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# Upscaled model for the diffusion/heterogeneous reaction in porous media: boundary layer problem

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## Abstract

Multi-species diffusion/heterogeneous reaction coupled problem in porous media involving a boundary layer problem is studied. The spectral approach developed in our previous work allows to derive a macroscopic model in the high Damköhler number regime combining homogenization technique and spectral approach. Such a homogenized model cannot describe the perturbation at the external boundary where the chemical equilibrium is not necessarily satisfied. We construct herein a modified model involving additional variables, which are rapidly-decaying functions, to capture the complex physics in the boundary layer. Numerical simulations underline the accuracy of the proposed correction in both steady and transient states.

*Keywords:* Homogenization, Diffusion/reaction problem, Spectral approach, Boundary layer problem

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## 1. Introduction

Reactive transport of multi-species in porous media, which is of major interest for many applications in numerous areas such as electrochemical systems, agronomy, geology, etc., has received considerable attention from the modeling point of view. Macroscopic models involving effective coefficients can be rigorously derived from upscaling approaches [1, 2, 3, 4, 5, 6, 7, 8, 9]. A challenging case refers to the predominant reaction situation when the medium exhibits a complex behavior

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7 and the effective coefficients in the macroscopic equations depend on reaction rates [1, 3, 10]. More  
8 sophisticated models are required to accurately describe the non-equilibrium state at very short  
9 times that are of the order of the characteristic reaction time [11, 12]. In spite of the difficulty,  
10 macroscopic models were derived by using the periodic homogenization technique and a spectral  
11 approach in our previous work [13, 14, 15]. However, the homogenization procedure imposes a  
12 spatial periodicity condition at the boundary of the unit cell. In this framework, the physics inside  
13 the porous domain can be accurately captured by the macroscopic models while at the outer surface  
14 of the domain, periodicity conditions cannot be respected. This leads to a boundary layer problem  
15 depending on the boundary condition type.

16 The boundary layer problems have been widely studied for elastic periodic composites [16, 17],  
17 for elastic beams [18], for elastic shells [19] or in a more general way in [20, 21]. Matine et al.  
18 [22, 23] proposed to extend this approach for thermal problem in periodic structures, to take into  
19 account the edge effects. However, to the best of our knowledge there is practically no work in the  
20 literature addressing the boundary layer problem for the coupling of predominating reaction and  
21 diffusion of multi-species in porous media.

22 In a sequence of papers, the coupling of diffusion/reaction of two species with different molecular  
23 diffusion coefficients has been studied combining periodic homogenization technique with a spectral  
24 approach [13, 14, 15, 24]. Concentrations of the initial pore-scale problem are expanded into a series  
25 development related to a spectral problem defined in a unit cell, yielding a new local problem to  
26 be homogenized. This approach is able to capture the complex coupling at short times when the  
27 chemical equilibrium is not reached. However, such a macroscopic model cannot provide information  
28 about the boundary layer that develops in the vicinity of the outer boundary due to the boundary  
29 conditions. In this work, corrections are added to the macroscopic model to take into account  
30 the boundary conditions at the outer boundary of the domain. In steady state, terms of the first  
31 order need to be corrected by introducing new variables whereas in transient regime, corrections  
32 at lower order are added to capture the perturbation in the boundary layer at short times. Such a  
33 modification implies new closure variables that must be solved over several unit cells from the edge  
34 of the domain. For larger distances, these decreasing functions vanish.

35 The paper is organized as follows. In Section 2, the main result of the upscaling procedure based  
36 on the spectral approach and homogenization technique for high Damköhler number is recalled.  
37 Section 3 is devoted to the development of the modified model in order to address the boundary layer

38 problem in both steady and transient regimes. Numerical simulations are performed in Section 4 to  
 39 validate the proposed model and to underline the importance of the correction terms. Conclusions  
 40 are drawn in Section 5.

## 41 2. Macroscopic model for high Damköhler number: a recall

42 In this section, the main steps and results of the homogenization procedure to derive the macro-  
 43 scopic equations for the diffusion-reaction problem, developed in a previous work [14] are recalled.  
 44 To simplify the notation, the superscript \* indicating dimensional quantities in the preceding refer-  
 45 ence is omitted.

46 A porous medium occupying a macroscopic domain  $\Omega$  with a characteristic length  $L$ , is composed  
 47 of an immobile fluid phase  $\Omega_f$  and of a rigid solid phase  $\Omega_s$  with a solid-fluid interface  $\Gamma_{fs}$ . The  
 48 medium is constituted of the repetition of a periodic elementary cell  $Y = Y_f \cup Y_s$  of characteristic  
 49 length  $l$ , composed of the fluid phase  $Y_f$  and the solid phase  $Y_s$  together with the solid-fluid interface  
 50  $\partial Y_{fs}$ . The boundary  $\partial Y = \partial Y_{fs} \cup \partial Y_e$  is constituted of the fluid-solid interface  $\partial Y_{fs}$  assumed to be  
 51 impervious and of the external interface  $\partial Y_e = \partial Y_{se} \cup \partial Y_{fe}$  separating two juxtaposed elementary  
 52 cells. The macroscopic and microscopic spatial coordinates are  $\mathbf{x} = (x_1, x_2, x_3)$  and  $\mathbf{y} = (y_1, y_2, y_3)$   
 53 respectively. The scale separation ( $l \ll L$ ) allows the introduction of the small parameter  $\varepsilon = l/L$ .

54 Let  $c_1$  and  $c_2$  be the concentrations of species  $A$  and  $B$  respectively. The transport is ruled by a  
 55 Fickian process. On the fluid-solid interface  $\Gamma_{fs}$ , linear chemical reactions exchange species  $A$  and  
 56  $B$ . The microscopic diffusion/reaction equations at the pore-scale are written as

$$\left\{ \begin{array}{ll} \frac{\partial c_1}{\partial t} - \nabla \cdot (\mathcal{D}_1 \nabla c_1) = 0 & \text{in } \Omega_f \\ \frac{\partial c_2}{\partial t} - \nabla \cdot (\mathcal{D}_2 \nabla c_2) = 0 & \text{in } \Omega_f \\ -\mathcal{D}_1 \nabla c_1 \cdot \mathbf{n}_{fs} = k_1 c_1 - k_2 c_2 & \text{at } \Gamma_{fs} \\ -\mathcal{D}_2 \nabla c_2 \cdot \mathbf{n}_{fs} = k_2 c_2 - k_1 c_1 & \text{at } \Gamma_{fs} \end{array} \right. \quad (1)$$

57 where  $\mathcal{D}_1$  and  $\mathcal{D}_2$  denote the diffusion coefficients of  $A$  and  $B$  respectively,  $k_1$  and  $k_2$  the reaction  
 58 rates. These coefficients have constant values during the process.  $\mathbf{n}_{fs}$  is the normal unit vector at  
 59 the solid/fluid interface pointing out of the fluid phase. The microscopic problem is completed by  
 60 the initial conditions for given values of  $c_1(t = 0)$  and  $c_2(t = 0)$  and the boundary conditions at  
 61 the outer edges of the domain. In this work, we only consider the Dirichlet conditions in which the  
 62 concentrations are given at the edges.

63 The initial model is transformed into a new problem associated with the following periodic  
64 spectral problem defined on the periodic unit cell  $Y$

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

65 where  $\psi_{1,n}(\mathbf{y})$  and  $\psi_{2,n}(\mathbf{y})$  represent the successive eigenfunctions sharing the same positive eigen-  
66 value  $\lambda_n$  ordered in ascending order with  $n \in \mathbb{N}$ . The eigenfunctions  $\psi_{1,n}(\mathbf{y})$  and  $\psi_{2,n}(\mathbf{y})$  are defined  
67 within a same multiplicative constant, which can be determined according to

$$k_1 \langle \psi_{1,n}^2 \rangle^f + k_2 \langle \psi_{2,n}^2 \rangle^f = k_1 + k_2 \quad (3)$$

68 where  $\langle \cdot \rangle^f$  denotes the volume average over the fluid phase.

69 For  $n = 0$ ,  $\lambda_0 = 0$  and the two eigenfunctions are constant satisfying the condition  $k_1 \psi_{1,0} -$   
70  $k_2 \psi_{2,0} = 0$ . They are given by

$$\psi_{1,0} = \sqrt{\frac{k_2}{k_1}}, \quad \psi_{2,0} = \sqrt{\frac{k_1}{k_2}} \quad (4)$$

71 Finally note that for  $n \geq 1$

$$\langle \psi_{1,n} \rangle^f + \langle \psi_{2,n} \rangle^f = 0 \quad (5)$$

72 resulting from the compatibility condition of Eqs. (2).

73  $c_i$  ( $i \in \{1, 2\}$ ) are then sought in an expansion related to the spectral problem (2) as follows

$$c_i(t, \mathbf{x}, \mathbf{y}) = \sum_{n=0}^{\infty} \psi_{i,n}(\mathbf{y}) \exp(-\lambda_n t) v_{i,n}(t, \mathbf{x}, \mathbf{y}) \quad (6)$$

74 with new variables  $v_{i,n}$  depending on time and position.

75 Let define the macroscopic Damköhler number  $\text{Da}_L$  as the ratio of the macroscopic diffusion  
76 time to the reaction one

$$\text{Da}_L = \frac{k_r L}{\mathcal{D}_r} \quad (7)$$

77 where  $k_r$  and  $\mathcal{D}_r$  denote reference reaction rate and diffusion coefficient. In [14], the Damköhler  
78 number appears naturally through the dimensional analysis which has been skipped in this summary

79 of the results. The reference time is chosen as the macroscopic diffusion time  $t_r = L^2/\mathcal{D}_r$ . The  
80 reader can refer to [14] for more details on the procedure.

81 It has been shown in [14] that for small Damköhler number of order  $\mathcal{O}(\varepsilon)$ , a classical homog-  
82 enization procedure can correctly predict the macroscopic laws. However, for higher Damköhler  
83 number of order  $\mathcal{O}(\varepsilon^0)$  or  $\mathcal{O}(\varepsilon^{-1})$ , special development is needed to precisely predict the behavior  
84 of diffusion/reaction mechanism for short time [14]. It should be noted that a slight difference  
85 between the two cases  $\mathcal{O}(\varepsilon^0)$  and  $\mathcal{O}(\varepsilon^{-1})$  comes from the closure problem in solid/fluid interface  
86 condition. In this work, we deal with the most interesting case of high Damköhler number with  
87  $\text{Da}_L = \mathcal{O}(\varepsilon^{-1})$ . By inserting (6) in the initial problem (1) and making use of the definition (7),  
88 performing a dimensional analysis, the  $\varepsilon$ -microscopic model for  $v_{i,n}$  in dimensional space reads as

$$\left\{ \begin{array}{l} \psi_{1,n}^2 \frac{\partial v_{1,n}^{(\varepsilon)}}{\partial t} = \nabla \cdot (\tilde{\mathcal{D}}_{1,n} \nabla v_{1,n}^{(\varepsilon)}) \quad \text{in } Y_f \\ \psi_{2,n}^2 \frac{\partial v_{2,n}^{(\varepsilon)}}{\partial t} = \nabla \cdot (\tilde{\mathcal{D}}_{2,n} \nabla v_{2,n}^{(\varepsilon)}) \\ -\tilde{\mathcal{D}}_{1,n} \nabla v_{1,n}^{(\varepsilon)} \cdot \mathbf{n}_{fs} = \varepsilon^{-1} k_2 \psi_{1,n} \psi_{2,n} (v_{1,n}^{(\varepsilon)} - v_{2,n}^{(\varepsilon)}) \quad \text{at } \partial Y_{fs} \\ -\tilde{\mathcal{D}}_{2,n} \nabla v_{2,n}^{(\varepsilon)} \cdot \mathbf{n}_{fs} = \varepsilon^{-1} k_1 \psi_{1,n} \psi_{2,n} (v_{2,n}^{(\varepsilon)} - v_{1,n}^{(\varepsilon)}) \end{array} \right. \quad (8)$$

89 with  $\tilde{\mathcal{D}}_{1,n} = \mathcal{D}_1 \psi_{1,n}^2$  and  $\tilde{\mathcal{D}}_{2,n} = \mathcal{D}_2 \psi_{2,n}^2$ . By collecting the terms in the different powers of  $\varepsilon$ , one  
90 leads to the following results.

91 • **Slow variables:** At the leading order, the solution of  $v$  is  $v_{1,n}^{(0)}(t, \mathbf{x}, \mathbf{y}) = v_{2,n}^{(0)}(t, \mathbf{x}, \mathbf{y}) =$   
92  $v_n^{(0)}(t, \mathbf{x})$ .

93 • **Fluctuation:** the solution for  $v_{1,n}^{(1)}$  and  $v_{2,n}^{(1)}$  are sought in the following form, to within one  
94 additive constant  $\hat{v}_n^{(1)}$  depending on  $t$  and  $\mathbf{x}$ <sup>1</sup>

$$\begin{aligned} v_{1,n}^{(1)} &= \chi_{1,n}(\mathbf{y}) \cdot \nabla_x v_n^{(0)}(t, \mathbf{x}) + \hat{v}_n^{(1)}(t, \mathbf{x}) \\ v_{2,n}^{(1)} &= \chi_{2,n}(\mathbf{y}) \cdot \nabla_x v_n^{(0)}(t, \mathbf{x}) + \hat{v}_n^{(1)}(t, \mathbf{x}) \end{aligned} \quad (9)$$

<sup>1</sup>This necessary condition comes from the right hand side of the associated boundary conditions in Eqs. (8)

95 where the vectors  $\chi_{1,n}$  and  $\chi_{2,n}$  satisfy the closure problem<sup>2</sup>

$$\left\{ \begin{array}{l} 0 = \nabla_y \cdot [\tilde{\mathcal{D}}_{1,n} (\mathbf{I} + \nabla_y \chi_{1,n})] \\ 0 = \nabla_y \cdot [\tilde{\mathcal{D}}_{2,n} (\mathbf{I} + \nabla_y \chi_{2,n})] \\ -\tilde{\mathcal{D}}_{1,n} \mathbf{n}_{fs} \cdot (\mathbf{I} + \nabla_y \chi_{1,n}) = k_2 \psi_{1,n} \psi_{2,n} (\chi_{1,n} - \chi_{2,n}) \\ -\tilde{\mathcal{D}}_{2,n} \mathbf{n}_{fs} \cdot (\mathbf{I} + \nabla_y \chi_{2,n}) = k_1 \psi_{1,n} \psi_{2,n} (\chi_{2,n} - \chi_{1,n}) \end{array} \right. \quad \begin{array}{l} \text{in } Y_f \\ \\ \text{at } \partial Y_{fs} \end{array} \quad (10)$$

96

97 The particular case  $n = 0$  corresponds to the eigenvalue  $\lambda_0 = 0$  and to the eigenfunctions (4).

98 In this case  $\chi_{1,0} \equiv \chi_{2,0} \equiv \chi$  and the local problem (10) reduces to the standard closure problem

$$\left\{ \begin{array}{l} \nabla_{yy}^2 \chi = 0 \\ (\mathbf{I} + \nabla_y \chi) \cdot \mathbf{n}_{fs} = 0 \end{array} \right. \quad \begin{array}{l} \text{in } Y_f \\ \text{at } \partial Y_{fs} \end{array} \quad (11)$$

99 This leads to

$$v_{1,0}^{(1)} = v_{2,0}^{(1)} = v_0^{(1)} = \chi(\mathbf{y}) \cdot \nabla_x v_0^{(0)}(t, \mathbf{x}) + \hat{v}_0^{(1)}(t, \mathbf{x}) \quad (12)$$

100 • **Macroscopic equation:** the macroscopic problem for  $v_n^{(0)}$  is derived as

$$\frac{\partial v_n^{(0)}}{\partial t} = \nabla_x \cdot (\mathbf{D}_{v,n} \cdot \nabla_x v_n^{(0)}) \quad (13)$$

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

$$\mathbf{D}_{v,n} = \frac{k_1}{k_1 + k_2} \langle \tilde{\mathcal{D}}_{1,n} (\mathbf{I} + (\nabla_y \chi_{1,n})^\top) \rangle^f + \frac{k_2}{k_1 + k_2} \langle \tilde{\mathcal{D}}_{2,n} (\mathbf{I} + (\nabla_y \chi_{2,n})^\top) \rangle^f \quad (14)$$

102 For  $n = 0$ , the effective tensor is given by

$$\mathbf{D}_{v,0} = \frac{k_1 \mathcal{D}_2 + k_2 \mathcal{D}_1}{k_1 + k_2} \langle \mathbf{I} + (\nabla_y \chi)^\top \rangle^f \quad (15)$$

103 • **Macroscopic equations for the concentrations:** As discussed in [14], only the two first  
104 eigenvalues  $\lambda_0 = 0$  and  $\lambda_1$  with their corresponding eigenfunctions are considered. In the asymptotic

---

<sup>2</sup>Here, rather than using the tensorial definition in [14] in which a transpose operator is needed, the index notation for the gradient of a vector defined in [25] is adopted.

105 development (6), the higher order terms can be ignored due to the exponential decay in time. The  
 106 averaged concentrations at the leading order are given by

$$\begin{aligned} \langle c_1^{(0)} \rangle^f &= \psi_{1,0} v_0^{(0)} + \langle \psi_{1,1} \rangle^f \exp(-\lambda_1 t) v_1^{(0)} \\ \langle c_2^{(0)} \rangle^f &= \psi_{2,0} v_0^{(0)} + \langle \psi_{2,1} \rangle^f \exp(-\lambda_1 t) v_1^{(0)} \end{aligned} \quad (16)$$

107 Omitting for the sake of simplicity the subscript (0) related to the scale order, using (13) for  $n = 0$   
 108 and  $n = 1$ , and considering the time derivative of (16) and the compatibility condition (5) for  $n = 1$   
 109 result in the following mass conservation equations at the leading order<sup>3</sup>:

$$\left\{ \begin{array}{l} \frac{\partial \langle c_1 \rangle^f}{\partial t} - \nabla_x \cdot \left( \frac{k_1 \mathbf{D}_{v,1} + k_2 \mathbf{D}_{v,0}}{k_1 + k_2} \cdot \nabla_x \langle c_1 \rangle^f \right) \\ - \nabla_x \cdot \left( \frac{k_2 (\mathbf{D}_{v,0} - \mathbf{D}_{v,1})}{k_1 + k_2} \cdot \nabla_x \langle c_2 \rangle^f \right) + \lambda_1 \frac{k_1 \langle c_1 \rangle^f - k_2 \langle c_2 \rangle^f}{k_1 + k_2} = 0 \\ \frac{\partial \langle c_2 \rangle^f}{\partial t} - \nabla_x \cdot \left( \frac{k_1 (\mathbf{D}_{v,0} - \mathbf{D}_{v,1})}{k_1 + k_2} \cdot \nabla_x \langle c_1 \rangle^f \right) \\ - \nabla_x \cdot \left( \frac{k_2 \mathbf{D}_{v,1} + k_1 \mathbf{D}_{v,0}}{k_1 + k_2} \cdot \nabla_x \langle c_2 \rangle^f \right) - \lambda_1 \frac{k_1 \langle c_1 \rangle^f - k_2 \langle c_2 \rangle^f}{k_1 + k_2} = 0 \end{array} \right. \quad (17)$$

110 Given the effective coefficient tensors  $\mathbf{D}_{v,0}$  and  $\mathbf{D}_{v,1}$ , and the initial and boundary conditions, the  
 111 coupled diffusion-reaction Eqs. (17) can be solved to compute the concentration profiles.

### 112 3. Boundary layer problem

113 The macroscopic model based on the homogenization technique relies on the periodic condition  
 114 hypothesis. As a consequence, it cannot capture the boundary layer problem developed in the  
 115 vicinity of the edge of the domain when an outer boundary condition of Dirichlet type is imposed.  
 116 In this section, corrections are made to precisely take into account this boundary layer in the  
 117 upscaled problem.

118 Let consider a parallelepiped rectangular porous medium with macro and microscopic coordi-  
 119 nates  $\{x_1, x_2, x_3\}$  and  $\{y_1, y_2, y_3\}$  respectively<sup>4</sup>. At the inlet boundary  $x_1 = 0$  (and  $y_1 = 0$ ),

<sup>3</sup>Eqs. (17) are dimensional equations corresponding to Eqs. (49) of [14], where the stars have been omitted.

<sup>4</sup>It should be noted that the semi-infinite domain  $x_1 \in [0, \infty]$ ,  $x_2, x_3 \in [-\infty, \infty]$  can be reduced to a parallelepiped when the periodic conditions in  $x_2$  and  $x_3$  directions are applied and a finite region in the vicinity of the boundary is considered for the boundary layer problem



120 Dirichlet conditions for the concentrations,  $c_1 = c_{1D}$  and  $c_2 = c_{2D}$  are imposed. The most inter-  
 121 esting case is when  $k_1 c_{1D} \neq k_2 c_{2D}$  corresponding to a non-equilibrium situation. This leads to  
 122 a thin boundary layer for the concentration profiles in the vicinity of the interface  $x_1 = 0$ . Our  
 123 main objective is to incorporate this layer in the upscaled model. To accomplish this task, we first  
 124 consider the development (6) with the two first orders in  $\varepsilon$  and the two first eigenvalues together  
 125 with the corresponding eigenfunctions:

$$\begin{aligned} c_1 &= \sqrt{\frac{k_2}{k_1}} (v_0^{(0)} + v_0^{(1)}) + \psi_{1,1}(\mathbf{y}) \exp(-\lambda_1 t) (v_1^{(0)} + v_{1,1}^{(1)}) \\ c_2 &= \sqrt{\frac{k_1}{k_2}} (v_0^{(0)} + v_0^{(1)}) + \psi_{2,1}(\mathbf{y}) \exp(-\lambda_1 t) (v_1^{(0)} + v_{2,1}^{(1)}) \end{aligned} \quad (18)$$

126 It should be noted that the formal parameter  $\varepsilon$  can be omitted for the calculation of the concentra-  
 127 tions. This is a quasi-exact solution in the domain, except for the boundary layer in the vicinity of  
 128 the interface where boundary conditions should be imposed for the variable  $v_0^{(0)}$  in order to solve  
 129 the problem (13). Two distinct problems related to the permanent and transient regimes need to  
 130 be considered.

### 131 3.1. Steady state

132 In the steady state when  $t \rightarrow \infty$ , only the first order variable  $v_0^{(0)}$  and second order variable  
 133  $v_0^{(1)}$ , both related to the zero eigenvalue, play a role in the boundary layer. To take into account  
 134 the boundary layer, the expansion of the concentrations needs to be improved in the sense of  
 135 [20]. Considering Dirichlet conditions, since two boundary values  $c_{1D}$  and  $c_{2D}$  are given for the  
 136 concentrations and only one variable  $v_0^{(0)}$  is involved at the interface, it is necessary to introduce  
 137 new boundary variables  $u_{1BL}^{(0)}(\mathbf{x}, \mathbf{y})$  and  $u_{2BL}^{(0)}(\mathbf{x}, \mathbf{y})$  at order  $\mathcal{O}(\varepsilon^0)$  and  $v_{0,BL}^{(1)}$  at order  $\mathcal{O}(\varepsilon^1)$  as

$$\begin{aligned} c_1 &= \sqrt{\frac{k_2}{k_1}} (v_0^{(0)} + v_0^{(1)} + v_{0,BL}^{(1)}) + u_{1BL}^{(0)} \\ c_2 &= \sqrt{\frac{k_1}{k_2}} (v_0^{(0)} + v_0^{(1)} + v_{0,BL}^{(1)}) + u_{2BL}^{(0)} \end{aligned} \quad (19)$$

138 It should be underlined that the boundary layer problem needs to be solved in a reduced fluid  
 139 domain  $Y_f^\dagger$  (with a corresponding solid/fluid interface  $\partial Y_{fs}^\dagger$ ) composed of the infinite repetition of  
 140 the unit cell  $Y$  in the direction  $Oy_1$  perpendicular to the edge.

141 3.1.1. Order  $\mathcal{O}(\varepsilon^0)$

142 Inserting (19) in the initial problem (1) in steady state, the problem for  $u_{1BL}^{(0)}$  and  $u_{2BL}^{(0)}$  in the  
 143 boundary layer at order  $\mathcal{O}(\varepsilon^{-2})$  in volume and  $\mathcal{O}(\varepsilon^{-1})$  at the interface reads as

$$\left\{ \begin{array}{l} 0 = \nabla_y \cdot (\mathcal{D}_1 \nabla_y u_{1BL}^{(0)}) \quad \text{in } Y_f^\dagger \\ 0 = \nabla_y \cdot (\mathcal{D}_2 \nabla_y u_{2BL}^{(0)}) \\ -\mathcal{D}_1 \nabla_y u_{1BL}^{(0)} \cdot \mathbf{n}_{fs} = k_1 u_{1BL}^{(0)} - k_2 u_{2BL}^{(0)} \quad \text{on } \partial Y_{fs}^\dagger \\ -\mathcal{D}_2 \nabla_y u_{2BL}^{(0)} \cdot \mathbf{n}_{fs} = k_2 u_{2BL}^{(0)} - k_1 u_{1BL}^{(0)} \end{array} \right. \quad (20)$$

144  $u_{1BL}^{(0)}$  and  $u_{2BL}^{(0)}$  are periodic in  $y_2$  and  $y_3$  and satisfy the following boundary conditions

$$\begin{aligned} y_1 = 0 \quad c_{1D} &= \sqrt{\frac{k_2}{k_1}} v_{0D}^{(0)} + u_{1BL}^{(0)}(y_1 = 0) \\ c_{2D} &= \sqrt{\frac{k_1}{k_2}} v_{0D}^{(0)} + u_{2BL}^{(0)}(y_1 = 0) \\ y_1 \rightarrow \infty \quad u_{1BL}^{(0)}(y_1) &\rightarrow 0 \\ u_{2BL}^{(0)}(y_1) &\rightarrow 0 \end{aligned} \quad (21)$$

145 where  $v_{0D}^{(0)}$  is the unknown Dirichlet condition value of  $v_0^{(0)}$  at  $y_1 = 0$ . The problem (20) can be  
 146 transformed by introducing the auxiliary variables

$$\begin{aligned} s_{BL}^{(0)} &= \mathcal{D}_1 u_{1BL}^{(0)} + \mathcal{D}_2 u_{2BL}^{(0)} \\ d_{BL}^{(0)} &= k_1 u_{1BL}^{(0)} - k_2 u_{2BL}^{(0)} \end{aligned} \quad (22)$$

147 Inserting the above definitions in (20), the problems for  $s_{BL}^{(0)}$  and  $d_{BL}^{(0)}$  are separate and given by

$$\left\{ \begin{array}{l} 0 = \Delta_{yy} s_{BL}^{(0)} \quad \text{in } Y_f^\dagger \\ 0 = \Delta_{yy} d_{BL}^{(0)} \\ -\nabla_y s_{BL}^{(0)} \cdot \mathbf{n}_{fs} = 0 \quad \text{on } \partial Y_{fs}^\dagger \\ -\nabla_y d_{BL}^{(0)} \cdot \mathbf{n}_{fs} = \left( \frac{k_1}{\mathcal{D}_1} + \frac{k_2}{\mathcal{D}_2} \right) d_{BL}^{(0)} \end{array} \right. \quad (23)$$

148  $s_{BL}^{(0)}$  and  $d_{BL}^{(0)}$  are also periodic in  $y_2$  and  $y_3$ . In addition, by using the definitions (22) of  $s_{BL}^{(0)}$  and  
 149  $d_{BL}^{(0)}$  in (21), one obtains the following boundary conditions

$$\begin{aligned} y_1 = 0 \quad s_{BL}^{(0)} &= \mathcal{D}_1 c_{1D} + \mathcal{D}_2 c_{2D} - \frac{k_1 \mathcal{D}_2 + k_2 \mathcal{D}_1}{\sqrt{k_1 k_2}} v_{0D}^{(0)} \\ d_{BL}^{(0)} &= d_D = k_1 c_{1D} - k_2 c_{2D} \\ y_1 \rightarrow \infty \quad s_{BL}^{(0)}(y_1) &\rightarrow 0 \\ d_{BL}^{(0)}(y_1) &\rightarrow 0 \end{aligned} \quad (24)$$

150 In steady state, the solution of the problem (23) for  $s_{BL}^{(0)}$  is a constant equal to 0 due to the boundary  
 151 condition (24) at  $y_1 \rightarrow \infty$ . From (24), the Dirichlet condition for  $v_0^{(0)}$  at  $y_1 = 0$  reads as

$$v_{0D}^{(0)} = \sqrt{k_1 k_2} \frac{\mathcal{D}_1 c_{1D} + \mathcal{D}_2 c_{2D}}{k_1 \mathcal{D}_2 + k_2 \mathcal{D}_1} \quad (25)$$

152 so that at the leading order, the boundary values of the concentrations imposed at  $x_1 = 0$  to  
 153 calculate the solution of the inner problem (17) are given by

$$\begin{cases} c_{1D}^{(0)} = \sqrt{\frac{k_2}{k_1}} v_{0D}^{(0)} = k_2 \frac{\mathcal{D}_1 c_{1D} + \mathcal{D}_2 c_{2D}}{k_1 \mathcal{D}_2 + k_2 \mathcal{D}_1} \\ c_{2D}^{(0)} = \sqrt{\frac{k_1}{k_2}} v_{0D}^{(0)} = k_1 \frac{\mathcal{D}_1 c_{1D} + \mathcal{D}_2 c_{2D}}{k_1 \mathcal{D}_2 + k_2 \mathcal{D}_1} \end{cases} \quad (26)$$

154 Inserting (25) into (21) gives the boundary values for  $u_{1BL}^{(0)}$  and  $u_{2BL}^{(0)}$

$$\begin{cases} u_{1BL}^{(0)}(y_1 = 0) = \mathcal{D}_2 \frac{k_1 c_{1D} - k_2 c_{2D}}{k_1 \mathcal{D}_2 + k_2 \mathcal{D}_1} \\ u_{2BL}^{(0)}(y_1 = 0) = \mathcal{D}_1 \frac{k_2 c_{2D} - k_1 c_{1D}}{k_1 \mathcal{D}_2 + k_2 \mathcal{D}_1} \end{cases} \quad (27)$$

155 It should be noted that the problem for  $d_{BL}^{(0)}$  in (23) and (24) is an exponential decay problem-type  
 156 involving a thin boundary layer affected by this correction.

157 To summarize, in steady state, at the order  $\mathcal{O}(\varepsilon^0)$ , to capture the boundary layer problem when  
 158 the Dirichlet conditions for the concentrations do not verify the equilibrium condition, the problems  
 159 for  $v_0^{(0)}$  (Eq. (13) for  $n = 0$ ) and for  $u_{1BL}^{(0)}$  and  $u_{2BL}^{(0)}$  (Eq. (20)) must be solved with the boundary  
 160 values for  $v_0^{(0)}$ ,  $u_{1BL}^{(0)}$  and  $u_{2BL}^{(0)}$  given by (25) and (27) respectively. The concentrations  $c_1$  and  $c_2$   
 161 must be adjusted by a thin boundary layer involving  $u_{1BL}^{(0)}$  and  $u_{2BL}^{(0)}$ .

### 162 3.1.2. Order $\mathcal{O}(\varepsilon^1)$

163 This correction comes from the fact that in the concentrations given by (18), the term  $v_0^{(1)}$  is not  
 164 uniform in space at the boundary  $y_1 = 0$ . Similarly to the expression (12) for  $v_0^{(1)}$ , the boundary  
 165 correction  $v_{0,BL}^{(1)}$  is sought in the form

$$v_{0,BL}^{(1)} = \boldsymbol{\omega} \cdot \nabla_x v_0^{(0)} \quad (28)$$

166 The vector  $\boldsymbol{\omega}$  periodic in  $y_2$  and  $y_3$  must satisfy the closure

$$\begin{cases} \nabla_{yy}^2 \boldsymbol{\omega} & = 0 & \text{in } Y_f^\dagger \\ -\nabla_y \boldsymbol{\omega} \cdot \mathbf{n} & = 0 & \text{on } \partial Y_{fs}^\dagger \end{cases} \quad (29)$$

167 At the boundary  $y_1 = 0$  in order to satisfy the boundary condition  $v_0^{(1)} + v_{0,BL}^{(1)} = 0$ , we impose

$$\boldsymbol{\omega} + \boldsymbol{\chi} = 0 \quad (30)$$

168 where  $\boldsymbol{\chi}$  is the solution of the closure problem (11). In the direction  $y_1$  of unit vector  $\mathbf{e}_1$ , for  
169  $y_1 \rightarrow \infty$ , a homogeneous Neuman condition is imposed

$$\nabla_y \boldsymbol{\omega} \cdot \mathbf{e}_1 = 0 \quad (31)$$

170 The vector  $\boldsymbol{\omega}$  will reach a constant value at large value of  $y_1$  resulting from the averaging of the  
171  $\boldsymbol{\omega} = -\boldsymbol{\chi}$  values at the interface  $y_1 = 0$ . As this constant value must be 0, the indetermination of  
172 the  $\boldsymbol{\chi}$  problem (11) is exploited subtracting this value from  $\boldsymbol{\omega}$ <sup>5</sup>.

173 In the particular case of a symmetrical unit cell, in the frame of the symmetry axes centered on  
174 the cell, imposing a null volume average ensures the unicity of  $\boldsymbol{\chi}$  where the components  $\chi_i$  are odd  
175 relative to  $y_i$  (and even relative to the other coordinates  $y_{j \neq i}$ ). Therefore, if the external surface  
176 of the medium coincides with the surface of the unit cell  $Y$  of normal  $\mathbf{e}_1$ ,  $\chi_1$  is null due to the  
177 combination of oddness and periodicity. Consequently,  $\omega_1 = 0$  on the surface  $y_1 = 0$  of  $Y^\dagger$ . Hence  
178  $\omega_1$  is identically null in  $Y_f^\dagger$ . In conclusion, if the gradient  $\nabla_x v_0^{(0)}$  is parallel to  $\mathbf{e}_1$ , the correction  
179  $v_{0,BL}^{(1)}$  is null over  $Y_f^\dagger$ .

### 180 3.2. Transient state

181 In the transient regime, the terms at order  $\mathcal{O}(\varepsilon)$  in (18) must be corrected to better describe the  
182 complex unsteady non-equilibrium effect in the boundary layer. It is important to note that due  
183 to the large Damköhler number, the physical coupling is affected by the boundary condition only  
184 for short times. Beyond this time, the steady state is established. The  $\mathcal{O}(\varepsilon^0)$ -corrective terms for  
185 the two concentrations  $u_{1,BL}^{(0)}$  and  $u_{2,BL}^{(0)}$  are now transient. We also introduce the  $\mathcal{O}(\varepsilon)$ -corrective  
186 terms  $v_{1,1BL}^{(1)}$  and  $v_{2,1BL}^{(1)}$  into the expression of the concentrations (18) as

$$\begin{aligned} c_1 &= \sqrt{\frac{k_2}{k_1}} \left( v_0^{(0)} + v_0^{(1)} + v_{0,BL}^{(1)} \right) + u_{1,BL}^{(0)} + \psi_{1,1}(\mathbf{y}) \exp(-\lambda_1 t) \left( v_1^{(0)} + v_{1,1}^{(1)} + v_{1,1BL}^{(1)} \right) \\ c_2 &= \sqrt{\frac{k_1}{k_2}} \left( v_0^{(0)} + v_0^{(1)} + v_{0,BL}^{(1)} \right) + u_{2,BL}^{(0)} + \psi_{2,1}(\mathbf{y}) \exp(-\lambda_1 t) \left( v_1^{(0)} + v_{2,1}^{(1)} + v_{2,1BL}^{(1)} \right) \end{aligned} \quad (32)$$

<sup>5</sup>We recall that the boundary conditions are imposed for  $c_1$  and  $c_2$  at the main order, that implies according to (19) that  $v_0^{(1)} + v_{0,BL}^{(1)} = 0$  at order  $\mathcal{O}(\varepsilon)$ .

187 3.2.1. Order  $\mathcal{O}(\varepsilon^0)$

188 Let define the characteristic short time  $\tau$  related to the macroscopic time  $t$  by  $\tau = \varepsilon^{-2}t$ . The  
 189 transient problem for  $u_{1BL}^{(0)}$  and  $u_{2BL}^{(0)}$  depending on  $\mathbf{y}$  then reads as

$$\left\{ \begin{array}{l} \frac{\partial u_{1BL}^{(0)}}{\partial \tau} = \nabla_{\mathbf{y}} \cdot (\mathcal{D}_1 \nabla_{\mathbf{y}} u_{1BL}^{(0)}) \quad \text{in } Y_f^\dagger \\ \frac{\partial u_{2BL}^{(0)}}{\partial \tau} = \nabla_{\mathbf{y}} \cdot (\mathcal{D}_2 \nabla_{\mathbf{y}} u_{2BL}^{(0)}) \\ -\mathcal{D}_1 \nabla_{\mathbf{y}} u_{1BL}^{(0)} \cdot \mathbf{n}_{fs} = k_1 u_{1BL}^{(0)} - k_2 u_{2BL}^{(0)} \quad \text{on } \partial Y_{fs}^\dagger \\ -\mathcal{D}_2 \nabla_{\mathbf{y}} u_{2BL}^{(0)} \cdot \mathbf{n}_{fs} = k_2 u_{2BL}^{(0)} - k_1 u_{1BL}^{(0)} \end{array} \right. \quad (33)$$

190 where  $u_{1BL}^{(0)}$  and  $u_{2BL}^{(0)}$  are periodic in  $y_2$  and  $y_3$  and satisfy the boundary conditions

$$\begin{aligned} y_1 = 0 \quad c_{1D} &= \sqrt{\frac{k_2}{k_1}} v_{0D}^{(0)} + u_{1BL}^{(0)}(y_1=0) + \psi_{1,1}(y_1=0) \exp(-\lambda_1 t) v_1^{(0)}(t, \mathbf{x})_{(y_1=0)} \\ c_{2D} &= \sqrt{\frac{k_1}{k_2}} v_{0D}^{(0)} + u_{2BL}^{(0)}(y_1=0) + \psi_{2,1}(y_1=0) \exp(-\lambda_1 t) v_1^{(0)}(t, \mathbf{x})_{(y_1=0)} \\ y_1 \rightarrow \infty \quad u_{1BL}^{(0)}(y_1) &\rightarrow 0 \\ &u_{2BL}^{(0)}(y_1) \rightarrow 0 \\ t = 0 \quad u_{1BL}^{(0)} = u_{2BL}^{(0)} &= 0 \end{aligned} \quad (34)$$

191 To solve the boundary problem and the upscaled model, the initial and boundary conditions  
 192 for  $v_0^{(0)}$ ,  $v_1^{(0)}$ ,  $u_{1BL}^{(0)}$  and  $u_{2BL}^{(0)}$  must be specified. The boundary values of  $v_0^{(0)}$ ,  $u_{1BL}^{(0)}$  and  $u_{2BL}^{(0)}$   
 193 should verify the steady state being given by (25) and (27). The boundary condition for  $v_1^{(0)}$  can  
 194 be legitimately adopted as  $v_1^{(0)}(y_1 = 0) = 0$ .

195 For the initial condition, owing to the compatibility condition (5) for  $n = 1$ , from (16) we obtain

$$\begin{aligned} v_0^{(0)}(t = 0, \mathbf{x}) &= \frac{\sqrt{k_1 k_2}}{k_1 + k_2} \left( \langle c_1^{(0)} \rangle^f(t = 0, \mathbf{x}) + \langle c_2^{(0)} \rangle^f(t = 0, \mathbf{x}) \right) \\ v_1^{(0)}(t = 0, \mathbf{x}) &= \frac{k_1 \langle c_1^{(0)} \rangle^f(t = 0, \mathbf{x}) - k_2 \langle c_2^{(0)} \rangle^f(t = 0, \mathbf{x})}{\langle \psi_{1,1} \rangle^f (k_1 + k_2)} \end{aligned} \quad (35)$$

196 It is legitimate to adopt that for  $\tau = 0$ , no correction is needed leading to  $u_{1BL}^{(0)}(\tau = 0, \mathbf{y}) =$   
 197  $u_{2BL}^{(0)}(\tau = 0, \mathbf{y}) = 0$ .

198 3.2.2. Order  $\mathcal{O}(\varepsilon^1)$

199 We now construct the closure problem for the  $\mathcal{O}(\varepsilon^1)$ -corrective terms. First note that the steady  
 200 state problem for  $v_{0,BL}^{(1)}$  remains unchanged. The problem for  $v_{1,1BL}^{(1)}$  and  $v_{2,1BL}^{(1)}$  to correct the terms  
 201  $v_{1,1}^{(1)}$  and  $v_{2,1}^{(1)}$  corresponding to the first non zero eigenvalue must be a transient problem. At short

202 times, inserting (32) in the initial problem (1) for  $c_1$  and  $c_2$ , the transient problem of  $v_{1,1BL}^{(1)}$  and  
 203  $v_{2,1BL}^{(1)}$  has the same form as the problem of  $v_{1,1}^{(1)}$  and  $v_{2,1}^{(1)}$  given by Eq. (8) written in  $\mathbf{y}$  coordinates  
 204 as<sup>6</sup>

$$\left\{ \begin{array}{l} \psi_{1,1}^2 \frac{\partial v_{1,1BL}^{(1)}}{\partial \tau} = \nabla_{\mathbf{y}} \cdot \left( \tilde{\mathcal{D}}_{1,1} \nabla_{\mathbf{y}} v_{1,1BL}^{(1)} \right) \quad \text{in } Y_f^\dagger \\ \psi_{2,1}^2 \frac{\partial v_{2,1BL}^{(1)}}{\partial \tau} = \nabla_{\mathbf{y}} \cdot \left( \tilde{\mathcal{D}}_{2,1} \nabla_{\mathbf{y}} v_{2,1BL}^{(1)} \right) \\ -\tilde{\mathcal{D}}_{1,1} \nabla_{\mathbf{y}} v_{1,1BL}^{(1)} \cdot \mathbf{n}_{fs} = k_2 \psi_{1,1} \psi_{2,1} (v_{1,1BL}^{(1)} - v_{2,1BL}^{(1)}) \quad \text{on } \partial Y_{fs}^\dagger \\ -\tilde{\mathcal{D}}_{2,1} \nabla_{\mathbf{y}} v_{2,1BL}^{(1)} \cdot \mathbf{n}_{fs} = k_1 \psi_{1,1} \psi_{2,1} (v_{2,1BL}^{(1)} - v_{1,1BL}^{(1)}) \end{array} \right. \quad (36)$$

205 Similar to the solution (9) for  $v_{1,1}^{(1)}$  and  $v_{2,1}^{(1)}$ , the solution of  $v_{1,1BL}^{(1)}$  and  $v_{2,1BL}^{(1)}$  is sought in the  
 206 form

$$\begin{aligned} v_{1,1BL}^{(1)} &= \zeta_1(\mathbf{y}, \tau) \cdot \nabla_{\mathbf{x}} v_1^{(0)}(\mathbf{x}, t) \\ v_{2,1BL}^{(1)} &= \zeta_2(\mathbf{y}, \tau) \cdot \nabla_{\mathbf{x}} v_1^{(0)}(\mathbf{x}, t) \end{aligned} \quad (37)$$

207 Inserting (37) into (36), noting that the slow variable  $v_1^{(0)}(\mathbf{x}, t)$  is independent on the short  
 208 characteristic time  $\tau$ , gives rise to the local unsteady problem of the vectors  $\zeta_1$  and  $\zeta_2$

$$\left\{ \begin{array}{l} \psi_{1,1}^2 \frac{\partial \zeta_1}{\partial \tau} = \nabla_{\mathbf{y}} \cdot \left( \tilde{\mathcal{D}}_{1,1} \nabla_{\mathbf{y}} \zeta_1 \right) \quad \text{in } Y_f^\dagger \\ \psi_{2,1}^2 \frac{\partial \zeta_2}{\partial \tau} = \nabla_{\mathbf{y}} \cdot \left( \tilde{\mathcal{D}}_{2,1} \nabla_{\mathbf{y}} \zeta_2 \right) \\ -\tilde{\mathcal{D}}_{1,1} \mathbf{n}_{fs} \cdot \nabla_{\mathbf{y}} \zeta_1 = k_2 \psi_{1,1} \psi_{2,1} (\zeta_1 - \zeta_2) \quad \text{on } \partial Y_{fs}^\dagger \\ -\tilde{\mathcal{D}}_{2,1} \mathbf{n}_{fs} \cdot \nabla_{\mathbf{y}} \zeta_2 = k_1 \psi_{1,1} \psi_{2,1} (\zeta_2 - \zeta_1) \end{array} \right. \quad (38)$$

209 complemented by the boundary condition at  $y_1 = 0$

$$\begin{aligned} \chi_{1,1} + \zeta_1 &= 0 \\ \chi_{2,1} + \zeta_2 &= 0 \end{aligned} \quad (39)$$

210 where  $\chi_{1,1}$  and  $\chi_{2,1}$  are solution of (10) for  $n = 1$ . This condition ensures that at the boundary,  
 211 the terms at order  $\mathcal{O}(\varepsilon)$  vanish so that only the terms at  $\mathcal{O}(\varepsilon^0)$  are considered for the boundary  
 212 values.

213 Given the solutions of the first order variables  $v_0^{(0)}$  and  $v_1^{(0)}$  and by solving the closure problems  
 214 (29) and (38), the  $\mathcal{O}(\varepsilon^1)$ -correction terms  $v_{0,BL}^{(1)}$ ,  $v_{1,1BL}^{(1)}$  and  $v_{2,1BL}^{(1)}$  can be computed.

<sup>6</sup>Starting again from Eq. (8) with the scaling  $\tau = \varepsilon^{-2}t$  on time, we would obtain (36) at order  $\mathcal{O}(\varepsilon)$ .

215 **4. Numerical simulations**

216 This section is devoted to the numerical validation of the proposed corrections to the upscaled  
 217 model by considering the boundary layer either in steady state or in transient regime. For this  
 218 purpose, a comparison between the numerical simulation of the corrected upscaled model and a  
 219 direct numerical simulation of the Pore Scale Model (PSM) will be performed.

220 A porous medium of size  $L \times l$  is constituted of  $N$  elementary cells of size  $l$ , composed of a  
 221 solid circular inclusion of radius  $R$  located at the center of each unit cell. The radius is constrained  
 222 by the porosity  $\varphi$ . The corresponding effective medium for the simulations of the macroscopic  
 equations is of the same size (see Fig. 1). At the inlet  $x_1 = 0$ , Dirichlet conditions are applied

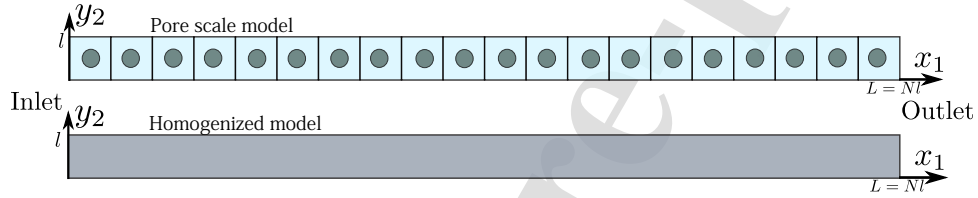


Figure 1: Porous medium and homogenized medium used in the numerical simulation.

223  
 224 for the concentrations  $c_1 = c_{1D}$  and  $c_2 = c_{2D}$ . A non-equilibrium condition at the boundary  
 225  $d_D = k_1 c_{1D} - k_2 c_{2D} \neq 0$  is studied. At the outlet  $x_1 = L$ , a zero value is imposed for the  
 226 concentrations. In addition, a periodicity condition is considered for the top and bottom boundaries.  
 227 The values of the physical parameters used are shown in Table 1. Note that the microscopic  
 228 Damköhler numbers that constrain the values of the reaction rates  $k_1$  and  $k_2$  are now defined as

$$\text{Da}_1 = \frac{k_1 l}{\mathcal{D}_1} \quad \text{and} \quad \text{Da}_2 = \frac{k_2 l}{\mathcal{D}_2} = \frac{\text{Da}_1 \alpha}{\beta} \quad (40)$$

229 with the ratios  $\alpha = k_2/k_1$  and  $\beta = \mathcal{D}_2/\mathcal{D}_1$ .

230 The numerical study is carried out using COMSOL Multiphysics software based on the finite  
 231 element method.

232 *4.1. Numerical results in steady state*

233 In steady state as  $t \rightarrow \infty$ , the corrections for the concentrations  $c_1$  and  $c_2$  are given by (19)  
 234 with additional variables  $u_{1BL}^{(0)}$  and  $u_{2BL}^{(0)}$  (recall that as mentioned in §3.1.2 for the symmetric cell  
 235 considered here the corrective term  $v_{0,BL}^{(1)}$  is identically zero). First, the macroscopic variable  $v_0^{(0)}$ ,

$l$	$N$	$\varphi$	$\mathcal{D}_1$	$\mathcal{D}_2$	$\beta$	$\text{Da}_1$	$k_1$	$\alpha$	$k_2$	$\text{Da}_2$	$c_{1D}$	$c_{2D}$
0.01	20	0.8	1	$\beta\mathcal{D}_1$	2	100	$\text{Da}_1\mathcal{D}_1/l$	2	$\alpha k_1$	$\text{Da}_1\alpha/\beta$	1	$c_{1D}$

Table 1: Parameters used in simulations.

236 solution of the homogenized diffusion problem (13) in steady state for  $n = 0$  with the homogenized  
 237 diffusion tensor given by (15), is computed in the effective medium. A Dirichlet boundary condition  
 238 (25) is applied at the inlet whereas  $v_0^{(0)} = 0$  is imposed at the outlet. If the concentrations values  
 239 imposed at the interface are  $c_{1D} = c_{2D} = 1$ , the imposed value for  $v_0^{(0)}$  corresponds to  $c_1^{(0)}(x_1 =$   
 240  $0) = 1.5$  and  $c_2^{(0)}(x_1 = 0) = 0.75$ . Secondly, given the field of  $v_0^{(0)}$ , the variable  $v_0^{(1)}$  is determined  
 241 from the solution (9) for  $n = 0$

$$v_0^{(1)} = \chi \cdot \nabla_x v_0^{(0)} \quad (41)$$

242 where  $\chi$  is solution of the closure problem (11) solved numerically on the unit cell.

243 Finally, the correction variables  $u_{1BL}^{(0)}$  and  $u_{2BL}^{(0)}$ , which are solutions of the local problem (20)  
 244 with the boundary conditions at the inlet given by (27) and a zero-value condition far from the  
 245 inlet, are solved in the microscopic pore-geometry for at least several unit cells from the inlet due  
 246 to the exponential-decay behavior of these functions. This point will be proved in the numerical  
 247 results in the sequel.

248 Let define the  $y_2$ -average operator of a function  $f$  as

$$\langle f \rangle_{y_2} = \frac{1}{l} \int_0^l f dy_2 \quad (42)$$

249 Figure 2(a) displays the variation of the  $y_2$ -averaged variables  $\langle u_{1BL}^0 \rangle_{y_2}$  and  $\langle u_{2BL}^0 \rangle_{y_2}$  with respect  
 250 to the position  $x_1/L$ . We can observe that the correction  $u_{1BL}^0$  (respectively  $u_{2BL}^0$ ) decreases  
 251 (respectively increases) rapidly and decays towards zero after several unit cells in the vicinity of the  
 252 inlet. Thus, this correction only affects a thin layer (boundary layer) from the edge whose thickness  
 253 depends on the Damköhler numbers. The variation of the difference  $\langle d_{BL}^0 \rangle_{y_2}$  with respect to  $x_1/L$   
 254 is plotted in Figure 2(b). It is clearly observed that a non-equilibrium state where  $\langle d_{BL}^0 \rangle_{y_2} \neq 0$  is  
 255 established in a thin boundary layer.

256 Given the solutions for  $v_0^{(0)}$ ,  $v_0^{(1)}$ ,  $u_{1BL}^{(0)}$  and  $u_{2BL}^{(0)}$ , knowing that  $v_{0,BL}^{(1)} \equiv 0$ , the  $y_2$ -averaged  
 257 concentrations  $\langle c_i \rangle_{y_2}$  of the corrected model can be computed from (19). In order to compare  
 258 these results with the solution of the original model, the non-corrected homogenized model (HM)



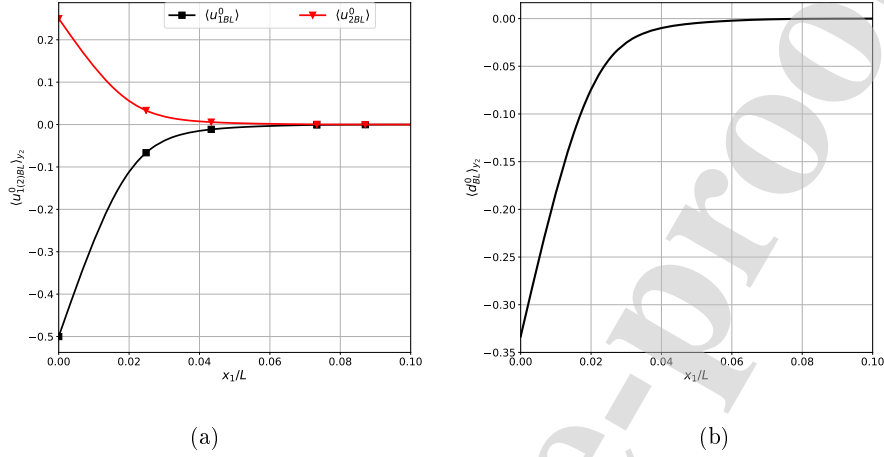


Figure 2: Variation of (a):  $\langle u_{1BL}^0 \rangle_{y_2}$  and  $\langle u_{2BL}^0 \rangle_{y_2}$  and (b):  $\langle d_{BL}^0 \rangle_{y_2}$  versus  $x_1/L$  for  $Da_1 = 100$ .

259 given by the system (17) is solved in the effective porous media. To do that, we first compute the  
 260 eigenvalue  $\lambda_1$  and the eigenfunctions  $\psi_{1,1}$  and  $\psi_{2,1}$  from the spectral problem (2) for  $n = 1$ . Given  
 261 the eigenfunctions, the closure problem (10) for  $\chi_{1,1}$  and  $\chi_{2,1}$  is solved in the unit cell to compute  
 262 the effective coefficient  $\mathbf{D}_{v,1}$  from (14) for  $n = 1$ . Moreover, the closure problem for  $\chi$  in (11) is  
 263 purely geometric and is solved in the unit cell to give the effective tensor  $\mathbf{D}_{v,0}$  from (15).

264 To validate the proposed corrections in steady state, a direct numerical simulation of the pore-  
 265 scale model (PSM) given in Eq. (1) is performed with the pore-scale geometry of Figure 1 to obtain  
 266 the concentration fields which are averaged over the  $y_2$  direction. Figure 3 displays the  $y_2$ -averaged  
 267 concentration profiles of  $\langle c_1 \rangle_{y_2}$  and  $\langle c_2 \rangle_{y_2}$  obtained from the corrected model (continuous line), the  
 268 original HM without correction (dotted line) and the PSM (line-marker). An excellent agreement  
 269 between the corrected model and the PSM is observed, which satisfactorily validates the proposed  
 270 model. The original HM solution fails to capture the complex physics in the boundary layer and  
 271 leads to an inaccurate prediction of the concentration fields in the entire domain. We can also  
 272 observe that  $\langle c_1 \rangle_{y_2}$  (respectively  $\langle c_2 \rangle_{y_2}$ ) increases (respectively decreases) quickly in the boundary  
 273 layer to attain a transition point delimiting the boundary zone.

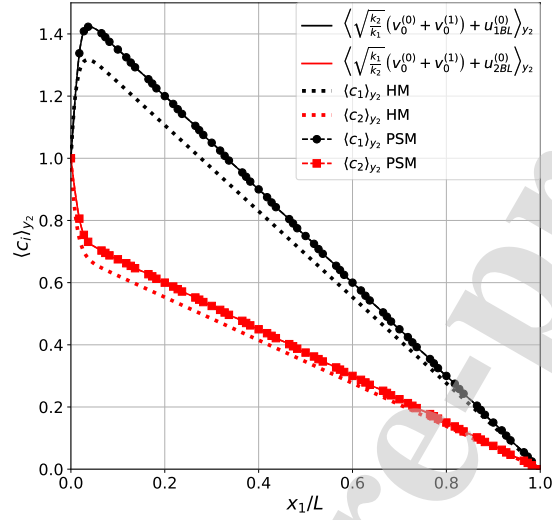


Figure 3:  $y_2$ -averaged concentrations versus  $x_1/L$  for  $Da_1 = 100$  obtained by the corrected model (line), the original HM (dotted line) and the PSM (line-marker).

#### 274 4.2. Numerical results in transient regime

275 The corrected solution for the concentrations involving additional variables at order  $\mathcal{O}(\varepsilon^1)$  in  
 276 transient regime is given by Eq. (32). To compute the concentrations, first we solve the transient  
 277 problems for the first-order variables  $v_0^{(0)}$  and  $v_1^{(0)}$  given by (13) with the initial conditions (35). In  
 278 addition, the Dirichlet boundary condition for  $v_0^{(0)}$  (25) is imposed at the inlet and  $v_0^{(0)} = 0$  at the  
 279 outlet whereas for  $v_1^{(0)}$ , the zero value is imposed on both boundaries. Given the fields of  $v_0^{(0)}$  and  
 280  $v_1^{(0)}$ , the  $\mathcal{O}(\varepsilon^1)$ -variables  $v_0^{(1)}$ ,  $v_{1,1}^{(1)}$  and  $v_{2,1}^{(1)}$  can be computed from the solution (9).

281 The first-order corrections  $u_{1,BL}^{(0)}$  and  $u_{2,BL}^{(0)}$  for the unsteady state in (33) can be solved on  
 282 several unit cells adjacent to the boundary with a boundary condition similar to that given in the  
 283 steady state and with a zero initial value. To compute the  $\mathcal{O}(\varepsilon^1)$ -correction variables, as  $v_{0,BL}^{(1)} \equiv 0$   
 284 accounting for the symmetry of the elementary cell considered (see section 3.1.2), for determining  
 285  $v_{1,1BL}^{(1)}$  and  $v_{2,1BL}^{(1)}$  given by (37), one has to solve the unsteady closure problem (38) for  $\zeta_1$  and  $\zeta_2$   
 286 with the corresponding boundary condition (39).

287 In order to validate the proposed corrected model, a direct numerical simulation of the PSM  
288 (Eq. 1) is numerically solved in the pore-scale geometry in transient regime. Initial values of the  
289 concentrations are imposed as  $c_1(t=0) = c_2(t=0) = 0.1$ , which corresponds to a non-equilibrium  
290 initial state. Parameters used in the simulation are given in Table 1. Moreover, macroscopic  
291 equations without correction (17) are also numerically solved in the same geometry.

292 Figure 4 shows the variation of the  $y_2$ -averaged concentrations  $\langle c_1 \rangle_{y_2}$  and  $\langle c_2 \rangle_{y_2}$  with time at  
293 different positions  $x_1 = [l/4, 2l, 3l]$ , obtained from the corrected model, the original homogenized  
294 model (HM) and the direct numerical simulation of the pore-scale model (PSM). Excellent agree-  
295 ment is obtained between the PSM and the corrected model for the three observation points located  
296 at different  $x_1$  positions, which satisfactorily validates the proposed transient model. At very short  
297 times when the local chemical reaction dominates the transport mechanism and the boundary layer  
298 is located very close to the surface, all three models predict the same results at the observation  
299 points. However, for longer times, when the boundary layer propagates through the domain, a  
300 difference between the original HM and the PSM appears and this is all the earlier as the position  
301 of the point is close to the surface at the left boundary.

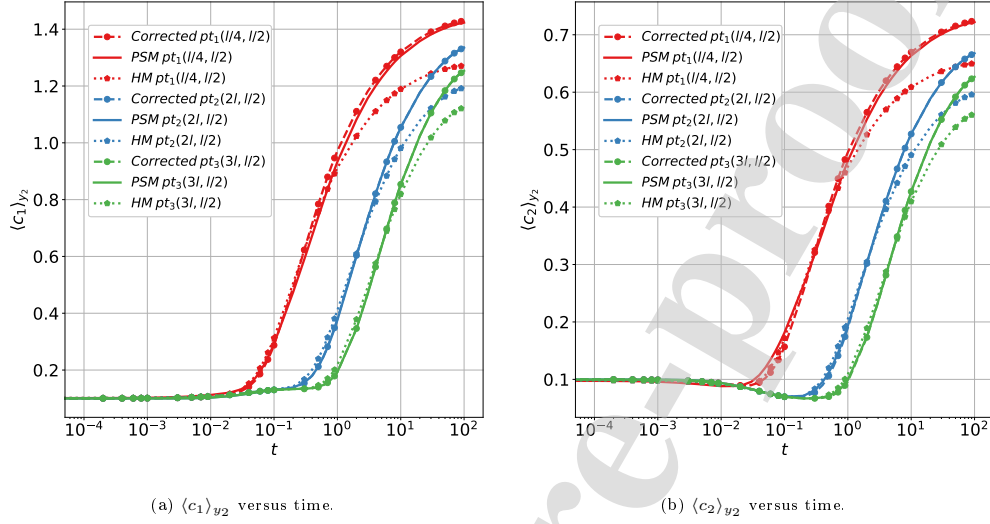


Figure 4: Concentration variation of (a)  $\langle c_1 \rangle_{y_2}$  and (b)  $\langle c_2 \rangle_{y_2}$  with time for different positions  $x_1 = [l/4, 2l, 3l]$ , obtained from the corrected model (dashed line-marker), PSM (line) and the original HM (dotted line-marker).

302 Figures 5 and 6 display the  $y_2$ -averaged concentration profiles of  $\langle c_1 \rangle_{y_2}$  and  $\langle c_2 \rangle_{y_2}$  with respect to  
 303  $x_1/L$  obtained from the three models at different times  $t$ . Small fluctuations in the concentrations  
 304 obtained by the corrected model are observed at the beginning of the process due to the periodic  
 305 variation of the eigenfunctions, which vanish with time. Again, the corrected model is in very good  
 306 agreement with the PSM while the original HM fails to reproduce the boundary layer behavior  
 307 correctly. As a result, this error propagates with time away from the boundary, leading to inaccurate  
 308 prediction of concentration profiles.

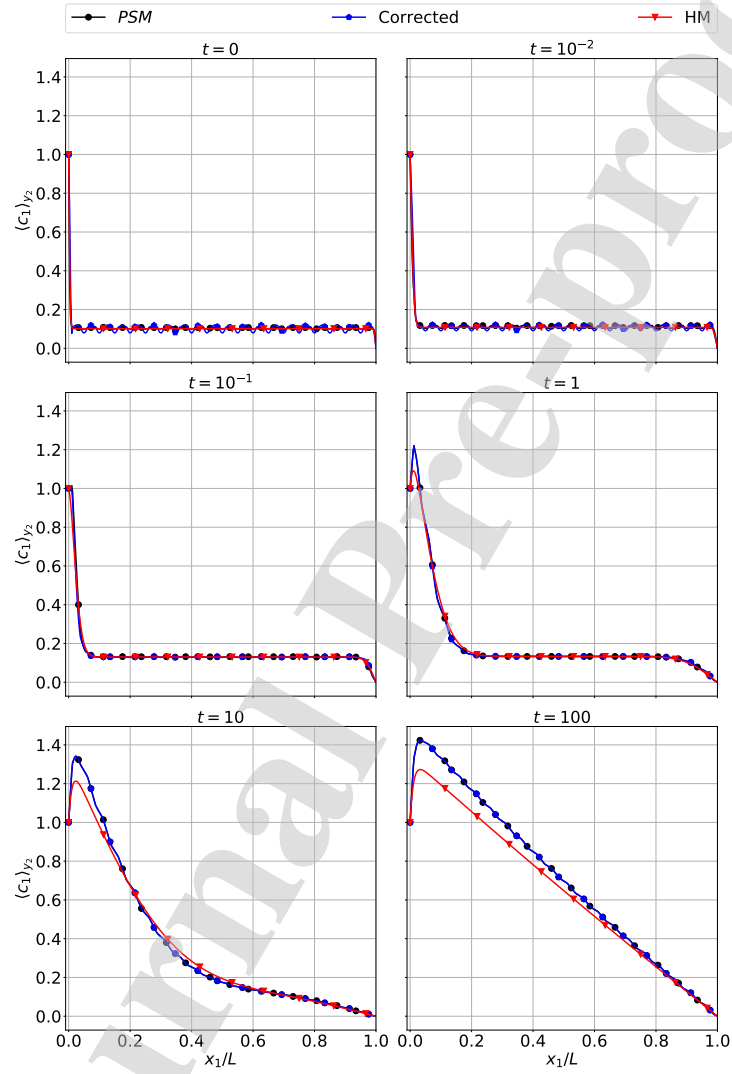


Figure 5: Concentration  $\langle c_1 \rangle_{y_2}$  versus  $x_1/L$  for different times.

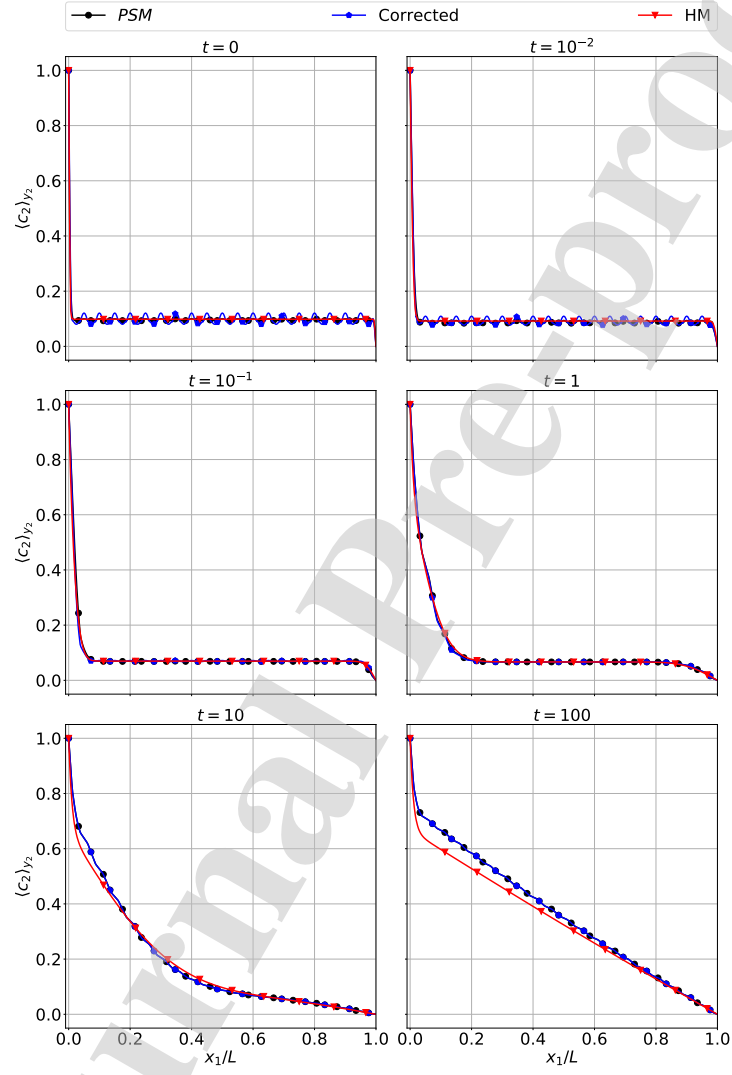


Figure 6: Concentration  $\langle c_2 \rangle_{y_2}$  versus  $x_1/L$  for different times.

309 Finally to quantify the role of each term in the solution (32), Figure 7a shows the profiles of the  
 310 terms corresponding to  $n = 0$  at very short times. The correction  $u_{1,BL}^{(0)}$  tends towards zero rapidly  
 311 from the boundary as shown previously and dominates the correction  $v_{0,BL}^{(1)}$ , which is of order  $\mathcal{O}(\varepsilon)$   
 312 in the general case and vanishes for symmetric elementary cells, which is the case here. Far from  
 313 the boundary, only the first-order variable  $v_0^{(0)}$  differs significantly from zero. In Figure 7b, the  
 314 terms corresponding to  $n = 1$  are plotted. The fluctuations are due to the periodic solution of the  
 315 eigenfunction  $\psi_{1,1}$ . Due to exponential decay, the terms disappear over time. We observe that the  
 316 time-dependent correction terms at this order are very small and can be neglected.

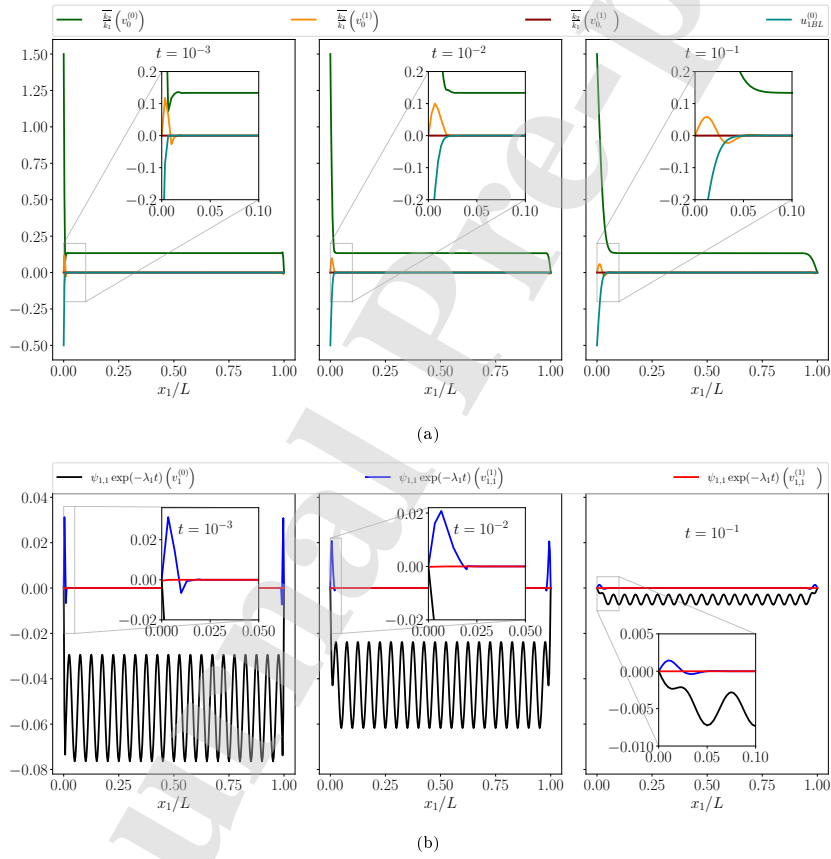


Figure 7: Corrective term profiles for different times.

## 317 5. Conclusion

318 The boundary layer problem for the coupled diffusion/reaction process for high Damköhler  
319 number in porous media has been studied. The macroscopic mass conservation law derived from  
320 the homogenization technique and based on a spectral approach represents a quasi-exact solution  
321 within the domain but fails to describe the physics in a thin layer near the surface when a non-  
322 equilibrium Dirichlet boundary condition is imposed. In this context, corrective terms have to be  
323 added to the concentrations for both steady state and transient regime.

324 In steady state, two corrective functions are introduced to adjust the first order variable corre-  
325 sponding to the null eigenvalue to capture the non-equilibrium state in the boundary layer. These  
326 terms decay exponentially from the boundary and need to be solved only on a few unit cells adjacent  
327 to the boundary. Numerical simulations prove that this correction is in excellent agreement with  
328 the direct numerical simulation of the pore-scale model.

329 In transient regime, the  $\mathcal{O}(\varepsilon)$ -variables need to be corrected with additional terms whose solu-  
330 tions involve new closure problems. Numerical results show a small contribution of these terms.

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- Boundary layer problem of diffusion/reaction process in porous media is studied
- Macro-model derived from homogenization technique and spectral approach is recalled
- Corrective terms are introduced to modify the concentration's expansion
- These terms decay rapidly from the boundary and are solved on several unit cells
- Numerical simulations highlight the role of the corrective terms in boundary layer

Journal Pre-proof

**Tien Dung Le:** Conceptualization; Methodology; Roles/Writing - original draft; Writing - review & editing, **Christian Moyné:** Conceptualization; Methodology; Roles/Writing - original draft, **Khaled Bourbatache:** Conceptualization; Methodology; Software; Roles/Writing - original draft; Writing - review & editing, **Olivier Millet:** Conceptualization; Methodology; Roles/Writing - original draft; Writing - review & editing

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**Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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