Upscaling Mass Transport with Homogeneous and Heterogeneous Reaction in Porous Media

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The upscaling process of mass transport with chemical reaction in porous media is carried out using the method of volume averaging under diffusive and dispersive conditions. We study cases in which the (first-order) reaction takes place in the fluid phase that saturates the porous medium or when the reaction occurs at the solid-fluid interface. The upscaling effort leads to average transport equations, which are expressed in terms of effective medium coefficients for (diffusive or dispersive) mass transport and reaction that are computed by solving the associated closure problems in representative unit cells. Our derivations show that mass transport effective coefficients depend, in general, of the nature and magnitude of the microscopic reaction rate coefficient as well as of the essential geometrical structure of the solid matrix and the flow rate. Furthermore, if the chemical reaction is homogeneous, the effective reaction rate coefficient is found to be simply the multiplication of its microscopic counterpart with the porosity; whereas, if the reaction is heterogeneous, the effective reaction coefficient is determined from a closure problem solution.

1. Introduction

Modeling of mass transport taking place across several levels of scales is, generally, carried out using upscaled models. Such models are expressed in terms of effective transport coefficients which contain information from the phenomenon in lower levels of scales. In cases involving diffusive or dispersive mass transport in absence of reaction, the effective coefficients have been obtained from well-established experimental and theoretical procedures (e.g. Baiker et al., 1982; Eidsath et al., 1983). Nevertheless, there is an open problem for transport under reactive conditions related to the dependence of the effective coefficients with the nature and magnitude of the reaction rate. This issue has been widely addressed in the literature with opposite conclusions. Supported in different theoretical or experimental evidences, on the one hand, there are works affirming that the effective transport coefficients are independent of the reaction rate (e.g. García-Ochoa and Santos, 1994; Zhang and Seaton, 1994); whereas on the other hand, some works state the opposite idea (e.g., Edwards et al., 1993; Valdés-Parada and Álvarez-Ramírez, 2010). In fact, even the magnitude of the dependency with the reaction rate is unclear. Motivated from these confusing results, in this work we extend the previous works by Valdés-Parada and Álvarez-Ramírez (2010) and by Ryan (1983) dealing with homogenous and heterogeneous reaction in porous

media, respectively. Particularly, we study a reactive porous system experiencing bulk or surface first-order reaction under diffusive and dispersive regimes. By using the method of volume averaging (MVA) (Whitaker, 1999), the upscaled equations are derived, and their corresponding effective transport coefficients are defined and predicted from the associated closure problem solution.

2. Diffusion with heterogeneous reaction

We commence by setting the microscopic description. It is considered a rigid homogeneous porous medium composed by a solid matrix (κ-phase) which is completely saturated with a fluid phase (γ-phase), such as the one sketched in Fig. 1. In this case, the microscale governing equations for mass transport of species A are

$$\frac{\partial c_{A\gamma}}{\partial t} = \nabla \cdot \left(D_\gamma \nabla c_{A\gamma} \right), \qquad \text{in the } \gamma\text{-phase} \tag{1}$$

$$-\mathbf{n}_{\gamma\kappa} \cdot D_\gamma \nabla c_{A\gamma} = k c_{A\gamma}, \qquad \text{at the } \gamma - \kappa \text{ interface} \tag{2}$$

where $c_{A\gamma}$ is the concentration of species A, D_γ is the molecular diffusivity, k is the heterogeneous reaction rate coefficient and $\mathbf{n}_{\gamma\kappa}$ is the unit normal vector directed from γ- to κ-phase. The statement of the microscopic problem is completed with the initial condition and the boundary conditions applying at the macroscopic boundaries of the system in Fig. 1, which are not provided here for brevity.
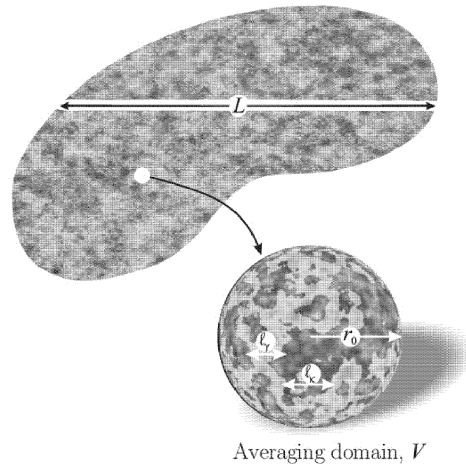

Averaging domain, V

Figure 1: Characteristic lengths of the system and sketch of the averaging domain.

It is clear that in solving the microscopic problem in the entire macroscopic domain represents a challenging task, and, commonly, it is enough to describe the transport in terms of average quantities. In this case it is convenient to use an upscaling process as

the MVA. In this way, after applying the MVA to the microscopic equations, we obtain (see details in Chap. 1 of Whitaker, 1999)

$$\varepsilon_\gamma \frac{\partial \langle c_{A\gamma} \rangle^\gamma}{\partial t} = \nabla \cdot \left(\varepsilon_\gamma \mathbf{D}_{eff} \cdot \nabla \langle c_{A\gamma} \rangle^\gamma \right) - a_v k_{eff} \langle c_{A\gamma} \rangle^\gamma \tag{3}$$

Here ε_γ is the porosity, $\langle c_{A\gamma} \rangle^\gamma$ is the intrinsic average concentration, a_v is the interfacial per unit volume, and $\mathbf{D}_{eff}$ and k_{eff} are the effective diffusivity tensor and reaction rate coefficient respectively, which are defined as

$$\mathbf{D}_{eff} = D_\gamma \left(\mathbf{I} + \frac{1}{V_\gamma} \int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa} \mathbf{b}_\gamma \, dA \right) \tag{4}$$

$$k_{eff} = k \left(1 + \frac{1}{A_{\gamma\kappa}} \int_{A_{\gamma\kappa}} s_\gamma \, dA \right) \tag{5}$$

where V_γ and $A_{\gamma\kappa}$ are the volume of the fluid phase and the interfacial area contained in the averaging domain V (see Fig. 1). In addition, $\mathbf{b}_\gamma$ and s_γ are the so-called closure variables, which arise from the solution of the associated closure problems (given in the Appendix) in unit cells representative of the microstructure. The dependency of the effective diffusivity and reaction rate coefficients with the cell Thiele modulus, $\varphi = \sqrt{kl / D_\gamma}$, and four types of unit cells is shown in Fig. 2. Note that D_{eff} depends moderately of the microstructure for $\varphi < 1$, and eventually equals to D_γ for $\varphi \gg 1$. In addition, our results show that k_{eff} / k is a decreasing function of the Thiele modulus and has a weak dependency with the microstructure and a moderate dependency with the porosity (not presented here).

3. Dispersion and reaction

3.1 Homogenous reaction
In this case, the microscopic governing equations are given by

$$\frac{\partial c_{A\gamma}}{\partial t} + \nabla \cdot \left(\mathbf{v}_\gamma c_{A\gamma} \right) = \nabla \cdot \left(D_\gamma \nabla c_{A\gamma} \right) - k_h c_{A\gamma}, \qquad \text{in the } \gamma\text{-phase} \tag{6}$$

$$-\mathbf{n}_{\gamma\kappa} \cdot D_\gamma \nabla c_{A\gamma} = 0, \qquad \text{at the } \gamma-\kappa \text{ interface} \tag{7}$$

Here $\mathbf{v}_\gamma$ represents the velocity field. Application of the MVA to the microscopic equations leads to the upscaled equation

$$\varepsilon_\gamma \frac{\partial \langle c_{A\gamma} \rangle^\gamma}{\partial t} + \nabla \cdot \left(\varepsilon_\gamma \langle \mathbf{v}_\gamma \rangle^\gamma \langle c_{A\gamma} \rangle^\gamma \right) = \nabla \cdot \left(\varepsilon_\gamma \mathbf{D}_\gamma^* \cdot \nabla \langle c_{A\gamma} \rangle^\gamma \right) - k_h \varepsilon_\gamma \langle c_{A\gamma} \rangle^\gamma \qquad (8)$$
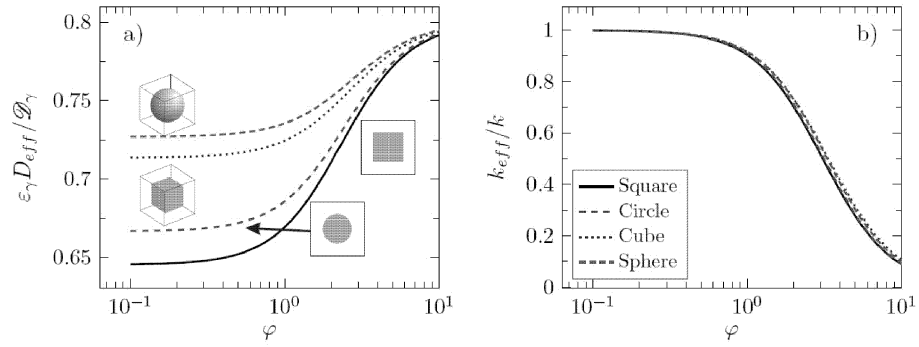

Figure 2: a) effective diffusivity and b) reaction rate coefficients as functions of the Thiele modulus φ using 2D and 3D unit cells and taking $\varepsilon_\gamma = 0.8$.

where the dispersion tensor $\mathbf{D}_\gamma^*$ is defined by

$$\mathbf{D}_\gamma^* = D_\gamma \left(\mathbf{I} + \frac{1}{V_\gamma} \int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa} \mathbf{f}_{\gamma h} dA \right) - \langle \tilde{\mathbf{v}}_\gamma \mathbf{f}_{\gamma h} \rangle^\gamma \qquad (9)$$

with $\tilde{\mathbf{v}}_\gamma$ being the spatial deviation of the velocity field and $\mathbf{f}_{\gamma h}$ the associated closure variable. Notice that, on the case at hand, the effective reaction rate coefficient is simply $k_h \varepsilon_\gamma$. In Fig. 3 we present the longitudinal and transverse components of the dispersion tensor as functions of the particle Péclet number, $Pe_p = \left\| \langle \mathbf{v}_\gamma \rangle^\gamma \right\| d_p \varepsilon_\gamma / \left[D_\gamma \left(1 - \varepsilon_\gamma \right) \right]$, the Thiele modulus for this case is $\phi = \sqrt{k_h l^2 / D_\gamma}$. As shown, the microstructure has a significant relevance, and increasing the reaction rate yields lower values of the effective dispersion coefficient.

3.2 Heterogeneous reaction
In this case the microscopic equation for mass transport is similar to Eq. (6), but without the reactive term whose effect is represented in the interfacial condition, Eq. (2). The use of the MVA leads to an upscaled equation similar to Eq. (8) with the reactive term in the form $a_v k_{eff}^* \langle c_{A\gamma} \rangle^\gamma$. For the sake of brevity we do not present the definition of the effective transport coefficients for the case on hand, because they have a similar definition as Eqs. (5) and (9), but with closure variables arising from different closure problems. In fact, it is enough to replace $\mathbf{f}_\gamma$ by $\mathbf{f}_{\gamma h}$ in Eq. (9), and k_{eff} by k_{eff}^* and g_γ by s_γ in Eq. (5). Our results show that the Péclet number has a weak influence over the

effective reaction rate and the results are similar to those presented in Fig. 2b). In the same way, the functionality of $\mathbf{D}_\gamma^*$ with the Péclet number, the Thiele modulus and the microstructure can be accurately represented by the results in Fig. 3.
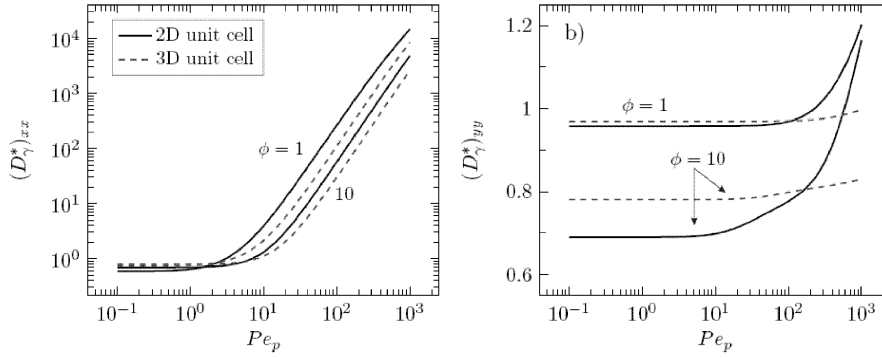

Figure 3: longitudinal and transverse components of the total dispersion tensor as a function of the Thiele modulus and the particle Péclet number. Taking $\varepsilon_\gamma = 0.37$ and using squared and cubic obstacles in the unit cells.

4. Conclusions

In this work, we have carried out the upscaling of mass transport coupled with a (first order) chemical reaction, involving diffusion and convection in porous media. Under the MVA framework, we have derived the upscaled equations expressed in terms of an effective (diffusive or dispersive) transport coefficient and an effective reaction rate coefficient, which are predicted by solving the associated closure problems in representative unit cells. In the basis of our results, the effective transport coefficients depend of the reaction rate, independently of the nature of the reaction, as well as of the microstructure. Moreover, for a homogeneous reaction the effective reaction rate coefficient is simply $\varepsilon_\gamma k_h$, whereas for the heterogeneous case, the effective reaction is determined from the solution of the associated closure problem.

Appendix

In a compact formulation, the closure variables solve the following boundary-value problems which are solved in unit cells as those shown in Fig. 2a):

$$\nabla \cdot D_\gamma \nabla \psi_\gamma = f, \quad \text{in the } \gamma\text{-phase} \tag{A-1}$$

$$-\mathbf{n}_{\gamma\kappa} \cdot D_\gamma \nabla \psi_\gamma = g, \qquad \text{at the } \gamma - \kappa \text{ interface} \tag{A-2}$$

$$\psi_\gamma(\mathbf{r}) = \psi_\gamma(\mathbf{r} + \mathbf{l}_i), \ i = 1,2,3, \qquad \text{periodicity} \tag{A-3}$$

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$$\langle \psi_\gamma \rangle^\gamma = 0, \quad \text{restriction} \tag{A-4}$$

where $\psi_\gamma = \mathbf{b}_\gamma, s_\gamma, \mathbf{f}_{\gamma h}, \mathbf{f}_\gamma, g_\gamma$, and

$$f = \begin{cases} -\dfrac{k}{V_\gamma} \displaystyle\int_{A_{\gamma\kappa}} \psi_\gamma dA, & \text{if } \psi_\gamma = \mathbf{b}_\gamma \\[2mm] -k\left(\dfrac{1}{V_\gamma} \displaystyle\int_{A_{\gamma\kappa}} \psi_\gamma dA + \dfrac{a_v}{\varepsilon_\gamma} \right), & \text{if } \psi_\gamma = s_\gamma \\[2mm] \tilde{\mathbf{v}}_\gamma + \mathbf{v}_\gamma \cdot \nabla\psi_\gamma + k_h \psi_\gamma, & \text{if } \psi_\gamma = \mathbf{f}_{\gamma h} \\[2mm] \tilde{\mathbf{v}}_\gamma + \mathbf{v}_\gamma \cdot \nabla\psi_\gamma - \dfrac{k}{V_\gamma} \displaystyle\int_{A_{\gamma\kappa}} \psi_\gamma dA, & \text{if } \psi_\gamma = \mathbf{f}_\gamma \\[2mm] \mathbf{v}_\gamma \cdot \nabla\psi_\gamma - k\left(\dfrac{1}{V_\gamma} \displaystyle\int_{A_{\gamma\kappa}} \psi_\gamma dA + \dfrac{a_v}{\varepsilon_\gamma} \right), & \text{if } \psi_\gamma = g_\gamma \end{cases} \tag{A-5}$$

$$g = \begin{cases} k\psi_\gamma + \mathbf{n}_{\gamma\kappa} D_\gamma, & \text{if } \psi_\gamma = \mathbf{b}_\gamma, \mathbf{f}_\gamma \\ k\left(\psi_\gamma + 1 \right), & \text{if } \psi_\gamma = s_\gamma, g_\gamma \\ \mathbf{n}_{\gamma\kappa} D_\gamma, & \text{if } \psi_\gamma = \mathbf{f}_{\gamma h} \end{cases} \tag{A-6}$$

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