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On the Upscaling of Reaction-Transport Processes in Porous Media with Fast Kinetics

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Abstract

We show that for transport-reaction systems with fast kinetics (in the limit of thermodynamic equilibrium), conventional volume averaging for determining effective kinetic parameters applies only when the macroscopic variable approaches its equilibrium value. Even under such conditions, computing the effective mass transfer coefficient requires solving an eigenvalue problem, coupling the local microstructure problem with the global. Two examples, one involving a simple advection-dissolution problem and another a drying problem in a pore network, illustrate the theoretical predictions. Similar considerations apply in the case of finite kinetics, when the macroscale concentration approaches an equilibrium value. In that case, the effective kinetic parameter is not equal to the local, as typically assumed, but it becomes a function of the local Thiele modulus.

Introduction

Mass transport with heterogeneous chemical reaction in porous media is important in a variety of applications in the physical, chemical, and engineering sciences. Transport is typically by advection and diffusion, with reaction occurring at the (usually) disordered pore surface. As a result of reaction, the pore morphology may also evolve, with examples ranging from gas-solid reactions [1] to the acidizing of carbonate rocks [2], [3]. A particular class of problems of interest to this paper involves fast heterogeneous reactions, where local thermodynamic equilibrium applies [4].

This problem arises in various contexts, for example in the solubilization of trapped Non-Aqueous Liquid Phases (NAPL) in soils [5], [6], or in the drying of a porous medium [7], [8], where the concentration at the source/sink interface can be considered as constant. In many of these applications, mass transfer is driven by the flow of a liquid in a porous medium. For example, this is the case in the remediation by the injection of a solvent, of groundwater aquifers contaminated by organic chemicals (NAPLs). The NAPL in the aquifer is usually trapped by capillarity in the form of immobile, disconnected ganglia, which act as contaminant sources of a generally disordered geometry. A similar situation arises in related dissolution or precipitation processes, involving mass transport between the pore surface and the injected fluid. In these problems, the kinetics at the interface are fast, and one can proceed with the assumption of local thermodynamic equilibrium (for example, the use of Henry's law at the source interface).

In view of the complexity of the pore space and/or the source-sink geometry, and the need for workable models, an important topic pursued for several years has been the development of effective models to scale-up the process from the micro (pore) scale to the macro (continuum) scale. While the upscaling of conventional diffusion-reaction systems has been researched for some time [9], the upscaling of dissolution-type processes has been rather recent. Of particular relevance in this context is the work of Quintard and Whitaker [10], to be hereafter referred to as QW, who applied volume averaging to derive effective mass transfer coefficients for the dissolution of trapped NAPLs in a porous medium with a periodic microstructure. Implicit to their approach are two important assumptions, scale separation at the microscale, and small gradients of the volume-averaged variable at the pore-network

scale. When local thermodynamic equilibrium applies, however, as in the present work, this requires that the volume-averaged concentration must also be close to its thermodynamic value. It will be shown in this paper that in this case, the unit-cell problem for calculating effective coefficients involves, in addition to the microstructure, gradients of the macroscopic concentration, thereby resulting in the coupling of micro- and macro-scale problems.

Volume averaging is one of two main methods for upscaling. It is closely related to homogenization [11], with which it shares the same foundation. Pioneering work in volume averaging in porous media has been done by Whitaker [9]. An alternative approach involving ensemble averages is based on the method of moments, applied for example in [12] to derive Darcy-scale diffusion-reaction coefficients. Stochastic theories for reactive transport in various contexts [13, 14] have also been developed, where the emphasis is on the (macroscopic) permeability heterogeneity, thus representing upscaling over a larger scale, however. In this paper, we will restrict our interest to volume averaging as particularly applied in the above-cited work of QW.

For volume-averaging to be meaningful, the averages so obtained should not depend on the averaging volume itself. In general, this requirement can be translated into two conditions, that the length scale of the averaging volume (associated with a macroscopic length L) be sufficiently larger than the correlation length of the microstructure, λ ,

$$\epsilon_1 \equiv \frac{\lambda}{L} \ll 1 \quad (1)$$

and that the upscaled variable vary slowly at the small scale

$$\epsilon_2 \equiv \lambda |\nabla \langle C_D \rangle| \ll 1 \quad (2)$$

where $\langle C_D \rangle$ represents a dimensionless upscaled variable. The correlation length λ expresses the scale over which microstructure variables are correlated. The first condition is simply a manifestation of the Central Limit Theorem. Microstructure variables, however, involve not only the pore surface geometry, which is usually process-independent, but also process-dependent variables, such as the upscaled concentration. Then, satisfying condition (2) will depend in general on process parameters, and possibly space and time.

In conventional reaction-diffusion systems in homogeneous media, constraint (2) can be enforced, if among other parameters, the local Thiele modulus is small, namely if the kinetics are sufficiently slow [9]. In the dissolution-precipitation processes of fast kinetics, of primary interest to this paper, however, the condition of local thermodynamic equilibrium precludes the existence of a small dimensionless parameter, that ensures the validity of (1) and (2). It follows that upscaling of such processes is inherently non-local, constraint (2) being satisfied only in the limit when the upscaled concentration approaches its thermodynamic equilibrium value. We will show that even under this condition, however, micro- and macro-scale problems still remain coupled. A similar situation exists for conventional reaction-diffusion processes, when the kinetics are not necessarily slow and the process approaches an equilibrium state. In the latter limit, constraint (2) is satisfied, even though the local Thiele modulus is not necessarily small. It will be shown that in this case as well, the resulting effective parameter derives from the solution of a problem coupling both local and global scales.

The paper is organized as follows: First, we provide a brief review of the upscaling constraints of the type (2) for a typical diffusion-reaction system. In this we will also draw an analogy with two-phase flow in porous media. Then, using the methodology of QW we will derive a problem at the unit cell for the computation of the effective mass transfer coefficient, in processes where local thermodynamic equilibrium applies. This problem is found to be different than in QW, as it depends also on the gradients of the macroscale variable, and can be cast in terms of an eigenvalue problem. Two simple examples, one involving advection-dissolution and another involving drying in a pore network, will next be presented to illustrate the coupling between scales and to show the quantitative effect in case this coupling is neglected. Finally, similar ideas and an illustrative example will be applied to reaction-diffusion systems with fast kinetics, where an equilibrium state is approached.

A Brief Background

Problems involving transport, reaction or other physicochemical processes in porous media, are controlled by two competing processes, one local and one non-local. The local process does not involve spatial gradients, and although involving fluctuating (and possibly random) phenomena, such as reaction at disordered surfaces, it is generally a stationary process. In the example of diffusion with heterogeneous reaction, the local process is the chemical reaction. The non-local process involves spatial gradients. For the example cited, this is diffusion. In the above, we have used the term non-local in the sense of upscaling involving gradients. The ratio in the magnitude between local and non-local “forces” is expressed by a dimensionless parameter, which in a reaction-diffusion system is the micro-scale Thiele modulus

$$\phi_l = \sqrt{\frac{k_e}{a_V D}} \quad (3)$$

Here, k_e is the heterogeneous reaction kinetic parameter, a_V is the pore surface area per unit volume and D is the diffusion coefficient. Recognizing that for relatively homogeneous media the specific surface area scales inversely with the microscale, $a_V \sim 1/l$, equation (3) expresses the ratio in the speed of reaction to that of diffusion in the microscale. In general, for negligible small-scale gradients in the upscaled variable, which here is the volume-average concentration, diffusion must be fast at the small scale, compared to reaction. Then, the homogenization constraint becomes

$$\phi_l \ll 1 \quad (4)$$

As ϕ_l increases, it becomes increasingly difficult to satisfy (2). An explicit coupling between the two scales arises, leading to a non-local description, in general. On the other hand, gradients of the macroscale variable can be small, regardless of the value of ϕ_l , if the system happens to approach an asymptotic equilibrium state (where reaction will cease). Then, the problem acquires characteristics similar to the dissolution problem, where local thermodynamic equilibrium applies. A measure of the competition between reaction and diffusion, but at the macroscale, is the conventional Thiele modulus

$$\phi = \sqrt{\frac{k_e L}{D}} \approx \phi_l \sqrt{\frac{L}{l}} \quad (5)$$

This classical reaction engineering parameter is, thus, the product of two terms, one of which must be small, according to (4), and the other large, according to (1), for conventional upscaling to apply.

It is instructive to draw a comparison, at this point, with immiscible, two-phase displacements in porous media, also a well-studied topic [15]. Here, the local “force” is capillarity, which controls fluid-fluid interfaces and their partition in the pore space, while the non-local “forces” are viscous. The ratio between viscous and capillary forces at the microscale is expressed through the capillary number

$$Ca = \frac{q\mu l}{l^2} \left(\frac{l}{\gamma} \right) = \frac{q\mu}{\gamma} \quad (6)$$

where q is a typical flow velocity, μ denotes viscosity and γ is the interfacial tension. Capillarity dominates at the small scale and conventional upscaling is valid if

$$Ca \ll 1 \quad (7)$$

This is the immiscible flow counterpart of (4). As in the corresponding reaction-diffusion example, a macroscopic capillary number can also be defined [16]

$$Ca_L = Ca \left(\frac{L}{\sqrt{k}} \right) \sim Ca \left(\frac{L}{l} \right) \quad (8)$$

where $k \sim l^2$ is the permeability of the porous medium, thus providing the analogue of the macroscopic Thiele modulus (5).

Pore-scale modeling, as well as experimental results from two-phase displacements, have shown that viscous effects at the small scale can be neglected provided that Ca is small, e.g. $Ca < O(10^{-4} - 10^{-5})$. A manifestation of this is the amount of the capillarity-trapped displaced phase (the “residual oil saturation”, typically denoted by S_{or}). As shown in Fig. 1 (taken from [15]), for values satisfying the constraint $Ca < O(10^{-5})$, S_{or} is independent of Ca , indicating dominance of capillary over viscous forces at the small scale. It is in this region that the conventional use of rate-independent flow and capillary parameters (and the

associated upscaled description, e.g. see [15]) is valid. Increasing Ca leads to decreasing S_{or} , indicating that viscous forces become progressively stronger at the microscale to overcome the trapping capillary forces. In this domain, rigorous upscaling methods are yet to be developed.

The microscale process efficiency in reaction-diffusion systems, analogous to S_{or} , is the classical effectiveness factor, η , which is the ratio of the reaction rate including diffusion to the rate if diffusion were instantaneous. Typical experimental results for the variation of η with the macroscale Thiele modulus are shown in Fig. 2 (taken from [17])(note that, compared to Fig. 1, here the plot is with respect to a macroscale parameter). For the same reasons as in the immiscible displacement problem, we expect that conventional upscaling is valid only when η remains constant, which from Fig. 2 implies the approximate condition $\phi < 0.2$. For larger values of ϕ , the validity of the conventional description should be questioned, although such a description is routinely practiced. Taking a typical ratio of characteristic scales $\frac{l}{L} \sim O(10^{-2})$, equation (5) provides the constraint $\phi_l < O(10^{-2})$, which is similar but not identical to the constraint on the capillary number. This analogy between reaction-diffusion and immiscible flow in porous media parallels earlier work by Yortsos and Sharma [18] and was first pointed out in [19].

The problem of mass transfer by advection and diffusion in the presence of sources (or sinks), embedded in a porous medium, is similar to the above, but also entails a key difference. Here, if the kinetics at the interface are fast, local thermodynamic equilibrium (for example, the use of Henry's law, etc.) applies, and in effect the local Thiele modulus (or the local Damköhler number) is infinitely large. Thus in this case, by necessity, the condition for homogenization becomes that the average concentration must be close to its thermodynamic equilibrium value. Therefore, enforcing this condition requires knowledge of the actual value of the macroscopic average, the evolution of which is sought, in turn. As a result, the two scales cannot be separated a priori and determining effective parameters requires the solution of a coupled problem. In the next section, we will follow closely the methodology of QW, near the limit where scale separation exists, but will derive a unit-cell boundary value problem that differs from that in QW. This problem involves macroscale gradients of the upscaled variable and will be shown to lead to an eigenvalue problem coupling both scales.

Formulation

We briefly summarize the problem of dissolution of a stationary phase in porous media and the volume-averaging approach, following QW. Denote by subscript β the flowing aqueous phase, by γ the trapped hydrocarbon (NAPL) phase, and by σ the solid porous matrix (Fig. 3). Under the assumption of slow dissolution rates, phases γ and σ are of fixed and stationary geometry. The pore-scale boundary value problem is described by an advection-diffusion equation

$$\frac{\partial C_\beta}{\partial t} + \nabla \cdot (\mathbf{v} C_\beta) = \mathcal{D} \nabla^2 C_\beta \quad (9)$$

in which C_β is the concentration of the dissolving species, t is time, $\mathbf{v}$ is the fluid velocity in the β -phase, and $\mathcal{D}$ is molecular diffusivity, considered constant. The solute is assumed at a sufficiently small concentration to not affect properties, such as density and viscosity.

Under the condition of thermodynamic equilibrium at the source interface, the solute concentration is constant and equal to its equilibrium value, C_{eq} ,

$$C_\beta = C_{eq} \quad \text{on} \quad A_{\beta\gamma} \quad (10)$$

where $A_{\beta\gamma}$ is the interface between trapped and flowing phases. The other boundary condition is zero flux at the interface $A_{\beta\sigma}$, between aqueous and solid phases

$$\mathbf{n}_{\beta\sigma} \cdot \nabla C_\beta = 0 \quad \text{on} \quad A_{\beta\sigma} \quad (11)$$

where $\mathbf{n}_{\beta\sigma}$ is the unit normal vector directed from the β -phase toward the σ -phase.

Define, next, the intrinsic volume average of concentration in the β -phase,

$$\langle C_\beta \rangle^\beta = \frac{1}{V_\beta} \int_{V_\beta} C_\beta dV \quad (12)$$

which is the quantity of interest, and where V_β is the β -phase averaging volume. Standard upscaling proceeds by decomposing the point concentration into its intrinsic average and a fluctuation

$$C_\beta = \langle C_\beta \rangle^\beta + C'_\beta \quad (13)$$

Following QW, and based on the assumption of uniform porosity and constant volume fractions, the governing equations for the average and the spatial deviation concentration read as follows

$$\begin{aligned} \epsilon_\beta \frac{\partial \langle C_\beta \rangle^\beta}{\partial t} + \langle \mathbf{v} \rangle^\beta \cdot \nabla \langle C_\beta \rangle^\beta + \nabla \cdot \langle \mathbf{v}' C'_\beta \rangle = \\ \epsilon_\beta \mathcal{D} \nabla^2 \langle C_\beta \rangle^\beta + \frac{\mathcal{D}}{\mathcal{V}} \nabla \cdot \left[\int_{A_{\beta\gamma}} \mathbf{n}_{\beta\gamma} C'_\beta dA + \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} C'_\beta dA \right] \\ + \frac{\epsilon_\beta \mathcal{D}}{V_\beta} \left[\int_{A_{\beta\gamma}} \mathbf{n}_{\beta\gamma} \cdot \nabla C'_\beta dA + \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \nabla C'_\beta dA \right] \end{aligned} \quad (14)$$

and

$$\begin{aligned} \epsilon_\beta \frac{\partial C'_\beta}{\partial t} + \langle \mathbf{v} \rangle^\beta \cdot \nabla C'_\beta + \mathbf{v}' \cdot \nabla \langle C'_\beta \rangle^\beta - \nabla \cdot \langle \mathbf{v}' C'_\beta \rangle = \\ \epsilon_\beta \mathcal{D} \nabla^2 C'_\beta - \frac{\mathcal{D}}{\mathcal{V}} \nabla \cdot \left[\int_{A_{\beta\gamma}} \mathbf{n}_{\beta\gamma} C'_\beta dA + \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} C'_\beta dA \right] \\ - \frac{\mathcal{D}}{\mathcal{V}} \left[\int_{A_{\beta\gamma}} \mathbf{n}_{\beta\gamma} \cdot \nabla C'_\beta dA + \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \nabla C'_\beta dA \right] \end{aligned} \quad (15)$$

where $\mathcal{V}$ is the averaging volume and ϵ_β is the volume fraction of the β -phase. The respective boundary conditions for the fluctuation become

$$C'_\beta = C_{eq} - \langle C_\beta \rangle^\beta \quad \text{on } A_{\beta\gamma} \quad (16)$$

and

$$\mathbf{n}_{\beta\sigma} \cdot \nabla C'_\beta = -\mathbf{n}_{\beta\sigma} \cdot \nabla \langle C_\beta \rangle^\beta \quad \text{on } A_{\beta\sigma} \quad (17)$$

Up to this point, the analysis is identical to QW.

Now, for the solution of (15)-(17), QW take the decomposition

$$C'_\beta = \mathbf{b}_f \cdot \nabla \langle C_\beta \rangle^\beta + s_\beta (C_{eq} - \langle C_\beta \rangle^\beta) \quad (18)$$

with the understanding that the macroscopic concentration and its gradient are linearly independent. However, implicit in the derivation that follows, and which allows to simplify

the equations considerably, is the important assumption that the intrinsic average varies little over the scale of the microstructure. In other words, that constraint (2) is applicable. It was pointed out above, that in the particular problem here, this is tantamount to assuming $\langle C_\beta \rangle^\beta \rightarrow C_{eq}$. In this limit, however, the macroscopic concentration and its gradient are *not* independent. To demonstrate this point consider the averaged equation in this limit and at steady-state. Then, for sufficiently large distances, $\langle C_\beta \rangle^\beta$ approaches its equilibrium value, C_{eq} , as an exponential function of x , where x is the coordinate aligned with the main flow direction, e.g. as

$$\langle C_\beta \rangle^\beta = C_{eq} - A \exp(-ax) \quad (19)$$

Here, A is a positive constant, and $a > 0$ is the non-zero positive root of a quadratic, involving among other parameters, the effective mass-transfer coefficient α , the determination of which is sought. Equation (19) shows that in the limit, where homogenization is expected to apply, the ratio $\frac{|\nabla \langle C_\beta \rangle^\beta|}{(C_{eq} - \langle C_\beta \rangle^\beta)}$ is a constant, indicating that the two variables are indeed not independent.

Given this observation, therefore, we will proceed with a substitution different than (18), by taking

$$C'_\beta = s_\beta (C_{eq} - \langle C_\beta \rangle^\beta) \quad (20)$$

For simplicity, in the following we will also assume that the flow velocity $\mathbf{v}$ is constant. Even though unrealistic for a typical porous medium, this assumption facilitates the presentation and allows for a simple illustration of the main points of this paper. It also does not detract from the generality of the conclusions to be reached, and can be relaxed if needed in the more general case. Using this assumption, introducing (20) into (15) and noting that the transient term is small, we then obtain the following problem for the closure variable s_β ,

$$\left[\mathbf{v}_\beta + 2\mathcal{D} \frac{\nabla \langle C_\beta \rangle^\beta}{(C_{eq} - \langle C_\beta \rangle^\beta)} \right] \cdot \nabla s_\beta - \left[\mathbf{v}_\beta \cdot \frac{\nabla \langle C_\beta \rangle^\beta}{(C_{eq} - \langle C_\beta \rangle^\beta)} - \mathcal{D} \frac{\nabla^2 \langle C_\beta \rangle^\beta}{(C_{eq} - \langle C_\beta \rangle^\beta)} \right] s_\beta = \mathcal{D} \nabla^2 s_\beta - \epsilon_\beta^{-1} \alpha \quad (21)$$

where $\mathbf{v}_\beta$ is the intrinsic velocity in the β -phase. Parameter α is given by the following expression

$$\alpha = \frac{\mathcal{D}}{\mathcal{V}} \left[\int_{A_{\beta\gamma}} \mathbf{n}_{\beta\gamma} \cdot \nabla s_\beta dA + \nabla \cdot \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} s_\beta dA - \frac{\nabla \langle C_\beta \rangle^\beta}{(C_{eq} - \langle C_\beta \rangle^\beta)} \cdot \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} s_\beta dA \right] \quad (22)$$

and includes a term for the interfacial transport between the dissolving (γ)-phase and the flowing aqueous (β)-phase. In deriving the above expression we assumed constant volume fractions and took account of the following boundary conditions

$$s_\beta = 1 \quad \text{on} \quad A_{\beta\gamma} \quad (23)$$

$$\mathbf{n}_{\beta\sigma} \cdot \nabla s_\beta + \mathbf{n}_{\beta\sigma} \cdot \frac{\nabla \langle C_\beta \rangle^\beta}{C_{eq} - \langle C_\beta \rangle^\beta} (1 - s_\beta) = 0 \quad \text{on} \quad A_{\beta\sigma} \quad (24)$$

These are supplemented with the self-consistency condition

$$\langle s_\beta \rangle^\beta = 0 \quad (25)$$

Both the boundary value problem (21) and the boundary condition (24) differ from those presented in QW. In the latter, only the first term in the LHS of (21) and the first term on the RHS of (22) are retained. In deriving their closure problem, QW neglect all terms associated with the gradients of $\langle C_\beta \rangle^\beta$, as being small within the microstructure. While this is indeed true for conventional upscaling, neglecting them in (21), (22) or (24), in fact requires the stronger condition that the ratio between the gradients and the deviation from the equilibrium concentration is small, namely that

$$\left| \frac{\nabla \langle C_\beta \rangle^\beta}{C_{eq} - \langle C_\beta \rangle^\beta} \right| \ll 1 \quad \text{and} \quad \left| \frac{\nabla^2 \langle C_\beta \rangle^\beta}{C_{eq} - \langle C_\beta \rangle^\beta} \right| \ll 1 \quad (26)$$

A comparison with (19) shows that (26) does not in general apply, when macroscopic equilibrium is approached, even though this is the very limit where homogenization is to be valid.

In this limit the averaged equation is in turn expressed in terms of the simple steady-state expression

$$\mathbf{v} \cdot \nabla \langle C_\beta \rangle^\beta = \epsilon_\beta \mathcal{D} \nabla^2 \langle C_\beta \rangle^\beta + \alpha (C_{eq} - \langle C_\beta \rangle^\beta) \quad (27)$$

One notes that missing from this equation is the effective dispersion tensor, which cannot be obtained with the above formulation in this limit. If expressed in terms of a conventional advection-dispersion-reaction equation, however, the above can be re-written as

$$\mathbf{v} \cdot \nabla \langle C_\beta \rangle^\beta = \nabla \cdot (\mathcal{D}_\beta^* \nabla \langle C_\beta \rangle^\beta) + \alpha_{eff} (C_{eq} - \langle C_\beta \rangle^\beta) \quad (28)$$

where $\mathcal{D}_\beta^*$ is the effective macroscopic dispersion coefficient, obtained independently (for example using QW), and the effective reaction rate coefficient α_{eff} is

$$\alpha_{eff} = \alpha + \frac{\epsilon_\beta \mathcal{D} \nabla^2 \langle C_\beta \rangle^\beta - \nabla \cdot (\mathcal{D}_\beta^* \nabla \langle C_\beta \rangle^\beta)}{C_{eq} - \langle C_\beta \rangle^\beta} \quad (29)$$

Given α , the second term on the RHS of (29) can be evaluated by taking the limit of thermodynamic equilibrium and solving the macroscopic problem to obtain the ratios involving the macroscopic concentration gradients. In the general case, of course, one needs to also include in the problem for α the velocity fluctuations, which were omitted here. In the particular case where there is no flow field and the dispersion tensor becomes a scalar, we find, from this approach

$$\alpha_{eff} = \frac{\mathcal{D}_\beta^* \alpha}{\epsilon_\beta \mathcal{D}} \quad (30)$$

The closure problem (21)-(28) is an eigenvalue problem for α . In the absence of the new terms identified here (which consists of the entire LHS of (21), this problem is not an eigenvalue problem, and can be directly solved using the transformation

$$s_\beta = 1 + \alpha \psi \quad (31)$$

as shown by QW. Here, ψ satisfies the steady-state diffusion equation with a constant source term. Then, the solution for α is simply $\alpha = -\frac{1}{\langle \psi \rangle_\beta}$. Local and global problems are uncoupled. However, this is not the case when the gradient terms in (21) are retained. Then, the problem becomes an eigenvalue problem for α , coupling the two scales. We can illustrate this in the limit $\mathbf{v} = 0$ (for example in a drying application) and when the closure variable s_β does

not vary in the direction of the gradient of the concentration (namely when macroscopic equilibrium is approached). Using (21), (27) and (31) leads now to the eigenvalue problem

$$\mathcal{D}\nabla^2\psi = -\epsilon_\beta^{-1}\alpha\psi \quad (32)$$

with the homogeneous boundary conditions

$$\psi = 0 \quad \text{on} \quad A_{\beta\gamma} \quad (33)$$

and

$$\mathbf{n}_{\beta\sigma} \cdot \nabla\psi - \mathbf{n}_{\beta\sigma} \cdot \frac{\nabla\langle C_\beta \rangle^\beta}{C_{eq} - \langle C_\beta \rangle^\beta} \psi = 0 \quad \text{on} \quad A_{\beta\sigma} \quad (34)$$

Note also the implicit dependence on α in the second term in (34). The solution of this eigenvalue problem generally gives a discrete spectrum, the smallest eigenvalue of which is the desired value. Two illustrative examples will be shown below.

We are, thus, led to the conclusion that in the very limit where it is expected to be valid, the volume average methodology for processes with fast reactions, gives rise to additional terms, such as $\frac{\nabla\langle C_\beta \rangle^\beta}{C_{eq} - \langle C_\beta \rangle^\beta}$ and $\frac{\nabla^2\langle C_\beta \rangle^\beta}{C_{eq} - \langle C_\beta \rangle^\beta}$, which cannot be a priori discarded, thus coupling micro- and macro-scales.

Two Illustrative Examples

In this section, we will consider two illustrative examples, one involving a simple geometry, where advection diffusion and dissolution occur, and another involving drying in a pore network, where transport is by diffusion alone.

A simple advection-dissolution problem

Consider a structureless, two-dimensional “porous” medium, consisting of the strip $(0, \infty)$ and $(0, l)$ in the coordinate directions X and Y , respectively (Fig. 4). The dissolving interface (phase γ) is at $Y = 0$, while the solid interface (phase σ) is at $Y = l$. In the present example, the microstructure consists of the line $0 < Y < l$, hence volume averaging of the concentration means integrating over Y in $(0, l)$. As discussed above, the aqueous phase is

assumed to flow at a constant velocity $v_X = U$. For further simplicity, we will also consider only transverse diffusion and neglect longitudinal dispersion. In appropriate dimensionless notation, where all lengths are scaled with l , the steady-state advection-diffusion equation for this problem reads

$$\frac{\partial c}{\partial x} = \frac{1}{\text{Pe}} \frac{\partial^2 c}{\partial y^2} \quad (35)$$

where c is the dimensionless concentration of the dissolving species in the aqueous phase, and we introduced the Peclet number, $\text{Pe} = Ul/\mathcal{D}$. Using the corresponding boundary conditions

$$c = 1 \quad \text{at} \quad y = 0 \quad (36)$$

$$c = 0 \quad \text{at} \quad x = 0 \quad (37)$$

and

$$\frac{\partial c}{\partial y} = 0 \quad \text{at} \quad y = 1 \quad (38)$$

the solution of (35)-(38) is easily found

$$c(y, \xi) = 1 - 2 \sum_{n=0}^{\infty} \frac{e^{-a_n^2 \xi}}{a_n} \sin(a_n y) \quad (39)$$

Here $a_n = \frac{(2n+1)\pi}{2}$ and we introduced the rescaled variable $\xi = x/\text{Pe}$. Volume averaging of the concentration, which here is tantamount to transverse averaging across the main flow direction, then, yields

$$\langle c \rangle = 1 - 2 \sum_{n=0}^{\infty} \frac{e^{-a_n^2 \xi}}{a_n^2} \quad (40)$$

The volume-averaged macroscopic equation is read directly from the steady-state version of (28), in the absence of longitudinal dispersion, by taking $\mathcal{D}_\beta^* = \mathcal{D}$ and $\epsilon_\beta = 1$. We find

$$\frac{\partial \langle c \rangle}{\partial x} = \frac{\alpha l}{U} (1 - \langle c \rangle) \quad (41)$$

Finally, introducing (40) into (41) gives the following expression for the large-scale dimensionless mass transfer coefficient,

$$\alpha_D(\xi) \equiv \frac{\alpha l^2}{\mathcal{D}} = \frac{\sum_{n=0}^{\infty} e^{-a_n^2 \xi}}{\sum_{n=0}^{\infty} \frac{e^{-a_n^2 \xi}}{a_n^2}} \quad (42)$$

This result is plotted in Fig. 5. As expected, the effective mass transfer coefficient is in general non-local as it also depends on the distance from the origin ξ . At large ξ , which depending on Pe can be equivalent to several microstructure lengths, α_D approaches its asymptotic value, $\alpha_{D,\infty}$,

$$\alpha_D \rightarrow \alpha_{D,\infty} = \frac{\pi^2}{4} \quad (43)$$

Note that in that limit, we also have the condition $\langle c \rangle \rightarrow 1$, namely, the approach of the volume-averaged concentration to its equilibrium state.

The same result can be obtained from the solution of the new closure problem (21)-(25), derived above. For this, we will neglect again longitudinal diffusion in favor of transverse diffusion. In the same dimensionless notation, equation (21) reads

$$\frac{\partial s}{\partial \xi} - \frac{\frac{\partial \langle c \rangle}{\partial \xi}}{(1 - \langle c \rangle)} s = \frac{\partial^2 s}{\partial y^2} - \alpha_D \quad (44)$$

where we dropped subscript β for simplicity, have taken $\epsilon_\beta = 1$, and introduced the dimensionless mass transfer coefficient

$$\alpha_D = -\frac{\partial s}{\partial y} \Big|_{y=0} \quad (45)$$

The corresponding boundary conditions become

$$s = 1 \quad \text{at} \quad y = 0 \quad (46)$$

$$\frac{\partial s}{\partial y} = 0 \quad \text{at} \quad y = 1 \quad (47)$$

and the self-consistency condition is

$$\int_0^1 s dy = 0 \quad (48)$$

Consider now the solution when $\xi \gg 1$, which is the limit that must be taken in the volume-averaging approach, for the microstructure variable s to be independent of ξ . Taking into account the macroscale relation $\frac{\partial \langle c \rangle}{\partial \xi} = -(1 - \langle c \rangle) \frac{\partial s}{\partial y} \big|_{y=0}$, and using the substitution $s = 1 + \alpha_D \psi$, we obtain the eigenvalue problem

$$\psi'' = -\alpha_D \psi \quad (49)$$

with boundary conditions

$$\psi = 0 \quad \text{at} \quad y = 0 \quad \text{and} \quad \psi' = 0 \quad \text{at} \quad y = 1 \quad (50)$$

The eigenvalues of this problem are readily found to be

$$\alpha_D^{(n)} = \frac{(2n+1)^2 \pi^2}{4} \quad n = 0, \pm 1, \pm 2, \dots \quad (51)$$

The smallest eigenvalue ($n = 0$) gives the correct previous result for the dimensionless mass transfer coefficient, namely $\alpha_D^0 = \alpha_{D,\infty} = \frac{\pi^2}{4}$. The expression for s is obtained from the self-consistency condition and reads

$$s = 1 - \frac{\pi}{2} \sin\left(\frac{\pi y}{2}\right) \quad (52)$$

Thus, the solution of the eigenvalue problem coincides with the exact result, in the limit where it is indeed expected to be applicable. By contrast, in the corresponding closure problem of QW, the left-hand-side of (44) is neglected, in which case s has the simple solution

$$s = 1 - 3y + \frac{3y^2}{2} \quad (53)$$

The QW effective mass transfer coefficient for this problem is obtained from (53) and reads, $\alpha_{D,\infty} = 3$, a value which is larger than the true by about 25%.

Drying in a pore network

The second example to illustrate the above is drying of a liquid in a pore network. In recent years, many pore-network studies of drying have been conducted, where the effect

of various factors has been addressed (e.g. [7, 20]). In this example, we are interested in computing the effective mass transfer rate during drying. The motivation for this problem also arises from our previous study [8], where an effective continuum model was postulated.

For the purposes of this example, we will simplify the physical description by considering the often-used pore-network approximation. We take the porous medium to be represented as a regular network of bonds (pore throats) and sites (pore bodies). A liquid phase is randomly distributed in the sites of the pore network. All volume is assigned to sites, hence the liquid undergoing evaporation resides on sites only, which it fully occupies, for the sake of this example. Transport of vapor occurs by diffusion in the gas phase, across adjacent sites connected by bonds. For convenience, all bonds are taken with the same transport properties. Effects of convection, temperature, countercurrent diffusion, etc., are neglected. As is conventional in these types of problems, variables are defined in the sites of the lattice, over which the governing equations are also discretized. Due to the limited accessibility of the network, percolation phenomena are possible, and for the gas phase to be macroscopically connected, the fraction of sites occupied by the liquid must be below the value $1 - p_c$, where p_c is the site-percolation threshold.

Because of the assumed thermodynamic equilibrium at the liquid interface, the drying problem also belongs to the same class of fast interfacial kinetics, hence, as pointed out above, a volume-averaged description is generally non-local, except in places where the macroscopic vapor concentration approaches its equilibrium value. In dimensionless notation, the corresponding macroscale problem at steady-state reads from (27) as follows

$$\frac{d^2 \langle c \rangle}{dx^2} = \alpha_D (\langle c \rangle - 1) \quad (54)$$

where the dimensionless mass transfer coefficient is, now,

$$\alpha_D = \frac{\alpha l^2}{\epsilon_\beta \mathcal{D}} \quad (55)$$

the porosity ϵ_β corresponds to the accessible porosity of the gas phase (excluding trapped regions) and lengths have been scaled with the microscale l . The solution of (54) at large x has an exponential behavior similar to (19), with $a = \sqrt{\alpha_D}$. Substituting in (21) then leads to

$$-\alpha_D s_\beta = \nabla_D^2 s_\beta - \alpha_D \quad (56)$$

where we have considered that near the equilibrium limit, s_β is independent of x . For the solution of this problem, we use again the transformation $s_\beta = 1 + \alpha_D \psi$, which leads to

$$\nabla_D^2 \psi = -\alpha_D \psi \quad (57)$$

Solving the problem on the pore network requires discretizing the Helmholtz equation (57) over the lattice sites. In this context, therefore, only the boundary condition at the liquid-gas interface, equation (23), will be utilized. Thus, the eigenvalue problem is given by equation (57), valid over the gas-occupied sites, accompanied with the boundary condition $\psi = 0$ in liquid-occupied sites. This problem is a novel eigenvalue problem for the Laplace operator, in a region with boundaries randomly distributed over the lattice. It has some similarities with the classical problem in statistical physics of Anderson localization [21], but it is not the same. The problem was solved over a square lattice, which represents a cross-section of the pore-network in a direction perpendicular to x . The numerical procedure used will be described elsewhere.

Numerical results for a lattice of dimensions 40×40 are shown in Figure 6. In the figure, we plot the smallest eigenvalue obtained as a function of the liquid saturation S_l (fraction of sites occupied by the liquid), for various different realizations of the microstructure. The small lattice size reflects the computational cost in finding the eigenvalues in this random lattice problem, and it is itself reflected in the scatter shown in the figure. We expect a decrease of the scatter and the approach to a limiting curve as the lattice size increases. Plotted also are the results corresponding to QW for the same liquid configurations. These results have smaller scatter, and also much smaller computational cost. The approach of the QW results to a limiting deterministic curve as the lattice size increases was verified in simulations using a 400×400 lattice. Both sets of data show that α_D approaches zero at $S_l = 0$ and that it increases as S_l increases. In view of (55), however, the dimensional coefficient α would eventually decrease, at higher values of S_l , given that the accessible fraction of the gas phase ϵ_β decreases with S_l and vanishes at the percolation threshold. Both these limiting results are to be expected. We should remark that in Figure 6, we do

not mean to offer a comparison between the present theory and that of QW. For such a comparison it is necessary to evaluate α_{eff} which enters in equation (28). Although rather straightforward for our problem, which requires only the evaluation of the effective diffusion coefficient, this is a bit more elaborate for the QW formulation, for which the two additional vectors $\mathbf{u}$ and $\mathbf{d}$, entering in their theory, must be computed. This was not attempted here.

The Case of Finite Kinetics and Approach to an Equilibrium State

In the previous sections we investigated the application of volume averaging to the case of advection-reaction processes with fast kinetics, where the reactant (solute) concentration at the source remains constant and equal to its thermodynamic equilibrium value. We showed the following results: that in general a non-local description is necessary, that volume averaging in the conventional sense is possible only when the macroscopic variable approaches an equilibrium state, but that even under such conditions, the microscale problem to be solved is coupled with the macroscale. In the section to follow, we will extend these concepts to the case where the kinetics at the interface are not necessarily fast, but the macroscopic concentration does approach an equilibrium state.

One such problem of interest is steady-state advection with a first-order, heterogeneous reaction at the pore surface, which we will take to consume the injected species. The homogenization of a related problem but with transient diffusion (instead of advection) and reaction has been discussed in detail in Whitaker [9]. Under the two conditions of negligible transients and small local Thiele modulus (which is the earlier postulated condition (4)), the effective, macroscopic equation is the standard reaction-diffusion equation, where the effective kinetic parameter is identical to the local. As a result, there is no need to solve a boundary-value problem at the microscale for obtaining the effective kinetic coefficient. Now, consider a corresponding problem in which an equilibrium state is reached, for example, in the case when an injected reactant is ultimately fully consumed, not necessarily under slow kinetics. Under these conditions, and for the same reasons as in the above, the gradients of the macroscale concentration are not necessarily small compared to the actual values of the concentration, hence conventional homogenization does not apply.

To proceed, we follow the previous approach and first derive equations for the average

and the fluctuation. The analysis parallels closely [9], thus details will be omitted. To obtain the closure problem, however, we will take

$$C'_\beta = s_\beta \langle C_\beta \rangle^\beta \quad (58)$$

which again differs from the conventional (e.g. see Whitaker[9]). This leads to the following closure problem for s_β ,

$$\left[\mathbf{v}_\beta - 2\mathcal{D} \frac{\nabla \langle C_\beta \rangle^\beta}{\langle C_\beta \rangle^\beta} \right] \cdot \nabla s_\beta + \left[\mathbf{v}_\beta \cdot \frac{\nabla \langle C_\beta \rangle^\beta}{\langle C_\beta \rangle^\beta} - \mathcal{D} \frac{\nabla^2 \langle C_\beta \rangle^\beta}{\langle C_\beta \rangle^\beta} \right] s_\beta = \mathcal{D} \nabla^2 s_\beta - \epsilon_\beta^{-1} \alpha \quad (59)$$

where we have again neglected velocity variations, and where we have defined

$$\alpha = \frac{\mathcal{D}}{\mathcal{V}} \left[\nabla \cdot \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} s dA + \frac{\nabla \langle C_\beta \rangle^\beta}{\langle C_\beta \rangle^\beta} \cdot \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} s dA \right] - a_v k_e \quad (60)$$

This problem is to be solved subject to periodicity, the self-consistency condition, and the boundary condition

$$\mathbf{n}_{\beta\sigma} \cdot \nabla s_\beta + \left[\mathbf{n}_{\beta\sigma} \cdot \frac{\nabla \langle C_\beta \rangle^\beta}{\langle C_\beta \rangle^\beta} + \frac{k_e}{\mathcal{D}} \right] (1 + s_\beta) = 0 \quad \text{on } A_{\beta\sigma} \quad (61)$$

The corresponding effective equation, under conditions of steady-state advection and reaction reads now

$$\mathbf{v} \cdot \nabla \langle C_\beta \rangle^\beta = \epsilon_\beta \mathcal{D} \nabla^2 \langle C_\beta \rangle^\beta - \alpha \langle C_\beta \rangle^\beta \quad (62)$$

Given that the solution approaches an equilibrium state, we have a similar exponential decay as previously, $\langle C_\beta \rangle^\beta \sim A \exp(-ax)$. Then, the ratios involving the gradient terms in (59) cannot be neglected, unless $a \ll 1$, which however, coincides with the condition (4) of small Thiele modulus. Hence, in the general problem, even under the condition of slow variation of the macroscopic concentration, the effective kinetic parameter must be determined from a problem coupling local and global problems. The solution to the latter is demonstrated below with a simple example.

A simple advection-reaction problem

Consider the same geometry as in the dissolution problem (Fig. 4), with a first order reaction that acts as a sink at the $Y = 0$ boundary. A fluid is injected at $X = 0$ with constant concentration C_0 and at a uniform velocity U in the x -direction. The steady-state advection-diffusion equation, with negligible longitudinal diffusion and uniform velocity is, in appropriate dimensionless notation, the same as before

$$\frac{\partial c}{\partial x} = \frac{1}{\text{Pe}} \frac{\partial^2 c}{\partial y^2} \quad (63)$$

where c is normalized with respect to the injected concentration C_0 . The corresponding boundary conditions are

$$c = 1 \quad \text{at} \quad x = 0 \quad (64)$$

$$\frac{\partial c}{\partial y} = 0 \quad \text{at} \quad y = 1 \quad (65)$$

and

$$\frac{\partial c}{\partial y} = \frac{k_e l}{D} c \quad \text{at} \quad y = 0 \quad (66)$$

where we recognize the small-scale Thiele modulus $\phi_l^2 = \frac{k_e l}{D}$. Straightforward calculations show that the solution of (63) is

$$c = 2 \sum_{n=1}^{\infty} e^{-\alpha_n^2 \xi} \frac{(\phi_l^4 + \alpha_n^2) \cos(\alpha_n(1-y)) \sin \alpha_n}{(\phi_l^4 + \alpha_n^2) + \phi_l^2} \frac{1}{\alpha_n} \quad (67)$$

where ξ was introduced in the previous section, and α_n is the n^{th} positive root of the transcendental equation

$$\alpha \tan \alpha = \phi_l^2 \quad (68)$$

The volume-averaged macroscopic equation can be derived in a manner similar to equation (41), considering again that averaging is performed along the y -direction. We obtain,

$$\frac{\partial \langle c \rangle}{\partial x} = -\frac{k_e}{U} \langle c \rangle (1 + s|_{y=0}) \quad (69)$$

where $1 + s|_{y=0} = \frac{c|_{y=0}}{\langle c \rangle}$. In the above, one recognizes an effective Damköhler number, Da ,

$$\text{Da}(x) \equiv \frac{k_{eff}}{U} = \frac{k_e}{U} (1 + s|_{y=0}) \quad (70)$$

given in terms of the microscale variable s , which is in general non-local. Now, given the expression for c , one can determine the effective kinetic coefficient, and hence the effective Thiele modulus $\phi^2 = \frac{k_{eff}l}{D}$, by evaluating $\langle c \rangle$ and $c|_{y=0}$. We find

$$\phi^2 = \frac{\sum_{n=1}^{\infty} e^{-\alpha_n^2 \xi} \frac{(\phi_l^4 + \alpha_n^2)}{(\phi_l^4 + \alpha_n^2) + \phi_l^2} \sin^2 \alpha_n}{\sum_{n=1}^{\infty} e^{-\alpha_n^2 \xi} \frac{(\phi_l^4 + \alpha_n^2)}{(\phi_l^4 + \alpha_n^2) + \phi_l^2} \frac{\sin^2 \alpha_n}{\alpha_n^2}} \quad (71)$$

The solution of (71) is plotted in Fig. 7 as a function of the distance ξ . As in the example with the fast kinetics described previously, the effective coefficient is non-local. As the equilibrium state is reached, it approaches the asymptotic value

$$\phi \rightarrow \phi_{\infty} = \alpha_1 \quad (72)$$

where α_1 is the smallest positive root of (68). Interestingly, the latter depends on ϕ_l and gives

$$\phi_{\infty} \tan \phi_{\infty} = \phi_l^2 \quad (73)$$

Fig. 8 shows the variation of ϕ_{∞} with ϕ_l . We note that at small ϕ_l , we have the linear relationship $\phi_{\infty} = \phi_l$, as expected from the conventional theory. Indeed, in this limit (73) gives $\phi_{\infty} \approx \phi_l$, which leads to the classical result

$$k_{eff} = k_e \quad (74)$$

However, as ϕ_l increases, the effective Thiele modulus becomes smaller than ϕ_l , and saturates at the value $\pi/2$, as $\phi_l \rightarrow \infty$. The effective kinetic constant eventually becomes independent of the actual.

The same predictions can be reached by solving the eigenvalue problem (59) instead. For the sake of brevity, this will not be attempted here. It is worthwhile to note, however, that a behavior qualitatively similar to the above, and Fig. 8, is obtained if one were to follow the well-known approach in advection-reaction systems (e.g. [17]), where mass transport to the reacting surface is through steady-state diffusion across a boundary layer of thickness l . By equating diffusive and reaction fluxes, one finds the following well-known result

$$\phi^2 \equiv \frac{k_{eff}l}{\mathcal{D}} = \frac{\phi_l^2}{1 + \phi_l^2} \quad (75)$$

expressing the effective macroscopic parameter in terms of the microscale Thiele modulus. Equation (75) has a qualitatively similar behavior with ϕ_∞ above, namely the linear scaling $\phi = \phi_l$, at small ϕ_l , and the approach to an asymptotic value (here equal to 1) at large ϕ_l . However, both the variation with ϕ_l and the asymptotic value predicted are different compared to the problem discussed above (see Fig. 8), suggesting that one cannot circumvent the solution of the more complex problem. We expect a similar difference for the more general case, as well.

Concluding remarks

In this paper we showed that for advection-reaction systems with fast kinetics (at the limit of thermodynamic equilibrium), as, for example, in dissolution-type processes, conventional volume averaging does not apply, except in the limit where the macroscopic variable approaches its equilibrium value. While this is not unexpected, and in fact, it is implied in various previous works, the limit where the macroscale variable approaches thermodynamic equilibrium can still be homogenized by volume averaging. What is interesting is that the solution for the effective parameters in this case results from a closure problem, where the microscale and the macroscale are coupled. In this limit, the coupling is only algebraic and results into a generally non-linear eigenvalue problem for the effective kinetic parameter. This result is different from the conventional, as for example described in QW. Two examples, one involving a simple advection-dissolution problem and another a drying problem in a pore network, verify the theoretical predictions.

We also showed that systems with finite kinetics can also be homogenized in the limit where an equilibrium state is approached, even though the local Thiele modulus is not small. The analysis of a simple example presented reveals, in fact, that the effective kinetic parameter is not the same as the kinetic constant for the heterogeneous reaction, but it is a function of the local Thiele modulus itself, eventually saturating at large values of the latter. Similar results are expected for more complex microstructures. The limiting behavior mimics that of a simple advection-reaction problem, where diffusion is across a constant boundary layer. While qualitatively similar, however, the precise dependence requires the solution of an eigenvalue problem, which was derived above.

Given that the process under consideration is very near equilibrium, the utility of the above results can be questioned. In response we claim that these do yield the correct results for the case when homogenization is expected to apply. For tackling the more general problem, where the process is far from equilibrium and the homogenization constraints do not apply, different approaches are needed. Some have already appeared in the literature involving integro-differential equations, moment expansions and/or non-local parameters. An alternative approach of some promise is to use transverse averaging across the main direction where the macroscale variable changes. This alternative is currently under consideration.

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Figure 1: The variation of the residual (trapped) saturation, S_{or} , in two-phase displacements in porous media vs. the capillary number of the displacement. The value is normalized with its limiting value at low Ca .

Figure 2: The effectiveness factor, η , versus the macroscale Thiele modulus corresponding to a first-order reaction. The dots represent values for pellets of various shapes.

Figure 3: Schematic representation of the porous medium with a distributed dissolving (NAPL) liquid phase.

Figure 4: A simple, two-dimensional, structureless “porous” medium for the example of advection-dissolution.

Figure 5: The variation of the dimensionless effective mass transfer coefficient with distance, for the geometry of Fig. 4. Note the saturation to an asymptotic value.

Figure 6: The variation of the dimensionless effective mass transfer coefficient as a function of the liquid saturation S_l , for a model problem of drying in a pore-network. Values of α_D obtained from the present theory are denoted by dots, those from QW by open circles. The scatter reflects the different realizations taken and the small size of the network (40×40).

Figure 7: The variation of the effective Thiele modulus with distance and for different values of the local Thiele modulus, for a simple first-order reaction-advection problem, in a geometry similar to Fig. 4. Note the saturation to a ϕ_l -dependent limiting value.

Figure 8: The limiting value of the effective Thiele modulus, ϕ_∞ , as a function of the local Thiele modulus, ϕ_l . Note the linear variation at small ϕ_l and the approach to the constant $\pi/2$ at large ϕ_l . For comparison, plotted also is the prediction from (75) denoted by a dashed line.