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Homogenization of a pore scale model for precipitation and dissolution in porous media

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Abstract

In this paper we employ homogenization techniques to provide a rigorous derivation of the Darcy scale model for precipitation and dissolution in porous media. The starting point is the pore scale model in [13], which is a coupled system of evolution equations, involving a parabolic equation which models ion transport in the fluid phase of a periodic porous medium, coupled to an ordinary differential equations modeling dissolution and precipitation at the grains boundary.

The main challenge is in dealing with the dissolution and precipitation rates, which involve a monotone but possibly discontinuous function. In order to pass to the limit in these rate functions at the boundary of the grains, we prove strong two scale convergence for the concentrations at the microscopic boundary and use refined arguments in order to identify the form of the macroscopic dissolution rate, which is again a discontinuous function. The resulting upscaled model is consistent with the Darcy scale model proposed in [20].

1 Introduction

In this paper, we employ rigorous homogenization techniques to derive the Darcy scale model for dissolution and precipitation in a porous medium. The starting point is the micro (pore) scale model analyzed in [13, 36], where the existence and uniqueness of a solution are proved. The challenging part is due to the dissolution and precipitation, involving non-Lipschitz, possibly discontinuous rates, and leading to solutions lacking regularity. Using homogenization techniques, here we give a rigorous derivation of the macro scale counterpart, which is in good agreement with the Darcy scale model proposed empirically in [20].

At the micro scale, the medium consists of periodically repeating solid grains surrounded by voids (the pores). The pore space forms a periodically perforated domain (the grains

being the perforations in the domain) which is completely filled by a fluid (e.g. water). The fluid is flowing around the solid grains, transporting solutes, which are dissolved ions. The solute may further diffuse in the fluid, whereas at the grain surfaces, the solute may react and precipitate, forming a thin layer of an immobile species (salt) attached to these boundaries. The reverse process of dissolution is also possible.

Encountered at the boundary of the perforations, the precipitation process is modeled by a rate function that is monotone and Lipschitz continuous with respect to the solute concentrations. This is consistent with the mass action kinetics. Concerning dissolution, at sites on the grain boundary where precipitate is present, it will be dissolved at a constant rate. A special situation is encountered when no precipitate is present at one site, when no dissolution is possible. Besides, at such a location a precipitate layer (meaning an effective occurrence of the immobile species) is only possible if the fluid is "oversaturated". This means that the precipitation rate exceeds a threshold value, the so-called solubility product. In the "undersaturated" regime, when the precipitation rate is below the solubility product, no effective gain in the precipitate is possible. This can be seen as an instantaneous dissolution of any precipitate formed in undersaturated conditions, so the overall result of these processes encountered at the time scale of interest is null. In other words, the precipitation rate is in balance with the dissolution rate. Between oversaturation and undersaturation, the precipitation rate equals the solubility product, which is an equilibrium value. In this case neither precipitation nor dissolution is encountered.

Note that the undersaturated regime is encountered for any value of the precipitation rate that is below the solubility product. Since the overall rate is zero, at sites where no precipitate is present, the dissolution rate should take a value between zero (no dissolution) and the equilibrium one (the solubility product), in order to balance the dissolution rate. In literature ([20, 12, 11, 10]) this has been modelled by taking the dissolution rate as a member of a multi-valued graph (a scaled Heaviside graph). Further, in [13, 36] the existence and uniqueness of the micro scale model has been studied along a sequence of a regularised Heaviside graph. Passing the regularisation parameter to zero, the limit dissolution rate becomes a discontinuous function. In this paper, this limit function is taken to model the dissolution rate.

The major challenge in the present work is in dealing with the dissolution rate that is non-Lipschitz and may even become discontinuous. This poses difficulties in obtaining the convergence of the precipitation and dissolution rates, and the correct identification of their limits. In particular, we follow the ideas in [30] and [26] and show the strong two-scale convergence of the species at the grain boundaries. This is based on unfolding/localization operators [5, 6], and allows us to identify the limit of the (pore scale) dissolution rate.

1.1 Literature review

The macro scale model for the present problem has been proposed in [20] and further discussed in [10, 11, 12], where the main focus is related to travelling waves. Its pore scale counterpart has been analyzed in [13] and [36], where existence and uniqueness results are obtained. Furthermore, in [13] a two dimensional strip was considered as a model geometry for deriving rigorously the macro scale model by a transversal averaging procedure.

One important assumption here is that the layer of the species attached to the grain boundaries (the precipitate) is very thin compared to the pore thickness, so eventual changes in the geometry at the pore-scale can be neglected. This allows decoupling the equations modelling the flow from those describing the chemical processes. This assumption is justified whenever the density of the deposited layer is very large compared to the typical density of the solute. Contrary to this, [22, 32, 33, 34]) consider the alternative approach, where the precipitate layer induces non-negligible changes in the pores, leading to a model involving free boundaries at the micro scale. In this context and for a simplified geometry, upscaled models are derived formally in [33] for moderate *Péclet* numbers. The same situation, but now under a dominated transport regime - high *Péclet* numbers, is considered in [22]. The upscaled model is similar to Taylor dispersion, and includes the effects of the changing geometry and of the reactions at the micro scale. Similar models are also obtained in [35] for biofilm growth, in [39] for drug release from collagen matrices and in [37] for a reactive flow model involving an evolving microstructure. In [35, 39] a level set function is used to describe the unknown microstructure (a free boundary) and a formal approach is used to obtain the upscaled model. In contrast, in [37] the evolution of the microstructure is assumed to be a priori known but a rigorous approach is used for the upscaling. For the domain with rough boundaries, the effective boundary conditions for the dissolution and precipitation model involving free and rough boundaries are obtained formally in [25].

The dissolution and precipitation model under discussion here refers to the situation when the precipitate does not affect the domain. For such a model, in domains with rough boundaries, effective boundary conditions are derived rigorously in [21]. This model has also been subjected to algorithmic developments and numerical analysis. We recall that the convergence of numerical schemes is analyzed in [9] for the micro scale model, and in [24, 23] for the macro scale model.

The Darcy scale model in [20] was derived rigorously in [13] for a simplified setting: a two-dimensional strip. In this case, a simple transversal averaging procedure can be applied and a one-dimensional Darcy model is derived. Here we consider a more general situation, when the porous medium is modeled by a periodically perforated domain in $\mathbb{R}^d (d = 2, 3, \dots)$. Clearly, this requires a different upscaling approach and the techniques for 2D-thin strip can not be used. For the rigorous derivation of the macroscopic model, we use the two-scale convergence concept developed in [2, 31] and extended further in [29] to include model components defined

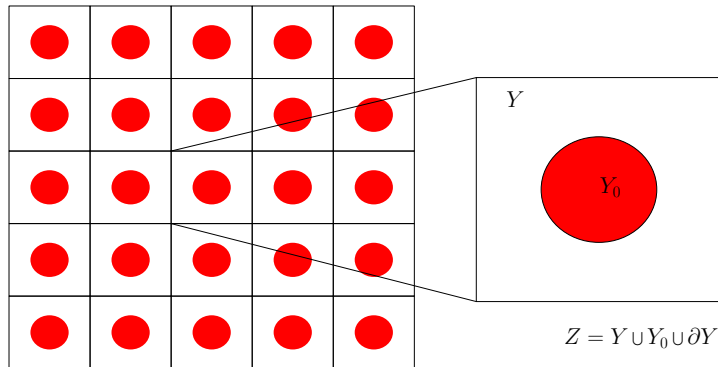


Figure 1: Left: the porous medium Ω consisting of ε -scaled perforated cells distributed periodically; the total void space is Ω^ε . Right: a reference cell containing the flow/reactive transport part (the pore Y) and the perforation (the solid grain) Y_0 separated by the interface Γ_G . Note that the geometry remains fixed in time for a given ε .

on lower dimensional manifolds (the grain boundaries).

We mention [17, 18] for pioneering works on rigorous homogenization of reactive flow models, including the derivation of upscaled models from well-posed microscopic (pore-scale) models. Since then many publications have considered similar problems; we restrict here to mention papers that are very close to the present contribution. The coupled flow and transport models for miscible displacement has been treated in [16]. Non-Lipschitz but continuous reaction rates are considered in [8], but for one species. In [29] and [26] the two-scale convergence framework is extended for variables defined on lower-dimensional manifolds. Rigorous homogenization results for reactive flows including adsorption and desorption at the boundaries of the perforations, but in dominating flow regime (high Peclet numbers) are obtained in [3, 4, 28]. The two-scale convergence approach has been extended to include the mechanics of the porous media and finds application in several fields including the biological, mechanical etc. A recent work dealing with combining the reactive flow with the mechanics of cells is [19]. Similarly, the effect of electric field on the reactive transport of ions has been included in [38, 41] with [38] dealing with Stokes flow coupled to a reactive transport model. Of particular relevance to the present work is the work of [26] where non-linear reaction terms on the surface are treated using the techniques of periodic unfolding.

2 Setting of the model

Let $\varepsilon > 0$ be a sequence of strictly positive numbers tending to zero, with the property that $\frac{1}{\varepsilon} \in \mathbb{N}$. Let $[0, T]$ denote a time interval, with $T > 0$.

We consider here a three-dimensional domain $\Omega = (0, 1)^3$, but extending this work to

any d -dimensional case is straightforward. Ω consists of two subdomains: the perforations (representing the solid grains) and the perforated domain (the pore space) filled with fluid and where flow, diffusion and transport is taking place, see Fig 1. At the micro scale, the domain of interest (the fluid part) is denoted by Ω^ε , and the boundary of the perforations by Γ_G^ε . Thus, the boundary of the domain Ω^ε consists of two parts

$$\partial\Omega^\varepsilon = \partial\Omega \cup \Gamma_G^\varepsilon.$$

The outer unit normal to $\partial\Omega^\varepsilon$ is denoted by ν .

The microscopic structure of Ω^ε and Γ_G^ε is periodic, and is obtained by the repetition of the standard cell $Z = (0, 1)^3$ scaled with the small parameter ε . We denote by Y and Y_0 the fluid part, respectively the perforation in Z . On ∂Y_0 , we denote by ν the unit normal to Γ_G pointing into the perforation Y_0 . We assume that

1. $\bar{Y}_0 \subset Z$, $Y = Z \setminus \bar{Y}_0$,
2. Y_0 is a set of strictly positive measure, with piecewise smooth boundary $\Gamma_G = \partial Y_0$.

Let

$$E_s := \bigcup_{k \in \mathbb{Z}^3} \bar{Y}_0^k = \bigcup_{k \in \mathbb{Z}^3} \overline{(Y_0 + k)}.$$

Then the fluid part of the porous medium Ω^ε and the total boundary of the perforations Γ_G^ε are defined as follows:

$$\Omega^\varepsilon = \Omega \setminus \varepsilon E_s, \quad \Gamma_G^\varepsilon = \Omega \cap \varepsilon \bigcup_{k \in \mathbb{Z}^3} \partial Y_0^k.$$

Finally, for any $t \in (0, T]$ we define

$$Q^t = (0, t] \times Q,$$

where Q is one of the sets Ω , Ω^ε , Γ_G , Γ_G^ε or $\partial\Omega$.

2.1 The micro scale model

Let us now formulate the equations which model the processes at the microscopic level. The microscopic model contains two components: the equations for the flow, and the equations for the reactive transport. For the flow, we consider the Stokes system

$$\begin{cases} \varepsilon^2 \Delta \mathbf{q}^\varepsilon &= \nabla P^\varepsilon, \\ \nabla \cdot \mathbf{q}^\varepsilon &= 0, \end{cases} \quad (2.1)$$

for all $x \in \Omega^\varepsilon$. In the above (2.1), \mathbf{q}^ε stands for the fluid velocity, P^ε denotes the pressure inside the fluid. With a proper scaling, when bringing the model to a dimensionless form the

dynamic viscosity becomes ε^2 (see e.g. [15], p. 45). We complement Stokes equations by assigning no-slip boundary conditions at the boundary of the perforations and given Dirichlet boundary conditions at the outer boundary $\partial\Omega$,

$$\mathbf{q}^\varepsilon = 0, \quad \text{on } \Gamma_G^\varepsilon, \quad \text{and} \quad \mathbf{q}^\varepsilon = \mathbf{q}_D, \quad \text{on } \partial\Omega, \quad (2.2)$$

where \mathbf{q}_D is such that $\int_{\partial\Omega} \boldsymbol{\nu} \cdot \mathbf{q}_D = 0$. As mentioned above, we assume that the chemical processes neither change the micro scale geometry, nor the fluid properties. Therefore the flow component does not depend on the other components of the model, and can be completely decoupled. This means that one can solve first the Stokes system (2.1) with the given boundary conditions (2.2) to obtain the fluid velocity \mathbf{q}^ε .

The main interest in this paper is in the subsystem modeling the chemical processes. This takes into account two solute (mobile) species, which are transported by the fluid. In the fluid, these species are diffusing, but no reactions are taking place there. The corresponding model is therefore a convection-diffusion equation in the fluid part Ω_ε . Following [20, 13], we simplify the analysis by considering only one immobile species, having the concentration u^ε . This is justified if the two species are having the same diffusion coefficient. Accounting for more species is fairly straightforward.

The chemical processes are encountered at the boundary of perforations, where the mobile species react forming the precipitate. The reaction result is an immobile species (the precipitate) attached to this boundary and having the concentration v^ε . The precipitate may be dissolved, becoming a source of mobile species in the fluid. As given in the mathematical model (2.3) below, the precipitation and dissolution are rates in the ordinary differential equation defined in every location on the boundary of perforations. Finally, the partial differential equation and the ordinary one are coupled through the boundary conditions.

With the concentrations u^ε and v^ε introduced above, the reactive transport is described by the following equations

$$\left\{ \begin{array}{ll} \partial_t u^\varepsilon + \nabla \cdot (\mathbf{q}^\varepsilon u^\varepsilon - D \nabla u^\varepsilon) = 0, & \text{in } \Omega^{\varepsilon T}, \\ -D \boldsymbol{\nu} \cdot \nabla u^\varepsilon = \varepsilon n \partial_t v^\varepsilon, & \text{on } \Gamma_G^{\varepsilon T}, \\ \partial_t v^\varepsilon = k(r(u^\varepsilon) - w^\varepsilon), & \text{on } \Gamma_G^{\varepsilon T}, \\ w^\varepsilon \in H(v^\varepsilon), & \text{on } \Gamma_G^{\varepsilon T}. \end{array} \right. \quad (2.3)$$

The system (2.3) is complemented by the following initial and boundary conditions,

$$\left\{ \begin{array}{ll} u^\varepsilon(0, \cdot) = u_I & \text{in } \Omega^\varepsilon, \\ v^\varepsilon(0, \cdot) = v_I & \text{on } \Gamma_G^\varepsilon, \\ u^\varepsilon = 0, & \text{on } \partial\Omega^T, \end{array} \right. \quad (2.4)$$

As mentioned above, \mathbf{q}^ε solves the Stokes system (2.1)-(2.2), which is not affected by the chemistry and therefore we assume it given. Hence, the unknowns of the microscopic model are u^ε , v^ε , and w^ε . In particular, w^ε describes the dissolution rate; the specific choice in (2.3)₄ will be explained below. Note that u^ε is defined in the domain Ω^ε , while v^ε and w^ε are defined on the boundaries of perforations, Γ_G^ε . The physical constant D is a (given) diffusion coefficient, assumed constant. Further, k is a dimensionless reaction rate constant, which we assume of moderate order w.r.t. ε and is normalized to 1. In physical sense, this means that the precipitation sites are homogeneous. Also note that assuming that D and k are moderate w.r.t. ε implies that the time scales of diffusion, transport and chemical processes are of the same order. Finally, n is a constant denoting the valence of the solute and for simplicity, we will be taking it as 1.

Clearly, (2.3)₂ relates the change in the precipitate to the normal flux of the ions at the boundaries, assuming the no-slip boundary condition for \mathbf{q}^ε . Also observe the appearance of ε in the boundary flux. As will be seen below, this allows to control the growth of the precipitate when passing to the limit in the homogenization step. We refer to Chapter 1 of [15] for a justification of this choice based on the geometry of the pores, and to [13], Remark 1.2 for an equivalent interpretation.

We proceed now by explaining the precipitation rate $r(u^\varepsilon)$ and the dissolution rate w^ε appearing in the last two equations of (2.3). We assume first that

Assumptions on r

The precipitation rate r depends on the solute concentration, where

$$r : \mathbb{R} \rightarrow [0, \infty) \text{ is locally Lipschitz in } \mathbb{R}. \quad (\text{A.1})$$

There exists a unique $u_* \geq 0$, such that

$$r(u^\varepsilon) = \begin{cases} 0 & \text{for } u^\varepsilon \leq u_*, \\ \text{strictly increasing for } & u^\varepsilon \geq u_* \quad \text{with } r(\infty) = \infty. \end{cases} \quad (\text{A.2})$$

An example where these assumptions are fulfilled is given in [20], where a model based on mass-action kinetics is considered. Note that a value $u^* > 0$ exists such that

$$r(u^*) = 1.$$

With the proper scaling, this value is exactly the solubility product mentioned in the introduction. As explained, this value is taken at an equilibrium concentration: if $u^\varepsilon(t, x) = u^*$, neither precipitation, nor dissolution is encountered in x at time t .

Finally, the dissolution rate satisfies

$$w^\varepsilon \in H(v^\varepsilon), \quad (2.5)$$

where $H(\cdot)$ denotes the Heaviside graph,

$$H(u) = \begin{cases} \{0\} & \text{if } u < 0, \\ [0, 1] & \text{if } u = 0, \\ \{1\} & \text{if } u > 0. \end{cases} \quad (2.6)$$

This means that whenever precipitate is present, hence $v^\varepsilon(t, x) > 0$, in this point dissolution is encountered at a constant rate, 1 by scaling. One may view this as a surface process: it does not matter how much precipitate is present in one location x on the boundary of perforations at some time t , the dissolution will be encountered strictly at the surface of the precipitate and not in the interior. A more interesting situation appears at sites where the precipitate is absent, thus $v^\varepsilon(t, x) = 0$. Then a value has to be specified for the dissolution rate $w^\varepsilon(t, x) \in [0, 1]$. Two important features should be accounted for: no dissolution is allowed whenever precipitate is absent, and further no precipitation should be encountered in the *undersaturated* regime, when $u^\varepsilon(t, x) < u^*$. As explained in [13, 20, 36], whenever $v^\varepsilon = 0$, the rate w^ε depends also on the solute concentration u^ε at the boundary. Specifically, in the *oversaturated* regime, when $u^\varepsilon > u^*$ (the value u^* being introduced above) we take $w^\varepsilon = 1$. Since $r(u^\varepsilon) > 1$, this means that the overall precipitation/dissolution rate is strictly positive, resulting in a net gain in the precipitate. In the undersaturated regime one has $u^\varepsilon < u^*$, thus $r(u^\varepsilon) \leq 1$. Then the solute concentration cannot support an effective gain in precipitate, and the overall rate remains 0. In particular, dissolution should be avoided in this case. To achieve this, we take $w^\varepsilon = r(u^\varepsilon) \in [0, 1)$ and the overall rate becomes 0. Finally, since $r(u^*) = 1$, the case $u^\varepsilon = u^*$ leads to an equilibrium, regardless of the value of v^ε . This can be summarized as

$$w^\varepsilon = \begin{cases} 0 & \text{if } v^\varepsilon < 0, \\ \min\{r(u^\varepsilon), 1\} & \text{if } v^\varepsilon = 0, \\ 1 & \text{if } v^\varepsilon > 0. \end{cases} \quad (2.7)$$

The dissolution rate is defined for unphysical, negative values of v^ε for the sake of completeness. We will prove below that whenever the initial precipitate concentration is non-negative, no negative concentrations can be obtained. Note that in the above relation, $w^\varepsilon \in H(v^\varepsilon)$ is a discontinuous function of v^ε and not an inclusion (in contrast to (2.5)-(2.6), the value of w^ε is well specified in the case $v^\varepsilon = 0$). This choice is justified also from mathematical point of view, as regularization arguments employed in [13] for obtaining the existence of a solution lead to the above form for w^ε .

2.2 The variational formulation of the microscopic problem

When defining a weak solution we use common notations in the functional analysis: with Q being either Ω , Ω^ε , $\partial\Omega$, Γ_G or Γ_G^ε , we denote by $L^2(Q)$ the square-integrable functions on Q (in the sense of Lebesgue). For $Q = \Omega^\varepsilon$ or $Q = \Omega$, the space $H_0^1(Q)$ restricts the space $H^1(Q)$ of functions having all first order partial derivatives in L^2 to those elements vanishing on $\partial\Omega$ (in the sense of traces). $(\cdot, \cdot)_Q$ stands for the scalar product in $L^2(Q)$; if $Q = \Omega^\varepsilon$ or $Q = \Omega$, it also denotes the duality pairing between $H_0^1(Q)$ and $H^{-1}(Q)$ – the dual of $H_0^1(Q)$. The corresponding norm is denoted by $\|\cdot\|_Q$, or simply $\|\cdot\|$ (where self understood). By $L^\infty(Q)$ we mean functions that are essentially bounded on Q , and the essential supremum is denoted by $\|u\|_{\infty, Q}$. Further, for a Banach space V we denote by $L^2(0, T; V)$ the corresponding Bochner space equipped with the standard inner product (where applicable) and norm. Besides, χ_I denotes the characteristic function of the set I .

Before stating the definition of a weak solution, we introduce the function spaces

$$\begin{aligned} \mathcal{U}^\varepsilon &:= \{u \in L^2(0, T; H_0^1(\Omega^\varepsilon)) \quad : \quad \partial_t u \in L^2(0, T; H^{-1}(\Omega^\varepsilon))\}, \\ \mathcal{V}^\varepsilon &:= H^1(0, T; L^2(\Gamma_G^\varepsilon)), \\ \mathcal{W}^\varepsilon &:= \{w \in L^\infty(\Gamma_G^{\varepsilon T}) \quad : \quad 0 \leq w \leq 1\}. \end{aligned}$$

Then a weak solution is introduced in

Definition 2.1. *A triple $(u^\varepsilon, v^\varepsilon, w^\varepsilon) \in \mathcal{U}^\varepsilon \times \mathcal{V}^\varepsilon \times \mathcal{W}^\varepsilon$ is called a weak solution to (2.3)-(2.4) if $u^\varepsilon(0, \cdot) = u_I$, $v^\varepsilon(0, \cdot) = v_I$,*

$$\begin{aligned} (\partial_t u^\varepsilon, \phi)_{\Omega^{\varepsilon T}} + D(\nabla u^\varepsilon, \nabla \phi)_{\Omega^{\varepsilon T}} - (\mathbf{q}^\varepsilon u^\varepsilon, \nabla \phi)_{\Omega^{\varepsilon T}} &= -\varepsilon(\partial_t v^\varepsilon, \phi)_{\Gamma_G^{\varepsilon T}}, \\ (\partial_t v^\varepsilon, \theta)_{\Gamma_G^{\varepsilon T}} &= (r(u^\varepsilon) - w^\varepsilon, \theta)_{\Gamma_G^{\varepsilon T}}, \end{aligned} \tag{2.8}$$

for all $(\phi, \theta) \in L^2(0, T; H_0^1(\Omega^\varepsilon)) \times L^2((0, T) \times \Gamma_G^\varepsilon)$, and w^ε satisfies (2.7) a.e. in $\Gamma_G^{\varepsilon T}$.

For the boundary and initial conditions we assume the following

$$u_I \in H_0^1(\Omega), v_I \in H^1(\Omega), \text{ and } 0 \leq u_I, v_I \leq M_0 \text{ a.e.}, \tag{A.3}$$

with an ε -independent constant $M_0 > 0$. Further, w_I satisfies (2.7).

Note that u_I, v_I are defined in the entire Ω . In Definition 2.1 above, the initial conditions are the restrictions of u_I and v_I to Ω^ε , respectively, Γ_G^ε . Since u^ε and v^ε are also continuous in time vector valued functions, the initial conditions make sense. Further, the initial precipitation concentration v_I is assumed in $H^1(\Omega)$ and for the micro scale model, we consider its trace on Γ_G^ε . For simplicity we considered homogeneous conditions on $\partial\Omega$, but the extension to non-homogeneous ones can be carried out without major difficulties.

The existence of weak solutions to (2.3)-(2.7) is proved in [13] (see Th. 2.21) by regular-

izing the Heaviside graph. Clearly, the solutions of the regularized problems depend on the regularization parameter. Passing this parameter to zero, one obtains a convergent sequence of solutions; its limit is a weak solution to the original problem, in the sense of Definition 2.1. Furthermore, the uniqueness of a solution is obtained in [36] ((Th. 2, Cor. 1) by proving the following contraction result with respect to the initial values

Theorem 2.1. *Assume (A.1) and (A.2) and let $(u^{(i)\varepsilon}, v^{(i)\varepsilon}, w^{(i)\varepsilon}) \in \mathcal{U}^\varepsilon, \mathcal{V}^\varepsilon, \mathcal{W}^\varepsilon, i = 1, 2$ be two solutions in the sense of Definition 2.1, obtained for the initial values $u_I^{(i)}, v_I^{(i)}$ ($i = 1, 2$) respectively. Then for any $t \in (0, T]$ it holds*

$$\begin{aligned} \int_{\Omega^\varepsilon} |u^{(1)\varepsilon}(t, x) - u^{(2)\varepsilon}(t, x)| dx + \varepsilon \int_{\Gamma_G^\varepsilon} |v^{(1)\varepsilon}(t, s) - v^{(2)\varepsilon}(t, s)| ds \\ \leq \int_{\Omega^\varepsilon} |u_I^{(1)}(x) - u_I^{(2)}(x)| dx + \varepsilon \int_{\Gamma_G^\varepsilon} |v_I^{(1)}(s) - v_I^{(2)}(s)| ds \end{aligned} \quad (2.9)$$

3 The macroscopic model and the main result

In this paper, we let $\varepsilon \rightarrow 0$ and investigate the limit behaviour of the solutions to the microscopic system (2.1)-(2.2), (2.3)-(2.4). The main result is in proving the convergence of the micro-scale reactive transport model in (2.3) to the unique solution to the homogenized (macroscopic) system of differential equations (3.4)-(3.5) defined below.

For completeness, we start by mentioning existing results for the flow component. The macroscopic variables (\mathbf{q}, P) satisfy the Darcy law

$$\nabla \cdot \mathbf{q} = 0, \quad \mathbf{q} = -K \nabla P, \quad (3.1)$$

for $x \in \Omega$, and boundary condition

$$-K \nabla P \cdot \nu = q_D \cdot \nu,$$

for $x \in \partial\Omega$. The permeability tensor K has the components

$$k_{ij} = \frac{1}{|Y|} \int_Y \chi_i^j(y) dy, \quad \text{for all } i, j \in \{1, 2, 3\}, \quad (3.2)$$

where χ_i^j is the i -th component of $\boldsymbol{\chi}^j = (\chi_1^j, \chi_2^j, \chi_3^j)$ solving the cell problems ($j \in \{1, 2, 3\}$)

$$(P_j^D) \begin{cases} -\Delta_y \boldsymbol{\chi}^j(y) &= \nabla_y \Pi^j(y) + \mathbf{e}_j, & \text{in } Y \\ \nabla_y \cdot \boldsymbol{\chi}^j(y) &= 0, & \text{in } Y \\ \boldsymbol{\chi}^j(y) &= 0, & \text{on } \Gamma_G \\ \boldsymbol{\chi}^j, \Pi^j &\text{ are } Z\text{-periodic.} \end{cases} \quad (3.3)$$

As shown in the L. Tartar's Appendix of [40] (also see Propositions 4 and 6 of [18]), \mathbf{q}^ε is uniformly bounded in the $L^2(\Omega^\varepsilon)$ norm. With χ^ε being the indicator function for Ω^ε , the extension $\chi^\varepsilon \mathbf{q}^\varepsilon$ has a weak limit \mathbf{q} solving the Darcy model (3.1).

The homogenized model component referring to the reactive transport, the solution triple (u, v, w) representing the upscaled solute concentration, precipitate concentration, and the macroscopic dissolution rate are solution to the system

$$\begin{cases} \partial_t \left(u + \frac{|\Gamma_G|}{|Y|} v \right) &= \nabla \cdot (S \nabla u - \mathbf{q} u), \\ \partial_t v &= (r(u) - w), \\ w &\in H(v), \end{cases} \quad (3.4)$$

for all $x \in \Omega$ and $t \in (0, T]$. In addition, analogous to (2.7), macroscopic w satisfies,

$$w = \begin{cases} 0 & \text{if } v < 0, \\ \min\{r(u), 1\} & \text{if } v = 0, \\ 1 & \text{if } v > 0. \end{cases} \quad (3.5)$$

The components of the diffusion tensor S are defined by

$$(S)_{i,j} = D \left[\delta_{ij} + \frac{1}{|Y|} \int_Y \partial_{y_j} \xi_i dy \right], \quad \text{for all } i, j \in \{1, 2, 3\}. \quad (3.6)$$

The functions ξ_i are solutions of the following cell problems ($i \in \{1, 2, 3\}$)

$$(P_i^C) \begin{cases} -\Delta \xi_i &= 0 & \text{in } Y, \\ \boldsymbol{\nu} \cdot \nabla \xi_i &= \boldsymbol{\nu} \cdot \mathbf{e}_i & \text{on } \Gamma_G \\ \xi_i \text{ is } Z \text{ periodic} &\text{ and } \int \xi_i dy = 0. \end{cases} \quad (3.7)$$

The system (3.4) is complemented by the boundary and initial conditions

$$\begin{cases} u(0, \cdot) = u_I & \text{in } \Omega, \\ v(0, \cdot) = v_I & \text{in } \Omega, \\ u = 0, & \text{on } \partial\Omega^T \end{cases} \quad (3.8)$$

As for the macro scale model, we are interested in the reactive transport component of the upscaled model, for which a weak solution is defined below.

Definition 3.1. *A triple (u, v, w) with $u \in L^2(0, T; H_0^1(\Omega))$; $\partial_t u \in L^2(0, T; H^{-1}(\Omega))$, $v \in H^1(0, T; L^2(\Omega))$, $w \in L^\infty(0, T; L^2(\Omega))$ is called a weak solution to (3.4)-(3.8) if $(u(0), v(0)) = (u_I, v_I)$, and*

$$\begin{aligned} (\partial_t u, \phi)_{\Omega^T} + D(S\nabla u, \nabla \phi)_{\Omega^T} &= (\mathbf{q}u, \nabla \phi)_{\Omega^T} - \frac{|\Gamma_G|}{|Y|} (\partial_t v, \phi)_{\Omega^T}, \\ (\partial_t v, \theta)_{L^2(\Omega^T)} &= (r(u) - w, \theta)_{L^2(\Omega^T)}, \\ w &\in H(v), \text{ satisfying (3.5)} \end{aligned} \quad (3.9)$$

for all $(\phi, \theta) \in L^2(0, T; H_0^1(\Omega)) \times L^2(0, T; L^2(\Omega))$.

The main result is as follows:

Theorem 3.1. *As $\varepsilon \searrow 0$, the sequence of micro-scale weak solutions $(u^\varepsilon, v^\varepsilon, w^\varepsilon)$ of problem (2.7) - (2.8) converges to the unique weak solution (u, v, w) of the upscaled model (3.9).*

The notion of convergence will be made more precise in the following sections. We remark that the effective solution (u, v, w) does not depend on the microscopic variable $y \in \Gamma_G$. This results from the fact that initial conditions are considered homogeneous and the processes at the boundaries of perforations are also homogeneous. Finally, since the flow component is completely decoupled from the reactive transport, it is sufficient to quote existing results for the transition from the micro scale (Stokes) model to the upscaled (Darcy) one. In this sense we refer to [1, 15, 40], where two-scale convergence results have been obtained (see e.g. Theorem 1.4 in [15]).

4 Uniform estimates for the microscopic solutions and extension properties

First, we provide estimates for the solutions of the microscopic problem that are uniform with respect to ε . These will allow passing to the limit $\varepsilon \searrow 0$, and obtaining the solution to the homogenized model. In doing so, we recall the a-priori estimates obtained in [13], without considering particularly the homogenization problem. According to Remarks 2.12 and 2.14

of [13], in the case of a periodically perforated medium (this being the situation here), these estimates are ε -uniform. From [13, 36] one has:

Theorem 4.1. *Assume (A.1) and (A.2), there exists a unique weak solution to (2.3)-(2.7) in the sense of Definition 2.1. Moreover, this solution satisfies the following estimates*

$$0 \leq u^\varepsilon, v^\varepsilon \leq M, \quad 0 \leq w^\varepsilon \leq 1, \quad (4.1)$$

$$\begin{aligned} \|u^\varepsilon\|_{L^\infty(0,T;L^2(\Omega^\varepsilon))}^2 + \|\nabla u^\varepsilon\|_{L^2(\Omega^\varepsilon T)}^2 + \|\partial_t u^\varepsilon\|_{L^2(0,T;H^{-1}(\Omega^\varepsilon))}^2 \\ + \varepsilon \|v^\varepsilon\|_{L^\infty(0,T;L^2(\Gamma_G^\varepsilon))}^2 + \varepsilon \|\partial_t v^\varepsilon\|_{L^2(\Gamma_G^\varepsilon T)}^2 \leq C, \end{aligned} \quad (4.2)$$

where the constants $C > 0$ and $M > 0$ are independent of ε .

Remark 4.1. *In the above reference [13], the above estimates are derived under the assumption of the flow \mathbf{q}^ε being uniformly bounded in L^∞ norm. However, a slight change of arguments in the proof of Lemma 2.11 that gives these estimates in [13] shows that this assumption can be relaxed to have only uniform L^2 bound which is available for Stokes model as remarked before (see [1, 15, 18]). This is immediate in the case of homogeneous Dirichlet boundary data for the flow as has been assumed here (in the case of inhomogeneous Dirichlet boundary data for \mathbf{q}^ε , it is straightforward to extend the same result by assuming L^2 smoothness of the gradient of the extension of the boundary data). To see this, note that from Lemma 2.7, Cor. 2.8 in [13], the L^∞ estimates for $u^\varepsilon, v^\varepsilon$ depend only on the initial and boundary data and is independent of the bounds on \mathbf{q}^ε . Using this in equation (2.16) from [13], the bound on $\partial_t u^\varepsilon$ is easily obtained with \mathbf{q}^ε being L^2 bounded. We spare the full details.*

For passing to the limit in the nonlinear reaction terms, especially on Γ_G^ε , one needs strong convergence for the solute concentration u^ε with respect to appropriate topologies. A first step in obtaining this is to extend u^ε and $\partial_t u^\varepsilon$ from Ω^ε to the entire domain Ω . Since Ω^ε is connected and has a Lipschitz boundary, there exists a linear and bounded extension operator

$$\begin{aligned} F_\varepsilon : L^2(0, T; H^1(\Omega^\varepsilon)) &\rightarrow L^2(0, T; H^1(\Omega)) \\ u^\varepsilon &\mapsto \tilde{u}^\varepsilon \end{aligned}$$

which preserves the estimates on the solution u^ε from Theorem 4.1, excepting that one for the time derivative, see e.g. [7]. Concerning the time derivative, we consider the following extension, see [27, 14]: For a function $u^\varepsilon \in L^2(0, T; H^1(\Omega^\varepsilon))$ with $\partial_t u^\varepsilon \in L^2(0, T; H^{-1}(\Omega^\varepsilon))$, the extension of the time derivative is defined by $\partial_t (\chi_{\Omega^\varepsilon} u^\varepsilon)$, where $\chi_{\Omega^\varepsilon}$ is the characteristic function of Ω^ε . For this extension the following holds

$$(\partial_t (\chi_{\Omega^\varepsilon} u^\varepsilon), \phi)_\Omega = (\partial_t u^\varepsilon(t), \phi \chi_{\Omega^\varepsilon})_{\Omega^\varepsilon} \text{ for all } \phi \in H^1(\Omega) \text{ and a.e. } t \in (0, T),$$

and we have the estimate

$$\|\partial_t (\chi_{\Omega^\varepsilon} u^\varepsilon)\|_{L^2(0,T;H^{-1}(\Omega))} \leq \|\partial_t u^\varepsilon\|_{L^2(0,T;H^{-1}(\Omega^\varepsilon))}. \quad (4.3)$$

5 Compactness of the microscopic solutions

To pass to the limit in the microscopic equations, we will use the notions of two-scale convergence and unfolding operator. Let us first recall the definitions of these concepts. The concept of two-scale convergence was introduced in [2, 31] and later extended to periodic surfaces in [29]. We give here the version of two-scale convergence for time depending functions.

Definition 5.1. *A sequence $u^\varepsilon \in L^2((0,T) \times \Omega)$ is said to converge two-scale (weakly) to a limit $u \in L^2((0,T) \times \Omega \times Z)$ iff*

$$\lim_{\varepsilon \searrow 0} \int_0^T \int_{\Omega} u^\varepsilon(t, x) \phi(t, x, \frac{x}{\varepsilon}) dx dt = \int_0^T \int_{\Omega} \int_Z u(t, x, y) \phi(t, x, y) dy dx dt$$

for all $\phi \in C([0, T] \times \bar{\Omega}; C_{per}^\infty(\bar{Z}))$.

Definition 5.2. *A sequence $v^\varepsilon \in L^2((0,T) \times \Gamma_G^\varepsilon)$ is said to converge two-scale to a limit $v \in L^2((0,T) \times \Omega \times \Gamma_G)$ iff*

$$\lim_{\varepsilon \searrow 0} \varepsilon \int_0^T \int_{\Gamma_G^\varepsilon} v^\varepsilon(t, x) \phi(t, x, \frac{x}{\varepsilon}) dx dt = \int_0^T \int_{\Omega} \int_{\Gamma_G} v(t, x, y) \phi(t, x, y) d\sigma_y dx dt$$

$\phi \in C([0, T] \times \bar{\Omega}; C_{per}^\infty(\Gamma))$.

A weakly convergent sequence $v^\varepsilon \in L^2((0,T) \times \Gamma_G^\varepsilon)$ converges strongly in the two-scale sense on Γ_G^ε , if additionally there holds

$$\lim_{\varepsilon \searrow 0} \sqrt{\varepsilon} \|v^\varepsilon\|_{L^2((0,T) \times \Gamma_G^\varepsilon)} = \|v\|_{L^2((0,T) \times \Omega \times \Gamma_G)}.$$

Especially to handle the nonlinear terms on Γ_G^ε , we need the strong two scale convergence. To prove such results, we employ the characterization of two-scale convergence by means of the unfolding operator, see e.g. [5, 6, 26].

Definition 5.3. *For a given $\varepsilon > 0$, we define a boundary unfolding operator D^ε mapping measurable functions on $(0, T) \times \Gamma_G^\varepsilon$ to measurable functions on $(0, T) \times \Omega \times \Gamma_G$ by*

$$D^\varepsilon f(t, x, y) = f\left(t, \varepsilon \left[\frac{x}{\varepsilon}\right] + \varepsilon y\right), \quad y \in \Gamma_G, \quad (t, x) \in (0, T) \times \Omega.$$

The relation between two-scale convergence and convergence of the unfolded sequence is given in the following lemma.

Lemma 5.1. *For a sequence $v^\varepsilon \in L^2((0, T) \times \Gamma_G^\varepsilon)$ with $\sqrt{\varepsilon} \|v^\varepsilon\|_{L^2((0, T) \times \Gamma_G^\varepsilon)} \leq C$ the following statements are equivalent*

(i) $v^\varepsilon \rightarrow v$ weakly/strongly in the two scale sense on Γ_G^ε .

(ii) $D^\varepsilon v^\varepsilon \rightarrow v$ weakly/strongly in $L^2((0, T) \times \Omega \times \Gamma_G)$.

Based on the estimates proved in the preceding section, the following compactness properties of the microscopic solutions are proved.

Lemma 5.2. *There exists limit functions*

$$\begin{aligned} u &\in L^2(0, T; H^1(\Omega)), & \partial_t u &\in L^2(0, T; H^{-1}(\Omega)), & u_1 &\in L^2(0, T; L^2(\Omega; H_{\text{per}}^1(Z))), \\ v &\in L^2((0, T) \times \Omega \times \Gamma_G), & \partial_t v &\in L^2((0, T) \times \Omega \times \Gamma_G), & w &\in L^2((0, T) \times \Omega \times \Gamma_G), \end{aligned}$$

such that up to a subsequence

1. $\tilde{u}^\varepsilon \rightharpoonup u$ weakly in $L^2(0, T; H^1(\Omega))$,
2. \tilde{u}^ε two-scale converges to u ,
3. $\nabla \tilde{u}^\varepsilon$ two-scale converges to $\nabla_x u + \nabla_y u_1$,
4. $\partial_t (\chi_{\Omega^\varepsilon} u^\varepsilon) \rightharpoonup |Y| \partial_t u$ weakly in $L^2(0, T; H^{-1}(\Omega))$,
5. $\tilde{u}^\varepsilon \rightarrow u$ strongly in $L^2((0, T) \times \Omega)$,
6. v^ε two-scale converges to v ,
7. $\partial_t v^\varepsilon$ two-scale converges to $\partial_t v$,
8. w^ε two-scale converges to w .

We will later show that these limit functions satisfy the upscaled model (3.9); for economy we retain the same notations for the variables solving the upscaled model.

Proof. The first result follows directly by using estimates (4.2) and the properties of the extension operator F_ε . The results in items 2. and 3. follow from standard compactness arguments in [2]. To show 4., we observe that (4.3) and the estimate of the time derivative in (4.2) imply the existence of a limit function $\zeta \in L^2(0, T; H^{-1}(\Omega))$, such that up to a subsequence $\partial_t (\chi_{\Omega^\varepsilon} u^\varepsilon)$ converges weakly to ζ in $L^2(0, T; H^{-1}(\Omega))$. Integration by parts in time and 2. shows that $\zeta = |Y| \partial_t u$. The strong convergence of \tilde{u}^ε in $L^2((0, T) \times \Omega)$ follows from [27]. The convergence results from items 6. to 8. follow from standard compactness results for sequences defined on periodic surfaces, see e.g. [29] and estimates (4.2). \square

Using the compactness results from Lemma 5.2, we are able to show the convergence of the nonlinear term on Γ_G^ε modeling the precipitation process.

Corollary 5.1. *The function $r(u^\varepsilon)$ converges strongly in two-scale to $r(u)$.*

Proof. Using the Lipschitz continuity of r and the trace inequality from [17] Lemma 3, we obtain

$$\varepsilon \|r(u^\varepsilon) - r(u)\|_{\Gamma_G^\varepsilon}^2 \leq C\varepsilon \|u^\varepsilon - u\|_{\Gamma_G^\varepsilon}^2 \leq C(\|\tilde{u}^\varepsilon - u\|_{L^2((0,T)\times\Omega)}^2 + \varepsilon^2 \|\nabla(\tilde{u}^\varepsilon - u)\|_{L^2((0,T)\times\Omega)}^2).$$

Lemma 5.2 implies the strong convergence of \tilde{u}^ε to u in $L^2((0,T)\times\Omega)$. As stated before, the estimates (4.2) carry over to the extension \tilde{u} and hence $\|\nabla(\tilde{u}^\varepsilon - u)\|_{L^2((0,T)\times\Omega)}$ is bounded. This yields

$$\lim_{\varepsilon \searrow 0} \varepsilon \|r(u^\varepsilon) - r(u)\|_{\Gamma_G^\varepsilon}^2 = 0. \quad (5.1)$$

Moreover, by Lemma 1.3.2 in [29], we have that for any function $f \in C^0(\bar{\Omega}; C_{\text{per}}^0(\Gamma_G))$ there holds

$$\lim_{\varepsilon \searrow 0} \varepsilon \int_{\Gamma_G^\varepsilon} f\left(x, \frac{x}{\varepsilon}\right) dx = \int_{\Omega} \int_{\Gamma_G} f(x, y) dx dy.$$

This result can be extended to functions $f \in L^2((0,T)\times\Omega; C_{\text{per}}^0(\Gamma_G))$. Using these results, we obtain for all $\phi \in C^0((0,T)\times\Omega; C_{\text{per}}^0(\Gamma_G))$

$$\begin{aligned} & \left| \int_{\Gamma_G^\varepsilon} \varepsilon r(u^\varepsilon) \phi\left(x, \frac{x}{\varepsilon}\right) dx dt - \int_{\Omega^T} \int_{\Gamma_G} r(u) \phi(x, y) dy dx dt \right| \leq \\ & \int_{\Gamma_G^\varepsilon} \left| \varepsilon (r(u^\varepsilon) - r(u)) \phi\left(x, \frac{x}{\varepsilon}\right) \right| dx dt + \left| \int_{\Gamma_G^\varepsilon} \varepsilon r(u) \phi\left(x, \frac{x}{\varepsilon}\right) dx dt - \int_{\Omega^T} \int_{\Gamma_G} r(u) \phi(x, y) dy dx dt \right| \\ & \rightarrow 0. \end{aligned}$$

The weak two-scale convergence together with (5.1) then imply the strong two-scale convergence of $r(u^\varepsilon)$ to $r(u)$. Thus, the corollary is proved. \square

Let us now turn our attention to the limit of the nonlinear precipitation rate w^ε . Observe that the two-scale convergence of w^ε to w does not provide the explicit form for the function w stated in (3.5). Identifying the form of w requires new arguments due to w^ε being possibly discontinuous in v^ε . This is done in two steps. First, we prove the strong two-scale convergence of v^ε to v . In doing so we use the unfolding operator and the monotonicity of w^ε . In a second step, we use the strong two-scale convergence of v^ε to analyze different cases which arise when the limit v takes the value zero or is positive.

Theorem 5.1. *The sequence v^ε converges to v strongly in the two-scale sense on Γ_G^ε , or equivalently, $D^\varepsilon v^\varepsilon$ converges strongly to v in $L^2((0, T) \times \Omega \times \Gamma_G)$.*

Proof. Let us recall (2.7), and note that $w^\varepsilon(v^\varepsilon)$ is monotonically increasing with respect to v^ε . This also implies that $D^\varepsilon w^\varepsilon$ is monotone with respect to $D^\varepsilon v^\varepsilon$. With the change in variable $x \mapsto \varepsilon[\frac{x}{\varepsilon}] + \varepsilon y$, $y \in \Gamma_G$ the equation (2.8)₂ reads on the fixed domain $(0, T) \times \Omega \times \Gamma_G$

$$\partial_t D^\varepsilon v^\varepsilon = D^\varepsilon r(u^\varepsilon) - D^\varepsilon w^\varepsilon.$$

We will prove below that the unfolded sequence $D^\varepsilon v^\varepsilon$ is a Cauchy sequence and hence will converge strongly in $L^2((0, T) \times \Omega \times \Gamma_G)$. Our approach is close to that used in [26] (also see [30] for similar results by using translation estimates). The strong convergence of $D^\varepsilon r(u^\varepsilon)$ to $r(u)$ in $L^2((0, T) \times \Omega \times \Gamma_G)$ and the monotonicity of $D^\varepsilon w^\varepsilon$ will be used to obtain this. Let m, n be two natural number with $n > m$. Now $T^{\varepsilon n} v^{\varepsilon n} - T^{\varepsilon m} v^{\varepsilon m}$ satisfies

$$\begin{aligned} & \frac{d}{dt} \|T^{\varepsilon n} v^{\varepsilon n} - T^{\varepsilon m} v^{\varepsilon m}\|_{L^2(\Gamma_G \times \Omega)}^2 = \\ & \int_{\Gamma_G \times \Omega} \{T^{\varepsilon n} v^{\varepsilon n} - T^{\varepsilon m} v^{\varepsilon m}\} \{T^{\varepsilon n} r(u^{\varepsilon n}) - T^{\varepsilon n} w^{\varepsilon n} - T^{\varepsilon m} r(u^{\varepsilon m}) + T^{\varepsilon m} w^{\varepsilon m}\} dx dy. \end{aligned} \quad (5.2)$$

Noting that (2.7) gives monotonicity of $D^\varepsilon w^\varepsilon$ with respect to $D^\varepsilon v^\varepsilon$, we have

$$(T^{\varepsilon n} v^{\varepsilon n} - T^{\varepsilon m} v^{\varepsilon m})(T^{\varepsilon n} w^{\varepsilon n} - T^{\varepsilon m} w^{\varepsilon m}) \geq 0. \quad (5.3)$$

Using (5.3) in (5.2), the right hand side is estimated as

$$\begin{aligned} & \frac{d}{dt} \|T^{\varepsilon n} v^{\varepsilon n} - T^{\varepsilon m} v^{\varepsilon m}\|_{L^2(\Gamma_G \times \Omega)}^2 \\ & \leq \int_{\Gamma_G \times \Omega} \{T^{\varepsilon n} v^{\varepsilon n} - T^{\varepsilon m} v^{\varepsilon m}\} \{T^{\varepsilon n} r(u^{\varepsilon n}) - T^{\varepsilon m} r(u^{\varepsilon m})\} dx dy \\ & \leq \frac{1}{2} \|T^{\varepsilon n} v^{\varepsilon n} - T^{\varepsilon m} v^{\varepsilon m}\|_{L^2(\Gamma_G \times \Omega)}^2 + \frac{1}{2} \|T^{\varepsilon n} r(u^{\varepsilon n}) - T^{\varepsilon m} r(u^{\varepsilon m})\|_{L^2(\Gamma_G \times \Omega)}^2. \end{aligned}$$

Now integrate in time and notice that as $(n, m) \rightarrow \infty$, due to strong convergence of $D^\varepsilon r(u^\varepsilon)$ the second term goes to 0 uniformly. Using Gronwall's lemma we conclude that

$$\|T^{\varepsilon n} v^{\varepsilon n} - T^{\varepsilon m} v^{\varepsilon m}\|_{L^2(\Gamma_G^T \times \Omega_h)}^2 \rightarrow 0 \text{ as } n, m \rightarrow \infty$$

uniformly and hence establishing the strong convergence of $D^\varepsilon v^\varepsilon$ in $L^2((0, T) \times \Omega \times \Gamma_G)$. \square

Let us now prove that w has the structure of (3.5).

Theorem 5.2. *The limit function w from Lemma 5.2 satisfies $w \in H(v)$ and we have*

$$w = \begin{cases} 1, & v > 0, \\ \min(r(u), 1), & v = 0, \\ 0, & v < 0. \end{cases} \quad (5.4)$$

Proof. We first recall that

$$\begin{aligned} D^\varepsilon r(u^\varepsilon) &\rightarrow r(u) \quad \text{strongly in } L^2((0, T) \times \Omega \times \Gamma_G), \\ D^\varepsilon v^\varepsilon &\rightarrow v \quad \text{strongly in } L^2((0, T) \times \Omega \times \Gamma_G), \\ D^\varepsilon w^\varepsilon &\rightarrow w \quad \text{weakly in } L^2((0, T) \times \Omega \times \Gamma_G), \\ D^\varepsilon w^\varepsilon &\in H(D^\varepsilon v^\varepsilon) \text{ and satisfies (2.7)}. \end{aligned}$$

Since $D^\varepsilon v^\varepsilon \rightarrow v$ strongly in $L^2((0, T) \times \Omega \times \Gamma_G)$ we have $D^\varepsilon v^\varepsilon \rightarrow v$ a.e.. According to Theorem 4.1, $D^\varepsilon v^\varepsilon$ is non-negative and converges strongly to v implying v is also non-negative. We have only two situations, either $v(t, x, y) > 0$ or $v(t, x, y) = 0$. In the first case and with $\mu := v(t, x, y)/2 > 0$, the pointwise convergence implies the existence of an $\varepsilon_\mu > 0$ such that $D^\varepsilon v^\varepsilon > \mu$ for all $\varepsilon \leq \varepsilon_\mu$. Then for any $\varepsilon \leq \varepsilon_\mu$ we have $D^\varepsilon w^\varepsilon = 1$ implying $w = 1$.

For a.e. (t, x, y) such that $v(t, x, y) = 0$, we have the following situations:

(a) $u(t, x) > u^*$

From the convergence of $D^\varepsilon u^\varepsilon(t, x, y)$, there exists an ε^* such that for $\varepsilon \leq \varepsilon^*$, we have $D^\varepsilon u^\varepsilon(t, x, y) > u^*$. This gives, using monotonicity of r , $r(D^\varepsilon u^\varepsilon)(t, x, y) > 1$ and recall the definition (2.7) to obtain $D^\varepsilon w^\varepsilon(t, x, y) = 1$. This implies that $D^\varepsilon w^\varepsilon(t, x, y) \rightarrow 1$.

(b) $u(t, x) \in [0, u^*)$

Again the convergence of $D^\varepsilon u^\varepsilon(t, x, y)$ implies that for small enough ε , $D^\varepsilon u^\varepsilon(t, x, y) \in [0, u^*)$. In this case, $r(D^\varepsilon u^\varepsilon)(t, x, y) \leq 1$ leading to $D^\varepsilon w^\varepsilon = r(D^\varepsilon u^\varepsilon)$ using (2.7). With continuity of r , we get $D^\varepsilon w^\varepsilon(t, x, y)$ converges to $r(u)(t, x)$.

(c) $u(t, x) = u^*$

Using similar arguments as above, $r(u)(t, x) = 1$ and $r(D^\varepsilon u^\varepsilon)(t, x, y) \rightarrow 1$. Hence, $D^\varepsilon w^\varepsilon(t, x, y) = \min(r(D^\varepsilon u^\varepsilon), 1) \rightarrow 1$.

In line with the micro scale model we define $w = 0$ for $v < 0$. Collecting the above cases, $D^\varepsilon w^\varepsilon$ converges a.e. to \tilde{w} where

$$\tilde{w} = \begin{cases} 1, & v > 0, \\ \min(r(u), 1), & v = 0, \\ 0, & v < 0. \end{cases} \quad (5.5)$$

Combining this with the weak-* convergence of $D^\varepsilon w^\varepsilon$ to w , we get $w = \tilde{w}$. This completes the identification of w satisfying (3.5). \square

6 Derivation of the macroscopic model.

In this section, we use the convergence results derived above to pass to the limit in the microscopic mode for $\varepsilon \searrow 0$. The following theorem holds.

Theorem 6.1. *The limit triple (u, v, w) obtained in Lemma 5.2 is the solution to the upscaled model (3.9).*

Proof. We first pass to the limit in (2.8)₂. Using the convergence results 7. and 8. from Lemma 5.2, and the Corollary 5.1, we immediately obtain (3.9)₂. Since (3.9)₃ is proved in Theorem 5.2, it remains to derive the macroscopic equation (3.9)₁. For this purpose, let $\phi \in C_0^\infty(0, T)$ and $\psi \in H^1(\Omega)$, and consider (2.8)₁ in the following equivalent form

$$\begin{aligned} & \int_0^T (\partial_t (\chi_{\Omega^\varepsilon} u^\varepsilon), \psi)_\Omega \phi(t) dt + D \int_0^T (\nabla \tilde{u}^\varepsilon, \chi^\varepsilon \nabla \psi)_\Omega \phi(t) dt - \int_0^T (\mathbf{q}^\varepsilon \chi^\varepsilon \tilde{u}^\varepsilon, \nabla \psi)_\Omega \phi(t) dt \\ & = -\varepsilon \int_0^T (\partial_t v^\varepsilon, \psi)_{\Gamma_G^\varepsilon} \phi(t) dt, \end{aligned} \quad (6.1)$$

where χ^ε is the characteristic function for Ω^ε . Now, we choose as test function $\psi(x) = \psi_0(x) + \varepsilon \psi_1(x, \frac{x}{\varepsilon})$ with $\psi_0 \in C_0^\infty(\Omega)$ and $\psi_1 \in C_0^\infty(\Omega; C_{\text{per}}^\infty(Z))$. This gives

$$\begin{aligned} & \int_0^T (\partial_t (\chi_{\Omega^\varepsilon} u^\varepsilon), \psi_0 + \varepsilon \psi_1(\cdot, \frac{\cdot}{\varepsilon}))_\Omega \phi(t) dt \\ & + D \int_0^T (\nabla \tilde{u}^\varepsilon, \chi^\varepsilon (\nabla \psi_0 + \varepsilon \nabla_x \psi_1(\cdot, \frac{\cdot}{\varepsilon}) + \nabla_y \psi_1(\cdot, \frac{\cdot}{\varepsilon})))_\Omega \phi(t) dt \\ & - \int_0^T (\mathbf{q}^\varepsilon \chi^\varepsilon \tilde{u}^\varepsilon, \nabla \psi_0 + \varepsilon \nabla_x \psi_1(\cdot, \frac{\cdot}{\varepsilon}) + \nabla_y \psi_1(\cdot, \frac{\cdot}{\varepsilon}))_\Omega \phi(t) dt \\ & = -\varepsilon \int_0^T (\partial_t v^\varepsilon, \psi_0 + \varepsilon \psi_1(\cdot, \frac{\cdot}{\varepsilon}))_{\Gamma_G^\varepsilon} \phi(t) dt, \end{aligned} \quad (6.2)$$

For $\varepsilon \searrow 0$ and using Lemma 5.2 and (3.9)₂, we obtain

$$\begin{aligned} & -|Y| \int_0^T (\partial_t u, \psi_0) \phi(t) dt + D \int_0^T \int_{\Omega \times Y} (\nabla_x u(t, x) + \nabla_y u_1(t, x, y), \nabla_x \psi_0(x) + \nabla_y \psi_1(x, y)) \phi(t) dt \\ & -|Y| \int_0^T \int_\Omega \mathbf{q}(x) u(t, x) \nabla \psi_0(x) \phi(t) dt + |\Gamma_G| \int_0^T \int_\Omega (r(u) - w, \psi_0) \phi(t) dt = 0. \end{aligned}$$

Note that to pass to the limit in the convective term in (6.2), we used the weak convergence of $\chi^\varepsilon \mathbf{q}^\varepsilon$ to \mathbf{q} (see e.g. the proof of Proposition 14 in [18]). The above equation is equivalent to the macroscopic equation (3.9)₁, where the homogenized matrix S is given by (3.6), see e.g. [2]. This completes the proof of the theorem. \square

7 Uniqueness of the macroscopic model

We conclude with a uniqueness argument.

Theorem 7.1. *Problem (3.4)-(3.8) has a unique solution.*

Proof. Assume that there exist two solution triples (u_1, v_1, w_1) and (u_2, v_2, w_2) . Define:

$$U := u_1 - u_2, \quad V := v_1 - v_2, \quad W := w_1 - w_2.$$

Clearly, at $t = 0$, we have $U(0, x) = V(0, x) = W(0, x) = 0$ for all $x \in \Omega$. In terms of the differences defined above, we have the resulting equations as:

$$(\partial_t U, \phi) + (DS \nabla U, \nabla \phi) + (\nabla \cdot (\mathbf{q}U), \phi) = -\frac{|\Gamma_G|}{|Y|} (r(u_1) - r(u_2) - W, \phi), \quad (7.1)$$

$$(\partial_t V, \theta) = (r(u_1) - r(u_2) - W, \theta), \quad (7.2)$$

for all $(\phi, \theta) \in L^2(0, T, H_0^1(\Omega)) \times L^2(0, T; L^2(\Omega))$.

The uniqueness is proved as follows: first we use (7.2) to estimate V in terms of U . This estimate can be then used in (7.1) to show that for all t , the norm of $U(t)$ is bounded by the initial condition, which is zero here. This establishes the uniqueness for U and thereby for V from the previous estimate. The uniqueness for W follows directly from (3.5).

Taking $\theta = \chi_{(0,t)} V$ in (7.2) gives

$$\frac{1}{2} \|V(t, \cdot)\|^2 = \int_0^t \int_{\Omega} (r(u_1) - r(u_2)) V(s, x) dx ds - \int_0^t \int_{\Omega} WV(s, x) dx ds.$$

Since $w_i \in H(v_i)$ and $H(\cdot)$ is monotone, WV is non-negative. The integral in the last term is thus non-negative. Using the Lipschitz continuity of r , this gives

$$\frac{1}{2} \|V(t, \cdot)\|^2 \leq \frac{1}{2} \int_0^t L_r^2 \|U(s, \cdot)\|^2 ds + \frac{1}{2} \int_0^t \|V(s, \cdot)\|^2 ds.$$

Employing Gronwall's inequality one gets

$$\|V(t, \cdot)\|^2 \leq C \exp(t) \int_0^t \|U(s, \cdot)\|^2 ds \leq C(T) \int_0^t \|U(s, \cdot)\|^2 ds. \quad (7.3)$$

The above estimate bounds V in terms of U and will be used below to estimate U in terms of initial conditions. Letting $t \in (0, T]$ fixed arbitrary and with $\psi \in H_0^1(\Omega)$, taking $\phi = \theta = \chi_{(0,t)} \psi$ in (7.1) - (7.2), multiplying the second by $\frac{|\Gamma_G|}{|Y|}$ and adding it to the first, since U and V are both 0 at $t = 0$ one gets

$$(U(t), \psi) + (DS \int_0^t \nabla U(s) ds, \nabla \psi) + \frac{|\Gamma_G|}{|Y|} (V(t), \psi) = -(\mathbf{q} \int_0^t \nabla U(s) ds, \psi).$$

Here we have used the fact that \mathbf{q} is divergence free and does not depend on time. Now we choose $\psi(x) = U(t, x)$ to obtain

$$\begin{aligned} \|U(t, \cdot)\|^2 + D \left(S \int_0^t \nabla U(s, \cdot) ds, \nabla U(t, \cdot) \right) + \frac{|\Gamma_G|}{|Y|} (V(t, \cdot), U(t, \cdot)) \\ \leq -(S^{1/2} \int_0^t \nabla U(s) ds, S^{-1/2} \mathbf{q} U(t, x)) \\ \leq \frac{\mu}{2} \left\| S^{1/2} \int_0^t \nabla U(s, \cdot) \right\|^2 + \frac{2M_q^2}{\mu \alpha_S} \|U(t, \cdot)\|^2, \end{aligned}$$

where $\mu > 0$ is any positive constant. In the above, we have used that S is symmetric positive definite, and hence, there exists $\alpha_S > 0$ such that $(S\xi, \xi) > \alpha_S (\xi, \xi)$ for any $\xi \in \mathbb{R}^3$.

From (7.3) and choosing μ properly, a $C > 0$ exists s.t.

$$\|U(t, \cdot)\|^2 + 2D \left(S \int_0^t \nabla U(s, \cdot) ds, \nabla U(t, \cdot) \right) \leq C \left(\int_0^t \|U(z, \cdot)\|^2 dz + D \left\| S^{1/2} \int_0^t \nabla U(s, \cdot) \right\|^2 \right).$$

With

$$E(t) := \int_0^t \|U(s, \cdot)\|^2 ds + D \left\| S^{1/2} \int_0^t \nabla U(s, \cdot) ds \right\|^2,$$

the above becomes

$$E'(t) \leq C E(t).$$

Clearly, $E(0) = 0$ and $E(t) \geq 0$ for all t , which immediately gives $E(t) = 0$ for all t . This ensures that $U(t) = 0$ and, by (7.3), $V(t) = 0$. This concludes the proof of uniqueness. \square

Remark 7.1. *Recall that the flow problem is independent of the transport variables. The above derivation of the limit equations and the uniqueness result provide an independent proof for the existence and uniqueness of the upscaled model involving both flow and transport (3.1) - (3.8).*

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