

# DERIVATION OF A MACROSCOPIC MODEL FOR TRANSPORT OF STRONGLY SORBED SOLUTES IN THE SOIL USING HOMOGENIZATION THEORY

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**Abstract.** In this paper we derive a model for the diffusion of strongly sorbed solutes in soil taking into account diffusion within both the soil fluid phase and the soil particles. The model takes into account the effect of solutes being bound to soil particle surfaces by a reversible nonlinear reaction. Effective macroscale equations for the solute movement in the soil are derived using homogenization theory. In particular we use the unfolding method to prove the convergence of nonlinear reaction terms in our system. We use the final, homogenized model to estimate the effect of solute dynamics within soil particles on plant phosphate uptake by comparing our double-porosity model to the more commonly used single porosity model. We find that there are significant qualitative and quantitative differences in the predictions of the models. This highlights the need for careful experimental and theoretical treatment of the plant-soil interaction when trying to understand solute losses from the soil.

**1. Introduction.** Recent reports predicting global food shortages highlight the need for us to develop a good understanding of the main processes that control crop growth, such as the bioavailability of nutrients in the soil. One of the commonest limiting nutrients, particularly in Africa, is phosphate. This is often so strongly bound to the soil as to make it almost immobile [24]. If a solute equilibrates rapidly with the soil at the local, soil-particle, scale then it is possible to treat the soil as homogeneous at that scale and use the standard single-porosity model for diffusion in the soil, [24]. However experimental results, [16], [23], indicate that for strongly-sorbed solutes, which are immobile on soil surfaces, and which may undergo slow sorption reactions, local equilibration is far slower and needs to be taken into account explicitly.

In this paper we present the derivation of a model for transport of strongly sorbed solutes in the soil considering the physical processes and geometrical properties at the scale of a single soil particle, Section 3. In contrast to existing models, we describe the movement of solutes by diffusion in both the solution and the soil particles. We also consider nonlinear, non-equilibrium reactions of the solute at the particle surface and inside the particles. The complexity of the microscopic system means that effective numerical simulations on the time and length scale of practical interest are not possible. Applying two-scale convergence, introduced in [1], [19], [25], and extended to sequences of functions defined on  $\varepsilon$ -periodic hypersurfaces in [2], [17], we derive a macroscopic model in Section 6. The main mathematical difficulty and novelty of the results presented in this paper is to prove the

convergence of the nonlinear terms in the model. Using the unfolding method, [4, 6, 7, 8, 15, 18], and the structure of the equations we show in Lemma 5.4 the two-scale convergence of the nonlinear functions. The macroscopic model depends crucially on the ratio between diffusion coefficients in the inter-particle  $D_e$  and intra-particle  $D_i$  spaces. If  $D_i/D_e \approx \varepsilon^2$ , where  $\varepsilon$  denotes the ratio of the size of the single particle domain relative to the whole soil sample size, then macroscopic model we obtain is a double-porosity model which is fully analysed in this article. For other cases we find that when  $D_i/D_e \approx \varepsilon$  solute concentrations are independent of microscopic variable, and the microscopic structure of the model influences only the new macroscopic diffusion coefficient and the reaction terms. When  $D_i/D_e \approx \varepsilon^3$  the processes in the inter-particle and intra-particle spaces are decoupled. Thus, for  $D_i/D_e \approx \varepsilon$  and  $D_i/D_e \approx \varepsilon^3$  single-porosity models are obtained. The macroscopic equations for the latter two cases are formulated in Section 9.

Whilst no suitable model for the experimental system discussed in this paper exists there is some relevant previous theoretical work specialised for other experimental systems. For instance, the derivation of a linear double-porosity model for single-phase flow in a fractured porous media using the theory of multiscale analysis has been presented in [4]. A formal asymptotic expansion ansatz was applied in [3] to derive a macroscopic model for incompressible two-phase flow in a double porous reservoir. To derive this model rigorously the authors in [6] used two-scale convergence, the unfolding method, knowledge of the macroscopic system derived in [3], and the monotonicity of the nonlinear diffusion operator. In [11] the authors described a model for diffusion, convection and nonlinear reactions in a periodic array of cells with permeable membranes. The concept of two-scale convergence coupled with monotonicity methods, compensated compactness and special structure of the nonlinear functions were used to deal with convergence in the nonlinear terms. The result obtained in [11] differs from the analysis presented in this article due to the special structure of the nonlinear functions inside the microstructure (cells), the absence of nonlinear reactions on the surface of the microstructures, and different transmission conditions between the free fluid domain (intercellular space) and particle (cell).

**2. Main results.** Considering the physical processes on the scale of a single soil particle we derive in Section 3 the microscopic dimensionless model for solute transport in the soil

$$\begin{aligned}
\partial_t L_e^\varepsilon - \nabla \cdot (\mathcal{D}^\varepsilon \nabla L_e^\varepsilon) &= 0 && \text{in } \Omega_0^\varepsilon \\
\theta_i \partial_t L_i^\varepsilon - \varepsilon^2 \nabla \cdot (\bar{\mathcal{D}}^\varepsilon \nabla L_i^\varepsilon) &= -G_f^\varepsilon(t, x, L_i^\varepsilon, S_{if}^\varepsilon) - G_s^\varepsilon(t, x, L_i^\varepsilon, S_{is}^\varepsilon) && \text{in } \Omega_1^\varepsilon, \\
\partial_t S_e^\varepsilon = F^\varepsilon(t, x, L_e^\varepsilon, S_e^\varepsilon) &\quad \text{on } \Gamma_1^\varepsilon, && \partial_t S_i^\varepsilon = G^\varepsilon(t, x, L_i^\varepsilon, S_i^\varepsilon) \quad \text{in } \Omega_1^\varepsilon
\end{aligned} \tag{2.1}$$

with boundary and initial conditions

$$\begin{aligned}
L_e^\varepsilon &= L_i^\varepsilon \quad \text{and} \quad \mathcal{D}^\varepsilon \nabla L_e^\varepsilon \cdot \nu = \varepsilon^2 \bar{\mathcal{D}}^\varepsilon \nabla L_i^\varepsilon \cdot \nu - \varepsilon F_f^\varepsilon(t, x, L_e^\varepsilon, S_{ef}^\varepsilon) - \varepsilon F_s^\varepsilon(t, x, L_e^\varepsilon, S_{es}^\varepsilon) \quad \text{on } \Gamma_1^\varepsilon, \\
\nabla L_e^\varepsilon \cdot \nu &= 0 \quad \text{on } \Gamma_2^\varepsilon, \quad L_e^\varepsilon = L_{eD} \quad \text{on } \partial\Omega_D, \quad \nabla L_e^\varepsilon \cdot \nu = 0 \quad \text{on } \partial\Omega_N, \quad (2.2) \\
L_e^\varepsilon(0, x) &= L_{e0}^\varepsilon(x) \quad \text{in } \Omega_0^\varepsilon, \quad L_i^\varepsilon(0, x) = L_{i0}^\varepsilon(x) \quad \text{in } \Omega_1^\varepsilon, \\
S_e^\varepsilon(0, x) &= S_{e0}^\varepsilon(x) \quad \text{on } \Gamma_1^\varepsilon, \quad S_i^\varepsilon(0, x) = S_{i0}^\varepsilon(x) \quad \text{in } \Omega_1^\varepsilon,
\end{aligned}$$

where  $S_e^\varepsilon = (S_{ef}^\varepsilon, S_{es}^\varepsilon)^T$ ,  $S_i^\varepsilon = (S_{if}^\varepsilon, S_{is}^\varepsilon)^T$ ,  $F^\varepsilon = (F_f^\varepsilon, F_s^\varepsilon)^T$ ,  $G^\varepsilon = (G_f^\varepsilon, G_s^\varepsilon)^T$ .

Applying the techniques of homogenization we derive rigorously in Section 6 the macroscopic double-porosity model defined on the scale of the whole soil domain

$$\begin{aligned}
|Y_0| \partial_t L_e - \nabla \cdot (A_{hom} \nabla L_e) &= \int_{\Gamma_1} \left( \bar{\mathcal{D}} \nabla_y L_i(t, x, y) \cdot \nu - F_f(t, y, L_e, S_{ef}) - F_s(t, y, L_e, S_{es}) \right) d\gamma \quad \text{in } \Omega, \\
\theta_i \partial_t L_i - \nabla_y \cdot (\bar{\mathcal{D}} \nabla_y L_i) &= -G_f(t, y, L_i, S_{if}) - G_s(t, y, L_i, S_{is}) \quad \text{in } Y_1 \times \Omega, \quad (2.3) \\
\partial_t S_e &= F(t, y, L_e, S_e) \quad \text{in } \Gamma_1 \times \Omega, \quad \partial_t S_i = G(t, y, L_i, S_i) \quad \text{in } Y_1 \times \Omega,
\end{aligned}$$

with boundary and initial conditions

$$\begin{aligned}
L_i &= L_e \quad \text{on } \Gamma_1 \times \Omega, \quad L_e = L_{eD} \quad \text{on } \partial\Omega_D, \quad \nabla L_e \cdot \nu = 0 \quad \text{on } \partial\Omega_N, \\
L_e(0, x) &= L_{e0}(x) \quad \text{in } \Omega, \quad L_i(0, x, y) = L_{i0}(y) \quad \text{in } Y_1 \times \Omega, \quad (2.4) \\
S_e(0, x, y) &= S_{e0}(y) \quad \text{in } \Gamma_1 \times \Omega, \quad S_i(0, x, y) = S_{i0}(y) \quad \text{in } Y_1 \times \Omega,
\end{aligned}$$

and matrix  $A_{hom}$  is defined by  $a_{ij} = \sum_{k=1}^3 \int_{Y_0} (D_{ij}(t, y) + D_{ik}(t, y) \partial_{y_k} w_j) dy$ , where  $w_j$  are solutions of unit cell problems

$$\begin{aligned}
-\nabla_y \cdot (\mathcal{D}(t, y) \nabla_y w_j) &= \sum_{k=1}^3 \partial_{y_k} D_{kj}(t, y) \quad \text{in } Y_0, \quad (2.5) \\
-\mathcal{D}(t, y) \nabla_y w_j \cdot \nu &= \sum_{k=1}^3 D_{kj}(t, y) \nu_k \quad \text{on } \Gamma_1 \cup \Gamma_2, \quad w_j \quad \text{periodic in } Z, \quad \int_{Y_0} w_j dy = 0.
\end{aligned}$$

Here  $F = (F_f, F_s)^T$ ,  $G = (G_f, G_s)^T$ ,  $S_e = (S_{ef}, S_{es})^T$ ,  $S_i = (S_{if}, S_{is})^T$ . Thus the macroscopic model includes a rigorously derived relationship between the effective diffusion coefficients and microscopic physical properties of the soil and soil chemical reactions. We contrast the equations (2.3)-(2.4) above with the standard single porosity equilibrium reaction model describing the solute movement in the soil. This model, presented in [24], is

$$\begin{aligned}
(|Y_0| + \theta_i |Y_1| + \bar{\beta}) \partial_t L_e - \nabla \cdot (A_{hom} \nabla L_e) &= 0 \quad \text{in } (0, T) \times \Omega, \quad (2.6) \\
L_e &= L_{eD} \quad \text{on } (0, T) \times \partial\Omega_D, \quad \nabla L_e \cdot \nu = 0 \quad \text{on } (0, T) \times \partial\Omega_N, \quad L_e(0, x) = L_{e0}(x) \quad \text{in } \Omega,
\end{aligned}$$

where  $\bar{\beta}$  is the buffer power of the soil (the equilibrium exchange constant in the linear reaction). Due to the linearity of these equations, and given  $L_{e0} = 0$ , the one dimensional solution for the soil column has the form  $L_e = L_{eD} \exp(-x_1^2/4Dt)$ , where  $D = A_{hom}/(|Y_0| + \theta_i|Y_1| + \bar{\beta})$ . Thus, a plot of  $\log(L_e/L_{eD})$  against  $x_1^2/t$  will be a straight line and the slope of it can be used to determine  $D$  from the experimental data. However, in [16], the experimental results for Andosol and Cambisol could not be fitted with straight line. This is a strong experimental indication that the intraparticle dynamics is important at the soil column scale and a new double-porosity models with inter- and intra-particle reactions is needed. A non-linear relationship between the logarithm of the solute concentration and  $x_1^2/t$  has been predicted by a model in which the soil was represented as a hollow cylinder with parallel inter- and intra-aggregate pathways in the central and outer band of the cylinder, [23]. However this model gives a poor representation of the morphology of a real soil and the microscopic processes were not considered in the model.

In Section 7 we consider phosphate as an example of a strongly sorbed solute and present numerical solution of the double-porosity model (2.3), (2.4). We compare numerical results for (2.3), (2.4), with and without slow reactions, with numerical solutions of the standard model (2.6).

**3. Derivation of the microscopic model.** We consider the soil to be a double porous material consisting of porous soil particles that are separated by water and air, see Figure 3.1.

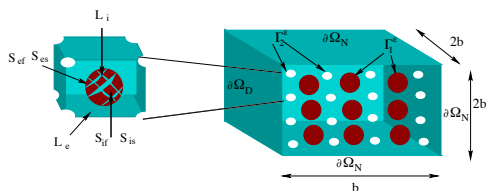


FIG. 3.1. *Representative single soil particle surrounded by solution and air. Periodically repeated particles in the soil*

We distinguish between the solute concentration in water between soil particles  $L_e^*$ ,  $\mu\text{mol}/\text{cm}^3$ , and inside each particle  $L_i^*$ ,  $\mu\text{mol}/\text{cm}^3$  and between adsorption to the surface of a particle and to the surfaces inside the porous particle. It is known that adsorption and desorption of strongly sorbed solutes can be fast in comparison to diffusion, [23]. We consider fast and slow absorbed concentrations  $S_{ef}^*$  and  $S_{es}^*$ ,  $\mu\text{mol}/\text{cm}^2$  on the particle surfaces,  $S_{if}^*$  and  $S_{is}^*$ ,  $\mu\text{mol}/\text{cm}^2$  on the surfaces inside the particle.

The solute concentration in the water in the inter-particle space is changing due to diffusion, fast and slow reactions on the particle surface, and due to the flux into the particle,

$$\partial_{t^*} L_e^* - \nabla \cdot (D_e \nabla L_e^*) = 0 \quad \text{in solution around particle, (3.1)}$$

$$D_e \nabla L_e^* \cdot \nu = D_i \nabla L_i^* \cdot \nu - \partial_{t^*} (\zeta_e S_{ef}^*) - \partial_{t^*} (\zeta_e S_{es}^*) \quad \text{on particle surface, (3.2)}$$

$$L_e^* = L_i^* \quad \text{on particle surface, (3.3)}$$

where  $D_e(t^*, x^*) = D_0 d_e(t^*, x^*)$  is diffusion of solute in water,  $D_i(t^*, x^*) = f_i \theta_i D_0 d_i(t^*, x^*)$  is diffusion of solute inside the particle,  $f_i$  is the impedance factor of the particle,  $\nu$  is the particle boundary normal vector pointing inside the particle,  $\varsigma_e$  is the fraction of the particle surface area which is solid. In general in experiments diffusion coefficients are constant, i.e.  $d_e \equiv 1$ ,  $d_i \equiv 1$ . However, we will consider  $D_e$  and  $D_i$  to be dependent on  $t^*$ ,  $x^*$ , because we can conduct our analysis for this case and also we can envisage a case when solute diffusion depends on nonhomogeneous hydrodynamic or chemical properties of the soil. For the fast and slow adsorbed concentrations on the particle surface we take

$$\partial_{t^*}(\varsigma_e S_{ef}^*) = \varsigma_e F_f^*(t^*, x^*, L_e^*, S_{ef}^*) \quad \text{and} \quad \partial_{t^*}(\varsigma_e S_{es}^*) = \varsigma_e F_s^*(t^*, x^*, L_e^*, S_{es}^*) \quad \text{on particle surface,} \quad (3.4)$$

where  $F_f^*$  and  $F_s^*$  are reaction kinetics for fast and slow adsorbed solute concentration, respectively.

The solute concentration in the water fraction inside the particle is changing due to diffusion, adsorption and desorption on the solid surface inside the particle, and the flux of the solute concentration from interparticle to intraparticle domain, covered already in (3.2) and (3.3),

$$\partial_{t^*}(\theta_i L_i^*) - \nabla \cdot (D_i \nabla L_i^*) = -\partial_{t^*}(\varsigma_i S_{if}^*) - \partial_{t^*}(\varsigma_i S_{is}^*) \quad \text{inside the particle.} \quad (3.5)$$

The adsorbed concentration inside the particle is given by

$$\partial_{t^*}(\varsigma_i S_{if}^*) = \varsigma_i G_f^*(t^*, x^*, L_i^*, S_{if}^*) \quad \text{and} \quad \partial_{t^*}(\varsigma_i S_{is}^*) = \varsigma_i G_s^*(t^*, x^*, L_i^*, S_{is}^*) \quad \text{inside the particle,} \quad (3.6)$$

where  $G_f^*$  and  $G_s^*$  are reactions kinetics for fast and slow adsorbed solute concentrations,  $\varsigma_i$ ,  $\text{cm}^2/\text{cm}^3$ , is the internal surface area density, i.e. surface area inside the particle per volume of particle,  $\theta_i$ ,  $\text{cm}^3/\text{cm}^3$ , is the particle porosity, i.e. volume of water inside the particle per volume of particle.

We consider the model in  $\tilde{\Omega} = \{(x_1^*, x_2^*, x_3^*) \in (0, b) \times (-b, b)^2\}$ . We will pose on  $\partial\tilde{\Omega}_D = \{x_1 = 0\}$  Dirichlet or non-zero Neumann boundary conditions and on  $\partial\tilde{\Omega}_N$  zero Neumann boundary conditions. We nondimensionalise the equations by setting  $t^* = [t]t$ ,  $\mathbf{x}^* = [x]\mathbf{y}$ ,  $L_e^* = [L_e]L_e$ ,  $L_i^* = [L_i]L_i$ ,  $S_{ef}^* = [S_{ef}]S_{ef}$ ,  $S_{es}^* = [S_{es}]S_{es}$ ,  $S_{if}^* = [S_{if}]S_{if}$ , and  $S_{is}^* = [S_{is}]S_{is}$ . In a representative experiment, [23], the length of the domain containing a particle with radius  $a = 9.98 \cdot 10^{-3}$  cm surrounded by solution and air is  $l = 0.02$  cm, and the length of the whole soil sample domain is  $b = 1$  cm. We are interested in the processes which occur on a time scale associated with the whole domain, thus we choose a timescale for diffusion that takes place on a soil sample scale  $[t] = \frac{b^2}{D_0}$ . In order to see the influence of the diffusion inside the particle on the behaviour of the whole system we choose as the scale for space  $[x] = l$ . Due to the continuity condition  $L_e^* = L_i^*$  it is convenient to choose  $[L_e] = [L_i]$

and as representative concentration  $[L_e] = 1\mu\text{mol}/\text{cm}^3$ . Considering the difference in the dimensions, we choose  $[S_{ef}] = [S_{es}] = [L_e]\frac{[x]}{\varsigma_e}$  and  $[S_{if}] = [S_{is}] = [L_i]/\varsigma_i$ . The dimensionless functions in the equations are  $\mathcal{D}(t, y) = d_e(\frac{b^2}{D_0}t, ly)$ ,  $F_j(t, y, L_e, S_{ej}) = \frac{b^2}{D_0[S_{ej}]}F_j^*(\frac{b^2}{D_0}t, ly, L_e[L_e], S_{ej}[S_{ej}])$ ,  $G_j(t, y, L_i, S_{ij}) = \frac{b^2}{D_0[S_{ij}]}G_j^*(\frac{b^2}{D_0}t, ly, L_i[L_i], S_{ij}[S_{ij}])$ ,  $j = f, s$ . The typical relation between diffusion inside the particle and in the free fluid  $\frac{D_i}{D_0} \sim 2 \cdot 10^{-4}$  is comparable to  $\varepsilon^2$ , with  $\varepsilon = l/b$ . Thus  $\bar{\mathcal{D}}(t, y) = \frac{D_i(\frac{b^2}{D_0}t, ly)}{D_0\varepsilon^2}$  is of order one. The geometric microstructure within the dimensionless domain  $\Omega = (0, 1) \times (-1, 1)^2$  is obtained by intersecting the  $\varepsilon$ -multiple  $\varepsilon Z$  with  $\Omega$ , where  $Z = [0, 1]^3$  a ‘‘unit cell’’ with respect to fast variable  $y = \frac{x}{\varepsilon}$ . We consider  $Y_1, Y_2 \subset Z$ ,  $\bar{Y}_1 \cap \bar{Y}_2 = \emptyset$ , with smooth boundaries  $\Gamma_1, \Gamma_2$ , where  $Y_1$  denote the single soil particle,  $Y_2$  the air fraction, and  $Y_0 = Z \setminus (\bar{Y}_1 \cup \bar{Y}_2)$  the free fluid part. Then define  $\Omega_1^\varepsilon = \cup\{\varepsilon Y_1^k | \varepsilon Z^k \subset \Omega, k \in \mathbb{Z}^3\}$ ,  $\Omega_2^\varepsilon = \cup\{\varepsilon Y_2^k | \varepsilon Z^k \subset \Omega, k \in \mathbb{Z}^3\}$ , with  $Z^k = Z + \sum_{i=1}^3 k_i e_i$ , and  $\Omega_0^\varepsilon = \Omega \setminus (\bar{\Omega}_1^\varepsilon \cup \bar{\Omega}_2^\varepsilon)$ ,  $\Gamma_1^\varepsilon = \cup\{\varepsilon \Gamma_1^k | \varepsilon Z^k \subset \Omega, k \in \mathbb{Z}^3\}$ ,  $\Gamma_2^\varepsilon = \cup\{\varepsilon \Gamma_2^k | \varepsilon Z^k \subset \Omega, k \in \mathbb{Z}^3\}$ , where  $Y_1^k, Y_2^k, \Gamma_1^k, \Gamma_2^k$  are maps of  $Y_1, Y_2, \Gamma_1, \Gamma_2$  in  $Z^k$ .

The coefficients in the equations and initial conditions are defined by  $Z$ -periodic functions:  $\mathcal{D}^\varepsilon = (D_{i,j}^\varepsilon)$  with  $D_{i,j}^\varepsilon(t, x) = D_{i,j}(t, \frac{x}{\varepsilon})$ ,  $\bar{\mathcal{D}}^\varepsilon = (\bar{D}_{i,j}^\varepsilon)$  with  $\bar{D}_{i,j}^\varepsilon(t, x) = \bar{D}_{i,j}(t, \frac{x}{\varepsilon})$ ,  $F^\varepsilon(t, x, \eta, \xi) = F(t, \frac{x}{\varepsilon}, \eta, \xi)$ ,  $G^\varepsilon(t, x, \eta, \xi) = G(t, \frac{x}{\varepsilon}, \eta, \xi)$  for  $t \in (0, T)$ ,  $\eta \in \mathbb{R}$ ,  $\xi \in \mathbb{R}^2$ , and  $L_{i0}^\varepsilon(x) = L_{i0}(\frac{x}{\varepsilon})$ ,  $S_{e0}^\varepsilon(x) = (S_{ef0}(\frac{x}{\varepsilon}), S_{es0}(\frac{x}{\varepsilon}))^T$ ,  $S_{i0}^\varepsilon(x) = (S_{if0}(\frac{x}{\varepsilon}), S_{is0}(\frac{x}{\varepsilon}))^T$ . Incorporating the nondimensionalization and the above notations into equations (3.1)–(3.6) we obtain the microscopic model (2.1)–(2.2).

**4. Existence of solution of microscopic model. A priori estimates.** We start the analysis with the definition of a weak solution and the existence result for the problem (2.1), (2.2). Then we derive a priori estimates for sequences  $L_e^\varepsilon, L_i^\varepsilon, S_{ef}^\varepsilon, S_{es}^\varepsilon, S_{if}^\varepsilon, S_{is}^\varepsilon$  uniformly with respect to  $\varepsilon$ .

*Assumption 4.1.*

1. The matrices  $\mathcal{D}, \bar{\mathcal{D}}$  are symmetric, elliptic,  $(\mathcal{D}(t, y)\xi, \xi) \geq d_0|\xi|^2$ ,  $(\bar{\mathcal{D}}(t, y)\xi, \xi) \geq \bar{d}_0|\xi|^2$  for  $d_0, \bar{d}_0 > 0$ ,  $\xi \in \mathbb{R}^3$ , a.a.  $(t, y) \in (0, T) \times Z$ ,  $\mathcal{D} \in L^\infty((0, T) \times Z)^{3 \times 3}$ ,  $\bar{\mathcal{D}} \in L^\infty(0, T; W^{1, \infty}(Z))^{3 \times 3}$ ,  $\partial_t \mathcal{D}, \partial_t \bar{\mathcal{D}} \in L^\infty((0, T) \times Z)^{3 \times 3}$ .
2. The function  $F(t, y, \eta, \xi) : (0, T) \times \Gamma_1 \times \mathbb{R} \times \mathbb{R}^2 \rightarrow \mathbb{R}^2$  is continuous and Lipschitz continuous in  $\xi, \eta$  uniformly in  $t, y$ , i.e.  $|F_j(t, y, \eta_1, \xi_1) - F_j(t, y, \eta_2, \xi_2)| \leq c(|\eta_1 - \eta_2| + |\xi_1 - \xi_2|)$ ,  $j = f, s$ , and  $\mathcal{F}_j, \partial_\eta \mathcal{F}_j = F_j$ , is such that  $\partial_\xi \mathcal{F}_j$  is sublinear, i.e.  $|\partial_\xi \mathcal{F}_j(t, y, \eta, \xi)| \leq c(1 + |\xi| + |\eta|)$ ,  $|\mathcal{F}_j(t, y, \eta, \xi)| \leq c(1 + |\xi|^2 + |\eta|^2)$ , and  $|\partial_t \mathcal{F}_j(t, y, \eta, \xi)| \leq c(1 + |\xi|^2 + |\eta|^2)$ .
3. The function  $G(t, y, \eta, \xi) : (0, T) \times Y_1 \times \mathbb{R} \times \mathbb{R}^2 \rightarrow \mathbb{R}^2$  is continuous and Lipschitz continuous in  $\xi, \eta$  uniformly in  $t, y$ , i.e.  $|G_j(t, y, \eta_1, \xi_1) - G_j(t, y, \eta_2, \xi_2)| \leq c(|\eta_1 - \eta_2| + |\xi_1 - \xi_2|)$ ,  $j = f, s$ .
4. The Dirichlet boundary data satisfies  $L_{eD} \in H^1(0, T; H^1(\Omega))$ .
5.  $L_{e0}^\varepsilon \in H^1(\Omega)$ ,  $L_{e0}^\varepsilon \rightarrow L_{e0}$  weakly in  $H^1(\Omega)$ ,  $L_{i0} \in H^1(Z)$ ,  $S_{e0} \in L^2(\Gamma_1)^2$ ,  $S_{i0} \in L^2(Y_1)^2$ .

For definition of a weak solution of model (2.1), (2.2) we consider the function space

$$W^\varepsilon = \{(\phi_1, \phi_2) : \phi_1 \in H^1(\Omega_0^\varepsilon), \phi_1 = 0 \text{ on } \partial\Omega_D, \phi_2 \in H^1(\Omega_1^\varepsilon), \text{ and } \phi_1 = \phi_2 \text{ on } \Gamma_1^\varepsilon\}.$$

DEFINITION 4.2. *Functions  $L_e^\varepsilon$ ,  $L_i^\varepsilon$ ,  $S_e^\varepsilon$ , and  $S_i^\varepsilon$  are solutions of the microscopic model (2.1), (2.2) if  $(L_e^\varepsilon - L_{eD}, L_i^\varepsilon - L_{eD}) \in L^2(0, T; W^\varepsilon)$ ,  $\partial_t L_e^\varepsilon \in L^2((0, T) \times \Omega_0^\varepsilon)$ ,  $\partial_t L_i^\varepsilon \in L^2((0, T) \times \Omega_1^\varepsilon)$ ,  $S_e^\varepsilon \in H^1(0, T; L^2(\Gamma_1^\varepsilon)^2)$ ,  $S_i^\varepsilon \in H^1(0, T; L^2(\Omega_1^\varepsilon)^2)$  such that*

$$\begin{aligned} & \int_0^T \int_{\Omega_0^\varepsilon} (\partial_t L_e^\varepsilon \phi_1 + \mathcal{D}^\varepsilon \nabla L_e^\varepsilon \nabla \phi_1) dx dt + \int_0^T \int_{\Omega_1^\varepsilon} (\theta_i \partial_t L_i^\varepsilon \phi_2 + \varepsilon^2 \bar{\mathcal{D}}^\varepsilon \nabla L_i^\varepsilon \nabla \phi_2) dx dt \\ &= - \int_0^T \int_{\Gamma_1^\varepsilon} \varepsilon (F_f^\varepsilon(L_e^\varepsilon, S_{ef}^\varepsilon) + F_s^\varepsilon(L_e^\varepsilon, S_{es}^\varepsilon)) \phi_1 d\gamma dt - \int_0^T \int_{\Omega_1^\varepsilon} (G_f^\varepsilon(L_i^\varepsilon, S_{if}^\varepsilon) + G_s^\varepsilon(L_i^\varepsilon, S_{is}^\varepsilon)) \phi_2 dx dt, \quad (4.1) \\ & \int_0^T \int_{\Gamma_1^\varepsilon} \partial_t S_e^\varepsilon \psi d\gamma dt = \int_0^T \int_{\Gamma_1^\varepsilon} F^\varepsilon(L_e^\varepsilon, S_e^\varepsilon) \psi d\gamma dt, \quad \int_0^T \int_{\Omega_1^\varepsilon} \partial_t S_i^\varepsilon \tilde{\psi} dx dt = \int_0^T \int_{\Omega_1^\varepsilon} G^\varepsilon(L_i^\varepsilon, S_i^\varepsilon) \tilde{\psi} dx dt, \end{aligned}$$

for  $\phi = (\phi_1, \phi_2) \in L^2(0, T; W^\varepsilon)$ ,  $\psi \in L^2((0, T) \times \Gamma_1^\varepsilon)^2$ ,  $\tilde{\psi} \in L^2((0, T) \times \Omega_1^\varepsilon)^2$ , and  $L_e^\varepsilon \rightarrow L_{e0}^\varepsilon$ ,  $L_i^\varepsilon \rightarrow L_{i0}^\varepsilon$ ,  $S_e^\varepsilon \rightarrow S_{e0}^\varepsilon$ ,  $S_i^\varepsilon \rightarrow S_{i0}^\varepsilon$  as  $t \rightarrow 0$  in  $L^2$ .

THEOREM 4.3. *Under Assumption 4.1 for every fixed  $\varepsilon > 0$  there exist unique solution of (2.1)-(2.2).*

*Proof.* The existence of solution of (2.1), (2.2) is equivalent to the existence of a fixed point of  $K$  defined on  $L^2((0, T) \times \Gamma_1^\varepsilon) \times L^2((0, T) \times \Omega_1^\varepsilon)$  by  $(L_e^{n,\varepsilon}, L_i^{n,\varepsilon}) = K(L_e^{n-1,\varepsilon}, L_i^{n-1,\varepsilon})$ , where  $L_e^{n,\varepsilon}, L_i^{n,\varepsilon}$  are solutions of

$$\partial_t L_e^{n,\varepsilon} - \nabla \cdot (\mathcal{D}^\varepsilon \nabla L_e^{n,\varepsilon}) = 0 \quad \text{in } \Omega_0^\varepsilon \quad (4.2)$$

$$\theta_i \partial_t L_i^{n,\varepsilon} - \varepsilon^2 \nabla \cdot (\bar{\mathcal{D}}^\varepsilon \nabla L_i^{n,\varepsilon}) = -G_f^\varepsilon(t, x, L_i^{n-1,\varepsilon}, S_{if}^{n,\varepsilon}) - G_s^\varepsilon(t, x, L_i^{n-1,\varepsilon}, S_{is}^{n,\varepsilon}) \quad \text{in } \Omega_1^\varepsilon, \quad (4.3)$$

$$\partial_t S_e^{n,\varepsilon} = F^\varepsilon(t, x, L_e^{n-1,\varepsilon}, S_e^{n,\varepsilon}) \quad \text{on } \Gamma_1^\varepsilon, \quad \partial_t S_i^{n,\varepsilon} = G^\varepsilon(t, x, L_i^{n-1,\varepsilon}, S_i^{n,\varepsilon}) \quad \text{in } \Omega_1^\varepsilon, \quad (4.4)$$

$$L_e^{n,\varepsilon} = L_i^{n,\varepsilon}, \quad \mathcal{D}^\varepsilon \nabla L_e^{n,\varepsilon} \cdot \nu = \varepsilon^2 \bar{\mathcal{D}}^\varepsilon \nabla L_i^{n,\varepsilon} \cdot \nu - \varepsilon (F_f^\varepsilon(L_e^{n-1,\varepsilon}, S_{ef}^{n,\varepsilon}) + F_s^\varepsilon(L_e^{n-1,\varepsilon}, S_{es}^{n,\varepsilon})) \quad \text{on } \Gamma_1^\varepsilon, \quad (4.5)$$

with boundary, initial conditions (2.2). For given  $L_e^{n-1,\varepsilon} \in L^2((0, T) \times \Gamma_1^\varepsilon)$ ,  $L_i^{n-1,\varepsilon} \in L^2((0, T) \times \Omega_1^\varepsilon)$  due to Lipschitz continuity of the right hand side, there exist solutions of ordinary differential equations (4.4),  $S_e^\varepsilon \in H^1(0, T; L^2(\Gamma_1^\varepsilon)^2)$ ,  $S_i^\varepsilon \in H^1(0, T; L^2(\Omega_1^\varepsilon)^2)$ . Then, using the Galerkin method, [12], we obtain a solution of the parabolic problem (4.2), (4.3), (4.5), (2.2),  $(L_e^\varepsilon - L_{eD}, L_i^\varepsilon - L_{eD}) \in L^2(0, T; W^\varepsilon)$ ,  $L_e^\varepsilon \in H^1(0, T; L^2(\Omega_0^\varepsilon))$ ,  $L_i^\varepsilon \in H^1(0, T; L^2(\Omega_1^\varepsilon))$ . The compactness of the embedding of  $L^2(0, T; W^\varepsilon) \cap (H^1(0, T; L^2(\Omega_0^\varepsilon)) \times H^1(0, T; L^2(\Omega_1^\varepsilon)))$  in  $L^2((0, T) \times \Gamma_1^\varepsilon) \times L^2((0, T) \times \Omega_1^\varepsilon)$ , [13], a

priori estimates similar as in Lemma 4.4, and Schauder fixed point theorem imply the existence of a fixed point of  $K$ .

To prove uniqueness for (2.1), (2.2) we consider the equations for the difference of two solutions. Using the ellipticity and Lipschitz continuity of  $F$  and  $G$ , assumptions 4.1.1, 4.1.2, 4.1.3, implies

$$\int_0^T \int_{\Omega_0^\varepsilon} |L_{e,1}^\varepsilon - L_{e,2}^\varepsilon|^2 dxdt + \varepsilon \int_0^T \int_{\Gamma_1^\varepsilon} |S_{e,1}^\varepsilon - S_{e,2}^\varepsilon|^2 d\gamma dt + \int_0^T \int_{\Omega_1^\varepsilon} (|L_{i,1}^\varepsilon - L_{i,2}^\varepsilon|^2 + |S_{i,1}^\varepsilon - S_{i,2}^\varepsilon|^2) dxdt \leq 0,$$

and  $L_{e,1}^\varepsilon = L_{e,2}^\varepsilon$ ,  $S_{e,1}^\varepsilon = S_{e,2}^\varepsilon$ ,  $L_{i,1}^\varepsilon = L_{i,2}^\varepsilon$ ,  $S_{i,1}^\varepsilon = S_{i,2}^\varepsilon$  a.e. in  $(0, T) \times \Omega_0^\varepsilon$ , in  $(0, T) \times \Gamma_1^\varepsilon$ , and in  $(0, T) \times \Omega_1^\varepsilon$ , respectively.  $\square$

LEMMA 4.4. *For solution of (2.1), (2.2) we have the estimates*

$$\begin{aligned} & \|L_e^\varepsilon\|_{L^\infty((0,T)\times\Omega_0^\varepsilon)} + \|\nabla L_e^\varepsilon\|_{L^2((0,T)\times\Omega_0^\varepsilon)} + \varepsilon^{1/2} \|S_e^\varepsilon\|_{L^\infty(0,T;L^2(\Gamma_1^\varepsilon))} \leq C, \\ & \|L_i^\varepsilon\|_{L^\infty((0,T)\times\Omega_1^\varepsilon)} + \varepsilon \|\nabla L_i^\varepsilon\|_{L^2((0,T)\times\Omega_1^\varepsilon)} + \|S_i^\varepsilon\|_{L^\infty(0,T;L^2(\Omega_1^\varepsilon))} \leq C, \\ & \|\partial_t L_e^\varepsilon\|_{L^2((0,T)\times\Omega_0^\varepsilon)} + \varepsilon^{1/2} \|\partial_t S_e^\varepsilon\|_{L^2((0,T)\times\Gamma_1^\varepsilon)} + \|\partial_t L_i^\varepsilon\|_{L^2((0,T)\times\Omega_1^\varepsilon)} + \|\partial_t S_i^\varepsilon\|_{L^2((0,T)\times\Omega_1^\varepsilon)} \leq C. \end{aligned}$$

with constant  $C$  independent of  $\varepsilon$ .

*Proof.* We consider  $(L_e^\varepsilon - L_{eD}, L_i^\varepsilon - L_{eD})$ ,  $S_e^\varepsilon$ ,  $S_i^\varepsilon$  as test functions in the equations (4.1). Using ellipticity assumption 4.1.1, the sublinearity of  $F$  and  $G$ , which follows from Lipschitz continuity, assumption 4.1.2 and 4.1.3, and Young inequality, we obtain for any  $\tau \in [0, T]$

$$\begin{aligned} & \int_0^\tau \int_{\Omega_0^\varepsilon} (\partial_t |L_e^\varepsilon|^2 + 2d_0 |\nabla L_e^\varepsilon|^2) dxdt + \int_0^\tau \int_{\Omega_1^\varepsilon} (\theta_i \partial_t |L_i^\varepsilon|^2 + \varepsilon^2 2\bar{d}_0 |\nabla L_i^\varepsilon|^2) dxdt \leq \int_{\Omega_0^\varepsilon} (\delta |L_e^\varepsilon(\tau)|^2 + \frac{1}{\delta} |L_{eD}(\tau)|^2) dx \\ & + \int_{\Omega_0^\varepsilon} (|L_{eD}(0)|^2 + |L_{e0}^\varepsilon|^2) dx + \int_0^\tau \int_{\Omega_0^\varepsilon} (|L_e^\varepsilon|^2 + |\partial_t L_{eD}|^2 + d_1 (\delta |\nabla L_e^\varepsilon|^2 + \frac{1}{\delta} |\nabla L_{eD}|^2)) dxdt + \int_{\Omega_1^\varepsilon} \delta |L_i^\varepsilon(\tau)|^2 dx \\ & + \int_{\Omega_1^\varepsilon} (\frac{1}{\delta} |L_{eD}(\tau)|^2 + |L_{eD}(0)|^2 + |L_{i0}^\varepsilon|^2) dx + \int_0^\tau \int_{\Omega_1^\varepsilon} (|L_i^\varepsilon|^2 + |\partial_t L_{eD}|^2 + \varepsilon^2 \bar{d}_1 (\delta |\nabla L_i^\varepsilon|^2 + \frac{1}{\delta} |\nabla L_{eD}|^2)) dxdt \\ & + C_1 \int_0^\tau \int_{\Gamma_1^\varepsilon} \varepsilon (1 + |L_e^\varepsilon|^2 + |S_e^\varepsilon|^2 + |L_{eD}|^2) d\gamma dt + C_2 \int_0^\tau \int_{\Omega_1^\varepsilon} (1 + |L_i^\varepsilon|^2 + |S_i^\varepsilon|^2 + |L_{eD}|^2) dxdt, \end{aligned}$$

where  $d_1 = \sup_{t,y} |\mathcal{D}(t,y)|$ ,  $\bar{d}_1 = \sup_{t,y} |\bar{\mathcal{D}}(t,y)|$ . Sublinearity of  $F$  and  $G$  and the Gronwall Lemma imply

$$\|S_e^\varepsilon(\tau)\|_{L^2(\Gamma_1^\varepsilon)}^2 \leq c_1 + c_2 \|L_e^\varepsilon\|_{L^2((0,\tau)\times\Gamma_1^\varepsilon)}^2, \quad \|S_i^\varepsilon(\tau)\|_{L^2(\Omega_1^\varepsilon)}^2 \leq c_3 + c_4 \|L_i^\varepsilon\|_{L^2((0,\tau)\times\Omega_1^\varepsilon)}^2.$$

In the estimate of the boundary integral we use the inequality, see [10] for the proof,

$$\varepsilon \|v^\varepsilon\|_{L^2(\Gamma_1^\varepsilon)}^2 \leq C_3 (\|v^\varepsilon\|_{L^2(\Omega_0^\varepsilon)}^2 + \varepsilon^2 \|\nabla v^\varepsilon\|_{L^2(\Omega_0^\varepsilon)}^2).$$



Then, choosing  $\delta$  such that  $2d_0 - \delta d_1 - C_1 C_3 \varepsilon^2 \geq \alpha > 0$ ,  $2\bar{d}_0 - \delta \bar{d}_1 \geq \alpha > 0$  and applying the Gronwall lemma we obtain the estimates for  $|L_e^\varepsilon|$ ,  $|L_i^\varepsilon|$ ,  $|S_e^\varepsilon|$ ,  $|S_i^\varepsilon|$ ,  $|\nabla L_e^\varepsilon|$ , and  $|\nabla L_i^\varepsilon|$ .

To derive the estimates for the time derivatives we use  $(\partial_t(L_e^\varepsilon - L_{eD}), \partial_t(L_i^\varepsilon - L_{eD}))$ ,  $\partial_t S_e^\varepsilon$ , and  $\partial_t S_i^\varepsilon$  as test functions and estimate the integrals in the same manner as in the first part. The only difference is in the estimate of the integral over  $\Gamma_1^\varepsilon$ . The assumption 4.1.2 on  $F$  implies for  $j = f, s$

$$\begin{aligned} \int_0^\tau \int_{\Gamma_1^\varepsilon} F_j^\varepsilon(t, x, L_e^\varepsilon, S_{ej}^\varepsilon) \partial_t L_e^\varepsilon d\gamma dt &= \int_0^\tau \int_{\Gamma_1^\varepsilon} \frac{d}{dt} \mathcal{F}_j^\varepsilon d\gamma dt - \int_0^\tau \int_{\Gamma_1^\varepsilon} (\partial_t \mathcal{F}_j^\varepsilon + \partial_\xi \mathcal{F}_j^\varepsilon \partial_t S_{ej}^\varepsilon) d\gamma dt \\ &\leq c_1 \int_{\Gamma_1^\varepsilon} (1 + |L_e^\varepsilon(t)|^2 + |S_{ej}^\varepsilon(t)|^2 + |L_{e0}|^2 + |S_{ej0}|^2) d\gamma_x + c_2 \int_0^\tau \int_{\Gamma_1^\varepsilon} (1 + |L_e^\varepsilon|^2 + |S_{ej}^\varepsilon|^2 + |\partial_t S_{ej}^\varepsilon|^2) d\gamma_x dt. \end{aligned}$$

□

**5. Convergence of solutions of the microscopic problem as  $\varepsilon \rightarrow 0$ .** We extend  $L_e^\varepsilon$ , defined on a connected domain  $\Omega_0^\varepsilon$ , onto whole  $\Omega$ , see [9] or [10], and the  $H^1$ -norm of the extension  $\tilde{L}_e^\varepsilon$  is controlled by the  $H^1$ -norm of the original function  $L_e^\varepsilon$  with constant independent on  $\varepsilon$ . For  $L_e^\varepsilon \in L^2(0, T; H^1(\Omega_0^\varepsilon))$  we define  $\bar{L}_e^\varepsilon(\cdot, t) := \tilde{L}_e^\varepsilon(\cdot, t)$  for a.a.  $t$ . Since the extension operator is linear and bounded  $\bar{L}_e^\varepsilon \in L^2(0, T; H^1(\Omega))$ . We identify  $L_e^\varepsilon$  with the extension  $\bar{L}_e^\varepsilon$ .

LEMMA 5.1. [15] For a function  $v^\varepsilon \in H^{\beta, 2}(\Omega_0^\varepsilon)$  with  $\frac{1}{2} < \beta < 1$  the following estimate holds

$$\varepsilon \|v^\varepsilon\|_{L^2(\Gamma_1^\varepsilon)}^2 \leq C \|v^\varepsilon\|_{L^2(\Omega_0^\varepsilon)}^2 + C \varepsilon^{2\beta} \int_{\Omega_0^\varepsilon} \int_{\Omega_0^\varepsilon} \frac{|v^\varepsilon(x_1) - v^\varepsilon(x_2)|^2}{|x_1 - x_2|^{n+2\beta}} dx_1 dx_2,$$

where  $C$  is a constant independent on  $\varepsilon$ .

LEMMA 5.2. There exist functions  $L_e, L_{e1}, L_i, S_e, S_i$  such that (up to a subsequence)

$$\begin{aligned} L_e^\varepsilon &\rightarrow L_e && \text{weakly in } L^2(0, T; H^1(\Omega)), \text{ strongly in } L^2(0, T; H^{\beta, 2}(\Omega)), \quad 1/2 < \beta < 1, \\ \varepsilon \|L_e^\varepsilon - L_e\|_{L^2((0, T) \times \Gamma_1^\varepsilon)}^2 &\rightarrow 0 && \text{as } \varepsilon \rightarrow 0, \\ \partial_t L_e^\varepsilon &\rightarrow \partial_t L_e && \text{weakly in } L^2((0, T) \times \Omega), \\ L_e^\varepsilon &\rightarrow L_e, \quad \partial_t L_e^\varepsilon \rightarrow \partial_t L_e, \quad \nabla L_e^\varepsilon \rightarrow \nabla_x L_e + \nabla_y L_{e1} && \text{two-scale, } L_{e1} \in L^2((0, T) \times \Omega, H_{per}^1(Z)/\mathbb{R}), \\ L_i^\varepsilon &\rightarrow L_i, \quad \partial_t L_i^\varepsilon \rightarrow \partial_t L_i, \quad \varepsilon \nabla L_i^\varepsilon \rightarrow \nabla_y L_i && \text{two-scale as } \varepsilon \rightarrow 0, \\ &&& L_i \in L^2((0, T) \times \Omega; H_{per}^1(Y_1)) \cap H^1(0, T, L^2(\Omega \times Y_1)), \\ S_e^\varepsilon &\rightarrow S_e, \quad \partial_t S_e^\varepsilon \rightarrow \partial_t S_e && \text{two-scale as } \varepsilon \rightarrow 0, \quad S_e, \partial_t S_e \in L^2((0, T) \times \Omega \times \Gamma_1), \\ S_i^\varepsilon &\rightarrow S_i, \quad \partial_t S_i^\varepsilon \rightarrow \partial_t S_i && \text{two-scale as } \varepsilon \rightarrow 0, \quad S_i, \partial_t S_i \in L^2((0, T) \times \Omega \times Y_1). \end{aligned}$$

*Proof.* From a priori estimates in Lemma 4.4, we obtain convergences  $L_e^\varepsilon$  to  $L_e$  in  $L^2(0, T; H^1(\Omega))$ ,  $\partial_t L_e^\varepsilon$  to  $\partial_t L_e$  in  $L^2((0, T) \times \Omega)$  weakly and  $L_e^\varepsilon$  to  $L_e$  in  $L^\infty(0, T; L^2(\Omega))$  \*-weakly. To obtain strong convergence of  $L_e^\varepsilon$  in  $L^2(0, T; H^{\beta, 2}(\Omega))$ ,  $\frac{1}{2} < \beta < 1$ , we use the compact embedding of  $H^1(\Omega)$  in  $H^{\beta, 2}(\Omega)$  and the Lions-Aubin Lemma, [13]. Applying Lemma 5.1 we obtain  $\varepsilon \|L_e^\varepsilon - L_e\|_{L^2((0, T) \times \Gamma_1^\varepsilon)}^2 \leq C \|L_e^\varepsilon - L_e\|_{L^2(0, T; H^{\beta, 2}(\Omega_0^\varepsilon))}^2 \leq C \|L_e^\varepsilon - L_e\|_{L^2(0, T; H^{\beta, 2}(\Omega))}^2 \rightarrow 0$  for  $\varepsilon \rightarrow 0$ . Since  $L_e^\varepsilon$  is bounded in  $L^2(0, T; H^1(\Omega))$  the compactness theorem, [1], [17], [19], implies the two-scale convergence of  $L_e^\varepsilon$  to the same function  $L_e$  and the existence of a function  $L_{e1} \in L^2((0, T) \times \Omega; H_{per}^1(Z)/\mathbb{R})$  such that  $\nabla L_e^\varepsilon(t, x)$  two-scale converges to  $\nabla_x L_e(t, x) + \nabla_y L_{e1}(t, x, y)$ . From boundedness of  $L_e^\varepsilon$  and  $\varepsilon \nabla L_e^\varepsilon$ , applying again the compactness theorem, we obtain that  $L_i^\varepsilon(t, x) \rightarrow L_i(t, x, y)$  and  $\varepsilon \nabla L_i^\varepsilon(t, x) \rightarrow \nabla_y L_i(t, x, y)$  in two-scale sense and  $L_i \in L^2((0, T) \times \Omega; H_{per}^1(Y_1))$ . Invoking the convergence theorems for bounded sequences in  $L^2((0, T) \times \Omega)$ ,  $L^2((0, T) \times \Gamma_1^\varepsilon)$  and  $L^2((0, T) \times \Omega_1^\varepsilon)$  (see [1], [2], [17]) we obtain the two-scale convergence of  $\partial_t L_e^\varepsilon$ ,  $S_e^\varepsilon$ ,  $\partial_t S_e^\varepsilon$ ,  $\partial_t L_i^\varepsilon$ ,  $S_i^\varepsilon$ , and  $\partial_t S_i^\varepsilon$ .  $\square$

The weak two-scale convergence of  $S_e^\varepsilon$ ,  $L_i^\varepsilon$ ,  $S_i^\varepsilon$  does not allow to pass to the limit in the nonlinear functions. Using the unfolding method, [4], [6], [7], [8], [15], [18], and the structure of the equations we prove the convergence of the nonlinear terms.

DEFINITION 5.3. Define the unfolding operator  $\mathcal{T}_b^\varepsilon : L^p((0, T) \times \Gamma_1^\varepsilon) \rightarrow L^p((0, T) \times \Omega \times \Gamma_1)$ ,  $p \in [1, \infty]$ , by

$$(\mathcal{T}_b^\varepsilon u)(t, x, y) = u(t, c^\varepsilon(x) + \varepsilon y) \quad \text{for } (t, x, y) \in (0, T) \times \Omega \times \Gamma_1, \quad c^\varepsilon(x) = \varepsilon \left\lfloor \frac{x}{\varepsilon} \right\rfloor,$$

and  $\mathcal{T}^\varepsilon : L^p((0, T) \times \Omega_1^\varepsilon) \rightarrow L^p((0, T) \times \Omega \times Y_1)$ ,  $p \in [1, \infty]$ , by

$$(\mathcal{T}^\varepsilon u)(t, x, y) = u(t, c^\varepsilon(x) + \varepsilon y) \quad \text{for } (t, x, y) \in (0, T) \times \Omega \times Y_1, \quad c^\varepsilon(x) = \varepsilon \left\lfloor \frac{x}{\varepsilon} \right\rfloor.$$

LEMMA 5.4.  $F^\varepsilon(t, x, L_e^\varepsilon, S_e^\varepsilon) \rightarrow F(t, y, L_e, S_e)$  and  $G^\varepsilon(t, x, L_i^\varepsilon, S_i^\varepsilon) \rightarrow G(t, y, L_i, S_i)$  converge two-scale as  $\varepsilon \rightarrow 0$ .

*Proof.* The change of the variables  $x \rightarrow \varepsilon y + c^\varepsilon(x)$ , the periodicity of  $F$ ,  $G$  in the second argument, and the periodicity of the initial data imply

$$\mathcal{T}_b^\varepsilon F^\varepsilon = F\left(t, \frac{c_\varepsilon(x) + \varepsilon y}{\varepsilon}, L_e^\varepsilon(t, c_\varepsilon(x) + \varepsilon y), S_e^\varepsilon(t, c_\varepsilon(x) + \varepsilon y)\right) = F(t, y, \mathcal{T}_b^\varepsilon L_e^\varepsilon, \mathcal{T}_b^\varepsilon S_e^\varepsilon), \quad (5.1)$$

$$\mathcal{T}^\varepsilon G^\varepsilon = G\left(t, \frac{c_\varepsilon(x) + \varepsilon y}{\varepsilon}, L_i^\varepsilon(t, c_\varepsilon(x) + \varepsilon y), S_i^\varepsilon(t, c_\varepsilon(x) + \varepsilon y)\right) = G(t, y, \mathcal{T}^\varepsilon L_i^\varepsilon, \mathcal{T}^\varepsilon S_i^\varepsilon), \quad (5.2)$$

$$(\mathcal{T}^\varepsilon L_{i0}^\varepsilon)(x, y) = L_{i0}(y), \quad (\mathcal{T}^\varepsilon S_{i0}^\varepsilon)(x, y) = S_{i0}(y), \quad (\mathcal{T}_b^\varepsilon S_{e0}^\varepsilon)(x, y) = S_{e0}(y),$$

and, using  $\mathcal{T}^\varepsilon(uv) = \mathcal{T}^\varepsilon(u)\mathcal{T}^\varepsilon(v)$ ,  $\nabla_y \mathcal{T}^\varepsilon(u) = \varepsilon \mathcal{T}^\varepsilon(\nabla u)$ , the equations for  $\mathcal{T}_b^\varepsilon S_e^\varepsilon$ ,  $\mathcal{T}^\varepsilon S_i^\varepsilon$ , and  $\mathcal{T}^\varepsilon L_i^\varepsilon$

$$\begin{aligned} \partial_t \mathcal{T}_b^\varepsilon S_e^\varepsilon &= F(t, y, \mathcal{T}_b^\varepsilon L_e^\varepsilon, \mathcal{T}_b^\varepsilon S_e^\varepsilon) \quad \text{in } (0, T) \times \Omega \times \Gamma_1, & \partial_t \mathcal{T}^\varepsilon S_i^\varepsilon &= G(t, y, \mathcal{T}^\varepsilon L_i^\varepsilon, \mathcal{T}^\varepsilon S_i^\varepsilon) \quad \text{in } (0, T) \times \Omega \times Y_1, \\ \mathcal{T}_b^\varepsilon S_e^\varepsilon(0, x, y) &= S_{e0}(y) \quad \text{in } \Omega \times \Gamma_1, & \mathcal{T}^\varepsilon S_i^\varepsilon(0, x, y) &= S_{i0}(y) \quad \text{in } \Omega \times Y_1, \\ \theta_i \partial_t \mathcal{T}^\varepsilon L_i^\varepsilon - \nabla_y \cdot (\bar{\mathcal{D}}(y) \nabla_y \mathcal{T}^\varepsilon L_i^\varepsilon) &= -G_f(t, y, \mathcal{T}^\varepsilon L_i^\varepsilon, \mathcal{T}^\varepsilon S_{if}^\varepsilon) - G_s(t, y, \mathcal{T}^\varepsilon L_i^\varepsilon, \mathcal{T}^\varepsilon S_{is}^\varepsilon) \quad \text{in } (0, T) \times \Omega \times Y_1, \\ \mathcal{T}_b^\varepsilon L_i^\varepsilon &= \mathcal{T}_b^\varepsilon L_e^\varepsilon \quad \text{on } (0, T) \times \Omega \times \Gamma_1, & \mathcal{T}^\varepsilon L_i^\varepsilon(0, x, y) &= L_{i0}(y) \quad \text{in } \Omega \times Y_1. \end{aligned}$$

We consider the difference of the equations for  $\mathcal{T}_b^{\varepsilon_m} S_e^{\varepsilon_m}$  and  $\mathcal{T}_b^{\varepsilon_n} S_e^{\varepsilon_n}$ , for  $\mathcal{T}^{\varepsilon_m} S_i^{\varepsilon_m}$  and  $\mathcal{T}^{\varepsilon_n} S_i^{\varepsilon_n}$ , use as test functions corresponding differences of solutions and apply the Gronwall inequality,

$$\sup_{(0, T)} \|\mathcal{T}_b^{\varepsilon_m} S_e^{\varepsilon_m} - \mathcal{T}_b^{\varepsilon_n} S_e^{\varepsilon_n}\|_{L^2(\Omega \times \Gamma_1)}^2 \leq c_1 \|\mathcal{T}_b^{\varepsilon_m} L_e^{\varepsilon_m} - \mathcal{T}_b^{\varepsilon_n} L_e^{\varepsilon_n}\|_{L^2((0, T) \times \Omega \times \Gamma_1)}^2, \quad (5.3)$$

$$\sup_{(0, T)} \|\mathcal{T}^{\varepsilon_m} S_i^{\varepsilon_m} - \mathcal{T}^{\varepsilon_n} S_i^{\varepsilon_n}\|_{L^2(\Omega \times Y_1)}^2 \leq c_2 \|\mathcal{T}^{\varepsilon_m} L_i^{\varepsilon_m} - \mathcal{T}^{\varepsilon_n} L_i^{\varepsilon_n}\|_{L^2((0, T) \times \Omega \times Y_1)}^2. \quad (5.4)$$

If we show that  $\mathcal{T}_b^\varepsilon L_e^\varepsilon$  and  $\mathcal{T}^\varepsilon L_i^\varepsilon$  are strongly convergent, then this also implies the strong convergence of  $\mathcal{T}_b^\varepsilon S_e^\varepsilon$  and  $\mathcal{T}^\varepsilon S_i^\varepsilon$ . Due to norm conservation properties of the unfolding operator, [4], [15], and the strong convergence of  $L_e^\varepsilon$  on  $\Gamma_1^\varepsilon$ , Lemma 5.2, we obtain

$$\|\mathcal{T}_b^\varepsilon L_e^\varepsilon - \mathcal{T}_b^\varepsilon L_e\|_{L^2((0, T) \times \Omega \times \Gamma_1)}^2 = \varepsilon \|L_e^\varepsilon - L_e\|_{L^2((0, T) \times \Gamma_1^\varepsilon)}^2 \rightarrow 0 \quad \text{as } \varepsilon \rightarrow 0.$$

Since, for  $L_e$  independent on  $y$ ,  $\mathcal{T}_b^{\varepsilon_n} L_e \rightarrow L_e$  strongly in  $L^2((0, T) \times \Omega \times \Gamma_1)$  (see [4], [15]) we have

$$\begin{aligned} \int_0^T \int_{\Omega \times \Gamma_1} |\mathcal{T}_b^{\varepsilon_m} L_e^{\varepsilon_m} - \mathcal{T}_b^{\varepsilon_n} L_e^{\varepsilon_n}|^2 d\gamma_y dx dt &\leq \varepsilon_n \int_0^T \int_{\Gamma_1^{\varepsilon_n}} |L_e^{\varepsilon_n} - L_e|^2 d\gamma dt + \varepsilon_m \int_0^T \int_{\Gamma_1^{\varepsilon_m}} |L_e^{\varepsilon_m} - L_e|^2 d\gamma dt \\ &+ \int_0^T \int_{\Omega \times \Gamma_1} (|\mathcal{T}_b^{\varepsilon_n} L_e - L_e|^2 + |\mathcal{T}_b^{\varepsilon_m} L_e - L_e|^2) d\gamma_y dx dt \rightarrow 0 \quad \text{as } \varepsilon_n, \varepsilon_m \rightarrow 0. \end{aligned} \quad (5.5)$$

Now we will show that  $\mathcal{T}^\varepsilon L_i^\varepsilon$  is a Cauchy sequence and converges strongly to  $L_i$  in  $L^2((0, T) \times \Omega \times Y_1)$ .

We can write  $\mathcal{T}^{\varepsilon_m} L_i^{\varepsilon_m} - \mathcal{T}^{\varepsilon_n} L_i^{\varepsilon_n} = h^{\varepsilon_m, \varepsilon_n} + k^{\varepsilon_m, \varepsilon_n}$ , where  $k^{\varepsilon_m, \varepsilon_n}$  and  $h^{\varepsilon_m, \varepsilon_n}$  are solutions of

$$\begin{aligned} \theta_i \partial_t k^{\varepsilon_m, \varepsilon_n} - \nabla_y \cdot (\bar{\mathcal{D}}(y) \nabla_y k^{\varepsilon_m, \varepsilon_n}) &= -(G_f(y, \mathcal{T}^{\varepsilon_m} L_i^{\varepsilon_m}, \mathcal{T}^{\varepsilon_m} S_{if}^{\varepsilon_m}) - G_f(y, \mathcal{T}^{\varepsilon_n} L_i^{\varepsilon_n}, \mathcal{T}^{\varepsilon_n} S_{if}^{\varepsilon_n})) \\ &\quad - (G_s(y, \mathcal{T}^{\varepsilon_m} L_i^{\varepsilon_m}, \mathcal{T}^{\varepsilon_m} S_{is}^{\varepsilon_m}) - G_s(y, \mathcal{T}^{\varepsilon_n} L_i^{\varepsilon_n}, \mathcal{T}^{\varepsilon_n} S_{is}^{\varepsilon_n})), \end{aligned} \quad (5.6)$$

$$k^{\varepsilon_m, \varepsilon_n} = 0 \quad \text{on } (0, T) \times \Omega \times \Gamma_1, \quad k^{\varepsilon_m, \varepsilon_n}(0) = 0 \quad \text{in } \Omega \times Y_1, \quad (5.7)$$

and

$$\theta_i \partial_t h^{\varepsilon_m, \varepsilon_n} - \nabla_y \cdot (\bar{\mathcal{D}}(y) \nabla_y h^{\varepsilon_m, \varepsilon_n}) = 0 \quad \text{in } (0, T) \times \Omega \times Y_1, \quad (5.8)$$

$$h^{\varepsilon_m, \varepsilon_n} = \mathcal{T}_b^{\varepsilon_m} L_e^{\varepsilon_m} - \mathcal{T}_b^{\varepsilon_n} L_e^{\varepsilon_n} \quad \text{on } (0, T) \times \Omega \times \Gamma_1, \quad h^{\varepsilon_m, \varepsilon_n}(0) = 0 \quad \text{in } \Omega \times Y_1, \quad (5.9)$$

The main idea is to estimate  $\|\mathcal{T}^{\varepsilon_m} L_i^{\varepsilon_m} - \mathcal{T}^{\varepsilon_n} L_i^{\varepsilon_n}\|_{L^2((0,T) \times \Omega \times Y_1)}$  by  $\|\mathcal{T}_b^{\varepsilon_m} L_i^{\varepsilon_m} - \mathcal{T}_b^{\varepsilon_n} L_i^{\varepsilon_n}\|_{L^2((0,T) \times \Omega \times \Gamma_1)}$   $= \|\mathcal{T}_b^{\varepsilon_m} L_e^{\varepsilon_m} - \mathcal{T}_b^{\varepsilon_n} L_e^{\varepsilon_n}\|_{L^2((0,T) \times \Omega \times \Gamma_1)}$  and use the strong convergence of  $L_e^\varepsilon$ . This idea to estimate  $L^2$ -norm via boundary data comes from transposition method, [14]. Similar idea was used in [18] to show the convergence of nonlinear reactions defined in a thin membrane. We consider

$$\begin{aligned} -\theta_i \partial_t d^{\varepsilon_m, \varepsilon_n} - \nabla_y \cdot (\bar{\mathcal{D}}(y) \nabla_y d^{\varepsilon_m, \varepsilon_n}) &= h^{\varepsilon_m, \varepsilon_n} && \text{in } (0, T) \times \Omega \times Y_1, \\ d^{\varepsilon_m, \varepsilon_n} &= 0 && \text{on } (0, T) \times \Omega \times \Gamma_1, \quad d^{\varepsilon_m, \varepsilon_n}(T, x, y) = 0 \quad \text{in } \Omega \times Y_1. \end{aligned} \quad (5.10)$$

From regularity theory for parabolic equations, [12], where  $x \in \Omega$  is a parameter, for  $h^{\varepsilon_m, \varepsilon_n} \in L^2((0, T) \times \Omega \times Y_1)$  we have that  $d^{\varepsilon_m, \varepsilon_n} \in L^2((0, T) \times \Omega; H^2(Y_1))$  and

$$\begin{aligned} \|d^{\varepsilon_m, \varepsilon_n}\|_{L^\infty(0, T; L^2(\Omega \times Y_1))} + \|\nabla_y d^{\varepsilon_m, \varepsilon_n}\|_{L^2((0, T) \times \Omega \times Y_1)} + \|\nabla_y^2 d^{\varepsilon_m, \varepsilon_n}\|_{L^2((0, T) \times \Omega \times Y_1)} \\ \leq C \|h^{\varepsilon_m, \varepsilon_n}\|_{L^2((0, T) \times \Omega \times Y_1)}. \end{aligned} \quad (5.11)$$

Using now  $h^{\varepsilon_m, \varepsilon_n}$  as test function in the equation (5.10) and taking into account that  $d^{\varepsilon_m, \varepsilon_n} = 0$  on  $(0, T) \times \Omega \times \Gamma_1$ , we obtain the following equality

$$\begin{aligned} \int_0^T \int_{\Omega \times Y_1} |h^{\varepsilon_m, \varepsilon_n}|^2 dy dx dt = \int_0^T \int_{\Omega \times Y_1} d^{\varepsilon_m, \varepsilon_n} (\theta_i \partial_t h^{\varepsilon_m, \varepsilon_n} - \nabla_y \cdot (\bar{\mathcal{D}}(y) \nabla_y h^{\varepsilon_m, \varepsilon_n})) dy dx dt \\ - \int_0^T \int_{\Omega \times \Gamma_1} \bar{\mathcal{D}}(y) \nabla_y d^{\varepsilon_m, \varepsilon_n} \cdot \nu h^{\varepsilon_m, \varepsilon_n} d\gamma_y dx dt. \end{aligned}$$

Due to (5.8) the first integral on the right hand side is zero. Then using in the second integral the trace theorem applied to  $\nabla_y d^{\varepsilon_m, \varepsilon_n} \cdot \nu$ , the estimate (5.11) and the boundary condition in (5.9) we obtain

$$\|h^{\varepsilon_m, \varepsilon_n}\|_{L^2((0, T) \times \Omega \times Y_1)} \leq C \|\mathcal{T}_b^{\varepsilon_m} L_e^{\varepsilon_m} - \mathcal{T}_b^{\varepsilon_n} L_e^{\varepsilon_n}\|_{L^2((0, T) \times \Omega \times \Gamma_1)}. \quad (5.12)$$

Now we test (5.6) with  $k^{\varepsilon_m, \varepsilon_n}$ , use the Lipschitz continuity of  $G$ , the estimate (5.4), the boundary condition in (5.7), the fact  $\mathcal{T}^{\varepsilon_m} L_i^{\varepsilon_m} - \mathcal{T}^{\varepsilon_n} L_i^{\varepsilon_n} = h^{\varepsilon_m, \varepsilon_n} + k^{\varepsilon_m, \varepsilon_n}$ , and obtain for  $\tau \in [0, T]$

$$\int_0^\tau \int_{\Omega \times Y_1} \left( \frac{1}{2} \partial_t |k^{\varepsilon_m, \varepsilon_n}|^2 + \bar{\mathcal{D}}(y) \nabla_y k^{\varepsilon_m, \varepsilon_n} \nabla_y k^{\varepsilon_m, \varepsilon_n} \right) dy dx dt \leq C \int_0^\tau \int_{\Omega \times Y_1} (|h^{\varepsilon_m, \varepsilon_n}|^2 + |k^{\varepsilon_m, \varepsilon_n}|^2) dy dx dt.$$

The ellipticity of  $\bar{\mathcal{D}}$  and the Gronwall Lemma implies

$$\sup_{(0, T)} \|k^{\varepsilon_m, \varepsilon_n}\|_{L^2(\Omega \times Y_1)}^2 \leq C (\|h^{\varepsilon_m, \varepsilon_n}\|_{L^2((0, T) \times \Omega \times Y_1)}^2 + \|k^{\varepsilon_m, \varepsilon_n}(0)\|_{L^2(\Omega \times Y_1)}^2).$$

The expression for  $\mathcal{T}^{\varepsilon_m} L_i^{\varepsilon_m} - \mathcal{T}^{\varepsilon_n} L_i^{\varepsilon_n}$ , the last estimate and (5.12) yield

$$\begin{aligned} & \|\mathcal{T}^{\varepsilon_m} L_i^{\varepsilon_m} - \mathcal{T}^{\varepsilon_n} L_i^{\varepsilon_n}\|_{L^2((0,T) \times \Omega \times Y_1)}^2 \leq \|h^{\varepsilon_m, \varepsilon_n}\|_{L^2((0,T) \times \Omega \times Y_1)}^2 + \|k^{\varepsilon_m, \varepsilon_n}\|_{L^2((0,T) \times \Omega \times Y_1)}^2 \\ & \leq C \|\mathcal{T}_b^{\varepsilon_m} L_e^{\varepsilon_m} - \mathcal{T}_b^{\varepsilon_n} L_e^{\varepsilon_n}\|_{L^2((0,T) \times \Omega \times \Gamma_1)}^2 \rightarrow 0 \text{ as } \varepsilon \rightarrow 0. \end{aligned} \quad (5.13)$$

The estimates (5.3), (5.4), (5.5), and (5.13) and the fact that weak limit of unfolded sequence and two-scale limit of original sequence are equal a.e., [6], [15], imply the strong convergence  $\mathcal{T}_b^\varepsilon L_e^\varepsilon \rightarrow L_e$ ,  $\mathcal{T}_b^\varepsilon S_e^\varepsilon \rightarrow S_e$  in  $L^2((0, T) \times \Omega \times \Gamma_1)$ , and  $\mathcal{T}^\varepsilon L_i^\varepsilon \rightarrow L_i$ ,  $\mathcal{T}^\varepsilon S_i^\varepsilon \rightarrow S_i$  in  $L^2((0, T) \times \Omega \times Y_1)$ . Thus  $F(t, y, \mathcal{T}_b^\varepsilon L_e^\varepsilon, \mathcal{T}_b^\varepsilon S_e^\varepsilon) \rightarrow F(t, y, L_e, S_e)$  a.e. in  $(0, T) \times \Omega \times \Gamma_1$ ,  $G(t, y, \mathcal{T}^\varepsilon L_i^\varepsilon, \mathcal{T}^\varepsilon S_i^\varepsilon) \rightarrow G(t, y, L_i, S_i)$  a.e. in  $(0, T) \times \Omega \times Y_1$ . From estimates for  $L_e^\varepsilon$ ,  $S_e^\varepsilon$ ,  $L_i^\varepsilon$ ,  $S_i^\varepsilon$  and sublinearity of  $F$  and  $G$  we obtain

$$\begin{aligned} & \|F(t, y, \mathcal{T}_b^\varepsilon L_e^\varepsilon, \mathcal{T}_b^\varepsilon S_e^\varepsilon)\|_{L^2((0,T) \times \Omega \times \Gamma_1)^2} \leq C, \quad \|G(t, y, \mathcal{T}^\varepsilon L_i^\varepsilon, \mathcal{T}^\varepsilon S_i^\varepsilon)\|_{L^2((0,T) \times \Omega \times Y_1)^2} \leq C, \\ & \varepsilon^{1/2} \|F^\varepsilon(t, x, L_e^\varepsilon, S_e^\varepsilon)\|_{L^2((0,T) \times \Gamma_1^\varepsilon)^2} \leq C, \quad \|G^\varepsilon(t, x, L_i^\varepsilon, S_i^\varepsilon)\|_{L^2((0,T) \times \Omega_1^\varepsilon)^2} \leq C. \end{aligned}$$

Thus, using (5.1), (5.2),  $\mathcal{T}_b^\varepsilon F \rightarrow F$  weakly in  $L^2((0, T) \times \Omega \times \Gamma_1)^2$ ,  $\mathcal{T}^\varepsilon G \rightarrow G$  weakly in  $L^2((0, T) \times \Omega \times Y_1)^2$ , and  $F^\varepsilon \rightarrow F^*$ ,  $G^\varepsilon \rightarrow G^*$  in the two-scale sense. Due to the relation between weak limit of unfolded sequence and two-scale limit of original sequence we have  $F = F^*$  and  $G = G^*$  a.e.  $\square$

**6. Macroscopic model.** Using the two-scale convergence we derive macroscopic equations for the microscopic model (2.1), (2.2).

**DEFINITION 6.1.** *The functions  $L_e$ ,  $L_i$ ,  $S_e$ ,  $S_i$  are solutions of the macroscopic model (2.3)–(2.4) if  $(L_e - L_{eD}, L_i - L_{iD}) \in L^2(0, T; W)$ ,  $\partial_t L_e \in L^2((0, T) \times \Omega)$ ,  $\partial_t L_i \in L^2((0, T) \times \Omega \times Y_1)$ ,  $S_e \in H^1(0, T; L^2(\Omega \times \Gamma_1)^2)$ ,  $S_i \in H^1(0, T; L^2(\Omega \times Y_1)^2)$  such that*

$$\begin{aligned} & \int_0^T \int_\Omega \left( |Y_0| \partial_t L_e \phi_1 + A_{hom} \nabla_x L_e \nabla_x \phi_1 + \int_{\Gamma_1} (F_f(t, y, L_e, S_{ef}) + F_s(t, y, L_e, S_{es})) d\gamma_y \phi_1 \right) dx dt \\ & = \int_0^T \int_\Omega \int_{\Gamma_1} \bar{\mathcal{D}}(t, y) \nabla_y L_i \cdot \nu d\gamma_y \phi_1 dx dt, \quad (6.1) \\ & \int_0^T \int_{\Omega \times Y_1} \left( \theta_i \partial_t L_i \phi_2 + \bar{\mathcal{D}} \nabla_y L_i \nabla_y \phi_2 + (G_f(t, y, L_i, S_{if}) + G_s(t, y, L_i, S_{is})) \phi_2 \right) dy dx dt = 0, \\ & \int_0^T \int_{\Omega \times \Gamma_1} (\partial_t S_e - F(t, y, L_e, S_e)) \psi_1 d\gamma_y dx dt = 0, \quad \int_0^T \int_{\Omega \times Y_1} (\partial_t S_i - G(t, y, L_i, S_i)) \psi_2 dy dx dt = 0 \end{aligned}$$

for  $(\phi_1, \phi_2) \in L^2(0, T, W)$ ,  $\psi_1 \in L^2((0, T) \times \Omega \times \Gamma_1)^2$ ,  $\psi_2 \in L^2((0, T) \times \Omega \times Y_1)^2$ .

Here  $W = \{(\phi_1, \phi_2) : \phi_1 \in H^1(\Omega), \phi_2 \in L^2(\Omega; H_{per}^1(Y_1)), \phi_1 = 0 \text{ on } \partial\Omega_D, \phi_1 = \phi_2|_{\Gamma_1} \text{ in } \Omega\}$ .

**THEOREM 6.2.** *The sequence of solutions of the microscopic model (2.1), (2.2) two-scale converge as  $\varepsilon \rightarrow 0$  to the solution of the macroscopic problem (2.3), (2.4).*

*Proof.* Using in equations (4.1) test functions  $\phi(t, x) = \varphi_0(t, x) + \varepsilon\varphi_1(t, x, \frac{x}{\varepsilon}) + \Psi(t, x, \frac{x}{\varepsilon})$ ,  $\varphi_0 \in C^\infty((0, T) \times \Omega)$ ,  $\varphi_1 \in C^\infty((0, T) \times \Omega; C_{per}^\infty(Z))$ ,  $\varphi_0 = 0$ ,  $\varphi_1 = 0$  on  $\partial\Omega_D$ ,  $\Psi(t, x, \frac{x}{\varepsilon}) \in C^\infty((0, T) \times \Omega; C_{per}^\infty(Z))$ ,  $\Psi = 0$  for  $y \in Z \setminus Y_1$ ,  $\psi_1 \in C^\infty((0, T) \times \Omega; C_{per}^\infty(\Gamma_1))^2$ ,  $\psi_2 \in C^\infty((0, T) \times \Omega; C_{per}^\infty(Y_1))^2$ , and passing to the two-scale limit applying Lemma 5.2 and Lemma 5.4 yields,

$$\begin{aligned} & \int_0^T \int_{\Omega} \left( |Y_0| \partial_t L_e \varphi_0 + \int_{Y_0} \mathcal{D}(t, y) (\nabla_x L_e + \nabla_y L_{e1}) (\nabla_x \varphi_0 + \nabla_y \varphi_1) dy \right) dx dt + \\ & \int_0^T \int_{\Omega \times Y_1} \left( \theta_i \partial_t L_i (\varphi_0 + \Psi) + \bar{\mathcal{D}}(t, y) \nabla_y L_i \nabla_y \Psi + (G_f(t, y, L_i, S_{if}) + G_s(t, y, L_i, S_{is})) (\varphi_0 + \Psi) \right) dy dx dt \\ & = - \int_0^T \int_{\Omega \times \Gamma_1} (F_f(t, y, L_e, S_{ef}) + F_s(t, y, L_e, S_{es})) \varphi_0 d\gamma_y dx dt, \\ & \int_0^T \int_{\Omega \times \Gamma_1} (\partial_t S_e - F(t, y, L_e, S_e)) \psi_1 d\gamma_y dx dt = 0, \quad \int_0^T \int_{\Omega \times Y_1} (\partial_t S_i - G(t, y, L_i, S_i)) \psi_2 dy dx dt = 0. \end{aligned}$$

Choosing  $\Psi = 0$  we obtain the equation for  $L_e$

$$\begin{aligned} & \int_0^T \int_{\Omega} \left( |Y_0| \partial_t L_e + \int_{\Gamma_1} (F_f + F_s) d\gamma_y \right) \varphi_0 + \int_{Y_0} \mathcal{D}(\nabla_x L_e + \nabla_y L_{e1}) (\nabla_x \varphi_0 + \nabla_y \varphi_1) dy \right) dx dt \\ & = - \int_0^T \int_{\Omega \times Y_1} (\theta_i \partial_t L_i + G_f(t, y, L_i, S_{if}) + G_s(t, y, L_i, S_{is})) \varphi_0 dy dx dt. \end{aligned} \quad (6.2)$$

Then the equation for  $L_i$  reads

$$\theta_i \partial_t L_i - \nabla_y \cdot (\bar{\mathcal{D}} \nabla_y L_i) = -G_f(t, y, L_i, S_{if}) - G_s(t, y, L_i, S_{is}).$$

Testing the last equation with  $\varphi_0(t, x)$  we obtain that

$$\int_0^T \int_{\Omega \times Y_1} (\theta_i \partial_t L_i + G_f(t, y, L_i, S_{if}) + G_s(t, y, L_i, S_{is})) \varphi_0 dy dx dt = - \int_0^T \int_{\Omega \times \Gamma_1} \bar{\mathcal{D}} \nabla_y L_i \cdot \nu \varphi_0 d\gamma_y dx dt.$$

To determinate the unknown function  $L_{e1} \in L^2((0, T) \times \Omega; H_{per}^1(Z)/\mathbb{R})$ , we set  $\varphi_0 = 0$  in (6.2)

$$\int_0^T \int_{\Omega \times Y_0} \mathcal{D}(t, y) (\nabla_x L_e(t, x) + \nabla_y L_{e1}(t, x, y)) \nabla_y \varphi_1(t, x, y) dy dx dt = 0$$

for all  $\varphi_1 \in C^\infty((0, T) \times \Omega; C_{per}^\infty(Z))$ . From this follows that  $L_{e1}$  depends linearly on  $\nabla_x L_e$ , and can be written in the form  $L_{e1} = \sum_{j=1}^3 \frac{\partial L_e}{\partial x_j} \cdot w_j$ , where the functions  $w_j$  are defined as solutions of the cell problems (2.5). Next, setting  $\varphi_1 = 0$ , and together with

$$\int_0^T \int_\Omega \int_{Y_0} \sum_{i,j=1}^3 D_{ij}(\partial_{x_i} L_e + \sum_{k=1}^3 \partial_{y_i} w_k \partial_{x_k} L_e) \partial_{x_j} \varphi_0 dy dx dt = \int_0^T \int_\Omega \sum_{i,j=1}^3 a_{ij} \partial_{x_i} \varphi_0 \partial_{x_j} L_e dy dx dt$$

and  $a_{ij} = \sum_{k=1}^3 \int_{Y_0} (D_{ij}(t, y) + D_{ik}(t, y) \partial_{y_k} w_j) dy$ , we obtain the equation for  $L_e$ .

To show that the limit functions fulfil the initial conditions we consider  $\phi \in C_0^\infty(\Omega \times Y_1)$ ,  $\xi \in C^\infty([0, T])$ ,  $\xi(T) = 0$  and obtain

$$\int_0^T \int_{\Omega_\varepsilon^\varepsilon} \partial_t L_i^\varepsilon \phi(x, \frac{x}{\varepsilon}) \xi(t) dx dt = - \int_{\Omega_\varepsilon^\varepsilon} L_{i0}(\frac{x}{\varepsilon}) \phi(x, \frac{x}{\varepsilon}) \xi(0) dx - \int_0^T \int_{\Omega_\varepsilon^\varepsilon} L_i^\varepsilon \phi(x, \frac{x}{\varepsilon}) \partial_t \xi(t) dx dt.$$

Using two-scale convergence we can pass to the limit for  $\varepsilon \rightarrow 0$  and obtain the initial conditions. Similarly, we obtain the initial conditions for  $L_e$ ,  $S_e$  and  $S_i$ . To show that  $L_i = L_e$  on  $\Gamma_1$  we consider

$$\lim_{\varepsilon \rightarrow 0} \int_0^T \int_{\Omega_\varepsilon^\varepsilon} \varepsilon \nabla L_i^\varepsilon(t, x) \phi(t, x \frac{x}{\varepsilon}) dx dt = \int_0^T \int_{\Omega \times Y_1} \nabla_y L_i(t, x, y) \phi(t, x, y) dy dx dt.$$

On the other hand, using  $L_i^\varepsilon = L_e^\varepsilon$  on  $\Gamma_1^\varepsilon$  and two-scale convergence of  $L_e^\varepsilon$  on  $\Gamma_1^\varepsilon$  we have

$$\begin{aligned} & \lim_{\varepsilon \rightarrow 0} \left( - \int_0^T \int_{\Omega_\varepsilon^\varepsilon} L_i^\varepsilon(t, x) (\varepsilon \nabla_x \phi(t, x, \frac{x}{\varepsilon}) + \nabla_y \phi(t, x, \frac{x}{\varepsilon})) dx dt + \varepsilon \int_0^T \int_{\Gamma_1^\varepsilon} L_i^\varepsilon(t, x) \phi(t, x, \frac{x}{\varepsilon}) \cdot \nu d\gamma_x dt \right) \\ &= - \int_0^T \int_{\Omega \times Y_1} L_i(t, x, y) \nabla_y \phi(t, x, y) dx dt + \int_0^T \int_{\Omega \times \Gamma_1} L_e(t, x) \phi(t, x, y) \cdot \nu d\gamma_y dx dt. \end{aligned}$$

We used here that  $\lim_{\varepsilon \rightarrow 0} \varepsilon \int_0^T \int_{\Gamma_1^\varepsilon} L_e^\varepsilon \phi(t, x, \frac{x}{\varepsilon}) d\gamma_x dt = \int_0^T \int_{\Omega \times \Gamma_1} L_e(t, x) \phi(t, x, y) d\gamma_y dx dt$ . The last convergence follows from  $\varepsilon \int_0^T \int_{\Gamma_1^\varepsilon} |L_e^\varepsilon - L_e| |\phi(t, x \frac{x}{\varepsilon})| d\gamma_x dt \leq \varepsilon \|L_e^\varepsilon - L_e\|_{\Gamma_1^\varepsilon} \|\phi\|_{\Gamma_1^\varepsilon} \rightarrow 0$  (due to Lemma 5.2) and the two-scale convergence of  $L_e$  on  $\Gamma_1^\varepsilon$ .  $\square$

**7. Numerical simulation of the model.** In this section we present numerical solutions of the macroscopic model applied to a specific experimental situation. We consider a column of moist soil of uniform bulk density with uniformly-spaced porous spherical soil particles, surrounded by solution and gas spaces. The radius of the soil particles is determined by the sieve mesh size, used to make the soil column, [16, 20]. The particle porosity is determined by the bulk density. As an example of strongly sorbed solute we consider phosphate,  $H_2PO_4^-$ , and specify the functions in the

framework (2.3), (2.4). There are two standard setups for diffusion-reaction experiments of strongly sorbed solutes: 1) a constant solute concentration is maintained at one of the boundaries; 2) two soil pieces with different initial concentrations are joined together. The first setup can be modelled prescribing Dirichlet boundary condition. The second situation is defined by nonhomogeneous initial conditions. Another situation the model could address is the interaction between soil and plant roots. This can be modeled by flux boundary condition defining phosphate uptake by roots. We consider here linearised uptake kinetic  $D_e \nabla L_e \cdot \nu = -F_m(L_e - L_{e,min})$ , where  $F_m$  is the uptake constant, and  $L_{e,min}$  is the minimum phosphate concentration in the soil, below which no uptake occurs, [24]. We would like to point out, that all the mathematical results proved above can be easily assigned to linear or sublinear Neumann boundary conditions for  $L_e$  at  $\partial\Omega_D$ . We assume that diffusion coefficients are constant.

We consider two main types of kinetics for chemical reactions:

1. Michealis-Menton kinetics, i.e. for  $K_f^j > 0$ ,  $K_m^j > 0$ ,  $k_b^j > 0$ ,  $F_f^j > 0$ ,  $F_m^j > 0$ ,  $f_b^j > 0$

$$F_j(L_e, S_{ej}) = \frac{K_f^j L_e}{K_m^j + L_e} - k_b^j S_{ej}, \quad G_j(L_i, S_{ij}) = \frac{F_f^j L_i}{F_m^j + L_i} - f_b^j S_{ij}, \quad \text{for } j = f \text{ and } j = s.$$

2. Freudlich type kinetics, i.e. for  $\gamma_a^j > 0$ ,  $\gamma_d^j > 0$ ,  $\zeta_a^j > 0$ ,  $\zeta_d^j > 0$

$$F_j(L_e, S_{ej}) = \gamma_a^j L_e^\alpha - \gamma_d^j S_{ej}, \quad G_j(L_i, S_{ij}) = \zeta_a^j L_i^\alpha - \zeta_d^j S_{ij}, \quad \text{for } 0 < \alpha \leq 1, \quad \text{for } j = f \text{ and } j = s.$$

In order to apply our theory for given functions, we have to verified the assumptions 4.1.2 and 4.1.3 on  $F$  and  $G$ . It can be easily seen that the Michaelis-Menten kinetic is Lipschitz continuous. We have also  $\mathcal{F}_j(L_e, S_{ej}) = K_f^j L_e - K_f^j K_m^j \ln(K_m^j + L_e) - k_b^j L_e S_{ej}$  and  $\mathcal{F}_j$  is sublinear for nonnegative  $L_e$ . Linear Freudlich kinetics fulfil all the assumptions. However, if  $0 < \alpha < 1$  the Freudlich kinetics is Lipschitz continuous and  $\mathcal{F}_j = \gamma_a^j \frac{1}{1+\alpha} L_e^{\alpha+1} - \gamma_d^j L_e S_{ej}$  fulfils the assumption 4.1.2 only for strictly nonzero functions, i.e. for  $L_e \geq \mu$ ,  $L_i \geq \mu$ ,  $S_{ej} \geq \mu$ , and  $S_{ij} \geq \mu$  for some constant  $\mu > 0$ . From boundary rectangles theory for reaction-diffusion equations, [22], it follows that for initial and boundary data such that  $L_{e0} \geq \mu_1 > 0$ ,  $L_{i0} \geq \mu_1 > 0$ ,  $S_{ej0} \geq \mu_2 > 0$ ,  $S_{ij0} \geq \mu_2 > 0$ ,  $L_{eD} \geq \mu_3 > 0$ ,  $L_{e,min} \geq \mu_4 > 0$ , there exists  $\mu > 0$  which bounds the solution of (2.3)-(2.4) from below.

Based on equilibrium experiments for phosphate that reveal  $S = \beta L^\alpha$ ,  $S$  - sorbed solute concentration,  $L$  - solute concentration in solution, we consider Freundlich type reaction kinetics

$$\partial_{t^*}(\varsigma_e S_{ej}^*) = \varsigma_e F_j^*(L_e^*, S_{ej}^*) = \varsigma_e (\gamma_a^j L_e^{*,\alpha} - \gamma_d^j S_{ej}^*), \quad \partial_{t^*}(\varsigma_i S_{ij}^*) = \varsigma_i G_j^*(L_i^*, S_{ij}^*) = \varsigma_i (\zeta_a^j L_i^{*,\alpha} - \zeta_d^j S_{ij}^*).$$

The nondimensional reactions, using the scales in Section 3, are given by

$$\partial_t S_{ej} = F_j(L_e, S_{ej}) = \bar{\gamma}_a^j L_e^\alpha - \bar{\gamma}_d^j S_{ej} \text{ in } \Omega \times \Gamma_1, \quad \partial_t S_{ij} = G_j(L_i, S_{ij}) = \bar{\zeta}_a^j L_i^\alpha - \bar{\zeta}_d^j S_{ij} \text{ in } \Omega \times Y_1,$$



where  $\bar{\gamma}_d^j = \gamma_d^j [L_e]^{\alpha-1} \varsigma_e b^2 / (l D_0)$ ,  $\bar{\gamma}_d^j = \gamma_d^j b^2 / D_0$ ,  $\bar{\zeta}_d^j = \zeta_d^j [L_i]^{\alpha-1} \varsigma_i b^2 / D_0$ , and  $\bar{\zeta}_d^j = \zeta_d^j b^2 / D_0$ . Under the assumption  $\bar{\gamma}_d^f = \bar{\zeta}_d^f = \gamma_d^f b^2 / D_0 = \zeta_d^f b^2 / D_0 = 1/\delta \gg 1$ , i.e. desorption in the fast reaction is very fast in comparison to the diffusion, we obtain  $\delta \partial_t S_{ef} = \varsigma_e \gamma_d^f / (l \gamma_d^f) L_e^\alpha - S_{ef}$ ,  $\delta \partial_t S_{if} = \varsigma_i \zeta_d^f / \zeta_d^f L_i^\alpha - S_{if}$ . It implies that the fast reactions can be assumed at the leading order to be in the equilibrium and

$$S_{ef} = \varsigma_e \gamma_d^f / (l \gamma_d^f) L_e^\alpha, \quad S_{if} = \varsigma_i \zeta_d^f / \zeta_d^f L_i^\alpha. \quad (7.1)$$

The geometry  $\Omega = (0, 1) \times (-1, 1)^2$  and the constant coefficients imply that the only nonhomogeneous direction is the direction of  $x_1$  due to Dirichlet or non-zero Neumann boundary conditions, or nonhomogeneous in  $x_1$ -direction initial conditions. We use this symmetry to reduce (2.3) to one dimensional equations for  $L_e$  and  $L_i$ , (we identified here  $x_1$  with  $x$ ),

$$\begin{aligned} (|Y_0| + |\Gamma_1| \frac{\varsigma_e}{l} \frac{\gamma_d^f}{\gamma_d^f} \alpha L_e^{\alpha-1}) \partial_t L_e - A_{hom} \partial_x^2 L_e &= -|\Gamma_1| (\bar{D} \partial_r L_i(t, x, r)|_{r=r_0} + \bar{\gamma}_d^s L_e^\alpha - \bar{\gamma}_d^s S_{es}) \quad \text{in } (0, 1), \\ (\theta_i + \frac{\varsigma_i \zeta_d^f}{\zeta_d^f} \alpha L_i^{\alpha-1}) \partial_t L_i - \bar{D} \frac{1}{r^2} \partial_r (r^2 \partial_r L_i) &= -(\bar{\zeta}_d^s L_i^\alpha - \bar{\zeta}_d^s S_{is}) \quad \text{in } (0, r_0) \times (0, 1), \\ \partial_t S_{es} = \bar{\gamma}_d^s L_e^\alpha - \bar{\gamma}_d^s S_{es} \quad \text{in } (0, 1), \quad \partial_t S_{is} = \bar{\zeta}_d^s L_i^\alpha - \bar{\zeta}_d^s S_{is} &\quad \text{in } (0, r_0) \times (0, 1), \end{aligned} \quad (7.2)$$

with boundary and initial conditions

$$\begin{aligned} L_i &= L_e \quad \text{on } (0, T) \times \{r = r_0\} \times (0, 1), \\ A_{hom} \partial_x L_e &= \bar{F} (L_e - L_{e,min}) \quad \text{on } (0, T) \times \{x = 0\}, \quad \nabla L_e \cdot \nu = 0 \quad \text{on } (0, T) \times \{x = 1\}, \\ L_e(0, x) &= L_{e0}, \quad S_{es}(0, x) = S_{es0} = \frac{\varsigma_e}{l} \frac{\gamma_d^s}{\gamma_d^s} L_{e0}^\alpha \quad \text{in } (0, 1), \\ L_i(0, x, r) &= L_{i0} = L_{e0}, \quad S_{is}(0, x, r) = S_{is0} = \varsigma_i \frac{\zeta_d^s}{\zeta_d^s} L_{i0}^\alpha \quad \text{in } (0, r_0) \times (0, 1). \end{aligned} \quad (7.3)$$

where  $\bar{F} = F_m b / D_0$ ,  $r_0$  is the radius of the particle  $Y_1 \subset Z$ . We compare numerical results for (7.2)–(7.3) and (2.6) with  $\bar{\beta} = \beta \alpha L_e^{\alpha-1}$  and  $A_{hom} \partial_x L_e = \bar{F} (L_e - L_{e,min})$  on  $\partial \Omega_D = \{x = 0\}$ .

The constants in the equations are taken from the experimental literature [5, 16, 20, 21, 23, 24].

- particle radius in the unit cell is  $r_0 = 0.499$ , soil particle radius is  $a = r_0 \cdot \varepsilon \cdot b = 9.98 \cdot 10^{-3}$  cm, radius of air particle is  $r_a = 0.0073$  cm,  $b = 1$  cm,  $\Gamma_1 = 3.129$ ,  $\theta_i = 0.2025$ ,  $l = 0.02$  cm;
- assuming cylindrical pores inside the particle of radius  $\lambda$  and length  $\tilde{a}$  we estimate  $\varsigma_e = (\tilde{a}^2 - \pi \lambda^2 n) / \tilde{a}^2$ , where  $n$  is the number of pores in the particle,  $\varsigma_i = 6\pi \lambda \tilde{a} n / a^3$ ,  $\theta_i = 3\pi \lambda^2 \tilde{a} n / a^3$ ;  $\varsigma_e = 1 - 3\theta_i = 0.393$ ,  $\varsigma_i = 2\theta_i / \lambda = 2\theta_i \cdot 10^4 \text{ cm}^2 \text{ cm}^{-3}$  for  $\lambda = 10^{-4}$  cm;
- $S = \beta L^\alpha$  implies  $\frac{\gamma_d^f}{\gamma_d^f} = \beta_e^f$ ,  $\frac{\zeta_d^f}{\zeta_d^f} = \beta_i^f$ ,  $\frac{\gamma_d^s}{\gamma_d^s} = \beta_e^s$ ,  $\frac{\zeta_d^s}{\zeta_d^s} = \beta_i^s$ ;  $\beta_i = \frac{\beta}{1 + \varsigma_i \lambda / \varsigma_e}$ ,  $\beta_e = \frac{\beta}{1 + \varsigma_e / (\varsigma_i \lambda)}$ ,  $\beta = |\Gamma_1| \frac{\varsigma_e}{l} (\beta_e^f + \beta_e^s) + \varsigma_i (\beta_i^f + \beta_i^s)$ ; for  $\alpha = 1$ :  $\beta^f = 8.95$  cm,  $\beta^s = 26.86$  cm,  $\gamma_d^s = \zeta_d^s =$

$$2.6 \cdot 10^{-3} \frac{D_0}{b^2} \text{ s}^{-1}, \gamma_a^s = 0.09 \frac{l}{\zeta_e} \frac{D_0}{b^2} \text{ cm/s}, \zeta_a^s = 7.55 \frac{1}{\zeta_i} \frac{D_0}{b^2} \text{ cm/s}, \bar{\beta} = \beta = 2200;$$

$$\text{for } \alpha = 0.49: \beta^f = 0.0895 \text{ cm}, \beta^s = 0.269 \text{ cm}, \gamma_d^s = \zeta_d^s = 0.26 \frac{D_0}{b^2} \text{ s}^{-1}, \gamma_a^s = 0.09 \frac{l}{\zeta_e} \frac{D_0}{b^2} \text{ cm/s},$$

$$\zeta_a^s = 7.55 \frac{1}{\zeta_i} \frac{D_0}{b^2} \text{ cm/s}, \bar{\beta} = \beta \alpha L_e^{\alpha-1}, \beta = 22;$$

- $f_i = 10^{-3}$ ,  $\bar{D} = f_i \theta_i b^2 / l^2 = 0.506$ ,  $A_{hom} = 0.172$ ,  $D_0 = 9 \cdot 10^{-6} \text{ cm}^2/\text{s}$ ,

$$F_m = 5.6 \cdot 10^{-2} \text{ cm/s}, L_{e,min} = 10^{-4} \mu\text{mol}/\text{cm}^3, L_{e0} = L_{i0} = 10^{-3} \mu\text{mol}/\text{cm}^3.$$

The total amount of solute per unit soil volume is the sum of solute concentration in the fluid part multiplied by porosity plus the sum of the absorbed concentration multiplied by the surface density:

$$\begin{aligned} C &= |Y_0| L_e^* + \int_{\Gamma_1} \frac{\zeta_e}{l} (S_{ef}^* + S_{es}^*) d\gamma + \int_{Y_1} (\theta_i L_i^* + \zeta_i (S_{if}^* + S_{is}^*)) dy & C &= (|Y_0| + \theta_i |Y_1| + \bar{\beta}) L_e - \text{total} \\ &= |Y_0| L_e + |\Gamma_1| \left( \frac{\zeta_e}{l} \frac{\gamma_d^f}{\gamma_d^f} L_e^\alpha + S_{es} \right) + \int_{Y_1} (\theta_i L_i + \zeta_i \frac{\zeta_d^f}{\zeta_d^f} L_i^\alpha + S_{is}) dy, & & \text{amount for standard model.} \end{aligned}$$

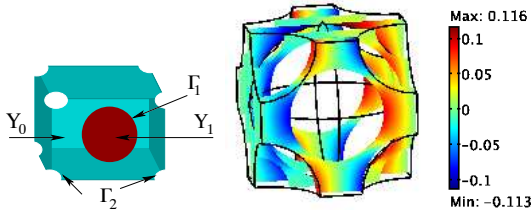


FIG. 7.1. Numerical solution of unit cell problem  $w_2$ .

In order to define the macroscopic diffusion coefficient  $A_{hom}$ ,  $A_{hom}^{ij} = |Y_0| \delta_{ij} + \int_{Y_0} \partial_{y_i} w_j dy$ , we calculate using Comsol Multiphysics the solutions of unit cell problems,

$$\begin{aligned} \Delta_y w_j &= 0 \text{ in } Y_0, \quad \nabla_y w_j \cdot \nu = -e_j \nu \text{ on } \Gamma_1 \cup \Gamma_2, \\ w_j &\text{ is periodic in } Z, \quad \int_{Y_0} w_j dy = 0. \end{aligned}$$

The symmetry of  $Y_0$  implies  $\int_{Y_0} \partial_{y_1} w_1(y) dy = \int_{Y_0} \partial_{y_2} w_2(y) dy = \int_{Y_0} \partial_{y_3} w_3(y) dy = -0.102$  and  $A_{hom} = 0.172$ . Equations (7.2) are solved using finite-difference approximations for the space derivatives. The second order partial derivatives with respect to  $x$  and  $y$  were discretized using the second order central difference. The resulting ordinary differential equations were solved by Matlab ODE solver ode15s.

**8. Conclusion.** One of the fundamental questions in experimental soil science is the definition of the minimal model that is appropriate for any given experimental setting and measurements. It has been difficult to decide in which case intraparticle diffusion pathways and/or at which level nonlinear binding reactions for solutes to particle surfaces should be included. The chemical processes in the soil were classically modeled by the standard single-porosity model, Eq (2.6), linked up to large speciation packages such as MIN3P, PHREEQC, where the nonlinear reactions are incorporated. However, these models can not explain the effects observed in the experiments on the Cambisol and Andosol soils (some of the most common soils in Wales and Japan) for phosphate diffusion, [16]. In

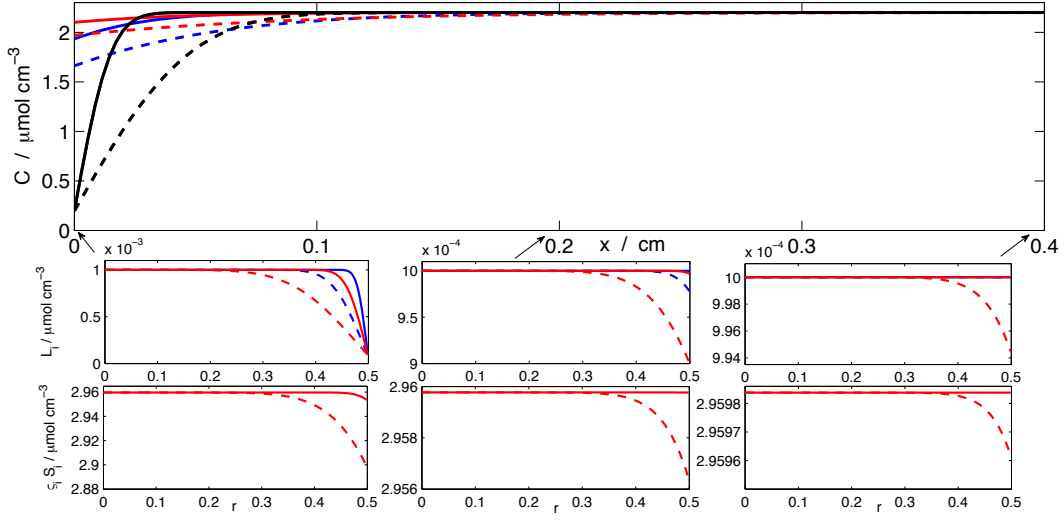


FIG. 7.2. Numerical solution for  $\alpha = 1$ ,  $C$ -complete solute amount in soil;  $L_i$ -concentration of phosphate in intra-particle space,  $\varsigma_i S_i$ -amount of phosphate adsorbed inside particle for  $x = 0$ ,  $x = 0.2$ ,  $x = 0.4$  cm as indicated with arrows; black lines- standard model, eq. (2.6); red lines- double-porosity model with slow reactions; blue lines- double-porosity model without slow reactions ( $\bar{\gamma}_a^s = \bar{\gamma}_d^s = \bar{\zeta}_a^s = \bar{\zeta}_d^s = 0$ ), eq. (7.2)-(7.3); solid lines -  $T = 10^5$  s, dashed lines -  $T = 10^6$  s.

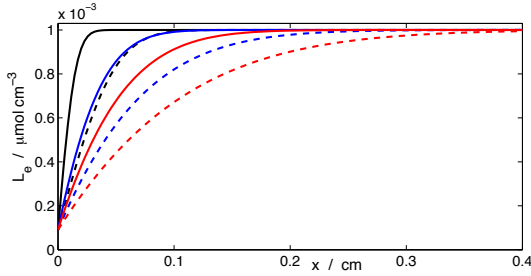


FIG. 7.3. Numerical solution for  $\alpha = 1$ ,  $L_e$ - concentration of phosphate in inter-particle space; black- standard model; red- double-porosity model with slow reactions; blue- double-porosity model without slow reactions; solid lines -  $T = 10^5$  s, dashed lines -  $T = 10^6$  s.

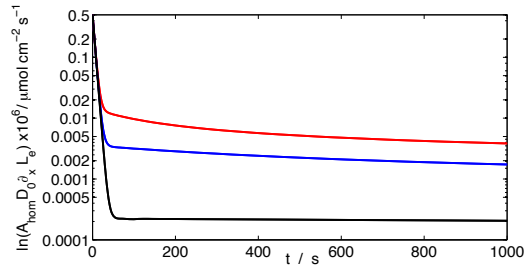


FIG. 7.4. Numerical solution for  $\alpha = 1$ ,  $L_e$ - concentration of phosphate in inter-particle space; black - standard model; red - double-porosity model with slow reactions, blue - double-porosity model without slow reactions.

the present article we derived and discussed a macroscopic model for transport of strongly sorbed solute in the soil by considering intraparticle diffusion and slow and fast binding reactions on the soil particle surfaces and inside the particles. The homogenization procedure resulted in a double-

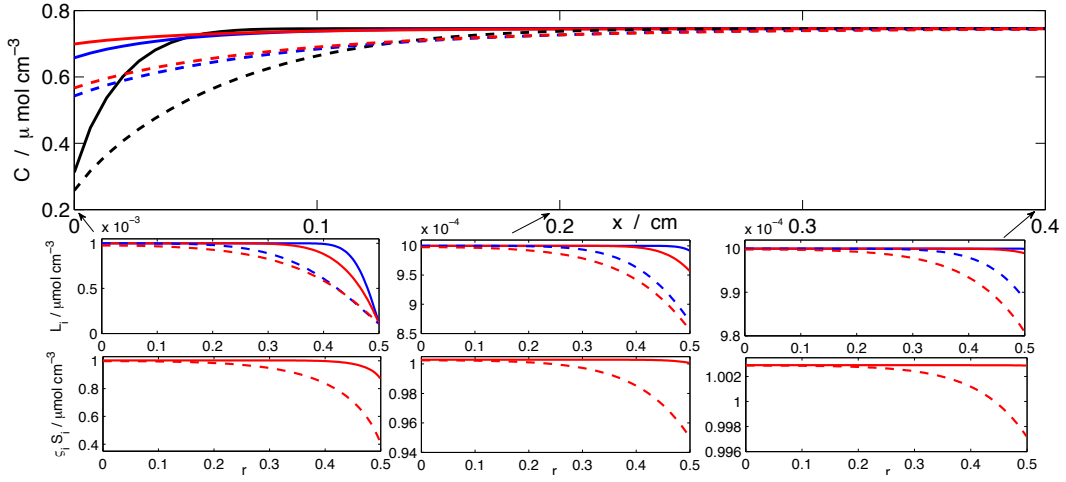


FIG. 7.5. Numerical solution for  $\alpha = 0.49$ ,  $C$ - complete solute amount in soil;  $L_i$ - concentration of phosphate in intra-particle space,  $S_i$ - amount of phosphate adsorbed inside particle for  $x = 0, x = 0.2, x = 0.4$  cm as indicated with arrows; black lines - standard model, eq. (2.6); red lines - double-porosity model with slow reactions; blue lines - double-porosity model without slow reactions ( $\bar{\gamma}_a^s = \bar{\gamma}_d^s = \bar{\zeta}_a^s = \bar{\zeta}_d^s = 0$ ), eq. (7.2)-(7.3); solid lines -  $T = 10^5$  s, dashed lines -  $T = 10^6$  s.

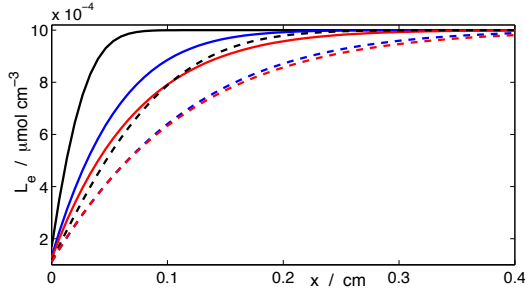


FIG. 7.6. Numerical solution for  $\alpha = 0.49$ ,  $L_e$ - concentration of phosphate in inter-particle space; black - standard model; red- double-porosity model with slow reactions; blue- double-porosity model without slow reactions; solid lines -  $T = 10^5$  s, dashed lines -  $T = 10^6$  s.

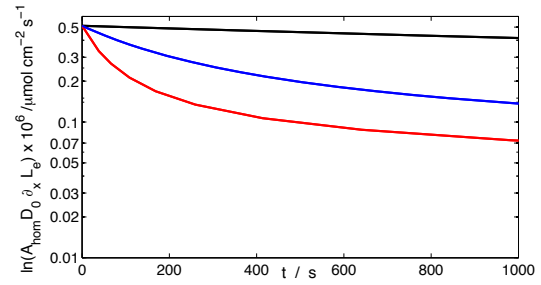


FIG. 7.7. Numerical solution for  $\alpha = 0.49$ ,  $L_e$ - concentration of phosphate in inter-particle space; black - standard model; red - double-porosity model with slow reactions; blue - double-porosity model without slow reactions.

porosity model with source/sink terms that represented the average reactions on the particle surface and average flux into the particle. Within the framework of rigorous derivation of the macroscopic equations we also found that the double-porosity model is important when the ratio of the diffusion coefficient within the particle to the diffusion in the fluid is comparable to the square of the relative

size of the single particle domain to the size of the soil sample. To our knowledge this is the first time such systematic analysis has been performed and our model is already being applied to interpret experimental findings in [16], [20], and [23].

As an example of the experimental situation, we have considered the transport of phosphate in the soil and its uptake by plant roots. We present the results for a linear binding reaction and compare the double-porosity model results to standard impeded phosphate model, Eq. (2.6), and double-porosity model without the slow reaction. The three predictions of the overall amount of phosphate in the soil differ significantly. Whilst the standard model predicts that there is a sharp gradient of phosphate around the root, the double-porosity model shows much smaller gradients because of much larger capacity of the soil particles to buffer and resupply nutrients into solution (Figure 7.2). The soil solution phosphate concentration for the three models is presented in Figure 7.3, and again, we can see that the results of the three models are quantitatively and qualitatively very different. The concentration gradients in the case of the double-porosity models are much smaller than in the case of standard model. As a result, the predictions about the rate of phosphate uptake, shown on Figure 7.4 are significantly different. Similar pattern of differences between double-porosity models and the standard model is apparent also in the case of nonlinear Freundlich type binding reactions (shown on Figures 7.5-7.7), although the differences in predicted phosphate uptake rates by plant are much smaller in the case of non-linear reactions than in the case of linear reactions.

This work emphasises the importance of starting, if it at all possible, from the microscopic description of the physical and/or biological processes and then deriving the effective macroscopic equations. The numerical results underline also the need for integrated studies of soil and plant interaction since the standard soil model will provide different estimates for root surface nutrient uptake properties as the new more adequate for solute transport in the soil double-porosity model.

**9. Macroscopic equations for  $D_i/D_0 \sim \varepsilon$  and  $D_i/D_0 \sim \varepsilon^3$ .** If we assume  $D_i/D_0 \sim \varepsilon$  then the nondimensional microscopic model equivalent to (2.1), (2.2), with  $\bar{D} = D_i/(D_0\varepsilon)$ , becomes

$$\begin{aligned}
\partial_t L_e - \Delta L_e &= 0 && \text{in } \Omega_0^\varepsilon, \\
L_e &= L_i, \quad \nabla L_e \cdot \nu = \varepsilon \bar{D} \nabla L_i \cdot \nu - \varepsilon \partial_t S_{ef} - \varepsilon \partial_t S_{es} && \text{on } \Gamma_1^\varepsilon, \\
\partial_t S_{ef} &= F_f(L_e, S_{ef}), \quad \partial_t S_{es} = F_s(L_e, S_{es}) && \text{on } \Gamma_1^\varepsilon, \\
\partial_t (\theta_i L_i) - \varepsilon \bar{D} \Delta L_i &= -\partial_t S_{if} - \partial_t S_{is} && \text{in } \Omega_1^\varepsilon, \\
\partial_t S_{if} &= G_f(L_i, S_{if}), \quad \partial_t S_{is} = G_s(L_i, S_{is}) && \text{in } \Omega_1^\varepsilon, \\
\nabla L_e \cdot \nu &= 0 && \text{on } \Gamma_2^\varepsilon,
\end{aligned} \tag{9.1}$$

Using the formal asymptotic expansion Ansatz

$$L_l = L_l^0(x, y) + \varepsilon L_l^1(x, y) + \varepsilon^2 L_l^2(x, y) + \dots, \quad S_{lj} = S_{lj}^0(x, y) + \varepsilon S_{lj}^1(x, y) + \varepsilon^2 S_{lj}^2(x, y) + \dots, \quad (9.2)$$

where  $l = e$  or  $l = i$  and  $j = f$  or  $j = s$ ,  $L_l^k(x, y)$  and  $S_{lj}^k(x, y)$ ,  $k = 0, 1, 2, \dots$ , are periodic in  $\mathbf{y} = \frac{\mathbf{x}}{\varepsilon}$ ,  $\nabla = \nabla_x + \frac{1}{\varepsilon} \nabla_y$ , we derive the macroscopic equations and obtain for  $L(x) = L_i^0(x) = L_e^0(x)$

$$\begin{aligned} \left( \frac{|Y_0|}{|Z|} + \frac{|Y_1|\theta_i}{|Z|} \right) \partial_t L - \nabla_x \cdot (A_{hom} \nabla_x L) &= -\frac{1}{|Z|} \int_{\Gamma_1} (\partial_t S_{ef}^0 + \partial_t S_{es}^0) d\gamma - \frac{1}{|Z|} \int_{Y_1} (\partial_t S_{if}^0 + \partial_t S_{is}^0) dy, \\ \partial_t S_{ef}^0 &= F_f(L, S_{ef}^0), \quad \partial_t S_{es}^0 = F_s(L, S_{es}^0) && \text{in } \Omega \times \Gamma_1, \\ \partial_t S_{if}^0 &= G_f(L, S_{if}^0), \quad \partial_t S_{is}^0 = G_s(L, S_{is}^0) && \text{in } \Omega \times Y_1, \end{aligned} \quad (9.3)$$

where  $A_{hom}^{ij} = \frac{|Y_0|}{|Z|} \delta_{ij} + \frac{1}{|Z|} \int_{Y_0} \partial_{y_i} w_j(y) dy$  and  $w_j$  are solutions of cell problems similar to (2.5). Thus, when  $\frac{D_i}{D_0} \sim \varepsilon$  only reactions inside the particle are important on the macroscopic scale and the spatial distribution of the concentration inside the particle equilibrates very fast.

For  $D_i/D_0 \sim \varepsilon^3$  using the asymptotic expansion Ansatz we obtain macroscopic equations

$$\begin{aligned} \frac{|Y_0|}{|Z|} \partial_t L_e^0 - \nabla_x \cdot (A_{hom} \nabla_x L_e^0) &= -\frac{1}{|Z|} \int_{\Gamma_1} (\partial_t S_{ef}^0 + \partial_t S_{es}^0) d\gamma && \text{in } \Omega, \\ \partial_t S_{ef}^0 &= F_f(L_e^0, S_{ef}^0), \quad \partial_t S_{es}^0 = F_s(L_e^0, S_{es}^0) && \text{in } \Omega \times \Gamma_1, \\ \partial_t L_i^0 &= -\partial_t S_{if}^0 - \partial_t S_{is}^0, \quad \partial_t S_{if}^0 = G_f(L_i^0, S_{if}^0), \quad \partial_t S_{is}^0 = G_s(L_i^0, S_{is}^0) && \text{in } \Omega \times Y_1. \end{aligned}$$

The diffusion into and inside the particle can not be seen on the macroscopic scale. The equations inside the particle are not coupled with the macroscopic equations in the interparticle space and prescribe the time evolution of the initial concentrations inside the particle.

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