SIAM J. APPL. MATH.
Vol. 70, No. 7, pp. 2097–2118

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

MARIYA PTASHNYK† AND TIINA ROOSE‡

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 plant-soil interaction when trying to understand solute losses from the soil.

Key words. homogenization, reaction-diffusion systems, reactive flows, unfolding method, double porosity, strongly sorbed solutes

AMS subject classifications. 35B27, 35K57, 74Q10, 76S05, 80A32

DOI. 10.1137/080729591

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], [20] 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; see 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, nonequilibrium 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 scales of practical interest are not possible. Applying two-scale convergence, introduced in [1], [19], [25] and extended to sequences of functions defined on ε-periodic hypersurfaces in [2], [17], we derive a macroscopic model in section 6. The main mathematical difficulty and novelty of the

*Received by the editors July 8, 2008; accepted for publication (in revised form) January 13, 2010; published electronically April 14, 2010.

http://www.siam.org/journals/siap/70-7/72959.html

†Department of Mathematics I, RWTH Aachen University, Aachen, Germany (ptashnyk@math1.rwth-aachen.de). This author's research was funded by the BBSRC grant BB/C518014.

‡School of Mathematics, University of Southhampton, Southampton, SO17 1BJ, United Kingdom (t.roose@soton.ac.uk). This author's research was supported by a Royal Society University Research Fellowship.

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 interparticle D_e and intraparticle D_i spaces. If $D_i/D_e \approx \varepsilon^2$, where ε denotes the ratio of the size of the single-particle domain relative to the whole soil sample size, then the macroscopic model we obtain is a double-porosity model which is fully analyzed in this article. For other cases we find that when $D_i/D_e \approx \varepsilon$, solute concentrations are independent of the 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 interparticle and intraparticle 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.

While no suitable model for the experimental system discussed in this paper exists, there is some relevant previous theoretical work specialized 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 microstructures (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,

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

with boundary and initial conditions

(2.2)

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

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

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,

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

with boundary and initial conditions

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

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

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

Here $F = (F_f, F_s)^T$, $G = (G_f, G_s)^T$, $S_e = (S_{ef}, S_{es})^T$, and $S_i = (S_{if}, S_{is})^T$. 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 (2.3)–(2.4) with the standard single-porosity equilibrium reaction model describing the solute movement in the soil. This model, presented in [24], is

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

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 model with inter- and intraparticle reactions is needed. A nonlinear relationship between the logarithm of the solute concentration and x_1^2/t has been predicted by a

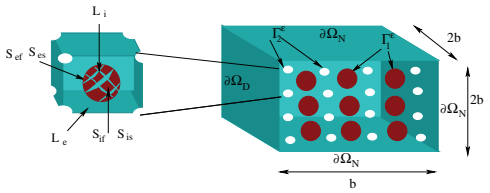

FIG. 1. *Representative single soil particle surrounded by solution and air. Periodically repeated particles in the soil.*

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 [20]. However, this model gives a poor representation of the morphology of 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 solutions 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 1.

We distinguish between the solute concentration in water between soil particles L_e^*, μmol/cm^3, and inside each particle L_i^*, μmol/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 [20]. We consider fast and slow absorbed concentrations S_{ef}^* and S_{es}^*, μmol/cm^2 on the particle surfaces, S_{if}^* and S_{is}^*, μmol/cm^2 on the surfaces inside the particle.

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

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

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

$$L_e^* = L_i^* \qquad \text{on particle surface,} \tag{3.3}$$

where $D_e(t^*, x^*) = D_0 d_e(t^*, x^*)$ is diffusion of solute in water, $D_i(t^*, x^*) = f_i \theta_i D_0 d_i \cdot(t^*, x^*)$ is diffusion of solute inside the particle, f_i is the impedance factor of the particle, ν is the particle boundary normal vector pointing inside the particle, and ς_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

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

on the particle surface, 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),

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

The adsorbed concentration inside the particle is given by

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

inside the particle, where G_f^* and G_s^* are reaction kinetics for fast- and slow-adsorbed solute concentrations, ς_i, $\mathrm{cm}^2/\mathrm{cm}^3$, is the internal surface area density, i.e., surface area inside the particle per volume of particle, and θ_i, $\mathrm{cm}^3/\mathrm{cm}^3$, 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 nonzero Neumann boundary conditions and on $\partial\tilde{\Omega}_N$ zero Neumann boundary conditions. We nondimensionalize 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 [20], 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 time scale 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 behavior 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, $[L_e] = 1\mu\mathrm{mol}/\mathrm{cm}^3$. 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 ε^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 ε-multiple εZ with Ω, where $Z = [0, 1]^3$, a "unit cell" with respect to fast variable $y = \frac{x}{\varepsilon}$. We consider $Y_1, Y_2 \subset Z$, $\overline{Y_1} \cap \overline{Y_2} = \emptyset$, with smooth boundaries Γ_1, Γ_2, where Y_1 denote the single soil particle, Y_2 the air fraction, and $Y_0 = Z \setminus (\overline{Y_1} \cup \overline{Y_2})$ 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 $\Omega_0^\varepsilon = \Omega \setminus (\bar{\Omega}_1^\varepsilon \cup \bar{\Omega}_a^\varepsilon)$, $\Gamma_1^\varepsilon = \cup\{\varepsilon\Gamma_1^k | \varepsilon Z^k \subset \Omega, k \in \mathbb{Z}^3\}$, $\Gamma_2^\varepsilon = \cup\{\varepsilon\Gamma_2^k | \varepsilon Z^k \subset \Omega, k \in \mathbb{Z}^3\}$, where Y_1^k, Y_2^k, Γ_1^k, Γ_2^k are maps of Y_1, Y_2, Γ_1, Γ_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 notation into (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^ε, L_i^ε, S_{ef}^ε, S_{es}^ε, S_{if}^ε, S_{is}^ε uniformly with respect to ε.

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 $F(t,y,\eta,\xi) : (0,T)\times\Gamma_1\times\mathbb{R}\times\mathbb{R}^2 \to \mathbb{R}^2$ is continuous and Lipschitz continuous in ξ, η 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 $G(t,y,\eta,\xi) : (0,T)\times Y_1\times\mathbb{R}\times\mathbb{R}^2 \to \mathbb{R}^2$ is continuous and Lipschitz continuous in ξ, η 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. $L_{e0}^\varepsilon \in H^1(\Omega)$, $L_{e0}^\varepsilon \to L_{e0}$ 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^ε, L_i^ε, S_e^ε, and S_i^ε 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*

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

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 $L_e^\varepsilon \to L_{e0}^\varepsilon$, $L_i^\varepsilon \to L_{i0}^\varepsilon$, $S_e^\varepsilon \to S_{e0}^\varepsilon$, $S_i^\varepsilon \to S_{i0}^\varepsilon$ as $t \to 0$ in L^2.

THEOREM 4.3. *Under Assumption* 4.1*, for every fixed $\varepsilon > 0$ there exists a unique solution of* (2.1)–(2.2).

Proof. The existence of a 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

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

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

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

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

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 (4.5), $S_e^\varepsilon \in H^1(0,T;L^2(\Gamma_1^\varepsilon)^2)$, $S_i^\varepsilon \in H^1(0,T;L^2(\Omega_1^\varepsilon)^2)$. Then, using the Galerkin method [12], we obtain a solution of the parabolic problem (4.2), (4.4), (4.6), (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 to those in Lemma 4.4, and the 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, and 4.1.3 imply

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

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. ∎

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

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

with constant C independent of ε.

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

$$\begin{aligned} &\int_0^\tau \int_{\Omega_0^\varepsilon} (\partial_t |L_e^\varepsilon|^2 + 2d_0 |\nabla L_e^\varepsilon|^2) dxdt + \int_0^\tau \int_{\Omega_1^\varepsilon} (\theta_i \partial_t |L_i^\varepsilon|^2 + \varepsilon^2 2\bar{d}_0 |\nabla L_i^\varepsilon|^2) dxdt \\ &\le \int_{\Omega_0^\varepsilon} \left(\delta |L_e^\varepsilon(\tau)|^2 + \frac{1}{\delta} |L_{eD}(\tau)|^2 \right) dx \end{aligned}$$

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

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

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

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

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

Then, choosing δ such that $2d_0-\delta d_1-C_1C_3\varepsilon^2\ge\alpha>0$, $2\bar{d}_0-\delta\bar{d}_1\ge\alpha>0$ 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 Γ_1^ε. Assumption 4.1.2 on F implies for $j=f,s$

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

5. Convergence of solutions of the microscopic problem as $\varepsilon\to 0$. We extend L_e^ε, defined on a connected domain Ω_0^ε, onto whole Ω (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^ε with constant independent on ε. 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^ε with the extension $\bar{L}_e^\varepsilon$.

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

$$\varepsilon||v^\varepsilon||^2_{L^2(\Gamma_1^\varepsilon)}\le C||v^\varepsilon||^2_{L^2(\Omega_0^\varepsilon)}+C\varepsilon^{2\beta}\int_{\Omega_0^\varepsilon}\int_{\Omega_0^\varepsilon}\frac{|v^\varepsilon(x_1)-v^\varepsilon(x_2)|^2}{|x_1-x_2|^{n+2\beta}}dx_1dx_2,$$

where C is a constant independent of ε.

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

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

Proof. From a priori estimates in Lemma 4.4, we obtain convergences L_e^ε 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^ε to L_e in $L^\infty(0,T;L^2(\Omega))$ $*$-weakly. To obtain strong convergence of L_e^ε 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 $\varepsilon\|L_e^\varepsilon - L_e\|^2_{L^2((0,T)\times\Gamma_1^\varepsilon)} \le C\|L_e^\varepsilon - L_e\|^2_{L^2(0,T;H^{\beta,2}(\Omega_0^\varepsilon))} \le C\|L_e^\varepsilon - L_e\|^2_{L^2(0,T;H^{\beta,2}(\Omega))} \to 0$ for $\varepsilon\to 0$. Since L_e^ε is bounded in $L^2(0,T;H^1(\Omega))$, the compactness theorem [1], [17], [19] implies the two-scale convergence of L_e^ε to the same function L_e and the existence of a function $L_{e1}\in L^2((0,T)\times\Omega; H^1_{per}(Z)/\mathbb{R})$ 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_i^ε and $\varepsilon\nabla L_i^\varepsilon$, applying again the compactness theorem, we obtain that $L_i^\varepsilon(t,x)\to L_i(t,x,y)$ and $\varepsilon\nabla L_i^\varepsilon(t,x)\to\nabla_y L_i(t,x,y)$ in the two-scale sense and $L_i\in L^2((0,T)\times\Omega; H^1_{per}(Y_1))$. 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^ε, $\partial_t S_e^\varepsilon$, $\partial_t L_i^\varepsilon$, S_i^ε, and $\partial_t S_i^\varepsilon$. □

The weak two-scale convergence of S_e^ε, L_i^ε, S_i^ε does not allow us 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 $\mathcal{T}_b^\varepsilon : L^p((0,T)\times\Gamma_1^\varepsilon)\to L^p((0,T)\times\Omega\times\Gamma_1)$, $p\in[1,\infty]$, by*

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

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

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

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

Proof. The change of the variables $x\to\varepsilon y + c^\varepsilon(x)$, the periodicity of F, G in the

second argument, and the periodicity of the initial data imply

$$(5.1)\ \mathcal{T}_b^\varepsilon F^\varepsilon = F\left(t, \frac{c_\varepsilon(x)+\varepsilon y}{\varepsilon}, L_e^\varepsilon(t, c_\varepsilon(x)+\varepsilon y), S_e^\varepsilon(t, c_\varepsilon(x)+\varepsilon y)\right)$$
$$= F(t, y, \mathcal{T}_b^\varepsilon L_e^\varepsilon, \mathcal{T}_b^\varepsilon S_e^\varepsilon),$$
$$(5.2)\ \mathcal{T}^\varepsilon G^\varepsilon = G\left(t, \frac{c_\varepsilon(x)+\varepsilon y}{\varepsilon}, L_i^\varepsilon(t, c_\varepsilon(x)+\varepsilon y), S_i^\varepsilon(t, c_\varepsilon(x)+\varepsilon y)\right)$$
$$= G(t, y, \mathcal{T}^\varepsilon L_i^\varepsilon, \mathcal{T}^\varepsilon S_i^\varepsilon),$$
$$(\mathcal{T}^\varepsilon L_{i0}^\varepsilon)(x,y) = L_{i0}(y), \quad (\mathcal{T}^\varepsilon S_{i0}^\varepsilon)(x,y) = S_{i0}(y), \quad (\mathcal{T}_b^\varepsilon S_{e0}^\varepsilon)(x,y) = S_{e0}(y),$$

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

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

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:

$$(5.3)\ \sup_{(0,T)} ||\mathcal{T}_b^{\varepsilon_m} S_e^{\varepsilon_m} - \mathcal{T}_b^{\varepsilon_n} S_e^{\varepsilon_n}||^2_{L^2(\Omega\times\Gamma_1)} \le c_1 ||\mathcal{T}_b^{\varepsilon_m} L_e^{\varepsilon_m} - \mathcal{T}_b^{\varepsilon_n} L_e^{\varepsilon_n}||^2_{L^2((0,T)\times\Omega\times\Gamma_1)},$$
$$(5.4)\ \sup_{(0,T)} ||\mathcal{T}^{\varepsilon_m} S_i^{\varepsilon_m} - \mathcal{T}^{\varepsilon_n} S_i^{\varepsilon_n}||^2_{L^2(\Omega\times Y_1)} \le c_2 ||\mathcal{T}^{\varepsilon_m} L_i^{\varepsilon_m} - \mathcal{T}^{\varepsilon_n} L_i^{\varepsilon_n}||^2_{L^2((0,T)\times\Omega\times Y_1)}.$$

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^ε on Γ_1^ε (Lemma 5.2), we obtain

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

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

$$(5.5)\ \int_0^T \int_{\Omega\times\Gamma_1} |\mathcal{T}_b^{\varepsilon_m} L_e^{\varepsilon_m} - \mathcal{T}_b^{\varepsilon_n} L_e^{\varepsilon_n}|^2 \, d\gamma_y dx dt$$
$$\le \varepsilon_n \int_0^T \int_{\Gamma_1^{\varepsilon_n}} |L_e^{\varepsilon_n} - L_e|^2 d\gamma dt + \varepsilon_m \int_0^T \int_{\Gamma_1^{\varepsilon_m}} |L_e^{\varepsilon_m} - L_e|^2 d\gamma dt$$
$$+ \int_0^T \int_{\Omega\times\Gamma_1} (|\mathcal{T}_b^{\varepsilon_n} L_e - L_e|^2 + |\mathcal{T}_b^{\varepsilon_m} L_e - L_e|^2)\, d\gamma_y dx dt \to 0 \text{ as } \varepsilon_n, \varepsilon_m \to 0.$$

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

$$\begin{aligned}(5.6)\quad \theta_i\partial_t k^{\varepsilon_m,\varepsilon_n} &- \nabla_y\cdot(\bar{\mathcal{D}}(y)\nabla_y k^{\varepsilon_m,\varepsilon_n})\\ &= -\big(G_f(y,\mathcal{T}^{\varepsilon_m}L_i^{\varepsilon_m},\mathcal{T}^{\varepsilon_m}S_{if}^{\varepsilon_m}) - G_f(y,\mathcal{T}^{\varepsilon_n}L_i^{\varepsilon_n},\mathcal{T}^{\varepsilon_n}S_{if}^{\varepsilon_n})\big)\\ &\quad -\big(G_s(y,\mathcal{T}^{\varepsilon_m}L_i^{\varepsilon_m},\mathcal{T}^{\varepsilon_m}S_{is}^{\varepsilon_m}) - G_s(y,\mathcal{T}^{\varepsilon_n}L_i^{\varepsilon_n},\mathcal{T}^{\varepsilon_n}S_{is}^{\varepsilon_n})\big),\\ (5.7)\qquad & k^{\varepsilon_m,\varepsilon_n}=0 \quad \text{on } (0,T)\times\Omega\times\Gamma_1, k^{\varepsilon_m,\varepsilon_n}(0)=0 \quad \text{in } \Omega\times Y_1,\end{aligned}$$

and

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

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

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^{ε}. This idea to estimate the L^2-norm via boundary data comes from the transposition method [14]. A similar idea was used in [18] to show the convergence of nonlinear reactions defined in a thin membrane. We consider

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

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

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

Using now $h^{\varepsilon_m,\varepsilon_n}$ as a test function in (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:

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

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

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

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

$$\begin{aligned}&\int_0^\tau\int_{\Omega\times Y_1}\left(\frac{1}{2}\partial_t|k^{\varepsilon_m,\varepsilon_n}|^2 + \bar{\mathcal{D}}(y)\nabla_y k^{\varepsilon_m,\varepsilon_n}\nabla_y k^{\varepsilon_m,\varepsilon_n}\right)dydxdt\\ &\qquad\le C\int_0^\tau\int_{\Omega\times Y_1}\big(|h^{\varepsilon_m,\varepsilon_n}|^2 + |k^{\varepsilon_m,\varepsilon_n}|^2\big)dydxdt.\end{aligned}$$

The ellipticity of $\bar{D}$ and the Gronwall lemma imply

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

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

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

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

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

Thus, using (5.2), (5.3), $\mathcal{T}_b^\varepsilon F \to F$ weakly in $L^2((0,T)\times\Omega\times\Gamma_1)^2$, $\mathcal{T}^\varepsilon G \to G$ weakly in $L^2((0,T)\times\Omega\times Y_1)^2$, and $F^\varepsilon \to F^*$, $G^\varepsilon \to G^*$ in the two-scale sense. Due to the relation between the weak limit of the unfolded sequence and the two-scale limit of the original sequence, we have $F = F^*$ and $G = G^*$ a.e. ∎

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* $(L_e - L_{eD}, L_i - L_{eD}) \in L^2(0,T;W)$, $\partial_t L_e \in L^2((0,T)\times\Omega)$, $\partial_t L_i \in L^2((0,T)\times\Omega\times Y_1)$, $S_e \in H^1(0,T;L^2(\Omega\times\Gamma_1)^2)$, $S_i \in H^1(0,T;L^2(\Omega\times Y_1)^2)$ *such that*

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

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

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

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

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

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

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

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

$$\begin{aligned}
&\int_0^T\int_{\Omega\times Y_1}(\theta_i\partial_t L_i+G_f(t,y,L_i,S_{if})+G_s(t,y,L_i,S_{is}))\varphi_0\,dydxdt\\
&\qquad=-\int_0^T\int_{\Omega\times\Gamma_1}\bar{\mathcal{D}}\nabla_y L_i\cdot\nu\,\varphi_0\,d\gamma_y dxdt.
\end{aligned}$$

To determine the unknown function $L_{e1}\in L^2((0,T)\times\Omega;H^1_{\rm per}(Z)/\mathbb{R})$, 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 $\varphi_1 \in C^\infty((0,T)\times\Omega; C^\infty_{per}(Z))$. From this it 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

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

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 fulfill 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

$$\int_0^T \int_{\Omega_1^\varepsilon} \partial_t L_i^\varepsilon \phi\left(x, \frac{x}{\varepsilon}\right)\xi(t)\, dx dt = -\int_{\Omega_1^\varepsilon} L_{i0}\left(\frac{x}{\varepsilon}\right)\phi\left(x,\frac{x}{\varepsilon}\right)\xi(0)\, dx$$
$$- \int_0^T \int_{\Omega_1^\varepsilon} L_i^\varepsilon \phi\left(x,\frac{x}{\varepsilon}\right)\partial_t\xi(t)\, dx dt.$$

Using two-scale convergence, we can pass to the limit for $\varepsilon \to 0$ 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 Γ_1, we consider

$$\lim_{\varepsilon\to 0}\int_0^T \int_{\Omega_1^\varepsilon} \varepsilon \nabla L_i^\varepsilon(t,x)\phi\left(t, x\frac{x}{\varepsilon}\right) dx dt = \int_0^T \int_{\Omega\times Y_1} \nabla_y L_i(t,x,y)\phi(t,x,y) dy dx dt.$$

On the other hand, using $L_i^\varepsilon = L_e^\varepsilon$ on Γ_1^ε and two-scale convergence of L_e^ε on Γ_1^ε, we have

$$\lim_{\varepsilon\to 0}\Big(-\int_0^T \int_{\Omega_1^\varepsilon} L_i^\varepsilon(t,x)\left(\varepsilon\nabla_x\phi\left(t,x,\frac{x}{\varepsilon}\right) + \nabla_y\phi\left(t,x,\frac{x}{\varepsilon}\right)\right) dx dt$$
$$+\varepsilon\int_0^T \int_{\Gamma_1^\varepsilon} L_i^\varepsilon(t,x)\phi\left(t,x,\frac{x}{\varepsilon}\right)\cdot\nu\, d\gamma_x dt\Big)$$
$$= -\int_0^T \int_{\Omega\times Y_1} L_i(t,x,y)\nabla_y\phi(t,x,y)\, dx dt + \int_0^T \int_{\Omega\times\Gamma_1} L_e(t,x)\phi(t,x,y)\cdot\nu\, d\gamma_y dx dt.$$

We used here that $\lim_{\varepsilon\to 0}\varepsilon\int_0^T\int_{\Gamma_1^\varepsilon} L_e^\varepsilon\,\phi(t,x,\frac{x}{\varepsilon})\, d\gamma_x dt = \int_0^T\int_{\Omega\times\Gamma_1} L_e(t,x)\phi(t,x,y) d\gamma_y \cdot dx dt$. The last convergence follows from $\varepsilon\int_0^T\int_{\Gamma_1^\varepsilon}|L_e^\varepsilon - L_e||\phi(t,x\frac{x}{\varepsilon})| d\gamma_x dt \le \varepsilon||L_e^\varepsilon - L_e||_{\Gamma_1^\varepsilon}||\phi||_{\Gamma_1^\varepsilon} \to 0$ (due to Lemma 5.2) and the two-scale convergence of L_e on Γ_1^ε. □

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], [21]. 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 of (2.3)–(2.4). There are two standard set-ups 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 set-up can be modeled prescribing the 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 the flux boundary condition defining phosphate uptake by roots. We consider here linearized 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. Michaelis–Menton kinetics, i.e., for $K_f^j > 0$, $K_m^j > 0$, $k_b^j > 0$, $F_f^j > 0$, $F_m^j > 0$, $f_b^j > 0$:

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

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

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

In order to apply our theory for given functions, we have to verifiy 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 fulfill all the assumptions. However, if $0 < \alpha < 1$, the Freudlich kinetics are Lipschitz continuous and $\mathcal{F}_j = \gamma_a^j \frac{1}{1+\alpha} L_e^{\alpha+1} - \gamma_d^j L_e S_{ej}$ fulfills Assumption 4.1.2 only for strictly nonzero functions, i.e., for $L_e \ge \mu$, $L_i \ge \mu$, $S_{ej} \ge \mu$, and $S_{ij} \ge \mu$ for some constant $\mu > 0$. From boundary rectangles theory for reaction-diffusion equations [23], it follows that for initial and boundary data such that $L_{e0} \ge \mu_1 > 0$, $L_{i0} \ge \mu_1 > 0$, $S_{ej0} \ge \mu_2 > 0$, $S_{ij0} \ge \mu_2 > 0$, $L_{eD} \ge \mu_3 > 0$, $L_{e,min} \ge \mu_4 > 0$, 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

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

The nondimesional reactions, using the scales in section 3, are given by

$$\partial_t S_{ej} = F_j(L_e, S_{ej}) = \bar\gamma_a^j L_e^\alpha - \bar\gamma_d^j S_{je} \quad \text{in } \Omega \times \Gamma_1,$$
$$\partial_t S_{ij} = G_j(L_i, S_{ij}) = \bar\zeta_a^j L_i^\alpha - \bar\zeta_d^j S_{ji} \quad \text{in } \Omega \times Y_1,$$

where $\bar\gamma_a^j = \gamma_a^j [L_e]^{\alpha-1}\varsigma_e b^2/(l\,D_0)$, $\bar\gamma_d^j = \gamma_d^j b^2/D_0$, $\bar\zeta_a^j = \zeta_a^j [L_i]^{\alpha-1}\varsigma_i b^2/D_0$, 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 diffusion, we obtain $\delta\,\partial_t S_{ef} = \varsigma_e\gamma_a^f/(l\,\gamma_d^f)\,L_e^\alpha - S_{ef}$, $\delta\,\partial_t S_{if} = \varsigma_i\zeta_a^f/\zeta_d^f\,L_i^\alpha - S_{if}$. It implies that the fast reactions can be assumed at leading order to be in the equilibrium and

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

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 nonzero 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):

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

with boundary and initial conditions

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

where $\bar F = F_m b/D_0$ and 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], [21], [22], [20], [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, $\Gamma_1 = 3.129$, $\theta_i = 0.2025$, and $l = 0.02$ cm.
- Assuming cylindrical pores inside the particle of radius λ 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, $\varsigma_i = 6\pi\lambda\tilde a n/a^3$, $\theta_i = 3\pi\lambda^2\tilde a n/a^3$; $\varsigma_e = 1 - 3\theta_i = 0.393$, $\varsigma_i = 2\theta_i/\lambda = 2\theta_i\cdot 10^4$ cm^2 cm^{-3} for $\lambda = 10^{-4}$ cm.
- $S = \beta L^\alpha$ implies $\frac{\gamma_a^f}{\gamma_d^f} = \beta_e^f$, $\frac{\zeta_a^f}{\zeta_d^f} = \beta_i^f$, $\frac{\gamma_a^s}{\gamma_d^s} = \beta_e^s$, $\frac{\zeta_a^s}{\zeta_d^s} = \beta_i^s$; $\beta_i = \frac{\beta}{1+\varsigma_i\lambda/\varsigma_e}$, $\beta_e = \frac{\beta}{1+\varsigma_e/(\varsigma_i\lambda)}$, $\beta = |\Gamma_1|\frac{\varsigma_e}{l}(\beta_e^f + \beta_e^s) + \varsigma_i(\beta_i^f + \beta_i^s)$; for $\alpha = 1$, $\beta^f = 8.95$

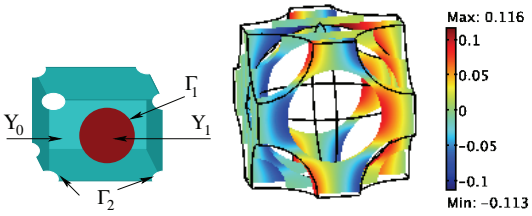

FIG. 2. *Numerical solution of unit cell problem* w_2.

cm, $\beta^s = 26.86$ cm, $\gamma_d^s = \zeta_d^s = 2.6 \cdot 10^{-3} \frac{D_0}{b^2}$ s^{-1}, $\gamma_a^s = 0.09 \frac{l}{\varsigma_e} \frac{D_0}{b^2}$ cm/s, $\zeta_a^s = 7.55 \frac{1}{\varsigma_i} \frac{D_0}{b^2}$ cm/s, $\bar{\beta} = \beta = 2200$; for $\alpha = 0.49$, $\beta^f = 0.0895$ cm, $\beta^s = 0.269$ cm, $\gamma_d^s = \zeta_d^s = 0.26 \frac{D_0}{b^2}$ s^{-1}, $\gamma_a^s = 0.09 \frac{l}{\varsigma_e} \frac{D_0}{b^2}$ cm/s, $\zeta_a^s = 7.55 \frac{1}{\varsigma_i} \frac{D_0}{b^2}$ cm/s, $\bar{\beta} = \beta \alpha L_e^{\alpha - 1}$, $\beta = 22$.

- $f_i = 10^{-3}$, $\bar{D} = f_i \theta_i b^2 / l^2 = 0.506$, $A_{hom} = 0.172$, $D_0 = 9 \cdot 10^{-6}$ cm^2/s, $F_m = 5.6 \cdot 10^{-2}$ cm/s, $L_{e,min} = 10^{-4}$ $\mu mol/\text{cm}^3$, $L_{e0} = L_{i0} = 10^{-3} \mu mol/\text{cm}^3$.

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:

$$C = |Y_0| L_e^* + \int_{\Gamma_1} \frac{\varsigma_e}{l} (S_{ef}^* + S_{es}^*) d\gamma + \int_{Y_1} (\theta_i L_i^* + \varsigma_i (S_{if}^* + S_{is}^*)) dy$$

$$= |Y_0| L_e + |\Gamma_1| \left(\frac{\varsigma_e}{l} \frac{\gamma_a^f}{\gamma_d^f} L_e^\alpha + S_{es} \right) + \int_{Y_1} \left(\theta_i L_i + \varsigma_i \frac{\zeta_a^f}{\zeta_d^f} L_i^\alpha + S_{is} \right) dy,$$

$C = (|Y_0| + \theta_i |Y_1| + \bar{\beta}) L_e$ – total amount for standard model.

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,

$$\Delta_y w_j = 0 \ \text{ in } Y_0, \quad \nabla_y w_j \cdot \nu = -e_j \nu \ \text{ on } \Gamma_1 \cup \Gamma_2,$$

$$w_j \text{ is periodic in } Z, \quad \int_{Y_0} w_j \, dy = 0.$$

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, (2.6), linked up to large speciation packages such as MIN3P, PHREEQC, where the nonlinear reactions are incorporated. However, these models cannot explain the effects observed in the experiments on the Cambisol and Andosol soils (some of the most common soils in Wales and Japan) for

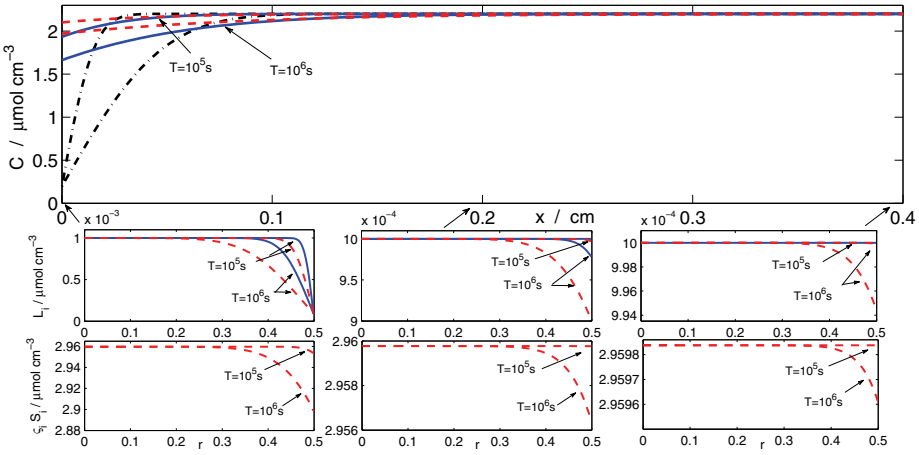

FIG. 3. *Numerical solution for* $\alpha = 1$. *C is the complete solute amount in soil;* L_i *is the concentration of phosphate in intraparticle space;* $\varsigma_i S_i$ *is the amount of phosphate adsorbed inside particle for* $x = 0$, $x = 0.2$, $x = 0.4$ *cm as indicated with arrows; dot-dash lines are the standard model,* (2.6)*; dashed lines are the double-porosity model with slow reactions; solid lines are the double-porosity model without slow reactions* ($\bar{\gamma}_a^s = \bar{\gamma}_d^s = \bar{\zeta}_a^s = \bar{\zeta}_d^s = 0$), (7.2)–(7.3).

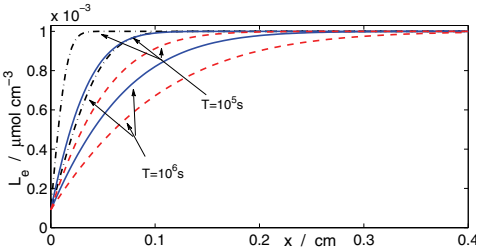

FIG. 4. *Numerical solution for* $\alpha = 1$. L_e *is the concentration of phosphate in interparticle space; dot-dash lines are the standard model; dashed lines are the double-porosity model with slow reactions; solid lines are the double-porosity model without slow reactions.*

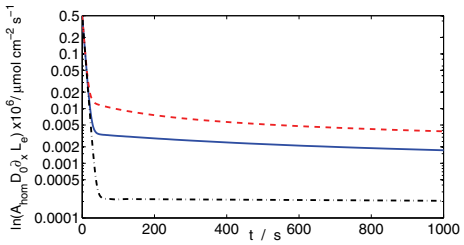

FIG. 5. *Numerical solution for* $\alpha = 1$. L_e *is the concentration of phosphate in interparticle space; dot-dash lines are the standard model; dashed lines are the double-porosity model with slow reactions; solid lines are the double-porosity model without slow reactions.*

phosphate diffusion [16]. In 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-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], [21], and [20].

As an example of the experimental situation, we have considered the transport

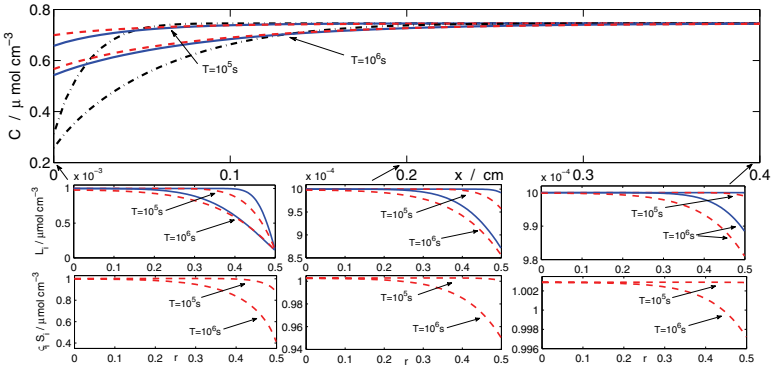

FIG. 6. *Numerical solution for $\alpha = 0.49$. C is the complete solute amount in soil; L_i is the concentration of phosphate in intraparticle space; $\varsigma_i S_i$ is the amount of phosphate adsorbed inside particle for $x = 0$, $x = 0.2$, $x = 0.4$ cm as indicated with arrows; dot-dash lines are the standard model,* (2.6)*; dashed lines are the double-porosity model with slow reactions; solid lines are the double-porosity model without slow reactions ($\bar{\gamma}_a^s = \bar{\gamma}_d^s = \bar{\zeta}_a^s = \bar{\zeta}_d^s = 0$),* (7.2)–(7.3).

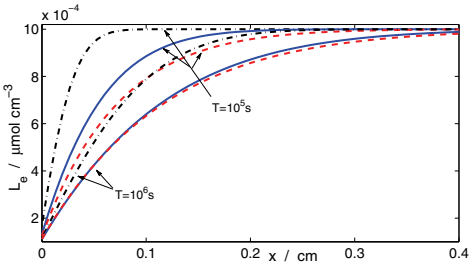

FIG. 7. *Numerical solution for $\alpha = 0.49$. L_e is the concentration of phosphate in interparticle space; dot-dash lines are the standard model; dashed lines are the double-porosity model with slow reactions; solid lines are the double-porosity model without slow reactions.*

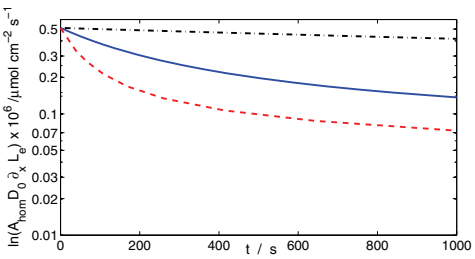

FIG. 8. *Numerical solution for $\alpha = 0.49$. L_e is the concentration of phosphate in interparticle space; dot-dash lines are the standard model; dashed lines are the double-porosity model with slow reactions; solid lines are the double-porosity model without slow reactions.*

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 the standard impeded phosphate model, (2.6), and the double-porosity model without the slow reaction. The three predictions of the overall amount of phosphate in the soil differ significantly. While 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 3). The soil solution phosphate concentration for the three models is presented in Figure 4, 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 the standard model. As a result, the predictions about the rate of phosphate uptake, shown in Figure 5 are significantly different. A 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 in Figures 6–8), although the

differences in predicted phosphate uptake rates by plants are much smaller in the case of nonlinear reactions than in the case of linear reactions.

This work emphasizes the importance of starting, if at all possible, from the microscopic description of the physical and/or biological processes and then deriving the effective macroscopic equations. The numerical results also underline 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 nondimesional 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

$$
\begin{aligned}
L_l &= L_l^0(x,y) + \varepsilon L_l^1(x,y) + \varepsilon^2 L_l^2(x,y) + \cdots,\\
S_{lj} &= S_{lj}^0(x,y) + \varepsilon S_{lj}^1(x,y) + \varepsilon^2 S_{lj}^2(x,y) + \cdots,
\end{aligned} \tag{9.2}
$$

where $l = e$ or $l = i$ and $j = f$ or $j = s$, $L_l^k(x,y)$ and $S_{lj}^k(x,y)$, $k = 0, 1, 2, \ldots$, 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 $L(x) = L_i^0(x) = L_e^0(x)$

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

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 quickly.

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

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

The diffusion into and inside the particle cannot 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.

Acknowledgments. We would like to acknowledge the help of Prof. G. Kirk from Cranfield University on the experimental soil science and mentorship during this project, and we thank Dr. Y. Golovaty, Dr. D. C. Smith, and Dr. F. Davidson for editorial assistance.

REFERENCES

[1] G. Allaire, *Homogenization and two-scale convergence*, SIAM J. Math. Anal., 23 (1992), pp. 1482–1518.

[2] G. Allaire, A. Damlamian, and U. Hornung, *Two-scale convergence on periodic surfaces and applications*, in Proceeding of the Internatational Conference on Mathematical Modelling of Flow through Porous Media, A. Bourgeat et al., eds., World Scientific, Singapore, 1996, pp. 15–25.

[3] T. Arbogast, J. Douglas, Jr., and U. Hornung, *Modeling of naturally fractured reservoirs by formal homogenization techniques*, in Frontiers in Pure and Applied Mathematics, R. Dautray, ed., North–Holland, Amsterdam, 1991, pp. 1–19.

[4] T. Arbogast, J. Douglas, Jr., and U. Hornung, *Derivation of the double porosity model of single phase flow via homogenization theory*, SIAM J. Math. Anal., 21 (1990), pp. 823–836.

[5] S. A. Barber, *Soil Nutrient Bioavailability. A Mechanistic Approach*, Wiley-Interscience, New York, 1984.

[6] A. Bourgeat, S. Luckhaus, and A. Mikelić, *Convergence of the homogenization process for a double-porosity model of immiscible two-phase flow*, SIAM J. Math. Anal., 27 (1996), pp. 1520–1543.

[7] D. Cioranescu, A. Damlamian, and G. Griso, *Periodic unfolding and homogenization*, C. R. Math. Acad. Sci. Paris, 335 (2002), pp. 99–104.

[8] D. Cioranescu, P. Donato, and R. Zaki, *Periodic unfolding and Robin problems in perforated domains*, C. R. Math. Acad. Sci. Paris, 342 (2006), pp. 469–474.

[9] D. Cioranescu and J. Saint Jean Paulin, *Homogenization in Open Sets with Holes*, J. Math. Anal. Appl., 71 (1979), pp. 590–607.

[10] U. Hornung and W. Jäger, *Diffusion, convection, adsorption, and reaction of chemicals in porous media*, J. Differential Equations, 92 (1991), pp. 199–225.

[11] U. Hornung, W. Jäger, and A. Mikelić, *Reactive transport through an array of cells with semi-permeable membranes*, Math. Model. Numer. Anal., 28 (1994), pp. 59–94.

[12] O. A. Ladyzenskaja, V. A. Solonnikov, and N. N. Uralceva, *Linear and Quasi-linear Equations of Parabolic Type*, AMS, Providence, RI, 1968.

[13] J.-L. Lions, *Quelques méthodes de résolution des problèmes aux limites non linéaires*, Dunod, Paris, 1969.

[14] J.-L. Lions and E. Magenes, *Nonhomogeneous Boundary Value Problems and Applications*, Springer-Verlag, Berlin, Heidelberg, New York, 1972.

[15] A. Marciniak-Czochra and M. Ptashnyk, *Derivation of a macroscopic receptor-based model using homogenization techniques*, SIAM J. Math. Anal., 40 (2008), pp. 215–237.

[16] N. Moritsuka, M. Ptashnyk, T. Roose, D. L. Jones, and G. J. D. Kirk, *Diffusion of strongly sorbed solutes in soil: Experimental testing of dual porosity model*, European J. Soil Sci., submitted.

[17] M. Neuss-Radu, *Some extensions of two-scale convergence*, C. R. Acad. Sci. Paris Sér. I Math., 332 (1996), pp. 899–904.

[18] M. Neuss-Radu and W. Jäger, *Effective transmission conditions for reaction-diffusion processes in domains separated by an interface*, SIAM J. Math. Anal., 39 (2007), pp. 687–720.

[19] G. Nguetseng, *A general convergence result for a functional related to the theory of homogenization*, SIAM J. Math. Anal., 20 (1989), pp. 608–623.

[20] P. H. Nye and S. Staunton, *The self-diffusion of strongly adsorbed anions in soil: Two-path model to simulate restricted access to exchange sites*, European J. Soil Sci., 45 (1994), pp. 145–152.

[21] M. Ptashnyk, T. Roose, and G. J. D. Kirk, *Diffusion of strongly sorbed solutes in soil: A dual porosity model allowing for slow access to sorption sites and time-dependent sorption*

reactions, European J. Soil Sci., 61 (2010), pp. 108–119.
[22] T. Roose, A. C. Fowler, and P. R. Darrah, *A mathematical model of plant nutrient uptake*, J. Math. Biol., 42 (2001), pp. 347–360.
[23] J. Smoller, *Shock Waves and Reaction-Diffusion Equations*. Springer-Verlag, New York, 1994.
[24] P. B. Tinker and P. H. Nye, *Solute Movement in the Rhizosphere*, Oxford University Press, New York, Oxford, UK, 2000.
[25] V. V. Zhikov, *On an extension and an application of the two-scale convergence method*, Sb. Math., 191 (2000), pp. 973–1014.