fs}^* \\ -\mathcal{D}_2^* \nabla^* (\psi_{2,n}^* v_{2,n}^*) \cdot \mathbf{n}_{fs} = k_2^* \psi_{2,n}^* v_{2,n}^* - k_1^* \psi_{1,n}^* v_{1,n}^* & \text{at } \partial Y_{fs}^*. \end{cases} \quad (7)$$

Multiplying (7a) by $\psi_{i,n}^*$ gives

$$\begin{aligned} \psi_{i,n}^{*2} \frac{\partial v_{i,n}^*}{\partial t^*} - \lambda_n^* \psi_{i,n}^{*2} v_{i,n}^* &= \psi_{i,n}^* \nabla^* \cdot [\mathcal{D}_i^* \nabla^* (\psi_{i,n}^* v_{i,n}^*)] \\ &= \psi_{i,n}^* \nabla^* \cdot (\mathcal{D}_i^* \psi_{i,n}^* \nabla^* v_{i,n}^* + \mathcal{D}_i^* v_{i,n}^* \nabla^* \psi_{i,n}^*) \\ &= \psi_{i,n}^{*2} \nabla^* \cdot (\mathcal{D}_i^* \nabla^* v_{i,n}^*) + 2\mathcal{D}_i^* \psi_{i,n}^* \nabla^* \psi_{i,n}^* \cdot \nabla^* v_{i,n}^* \\ &\quad + \psi_{i,n}^* v_{i,n}^* \nabla^* \cdot (\mathcal{D}_i^* \nabla^* \psi_{i,n}^*) \\ &= \nabla^* \cdot (\mathcal{D}_i^* \psi_{i,n}^{*2} \nabla^* v_{i,n}^*) + \psi_{i,n}^* v_{i,n}^* \nabla^* \cdot (\mathcal{D}_i^* \nabla^* \psi_{i,n}^*). \end{aligned} \quad (8)$$

Using spectral problem (3a) and (3b), the last terms of the left and right hand sides of (8) cancel out. It yields

$$\psi_{i,n}^{*2} \frac{\partial v_{i,n}^*}{\partial t^*} = \nabla^* \cdot (\mathcal{D}_i^* \psi_{i,n}^{*2} \nabla^* v_{i,n}^*). \quad (9)$$

On the other hand, multiplying the interface condition (7b) by $\psi_{1,n}^*$ and using the boundary condition (3c), yields

$$\begin{aligned} k_1^* \psi_{1,n}^* v_{1,n}^* - k_2^* \psi_{1,n}^* \psi_{2,n}^* v_{2,n}^* &= -\mathbf{n}_{fs} \cdot \mathcal{D}_1^* \psi_{1,n}^* \nabla^* (\psi_{1,n}^* v_{1,n}^*) \\ &= -\mathbf{n}_{fs} \cdot (\mathcal{D}_1^* \psi_{1,n}^{*2} \nabla^* v_{1,n}^* + \mathcal{D}_1^* \psi_{1,n}^* v_{1,n}^* \nabla^* \psi_{1,n}^*) \\ &= -\mathbf{n}_{fs} \cdot (\mathcal{D}_1^* \psi_{1,n}^{*2} \nabla^* v_{1,n}^*) + \psi_{1,n}^* v_{1,n}^* (k_1^* \psi_{1,n}^* - k_2^* \psi_{2,n}^*). \end{aligned} \quad (10)$$

We finally obtain the interface condition for $v_{1,n}^*$

$$-\mathcal{D}_1^* \psi_{1,n}^{*2} \nabla^* v_{1,n}^* \cdot \mathbf{n}_{fs} = k_2^* \psi_{1,n}^* \psi_{2,n}^* (v_{1,n}^* - v_{2,n}^*) \quad \text{at } \partial Y_{fs}^*. \quad (11)$$

A similar development can be performed to obtain the interface condition for $v_{2,n}^*$. Let define $\tilde{\mathcal{D}}_{1,n}^* = \mathcal{D}_1^* \psi_{1,n}^{*2}$ and $\tilde{\mathcal{D}}_{2,n}^* = \mathcal{D}_2^* \psi_{2,n}^{*2}$. The microscopic problem of $v_{1,n}^*$ and $v_{2,n}^*$ to be homogenized is now written as

$$\begin{cases} \psi_{1,n}^{*2} \frac{\partial v_{1,n}^*}{\partial t^*} = \nabla^* \cdot (\tilde{\mathcal{D}}_{1,n}^* \nabla^* v_{1,n}^*) & \text{in } Y_f^* \\ \psi_{2,n}^{*2} \frac{\partial v_{2,n}^*}{\partial t^*} = \nabla^* \cdot (\tilde{\mathcal{D}}_{2,n}^* \nabla^* v_{2,n}^*) & \\ -\tilde{\mathcal{D}}_{1,n}^* \nabla^* v_{1,n}^* \cdot \mathbf{n}_{fs} = k_2^* \psi_{1,n}^* \psi_{2,n}^* (v_{1,n}^* - v_{2,n}^*) & \text{at } \partial Y_{fs}^* \\ -\tilde{\mathcal{D}}_{2,n}^* \nabla^* v_{2,n}^* \cdot \mathbf{n}_{fs} = k_1^* \psi_{1,n}^* \psi_{2,n}^* (v_{2,n}^* - v_{1,n}^*). & \end{cases} \quad (12)$$

The initial problem (2) has been transformed into n diffusion problems in the unit cell with a spatially periodic diffusion coefficient. The main difference is in the form of the boundary condition at the interface ∂Y_{fs}^* , which will allow the homogenization of the problem.

3. Periodic homogenization procedure

Our aim now is to upscale the microscopic model (12) for $v_{i,n}^*$ in order to construct the average mass conservation equations at the macroscale. This task is accomplished through the formal homogenization procedure.

3.1. Dimensional analysis

A dimensional analysis of the equations is first performed. Let $c_r, \mathcal{D}_r, k_r, \psi_r, v_r$ be the reference quantities of concentrations, diffusion coefficients, reaction rates, eigenfunctions $\psi_{i,n}^*$ and unknown functions $v_{i,n}^*$.

Defining the dimensionless quantity as $f = f^*/f_r$, where f_r is the reference quantity of the variable f^* , we have

$$x = \frac{x^*}{L}, \quad y = \frac{y^*}{l}, \quad c_{i,n} = \frac{c_{i,n}^*}{c_r}, \quad D_i = \frac{D_i^*}{\mathcal{D}_r}, \quad k_i = \frac{k_i^*}{k_r}, \quad \psi_{i,n} = \frac{\psi_{i,n}^*}{\psi_r}, \quad v_{i,n} = \frac{v_{i,n}^*}{v_r}. \quad (13)$$

It must be quoted that $\psi_{i,n}^*$ are dimensionless variables so that $\psi_r = 1$ and $v_{i,n}^*$ has the dimension of concentration (noting that $v_{i,n}^*$ is solution of a diffusion equation (12)).

The reference length scale is chosen as the macroscopic length L so that we have:

$$\nabla^* = \frac{\nabla}{L}, \quad \nabla^* \cdot = \frac{\nabla \cdot}{L} \quad (14)$$

Finally, the reference time is chosen as the macroscopic diffusive time

$$t_r = \frac{L^2}{\mathcal{D}_r} \quad (15)$$

Using (13), (14) and (15), from (12) the dimensionless microscopic problem for $v_{1,n}$ and $v_{2,n}$ can be written as

$$\left\{ \begin{array}{l} \psi_{1,n}^2 \frac{\partial v_{1,n}}{\partial t} = \nabla \cdot \left(\tilde{\mathcal{D}}_{1,n} \nabla v_{1,n} \right) \quad \text{in } Y_f \\ \psi_{2,n}^2 \frac{\partial v_{2,n}}{\partial t} = \nabla \cdot \left(\tilde{\mathcal{D}}_{2,n} \nabla v_{2,n} \right) \\ -\tilde{\mathcal{D}}_{1,n} \nabla v_{1,n} \cdot \mathbf{n}_{fs} = \text{Da}_L k_2 \psi_{1,n} \psi_{2,n} (v_{1,n} - v_{2,n}) \quad \text{at } \partial Y_{fs} \\ -\tilde{\mathcal{D}}_{2,n} \nabla v_{2,n} \cdot \mathbf{n}_{fs} = \text{Da}_L k_1 \psi_{1,n} \psi_{2,n} (v_{2,n} - v_{1,n}) \end{array} \right. \quad (16)$$

where Da_L represents the macroscopic Damköhler number defined as the ratio of the macroscopic diffusion time to the reaction one

$$\text{Da}_L = \frac{k_r L}{\mathcal{D}_r} \quad (17)$$

3.2. Reduction to a one-scale problem

To proceed within the periodic homogenization framework, the above problem needs to be reduced to a one-scale problem in considering three different scenarios related to the order of magnitude of the Damköhler number:

- Case 1: predominating reaction rates when $\text{Da}_L = \mathcal{O}(\varepsilon^{-1})$
- Case 2: diffusion and reaction of the same order when $\text{Da}_L = \mathcal{O}(\varepsilon^0)$
- Case 3: dominant diffusion when $\text{Da}_L = \mathcal{O}(\varepsilon)$

where $\varepsilon = l/L$ denotes the scale ratio and ε^p , $p \in \mathbb{Z}$ the reference scale of comparison to reduce the problem to a one-scale problem.

The results of the upscaling procedures for the three different orders of magnitude of the Damköhler number are summarized in Result 1, Result 2 and Result 3 at the end of each section.

3.3. Asymptotic expansion

To perform the asymptotic expansion, the perturbation parameter $\varepsilon = l/L$ is assumed to be small. Thus, we postulate the ansatz

$$f^{(\varepsilon)}(\mathbf{x}, \mathbf{y}, t) = \sum_{k=0}^{\infty} \varepsilon^k f^{(k)}(\mathbf{x}, \mathbf{y}, t) \quad (18)$$

where the functions $f^{(k)} = f^{(k)}(\mathbf{x}, \mathbf{y}, t)$ ($k = 0, 1, 2, \dots$) are \mathbf{y} -periodic. The differential operators are given by

$$\begin{aligned} \nabla f^{(\varepsilon)}(\mathbf{x}, \mathbf{y}, t) &= \nabla_x f^{(\varepsilon)}(\mathbf{x}, \mathbf{y}, t) + \varepsilon^{-1} \nabla_y f^{(\varepsilon)}(\mathbf{x}, \mathbf{y}, t) \\ \nabla \cdot f^{(\varepsilon)}(\mathbf{x}, \mathbf{y}, t) &= \nabla_x \cdot f^{(\varepsilon)}(\mathbf{x}, \mathbf{y}, t) + \varepsilon^{-1} \nabla_y \cdot f^{(\varepsilon)}(\mathbf{x}, \mathbf{y}, t). \end{aligned} \quad (19)$$

Finally, the average, intrinsic average and area average operators in the unit cell are defined as

$$\langle f \rangle = \frac{1}{|Y|} \int_Y f dV; \quad \langle f \rangle^f = \frac{1}{|Y_f|} \int_{Y_f} f dV; \quad \langle f \rangle^{fs} = \frac{1}{|\partial Y_{fs}|} \int_{\partial Y_{fs}} f dS. \quad (20)$$

4. Case 1: homogenized model for predominant reaction

The predominant reaction with $\text{Da}_L = \mathcal{O}(\varepsilon^{-1})$ is the most interesting case in which the classical homogenization procedure fails to predict the macroscopic conservation laws for short time as discussed in [15] and in section 4.3.

4.1. Asymptotic expansion

Considering $\text{Da}_L = \mathcal{O}(\varepsilon^{-1})$, the ε -microscopic model of Eqs. (16) is written as

$$\left\{ \begin{array}{l} \psi_{1,n}^2 \frac{\partial v_{1,n}^{(\varepsilon)}}{\partial t} = \nabla \cdot \left(\tilde{\mathcal{D}}_{1,n} \nabla v_{1,n}^{(\varepsilon)} \right) \quad \text{in } Y_f \\ \psi_{2,n}^2 \frac{\partial v_{2,n}^{(\varepsilon)}}{\partial t} = \nabla \cdot \left(\tilde{\mathcal{D}}_{2,n} \nabla v_{2,n}^{(\varepsilon)} \right) \\ -\tilde{\mathcal{D}}_{1,n} \nabla v_{1,n}^{(\varepsilon)} \cdot \mathbf{n}_{fs} = \varepsilon^{-1} k_2 \psi_{1,n} \psi_{2,n} (v_{1,n}^{(\varepsilon)} - v_{2,n}^{(\varepsilon)}) \quad \text{at } \partial Y_{fs} \\ -\tilde{\mathcal{D}}_{2,n} \nabla v_{2,n}^{(\varepsilon)} \cdot \mathbf{n}_{fs} = \varepsilon^{-1} k_1 \psi_{1,n} \psi_{2,n} (v_{2,n}^{(\varepsilon)} - v_{1,n}^{(\varepsilon)}). \end{array} \right. \quad (21)$$

In particular, for $n = 0$ corresponding to the eigenvalue $\lambda_0 = 0$, the eigenfunctions defined to within one multiplicative constant are given by:

$$\psi_{1,0} = \sqrt{\frac{k_2}{k_1}} \quad \text{and} \quad \psi_{2,0} = \sqrt{\frac{k_1}{k_2}}. \quad (22)$$

This expression satisfies the normalization condition (31) that will be imposed later.

Using the asymptotic expansion (18) for the unknowns $v_{1,n}^{(\varepsilon)}$ and $v_{2,n}^{(\varepsilon)}$ and the expression (19) for the differential operators, the successive powers of ε in Eqs. (21) are now collected.

• Order $\mathcal{O}(\varepsilon^{-2})$

At order $\mathcal{O}(\varepsilon^{-2})$ in the volume and $\mathcal{O}(\varepsilon^{-1})$ at the interface, Eqs. (21) become

$$\left\{ \begin{array}{l} \nabla_y \cdot \left(\tilde{\mathcal{D}}_{1,n} \nabla_y v_{1,n}^{(0)} \right) = 0 \quad \text{in } Y_f \\ \nabla_y \cdot \left(\tilde{\mathcal{D}}_{2,n} \nabla_y v_{2,n}^{(0)} \right) = 0 \\ -\tilde{\mathcal{D}}_{1,n} \nabla_y v_{1,n}^{(0)} \cdot \mathbf{n}_{fs} = k_2 \psi_{1,n} \psi_{2,n} (v_{1,n}^{(0)} - v_{2,n}^{(0)}) \quad \text{at } \partial Y_{fs} \\ -\tilde{\mathcal{D}}_{2,n} \nabla_y v_{2,n}^{(0)} \cdot \mathbf{n}_{fs} = k_1 \psi_{1,n} \psi_{2,n} (v_{2,n}^{(0)} - v_{1,n}^{(0)}). \end{array} \right. \quad (23)$$

It is obvious that

$$v_{1,n}^{(0)}(t, \mathbf{x}, \mathbf{y}) = v_{2,n}^{(0)}(t, \mathbf{x}, \mathbf{y}) = v_n^{(0)}(t, \mathbf{x}) \quad (24)$$

is solution of the problem (23). The uniqueness of the solution can easily be proved for $n = 0$ when the eigenfunctions $\psi_{1,0}$ and $\psi_{2,0}$ are constant and positive². However, for $n > 0$ it is not straightforward and will not be proved in this work. Henceforth, we consider (24) as the solution of (23).

• **Order $\mathcal{O}(\varepsilon^{-1})$**

At order $\mathcal{O}(\varepsilon^{-1})$ in the volume and $\mathcal{O}(\varepsilon^0)$ at the interface, we have

$$\begin{cases} \nabla_y \cdot \left[\tilde{\mathcal{D}}_{1,n} \left(\nabla_x v_n^{(0)} + \nabla_y v_{1,n}^{(1)} \right) \right] = 0 & \text{in } Y_f \\ \nabla_y \cdot \left[\tilde{\mathcal{D}}_{2,n} \left(\nabla_x v_n^{(0)} + \nabla_y v_{2,n}^{(1)} \right) \right] = 0 & \\ -\tilde{\mathcal{D}}_{1,n} \left(\nabla_x v_n^{(0)} + \nabla_y v_{1,n}^{(1)} \right) \cdot \mathbf{n}_{fs} = k_2 \psi_{1,n} \psi_{2,n} (v_{1,n}^{(1)} - v_{2,n}^{(1)}) & \text{at } \partial Y_{fs} \\ -\tilde{\mathcal{D}}_{2,n} \left(\nabla_x v_n^{(0)} + \nabla_y v_{2,n}^{(1)} \right) \cdot \mathbf{n}_{fs} = k_1 \psi_{1,n} \psi_{2,n} (v_{2,n}^{(1)} - v_{1,n}^{(1)}) & \end{cases} \quad (25)$$

By linearity, the solution for $v_{1,n}^{(1)}$ and $v_{2,n}^{(1)}$ in \mathbf{y} is sought in the following form with a same additive constant $\widehat{v}_n^{(1)}$ depending on t and \mathbf{x}

$$\begin{aligned} v_{1,n}^{(1)} &= \boldsymbol{\chi}_{1,n} \cdot \nabla_x v_n^{(0)} + \widehat{v}_n^{(1)}(t, \mathbf{x}) \\ v_{2,n}^{(1)} &= \boldsymbol{\chi}_{2,n} \cdot \nabla_x v_n^{(0)} + \widehat{v}_n^{(1)}(t, \mathbf{x}) \end{aligned} \quad (26)$$

where the vectors $\boldsymbol{\chi}_{1,n}$ and $\boldsymbol{\chi}_{2,n}$ satisfy the following coupled problem

$$\begin{cases} 0 = \nabla_y \cdot \left[\tilde{\mathcal{D}}_{1,n} \left(\mathbf{I} + (\nabla_y \boldsymbol{\chi}_{1,n})^\top \right) \right] & \text{in } Y_f \\ 0 = \nabla_y \cdot \left[\tilde{\mathcal{D}}_{2,n} \left(\mathbf{I} + (\nabla_y \boldsymbol{\chi}_{2,n})^\top \right) \right] & \\ -\tilde{\mathcal{D}}_{1,n} \left(\mathbf{I} + \nabla_y \boldsymbol{\chi}_{1,n} \right) \cdot \mathbf{n}_{fs} = k_2 \psi_{1,n} \psi_{2,n} (\boldsymbol{\chi}_{1,n} - \boldsymbol{\chi}_{2,n}) & \text{at } \partial Y_{fs} \\ -\tilde{\mathcal{D}}_{2,n} \left(\mathbf{I} + \nabla_y \boldsymbol{\chi}_{2,n} \right) \cdot \mathbf{n}_{fs} = k_1 \psi_{1,n} \psi_{2,n} (\boldsymbol{\chi}_{2,n} - \boldsymbol{\chi}_{1,n}) & \end{cases} \quad (27)$$

where the superscript $^\top$ denotes a matrix transpose.

• **Order $\mathcal{O}(\varepsilon^0)$**

²Indeed, setting $U = v_{2,0}^{(0)} - v_{1,0}^{(0)}$, using (22), Eqs. (23) can be transformed to a Laplace equation for U with homogeneous Robin-Fourier boundary conditions similar to (35) that admits a unique solution $U = 0$ and therefore $v_{2,0}^{(0)} = v_{1,0}^{(0)}$.

At the leading order $\mathcal{O}(1)$ in the volume and $\mathcal{O}(\varepsilon^{-1})$ at the interface, the time-dependent problem for $v_n^{(0)}$ is written as

$$\left\{ \begin{array}{l} \psi_{1,n}^2 \frac{\partial v_n^{(0)}}{\partial t} = \nabla_y \cdot \left[\tilde{\mathcal{D}}_{1,n} \left(\nabla_y v_{1,n}^{(2)} + \nabla_x v_{1,n}^{(1)} \right) \right] \\ \quad + \nabla_x \cdot \left[\tilde{\mathcal{D}}_{1,n} \left(\nabla_y v_{1,n}^{(1)} + \nabla_x v_n^{(0)} \right) \right] \\ \psi_{2,n}^2 \frac{\partial v_n^{(0)}}{\partial t} = \nabla_y \cdot \left[\tilde{\mathcal{D}}_{2,n} \left(\nabla_y v_{2,n}^{(2)} + \nabla_x v_{2,n}^{(1)} \right) \right] \\ \quad + \nabla_x \cdot \left[\tilde{\mathcal{D}}_{2,n} \left(\nabla_y v_{2,n}^{(1)} + \nabla_x v_n^{(0)} \right) \right] \\ -\tilde{\mathcal{D}}_{1,n} \left(\nabla_y v_{1,n}^{(2)} + \nabla_x v_{1,n}^{(1)} \right) \cdot \mathbf{n}_{fs} = k_2 \psi_{1,n} \psi_{2,n} \left(v_{1,n}^{(2)} - v_{2,n}^{(2)} \right) \\ -\tilde{\mathcal{D}}_{2,n} \left(\nabla_y v_{2,n}^{(2)} + \nabla_x v_{2,n}^{(1)} \right) \cdot \mathbf{n}_{fs} = k_1 \psi_{1,n} \psi_{2,n} \left(v_{2,n}^{(2)} - v_{1,n}^{(2)} \right) \end{array} \right. \quad \begin{array}{l} \text{in } Y_f \\ \\ \\ \text{at } \partial Y_{fs} \end{array} \quad (28)$$

Averaging Eqs. (28a) and (28b) over the fluid phase of the unit cell, taking into account the interface conditions (28c) and (28d) and considering the solution (26) for $v_{i,n}^{(1)}$, we get

$$\left\{ \begin{array}{l} \langle \psi_{1,n}^2 \rangle^f \frac{\partial v_n^{(0)}}{\partial t} = \nabla_x \cdot \left[\left\langle \tilde{\mathcal{D}}_{1,n} \left(\mathbf{I} + (\nabla_y \chi_{1,n})^\top \right) \right\rangle^f \nabla_x v_n^{(0)} \right] \\ \quad - \frac{|\partial Y_{fs}|}{|Y_f|} \left\langle k_2 \psi_{1,n} \psi_{2,n} \left(v_{1,n}^{(2)} - v_{2,n}^{(2)} \right) \right\rangle^{fs} \\ \langle \psi_{2,n}^2 \rangle^f \frac{\partial v_n^{(0)}}{\partial t} = \nabla_x \cdot \left[\left\langle \tilde{\mathcal{D}}_{2,n} \left(\mathbf{I} + (\nabla_y \chi_{2,n})^\top \right) \right\rangle^f \nabla_x v_n^{(0)} \right] \\ \quad + \frac{|\partial Y_{fs}|}{|Y_f|} \left\langle k_1 \psi_{1,n} \psi_{2,n} \left(v_{1,n}^{(2)} - v_{2,n}^{(2)} \right) \right\rangle^{fs} \end{array} \right. \quad (29)$$

By adding these two above averaged equations previously multiplied by k_1 and k_2 respectively, we obtain

$$\begin{aligned} & \left(k_1 \langle \psi_{1,n}^2 \rangle^f + k_2 \langle \psi_{2,n}^2 \rangle^f \right) \frac{\partial v_n^{(0)}}{\partial t} = \\ & \nabla_x \cdot \left\{ \left[k_1 \left\langle \tilde{\mathcal{D}}_{1,n} \left(\mathbf{I} + (\nabla_y \chi_{1,n})^\top \right) \right\rangle^f + k_2 \left\langle \tilde{\mathcal{D}}_{2,n} \left(\mathbf{I} + (\nabla_y \chi_{2,n})^\top \right) \right\rangle^f \right] \cdot \nabla_x v_n^{(0)} \right\}. \end{aligned} \quad (30)$$

To ensure uniqueness of the spectral problem, the eigenfunctions are normalized by imposing

$$k_1 \langle \psi_{1,n}^2 \rangle^f + k_2 \langle \psi_{2,n}^2 \rangle^f = k_1 + k_2 \quad (31)$$

which leads to the macroscopic equation for $v_n^{(0)}$

$$\frac{\partial v_n^{(0)}}{\partial t} = \nabla_x \cdot (\mathbf{D}_{v,n} \cdot \nabla_x v_n^{(0)}) . \quad (32)$$

The effective diffusion tensor $\mathbf{D}_{v,n}$ is defined by

$$\mathbf{D}_{v,n} = \frac{k_1}{k_1 + k_2} \left\langle \tilde{\mathcal{D}}_{1,n} \left(\mathbf{I} + (\nabla_y \boldsymbol{\chi}_{1,n})^\top \right) \right\rangle^f + \frac{k_2}{k_1 + k_2} \left\langle \tilde{\mathcal{D}}_{2,n} \left(\mathbf{I} + (\nabla_y \boldsymbol{\chi}_{2,n})^\top \right) \right\rangle^f . \quad (33)$$

In particular for $n = 0$, the local problem (27) reduces to

$$\begin{cases} \nabla_y \cdot \left[\mathcal{D}_1 \left(\mathbf{I} + (\nabla_y \boldsymbol{\chi}_{1,0})^\top \right) \right] = 0 & \text{in } Y_f \\ \nabla_y \cdot \left[\mathcal{D}_2 \left(\mathbf{I} + (\nabla_y \boldsymbol{\chi}_{2,0})^\top \right) \right] = 0 & \\ -\mathcal{D}_1 \left(\mathbf{I} + \nabla_y \boldsymbol{\chi}_{1,0} \right) \cdot \mathbf{n}_{fs} = k_1 (\boldsymbol{\chi}_{1,0} - \boldsymbol{\chi}_{2,0}) & \text{at } \partial Y_{fs} \\ -\mathcal{D}_2 \left(\mathbf{I} + \nabla_y \boldsymbol{\chi}_{2,0} \right) \cdot \mathbf{n}_{fs} = k_2 (\boldsymbol{\chi}_{2,0} - \boldsymbol{\chi}_{1,0}) & \end{cases} \quad (34)$$

where the expression (22) is used for $\psi_{1,0}$ and $\psi_{2,0}$. Setting $\Theta = \boldsymbol{\chi}_{1,0} - \boldsymbol{\chi}_{2,0}$, it can be easily proven that Θ is solution of a Laplace equation with homogeneous Robin-Fourier boundary conditions

$$\begin{cases} \Delta_y \Theta = 0 & \text{in } Y_f \\ \nabla_y \Theta \cdot \mathbf{n}_{fs} + \beta \Theta = 0 & \text{at } \partial Y_{fs} \end{cases} \quad (35)$$

with $\beta = \frac{k_1}{\mathcal{D}_1} + \frac{k_2}{\mathcal{D}_2} > 0$, leading to $\Theta = 0$ and therefore to $\boldsymbol{\chi}_{1,0} = \boldsymbol{\chi}_{2,0} \equiv \boldsymbol{\chi}$.

In this case, the expression $\mathbf{D}_{v,0}$ reduces to the simple expression

$$\mathbf{D}_{v,0} = \frac{k_1 \mathbf{D}_2^{\text{eff}} + k_2 \mathbf{D}_1^{\text{eff}}}{k_1 + k_2} \quad (36)$$

where the effective coefficients are defined as

$$\begin{aligned} \mathbf{D}_1^{\text{eff}} &= \left\langle \mathcal{D}_1 \left(\mathbf{I} + (\nabla_y \boldsymbol{\chi})^\top \right) \right\rangle^f \\ \mathbf{D}_2^{\text{eff}} &= \left\langle \mathcal{D}_2 \left(\mathbf{I} + (\nabla_y \boldsymbol{\chi})^\top \right) \right\rangle^f \end{aligned} \quad (37)$$

and $\boldsymbol{\chi}$ is solution of the classical tortuosity problem

$$\begin{cases} \Delta_y \boldsymbol{\chi} = 0 & \text{in } Y_f \\ (\mathbf{I} + \nabla_y \boldsymbol{\chi}) \cdot \mathbf{n}_{fs} = 0 & \text{at } \partial Y_{fs} \\ \langle \boldsymbol{\chi} \rangle^f = 0 . \end{cases} \quad (38)$$

4.2. Back to concentrations

In the development (5) of the concentrations c_i^* , when the eigenvalues are well separated, it is legitimate to consider only the two first eigenvalues $\lambda_0^* = 0$ and λ_1^* with their corresponding eigenfunctions. At the leading order, we have³

$$\begin{aligned} c_1^{*(0)} &= \psi_{1,0}^* v_0^{*(0)} + \psi_{1,1}^* \exp(-\lambda_1^* t^*) v_1^{*(0)} \\ c_2^{*(0)} &= \psi_{2,0}^* v_0^{*(0)} + \psi_{2,1}^* \exp(-\lambda_1^* t^*) v_1^{*(0)}. \end{aligned} \quad (39)$$

In the sequel, to simplify the notations, the superscript (0) is henceforth omitted. It should be noted that the concentrations c_1^* and c_2^* at the order $\mathcal{O}(\varepsilon^0)$ are \mathbf{y}^* -dependent variables since $\psi_{1,1}^*$ and $\psi_{2,1}^*$ depend on \mathbf{y}^* .

Averaging (39) over the fluid phase of the unit cell gives

$$\begin{aligned} \langle c_1^* \rangle^f &= \psi_{1,0}^* v_0^* + \langle \psi_{1,1}^* \rangle^f \exp(-\lambda_1^* t^*) v_1^* \\ \langle c_2^* \rangle^f &= \psi_{2,0}^* v_0^* + \langle \psi_{2,1}^* \rangle^f \exp(-\lambda_1^* t^*) v_1^*. \end{aligned} \quad (40)$$

On the other hand, going back to dimensional variables from (32), we easily get

$$\frac{\partial v_n^*}{\partial t^*} = \nabla_{x^*}^* \cdot (\mathbf{D}_{v,n}^* \cdot \nabla_{x^*}^* v_n^*) \quad (41)$$

where from (33) and (36) the dimensional effective coefficients $\mathbf{D}_{v,0}^*$ and $\mathbf{D}_{v,1}^*$ are given by

$$\mathbf{D}_{v,0}^* = \frac{k_1^* \mathcal{D}_2^* + k_2^* \mathcal{D}_1^*}{k_1^* + k_2^*} \langle \mathbf{I} + (\nabla_{y^*}^* \chi^*)^\top \rangle^f \quad (42)$$

$$\mathbf{D}_{v,1}^* = \frac{k_1^*}{k_1^* + k_2^*} \left\langle \tilde{\mathcal{D}}_{1,1}^* \left[\mathbf{I} + (\nabla_{y^*}^* \chi_{1,1}^*)^\top \right] \right\rangle^f + \frac{k_2^*}{k_1^* + k_2^*} \left\langle \tilde{\mathcal{D}}_{2,1}^* \left[\mathbf{I} + (\nabla_{y^*}^* \chi_{2,1}^*)^\top \right] \right\rangle^f \quad (43)$$

The vectors $\chi_{1,1}^*$ and $\chi_{2,1}^*$ are solutions of the local problem

$$\begin{cases} \nabla_{y^*}^* \cdot \left[\tilde{\mathcal{D}}_{1,1}^* \left(\mathbf{I} + (\nabla_{y^*}^* \chi_{1,1}^*)^\top \right) \right] = 0 & \text{in } Y_f^* \\ \nabla_{y^*}^* \cdot \left[\tilde{\mathcal{D}}_{2,1}^* \left(\mathbf{I} + (\nabla_{y^*}^* \chi_{2,1}^*)^\top \right) \right] = 0 & \\ -\tilde{\mathcal{D}}_{1,1}^* \left(\mathbf{I} + \nabla_{y^*}^* \chi_{1,1}^* \right) \cdot \mathbf{n}_{fs} = k_2^* \psi_{1,1}^* \psi_{2,1}^* \left(\chi_{1,1}^* - \chi_{2,1}^* \right) & \text{at } \partial Y_{fs}^* \\ -\tilde{\mathcal{D}}_{2,1}^* \left(\mathbf{I} + \nabla_{y^*}^* \chi_{2,1}^* \right) \cdot \mathbf{n}_{fs} = k_1^* \psi_{1,1}^* \psi_{2,1}^* \left(\chi_{2,1}^* - \chi_{1,1}^* \right). & \end{cases} \quad (44)$$

³This choice discussed later is also explained by Eqs. (B.7) and (B.8) of Appendix B.

For $n = 0$, $\boldsymbol{\chi}^* = \boldsymbol{\chi}_{1,0}^* = \boldsymbol{\chi}_{2,0}^*$ is solution of the problem (38) in dimensional form with constant eigenfunctions corresponding to the eigenvalue $\lambda_0^* = 0$ given by

$$\psi_{1,0}^* = \sqrt{\frac{k_2^*}{k_1^*}}, \quad \psi_{2,0}^* = \sqrt{\frac{k_1^*}{k_2^*}}. \quad (45)$$

Using (41) for $n = 0$ and $n = 1$, the time derivative of Eq. (40a) yields

$$\begin{aligned} \frac{\partial \langle c_1^* \rangle^f}{\partial t^*} - \nabla_{x^*}^* \cdot (\mathbf{D}_{v,1}^* \cdot \nabla_{x^*}^* \langle c_1^* \rangle^f) + \lambda_1^* \langle c_1^* \rangle^f = \\ \psi_{1,0}^* \nabla_{x^*}^* \cdot [(\mathbf{D}_{v,0}^* - \mathbf{D}_{v,1}^*) \cdot \nabla_{x^*}^* v_0^*] + \lambda_1^* \psi_{1,0}^* v_0^*. \end{aligned} \quad (46)$$

A similar development for c_2^* gives

$$\begin{aligned} \frac{\partial \langle c_2^* \rangle^f}{\partial t^*} - \nabla_{x^*}^* \cdot (\mathbf{D}_{v,1}^* \cdot \nabla_{x^*}^* \langle c_2^* \rangle^f) + \lambda_1^* \langle c_2^* \rangle^f = \\ \psi_{2,0}^* \nabla_{x^*}^* \cdot [(\mathbf{D}_{v,0}^* - \mathbf{D}_{v,1}^*) \cdot \nabla_{x^*}^* v_0^*] + \lambda_1^* \psi_{2,0}^* v_0^*. \end{aligned} \quad (47)$$

Using the compatibility condition $\langle \psi_{1,1}^* \rangle^f + \langle \psi_{2,1}^* \rangle^f = 0$ of the spectral problem (3), we obtain from (40)

$$v_0^* = \frac{\langle c_1^* \rangle^f + \langle c_2^* \rangle^f}{\psi_{1,0}^* + \psi_{2,0}^*}. \quad (48)$$

To finish, inserting (48) into (46) and (47) leads to the following result of the average mass conservation equations.

Result 1. *For a predominant reaction corresponding to $Da_L = \mathcal{O}(\varepsilon^{-1})$, the concentrations at the leading order are solutions of the homogenized coupled diffusion-reaction problem*

$$\begin{aligned} \frac{\partial \langle c_1^* \rangle^f}{\partial t^*} - \nabla_{x^*}^* \cdot \left(\frac{k_1^* \mathbf{D}_{v,1}^* + k_2^* \mathbf{D}_{v,0}^*}{k_1^* + k_2^*} \cdot \nabla_{x^*}^* \langle c_1^* \rangle^f \right) \\ - \nabla_{x^*}^* \cdot \left(\frac{k_2^* (\mathbf{D}_{v,0}^* - \mathbf{D}_{v,1}^*)}{k_1^* + k_2^*} \cdot \nabla_{x^*}^* \langle c_2^* \rangle^f \right) + \lambda_1^* \frac{k_1^* \langle c_1^* \rangle^f - k_2^* \langle c_2^* \rangle^f}{k_1^* + k_2^*} = 0 \\ \frac{\partial \langle c_2^* \rangle^f}{\partial t^*} - \nabla_{x^*}^* \cdot \left(\frac{k_1^* (\mathbf{D}_{v,0}^* - \mathbf{D}_{v,1}^*)}{k_1^* + k_2^*} \cdot \nabla_{x^*}^* \langle c_1^* \rangle^f \right) \\ - \nabla_{x^*}^* \cdot \left(\frac{k_2^* \mathbf{D}_{v,1}^* + k_1^* \mathbf{D}_{v,0}^*}{k_1^* + k_2^*} \cdot \nabla_{x^*}^* \langle c_2^* \rangle^f \right) - \lambda_1^* \frac{k_1^* \langle c_1^* \rangle^f - k_2^* \langle c_2^* \rangle^f}{k_1^* + k_2^*} = 0 \end{aligned} \quad (49)$$

where the homogenized diffusion tensors $\mathbf{D}_{v,0}^*$ and $\mathbf{D}_{v,1}^*$ are defined by (42) and (43).

The above equations represent the macroscopic mass conservation law for the averaged concentrations with coupled diffusion terms and with an exchange term due to reaction depending on the first non-zero eigenvalue λ_1^* of the associated spectral problem.

4.3. Comparison with the classical periodic homogenization

The objective of this subsection is to compare the result obtained by the current approach with that reported in [15] using a classical homogenization procedure. Let consider only the first eigenvalue value $\lambda_0^* = 0$. Going back to dimensional concentrations and omitting the superscript (0) , we have from (39)

$$\begin{aligned} c_1^* &= \psi_{1,0}^* v_0^* \\ c_2^* &= \psi_{2,0}^* v_0^*. \end{aligned} \quad (50)$$

Therefore, the homogenization problem (32) for $n = 0$ leads obviously to

$$\frac{\partial c_i^*}{\partial t} = \nabla_{x^*}^* \cdot (\mathbf{D}_{v,0}^* \cdot \nabla_{x^*}^* c_i^*) \quad (51)$$

for $i = 1, 2$, where the homogenized diffusion tensor $\mathbf{D}_{v,0}^*$ is given by (42). The concentrations are related by the constraint

$$k_1^* c_1^* - k_2^* c_2^* = 0 \quad (52)$$

according to (50) and the expressions (45) of $\psi_{1,0}^*$ and $\psi_{2,0}^*$.

This result is also obtained by the classical homogenization approach as reported in [15]. It is important to notice that considering solely the first eigenvalue λ_0^* is only valid for long diffusion times and cannot handle boundary and initial conditions that does not verify the equilibrium condition⁴ (52). This point has been analyzed in [15]. The correction with the first non-zero eigenvalue λ_1^* enables to overcome this difficulty, which is the main interest of the approach proposed in this work leading to Result 1. According to expression (B.8) of Appendix B, it is clear that the gap with the equilibrium condition is described by the non-zero eigenvalues. Moreover, as the eigenvalues increase with n , the main information is contained in the first non-zero eigenvalue λ_1^* . Due to the exponential decay, the contribution of the other eigenvalues becomes rapidly negligible with time.

⁴In that case, we have a boundary layer problem that will be studied in a further work.

5. Homogenized model for diffusion-reaction of the same order

The intermediate case corresponds to diffusion and reaction characteristic times of the same order at the macroscale, i.e satisfying $\text{Da}_L = \mathcal{O}(\varepsilon^0)$.

5.1. Asymptotic expansion

Considering $\text{Da}_L = \mathcal{O}(\varepsilon^0)$, Eqs.(16) reduce to

$$\left\{ \begin{array}{l} \psi_{1,n}^2 \frac{\partial v_{1,n}^{(\varepsilon)}}{\partial t} = \nabla \cdot \left(\tilde{\mathcal{D}}_{1,n} \nabla v_{1,n}^{(\varepsilon)} \right) \quad \text{in } Y_f \\ \psi_{2,n}^2 \frac{\partial v_{2,n}^{(\varepsilon)}}{\partial t} = \nabla \cdot \left(\tilde{\mathcal{D}}_{2,n} \nabla v_{2,n}^{(\varepsilon)} \right) \\ -\tilde{\mathcal{D}}_{1,n} \nabla v_{1,n}^{(\varepsilon)} \cdot \mathbf{n}_{fs} = k_2 \psi_{1,n} \psi_{2,n} (v_{1,n}^{(\varepsilon)} - v_{2,n}^{(\varepsilon)}) \quad \text{at } \partial Y_{fs} \\ -\tilde{\mathcal{D}}_{2,n} \nabla v_{2,n}^{(\varepsilon)} \cdot \mathbf{n}_{fs} = k_1 \psi_{1,n} \psi_{2,n} (v_{2,n}^{(\varepsilon)} - v_{1,n}^{(\varepsilon)}). \end{array} \right. \quad (53)$$

In a similar fashion with the first case, the successive powers of ε are collected.

• Order $\mathcal{O}(\varepsilon^{-2})$

At order $\mathcal{O}(\varepsilon^{-2})$ in the volume and $\mathcal{O}(\varepsilon^{-1})$ on the interface ∂Y_{fs} , we get

$$\left\{ \begin{array}{l} \nabla_y \cdot \left(\tilde{\mathcal{D}}_{1,n} \nabla_y v_{1,n}^{(0)} \right) = 0 \quad \text{in } Y_f \\ \nabla_y \cdot \left(\tilde{\mathcal{D}}_{2,n} \nabla_y v_{2,n}^{(0)} \right) = 0 \\ -\tilde{\mathcal{D}}_{1,n} \nabla_y v_{1,n}^{(0)} \cdot \mathbf{n}_{fs} = 0 \quad \text{at } \partial Y_{fs} \\ -\tilde{\mathcal{D}}_{2,n} \nabla_y v_{2,n}^{(0)} \cdot \mathbf{n}_{fs} = 0 \end{array} \right. \quad (54)$$

leading straightforwardly to $v_{1,n}^{(0)}(t, \mathbf{x}, \mathbf{y}) = v_{1,n}^{(0)}(t, \mathbf{x})$ and $v_{2,n}^{(0)}(t, \mathbf{x}, \mathbf{y}) = v_{2,n}^{(0)}(t, \mathbf{x})$.

• Order $\mathcal{O}(\varepsilon^{-1})$

At order $\mathcal{O}(\varepsilon^{-1})$ in the volume and $\mathcal{O}(\varepsilon^0)$ on the interface, it yields

$$\left\{ \begin{array}{l} \nabla_y \cdot \left[\tilde{\mathcal{D}}_{1,n} \left(\nabla_x v_{1,n}^{(0)} + \nabla_y v_{1,n}^{(1)} \right) \right] = 0 \quad \text{in } Y_f \\ \nabla_y \cdot \left[\tilde{\mathcal{D}}_{2,n} \left(\nabla_x v_{2,n}^{(0)} + \nabla_y v_{2,n}^{(1)} \right) \right] = 0 \\ -\tilde{\mathcal{D}}_{1,n} \left(\nabla_x v_{1,n}^{(0)} + \nabla_y v_{1,n}^{(1)} \right) \cdot \mathbf{n}_{fs} = k_2 \psi_{1,n} \psi_{2,n} (v_{1,n}^{(0)} - v_{2,n}^{(0)}) \quad \text{at } \partial Y_{fs} \\ -\tilde{\mathcal{D}}_{2,n} \left(\nabla_x v_{2,n}^{(0)} + \nabla_y v_{2,n}^{(1)} \right) \cdot \mathbf{n}_{fs} = k_1 \psi_{1,n} \psi_{2,n} (v_{2,n}^{(0)} - v_{1,n}^{(0)}). \end{array} \right. \quad (55)$$

Averaging Eq. (55a) over the unit cell and using the divergence theorem together with the interface condition Eq. (55c), result in $\left(v_{1,n}^{(0)} - v_{2,n}^{(0)} \right) \langle \psi_{1,n} \psi_{2,n} \rangle^{fs} = 0$ as

$v_{1,n}^{(0)}$ and $v_{2,n}^{(0)}$ are \mathbf{y} -independent variables. The solution is $v_{1,n}^{(0)}(t, \mathbf{x}) = v_{2,n}^{(0)}(t, \mathbf{x}) \equiv v_n^{(0)}(t, \mathbf{x})$.

Coming back to problem (55), by linearity the solution for $v_{i,n}^{(1)}$ is sought in the form

$$v_{1,n}^{(1)} = \boldsymbol{\chi}_{1,n} \cdot \nabla_x v_n^{(0)} + \widehat{v}_{1,n}^{(1)}(t, \mathbf{x}) \quad (56)$$

$$v_{2,n}^{(1)} = \boldsymbol{\chi}_{2,n} \cdot \nabla_x v_n^{(0)} + \widehat{v}_{2,n}^{(1)}(t, \mathbf{x}) \quad (57)$$

where $\widehat{v}_{1,n}^{(1)}$ and $\widehat{v}_{2,n}^{(1)}$ are two additive constants depending on t and \mathbf{x} for the unit cell problem. $\boldsymbol{\chi}_{1,n}$ and $\boldsymbol{\chi}_{2,n}$ are solutions of the following cell problems

$$\begin{cases} \nabla_y \cdot \left[\widetilde{\mathcal{D}}_{1,n} \left(\mathbf{I} + (\nabla_y \boldsymbol{\chi}_{1,n})^\top \right) \right] = 0 & \text{in } Y_f \\ \nabla_y \cdot \left[\widetilde{\mathcal{D}}_{2,n} \left(\mathbf{I} + (\nabla_y \boldsymbol{\chi}_{2,n})^\top \right) \right] = 0 \\ -\widetilde{\mathcal{D}}_{1,n} \left(\mathbf{I} + \nabla_y \boldsymbol{\chi}_{1,n} \right) \cdot \mathbf{n}_{fs} = 0 & \text{at } \partial Y_{fs} \\ -\widetilde{\mathcal{D}}_{2,n} \left(\mathbf{I} + \nabla_y \boldsymbol{\chi}_{2,n} \right) \cdot \mathbf{n}_{fs} = 0. \end{cases} \quad (58)$$

It can be noticed that unlike case 1, the problems of $\boldsymbol{\chi}_{1,n}$ and $\boldsymbol{\chi}_{2,n}$ are independent and decoupled here. To ensure the uniqueness of the solution of $\boldsymbol{\chi}_{1,n}$ and $\boldsymbol{\chi}_{2,n}$, the supplementary condition of zero average in Y_f is added. This condition has no influence on the homogenized diffusion tensor, as only the gradient of $\boldsymbol{\chi}_{1,n}$ and $\boldsymbol{\chi}_{2,n}$ is involved.

For $n = 0$, the problem (58) reduces to the classical tortuosity problem (38).

• **Order $\mathcal{O}(\varepsilon^0)$**

Finally, at order $\mathcal{O}(\varepsilon^0)$ in the volume and $\mathcal{O}(\varepsilon^{-1})$ on the interface, we obtain

$$\begin{cases} \psi_{1,n}^2 \frac{\partial v_n^{(0)}}{\partial t} = \nabla_y \cdot \left[\widetilde{\mathcal{D}}_{1,n} \left(\nabla_y v_{1,n}^{(2)} + \nabla_x v_{1,n}^{(1)} \right) \right] \\ \quad + \nabla_x \cdot \left[\widetilde{\mathcal{D}}_{1,n} \left(\nabla_y v_{1,n}^{(1)} + \nabla_x v_n^{(0)} \right) \right] & \text{in } Y_f \\ \psi_{2,n}^2 \frac{\partial v_n^{(0)}}{\partial t} = \nabla_y \cdot \left[\widetilde{\mathcal{D}}_{2,n} \left(\nabla_y v_{2,n}^{(2)} + \nabla_x v_{2,n}^{(1)} \right) \right] \\ \quad + \nabla_x \cdot \left[\widetilde{\mathcal{D}}_{2,n} \left(\nabla_y v_{2,n}^{(1)} + \nabla_x v_n^{(0)} \right) \right] \\ -\widetilde{\mathcal{D}}_{1,n} \left(\nabla_y v_{1,n}^{(2)} + \nabla_x v_{1,n}^{(1)} \right) \cdot \mathbf{n}_{fs} = k_2 \psi_{1,n} \psi_{2,n} \left(v_{1,n}^{(1)} - v_{2,n}^{(1)} \right) & \text{at } \partial Y_{fs} \\ -\widetilde{\mathcal{D}}_{2,n} \left(\nabla_y v_{2,n}^{(2)} + \nabla_x v_{2,n}^{(1)} \right) \cdot \mathbf{n}_{fs} = k_1 \psi_{1,n} \psi_{2,n} \left(v_{2,n}^{(1)} - v_{1,n}^{(1)} \right). \end{cases} \quad (59)$$

A development similar to case 1 can be carried out to obtain the same macroscopic equation for $v_n^{(0)}$

$$\left(k_1 \langle \psi_{1,n}^2 \rangle^f + k_2 \langle \psi_{2,n}^2 \rangle^f\right) \frac{\partial v_n^{(0)}}{\partial t} = \nabla_x \cdot \left\{ \left[k_1 \langle \tilde{\mathcal{D}}_{1,n} \left(\mathbf{I} + (\nabla_y \chi_{1,n})^\top \right) \rangle^f + k_2 \langle \tilde{\mathcal{D}}_{2,n} \left(\mathbf{I} + (\nabla_y \chi_{2,n})^\top \right) \rangle^f \right] \cdot \nabla_x v_n^{(0)} \right\}. \quad (60)$$

Considering the normalization condition (31), we obtain Eq. (32). The difference between these two cases only comes from the closure problem for $\chi_{1,n}$ and $\chi_{2,n}$ as discussed previously, except for $n = 0$ where both cases share the same local problem for χ .

5.2. Back to concentrations

Going back to dimensional variables in order to obtain the macroscopic diffusion equations at the leading order for the concentrations $\langle c_1^* \rangle^f$ and $\langle c_2^* \rangle^f$ and proceeding in the same manner as in §4.2, the following result is obtained.

Result 2. *For a diffusion and reaction of the same order corresponding to $Da_L = \mathcal{O}(\varepsilon^0)$, the concentrations at the leading order are solutions of the homogenized coupled diffusion-reaction problem (49) similar to case 1. The only difference stems from the decoupled closure problem (58).*

5.3. Comparison with the classical periodic homogenization

As for case 1, considering only the first eigenvalue value $\lambda_0^* = 0$ and omitting the superscript $^{(0)}$ lead to

$$\begin{aligned} c_1^* &= \psi_{1,0}^* v_0^* \\ c_2^* &= \psi_{2,0}^* v_0^*. \end{aligned} \quad (61)$$

Therefore, the homogenized problem (32) for v_n^* is written as

$$\frac{\partial c_i^*}{\partial t} - \nabla_{x^*} \cdot \left[\left(\frac{k_1^* \mathbf{D}_2^{*\text{eff}} + k_2^* \mathbf{D}_1^{*\text{eff}}}{k_1^* + k_2^*} \right) \cdot \nabla_{x^*} c_i^* \right] = 0 \quad (62)$$

for $i = 1, 2$ with the constraint:

$$k_1^* c_1^* - k_2^* c_2^* = 0. \quad (63)$$

The homogenized tensors $\mathbf{D}_1^{\text{eff}}$ and $\mathbf{D}_2^{\text{eff}}$ are given by:

$$\begin{aligned}\mathbf{D}_1^{\text{eff}} &= \left\langle \mathcal{D}_1^* \left(\mathbf{I} + (\nabla_{y^*}^* \boldsymbol{\chi}^*)^\top \right) \right\rangle^f \\ \mathbf{D}_2^{\text{eff}} &= \left\langle \mathcal{D}_2^* \left(\mathbf{I} + (\nabla_{y^*}^* \boldsymbol{\chi}^*)^\top \right) \right\rangle^f\end{aligned}\tag{64}$$

where $\boldsymbol{\chi}^*$ is solution of the local problem (38).

Considering only the first eigenvalue $\lambda_0^* = 0$ in expression (5), the result of case 1 with predominant reaction is recovered. In addition, these homogenized equations can be obtained by a classical homogenization procedure (see [15]). Again, such a homogenized result is only valid for long diffusion times and must be corrected by an additional term corresponding to the first non-zero eigenvalue λ_1^* leading to Result 2 in order to capture the complex behavior of the diffusion/reaction processes at short times.

6. Dominant diffusion

The last case corresponds to a predominant diffusion for which $\text{Da}_L = \mathcal{O}(\varepsilon)$.

6.1. Asymptotic expansion of equations

For $\text{Da}_L = \mathcal{O}(\varepsilon)$, the ε -model reads as

$$\left\{ \begin{array}{ll} \psi_{1,n}^2 \frac{\partial v_{1,n}^{(\varepsilon)}}{\partial t} = \nabla \cdot \left(\tilde{\mathcal{D}}_{1,n} \nabla v_{1,n}^{(\varepsilon)} \right) & \text{in } Y_f \\ \psi_{2,n}^2 \frac{\partial v_{2,n}^{(\varepsilon)}}{\partial t} = \nabla \cdot \left(\tilde{\mathcal{D}}_{2,n} \nabla v_{2,n}^{(\varepsilon)} \right) & \\ -\tilde{\mathcal{D}}_{1,n} \nabla v_{1,n}^{(\varepsilon)} \cdot \mathbf{n}_{fs} = \varepsilon k_2 \psi_{1,n} \psi_{2,n} (v_{1,n}^{(\varepsilon)} - v_{2,n}^{(\varepsilon)}) & \text{at } \partial Y_{fs} \\ -\tilde{\mathcal{D}}_{2,n} \nabla v_{2,n}^{(\varepsilon)} \cdot \mathbf{n}_{fs} = \varepsilon k_1 \psi_{1,n} \psi_{2,n} (v_{2,n}^{(\varepsilon)} - v_{1,n}^{(\varepsilon)}) & \end{array} \right. \tag{65}$$

• Order $\mathcal{O}(\varepsilon^{-2})$

At order $\mathcal{O}(\varepsilon^{-2})$ in the volume and $\mathcal{O}(\varepsilon^{-1})$ on the interface, the problem reads as

$$\left\{ \begin{array}{ll} 0 = \nabla_y \cdot \left(\tilde{\mathcal{D}}_{1,n} \nabla_y v_{1,n}^{(0)} \right) & \text{in } Y_f \\ 0 = \nabla_y \cdot \left(\tilde{\mathcal{D}}_{2,n} \nabla_y v_{2,n}^{(0)} \right) & \\ 0 = -\tilde{\mathcal{D}}_{1,n} \nabla_y v_{1,n}^{(0)} \cdot \mathbf{n}_{fs} & \text{at } \partial Y_{fs} \\ 0 = -\tilde{\mathcal{D}}_{2,n} \nabla_y v_{2,n}^{(0)} \cdot \mathbf{n}_{fs} & \end{array} \right. \tag{66}$$

whose solutions are $v_{1,n}^{(0)}(t, \mathbf{x}, \mathbf{y}) = v_{1,n}^{(0)}(t, \mathbf{x})$ and $v_{2,n}^{(0)}(t, \mathbf{x}, \mathbf{y}) = v_{2,n}^{(0)}(t, \mathbf{x})$.

• **Order $\mathcal{O}(\varepsilon^{-1})$**

At order $\mathcal{O}(\varepsilon^{-1})$ in the volume and $\mathcal{O}(\varepsilon^0)$ on the interface, it yields

$$\begin{cases} 0 = \nabla_y \cdot \left[\tilde{\mathcal{D}}_{1,n} \left(\nabla_x v_{1,n}^{(0)} + \nabla_y v_{1,n}^{(1)} \right) \right] \\ 0 = \nabla_y \cdot \left[\tilde{\mathcal{D}}_{2,n} \left(\nabla_x v_{2,n}^{(0)} + \nabla_y v_{2,n}^{(1)} \right) \right] \\ 0 = -\tilde{\mathcal{D}}_{1,n} \left(\nabla_x v_{1,n}^{(0)} + \nabla_y v_{1,n}^{(1)} \right) \cdot \mathbf{n}_{fs} \\ 0 = -\tilde{\mathcal{D}}_{2,n} \left(\nabla_x v_{2,n}^{(0)} + \nabla_y v_{2,n}^{(1)} \right) \cdot \mathbf{n}_{fs} \end{cases} \quad \begin{array}{l} \text{in } Y_f \\ \\ \text{at } \partial Y_{fs} \end{array} \quad (67)$$

where the problems for $v_{1,n}^{(1)}$ and $v_{2,n}^{(1)}$ are decoupled. The solution is sought in the form

$$\begin{aligned} v_{1,n}^{(1)} &= \chi_{1,n} \cdot \nabla_x v_{1,n}^{(0)} + \hat{v}_{1,n}^{(1)}(t, \mathbf{x}) \\ v_{2,n}^{(1)} &= \chi_{2,n} \cdot \nabla_x v_{2,n}^{(0)} + \hat{v}_{2,n}^{(1)}(t, \mathbf{x}) \end{aligned}$$

where $\chi_{1,n}$ and $\chi_{2,n}$ satisfy the local problems

$$\begin{cases} 0 = \nabla_y \cdot \left[\tilde{\mathcal{D}}_{1,n} \left(\mathbf{I} + (\nabla_y \chi_{1,n})^\top \right) \right] \\ 0 = \nabla_y \cdot \left[\tilde{\mathcal{D}}_{2,n} \left(\mathbf{I} + (\nabla_y \chi_{2,n})^\top \right) \right] \\ 0 = -\tilde{\mathcal{D}}_{1,n} \left(\mathbf{I} + \nabla_y \chi_{1,n} \right) \cdot \mathbf{n}_{fs} \\ 0 = -\tilde{\mathcal{D}}_{2,n} \left(\mathbf{I} + \nabla_y \chi_{2,n} \right) \cdot \mathbf{n}_{fs} \end{cases} \quad \begin{array}{l} \text{in } Y_f \\ \\ \text{at } \partial Y_{fs} \end{array} \quad (68)$$

• **Order $\mathcal{O}(\varepsilon^0)$**

At the leading order, the problem is written as

$$\begin{cases} \psi_{1,n}^2 \frac{\partial v_{1,n}^{(0)}}{\partial t} = \nabla_y \cdot \left[\tilde{\mathcal{D}}_{1,n} \left(\nabla_y v_{1,n}^{(2)} + \nabla_x v_{1,n}^{(1)} \right) \right] \\ \quad + \nabla_x \cdot \left[\tilde{\mathcal{D}}_{1,n} \left(\nabla_y v_{1,n}^{(1)} + \nabla_x v_{1,n}^{(0)} \right) \right] \\ \psi_{2,n}^2 \frac{\partial v_{2,n}^{(0)}}{\partial t} = \nabla_y \cdot \left[\tilde{\mathcal{D}}_{2,n} \left(\nabla_y v_{2,n}^{(2)} + \nabla_x v_{2,n}^{(1)} \right) \right] \\ \quad + \nabla_x \cdot \left[\tilde{\mathcal{D}}_{2,n} \left(\nabla_y v_{2,n}^{(1)} + \nabla_x v_{2,n}^{(0)} \right) \right] \\ -\tilde{\mathcal{D}}_{1,n} \left(\nabla_y v_{1,n}^{(2)} + \nabla_x v_{1,n}^{(1)} \right) \cdot \mathbf{n}_{fs} = k_2 \psi_{1,n} \psi_{2,n} \left(v_{1,n}^{(0)} - v_{2,n}^{(0)} \right) \\ -\tilde{\mathcal{D}}_{2,n} \left(\nabla_y v_{2,n}^{(2)} + \nabla_x v_{2,n}^{(1)} \right) \cdot \mathbf{n}_{fs} = k_1 \psi_{1,n} \psi_{2,n} \left(v_{2,n}^{(0)} - v_{1,n}^{(0)} \right) \end{cases} \quad \begin{array}{l} \text{in } Y_f \\ \\ \text{at } \partial Y_{fs} \end{array} \quad (69)$$

Averaging Eqs. (69a-b) over the fluid phase of the unit cell and taking into account the interface conditions (69c-d) lead to

$$\left\{ \begin{array}{l} \langle \psi_{1,n}^2 \rangle^f \frac{\partial v_{1,n}^{(0)}}{\partial t} = \nabla_x \cdot \left(\langle \tilde{\mathcal{D}}_{1,n} \left(\mathbf{I} + (\nabla_y \chi_{1,n})^\top \right) \rangle^f \cdot \nabla_x v_{1,n}^{(0)} \right) \\ \quad - \frac{k_2 \left(v_{1,n}^{(0)} - v_{2,n}^{(0)} \right)}{|Y_f|} \int_{\partial Y_{fs}} \psi_{1,n} \psi_{2,n} dA \\ \langle \psi_{2,n}^2 \rangle^f \frac{\partial v_{2,n}^{(0)}}{\partial t} = \nabla_x \cdot \left(\langle \tilde{\mathcal{D}}_{2,n} \left(\mathbf{I} + (\nabla_y \chi_{2,n})^\top \right) \rangle^f \cdot \nabla_x v_{2,n}^{(0)} \right) \\ \quad - \frac{k_1 \left(v_{2,n}^{(0)} - v_{1,n}^{(0)} \right)}{|Y_f|} \int_{\partial Y_{fs}} \psi_{1,n} \psi_{2,n} dA. \end{array} \right. \quad (70)$$

6.2. Back to concentrations

When the chemical reaction is slow, the series development (5) can be limited to the first term corresponding to $n = 0$ and $\lambda_0^* = 0$, $\psi_{1,0}^*$ and $\psi_{2,0}^*$ being defined in (45). Since $v_{1,0}$ and $v_{2,0}$ are independent variables, it is legitimate to impose the initial conditions for the concentrations by using the initial conditions of $v_{1,0}$ and $v_{2,0}$. As a consequence, for $n \geq 1$ the initial conditions for $v_{1,n}$ and $v_{2,n}$ are null and the functions vanish.

The macroscopic mass conservation laws in dimensional space for the concentrations c_1^* and c_2^* at the leading order are obtained as follows

Result 3. *For dominant diffusion corresponding to $Da_L = \mathcal{O}(\varepsilon)$, the concentrations at the leading order are solutions of the homogenized coupled diffusion-reaction problem*

$$\left\{ \begin{array}{l} \frac{\partial c_1^*}{\partial t^*} = \nabla_{x^*} \cdot \left(\langle \mathcal{D}_1^* \left(\mathbf{I} + \nabla_{y^*} \chi^* \right) \rangle^f \cdot \nabla_{x^*} c_1^* \right) - \frac{|\partial Y_{fs}^*|}{|Y_f^*|} (k_1^* c_1^* - k_2^* c_2^*) \\ \frac{\partial c_2^*}{\partial t^*} = \nabla_{x^*} \cdot \left(\langle \mathcal{D}_2^* \left(\mathbf{I} + \nabla_{y^*} \chi^* \right) \rangle^f \cdot \nabla_{x^*} c_2^* \right) - \frac{|\partial Y_{fs}^*|}{|Y_f^*|} (k_2^* c_2^* - k_1^* c_1^*) \end{array} \right. \quad (71)$$

where χ^* is the solution of the classical local problem for diffusion (38).

It should be noted that such a result can also be obtained from a classical homogenization procedure [15].

7. Conclusions

A multiscale procedure has been developed to model the diffusion/reaction processes of two species in a periodic porous medium based on a spectral approach. The initial pore-scale problem is transformed into an auxiliary problem by expanding the concentrations in a series of eigenfunctions related to the spectral problem defined on the unit cell. The homogenization technique is then used to upscale the local problem to obtain the macroscopic laws. Three different cases, predominant reaction, reaction and diffusion of the same order of magnitude and dominant diffusion are studied.

For predominant reaction with a Damköhler number of order $\mathcal{O}(\varepsilon^{-1})$, the macroscopic equations exhibit a complex behavior characterized by a source term depending on the reaction rates introduced through the first non-zero eigenvalue and by coupled diffusion terms. If only the first null eigenvalue $\lambda_0 = 0$ is considered, the result of the classical homogenization procedure is recovered but the chemical equilibrium is then imposed everywhere in the fluid phase. Therefore, the classical homogenization procedure fails to predict the diffusion/reaction behavior at short reaction times. The correction induced by taking into account the non-zero eigenvalues allows us to overcome this difficulty. The proposed model is able to capture complex phenomena at short times when the chemical equilibrium is not established.

When the reaction time is of the same order as the diffusion time, *i.e.* $\text{Da}_L = \mathcal{O}(\varepsilon^0)$, macroscopic mass conservation laws are similar to the preceding first case ($\text{Da}_L = \mathcal{O}(\varepsilon^{-1})$). The only slight difference comes from the closure problems for the diffusivities where no coupled term between both species at the interface is present.

When the reaction is slow and the diffusion dominates, the spectral approach and the classical homogenization procedure give the same result. The macroscopic laws have a source term depending only on the specific area, reaction rates and average concentrations. The effective diffusion coefficients are independent of the reaction rates.

In future work, numerical simulations will be performed to show the potential of the current multiscale approach. Moreover, the convection problem will also be considered in the extension of this work.

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Appendix A. On the orthogonality of the eigenfunctions

Let us consider again the spectral problem (3) without superscript to simplify the notation

$$\begin{cases} -\nabla \cdot (\mathcal{D}_1 \nabla \psi_{1,m}) &= \lambda_m \psi_{1,m} & \text{in } Y_f \\ -\nabla \cdot (\mathcal{D}_2 \nabla \psi_{2,m}) &= \lambda_m \psi_{2,m} & \text{in } Y_f \\ -\mathcal{D}_1 \nabla \psi_{1,m} \cdot \mathbf{n}_{fs} &= k_1 \psi_{1,m} - k_2 \psi_{2,m} & \text{at } \partial Y_{fs} \\ -\mathcal{D}_2 \nabla \psi_{2,m} \cdot \mathbf{n}_{fs} &= k_2 \psi_{2,m} - k_1 \psi_{1,m} & \text{at } \partial Y_{fs}. \end{cases} \quad (\text{A.1})$$

We consider two eigenvalues λ_m et λ_n and the corresponding eigenfunctions $\psi_{1,m}$ and $\psi_{1,n}$ for the first species associated with the concentration c_1 . For the sake of simplicity, assume that the diffusion coefficients are constant⁵ on Y_f . We have

$$\begin{cases} \mathcal{D}_1 \nabla^2 \psi_{1,m} &= -\lambda_m \psi_{1,m} \\ \mathcal{D}_1 \nabla^2 \psi_{1,n} &= -\lambda_n \psi_{1,n}. \end{cases} \quad (\text{A.2})$$

By multiplying the first equation by $-\psi_{1,n}$ and the second one by $\psi_{1,m}$, integrating over the fluid phase of the unit cell and summing the two equations, we get for $n \neq m$

$$\int_{Y_f} (-\mathcal{D}_1 \psi_{1,n} \nabla^2 \psi_{1,m} + \mathcal{D}_1 \psi_{1,m} \nabla^2 \psi_{1,n}) dV = (\lambda_m - \lambda_n) \int_{Y_f} \psi_{1,m} \psi_{1,n} dV. \quad (\text{A.3})$$

The left-hand side transforms into

$$\begin{aligned} \int_{Y_f} (-\mathcal{D}_1 \psi_{1,n} \nabla^2 \psi_{1,m} + \mathcal{D}_1 \psi_{1,m} \nabla^2 \psi_{1,n}) dV &= \\ \mathcal{D}_1 \int_{Y_f} [\nabla \cdot (\psi_{1,m} \nabla \psi_{1,n}) - \nabla \cdot (\psi_{1,n} \nabla \psi_{1,m})] dV &= \\ = \mathcal{D}_1 \int_{\partial Y_f} [\psi_{1,m} \nabla \psi_{1,n} - \psi_{1,n} \nabla \psi_{1,m}] \cdot \mathbf{n}_f dS & \quad (\text{A.4}) \end{aligned}$$

where $\partial Y_f = \partial Y_{fe} \cup \partial Y_{fs}$. By periodicity, the integral vanishes on the external boundary ∂Y_{fe} . Accounting for the boundary condition on ∂Y_{fs} , we get from (A.3)

$$\begin{aligned} (\lambda_m - \lambda_n) \int_{Y_f} \psi_{1,m} \psi_{1,n} dV &= \int_{\partial Y_{fs}} [\psi_{1,m} (-k_1 \psi_{1,n} + k_2 \psi_{2,n}) \\ &\quad + \psi_{1,n} (k_1 \psi_{1,m} - k_2 \psi_{2,m})] dS \\ &= k_2 \int_{\partial Y_{fs}} (\psi_{1,m} \psi_{2,n} - \psi_{1,n} \psi_{2,m}) dS. \end{aligned} \quad (\text{A.5})$$

⁵A generalization to non-uniform diffusion coefficients does not present any difficulty.

Applying the same procedure for $\psi_{2,m}$ and $\psi_{2,n}$ yields

$$(\lambda_m - \lambda_n) \int_{Y_f} \psi_{2,m} \psi_{2,n} dV = k_1 \int_{\partial Y_{fs}} (\psi_{1,n} \psi_{2,m} - \psi_{1,m} \psi_{2,n}) dS. \quad (\text{A.6})$$

Combining relations (A.5) and (A.6), we obtain the orthogonality condition for $n \neq m$

$$\int_{Y_f} (k_1 \psi_{1,m} \psi_{1,n} + k_2 \psi_{2,m} \psi_{2,n}) dV = 0. \quad (\text{A.7})$$

Finally, taking into account the normalization condition (31) for the eigenfunctions

$$k_1 \langle \psi_{1,n}^2 \rangle^f + k_2 \langle \psi_{2,n}^2 \rangle^f = k_1 + k_2. \quad (\text{A.8})$$

The orthogonality condition for the eigenfunctions is written for $(n, m) \in \mathbb{N}^2$:

$$\int_{Y_f} (k_1 \psi_{1,n} \psi_{1,m} + k_2 \psi_{2,n} \psi_{2,m}) dV = (k_1 + k_2) \delta_{mn}. \quad (\text{A.9})$$

Appendix B. Importance of the first eigenvalue

At the main order for the concentrations, omitting the superscripts * and ⁽⁰⁾, as v_0 only depends on (t, \mathbf{x}) according to results⁶ 1 and 2, we have from (5)

$$\begin{cases} c_1(t, \mathbf{x}, \mathbf{y}) = \sqrt{\frac{k_2}{k_1}} v_0(t, \mathbf{x}) + \sum_{n=1}^{\infty} \psi_{1,n}(\mathbf{y}) \exp(-\lambda_n t) v_n(t, \mathbf{x}) \\ c_2(t, \mathbf{x}, \mathbf{y}) = \sqrt{\frac{k_1}{k_2}} v_0(t, \mathbf{x}) + \sum_{n=1}^{\infty} \psi_{2,n}(\mathbf{y}) \exp(-\lambda_n t) v_n(t, \mathbf{x}). \end{cases} \quad (\text{B.1})$$

Let us specify the initial values of $v_n(0, \mathbf{x})$ ($0 \leq n \leq \infty$) from the initial conditions for c_1 and c_2

$$\begin{cases} c_1(0, \mathbf{x}, \mathbf{y}) = \sqrt{\frac{k_2}{k_1}} v_0(0, \mathbf{x}) + \sum_{n=1}^{\infty} \psi_{1,n}(\mathbf{y}) v_n(0, \mathbf{x}) \\ c_2(0, \mathbf{x}, \mathbf{y}) = \sqrt{\frac{k_1}{k_2}} v_0(0, \mathbf{x}) + \sum_{n=1}^{\infty} \psi_{2,n}(\mathbf{y}) v_n(0, \mathbf{x}). \end{cases} \quad (\text{B.2})$$

⁶Results 1 and 2 have been obtained for moderate and high values of Damköhler number. For low values of Damköhler number, $v_{1,n}^{(0)}$ and $v_{2,n}^{(0)}$ depend on \mathbf{y} as well (Result 3) and this analysis is not valid.

Averaging the two above equations on Y_f , accounting for the compatibility condition of the spectral problem (3)

$$\langle \psi_{1,n} \rangle^f + \langle \psi_{2,n} \rangle^f = 0, \quad (\text{B.3})$$

we obtain

$$\langle c_1(0, \mathbf{x}, \mathbf{y}) \rangle^f + \langle c_2(0, \mathbf{x}, \mathbf{y}) \rangle^f = \left(\sqrt{\frac{k_2}{k_1}} + \sqrt{\frac{k_1}{k_2}} \right) v_0(0, \mathbf{x}). \quad (\text{B.4})$$

For $n \neq 0$, let us multiply the first equation (B.2) for c_1 by $k_1 \psi_{1,m}$ and the second equation for c_2 by $k_2 \psi_{2,m}$. By integration on the fluid domain Y_f , accounting for the orthogonality condition (A.9) and the compatibility condition (B.3), we get

$$v_n(0, \mathbf{x}) = \frac{\langle k_1 \psi_{1,n} c_1(0, \mathbf{x}, \mathbf{y}) + k_2 \psi_{2,n} c_2(0, \mathbf{x}, \mathbf{y}) \rangle^f}{k_1 + k_2}. \quad (\text{B.5})$$

If the initial conditions $c_1(0, \mathbf{x}, \mathbf{y}) \equiv c_1^{ini}(\mathbf{x})$ and $c_2(0, \mathbf{x}, \mathbf{y}) \equiv c_2^{ini}(\mathbf{x})$ are uniform in each cell (the initial distribution of the concentrations does not depend on \mathbf{y}), we have using the compatibility condition (B.3)

$$v_n(0, \mathbf{x}) = \frac{k_1 c_1^{ini}(\mathbf{x}) - k_2 c_2^{ini}(\mathbf{x})}{k_1 + k_2} \langle \psi_{1,n} \rangle^f. \quad (\text{B.6})$$

Finally, it is important to note that, due to the relation (B.3), the total concentration of the two chemical species is only given by the first term of the development (B.1)

$$\langle c_1 \rangle^f + \langle c_2 \rangle^f = \left(\sqrt{\frac{k_2}{k_1}} + \sqrt{\frac{k_1}{k_2}} \right) v_0(t, \mathbf{x}) \quad (\text{B.7})$$

whereas the deviation from the chemical equilibrium is given by

$$\begin{aligned} k_1 \langle c_1 \rangle^f - k_2 \langle c_2 \rangle^f &= \sum_{n=1}^{\infty} \left(k_1 \langle \psi_{1,n} \rangle^f - k_2 \langle \psi_{2,n} \rangle^f \right) \exp(-\lambda_n t) v_n(t, \mathbf{x}) \\ &= \sum_{n=1}^{\infty} (k_1 + k_2) \langle \psi_{1,n} \rangle^f \exp(-\lambda_n t) v_n(t, \mathbf{x}). \end{aligned} \quad (\text{B.8})$$

It clearly appears from (B.8) that deviation from chemical equilibrium at the main order is given by the first non-zero eigenvalue λ_1^* , which is the smaller one, due to

the fast exponential decay for the larger ones. That is the reason why in Results 1 and 2 only the first non-zero eigenvalue λ_1^* has been considered. Moreover, expression (B.8) reveals that if only the first zero eigenvalue $\lambda_0^* = 0$ is considered in the homogenized models, the chemical equilibrium is instantaneously imposed as the right hand side of (B.8) vanishes. That is in contradiction with the physics at (very) short times.

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