Macroscopic models for heterogeneous reactions in porous media

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Abstract

Derivation of coarse grained models for advection-diffusion processes in the presence of dominant surface reactions using homogenisation theory or volume averaging is often deemed unfeasible [1, 2] due to the strong coupling between scales that characterise such systems. In this work, we show how this problem can be circumvented by applying and extending the methods presented in Allaire and Raphael [3], Mauri [4]. Such process relies on the decomposition of the solution with the principal eigenvalue and eigenfunction of the non self-adjoint linear advection-diffusion operator, and on a two-scale asymptotic expansion. A set of cell problems and the corresponding macroscopic equation are obtained. The whole procedure is implemented and the cell problems are solved for arbitrarily complex periodic structures using the open-source finite volume library OpenFOAM®. We provide details on the implementation and test the methodology for two-dimensional periodic arrays of spheres, in a wide range of Péclet and surface Damköhler numbers. Results are compared to fully resolved numerical simulations, demonstrating the accuracy and generality of the upscaling approach. Noticeably, the effective transport parameters (dispersivity and velocity) can be significantly different from the non-reactive (conserved scalar) case, as the heterogeneity introduced by the reaction strongly affects the micro-scale profiles.

Keywords: Homogenisation, Reactive Transport, Upscaling, Pore-scale simulation, OpenFOAM®

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1. Introduction

Understanding the transport behaviour of porous media is important in a wide range of chemical processes (for example drying of paper pulp or flow through catalysts) and applications (subsurface flows, CO\textsubscript{2} storage, nuclear waste management, etc.) [5]. However, the study of transport phenomena in porous media is complicated by the broad range of excited space and time scales, which results in large (almost always unaffordable) computational requirements when simulating such systems at industrial or natural scales. Therefore, any precise simulation describing the local, pore-scale, phenomena would be of little practical applicability, without a robust methodology that leads to upscaled models.

In the following, we use the term ‘upscaling’ to describe the procedure leading to ‘upscaled models’ where the ‘fast’ (high wave number) components of the unknown fields are averaged out. Notice that often the terms ‘spatial filtering’ [6] or ‘coarse graining’ [7] are also employed in literature with a similar meaning.

A variety of methods can be employed to perform this upscaling procedure: asymptotic homogenisation [8, 9, 10] is a powerful and versatile tool for the upscaling of transport and reaction equations in porous and heterogeneous media. For example, Taylor dispersion in porous media has been approached in this way [11] and there have been attempts to account for heterogeneous (surface) reactions [12, 13].

1.1. Problem statement and dimensionless governing equations

Consider a porous medium occupying a region of space \( \hat{\Omega} \) associated with a characteristic length \( L \). We assume \( \hat{\Omega} \) to be composed of spatially repeated (periodic) unit cells \( \hat{\mathcal{Y}} \) with characteristic length (periodicity) \( \ell = \varepsilon L \ll 1 \). Each unit cell \( \hat{\mathcal{Y}} \) is then given by the union \( \hat{\mathcal{Y}} = \hat{\mathcal{Y}}_f \cup \hat{\mathcal{Y}}_s \), where \( \hat{\mathcal{Y}}_f \) and \( \hat{\mathcal{Y}}_s \) are the fluid and solid regions of \( \hat{\mathcal{Y}} \) respectively, separated by an interface \( \hat{\Gamma} \). Clearly, \( \hat{\mathcal{Y}}_f \) is generally not simply connected, while \( \hat{\mathcal{Y}}_s \) is a disconnected domain (for example, it may represent grains inside the porous medium). We are interested in the fluid flow and scalar transport in \( \hat{\mathcal{Y}}_f \), neglecting\(^1\) the solid region \( \hat{\mathcal{Y}}_s \) that is here represented only through its interface \( \hat{\Gamma} \). If such flow is well described by the Stokes equations (i.e., incompressible, low Reynolds number), it has been shown that the homogenisation procedure leads to the Darcy equation [11]. Therefore, in this work we will only deal with the scalar transport problem, assuming that the velocity field is prescribed, and the upscaled Darcy equation valid. We limit here to the case of periodic and non-moving porous media. However, some of these ideas can be extended to stochastic stationary multiscale random media, with Fourier/Bloch [15, 16] or numerical sampling [17] approaches, and to slowly varying or quasi-periodic media [18, 19]. These extensions will be considered in future studies.

Let us consider a generic (dimensional) scalar field \( \hat{c}(\hat{x}, t) \) defined in the fluid region \( \hat{\Omega}_f \) given by the \( \hat{\mathcal{Y}}_f \) of each cell that obeys the advection-diffusion equation:

\[
\begin{align*}
\frac{\partial \hat{c}}{\partial t} + \hat{\nabla} \cdot (\hat{\mathbf{v}} \hat{c}) &= \hat{\nabla} \cdot \left( \mathcal{D} \hat{\nabla} \hat{c} \right) \quad \hat{x} \in \hat{\Omega}_f \\
\mathcal{D} \hat{\nabla} \hat{c} \cdot \hat{n} &= -\kappa \hat{c} + \hat{g} \quad \hat{x} \in \hat{\Gamma}_\Omega
\end{align*}
\]

(1)

where \( \mathcal{D} \) is the molecular diffusion coefficient, \( \hat{\mathbf{v}}(\hat{x}) \) a solenoidal velocity field and \( \hat{g}(\hat{x}) \) is a known forcing (source) term at the boundary. The mixed boundary condition on the solid surface \( \hat{\Gamma}_\Omega \) (the union of the interfaces \( \hat{\Gamma} \) of all the unit cells) is, for the limit \( \kappa \to \infty \), equivalent to a homogeneous Dirichlet condition.

\(^1\)We do not consider here the case of conjugate transport in both regions that will be studied in future works\([14]\).
Equation 1 should be provided with a proper set of external boundary conditions (e.g., inlet/outlet). Since such boundary conditions are specific for each problem and should not concern the homogenisation procedure, we will not explicitly state them. However, it is important to notice that homogenisation fails in case the external boundary conditions play a significant role at the scale $\ell$ since the model with periodic unit cells $\hat{Y}$ would fail to be a realistic and mathematically consistent description of the porous medium as outlined in Auriault and Adler [11].

We now introduce a set of dimensionless quantities:

\begin{align*}
    x &= \frac{\hat{x}}{L}; \quad v = \frac{\hat{v}}{U} \quad c = \frac{\hat{c}}{c_0}; \quad t = \frac{L^2}{D} t; \quad g = \frac{\hat{g}}{\kappa c_0} \\
    \end{align*}

where $U$ is the system characteristic velocity and $c_0$ is characteristic value for particle concentration.

When the dimensionless quantities are substituted into equation 1, two dimensionless number arise:

- The Péclet number:
  \[ \text{Pe} = \frac{U \ell}{D} \]
  Which represents the ratio between inertial and diffusion time scales at the microscale.

- The second Damköhler number:
  \[ \text{Da}_\text{II} = \frac{\kappa \ell}{D} \]
  Which gives the ratio between the reaction and diffusion time scales at the microscale.

Thus, recalling that $\varepsilon = \ell/L$, we can write the advection-diffusion problem in dimensionless form:

\begin{align*}
    \left\{ \begin{array}{ll} 
    \frac{\partial c}{\partial t} + \nabla \cdot (\text{Pe} v c - \nabla c) &= 0 \quad x \in \Omega \\
    \nabla c \cdot n &= \text{Da}_\text{II} (g - c) \quad x \in \Gamma_\Omega
    \end{array} \right.
    \tag{5}
\end{align*}

1.2. Homogenisation via two-scale asymptotics

Following the standard two-scale asymptotic homogenisation method [20], we introduce a "fast" spatial variable $y$ defined as follows:

\[ y = \frac{x}{\varepsilon} \]

Then, $c$ is represented as $c(x, t) = c(x, y, t)$ and expanded into an asymptotic series of $\varepsilon$

\[ c(x, y, t) = \sum_{m=0}^{\infty} \varepsilon^m c_m (x, y, t) \]

Using 6 we obtain the following differentiation rule:

\[ \nabla c = \nabla_x c + \varepsilon^{-1} \nabla_y c \]

Furthermore, we consider the case of equally important advection and diffusion at large scales $\text{Pe} = \text{Pe}_L = O(1)$ without any loss of generality. Substituting into equation 5 and collecting terms of the same order $\varepsilon$ we obtain:

\[ \varepsilon^{-2} \left( \nabla_y \cdot (\text{Pe} v c_0 - \nabla_y c_0) \right) + \]

\[ \varepsilon^{-1} \left( \nabla_x \cdot (\text{Pe} v c_0 - \nabla_y c_0) - \nabla_y \cdot [\nabla_x c_0 + \nabla_y c_1 - \text{Pe} v c_1] \right) + \]

\[ \varepsilon^0 \left( \frac{\partial c_0}{\partial t} - \nabla_x \cdot [(\nabla_x c_0 + \nabla_y c_1)] - \nabla_y \cdot [(\nabla_x c_1 + \nabla_y c_2)] + \right. \]

\[ + \text{Pe} \nabla_x \cdot (v c_1) \right) = O(\varepsilon) \]
We apply the same expansion to the boundary condition in $\Gamma_\Omega$ for the homogeneous case $g = 0$:

$$(\nabla_x + \varepsilon^{-1}\nabla_y)(c_0 + \varepsilon^1 c_1 + \varepsilon^2 c_2) \cdot n = -\varepsilon^{-1} D_{\text{II}} c_0 + \varepsilon^1 c_1 + \varepsilon^2 c_2 + O(\varepsilon^3) \quad y \in \Gamma_\Omega$$  (9)

1.2.1. The failure of two-scale asymptotics

Collecting terms of order $O(\varepsilon^{-2})$ in equation 9 and (9), and considering that for an incompressible fluid $\nabla_y \cdot v = 0$, we obtain a problem in the unit cell:

$$\begin{align*}
\nabla_y \cdot (-\nabla_y c_0) &= 0 \quad y \in Y_f \\
\nabla_y c_0 \cdot n &= D_{\text{II}} c_0 \quad y \in \Gamma
\end{align*}$$  (10)

Generally, formal two-scale asymptotics can be applied to obtain a macro-scale equation (independent from the micro-scale), if the equation for the lowest order is solved by a function independent of $y$, i.e., $c_0 = c_0(x, t)$. This allows the subsequent order equations to simplify and to finally perform volume averaging to obtain a well-defined effective concentration. For example, in the case of $D_{\text{II}} = 0$ (impermeable non-reactive walls), the resulting homogeneous Neumann boundary condition would ensure that no dependence on $y$ is retained in $c_0$. Due to the geometry of the unit cell (periodicity and internal boundary), equation 10 is satisfied only for the trivial case $c_0 = 0$, thus removing the leading order term from the asymptotic expansion. This phenomenon is essentially triggered by a lack of separation of scales, i.e., the leading order of the asymptotic expansion directly depends upon the boundary conditions on $\Gamma$. Therefore, the problem cannot be homogenised using this formal expansion.

1.3. Goals and outline

In this work we show how the issue highlighted above, for this and other similar reactive transport problems, can be circumvented. We derive a homogenised equation using the technique developed by Allaire and Raphael [3] in the case of homogeneous surface reactions and we generalised it to include non-homogeneous boundary conditions of relevance for many engineering applications. Furthermore, we describe how the resulting upscaling algorithm can be implemented in the open-source C++ finite volume library OpenFOAM®.

This work is structured as follows: in Section 2 we present the approach of Allaire and Raphael and its extension. In section 3 we detail the numerical algorithm, and in section 4 we show how the method compares against fully resolved numerical simulation and present some results for the upscaled parameters obtained for a periodic arrays of spheres under different flow regimes. Eventually, we present conclusions and outlook on future directions in section 5.

2. Upscaling via scale decomposition

In order to upscale the advection-diffusion equation with reactive boundary conditions, we apply a decomposition method where the scalar field is appropriately separated into terms that account for exchange processes at different scales. In order to shorten our notation, we introduce the steady advection-diffusion operator:

$$\mathcal{L} = \nabla \cdot [P e v(x) - \nabla]$$  (11)

This allows us to rewrite equation (5) in a more succinct way:

$$\begin{align*}
\frac{\partial}{\partial t} + \mathcal{L} c(x, t) &= 0 \quad \forall x \in \Omega \\
\nabla c(x, t) \cdot n &= D_{\text{II}} c(x, t) \quad \forall x \in \Gamma_\Omega
\end{align*}$$  (12)

As already stated, we do not consider here other “external” boundary conditions, as if we were considering a “bulk” region where the dynamics is completely determined by the boundary conditions in $\Gamma_\Omega$. 

2.1. Spectral decomposition

By using the geometrical periodicity of the system, we can separate \( c(x, t) \) into a function \( \phi(x, t) \) periodic in \( Y \) and another function \( \omega(x, t) \), which is not necessarily periodic:

\[
c(x, t) = \phi(x) \omega(x, t)
\]  \hspace{1cm} (13)

The aim of decomposition (13) is to separate the part of \( c(x, t) \), that dominates at the microscale, and drives the mass exchange between \( \Omega \) and \( \Gamma_0 \), from the part that is responsible for the transport over long distances. We therefore choose \( \phi \) as the principal (i.e. first positive) eigenfunction of \( L \) in \( Y \), which satisfies:

\[
L \phi = \lambda \phi, \quad \forall x \in Y_f
\]

\[
\nabla \phi \cdot n = \text{D}_n \phi(x), \quad \forall x \in \Gamma
\]

(14)

with \( \phi > 0 \forall x \), and \( \lambda \) the associated principal eigenvalue. Therefore, \( \omega(x, t) \) can be thought as a reduced concentration, which compensates for the arbitrariness of our choice of \( \phi \).

Substituting back equation (13) into \( Lc \) (dropping the dependence on \( x \) and \( t \)) we obtain the operator that should be satisfied by \( \omega \):

\[
L(\phi \omega) = \nabla \cdot [\text{Pe} \phi \omega - \nabla (\phi \omega)]
\]

\[
= \nabla \cdot (\text{Pe} \phi \omega - \phi \nabla \omega - \omega \nabla \phi)
\]

\[
= \phi \nabla \cdot (\text{Pe} - \nabla) \omega + \omega \nabla \cdot (\text{Pe} - \nabla) \phi - \nabla \phi \cdot \nabla \omega
\]

\[
= \phi \nabla \omega + \omega \nabla \phi - \nabla \phi \cdot \nabla \omega
\]

\[
= \phi \nabla \omega + \omega \lambda \phi - \nabla \phi \cdot \nabla \omega
\]

(15)

While the term \( \omega \lambda \phi \) could be removed by mean of an appropriate transformation, the last term on the right-hand-side of equation (15), involving the dot product of \( \nabla \phi \) and \( \nabla \omega \), requires particular care. In order to recast the problem into a more familiar and tractable operator, we introduce the adjoint eigenproblem:

\[
L^\dagger (\phi^\dagger) = \lambda^\dagger (\phi^\dagger), \quad \forall x \in Y_f
\]

\[
\nabla \phi^\dagger \cdot n = \text{D}_n \phi^\dagger(x), \quad \forall x \in \Gamma
\]

(16)

where \( L^\dagger = -\nabla \cdot [\text{Pe} (\phi) + \nabla] \). It can be proved[3] that there exist one single real and positive eigenfunction for both the direct and adjoint problem, and the associated eigenvalue \( \lambda^\dagger = \lambda \) is real.

We therefore make use of the adjoint eigenfunction \( \phi^\dagger \) to obtain an equation for \( \omega \):

\[
\phi^\dagger L(\phi \omega) = \phi^\dagger \nabla \cdot (\text{Pe} \phi \omega - \phi \nabla \omega - \omega \nabla \phi)
\]

\[
= \nabla \cdot (\text{Pe} \phi \omega - \omega \phi^\dagger \phi \nabla \omega - \phi^\dagger \nabla \phi \omega)
\]

\[
+ (\phi \nabla \omega + \omega \nabla \phi) \cdot \nabla \phi^\dagger - \omega \phi^\dagger \nabla \cdot (\text{Pe} \phi^\dagger)
\]

\[
= \nabla \cdot (\text{Pe} \phi \omega - \omega \phi^\dagger \phi \nabla \omega - \phi^\dagger \nabla \phi \omega + \nabla \phi^\dagger \phi \omega)
\]

\[
- \omega \phi^\dagger \nabla \cdot (\text{Pe} \phi^\dagger + \nabla \phi^\dagger)
\]

\[
= \nabla \cdot (\text{Pe} \omega - \beta \nabla \omega) + \lambda^\dagger \beta \omega
\]

(17)

where, in the last step, we have used the definition of \( L^\dagger \), and we have introduced a dimensionless coefficient \( \beta(x) = \phi \phi^\dagger \) and a new velocity field:

\[
v^* = \beta \left( v - \nabla \phi + \nabla \phi^\dagger \right) = \beta v^+
\]

(18)

being \( v^+ \) the sum of the original velocity and the additional pseudo velocities arising from the spectral decomposition above.
Therefore, we can define a new advection-diffusion operator:
\[
\mathcal{L}^* = \nabla \cdot [v^* (x) - \beta(x) \nabla]
\]
and the equation for \(\omega\) then reads:
\[
\left[\beta \left( \frac{\partial}{\partial t} + \lambda \right) + \mathcal{L}^* \right] \omega = 0
\]
(20)
The modified operator \(\mathcal{L}^*\) possesses several good properties. In particular, the new velocity field \(v^*\) is divergence-free:
\[
\nabla \cdot v^* = \nabla \cdot \left( \phi \phi^\dagger + D \nabla \phi \right) + D \nabla \phi^\dagger (\nu \phi - D \nabla \phi) = -\phi \phi^\dagger \lambda + \phi \phi^\dagger \lambda = 0
\]
(21)
If we apply the same decomposition to the boundary condition in \(\Gamma\), it can be easily verified that, due to our choice of \(\phi\), the Robin (reactive) boundary condition is absorbed by \(\phi\), leaving a homogeneous Neumann (non-reactive) BC for \(\omega\):
\[
\nabla \omega \cdot n = 0
\]
(22)
Therefore, the spectral decomposition has the effect of moving the reaction term from the boundary to the bulk. It is easy to see now that equation (20) can be further simplified by mean of one additional transformation which takes into account the fast time scale related to \(\lambda\):
\[
\omega(x, t) = e^{-\lambda t} w(x, t) \rightarrow \phi(x) e^{-\lambda t} w(x, t)
\]
(23)
where the exponential takes into account the fast change in \(c\) due to the reaction. We can finally write an equation for the reduced concentration \(w\) together with a proper set of boundary conditions:
\[
\begin{cases}
\left( \beta \frac{\partial}{\partial t} + \mathcal{L}^* \right) w = 0, & \forall x \in \Omega \\
\nabla w \cdot n = 0, & \forall x \in \Gamma
\end{cases}
\]
(24)
Through this simple decomposition, we have obtained an equation for the reduced concentration with non-reactive (zero flux) on \(\Gamma\). This can be now upscaled using standard two-scale asymptotics.

2.2. Two-scales asymptotics with drift

Decomposition (23) introduced an auxiliary problem in the cell \(Y_f\) and clearly, the eigenfunction \(\phi\) and the adjoint \(\phi^\dagger\), by construction, can only depend on the small scale spatial variable \(y\), while \(w\) can vary on both scales. It is convenient to express the solution as:
\[
c(x, y, t) = e^{-\lambda t} \phi(y) w(x, y, t)
\]
(25)
The two-scale expansion of \(c\) turns out to be fully determined by considering the two scale expansion of \(w\) only. Since the governing equation for \(w\) does not have a Robin boundary condition, the limitation of standard asymptotics addressed in Section 1, can be avoided. We thus expand \(w\) into an asymptotic series of \(\varepsilon\) introducing a drift in \(w\) that accounts for the fast advective transport at the microscale:
\[
w(x - \varepsilon^{-1} Pe V^* t, y, t) = \sum_{m=0}^{\infty} \varepsilon^m w_m(x - \varepsilon^{-1} Pe V^* t, y, t)
\]
(26)
where the velocity $V^*$ is obtained during the homogenisation procedure as shown in [21]. The same expansion we derived in Section 1 is applied on equation 24 obtaining:

$$
\varepsilon^{-2} \left\{ \nabla_y \cdot (P\!e v^* w_0 - \beta \nabla_y w_0) \right\} + \\
\varepsilon^{-1} \left\{ P\!e \left[ -\beta V^* \cdot \nabla_x w_0 + \nabla_x \cdot (v^* w_0) + \nabla_y \cdot (v^* w_1) \right] \\
- \nabla_x \cdot (\beta \nabla_y w_0) - \nabla_y \cdot \left[ \beta (\nabla_x w_0 + \nabla_y w_1) \right] \right\} + \\
+ \varepsilon^0 \left( \beta \frac{\partial w_0}{\partial t} - \beta P\!e V^* \cdot \nabla_x w_1 + P\!e \nabla_x \cdot (v^* w_0) + P\!e \nabla_x \cdot (v^* w_2) - \\
- \nabla_x \cdot \left[ \beta (\nabla_x w_0 + \nabla_y w_1) \right] - \nabla_y \cdot \left[ \beta (\nabla_x w_0 + \nabla_y w_1) \right] \right\} = O(\varepsilon)
$$

(27)

The internal boundary condition is also expanded:

$$(\nabla_x + \varepsilon^{-1} \nabla_y)(w_0 + \varepsilon^1 w_1 + \varepsilon^2 w_2) \cdot n = 0$$

(28)

which corresponds to a homogeneous Neumann boundary condition for all the terms in the series.

**Terms of order $O(\varepsilon^{-2})$**

We can now collect the leading order terms of equation (27) and (9), which correspond to terms of order $O(\varepsilon^{-2})$

$$
\left\{ \begin{array}{l}
\nabla_y \cdot (P\!e v^* w_0 - \beta \nabla_y w_0) = 0 \quad y \in \Omega \\
\nabla_y w_0 \cdot n = 0 \quad y \in \Gamma
\end{array} \right.
$$

(29)

This problem allows the trivial solution $w_0 = w_0(x,t)$ since the homogeneous Neumann boundary condition ensures that no terms from "fast" scales appear in equations (29).

**Terms of order $O(\varepsilon^{-1})$**

Moving on to collect terms of order $O(\varepsilon^{-1})$, we obtain the following partial differential equation:

$$
\left\{ \begin{array}{l}
- \beta P\!e V^* \cdot \nabla_x w_0 + P\!e \nabla_x \cdot (v^* w_0) + \\
+ \nabla_y \cdot \left[ \beta (v^* w_1 - \nabla_x w_0 + \nabla_y w_1) \right] \quad y \in \Omega \\
\nabla_y w_1 + \nabla_x w_0 \cdot n = 0 \quad y \in \Gamma
\end{array} \right.
$$

(30)

This equation can be integrated over the unit cell to give:

$$
\int_{y_f} \left( \beta V^* - v^* \right) dy \cdot \nabla_x w_0 = \int_{y_f} \beta \left( V^* - v^* w_0 \right) dy \cdot \nabla_x w_0
$$

(31)

Assuming that the velocity field $v$ is solenoidal at the microscopic scale this can be simplified into an equation for the unknown upscaled effective velocity $V^*$:

$$
V^* = \frac{1}{\epsilon} \int_{y_f} v^*(y) dy = \langle v^* \rangle
$$

(32)
where we have defined the Favre average of the velocity field \( \langle v^+ \rangle \) and the effective porosity \( \epsilon \) as:

\[
\epsilon = \int dy
\]  

We now notice that when substituting (32) into equation (30), we can express the solution \( w_1 \) as:

\[
w_1 = \chi(y) \cdot \nabla_x w_0 + f_1(x)
\]  

where \( \chi \) is called first order corrector and \( f_1 \) is an arbitrary function of the macroscopic coordinate. Substituting equation (34) into equations (30) we obtain:

\[
\begin{align*}
- \nabla_y \cdot \left[ \beta \left( I + \nabla_y \chi \right) \right] + \text{Pe} v^\star \cdot \left( I + \nabla_y \chi \right) &= \text{Pe} \beta V^\star \quad y \in \mathcal{Y}_f \\
\left( I + \nabla_y \chi \right) \cdot n &= 0 \quad y \in \Gamma
\end{align*}
\]  

Equation (35) is often referred as the first order cell corrector, closure, or cell problem, since \( \chi \) appears in the expressions for the effective diffusion coefficient. It is important to notice that the first order corrector only depends on \( y \) and therefore, its governing equation can be defined in the unit cell \( \mathcal{Y} \) alone.

2.3. Upscaled equation

Finally, we collect the terms of order \( O(1) \) from equation (27):

\[
\begin{align*}
\langle \beta \rangle \frac{\partial w_0}{\partial t} + \beta \text{Pe}(v^+ - V^\star) \cdot \nabla_x w_1 + 3\text{Pe} \nabla_x (v^\star w_2) - \\
\nabla_x \cdot [\beta(\nabla_x w_0 + \nabla_y w_1)] - \nabla_y \cdot [\beta(\nabla_x w_1 + \nabla_y w_2)] &= \text{Pe} \beta V^\star \quad y \in \Omega \\
\nabla_x w_1 + \nabla_y w_2 \cdot n &= 0 \quad y \in \Gamma
\end{align*}
\]  

Equation (36) can be integrated over \( \mathcal{Y}_f \) to obtain:

\[
\langle \beta \rangle \frac{\partial w_0}{\partial t} - \nabla_x \cdot \left[ \langle \beta \rangle \left( I + \nabla_x \chi + \text{Pe} V^\star \chi - \text{Pe} v^\star \chi \right) \right] \cdot \nabla_x w_0 = 0
\]  

Without loss of generality\(^2\), we can take \( \beta \) such that:

\[
\langle \beta \rangle = 1
\]  

Furthermore, we can express an effective diffusivity tensor \( D^{\text{eff}} \) as:

\[
D^{\text{eff}} = \langle \beta \left( I + \nabla_x \chi + \text{Pe} V^\star \chi - \text{Pe} v^\star \chi \right) \rangle
\]  

The full form of the effective diffusion tensor is irrelevant since its effect on the homogenised solution is defined by its product with the Hessian matrix \( \nabla_x^2 w_0 \), so that only its symmetric part contributes in the equation. It is thus more convenient to express it in symmetric form. It can be shown [10] that the symmetric part of \( D^{\text{eff}} \) can be expressed as:

\[
D^{\text{eff}} = \langle \beta \left( I + \nabla_x \chi \right) \rangle \left( I + \nabla_x \chi \right)^T
\]  

Physically, this means that the dispersion due to the microscale velocity is concealed in the corrector \( \chi \), and it does not require to be accounted for in \( D^{\text{eff}} \)

\(^2\)Since both the direct and adjoint eigenfunctions can be defined up to a constant.
Finally, to include the effect of the exponential term in the decomposition of \( w \), we transform back the shifted spatial coordinate, and we let \( \varepsilon \to 0 \) to obtain the homogenised equation for \( \omega(x,t) = \omega_0(x,t) + O(\varepsilon) \):

\[
\frac{\partial \omega}{\partial t} + \nabla_x \cdot \left( \text{Pe}_L V^* \omega - D^\text{eff} \cdot \nabla_x \omega \right) = -\lambda \omega
\]  

(41)

where we have introduced the macroscopic Péclet number \( \text{Pe}_L = UL/D = \text{Pe}/\varepsilon \), which is evaluated at the macroscale. It should be noted that equation (41) is not immediately equivalent to the equation for the average concentration \( \langle c \rangle \).

In fact:

\[
\langle c \rangle = \langle \phi \omega \rangle = \frac{1}{\varepsilon} \int \phi(y) \omega(x,y,t) dy
\]  

(42)

However, employing expansion (26) and letting \( \varepsilon \to 0 \), at the leading order we have:

\[
\langle c \rangle = \frac{1}{\varepsilon} \int \phi(y) \omega(x,y,t) dy = \langle \phi \rangle \omega_0(x,t) + O(\varepsilon)
\]  

(43)

Finally, taking a \( \phi \) normalised over the fluid volume\(^3\), we can write the asymptotic limit:

\[
\langle c \rangle \sim \omega_0(x,t), \quad \varepsilon \to 0
\]  

(44)

and therefore rewrite a macroscopic equation for the first order approximation\(^5\) of \( \langle c \rangle \):

\[
\frac{\partial \langle c \rangle}{\partial t} + \nabla \cdot \left( \text{Pe}_L V^* \langle c \rangle - D^\text{eff} \cdot \nabla \langle c \rangle \right) = -\lambda \langle c \rangle
\]  

(45)

Alternatively, one can retain terms up to \( O(\varepsilon^2) \) and merely consider equation (41) as the equation for \( w_0 \), i.e. the leading order term. The average concentration can be corrected a-posteriori introducing a first order term:

\[
\langle c \rangle = \omega_0 + \varepsilon \langle \phi \chi \rangle \cdot \nabla \omega_0 + O(\varepsilon^2), \quad \varepsilon < 1
\]  

(46)

Equation 46 is often referred as the “first corrector equation” [9] but a direct solution would involve a third order macroscopic equation that is therefore not easily solvable.

### 2.4. Extension to inhomogeneous boundary conditions

In Section 2.1, we employed the homogeneity of the Robin boundary condition to define an eigenvalue problem for \( \phi \), which allows to evaluate the eigenvalue \( \lambda \). Thus, our approach, in the present formulation, fails when considering generic inhomogeneous boundary conditions, i.e. when \( g = g(x,y,t) \). However, the method can still be exploited when the inhomogeneous term is a function of \( x \) and \( y \) only through \( c \) and its gradient:

\[
g = g(c, \nabla c \cdot n) = a(c - c_T) + b \nabla c \cdot n
\]  

(47)

Specifically, one can write the boundary condition on \( \Gamma \) in the more familiar form:

\[
\nabla c \cdot n = -D_{\text{II}}^* (c - c_T), \quad D_{\text{II}}^* = \frac{(k - a)\ell}{D - b}, \quad b \neq D,
\]  

(48)

\( ^3 \)There is now a unique choice of \( \phi \) and \( \phi^\dagger \) such that \( \langle \phi \rangle = 1 \) and \( \langle \phi \phi^\dagger \rangle = 1 \).

\( ^5 \)The fact that we took the limit \( \varepsilon \to 0 \) is equivalent to state that we employed a local perturbation analysis. This has the consequence that equation 45 is expected to be valid only in the case in which the microscopic and macroscopic scales are totally separated and \( \ell \ll L \).
which gives the inhomogeneous Dirichlet boundary condition:

\[ c = c_T, \quad c_T = \frac{d}{\kappa - a}, \quad b = D \]

In case the inhomogeneous term is in the form given in equation 47, the linearity of advection-diffusion allows to define a new dimensionless concentration:

\[ c'(x) = c(x, t) - c_T \]

which satisfies our initial homogeneous problem. Thus, the analysis remains valid when the inhomogeneity can be expressed as an additive constant to the field \( c \).

It is important to notice that, while \( c_T \) can still be a function of the macroscopic coordinate and vary only at large scales, this method fails in case of inhomogeneous Neumann boundary conditions or in case of more general expressions for \( g \). Extension of this methodologies for such cases will be studied in our future works.

3. Numerical implementation of the upscaling method

The upscaling procedure explained above is implemented within the C++ opensource finite volume library OpenFOAM® [22] to solve the closure problems in general geometries. We motivate our choice of OpenFOAM® over other libraries with its wide diffusion both in the academic and industrial communities, and with the wide range of classes already available in the library and structured in an consistent object-oriented programming approach.

3.1. Overall structure of the algorithm

Figure 1 illustrates the overall algorithms, which consists on two main sequential operations:

i. Solving the spectral cell problem for the spectral (eigenvalue) direct and adjoint problems.

ii. Solving the cell corrector problem for the first order corrector \( \chi \).

As input, the algorithm requires an appropriate velocity field which can be obtained from native OpenFOAM® solver such as simpleFoam.
3.2. Power method for the spectral problem

Solving the spectral problems pose an additional complication with respect to standard power methods as the direct and adjoint problems are coupled through $\lambda$ and $\lambda^\dagger$ respectively, that should be equal. We propose an iterative segregated algorithm where the convergence of $\lambda$ is achieved through residual control. At each iteration $n$, the values of eigenfunctions and eigenvalues at iteration $n+1$ are calculated following a series of steps:

1. Compute $\phi^{n+1}$ and $\phi^{\dagger,n+1}$ from:
   \begin{align}
   \phi^{n+1} &= L^{-1}(\lambda^n \phi^n), \quad (51) \\
   \phi^{\dagger,n+1} &= (L^\dagger)^{-1}(\lambda^{\dagger,n} \phi^{\dagger,n}). \quad (52)
   \end{align}

   This operation may consist in nested iteration loops: solution of the linear systems and corrections for the non-orthogonal fluxes, non-linearities and explicit terms. The adjoint eigenvalue $\lambda^\dagger$ should tend to $\lambda$ for $n \to \infty$.

2. Update the eigenvalues using the Rayleigh quotient:
   \begin{align}
   \lambda^{n+1} &= \lambda^n \frac{\langle \phi^n \phi^n \rangle}{\langle \phi^{n+1} \phi^{n+1} \rangle}, \quad (53) \\
   \lambda^{\dagger,n+1} &= \frac{\langle \phi^{\dagger,n} \phi^{\dagger,n} \rangle}{\langle \phi^{\dagger,n+1} \phi^{\dagger,n+1} \rangle}.
   \end{align}

3. Normalise $\phi^{n+1}$ and $\phi^{\dagger,n+1}$:
   \begin{align}
   \phi^{n+1} &= \frac{\phi^{n+1}}{\langle \phi^{n+1} \phi^{n+1} \rangle}, \quad (54) \\
   \phi^{\dagger,n+1} &= \frac{\phi^{\dagger,n+1}}{\langle \phi^{\dagger,n+1} \phi^{\dagger,n+1} \rangle}.
   \end{align}

Notice that this normalisation is arbitrary and we will later re-normalise $\phi^{\dagger,n+1}$ to be consistent with equation 38.

4. Check convergence against a number of norms with user-defined tolerances. We choose to test both the residuals for $\phi$ and $\phi^\dagger$ defined as:
   \begin{align}
   \text{res}(\phi^{n+1}) &= \max \left( \frac{|\phi^{n+1}| - |\phi^n|}{|\phi^n|} \right), \quad \text{res}(\phi^{\dagger,n+1}) = \max \left( \frac{|\phi^{\dagger,n+1}| - |\phi^{\dagger,n}|}{|\phi^{\dagger,n}|} \right), \quad (55)
   \end{align}

   Where max is the maximum and the operator $|\cdot|$ denotes the absolute value. Clearly, the error on the eigenvalues is also a critical metrics to assess convergence:
   \begin{align}
   (\lambda\text{-error})^{n+1} &= \frac{|\lambda^{\dagger,n+1} - \lambda^{n+1}|}{\lambda^{n+1}}. \quad (56)
   \end{align}

   When all the metrics pass the convergence test (generally their value should be smaller than $10^{-5}$), the spectral solver exits the loop.

After convergence, the eigenfunctions need to be re-normalised to satisfy $\langle \phi \rangle = 1$ and $\langle \beta \rangle = 1$ to be consistent with our formulations. While no action needs to be taken for $\phi$, $\phi^\dagger$ is finally re-scaled simply dividing it by $\langle \phi^\dagger \phi \rangle$.

3.3. Numerical solution of the corrector problem

Finally, the corrector problem is solved iteratively (with the two nested loops described above). Since $\chi$ is gauge-invariant (i.e., defined up to a constant), from equation 44, we can make the approximation of $\langle c \rangle$ of order $O(\epsilon^2)$ by imposing $\langle \phi \chi \rangle = 0$. Thus, at each iteration $n$ we impose:
   \begin{align}
   \chi^{n+1} &= \chi^{n+\frac{1}{2}} - \langle \phi \chi^{n+\frac{1}{2}} \rangle, \quad (57)
   \end{align}

   where $\chi^{n+\frac{1}{2}}$ is calculated from the solution of the corrector problem before the gauge scaling.
4. Numerical results

4.1. Verification

We verify both our code and the upscaling methodology by direct comparison with spatial averaged data from fully resolved pore-scale simulations. Flow and scalar transport are solved in two dimensions for an array of 26 face-centred-cubic (FCC) cells (see Fig. 2) using the OpenFOAM® native solvers simpleFoam (classic Navier-Stokes solver employing the SIMPLE algorithm for pressure-velocity coupling) and scalarTransportFoam (standard advection-diffusion equation corresponding to equation 1). To implement the Robin boundary condition we follow [13].

When solving equation 1 at the pore-scale, we provide the following external boundary conditions:

\[ c(x = 0, y) = 1, \quad \frac{\partial c}{\partial x} \bigg|_{x=L} = 0, \]  

where \( x \) is the axial direction of the cell array and \( L \) is the domain length. We ensure the flow is in Stokes (viscous) regime by imposing a value of the Reynolds number \( \text{Re} < 10^{-3} \) everywhere. Steady-state results are then averaged over each cell and compared against prediction obtained from the ordinary differential equation (ODE):

\[ \frac{d}{dx} \left( V_x^e \langle c \rangle - D_{xx}^{\text{eff}} \frac{dc}{dx} \right) = -A\langle c \rangle, \]  

where \( V_x^e \) is the effective velocity in \( x \) and \( D_{xx}^{\text{eff}} \) is the axial component of the effective diffusivity tensor. Equation 59 is solved to spectral accuracy using the MATLAB® package Chebfun [24].

Choosing appropriate boundary conditions for equation 59 is not trivial, since we do not know the value of \( \langle c \rangle \) at \( x = 0 \). However, since our only objective is to evaluate the accuracy of this method, we just impose:

\[ \langle c \rangle(x = 0) = 1, \quad \frac{d\langle c \rangle}{dx} \bigg|_{x=L} = 0, \]  

and compare the results against fully developed (i.e., far from the inlet) pore-scale simulations with an appropriate rescaling. Therefore, all comparisons will be made dividing all values of \( \langle c \rangle \) obtained from pore-scale simulations with the value of \( \langle c \rangle \) at the 10th FCC cell, where the profile of \( c \) is well developed for all the simulations.

![Figure 2](image_url)  

Figure 2: Example results from a two-dimensional pore-scale simulation. For clarity, we show only a fraction of the FCC cells composing the computational domain.

We compute the coefficients in equation 59 using our novel solver from a single FCC cell. Fig. 3 shows the relevant fields arising from the solution of the cell problem. Notice that the eigenfunction \( \phi \) is Fig. 3a and the adjoint \( \phi^\dagger \) in Fig. 3b only differ for the direction of the advective component as expected from inspection of their governing equation.

Results from two pore-scale simulations are compared with solutions of equation 59 in Fig 4. Overall, the upscaling method provides excellent results, with little deviations from the pore-scale simulations. Notice that such agreement was obtained by rescaling the cell average concentration from the pore-scale simulations by an appropriate reference value (i.e., the value of an FCC cell in the asymptotic regime). Using this approach, we were able to test the accuracy of the method without an a complete knowledge of the external boundary conditions.
Figure 3: Results from the spectral and first order corrector solver for the FCC cell in the case $\text{Pe} = 100$, $\epsilon = 0.7$ and $\text{Da}_{II} = 962$. $u^*$ is the magnitude of $u$ and $\chi^*$ is the magnitude of $\chi$.

4.2. Parametric study - FCC array

We illustrate how the present method can be applied to large scale studies by studying the effect of Pe and $\text{Da}_{II}$ on the effective parameters of the homogenised transport equation. Results are presented in Figures 5, 6 and 7 for different porosities $\epsilon$. Furthermore, full numerical results are provided in the additional material.

We probe the range $\text{Da}_{II} \in [10^{-2}, 10^5]$ in order to capture both the limits tending to Neumann and Dirichlet boundary conditions. Effective parameters are scaled based on such limits, defining the 'primed' effective parameters as:

$$
\lambda' = \frac{\lambda - \lambda_N}{\lambda_D - \lambda_N}, \quad D' = \frac{D_{\text{eff}} - D_{\text{eff}}^N}{D_{\text{eff}}^D - D_{\text{eff}}^N}, \quad V' = \frac{V^* - V_N^*}{V_D^* - V_N^*},
$$

(61)

where the subscripts N and D indicate that the effective parameter has been calculated using Neumann or Dirichlet boundary conditions respectively. In the above equation, $\lambda_N = 0$ since it represents the non-reactive case.
Figure 4: Comparison of results from equation 59 against resolved pore-scale simulations. Here, $x$ is scaled with the length of an FCC cell such that the value of $x$ corresponds to the number of FCC cells.

Results from different values of $\epsilon$ show little variation in the profiles of $\lambda$, but reveal interesting behaviours for both the effective dispersion and velocity.

Specifically, the effective dispersion profiles do not show any consistent trend with the Péclet number, which indicates the complex interconnection between this and the Damköhler number on the effective transport properties. However, it can be seen that both $D_{xx}'$ and $D_{yy}'$ tend to occupy a larger range of values with decreasing porosity. This can be explained considering that the flow field becomes more tortuous when larger portions of the domain are occupied by the solid phase. Interestingly, we notice that the effective diffusion coefficient in reactive systems can be both larger or smaller with respect to the non-reactive case.

Another interesting feature predicted by this model, is a global minimum of the effective velocity in the range $Da_{II} \sim 10$ at high values of $\epsilon$ (maximum in $V_x'$). Such phenomenon is evident at low values of $\epsilon$ and $Pe$, where the effect of the reaction is stronger.

Overall, the results we presented lead to a better understanding of reactive flows through ordered arrays of cylinder and may provide useful hints for design of heat exchangers or catalysts.
Figure 5: Scaled effective parameters as a function of the microscopic parameters for $\varepsilon = 0.9$.

5. Conclusions

In this work, we presented a methodology for the upscaling of reactive transport in porous media based on the works of Allaire and Raphael [3] and Mauri [4]. Such upscaling procedure has been described in details for homogeneous boundary conditions and extended to simple non-homogeneous boundary conditions.

Furthermore, we implemented the method in the opensource library OpenFOAM® [22] and compared its predictions against fully resolved microscale simulations finding excellent agreement. This confirms the power and accuracy of homogenisation-based approaches to solve a range of ‘closure problems’.

Finally, we presented a parametric study of reactive transport in ordered arrays of cylinders to illustrate the usage of the proposed method and numerical code. We found that the effective parameters depend on the Péclet and Damköhler number in a complex manner and that the method is able to correctly recover the limiting cases of Dirichlet and Neumann boundary conditions.

While we restricted our numerical investigation to FCC configurations, the presented methodology and numerical code can be straightforwardly extended to any other geometry. In future works, we plan to use this method to study heat/mass transfer in random arrays of sphere and even homogeneous and wall bounded suspensions [25, 26].

From a theoretical point of view, future extension will also include the application to more complex, non-linear and electrokinetic boundary conditions [27]. These have important applications for electrokinetic energy conversion in...
Figure 6: Scaled effective parameters as a function of the microscopic parameters for $\epsilon = 0.7$.

nanofluidic channels [28].

As a final remark, we stress the fact we made our numerical code open source and freely available. This with the objective of extending the use of homogenisation-based techniques to a wider community and providing an "upscaling toolbox" with solid mathematical foundations.

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Figure 7: Scaled effective parameters as a function of the microscopic parameters for $\epsilon = 0.5$.

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