INFLUENCE OF INERTIAL EFFECTS ON DISPERSION AND EFFECTIVE REACTION IN POROUS MEDIA

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Abstract

In this work we develop, via volume averaging, the macroscale transport equation for a reactive chemical species undergoing a heterogeneous reaction with first-order kinetics. We describe the closure problem required to predict (1) the effective macroscale reaction rate, and (2) the effective dispersion tensor from the microscale geometry, chemical, and physical properties of the media. The effective parameters are computed for a 3D simple unit cell. Particular attention is given to the influence of inertial effects on the flow field and the resulting effective parameters.

1. INTRODUCTION

The influence of mass transfer on the effective rate of reaction in porous media has been studied for at least 60 years, beginning with the well-known work of Thiele [1]. A significant body of literature now exists on the determination of the effective reaction rate parameter, or, equivalently, the effectiveness factor for reactive transport in porous media systems via upscaling from the pore- to Darcy scales (e.g., [2, 4, 5]). A related, but lesser known phenomena is the influence of reaction on the effective transport properties of the medium. It has been illustrated that both the effective solute velocity [3, 4, 5] and the effective longitudinal dispersion coefficient [3, 4, 5, 6] are influenced by the reaction process. This means that, in general, there is no unique dispersion tensor for reacting solutes because the dispersion depends on the rate of reaction. However, it has been shown by Edwards et al. [3] that the influence of reaction is only important when the Thiele modulus is greater than 1, where the Thiele modulus is defined by

$$\phi = \sqrt{\ell_\beta k / D_\beta}$$

In the work reported here, we develop the macroscale transport equation for a solute undergoing heterogeneous reaction at a surface with a first-order reaction rate. Such reactions can occur in a variety of systems, such as monolithic catalysts, immobilized enzymes, or in systems with sparsely distributed biofilms that offer no resistance to mass transfer. The work presented here extends a previous study [2] by examining the influence of the flow field on these effective parameters when inertial contributions are important.
2. MICROSCALE DESCRIPTION

The pore-scale description of the problem can be written as follows

\[
\frac{\partial c_{A\beta}}{\partial t} + \nabla \cdot (\mathbf{v}_\beta c_{A\beta}) = \nabla \cdot (D_\beta \nabla c_{A\beta}), \quad \text{in the } \beta\text{-phase} \tag{2}
\]

B.C. 1
\[-(D_\beta \nabla c_{A\beta}) \cdot \mathbf{n}_{\beta\sigma} = k c_{A\beta}, \quad \text{at } A_{\beta\sigma} \tag{3}\]

B.C. 2
\[c_{A\beta} = C(x, t), \quad \text{at } A_{\beta e} \tag{4}\]

I.C.
\[c_{A\beta} = I(x), \quad \text{in the } \beta\text{-phase} \tag{5}\]

B.C. 3
\[\nabla \cdot (\rho \mathbf{v}_\beta \mathbf{v}_\beta) = -\nabla p_\beta + \mu_\beta \nabla^2 \mathbf{v}_\beta, \quad \text{in the } \beta\text{-phase} \tag{6}\]

B.C. 4
\[\mathbf{v}_\beta = 0, \quad \text{at } A_{\beta\sigma} \tag{7}\]

B.C. 5
\[p_\beta = P(x), \quad \text{at } A_{\beta e} \tag{9}\]

This set of equations, in principle, defines the balances for mass and momentum at the microscale. In addition, it is useful to define the following unitless groups

\[
Re = \frac{\rho \langle \mathbf{v}_\beta \rangle^\beta \ell_\beta}{\mu_\beta}, \quad Re_p = \frac{\rho \langle \mathbf{v}_\beta \rangle^\beta d_p}{\mu_\beta} \left( \frac{\epsilon_\beta}{1 - \epsilon_\beta} \right) \tag{10}
\]

\[
P_e = \frac{\langle \mathbf{v}_\beta \rangle^\beta \ell_\beta}{D_\beta}, \quad Pe_p = \frac{\langle \mathbf{v}_\beta \rangle^\beta d_p}{D_\beta} \left( \frac{\epsilon_\beta}{1 - \epsilon_\beta} \right) \tag{11}
\]

where \(Re\) and \(Re_p\) are the Reynolds number and particle Reynolds number, and \(P_e\) and \(Pe_p\) are the Péclet number and the particle Péclet number, respectively. The hydrodynamic fluid pressure is given by \(p_\beta = \hat{p}_\beta - \rho_\beta g z\), and \(\hat{p}_\beta\) is the total fluid pressure. For the remaining parameters, \(c_{A\beta}\) is the concentration, \(\mathbf{v}_\beta\) is the fluid velocity, \(D_\beta\) is the diffusion coefficient, \(k\) is the first-order reaction rate coefficient, \(\mu\) is the viscosity, \(p_\beta\) is the pressure, and \(\langle \mathbf{v}_\beta \rangle^\beta\) is the spatial average velocity (defined below). The boundaries \(A_{\beta\sigma}\) and \(A_{\beta e}\) represent the internal fluid-solid interface and the interface of the averaging volume with the fluid, respectively. These equations apply at the sub-pore scale, identified as ‘Level I’ in Fig 1.

Although conventionally the inertial term \(\nabla \cdot (\rho \mathbf{v}_\beta \mathbf{v}_\beta)\) is neglected in studies of flow and transport in porous media, it is included here to account for the inertial effects at the microscale.
media, there are many practical cases where this term is not negligible. In particular, high-
Re_p flows occur in a wide variety of applications, including gas adsorption [7], catalysis [8],
filtration [9], immobilized enzyme reactors [10], and subsurface remediation [11]. Unlike
many previous works on upscaling transport and reactions in porous media, we will not
discard the inertial term, so that the effective reaction rate and longitudinal dispersion
coefficient can be determined for non-inertial flow conditions.

3. UPSCALING VIA VOLUME AVERAGING

The essential features of ‘upscaling’ are reasonably simple; one attempts to develop a
macroscale representation of the system of interest by mathematically homogenizing the
microscale description. In the case of volume averaging (and similar methods, such as the
generalized Taylor-Aris-Brenner method [12] or the method of homogenization [13]), the
homogenization is conducted over a volume of the media, such as the volume V illustrated
in Fig 1, Level II. The result is a macroscale equation that applies at the Darcy scale,
and a set of ‘closure’ problems that indicate how the microscale and macroscale structure
and physics are related through effective parameters.

3.1. Averaging. For the method of volume averaging, the superficial and intrinsic spatial
averages are defined by

\[
\langle c_{A\beta} \rangle = \frac{1}{V} \int_{V_{\beta}} c_{A\beta} \, dV \quad \langle c_{A\beta} \rangle^\beta = \frac{1}{V_{\beta}} \int_{V_{\beta}} c_{A\beta} \, dV \tag{12}
\]

where \( V_{\beta} \) represents the volume of the fluid phase in the averaging volume \( V \). Note that
this also defines the porosity by the relation

\[
\varepsilon_{\beta} = \frac{V_{\beta}}{V} \tag{13}
\]

Similar averages can be defined for the velocity field. When the averages are applied to
the sub-pore-scale description given by Eqs. (2)-(9), the averages of the gradient operator
appear. In order to interchange the averaging and gradient operations, the averaging
theorem [14, 15, 16] (which can be though of as a generalization of the Liebnitz rule for
integration) is used

\[
\langle \nabla c_{A\beta} \rangle = \nabla \langle c_{A\beta} \rangle + \frac{1}{V} \int_{A_{\beta\sigma}} n_{\sigma} c_{A\beta} \, dA \tag{14}
\]

Finally, sub-pore-scale concentrations arise in the averaged equations, and it is convenient
to decompose these into a spatial average value plus a deviation from the spatial average.
These deviations are defined by [17]

\[
\tilde{c}_{A\beta} = \langle c_{A\beta} \rangle^\beta - c_{A\beta} \tag{15}
\]
\[
\tilde{v}_{\beta} = \langle v_{\beta} \rangle^\beta - v_{\beta} \tag{16}
\]
With these definitions, the averaging of Eqs (2)-(6) is straightforward; the details of the averaging can be found elsewhere [2], and we will only list the result here

\[
\frac{\partial \langle c_{A\beta} \rangle^\beta}{\partial t} + \langle \mathbf{v}_{\beta} \rangle^\beta \cdot \nabla \langle c_{A\beta} \rangle^\beta = \nabla \cdot (D_{\beta} \nabla \langle c_{A\beta} \rangle^\beta) + \varepsilon_{\beta}^{-1} \nabla \cdot \mathbf{f}_\beta + \varepsilon_{\beta}^{-1} \nabla \cdot \mathbf{\tilde{v}}_{\beta} \mathbf{\tilde{c}}_{A\beta} \tag{17}
\]

accumulation convection diffusion macrodiffusion

Here, we have defined the area per unit volume, \(a_v = A_{\beta \sigma} / V\), and the vector \(\mathbf{f}_\beta\) is given by

\[
\mathbf{f}_\beta = \frac{D_{\beta}}{V} \int_{A_{\beta \sigma}} \mathbf{n}_{\beta \sigma} \mathbf{\tilde{c}}_{A\beta} \, dA \tag{18}
\]

The development of Eq. (17) has required several approximations, and these are detailed in [2]. However, the approximations involved are generally valid if we have a separation of length scales, i.e.,

\[
\ell_{\beta} \ll r_0 \ll L \tag{19}
\]

The problem remaining with Eq. (17) is that the unknown deviations \(\mathbf{\tilde{c}}_{A\beta}\) appear, so the mass balance equation is not expressed entirely in terms of the dependent variable \(\langle c_{A\beta} \rangle^\beta\). To rectify this, we seek to determine \(\mathbf{\tilde{c}}_{A\beta}\) as a function of the spatial average \(\langle c_{A\beta} \rangle^\beta\). This process is conventionally known as ‘closure’; a brief overview of the closure is presented in the next section.

3.2. Closure. Equation (17) represents a macroscale transport equation for the reactive transport process associated with the averaging volume \(V\) provided that we can eliminate the explicit dependence upon the microscale concentration deviation, \(\mathbf{\tilde{c}}_{A\beta}\). The concentration deviations appear only in integral terms, so in this sense, one expects them to represent a macroscale quantity. In fact, these integrals are the terms that define the effective parameters that appear in the (closed) macroscale transport equation.

In order to eliminate the dependence on \(\mathbf{\tilde{c}}_{A\beta}\), one usually seeks to model the deviation terms in a representative volume of porous medium. Often, the essential features of the physics of the system can be captured with a representative volume that is highly abstracted from the actual structure of the porous medium. As an example, the well known solutions of Maxwell [18] and Rayleigh [19] give effective diffusion coefficients (or, equivalently, electrical conductivities) for isotropic media that depend primarily upon the volume fraction of the two media involved. These results were obtained for very simple media (essentially a periodic array of spheres in the case of Rayleigh), but they provide good representations for the effective diffusion coefficient even for more complex media [20].

For the closure of the problem posed here, we have adopted the simple unit cell shown in Fig 2(a). In order to develop a balance equation for \(\mathbf{\tilde{c}}_{A\beta}\), Eq (17) is subtracted from the sub-pore-scale equation Eq (2). Similarly, boundary conditions for this balance equation
can be constructed directly from the microscale boundary conditions and the decomposition given by Eq (15). The result is a set of equations for the concentration deviations that take the form

\[ \mathbf{v}_\beta \cdot \nabla \tilde{c}_{A\beta} + \tilde{\mathbf{v}}_\beta \cdot \nabla \langle c_{A\beta} \rangle^\beta = \nabla \cdot (\mathbf{D}_\beta \nabla \tilde{c}_{A\beta}) \]  
\[ + \varepsilon^{-1}_\beta a_v k \langle c_{A\beta} \rangle^\beta + \varepsilon^{-1}_\beta a_v k \frac{1}{A_{\beta\sigma}} \int \tilde{c}_{A\beta} \, dA \]  

(20)

Convective source

B.C. 1

\[ -\mathbf{D}_\beta \nabla \tilde{c}_{A\beta} \cdot \mathbf{n}_{\beta\sigma} - k \tilde{c}_{A\beta} = \mathbf{D}_\beta \nabla \langle c_{A\beta} \rangle^\beta \cdot \mathbf{n}_{\beta\sigma} + k \langle c_{A\beta} \rangle^\beta, \text{ at } A_{\beta\sigma} \]  

(21)

Reactive source

Diffusive source

Periodicity

\[ \tilde{c}_{A\beta}(\mathbf{r} + \mathbf{l}_i) = \tilde{c}_{A\beta}(\mathbf{r}) \]  

(22)

Constraint

\[ \mathbf{n}_{\beta\sigma} \]  

\[ \langle c_{A\beta} \rangle^\beta = 0 \]  

(23)

\[ \nabla \cdot (\rho \mathbf{v}_\beta) = \nabla p_\beta - \mu_\beta \nabla^2 \mathbf{v}_\beta \]  

(24)

\[ \nabla \cdot \mathbf{v}_\beta = 0, \text{ at } A_{\beta\sigma} \]  

(25)

\[ \mathbf{v}_\beta = 0, \text{ at } A_{\beta\sigma} \]  

(26)

\[ \mathbf{v}_\beta \]  

(27)

\[ p_\beta(\mathbf{r} + \mathbf{l}_i) = p_\beta(\mathbf{r}) + \delta_{jk} \Delta p, \text{ at } A_{\beta e} i = 1,2,3 \]  

(28)

\[ \tilde{\mathbf{v}}_\beta(\mathbf{r} + \mathbf{l}_i) = \tilde{\mathbf{v}}_\beta(\mathbf{r}), \text{ at } A_{\beta e} i = 1,2,3 \]  

(29)

Periodicity

\[ \langle \mathbf{v}_\beta \rangle^\beta = \mathbf{v}_0 \]  

(30)

Note that here we have (i) assumed that quasi-steady conditions apply to the closure problem, (ii) replaced the generic boundary condition given by Eq (4) with a condition of periodicity (where \( \mathbf{l}_i \) is a lattice vector defining the periodic structure), and (iii) imposed a constraint (Eq (24)) to set the level of the solution, which otherwise would contain an undetermined constant. Both the pressure and velocity fields are periodic; however, at one face (where \( \delta_{jk} = 1, j \) indexes all control faces, and \( k \) indicates the specified control face) a constant \( \Delta p \) is added to the periodic pressure so that there is a pressure gradient driving flow. The impact of the periodicity condition on the resulting solution is discussed at length elsewhere [21, 2, 22]; however, the influence of periodic boundaries has not been examined extensively for reactive systems. In particular, it is not clear that the periodic condition is the best one to use for systems where chemical species mass is not conserved.

FIGURE 2. (a) Simple 3D unit cell used for closure. (b) and (c) Velocity field for low and high values of \( Re_p \).
due to reactions. Although this important question deserves further research, it will not be addressed in additional detail here.

The solution to Eqs (20)-(24) can be expressed in terms of Green's functions [23]. When the separation of length scales required by Eq (19) is met, the solution to the boundary value problem can be represented generally by

$$\tilde{c}_{A\beta} = b_\beta \cdot \nabla \langle c_{A\beta} \rangle_\beta + s_\beta \langle c_{A\beta} \rangle_\beta$$  \hspace{1cm} (31)

where \(b_\beta\) and \(s_\beta\) are closure variables that can be interpreted as integrals of the Green's function and its gradient. The substitution of Eq (31) into Eqs (20)-(24) gives two linearly independent problems for the solution to the \(b_\beta\) and \(s_\beta\) fields. A detailed presentation of these closure problems has been given by Wood et al. [2]. Using the representation given by Eq (31), the closed form of the macroscale equation can be put in the form

$$\begin{align*}
\frac{\partial \langle c_{A\beta} \rangle_\beta}{\partial t} + v_{\text{eff}} \cdot \nabla \langle c_{A\beta} \rangle_\beta &= \nabla \cdot \left( D_{\beta} \nabla \langle c_{A\beta} \rangle_\beta \right) - \varepsilon^{-1}_\beta a_v \eta \langle c_{A\beta} \rangle_\beta \\
\text{accumulation} &\quad \text{convection} & \quad \text{diffusion} & \quad \text{reaction}
\end{align*}$$  \hspace{1cm} (32)

where the effective parameters are defined by

$$\eta = \left( 1 + \frac{1}{A_{\beta\sigma}} \int_{A_{\beta\sigma}} s_\beta \, dA \right)$$  \hspace{1cm} (33)

$$D_{\beta}^* = D_\beta \left( I + \frac{1}{V_\beta} \int_{A_{\beta\sigma}} n_{\beta\sigma} b_\beta \, dA \right) - \langle \tilde{v}_\beta b_\beta \rangle_\beta$$  \hspace{1cm} (34)

$$v_{\text{eff}} = \langle v_\beta \rangle_\beta - \frac{D_\beta}{V_\beta} \int_{A_{\beta\sigma}} n_{\beta\sigma} s_\beta \, dA + \frac{\varepsilon^{-1}_\beta a_v k \eta}{A_{\beta\sigma}} \int_{A_{\beta\sigma}} b_\beta \, dA - \langle \tilde{v}_\beta s_\beta \rangle_\beta$$  \hspace{1cm} (35)

Note that the effective reaction rate is given by \(k_{\text{eff}} = \eta k\), and the hydraulic diameter is taken as the characteristic length, \(\ell_\beta = 4V_\beta/A_{\beta\sigma} = 4\varepsilon_\beta/a_v\).

4. NUMERICAL SOLUTION TO THE CLOSURE PROBLEM

The closure problem described above was solved numerically to determine the effective reaction rate (or, equivalently, the effectiveness factor), and the effective longitudinal dispersion coefficient. The two linearly independent solutions that arise from substituting Eq (31) into Eqs (20)-(30) were solved for the simple unit cell illustrated in Fig 2(a). The commercial finite-element code COMSOL Multiphysics was used to determine the solution; convergence was determined using a heuristic convergence analysis via grid refinement. The parameters used for these simulations were as follows: \(\varepsilon_\beta = 0.376\), \(\ell = 1 \times 10^{-3}\) m, \(\ell_\beta = 0.54 \times 10^{-3}\) m, \(a_v = 2798\) m²/ m³, \(\rho = 1000\) kg/ m³, \(\mu = 1 \times 10^{-3}\) N · s/ m², \(D_\beta = 1 \times 10^{-9}\) m²/ s. Only a quarter of the domain needed to be simulated because of symmetry, and for this region approximately 10,000 elements were used to resolve the solutions. In the solution to the equations for the concentration deviations, a streamline upwind Petrov-Galerkin method (with tuning parameter \(\delta' = 0.02\)) was used to reduce oscillations.
4.1. Effectiveness Factor. In Fig 3, we have plotted the effectiveness factor versus $\phi^2$. At low values of $\phi^2$, the system is reaction-limited, and the effectiveness factor is 1. However, at $\phi^2 > 1$, reaction begins to dominate over mass transport, and the effectiveness factor decreases with increasing $\phi^2$. This behavior is similar to what is observed in microporous catalytic systems, although the shape of the curve is slightly different because the reaction in the system that we represent is at the fluid-solid interface, rather than within a porous solid.

One interesting feature that is illustrated in Fig 3 is the influence of the Péclet number on the effectiveness factor. The effectiveness factor gradually increases with increasing Péclet number. However, there is a significant increase in the effectiveness factor when the Péclet number approaches 1000. The Péclet and Reynolds numbers are related by the Schmidt number, i.e., $Re_p = Pe_p Sc$ where $Sc = \rho D_{\beta}/\mu_{\beta}$. For the system investigated here, $Sc = 1 \times 10^{-3}$, so the Reynolds number that is associated with this transition is approximately $Re_p = 1$. This indicates that the transition occurs when inertial effects begin to dominate over viscous effects in the momentum balance. This transition is more apparent in Fig 4, where we have plotted the effectiveness factor versus the Péclet number for a fixed value of $\phi^2$ ($\phi^2 = 10$). Here it is clear that there are essentially two transitions. First, there is a gradual increase in $\eta$ near $Pe_p = 1$, indicating the region where convection begins to dominate over diffusion. Then, there is a second, more dramatic increase in $\eta$ near $Pe_p = 1000 (Re_p = 1)$ where inertial effects begin to influence the structure of the flow field.

Although true turbulence in porous media would generally not be expected to occur until a Reynolds number of over 200 [24], inertial effects can have dramatic effects on the structure of the flow field well before turbulence is manifest. In Fig 2 parts (b) and (c), we have presented an illustration of the flow field for our unit cell at $Re_p = 0.1$ and $Re_p = 200$. At higher values of $Re_p$, the flow field can exhibit jets, and steady helical secondary flows, as can be seen in Fig 2(c). The rearrangement of the structure of the flow field leads to decreased resistance to mass transfer, and a subsequent increase in the effectiveness factor for a given value of $\phi^2$. The influence of the inertial effects can be seen in Fig 4, where we have plotted the effectiveness factor as a function of $Re_p$ for a fixed Thiele modulus ($\phi^2 = 10$).
Figure 4. The effectiveness factor $\eta$ as a function of the square of the Theile modulus, $\phi^2 = \ell_\beta k / D_\beta$.

Figure 5. The effective longitudinal dispersion coefficient as a function of the Péclet number: Comparison of closure simulations and experimental data.
4.2. Effective Longitudinal Dispersion Coefficient: Inertial Effects. When Eq (31) is substituted into the closure problem given by Eqs (20)-(30), the second of the two linearly independent solutions allows the prediction of the vector $b_\beta$. The components of the effective dispersion tensor can then be determined by Eq (34). Solutions for the effective longitudinal dispersion coefficient, $D_{xx}^*$ (with $k = 0$) were determined numerically using the finite element code COMSOL Multiphysics, as described above.

The longitudinal dispersion coefficient was determined for the unit cell over a range of Péclet numbers ($4 \times 10^{-2} < Pe_p < 2 \times 10^5$), and the results are compared with experimental data in Fig 2. In this plot, the influence of the inertial terms on the resulting predictions for $D_{xx}$ can be observed by the decrease in the slope of the curve with increasing $Pe_p$. For Péclet numbers in the range of approximately $10^1 < Pe_p < 10^3$, the slope of the curve is approximately 1.2. The relationship between the effective longitudinal dispersion coefficient and the Péclet number is a power law of the form $D_{xx}^*/D_\beta = \beta Pe_p^{1/2}$.

For Péclet numbers in the range of approximately $10^3 Pe_p < 10^5$, the slope of the curve decreases to approximately 0.95. Note that this corresponds to a range of Reynolds numbers of $10^0 < Re_p < 10^2$, which is the range that one would expect the inertial effects to begin to dominate. The effective dispersion tensor predicted from the simple unit cell does underpredict the value of $D_{xx}^*/D_\beta$ over much of the range of $Pe_p$; however, this is not entirely unexpected because the simple unit cell can not capture the effects of large-scale structure randomness that would occur in a real porous medium. Importantly, however, the correct power law exponent is predicted over the whole range that has been simulated. This is significant, because previously there have been few quantitative explanations for the decrease in the exponent of the curve at high values of $Pe_p$.

References


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