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# Homogenization of the linearized ionic transport equations in rigid periodic porous media<sup>a)</sup>

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In this paper we undertake the rigorous homogenization of a system of partial differential equations describing the transport of a  $N$ -component electrolyte in a dilute Newtonian solvent through a rigid porous medium. The motion is governed by a small static electric field and a small hydrodynamic force, which allows us to use O'Brien's linearized equations as the starting model. We establish convergence of the homogenization procedure and discuss the homogenized equations. Even if the symmetry of the effective tensor is known from the literature (Looker and Carnie<sup>1</sup>), its positive definiteness does not seem to be known. Based on the rigorous study of the underlying equations, we prove that the effective tensor satisfies Onsager properties, namely is symmetric positive definite. This result justifies the approach of many authors who use Onsager theory as starting point.

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## I. INTRODUCTION

The quasi-static transport of an electrolyte through an electrically charged porous medium is an important and well-known multiscale problem in geosciences and porous materials modeling. An  $N$ -component electrolyte is a dilute solution of  $N$  species of charged particles, or ions, in a fluid which saturates a rigid porous medium. In such a case, an electric field can generate a so-called electrokinetic flow. This electro-osmotic mechanism, which can facilitate or slow down fluid flowing through clays, is due to the *electric double layer* (EDL) which is formed as a result of the interaction of the ionized solution with static charges on the pore solid-liquid interfaces. The solute ions of opposite charge cluster near the interface, forming the *Stern layer*. Its typical thickness is of one ionic diameter. After the Stern layer the *electrostatic diffuse layer* or *Debye's layer* is formed, where the ion density

varies. The EDL is the union of Stern and diffuse layers. The thickness of the EDL is predicted by the Debye length  $\lambda_D$ , defined as the distance from the solid charged interface, where the thermal energy is equal to the electrokinetic potential energy. Usually,  $\lambda_D$  is smaller than 100 nanometers. Outside Debye's layer, in the remaining bulk fluid, the solvent can be considered as electrically neutral.

The ion distribution in the EDL is characterized using the electrokinetic potential  $\Psi$ . Its boundary value at the edge of Stern's layer is known as the zeta potential  $\zeta$ . In many situations it is rather the surface charge density  $\sigma$ , proportional to the normal derivative of  $\Psi$ , than  $\zeta$ , which is known. Under the presence of an external electric field  $\mathbf{E}$ , the charged fluid may acquire a plug flow velocity which is proportional to  $\mathbf{E}\zeta$  and given by the so-called Smoluchowski's formula. A more detailed, mathematically oriented, presentation of the fundamental concepts of electroosmotic flow in nanochannels can be found in the book<sup>2</sup> by Karniadakis et al., pages 447-470, from which we borrow the notations and definitions in this introduction.

In the case of porous media with large pores, the electro-osmotic effects are modeled by introducing an effective slip velocity at the solid-liquid interfaces, which comes from the Smoluchowski formula. In this setting, the effective behavior of the charge transport through spatially periodic porous media was studied by Edwards in<sup>3</sup>, using the volume averaging method.

On the other hand, in the case of clays, the characteristic pore size is also of the order of a few hundreds of nanometers or even less. Therefore the Debye's layer fills largely the pores and its effect cannot anymore be modeled by an effective slip boundary condition at the

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liquid-solid interface. Furthermore, it was confirmed experimentally (see e.g.<sup>4</sup>) that the bulk Navier-Stokes equations still hold for pores larger than 1 nanometer. Therefore, in the present paper we consider continuum equations at the microscopic level and, more precisely, we couple the incompressible Stokes equations for the fluid with the electrokinetic model made of a global electrostatic equation and one convection-diffusion equation for each type of ions.

The microscopic electro-chemical interactions in an  $N$ -component electrolyte in a dilute Newtonian solvent are now well understood and given by

$$\mathcal{E}\Delta\Psi = -N_A e \sum_{j=1}^N z_j n_j \quad \text{in } \Omega_p, \quad (1)$$

$$\mathcal{E}\nabla\Psi \cdot \nu = -\sigma \quad \text{on } \partial\Omega_p \setminus \partial\Omega, \quad (2)$$

$$\eta\Delta\mathbf{u} = \mathbf{f} + \nabla P + N_A e \sum_{j=1}^N z_j n_j \nabla\Psi \quad \text{in } \Omega_p, \quad (3)$$

$$\text{div } \mathbf{u} = 0 \quad \text{in } \Omega_p, \quad (4)$$

$$D_i \Delta n_i + \text{div} \left( e b_i z_i n_i \nabla\Psi - \mathbf{u} n_i \right) = 0 \quad \text{in } \Omega_p, \\ i = 1, \dots, N, \quad (5)$$

$$\mathbf{u} = 0 \quad \text{on } \partial\Omega_p \setminus \partial\Omega, \quad (6)$$

$$\left( D_i \nabla n_i + e b_i z_i n_i \nabla\Psi \right) \cdot \nu = 0 \quad \partial\Omega_p \setminus \partial\Omega, \quad i = 1, \dots, N. \quad (7)$$

where  $\Omega_p$  is the pore space of the porous medium  $\Omega$  and  $\nu$  is the unit exterior normal to  $\Omega_p$ . We recall that the equation (1) links the electrokinetic potential  $\Psi$  with the

electric charge density  $\rho_e = N_A e \sum_{j=1}^N z_j n_j$ . In the mo-

mentum equation (3), the electrokinetic force per unit volume  $\mathbf{f}_{EK} = \rho_e \nabla\Psi$  is taken into account. The unknowns  $(\mathbf{u}, P)$  denote, respectively, the fluid velocity and the pressure. Denoting by  $n_i$  the concentration of the  $i$ th species, each equation (5) is the  $i$ th mass conservation for a multicomponent fluid, in the absence of chemical reactions. The boundary condition (7) means that the normal component of the  $i$ th species ionic flux, given by  $\mathbf{j}_i = -D_i \nabla n_i - e b_i z_i n_i \nabla\Psi + \mathbf{u} n_i$ , vanishes at the pore boundaries. The various parameters appearing in (1)-(7) are defined in Table I. There is a liberty in choosing boundary conditions for  $\Psi$  on  $\partial\Omega_p \setminus \partial\Omega$  and following the literature we impose a nonhomogeneous Neumann condition with  $\sigma$  in (2), rather than Dirichlet's condition with  $\zeta$ .

For simplicity we assume that  $\Omega = (0, L)^d$  ( $d = 2, 3$  is the space dimension),  $L > 0$  and at the outer boundary  $\partial\Omega$  we set

$$\Psi + \Psi^{ext}(x), n_i, \mathbf{u} \text{ and } P \text{ are } L\text{-periodic.} \quad (8)$$

The applied exterior potential  $\Psi^{ext}(x)$  can typically be linear, equal to  $\mathbf{E} \cdot x$ , where  $\mathbf{E}$  is an imposed electrical

	QUANTITY	CHARACTERISTIC VALUE
e	electron charge	1.6e-19 C (Coulomb)
$D_i$	diffusivity of the $i$ th specie	$D_i \in (1.79, 9.31)e-09 \text{ m}^2/\text{s}$
$k_B$	Boltzmann constant	1.38e-23 J/K
$N_A$	Avogadro's constant	6.022e23 1/Mole
$T$	temperature	293° K (Kelvin)
$b_i$	electric mobility	$b_i = D_i/(k_B T) \text{ s/kg}$
$\mathcal{E}$	dielectric constant	708e-12 C/(mV)
$\eta$	dynamic viscosity	1e-3 kg/(m sec)
$\ell$	pore size	1e-6 m
$\lambda_D$	Debye's length	$\sqrt{\frac{\mathcal{E} k_B T}{N_A e^2 \sum_j n_j z_j}} \in (3, 300) \text{ nm}$
$z_j$	$j$ -th electrolyte valence	given integer
$\sigma$	surface charge density	C/m <sup>2</sup>
$\mathbf{f}$	given applied force	N/m <sup>3</sup>

TABLE I. *Data description*

field. Note that the applied exterior force  $\mathbf{f}$  in the Stokes equations (3) can also be interpreted as some imposed pressure drop or gravity force. Due to the complexity of the geometry and of the equations, it is necessary for engineering applications to upscale the system (1)-(8) and to replace the flow equations with a Darcy type law, including electro-osmotic effects.

It is a common practice to assume that the porous medium has a periodic microstructure. For such media formal two-scale asymptotic analysis of system (1)-(8) has been performed in many previous papers. Most of these works rely on a preliminary linearization of the problem which is first due to O'Brien et al.<sup>5</sup>. The earliest paper, considering only one ionic species, is<sup>6</sup>. It was further extended by Looker and Carnie in<sup>1</sup>. We also mention several important numerical works by Adler et al. in<sup>7, 8, 9, 10, 11, 12</sup> and<sup>13</sup>. Moynes and Murad considered the case of electro-osmosis in **deformable** periodic porous media without linearization in the series of articles<sup>14, 15, 16, 17</sup> and<sup>18</sup>. They obtained a homogenized system involving two-scale partial differential equations and presented numerical simulations.

Our goal here is to rigorously justify the homogenization of a linearized version of (1)-(8) in a **rigid** periodic porous medium and to clarify the analysis of the homogenized problem. We feel that our rigorous approach brings further light on the results obtained previously by the above mentioned authors.

In Section II we present the linearization, corresponding to the seminal work of O'Brien et al.<sup>5</sup>, and write the linearized system in a non-dimensional form. This allows us to write the microscopic  $\varepsilon$ -problem. Its solvability and the a priori estimates (uniform with respect to  $\varepsilon$ ) are obtained in Section III where we also state our main convergence result, Theorem 1. In Section IV, we present rigorous passing to the homogenization limit, namely we prove our Theorem 1. The homogenized problem, being identical to the one in<sup>1</sup>, is then studied and uniqueness questions are discussed. We finish Section IV with

a short discussion of the linear relation linking the ionic current, filtration velocity and ionic fluxes with gradients of the electrical potential, pressure and ionic concentrations. In other words, in Proposition 3 we prove that the so called **Onsager relation** (see e.g.<sup>19</sup>) is satisfied, namely the full homogenized tensor is symmetric positive definite. Finally in Section V we show that the two-scale convergence from Section IV is actually strong. It relies on a  $\Gamma$ -convergence type result, namely on the convergence of the associated energy. A numerical study of the obtained homogenized coefficients (including their sensitivities to various physical parameters) is the topic of further investigation and will appear later, together with a comparison with previous results in the literature.

## II. LINEARIZATION AND NON-DIMENSIONAL FORM

The electrolyte flows in response to the static electric potential  $\Psi^{ext}(x)$ , the constant surface charge density  $\sigma$  on the pore walls and the applied fluid force  $\mathbf{f}(x)$ . The magnitude of the applied fields  $\mathbf{f}$  and  $\Psi^{ext}$  is assumed to be sufficiently small to permit the linearization of the ionic transport (electrokinetic) equations. Then the system is only slightly perturbed from equilibrium and we are permitted to linearize (1)-(8). Following the calculations by O'Brien et al. from the seminal paper<sup>5</sup>, we write the electrokinetic unknowns as

$$n_i(x) = n_i^0(x) + \delta n_i(x), \quad \Psi(x) = \Psi^0(x) + \delta\Psi(x), \\ \mathbf{u}(x) = \mathbf{u}^0(x) + \delta\mathbf{u}(x), \quad P(x) = P^0(x) + \delta P(x),$$

where  $n_i^0, \Psi^0, \mathbf{u}^0, P^0$  are the equilibrium quantities, corresponding to  $\mathbf{f} = 0$  and  $\Psi^{ext} = 0$ . The  $\delta$  prefix indicates a perturbation. It is easy to check that, in the case  $\mathbf{f} = 0$  and  $\Psi^{ext} = 0$ , a solution of (1)-(8) is given by

$$\mathbf{u}^0 = 0, \quad P^0 = N_A k_B T \sum_{j=1}^N n_j^0, \\ n_j^0(x) = n_j^0(\infty) \exp\left\{-\frac{ez_j}{k_B T} \Psi^0(x)\right\}, \quad (9)$$

where  $n_i^0(\infty)$  are constants and  $\Psi^0$  is the solution of the Boltzmann-Poisson equation

$$\begin{cases} -\Delta\Psi^0 = \frac{N_A e}{\mathcal{E}} \sum_{j=1}^N n_j^0(\infty) \exp\left\{-\frac{ez_j}{k_B T} \Psi^0\right\} & \text{in } \Omega_p, \\ \mathcal{E} \nabla\Psi^0 \cdot \nu = -\sigma & \text{on } \partial\Omega_p \setminus \partial\Omega, \end{cases} \quad \Psi^0 \text{ is } L\text{-periodic.} \quad (10)$$

Motivated by the form of the Boltzmann equilibrium distribution and the calculation of  $n_i^0$ , we follow the lead of<sup>5</sup> and introduce a so-called ionic potential  $\Phi_i$  which is defined in terms of  $n_i$  by

$$n_i(x) = n_i^0(\infty) \exp\left\{-\frac{ez_j}{k_B T} (\Psi(x) + \Phi_i(x) + \Psi^{ext}(x))\right\}. \quad (11)$$

After linearization it leads to

$$\delta n_i(x) = -\frac{ez_j}{k_B T} n_i^0(x) (\delta\Psi(x) + \Phi_i(x) + \Psi^{ext}(x)). \quad (12)$$

Introducing (12) into (1)-(8) and linearizing yields the following equations for  $\delta\Psi, \delta\mathbf{u}, \delta P$  and  $\Phi_i$

$$-\Delta(\delta\Psi) + \frac{N_A e^2}{\mathcal{E} k_B T} \left( \sum_{j=1}^N z_j^2 n_j^0(x) \right) \delta\Psi = \\ -\frac{N_A e^2}{\mathcal{E} k_B T} \left( \sum_{j=1}^N z_j^2 n_j^0(x) (\Phi_j + \Psi^{ext}(x)) \right) \text{ in } \Omega_p, \quad (13)$$

$$\mathcal{E} \nabla \delta\Psi \cdot \nu = 0 \text{ on } \partial\Omega_p \setminus \partial\Omega, \quad (14)$$

$$\delta\Psi(x) + \Psi^{ext}(x) \text{ is } L\text{-periodic}, \quad (15)$$

$$\eta \Delta \delta\mathbf{u} - \nabla \left( \delta P + N_A e \sum_{j=1}^N z_j n_j^0 (\delta\Psi + \Phi_j + \Psi^{ext}(x)) \right) =$$

$$\mathbf{f} - N_A e \sum_{j=1}^N z_j n_j^0(x) (\nabla\Phi_j + \nabla\Psi^{ext}) \text{ in } \Omega_p, \quad (16)$$

$$\text{div} \delta\mathbf{u} = 0 \text{ in } \Omega_p, \quad \delta\mathbf{u} = 0 \text{ on } \partial\Omega_p \setminus \partial\Omega, \quad (17)$$

$$\delta\mathbf{u} \text{ and } \delta P \text{ are } L\text{-periodic}, \quad (18)$$

$$\text{div} (n_i^0 (eb_i z_i \nabla\Phi_i + eb_i z_i \nabla\Psi^{ext} + \delta\mathbf{u})) = 0 \text{ in } \Omega_p; \quad (19)$$

$$(\nabla\Phi_i + \nabla\Psi^{ext}) \cdot \nu = 0 \text{ on } \partial\Omega_p \setminus \partial\Omega; \quad (20)$$

$$\Phi_i \text{ is } L\text{-periodic}. \quad (21)$$

Note that the perturbed velocity is actually equal to the overall velocity and that it is convenient to introduce a global pressure  $p$

$$\delta\mathbf{u} = \mathbf{u}, \quad p = \delta P + N_A e \sum_{j=1}^N z_j n_j^0 (\delta\Psi + \Phi_j + \Psi^{ext}(x)). \quad (22)$$

It is important to remark that  $\delta\Psi$  does not enter equations (16)-(21) and thus is **decoupled** from the main unknowns  $\mathbf{u}, p$  and  $\Phi_i$ . The system (9), (10), (16)-(22) is the microscopic linearized system for the ionic transport in the papers by Adler et al.<sup>7, 8, 9, 10, 11, 12</sup> and<sup>13</sup> and in the work of Looker and Carnie<sup>1</sup>. Our Stokes system coincides with theirs after redefining the pressure.

**Remark 1.** *It is also possible to introduce the electrochemical potential, relative to the  $j$ -th component,  $\mu_j(x) = \mu_j^{ref} + \log n_j(x) + \frac{ez_j}{k_B T} \Psi(x)$ . Applying the same decomposition,  $\mu_j(x) = \mu_j^0(x) + \delta\mu_j(x)$ , it is easy to find that  $\mu_j^0(x)$  is a constant and  $\delta\mu_j(x) = -\frac{ez_j}{k_B T} (\Phi_j + \Psi^{ext}(x))$ .*

In order to obtain a **dimensionless** form of the equations (9), (10), (16)-(22), we first note that the known data are the characteristic pore size  $\ell$ , the surface charge density  $\sigma(x)$  (having the characteristic value  $\sigma_s$ ), the static electrical potential  $\Psi^{ext}$  and the applied fluid force  $\mathbf{f}$ . Following the textbook<sup>2</sup>, we introduce the ionic force parameter  $\alpha$  defined by  $\alpha = e\zeta/(k_B T)$ . Since it is not the zeta potential  $\zeta$  which is given, but the charge density  $\sigma$ , it makes sense to choose a characteristic  $\zeta$  by imposing

$\alpha = 1$ . This choice was taken in the articles by Adler et al. After<sup>2</sup>, we know that, at  $T = 293^\circ K$ ,  $\alpha = 1$  corresponds to the zeta potential  $\zeta = 0.0254V$ . The small parameter is  $\varepsilon = \frac{\ell}{L} \ll 1$ . Next, following again the non-dimensionalization from<sup>2</sup>, we introduce the parameter  $\beta$  relating the ionic energy parameter  $\alpha$  and the characteristic pore size  $\ell$  to the Debye-Hückel parameter  $\omega = 1/\lambda_D$ , as follows

$$\beta = \frac{(\omega\ell)^2}{\alpha} = \left(\frac{\ell}{\lambda_D}\right)^2.$$

For large  $\beta$  the electrical potential is concentrated in a diffuse layer next to the liquid/solid interface.

Using the definition of Debye's length from the Table I, we find out that the characteristic concentration is

$$n_c = \frac{\mathcal{E}k_B T}{N_A e^2 \lambda_D^2} = \beta \frac{\mathcal{E}k_B T}{N_A (\ell\lambda_D)^2}.$$

Note that the parameters  $n_j^0(\infty)$  should be compatible with  $n_c$ . Following<sup>2</sup>, we find out that for  $\ell = 1.5e - 6m$  and  $\lambda_D = 136nm$  one has  $n_c = 1e - 5M$  (Mole/liter).

Next we rescale the space variable by setting  $\Omega^\varepsilon = \Omega_p/L$  and  $x' = \frac{x}{L}$  (we shall drop the primes for simplicity in the sequel). Recalling that  $\zeta = k_B T/e$ , we introduce other characteristic quantities

$$p_c = n_c N_A \zeta e, \quad u_c = \beta \mathcal{E} \frac{\zeta^2}{\eta L}, \quad n_j^c = \frac{n_j^0(\infty)}{n_c},$$

and adimensionalized unknowns

$$p^\varepsilon = \frac{p}{p_c}, \quad \mathbf{u}^\varepsilon = \frac{\mathbf{u}}{u_c}, \quad \Phi_j^\varepsilon = \frac{\Phi_j}{\zeta}, \quad \Psi^\varepsilon = \frac{\Psi^0}{\zeta}, \quad n_j^\varepsilon = \frac{n_j^0}{n_c}.$$

We also define the rescaled electric potential  $\Psi^{ext,*}$ , the rescaled fluid force  $\mathbf{f}^*$  the ratio between electrical and thermal energy  $N_\sigma$  and the global Péclet number for the  $j$ -th species  $Pe_j$  by

$$\Psi^{ext,*} = \frac{\Psi^{ext}}{\zeta}, \quad \mathbf{f}^* = \frac{\mathbf{f}L}{p_c}, \quad N_\sigma = \frac{e\sigma_s \ell}{\mathcal{E}k_B T}, \quad Pe_j = \frac{\beta \mathcal{E} \zeta^2}{\eta D_j}.$$

For simplicity, in the sequel we denote by  $\mathbf{E}^*$  the electric field corresponding to the potential  $\Psi^{ext,*}$ , i.e.,

$$\mathbf{E}^*(x) = \nabla \Psi^{ext,*}(x).$$

Straightforward algebra then yields

$$\varepsilon^2 \Delta \mathbf{u}^\varepsilon - \nabla p^\varepsilon = \mathbf{f}^* - \sum_{j=1}^N z_j n_j^\varepsilon(x) (\nabla \Phi_j^\varepsilon + \mathbf{E}^*) \quad \text{in } \Omega^\varepsilon, \quad (23)$$

$$\mathbf{u}^\varepsilon = 0 \quad \text{on } \partial\Omega^\varepsilon \setminus \partial\Omega, \quad \text{div } \mathbf{u}^\varepsilon = 0 \quad \text{in } \Omega^\varepsilon, \quad (24)$$

$$\mathbf{u}^\varepsilon \quad \text{and} \quad p^\varepsilon \quad \text{are } 1 - \text{periodic in } x, \quad (25)$$

$$-\varepsilon^2 \Delta \Psi^\varepsilon = \beta \sum_{j=1}^N z_j n_j^\varepsilon(x) \quad \text{in } \Omega^\varepsilon; \quad (26)$$

$$n_j^\varepsilon(x) = n_j^c \exp\{-z_j \Psi^\varepsilon\}, \quad (27)$$

$$\varepsilon \nabla \Psi^\varepsilon \cdot \nu = -N_\sigma \sigma \quad \text{on } \partial\Omega^\varepsilon \setminus \partial\Omega, \quad (28)$$

$$\text{div} \left( n_j^\varepsilon(x) (\nabla \Phi_j^\varepsilon + \mathbf{E}^* + \frac{Pe_j}{z_j} \mathbf{u}^\varepsilon) \right) = 0 \quad \text{in } \Omega^\varepsilon; \quad (29)$$

$$(\nabla \Phi_j^\varepsilon + \mathbf{E}^*) \cdot \nu = 0 \quad \text{on } \partial\Omega^\varepsilon \setminus \partial\Omega, \quad (30)$$

$$\Psi^\varepsilon \quad \text{and} \quad \Phi_j^\varepsilon \quad \text{are } 1 - \text{periodic in } x. \quad (31)$$

System (23)-(31) is the adimensionalized scaled model that we are going to homogenize in the sequel. We assume that all constants appearing in (23)-(31) are independent of  $\varepsilon$ , namely  $N_\sigma$  and  $Pe_j$  are of order 1 with respect to  $\varepsilon$ . The assumption  $N_\sigma = \mathcal{O}(1)$  is classical in the literature<sup>14</sup> and<sup>1</sup>, while the assumption  $Pe_j = \mathcal{O}(1)$  is motivated by the following exemplary computation: if we take  $D_j = 1e - 9m^2/sec$ ,  $\ell = 1.5e - 6m$ ,  $\lambda_D = 136nm$  and the parameters values from Table I, then we find  $Pe_j = 2.77$ .

### III. UNIFORM A PRIORI ESTIMATES AND MAIN CONVERGENCE RESULT

Let us first make precise the geometrical structure of the porous medium. From now on we assume that  $\Omega^\varepsilon$  is an  $\varepsilon$ -periodic open subset of  $\mathbb{R}^d$ . It is built from  $(0, 1)^d$  by removing a periodic distributions of solid obstacles which, after rescaling, are all similar to the unit obstacle  $\Sigma^0$ . More precisely, the unit periodicity cell  $Y$  is identified with the flat unit torus  $\mathbb{T}^d$  on which we consider a smooth partition  $\Sigma^0 \cup Y_F$  where  $\Sigma^0$  is the solid part and  $Y_F$  is the fluid part. The liquid/solid interface is  $S = \partial\Sigma^0 \setminus \partial Y$ . The fluid part is assumed to be a smooth connected open subset (no assumption is made on the solid part). We define  $Y_\varepsilon^j = \varepsilon(Y_F + j)$ ,  $\Sigma_\varepsilon^j = \varepsilon(\Sigma^0 + j)$ ,  $S_\varepsilon^j = \varepsilon(S + j)$ ,  $\Omega^\varepsilon = \bigcup_{j \in \mathbb{Z}^d} Y_\varepsilon^j \cap \Omega$  and  $S_\varepsilon \equiv \partial\Omega^\varepsilon \setminus \partial\Omega = \bigcup_{j \in \mathbb{Z}^d} S_\varepsilon^j \cap \Omega$ .

The formal homogenization of the system (23)-(31) was undertaken in<sup>1</sup> by the method of two-scale asymptotic expansions. Introducing the fast variable  $y = x/\varepsilon$ , it assumes that the solution of (23)-(25) is given by

$$\begin{cases} \mathbf{u}^\varepsilon(x) = \mathbf{u}^0(x, y) + \varepsilon \mathbf{u}^1(x, y) + \dots, \\ p^\varepsilon(x) = p^0(x, y) + \varepsilon p^1(x, y) + \dots, \\ \Psi^\varepsilon(x) = \Psi^0(x, y) + \varepsilon \Psi^1(x, y) + \dots, \\ \Phi_j^\varepsilon(x) = \Phi_j^0(x, y) + \varepsilon \Phi_j^1(x, y) + \dots \end{cases}$$

They can be considered as a special case of the general expansions of this type from the papers by Moyné and Murad<sup>14, 15, 16, 18</sup>. Our aim is to give a mathematically rigorous justification of the homogenization results of Looker and Carnie<sup>1</sup>, and to shed some light on the analysis of the homogenized problem.

### A. Solvability of the $\varepsilon$ -problem and a priori estimates

We start by noticing that the problem (26)-(28) is independent of the rest. Since  $\Omega^\varepsilon$  is periodic as well as the coefficients and the boundary conditions, the solution is of the type

$$\Psi^\varepsilon(x) = \Psi^0\left(\frac{x}{\varepsilon}\right),$$

where  $\Psi^0(y)$  is the minimizer of the minimization problem

$$\inf_{\varphi \in V} J(\varphi), \quad (32)$$

with  $V = \{\varphi \in H^1(Y_F), \varphi \text{ is } 1\text{-periodic}\}$  and

$$J(\varphi) = \frac{1}{2} \int_{Y_F} |\nabla_y \varphi(y)|^2 dy + \beta \sum_{j=1}^N \int_{Y_F} n_j^c \exp\{-z_j \varphi\} dy + N_\sigma \int_S \sigma \varphi dS.$$

Note that  $J$  is strictly convex, which give the uniqueness of the minimizer. Nevertheless, for arbitrary non-negative  $\beta, n_j^c$  and  $N_\sigma$ ,  $J$  may be **not coercive** on  $V$  if all  $z_j$ 's have the same sign. Therefore, we must put a condition on the  $z_j$ 's so that the minimization problem (32) admits a solution. Following the literature, we impose the **bulk electroneutrality condition**

$$\sum_{j=1}^N z_j n_j^c = 0, \quad n_j^c > 0, \quad \beta > 0, \quad (33)$$

which guarantees that for  $\sigma = 0$ , the unique solution is  $\Psi^0 = 0$ . Note that other conditions are possible like having both positive and negative  $z_j$ 's. Under (33) it is easy to see that  $J$  is coercive on  $V$ .

Next difficulty is that the functional  $J$  is not defined on  $V$  (except for  $n = 1$ ), but on its proper subspace  $V_1 = \{\varphi \in H^1(Y_F), \exp\{\max_j |z_j| |\varphi|\} \in L^1(Y_F)\}$ . This situation makes the solvability of the problem (32) not completely obvious. The corresponding result was established in<sup>20</sup>, using a penalization, with a cut-off of the nonlinear terms and the application of the theory of pseudomonotone operators. It reads as follows:

**Lemma 1** (20). *Assume that the centering condition (33) holds true and  $\sigma \in L^2(S)$ . Then problem (32) has a*

*unique solution  $\Psi^0 \in V$  such that*

$$\sum_{j=1}^N z_j e^{-z_j \Psi^0} \in L^1(Y_F) \quad \text{and} \quad \Psi^0 \sum_{j=1}^N z_j e^{-z_j \Psi^0} \in L^1(Y_F).$$

*Furthermore,  $\Psi^0 \in H_{loc}^2(Y_F) \cap L^\infty(Y_F)$ . In particular,  $n_j^0 = n_j^c \exp\{-z_j \Psi^0\}$  satisfies the lower bound  $n_j^0(y) \geq C > 0$  in  $Y_F$ .*

Let now  $\sigma \in C^\infty(S)$ . Then further regularity of  $\Psi^0$  can be obtained by standard elliptic regularity in the Euler-Lagrange optimality condition of (32) which is similar to (10). Indeed, the right hand side in the equation (10) is bounded and using the smoothness of the geometry, we conclude that  $\Psi^0 \in W^{2,q}(Y_F)$  for every  $q < +\infty$ . By bootstrapping, we obtain that  $\Psi^0 \in C^\infty(\bar{Y}_F)$ .

Therefore we have

$$\Psi^\varepsilon(x) = \Psi^0\left(\frac{x}{\varepsilon}\right), \quad n_j^\varepsilon(x) = n_j^c \exp\{-z_j \Psi^\varepsilon(x)\}, \quad j = 1, \dots, N. \quad (34)$$

Having determined  $\Psi^\varepsilon$  and  $n_j^\varepsilon$ , we switch to the equations for  $\Phi_j^\varepsilon$ ,  $\mathbf{u}^\varepsilon$  and  $p^\varepsilon$ . These functions should satisfy the equations (23)-(25), (29)-(31) that we study by writing its variational formulation.

The functional spaces related to the velocity field are  $W^\varepsilon = \{\mathbf{z} \in H^1(\Omega^\varepsilon)^d, \mathbf{z} = 0 \text{ on } \partial\Omega^\varepsilon \setminus \partial\Omega, 1\text{-periodic in } x\}$  and

$$H^\varepsilon = \{\mathbf{z} \in W^\varepsilon, \operatorname{div} \mathbf{z} = 0 \text{ in } \Omega^\varepsilon\}.$$

Then, summing the variational formulation of (23)-(25) with that of (29)-(31) (weighted by  $z_j^2/\text{Pe}_j$ ) yields:

$$\begin{aligned} & \text{Find } \mathbf{u}^\varepsilon \in H^\varepsilon \text{ and } \{\Phi_j^\varepsilon\}_{j=1, \dots, N} \in H^1(\Omega^\varepsilon)^N, \\ & \quad \Phi_j^\varepsilon \text{ being } 1\text{-periodic, such that} \\ & a((\mathbf{u}^\varepsilon, \{\Phi_j^\varepsilon\}), (\xi, \{\phi_j\})) := \varepsilon^2 \int_{\Omega^\varepsilon} \nabla \mathbf{u}^\varepsilon : \nabla \xi dx + \\ & \quad + \sum_{j=1}^N z_j \int_{\Omega^\varepsilon} n_j^\varepsilon (\mathbf{u}^\varepsilon \cdot \nabla \phi_j - \xi \cdot \nabla \Phi_j^\varepsilon) dx + \\ & \quad + \sum_{j=1}^N \frac{z_j^2}{\text{Pe}_j} \int_{\Omega^\varepsilon} n_j^\varepsilon \nabla \Phi_j^\varepsilon \cdot \nabla \phi_j dx = \langle \mathcal{L}, (\xi, \{\phi_j\}) \rangle := \\ & \quad + \sum_{j=1}^N z_j \int_{\Omega^\varepsilon} n_j^\varepsilon \mathbf{E}^* \cdot \left( \xi - \frac{z_j}{\text{Pe}_j} \nabla \phi_j \right) dx - \int_{\Omega^\varepsilon} \mathbf{f}^* \cdot \xi dx, \end{aligned} \quad (35)$$

for any test functions  $\xi \in H^\varepsilon$  and  $\{\phi_j\}_{j=1, \dots, N} \in H^1(\Omega^\varepsilon)^N$ ,  $\phi_j$  being 1-periodic.

**Lemma 2.** *Let  $\mathbf{E}^*$  and  $\mathbf{f}^*$  be given elements of  $L^2(\Omega)^d$ . The variational formulation (35) admits a unique solution  $(\mathbf{u}^\varepsilon, \{\Phi_j^\varepsilon\}) \in H^\varepsilon \times H^1(\Omega^\varepsilon)^d$ , such that  $\Phi_j^\varepsilon$  are 1-periodic and  $\int_{\Omega^\varepsilon} \Phi_j^\varepsilon(x) dx = 0$ . Furthermore, there exists*



a constant  $C$ , which does not depend on  $\varepsilon$ ,  $\mathbf{f}^*$  and  $\mathbf{E}^*$ , such that the solution satisfies the following a priori estimates

$$\|\mathbf{u}^\varepsilon\|_{L^2(\Omega^\varepsilon)^d} + \varepsilon \|\nabla \mathbf{u}^\varepsilon\|_{L^2(\Omega^\varepsilon)^{d^2}} \leq C \left( \|\mathbf{E}^*\|_{L^2(\Omega)^d} + \|\mathbf{f}^*\|_{L^2(\Omega)^d} \right) \quad (36)$$

$$\max_{1 \leq j \leq N} \|\Phi_j^\varepsilon\|_{H^1(\Omega^\varepsilon)} \leq C \left( \|\mathbf{E}^*\|_{L^2(\Omega)^d} + \|\mathbf{f}^*\|_{L^2(\Omega)^d} \right). \quad (37)$$

*Proof.* It is clear that the bilinear form  $a$  and the linear form  $\mathcal{L}$  are continuous on our functional spaces. Furthermore for  $\xi = \mathbf{u}^\varepsilon$  and  $\phi_j = \Phi_j^\varepsilon$ , we find out that the second integral in the definition of  $a$  cancels. In fact one can prove that this term is antisymmetric. Hence, since  $n_j^\varepsilon \geq C > 0$ , the form  $a((\mathbf{u}^\varepsilon, \{\Phi_j^\varepsilon\}), (\mathbf{u}^\varepsilon, \{\Phi_j^\varepsilon\}))$  is elliptic with respect to the norm of  $H^\varepsilon \times \{\mathbf{z} \in H^1(\Omega^\varepsilon)^d, \mathbf{z} \text{ is 1-periodic}\}/\mathbb{R}$ . Now, the Lax-Milgram lemma implies existence and uniqueness for the problem (35).

The a priori estimates (36)-(37) follow by testing the problem (35) by the solution, using the  $L^\infty$ -estimate for  $\Psi^0$  and using the well-known scaled Poincaré inequality in  $\Omega^\varepsilon$  (see e.g. lemma 1.6 in section 3.1.3 of<sup>27</sup>)

$$\|\xi\|_{L^2(\Omega^\varepsilon)^d} \leq C\varepsilon \|\nabla \xi\|_{L^2(\Omega^\varepsilon)^{d^2}} \quad (38)$$

for any  $\xi \in H^\varepsilon$ .  $\square$

To simplify the presentation we use an extension operator from the perforated domain  $\Omega^\varepsilon$  into  $\Omega$  (although it is not necessary). As was proved in<sup>21</sup>, there exists such an extension operator  $T^\varepsilon$  from  $H^1(\Omega^\varepsilon)$  in  $H^1(\Omega)$  satisfying  $T^\varepsilon \phi|_{\Omega^\varepsilon} = \phi$  and the inequalities

$$\|T^\varepsilon \phi\|_{L^2(\Omega)} \leq C \|\phi\|_{L^2(\Omega^\varepsilon)}, \quad \|\nabla(T^\varepsilon \phi)\|_{L^2(\Omega)} \leq C \|\nabla \phi\|_{L^2(\Omega^\varepsilon)}$$

with a constant  $C$  independent of  $\varepsilon$ , for any  $\phi \in H^1(\Omega^\varepsilon)$ . We keep for the extended function  $T^\varepsilon \Phi_j^\varepsilon$  the same notation  $\Phi_j^\varepsilon$ .

We extend  $\mathbf{u}^\varepsilon$  by zero in  $\Omega \setminus \Omega^\varepsilon$ . It is well known that extension by zero preserves  $L^q$  and  $W_0^{1,q}$  norms for  $1 < q < \infty$ . Therefore, we can replace  $\Omega^\varepsilon$  by  $\Omega$  in (36).

The pressure field is reconstructed using de Rham's theorem<sup>22</sup> (it is thus unique up to an additive constant). Contrary to the velocity, a priori estimates for the pressure are not easy to obtain. Following the approach from<sup>23</sup>, we define the pressure extension  $\tilde{p}^\varepsilon$  by

$$\tilde{p}^\varepsilon = \begin{cases} p^\varepsilon & \text{in } \Omega^\varepsilon, \\ \frac{1}{|\varepsilon Y_F|} \int_{\varepsilon(Y_F+i)} p^\varepsilon & \text{in } \varepsilon(\Sigma^0 + i), \end{cases} \quad (39)$$

for each  $i$  such that  $\varepsilon(\Sigma^0 + i) \subset (0,1)^d$ . Note that the solid part of the porous medium  $\Omega$  is the union of all  $\varepsilon(\Sigma^0 + i) \subset (0,1)^d$ . Then, according to the fundamental result of Tartar<sup>25</sup> (see also<sup>26</sup> or section 3.1.3 in<sup>27</sup>), the pressure field  $p^\varepsilon$  satisfies uniform a priori estimates and do not oscillate.

**Lemma 3** (<sup>25</sup>). Let  $\tilde{p}^\varepsilon$  be defined by (39). Then it satisfies the estimates

$$\|\tilde{p}^\varepsilon - \frac{1}{|\Omega|} \int_\Omega \tilde{p}^\varepsilon dx\|_{L^2(\Omega)} \leq C \left( \|\mathbf{E}^*\|_{L^2(\Omega)^d} + \|\mathbf{f}^*\|_{L^2(\Omega)^d} \right),$$

$$\|\nabla \tilde{p}^\varepsilon\|_{H^{-1}(\Omega)^d} \leq C \left( \|\mathbf{E}^*\|_{L^2(\Omega)^d} + \|\mathbf{f}^*\|_{L^2(\Omega)^d} \right).$$

Furthermore, the sequence  $\{\tilde{p}^\varepsilon - \frac{1}{|\Omega|} \int_\Omega \tilde{p}^\varepsilon\}$  is strongly relatively compact in  $L^2(\Omega)$ .

## B. Strong and two-scale convergence for the solution to the $\varepsilon$ -problem

The velocity field is oscillatory and the appropriate convergence is the *two-scale convergence*, developed in<sup>28, 29</sup>. We just recall its definition and basic properties.

**Definition 1.** A sequence  $\{w^\varepsilon\} \subset L^2(\Omega)$  is said to two-scale converge to a limit  $w \in L^2(\Omega \times Y)$  if  $\|w^\varepsilon\|_{L^2(\Omega)} \leq C$ , and for any  $\varphi \in C_0^\infty(\Omega; C_{\text{per}}^\infty(Y))$  ("per" denotes 1-periodicity) one has

$$\lim_{\varepsilon \rightarrow 0} \int_\Omega w^\varepsilon(x) \varphi\left(x, \frac{x}{\varepsilon}\right) dx = \int_\Omega \int_Y w(x, y) \varphi(x, y) dy dx$$

Next, we give various useful properties of two-scale convergence.

**Proposition 1** (<sup>28</sup>). 1. From each bounded sequence  $\{w^\varepsilon\}$  in  $L^2(\Omega)$  one can extract a subsequence which two-scale converges to a limit  $w \in L^2(\Omega \times Y)$ .

2. Let  $w^\varepsilon$  and  $\varepsilon \nabla w^\varepsilon$  be bounded sequences in  $L^2(\Omega)$ . Then there exists a function  $w \in L^2(\Omega; H_{\text{per}}^1(Y))$  and a subsequence such that both  $w^\varepsilon$  and  $\varepsilon \nabla w^\varepsilon$  two-scale converge to  $w$  and  $\nabla_y w$ , respectively.

3. Let  $w^\varepsilon$  two-scale converge to  $w \in L^2(\Omega \times Y)$ . Then  $w^\varepsilon$  converges weakly in  $L^2(\Omega)$  to  $\int_Y w(x, y) dy$ .

4. Let  $\lambda \in L_{\text{per}}^\infty(Y)$ ,  $\lambda^\varepsilon = \lambda(x/\varepsilon)$  and let a sequence  $\{w^\varepsilon\} \subset L^2(\Omega)$  two-scale converge to a limit  $w \in L^2(\Omega \times Y)$ . Then  $\lambda^\varepsilon w^\varepsilon$  two-scale converges to the limit  $\lambda w$ .

5. Let  $\mathbf{v}^\varepsilon$  be a bounded sequence in  $L^2(\Omega)^d$  which two-scale converges to  $\mathbf{v} \in L^2(\Omega \times Y)^d$ . If  $\text{div } \mathbf{v}^\varepsilon(x) = 0$ , then  $\text{div}_y \mathbf{v}(x, y) = 0$  and  $\text{div}_x (\int_Y \mathbf{v}(x, y) dy) = 0$ .

Using the a priori estimates and the notion of two-scale convergence, we are able to prove our main convergence result for the solutions of system (23)-(31).

**Theorem 1.** Let  $n_j^\varepsilon$  be given by (34) and  $\{\mathbf{u}^\varepsilon, \{\Phi_j^\varepsilon\}_{j=1, \dots, N}\}$  be the variational solution of (35). We extend the velocity  $\mathbf{u}^\varepsilon$  by zero in  $\Omega \setminus \Omega^\varepsilon$  and the pressure  $p^\varepsilon$  by  $\tilde{p}^\varepsilon$ , given by (39) and normalized by  $\int_{\Omega^\varepsilon} \tilde{p}^\varepsilon = 0$ . Then there exist limits  $(\mathbf{u}^0, p^0) \in L^2(\Omega; H_{\text{per}}^1(Y)^d) \times L_0^2(\Omega)$  and

$\{\Phi_j^0, \Phi_j^1\}_{j=1, \dots, N} \in (H^1(\Omega) \times L^2(\Omega; H_{per}^1(Y)))^N$  such that the following convergences hold

$$\mathbf{u}^\varepsilon \rightarrow \mathbf{u}^0(x, y) \quad \text{in the two-scale sense} \quad (40)$$

$$\varepsilon \nabla \mathbf{u}^\varepsilon \rightarrow \nabla_y \mathbf{u}^0(x, y) \quad \text{in the two-scale sense} \quad (41)$$

$$\tilde{p}^\varepsilon \rightarrow p^0(x) \quad \text{strongly in } L^2(\Omega) \quad (42)$$

$$\{\Phi_j^\varepsilon\} \rightarrow \{\Phi_j^0(x)\} \quad \text{weakly in } H^1(\Omega) \quad \text{and strongly in } L^2(\Omega) \quad (43)$$

$$\{\nabla \Phi_j^\varepsilon\} \rightarrow \{\nabla_x \Phi_j^0(x) + \nabla_y \Phi_j^1(x, y)\} \quad \text{in the two-scale sense} \quad (44)$$

$$n_j^\varepsilon \rightarrow n_j^0(y) \quad \text{and} \quad \Psi^\varepsilon \rightarrow \Psi^0(y) \quad \text{in the two-scale sense.} \quad (45)$$

Furthermore,  $(\mathbf{u}^0, p^0, \{\Phi_j^0, \Phi_j^1\})$  is the unique solution of the two-scale homogenized problem

$$\begin{aligned} -\Delta_y \mathbf{u}^0(x, y) + \nabla_y p^1(x, y) &= -\nabla_x p^0(x) - \mathbf{f}^*(x) + \\ &\sum_{j=1}^N z_j n_j^0(y) (\nabla_x \Phi_j^0(x) + \nabla_y \Phi_j^1(x, y) + \\ &\mathbf{E}^*(x)) \quad \text{in } \Omega \times Y_F, \end{aligned} \quad (46)$$

$$\operatorname{div}_y \mathbf{u}^0(x, y) = 0 \quad \text{in } \Omega \times Y_F, \quad \mathbf{u}^0(x, y) = 0 \quad \text{on } \Omega \times S, \quad (47)$$

$$\operatorname{div}_x \left( \int_{Y_F} \mathbf{u}^0 dy \right) = 0 \quad \text{in } \Omega, \quad (48)$$

$$\begin{aligned} -\operatorname{div}_y \left( n_j^0(y) (\nabla_y \Phi_j^1(x, y) + \nabla_x \Phi_j^0(x) + \mathbf{E}^*(x) + \right. \\ \left. \frac{Pe_j}{z_j} \mathbf{u}^0) \right) = 0 \quad \text{in } \Omega \times Y_F, \end{aligned} \quad (49)$$

$$(\nabla_y \Phi_j^1 + \nabla_x \Phi_j^0 + \mathbf{E}^*) \cdot \nu(y) = 0 \quad \text{on } \Omega \times S, \quad (50)$$

$$\begin{aligned} -\operatorname{div}_x \left( \int_{Y_F} n_j^0(y) (\nabla_y \Phi_j^1 + \nabla_x \Phi_j^0 + \mathbf{E}^*(x) + \right. \\ \left. \frac{Pe_j}{z_j} \mathbf{u}^0) dy \right) = 0 \quad \text{in } \Omega, \end{aligned} \quad (51)$$

$$\Phi_j^0, \int_{Y_F} \mathbf{u}^0 dy \quad \text{and} \quad p^0 \quad \text{being 1-periodic in } x, \quad (52)$$

with periodic boundary conditions on the unit cell  $Y_F$  for all functions depending on  $y$ .

The limit problem introduced in Theorem 1 is called the two-scale and two-pressure homogenized problem, following the terminology of<sup>27, 30</sup>. It is well posed because the two incompressibility constraints (47) and (48) are exactly dual to the two pressures  $p^0(x)$  and  $p^1(x, y)$  which are their corresponding Lagrange multipliers.

Removing the  $y$  variable from the above two-scale limit problem and extracting the purely macroscopic homogenized problem will be done later in Proposition 3.

#### IV. PASSING TO THE LIMIT IN THE $\varepsilon$ PROBLEM AND THE HOMOGENIZED PROBLEM

This section is devoted to the proof of Theorem 1 and to the analysis of the homogenized problem (46)-(52). We start by rewriting the variational formulation (35) with a velocity test function which is not divergence-free, so we can still take into account the pressure

$$\begin{aligned} &\varepsilon^2 \int_{\Omega^\varepsilon} \nabla \mathbf{u}^\varepsilon : \nabla \xi dx - \int_{\Omega^\varepsilon} p^\varepsilon \operatorname{div} \xi dx + \\ &\sum_{j=1}^N \int_{\Omega^\varepsilon} z_j n_j^\varepsilon (-\xi \cdot \nabla \Phi_j^\varepsilon + \mathbf{u}^\varepsilon \cdot \nabla \phi_j) dx + \\ &\sum_{j=1}^N \frac{z_j^2}{Pe_j} \int_{\Omega^\varepsilon} n_j^\varepsilon \nabla \Phi_j^\varepsilon \cdot \nabla \phi_j dx = - \sum_{j=1}^N \frac{z_j^2}{Pe_j} \int_{\Omega^\varepsilon} n_j^\varepsilon \mathbf{E}^* \cdot \nabla \phi_j dx \\ &+ \sum_{j=1}^N \int_{\Omega^\varepsilon} z_j n_j^\varepsilon \mathbf{E}^* \cdot \xi dx - \int_{\Omega^\varepsilon} \mathbf{f}^* \cdot \xi dx, \end{aligned} \quad (53)$$

for any test functions  $\xi \in W^\varepsilon$  and  $\phi_j \in H^1(\Omega^\varepsilon)$ ,  $\phi_j$  being 1-periodic,  $1 \leq j \leq N$ . Of course, one keeps the divergence constraint  $\operatorname{div} \mathbf{u}^\varepsilon = 0$  in  $\Omega^\varepsilon$ . Next we define the two-scale test functions:

$$\begin{aligned} \xi^\varepsilon(x) &= \xi(x, x/\varepsilon), \quad \xi \in C_{per}^\infty(\Omega; H_{per}^1(Y)^d), \\ \xi &= 0 \quad \text{on } \Omega \times S, \quad \operatorname{div}_y \xi(x, y) = 0 \quad \text{on } \Omega \times Y, \end{aligned} \quad (54)$$

$$\begin{aligned} \phi_j^\varepsilon(x) &= \varphi_j(x) + \varepsilon \gamma_j(x, x/\varepsilon), \quad \varphi_j \in C_{per}^\infty(\Omega), \\ \gamma_j &\in C_{per}^\infty(\Omega; H_{per}^1(Y_F)). \end{aligned} \quad (55)$$

Recalling that  $n_j^\varepsilon(x) = n_j^0(x/\varepsilon)$  is like a two-scale test function, we can pass to the limit in (53), along the same lines as in the seminal papers<sup>28</sup> or<sup>27</sup>. By virtue of the a priori estimates in Lemmas 2 and 3, and using the compactness of Proposition 1, there exist a subsequence, still denoted by  $\varepsilon$ , and limits  $(\mathbf{u}^0, p^0, \{\Phi_j^0, \Phi_j^1\}) \in L^2(\Omega; H_{per}^1(Y)^d) \times L_0^2(\Omega) \times H^1(\Omega) \times L^2(\Omega; H_{per}^1(Y))$  such that the convergences in Theorem 1 are satisfied. Passing to the two-scale limit in (53) we get that the limit  $(\mathbf{u}^0, p^0, \{\Phi_j^0, \Phi_j^1\})$  satisfy the following two-scale variational formulation

$$\begin{aligned} &\int_{\Omega \times Y_F} \nabla_y \mathbf{u}^0(x, y) : \nabla_y \xi dx dy - \int_{\Omega \times Y_F} p^0(x) \operatorname{div}_x \xi dx dy \\ &+ \sum_{j=1}^N \int_{\Omega \times Y_F} z_j n_j^0(y) \left( -\xi(x, y) \cdot (\nabla_x \Phi_j^0(x) + \nabla_y \Phi_j^1(x, y)) \right. \\ &\quad \left. + \mathbf{u}^0(x, y) \cdot (\nabla_x \varphi_j(x) + \nabla_y \gamma_j(x, y)) \right) dx dy \\ &+ \sum_{j=1}^N \frac{z_j^2}{Pe_j} \int_{\Omega \times Y_F} n_j^0(y) (\nabla_x \Phi_j^0(x) + \nabla_y \Phi_j^1(x, y)) \cdot (\nabla_x \varphi_j(x) \\ &+ \nabla_y \gamma_j) dx dy = - \sum_{j=1}^N \frac{z_j^2}{Pe_j} \int_{\Omega \times Y_F} n_j^0(y) \mathbf{E}^*(x) \cdot (\nabla_x \varphi_j(x) + \end{aligned}$$

$$\begin{aligned} & \nabla_y \gamma_j(x, y)) \, dx dy + \sum_{j=1}^N \int_{\Omega \times Y_F} z_j n_j^0(y) \mathbf{E}^*(x) \cdot \xi(x, y) \, dx dy \\ & - \int_{\Omega \times Y_F} \mathbf{f}^*(x) \cdot \xi(x, y) \, dx dy, \end{aligned} \quad (56)$$

for any test functions  $\xi$  given by (54) and  $\{\varphi_j, \gamma_j\}$  given by (55). Furthermore the velocity  $\mathbf{u}^0(x, y)$  satisfies the incompressibility constraints (47) and (48).

The next step is to prove the well-posedness of (56) which will automatically implies that the entire sequence  $(\mathbf{u}^\varepsilon, p^\varepsilon, \{\Phi_j^\varepsilon\})$  converges by uniqueness of the limit.

**Proposition 2.** *The problem (56) with incompressibility constraints (47) and (48) has a unique solution*

$$L^2(\Omega; H_{per}^1(Y)^d) \times L_0^2(\Omega) \times (H^1(\Omega)/\mathbb{R} \times L^2(\Omega; H_{per}^1(Y)^d/\mathbb{R}))^N.$$

*Proof.* Following<sup>31</sup> (see also section 3.1.2 in<sup>27</sup>) we introduce the functional space for the velocities

$$V = \{\mathbf{u}^0(x, y) \in L_{per}^2(\Omega; H_{per}^1(Y)^d) \text{ satisfying (47)–(48)}\},$$

which is known to be orthogonal in  $L_{per}^2(\Omega; H_{per}^1(Y)^d)$  to the space of gradients of the form  $\nabla_x q(x) + \nabla_y q_1(x, y)$  with  $q(x) \in H_{per}^1(\Omega)/\mathbb{R}$  and  $q_1(x, y) \in L_{per}^2(\Omega; L_{per}^2(Y_F)/\mathbb{R})$ . We apply the Lax-Milgram lemma to prove the existence and uniqueness of  $(\mathbf{u}^0, p^0, \{\Phi_j^0, \Phi_j^1\})$  in  $V \times L_0^2(\Omega) \times H_{per}^1(\Omega)/\mathbb{R} \times L_{per}^2(\Omega; H_{per}^1(Y)^d/\mathbb{R})$ . The only point which requires to be checked is the coercivity of the bilinear form. We take  $\xi = \mathbf{u}^0$ ,  $\varphi_j = \Phi_j^0$  and  $\gamma_j = \Phi_j^1$  as the test functions in (56). Using the incompressibility constraints (48) and the anti-symmetry of the third integral in (56), we obtain the quadratic form

$$\begin{aligned} & \int_{\Omega \times Y_F} |\nabla_y \mathbf{u}^0(x, y)|^2 \, dx dy + \\ & \sum_{j=1}^N \frac{z_j^2}{\text{Pe}_j} \int_{\Omega \times Y_F} n_j^0(y) |\nabla_x \Phi_j^0(x) + \nabla_y \Phi_j^1(x, y)|^2 \, dx dy. \end{aligned} \quad (57)$$

Recalling from Lemma 1 that  $n_j^0(y) \geq C > 0$  in  $Y_F$ , it is easy to check that each term in the sum on the second line of (57) is bounded from below by

$$C \left( \int_{\Omega} |\nabla_x \Phi_j^0(x)|^2 \, dx + \int_{\Omega \times Y_F} |\nabla_y \Phi_j^1(x, y)|^2 \, dx dy \right),$$

which proves the coerciveness of the bilinear form in the required space.  $\square$

The next step is to recover the two-scale homogenized system (46)–(52) from the variational formulation (56). In order to get the Stokes equations (46) we choose  $\varphi_j = 0$  and  $\gamma_j = 0$  in (56). By a two-scale version of de Rham's theorem<sup>22</sup> (see<sup>31</sup> or lemma 1.5 in section 3.1.2 of<sup>27</sup>) we

deduce the existence of a pressure field  $p^1(x, y)$  in  $L^2(\Omega \times Y_F)$  such that

$$-\Delta_y \mathbf{u}^0 + \nabla_y p^1 = -\nabla_x p^0 - \mathbf{f}^* + \sum_{j=1}^N z_j n_j^0 (\nabla_x \Phi_j^0 + \nabla_y \Phi_j^1 + \mathbf{E}^*).$$

The incompressibility constraints (47) and (48) are simple consequences of passing to the two-scale limit in the equation  $\text{div} \mathbf{u}^\varepsilon = 0$  in  $\Omega^\varepsilon$ . To obtain the cell convection-diffusion equation (49) we now choose  $\xi = 0$  and  $\varphi_j = 0$  in (56) while the macroscopic convection-diffusion equation (51) is obtained by taking  $\xi = 0$  and  $\gamma_j = 0$ . This finishes the proof of Theorem 1.

It is important to separate the fast and slow scale, if possible. This was undertaken by Looker and Carnie in<sup>1</sup> introducing three different type of cell problems. We propose a different approach relying on only two type of cell problems. We believe our approach is more systematic and simpler, at least from a mathematical point of view. The main idea is to recognize in the two-scale homogenized problem (46)–(52) that there are two different macroscopic fluxes, namely  $(\nabla_x p^0(x) + \mathbf{f}^*(x))$  and  $\{\nabla_x \Phi_j^0(x) + \mathbf{E}^*(x)\}_{1 \leq j \leq N}$ . Therefore we introduce two family of cell problems, indexed by  $k \in \{1, \dots, d\}$  for each component of these fluxes. We denote by  $\{\mathbf{e}^k\}_{1 \leq k \leq d}$  the canonical basis of  $\mathbb{R}^d$ .

The first cell problem, corresponding to the macroscopic pressure gradient, is

$$\begin{aligned} -\Delta_y \mathbf{v}^{0,k}(y) + \nabla_y \pi^{0,k}(y) &= \mathbf{e}^k + \\ \sum_{j=1}^N z_j n_j^0(y) \nabla_y \theta_j^{0,k}(y) & \text{ in } Y_F \end{aligned} \quad (58)$$

$$\text{div}_y \mathbf{v}^{0,k}(y) = 0 \quad \text{in } Y_F, \quad \mathbf{v}^{0,k}(y) = 0 \quad \text{on } S, \quad (59)$$

$$-\text{div}_y \left( n_j^0(y) (\nabla_y \theta_j^{0,k}(y) + \frac{\text{Pe}_j}{z_j} \mathbf{v}^{0,k}(y)) \right) = 0 \quad \text{in } Y_F \quad (60)$$

$$\nabla_y \theta_j^{0,k}(y) \cdot \nu = 0 \quad \text{on } S. \quad (61)$$

The second cell problem, corresponding to the macroscopic diffusive flux, is for each species  $i \in \{1, \dots, N\}$

$$\begin{aligned} -\Delta_y \mathbf{v}^{i,k}(y) + \nabla_y \pi^{i,k}(y) &= \sum_{j=1}^N z_j n_j^0(y) (\delta_{ij} \mathbf{e}^k + \\ \nabla_y \theta_j^{i,k}(y)) & \text{ in } Y_F \end{aligned} \quad (62)$$

$$\text{div}_y \mathbf{v}^{i,k}(y) = 0 \quad \text{in } Y_F, \quad \mathbf{v}^{i,k}(y) = 0 \quad \text{on } S, \quad (63)$$

$$\begin{aligned} -\text{div}_y (n_j^0(y) (\delta_{ij} \mathbf{e}^k + \nabla_y \theta_j^{i,k}(y) + \\ \frac{\text{Pe}_j}{z_j} \mathbf{v}^{i,k}(y))) &= 0 \quad \text{in } Y_F \end{aligned} \quad (64)$$

$$(\delta_{ij} \mathbf{e}^k + \nabla_y \theta_j^{i,k}(y)) \cdot \nu = 0 \quad \text{on } S, \quad (65)$$

where  $\delta_{ij}$  is the Kronecker symbol. As usual the cell problems are complemented with periodic boundary conditions. The solvability of the cell problems (58)-(61) and (62)-(65) is along the same lines as the proof of Proposition 2. Then, we can decompose the solution of (46)-(52) as

$$\mathbf{u}^0(x, y) = \sum_{k=1}^d (-\mathbf{v}^{0,k}(y) \left( \frac{\partial p^0}{\partial x_k} + f_k^* \right) (x) + \sum_{i=1}^N \mathbf{v}^{i,k}(y) \left( E_k^* + \frac{\partial \Phi_i^0}{\partial x_k} \right) (x)) \quad (66)$$

$$p^1(x, y) = \sum_{k=1}^d (-\pi^{0,k}(y) \left( \frac{\partial p^0}{\partial x_k} + f_k^* \right) (x) + \sum_{i=1}^N \pi^{i,k}(y) \left( E_k^* + \frac{\partial \Phi_i^0}{\partial x_k} \right) (x)) \quad (67)$$

$$\Phi_j^1(x, y) = \sum_{k=1}^d (-\theta_j^{0,k}(y) \left( \frac{\partial p^0}{\partial x_k} + f_k^* \right) (x) + \sum_{i=1}^N \theta_j^{i,k}(y) \left( E_k^* + \frac{\partial \Phi_i^0}{\partial x_k} \right) (x)). \quad (68)$$

We now have to average (66)-(68) in order to get a purely macroscopic homogenized problem. From Remark 1 we recall the non-dimensional perturbation of the electrochemical potential

$$\delta \mu_j^\varepsilon = -z_j (\Phi_j^\varepsilon + \Psi^{ext,*})$$

and we introduce the ionic flux of the  $j$ th species

$$\mathbf{j}_j = \frac{z_j}{\text{Pe}_j} n_j^\varepsilon \left( \nabla \Phi_j^\varepsilon + \mathbf{E}^* + \frac{\text{Pe}_j}{z_j} \mathbf{u}^\varepsilon \right),$$

where  $\mathbf{E}^* = \nabla \Psi^{ext,*}$ , and we define the effective quantities

$$\mu_j^{eff}(x) = -z_j (\Phi_j^0(x) + \Psi^{ext,*}(x)),$$

$$\mathbf{j}_j^{eff}(x) = \frac{z_j}{\text{Pe}_j |Y_F|} \int_{Y_F} n_j^0(y) (\nabla_x \Phi_j^0(x) + \mathbf{E}^* + \nabla_y \Phi_j^1(x, y) + \frac{\text{Pe}_j}{z_j} \mathbf{u}^0(x, y)) dy,$$

$$\mathbf{u}^{eff}(x) = \frac{1}{|Y_F|} \int_{Y_F} \mathbf{u}^0(x, y) dy \quad \text{and} \quad p^{eff}(x) = p^0(x).$$

We are now able to write the homogenized or upscaled equations for the above effective fields.

**Proposition 3.** *The macroscopic equations are, for  $j = 1, \dots, N$ ,*

$$\text{div}_x \mathbf{u}^{eff} = 0 \quad \text{and} \quad \text{div}_x \mathbf{j}_j^{eff} = 0 \quad \text{in } \Omega, \\ \mathbf{u}^{eff}(x) \quad \text{and} \quad \mathbf{j}_j^{eff}(x) \quad 1 - \text{periodic},$$

with

$$\mathbf{u}^{eff} = - \sum_{i=1}^N \frac{\mathbb{J}_i}{z_i} \nabla_x \mu_i^{eff} - \mathbb{K} \nabla_x p^{eff} - \mathbb{K} \mathbf{f}^*, \quad (69)$$

where the matrices  $\mathbb{J}_i$  and  $\mathbb{K}$  are defined by their entries

$$\{\mathbb{J}_i\}_{lk} = \frac{1}{|Y_F|} \int_{Y_F} \mathbf{v}^{i,k}(y) \cdot \mathbf{e}^l dy, \\ \{\mathbb{K}\}_{lk} = \frac{1}{|Y_F|} \int_{Y_F} \mathbf{v}^{0,k}(y) \cdot \mathbf{e}^l dy,$$

and

$$\mathbf{j}_j^{eff} = - \sum_{i=1}^N \frac{\mathbb{D}_{ji}}{z_i} \nabla_x \mu_i^{eff} - \mathbb{L}_j \nabla_x p^{eff} - \mathbb{L}_j \mathbf{f}^*, \quad (70)$$

where the matrices  $\mathbb{D}_{ji}$  and  $\mathbb{L}_j$  are defined by their entries

$$\{\mathbb{D}_{ji}\}_{lk} = \frac{1}{|Y_F|} \int_{Y_F} n_j^0(y) (\mathbf{v}^{i,k}(y) + \frac{z_j}{\text{Pe}_j} (\mathbf{e}^k + \nabla_y \theta_j^{i,k}(y))) \cdot \mathbf{e}^l dy, \quad (71) \\ \{\mathbb{L}_j\}_{lk} = \frac{1}{|Y_F|} \int_{Y_F} n_j^0(y) \left( \mathbf{v}^{0,k}(y) + \frac{z_j}{\text{Pe}_j} \nabla_y \theta_j^{0,k}(y) \right) \cdot \mathbf{e}^l dy. \quad (72)$$

Furthermore, the overall tensor  $\mathcal{M}$ , such that  $\mathcal{J} = -\mathcal{M}\mathcal{F} - \mathcal{M}(\mathbf{f}^*, \{0\})$  with  $\mathcal{J} = (\mathbf{u}^{eff}, \{\mathbf{j}_j^{eff}\})$  and  $\mathcal{F} = (\nabla_x p^{eff}, \{\nabla_x \mu_j^{eff}/z_i\})$ , defined by

$$\mathcal{M} = \begin{pmatrix} \mathbb{K} & \mathbb{J}_1 & \dots & \mathbb{J}_N \\ \mathbb{L}_1 & \frac{\mathbb{D}_{11}}{z_1} & \dots & \frac{\mathbb{D}_{1N}}{z_N} \\ \vdots & \vdots & \ddots & \vdots \\ \mathbb{L}_N & \frac{\mathbb{D}_{N1}}{z_1} & \dots & \frac{\mathbb{D}_{NN}}{z_N} \end{pmatrix} \quad (73)$$

is symmetric positive definite.

The tensor  $\mathbb{K}$  is called permeability tensor,  $\mathbb{D}_{ji}$  are the electrodiffusion tensors. The symmetry of the tensor  $\mathcal{M}$  is equivalent to the famous Onsager's reciprocal relations.

**Remark 2.** *One of the important results of Looker and Carnie in their paper<sup>1</sup> is the proof of Onsager's reciprocal relations, i.e., the symmetry of  $\mathcal{M}$  (beware our definitions of  $\mathbb{K}, \mathbb{L}_j, \mathbb{J}_j$  and  $\mathbb{D}_{ji}$  that are slightly different from those of<sup>1</sup>). Our proof of the symmetry of  $\mathcal{M}$  in Proposition 3 is actually similar to that in<sup>1</sup> (the difference being that their cell problems have distinct definitions from ours). It is also proved in<sup>1</sup> that the diagonal blocks  $\mathbb{K}$  and  $\mathbb{D}_{jj}$  are positive definite. Nevertheless, the second law of thermodynamics requires that the full tensor  $\mathcal{M}$  be positive definite and it was not established in the literature. One of the novelty in our rigorous analysis is that Proposition 3 establishes the positive definite character of  $\mathcal{M}$ .*

**Remark 3.** *The homogenized equations in Proposition 3 form a symmetric elliptic system*

$$\operatorname{div}_x \{ \mathbb{K}(\nabla_x p^0 + \mathbf{f}^*) + \sum_{i=1}^N \mathbb{J}_i(\nabla_x \Phi_i^0 + \mathbf{E}^*) \} = 0 \quad \text{in } \Omega,$$

$$\operatorname{div}_x \{ \mathbb{L}_j(\nabla_x p^0 + \mathbf{f}^*) + \sum_{i=1}^N \mathbb{D}_{ji}(\nabla_x \Phi_i^0 + \mathbf{E}^*) \} = 0 \quad \text{in } \Omega,$$

with periodic boundary conditions. In particular it implies that the pressure field  $p^0$  is smoother than expected from the convergence in Theorem 1 since it belongs to  $H^1(\Omega)$ .

*Proof.* Averaging (66)-(68) on  $Y_F$  yields the macroscopic relations (69)-(72). The only thing to prove is that  $\mathcal{M}$  is symmetric positive. We start by showing that it is positive definite. For any collection of vectors  $\lambda^0, \{\lambda^i\}_{1 \leq i \leq N} \in \mathbb{R}^d$  let us introduce the following linear combinations of the cell solutions

$$\mathbf{v}^\lambda = \sum_{k=1}^d \left( \lambda_k^0 \mathbf{v}^{0,k} + \sum_{i=1}^N \lambda_k^i \mathbf{v}^{i,k} \right), \quad (74)$$

$$\theta_j^\lambda = \sum_{k=1}^d \left( \lambda_k^0 \theta_j^{0,k} + \sum_{i=1}^N \lambda_k^i \theta_j^{i,k} \right), \quad (75)$$

which satisfy a system of equations similar to (58)-(61) or (62)-(65) but with  $\lambda^0$  or  $\lambda^j$  instead of  $\mathbf{e}^k$  as right hand sides, namely

$$-\Delta_y \mathbf{v}^\lambda(y) + \nabla_y \pi^\lambda(y) = \lambda^0 + \sum_{j=1}^N z_j n_j^0(y) (\lambda^j + \nabla_y \theta_j^\lambda(y)) \quad \text{in } Y_F \quad (76)$$

$$\operatorname{div}_y \mathbf{v}^\lambda(y) = 0 \quad \text{in } Y_F, \quad \mathbf{v}^\lambda(y) = 0 \quad \text{on } S, \quad (77)$$

$$-\operatorname{div}_y \left( n_j^0(y) (\lambda^j + \nabla_y \theta_j^\lambda(y) + \frac{\operatorname{Pe}_j}{z_j} \mathbf{v}^\lambda(y)) \right) = 0 \quad \text{in } Y_F \quad (78)$$

$$(\lambda^j + \nabla_y \theta_j^\lambda(y)) \cdot \nu = 0 \quad \text{on } S, \quad (79)$$

Multiplying the Stokes equation (76) by  $\mathbf{v}^\lambda$ , the convection-diffusion equation (78) by  $\theta_j^\lambda$  and doing the same computation as the one that leads to (57), we obtain

$$\begin{aligned} & \int_{Y_F} \left( |\nabla_y \mathbf{v}^\lambda(y)|^2 + \sum_{j=1}^N \frac{z_j^2}{\operatorname{Pe}_j} n_j^0(y) |\nabla_y \theta_j^\lambda(y)|^2 \right) dy \\ &= \int_{Y_F} \lambda^0 \cdot \mathbf{v}^\lambda(y) dy + \sum_{i=1}^N \int_{Y_F} n_i^0(y) \lambda^i \cdot (z_i \mathbf{v}^\lambda(y) - \frac{z_i^2}{\operatorname{Pe}_i} \nabla_y \theta_i^\lambda(y)) dy. \end{aligned}$$

We modify the left hand side which is still a positive

quadratic form

$$\begin{aligned} & \int_{Y_F} \left( |\nabla_y \mathbf{v}^\lambda(y)|^2 + \sum_{j=1}^N \frac{z_j^2}{\operatorname{Pe}_j} n_j^0(y) |\nabla_y \theta_j^\lambda(y) + \lambda^j|^2 \right) dy \\ &= \int_{Y_F} \lambda^0 \cdot \mathbf{v}^\lambda dy + \sum_{i=1}^N \int_{Y_F} n_i^0 \lambda^i \cdot (z_i \mathbf{v}^\lambda + \frac{z_i^2}{\operatorname{Pe}_i} (\nabla_y \theta_i^\lambda + \lambda^i)) dy \\ &= \mathbb{K} \lambda^0 \cdot \lambda^0 + \sum_{i=1}^N \mathbb{J}_i \lambda^i \cdot \lambda^0 + \sum_{i,j=1}^N z_i \lambda^i \cdot \mathbb{D}_{ij} \lambda^j \\ &+ \sum_{i=1}^N z_i \lambda^i \cdot \mathbb{L}_i \lambda^0 = \mathcal{M}(\lambda^0, \{z_i \lambda^i\})^T \cdot (\lambda^0, \{z_i \lambda^i\})^T \quad (80) \end{aligned}$$

which proves the positive definite character of  $\mathcal{M}$ .

We now turn to the symmetry of  $\mathcal{M}$ . Similarly to (74)-(75), for  $\tilde{\lambda}^0, \{\tilde{\lambda}^i\}_{1 \leq i \leq N} \in \mathbb{R}^d$ , we define  $\mathbf{v}^{\tilde{\lambda}}$  and  $\theta_j^{\tilde{\lambda}}$ . Multiplying the Stokes equation for  $\mathbf{v}^\lambda$  by  $\mathbf{v}^{\tilde{\lambda}}$  and the convection-diffusion equation for  $\theta_j^\lambda$  by  $\theta_j^{\tilde{\lambda}}$  (note the skew-symmetry of this computation), then adding the two variational formulations yields

$$\begin{aligned} & \int_{Y_F} \left( \nabla_y \mathbf{v}^\lambda \cdot \nabla_y \mathbf{v}^{\tilde{\lambda}} + \sum_{j=1}^N \frac{z_j^2}{\operatorname{Pe}_j} n_j^0 \nabla_y \theta_j^\lambda \cdot \nabla_y \theta_j^{\tilde{\lambda}} \right) dy \\ &= \int_{Y_F} \lambda^0 \cdot \mathbf{v}^{\tilde{\lambda}} dy + \sum_{j=1}^N \int_{Y_F} z_j n_j^0 (\lambda^j \cdot \mathbf{v}^{\tilde{\lambda}} - \frac{z_j}{\operatorname{Pe}_j} \tilde{\lambda}^j \cdot \nabla_y \theta_j^{\tilde{\lambda}}) dy. \quad (81) \end{aligned}$$

Since (81) is symmetric in  $\lambda, \tilde{\lambda}$ , we deduce that

$$\begin{aligned} & \int_{Y_F} \lambda^0 \cdot \mathbf{v}^{\tilde{\lambda}} dy + \sum_{j=1}^N \int_{Y_F} z_j n_j^0 \left( \lambda^j \cdot \mathbf{v}^{\tilde{\lambda}} + \frac{z_j}{\operatorname{Pe}_j} \lambda^j \cdot \nabla_y \theta_j^{\tilde{\lambda}} \right) dy \\ &= \int_{Y_F} \tilde{\lambda}^0 \cdot \mathbf{v}^\lambda dy + \sum_{j=1}^N \int_{Y_F} z_j n_j^0 (\tilde{\lambda}^j \cdot \mathbf{v}^\lambda + \frac{z_j}{\operatorname{Pe}_j} \tilde{\lambda}^j \cdot \nabla_y \theta_j^\lambda) dy, \end{aligned}$$

which is equivalent to

$$\begin{aligned} & \lambda^0 \cdot \mathbb{K} \tilde{\lambda}^0 + \sum_{i=1}^N \lambda^0 \cdot \mathbb{J}_i \tilde{\lambda}^i + \sum_{j=1}^N z_j \lambda^j \cdot \left( \mathbb{L}_j \tilde{\lambda}^0 + \sum_{i=1}^N \mathbb{D}_{ji} \tilde{\lambda}^i \right) \\ &= \tilde{\lambda}^0 \cdot \mathbb{K} \lambda^0 + \sum_{i=1}^N \tilde{\lambda}^0 \cdot \mathbb{J}_i \lambda^i + \sum_{j=1}^N z_j \tilde{\lambda}^j \cdot \left( \mathbb{L}_j \lambda^0 + \sum_{i=1}^N \mathbb{D}_{ji} \lambda^i \right), \end{aligned}$$

or

$$\mathcal{M}(\tilde{\lambda}^0, \{z_i \tilde{\lambda}^i\})^T \cdot (\lambda^0, \{z_i \lambda^i\})^T = \mathcal{M}(\lambda^0, \{z_i \lambda^i\})^T \cdot (\tilde{\lambda}^0, \{z_i \tilde{\lambda}^i\})^T$$

from which we deduce the symmetry of  $\mathcal{M}$ .  $\square$

## V. STRONG CONVERGENCE AND CORRECTORS

Besides the standard convergences of the microscopic variables to the effective ones, we also prove the following convergences of the energies.

**Proposition 4.** *We have the following convergences in energy, for  $j = 1, \dots, N$ ,*

$$\begin{aligned} \lim_{\varepsilon \rightarrow 0} \varepsilon^2 \int_{\Omega^\varepsilon} |\nabla \mathbf{u}^\varepsilon|^2 dx &= \int_{\Omega \times Y_F} |\nabla_y \mathbf{u}^0(x, y)|^2 dy dx, \quad (82) \\ \lim_{\varepsilon \rightarrow 0} \int_{\Omega^\varepsilon} n_j^\varepsilon |\nabla \Phi_j^\varepsilon|^2 dx &= \int_{\Omega \times Y_F} n_j^0(y) |\nabla_x \Phi_j^0(x) + \\ &\quad \nabla_y \Phi_j^1(x, y)|^2 dx dy. \quad (83) \end{aligned}$$

*Proof.* The proof is standard (see Theorem 2.6 in<sup>28</sup>). We start from the energy equality corresponding to the variational equation (35):

$$\begin{aligned} \varepsilon^2 \int_{\Omega^\varepsilon} |\nabla \mathbf{u}^\varepsilon|^2 dx + \sum_{j=1}^N \frac{z_j^2}{\text{Pe}_j} \int_{\Omega^\varepsilon} n_j^\varepsilon |\nabla \Phi_j^\varepsilon|^2 dx &= \\ - \sum_{j=1}^N \frac{z_j^2}{\text{Pe}_j} \int_{\Omega^\varepsilon} n_j^\varepsilon \mathbf{E}^* \cdot \nabla \Phi_j^\varepsilon dx + \sum_{j=1}^N z_j \int_{\Omega^\varepsilon} n_j^\varepsilon \mathbf{E}^* \cdot \mathbf{u}^\varepsilon dx \\ - \int_{\Omega^\varepsilon} \mathbf{f}^* \cdot \mathbf{u}^\varepsilon dx. \quad (84) \end{aligned}$$

For the homogenized variational problem (56) the energy equality reads

$$\begin{aligned} \int_{\Omega \times Y_F} |\nabla_y \mathbf{u}^0|^2 dx dy + \sum_{j=1}^N \frac{z_j^2}{\text{Pe}_j} \int_{\Omega \times Y_F} n_j^0(y) |\nabla_x \Phi_j^0 + \\ \nabla_y \Phi_j^1|^2 dx dy = - \sum_{j=1}^N \frac{z_j^2}{\text{Pe}_j} \int_{\Omega \times Y_F} n_j^0(y) \mathbf{E}^* \cdot (\nabla_x \Phi_j^0 \\ + \nabla_y \Phi_j^1) dx dy + \sum_{j=1}^N z_j \int_{\Omega \times Y_F} n_j^0(y) \mathbf{E}^* \cdot \mathbf{u}^0 dx dy \\ - \int_{\Omega \times Y_F} \mathbf{f}^* \cdot \mathbf{u}^0 dx dy. \quad (85) \end{aligned}$$

In (84) we observe the convergence of the right hand side to the right hand side of (85). Next we use the lower semicontinuity of the left hand side with respect to the two-scale convergence and the equality (85) to conclude (82)-(83).  $\square$

**Theorem 2.** *The following strong two-scale convergences hold*

$$\lim_{\varepsilon \rightarrow 0} \int_{\Omega^\varepsilon} \left| \mathbf{u}^\varepsilon(x) - \mathbf{u}^0(x, \frac{x}{\varepsilon}) \right|^2 dx = 0 \quad (86)$$

and

$$\lim_{\varepsilon \rightarrow 0} \int_{\Omega^\varepsilon} \left| \nabla \left( \Phi_j^\varepsilon(x) - \Phi_j^0(x) - \varepsilon \Phi_j^1(x, \frac{x}{\varepsilon}) \right) \right|^2 dx = 0. \quad (87)$$

*Proof.* We first remark that the regularity of the solutions of the cell problems (58)-(61) and (62)-(65) implies that the functions  $\mathbf{u}^0(x, x/\varepsilon)$  and  $\Phi_j^1(x, x/\varepsilon)$  are measurable and well defined in  $H^1(\Omega)$ . We have

$$\begin{aligned} \int_{\Omega^\varepsilon} \varepsilon^2 |\nabla [\mathbf{u}^0(x, \frac{x}{\varepsilon})] - \nabla \mathbf{u}^\varepsilon(x)|^2 dx &= \int_{\Omega^\varepsilon} |[\nabla_y \mathbf{u}^0](x, \frac{x}{\varepsilon})|^2 dx \\ &\quad + \int_{\Omega^\varepsilon} \varepsilon^2 |\nabla \mathbf{u}^\varepsilon(x)|^2 dx - \\ &\quad 2 \int_{\Omega^\varepsilon} \varepsilon [\nabla_y \mathbf{u}^0](x, \frac{x}{\varepsilon}) \cdot \nabla \mathbf{u}^\varepsilon(x) dx + \mathcal{O}(\varepsilon). \quad (88) \end{aligned}$$

Using Proposition 4 for the second term in the right hand side of (88) and passing to the two-scale limit in the third term in the right hand side of (88), we deduce

$$\lim_{\varepsilon \rightarrow 0} \int_{\Omega^\varepsilon} \varepsilon^2 \left| \nabla \left( \mathbf{u}^\varepsilon(x) - \mathbf{u}^0(x, \frac{x}{\varepsilon}) \right) \right|^2 dx = 0$$

Using the scaled Poincaré inequality (38) in  $\Omega^\varepsilon$  (see the proof of Lemma 2) yields (86).

On the other hand, by virtue of Lemma 1,  $n_j^\varepsilon$  is uniformly positive, i.e., there exists a constant  $C > 0$ , which does not depend on  $\varepsilon$ , such that

$$\begin{aligned} \int_{\Omega^\varepsilon} \left| \nabla \left( \Phi_j^\varepsilon(x) - \Phi_j^0(x) - \varepsilon \Phi_j^1(x, \frac{x}{\varepsilon}) \right) \right|^2 dx &\leq C \\ \int_{\Omega^\varepsilon} n_j^\varepsilon \left| \nabla \left( \Phi_j^\varepsilon(x) - \Phi_j^0(x) - \varepsilon \Phi_j^1(x, \frac{x}{\varepsilon}) \right) \right|^2 dx &= 0. \quad (89) \end{aligned}$$

Developing the right hand side of (89) as we just did for the velocity and using the fact that  $n_j^\varepsilon(x) = n_j^0(x/\varepsilon)$  is a two-scale test function, we easily deduce (87).  $\square$

<sup>1</sup>Looker, J.R., Carnie S.L.: Homogenization of the ionic transport equations in periodic porous media. *Transp. Porous Media* **65** (2006), 107-131.

<sup>2</sup>Karniadakis G., Beskok A. and Aluru N.: *Microflows and Nanoflows. Fundamentals and Simulation. Interdisciplinary Applied Mathematics*, Vol. 29, Springer, New York, (2005).

<sup>3</sup>Edwards, D. A.: Charge transport through a spatially periodic porous medium: electrokinetic and convective dispersion phenomena, *Philos. Trans. R. Soc. Lond. A* **353** (1995), 205-242.

<sup>4</sup>Chan, D.Y. and Horn R.G.: The drainage of thin liquid films between solid surfaces, *J. Chem. Phys.* **83** (1985), 5311-5325.

<sup>5</sup>O'Brien, R. W. and White, L. R.: Electrophoretic mobility of a spherical colloidal particle, *J. Chem. Soc., Faraday Trans. 2* **74(2)** (1978), 1607-1626.

<sup>6</sup>Auriault, J. L. and Strzelecki, T.: On the electro-osmotic flow in a saturated porous medium, *Int. J. Engng Sci.* **19** (1981), 915-928.

<sup>7</sup>Adler, P. M. and Mityushev, V.: Effective medium approximation and exact formulae for electrokinetic phenomena in porous media, *J. Phys. A: Math. Gen.* **36** (2003), 391-404.

<sup>8</sup>Adler, P. M.: Macroscopic electroosmotic coupling coefficient in random porous media, *Math. Geol.* **33(1)** (2001), 63-93.

<sup>9</sup>Coelho, D., Shapiro, M., Thovert, J. F. and Adler, P. M.: Electro-osmotic phenomena in porous media, *J. Colloid Interface Sci.* **181** (1996), 169-90.

<sup>10</sup>Gupta, A.K., Coelho, D. and Adler, P.M.: Electroosmosis in porous solids for high zeta potentials, *Journal of Colloid and Interface Science* **303** (2006), 593-603.

- <sup>11</sup>Marino, S., Coelho, D., Békri, S. and Adler, P. M.: Electroosmotic phenomena in fractures, *J. Colloid Interface Sci.* **223** (2000), 292-304.
- <sup>12</sup>Marino, S., Shapiro, M. and Adler, P. M.: Coupled transports in heterogeneous media, *J. Colloid Interface Sci.* **243** (2001), 391-419.
- <sup>13</sup>Rosanne, M., Paszkuta, M. and Adler, P. M.: Electrokinetic phenomena in saturated compact clays, *Journal of Colloid and Interface Science*, **297** (2006), 353-364.
- <sup>14</sup>Moyne, C. and Murad, M.: Electro-chemo-mechanical couplings in swelling clays derived from a micro/macro-homogenization procedure, *Int. J. Solids Structures* **39** (2002), 6159-6190.
- <sup>15</sup>Moyne, C. and Murad, M.: Macroscopic behavior of swelling porous media derived from micromechanical analysis, *Transport Porous Media* **50** (2003), 127-151.
- <sup>16</sup>Moyne, C. and Murad, M.: A Two-scale model for coupled electro-chemomechanical phenomena and Onsager's reciprocity relations in expansive clays: I Homogenization analysis, *Transport Porous Media* **62** (2006), 333-380.
- <sup>17</sup>Moyne, C., Murad, M.: A two-scale model for coupled electro-chemo-mechanical phenomena and Onsager's reciprocity relations in expansive clays: II. Computational validation. *Transp. Porous Media* **63**(1) (2006), 13-56.
- <sup>18</sup>Moyne, C. and Murad, M.: A dual-porosity model for ionic solute transport in expansive clays, *Comput Geosci* **12** (2008), 47-82.
- <sup>19</sup>de Groot, S. R. and Mazur, P.: *Non-Equilibrium Thermodynamics*, North-Holland, Amsterdam, 1969.
- <sup>20</sup>Looker, J.R.: Semilinear elliptic Neumann problems and rapid growth in the nonlinearity. *Bull. Austral. Math. Soc.*, Vol. **74**, no.2, (2006), 161-175.
- <sup>21</sup>Acerbi, E., Chiadò Piat, V., Dal Maso, G. and Percivale D.: An extension theorem from connected sets, and homogenization in general periodic domains, *Nonlinear Anal.*, **18** (1992), 481-496.
- <sup>22</sup>Temam, R.: *Navier Stokes equations*, North Holland, Amsterdam (1977).
- <sup>23</sup>Lipton, R. and Avellaneda, M.: A Darcy Law for Slow Viscous Flow Past a Stationary Array of Bubbles, *Proc. Royal Soc. Edinburgh* **114A**, (1990), 71-79.
- <sup>24</sup>Sanchez-Palencia, E.: *Non-Homogeneous Media and Vibration Theory*, Lecture Notes in Physics 127, Springer Verlag, (1980).
- <sup>25</sup>Tartar, L.: *Convergence of the Homogenization Process*, *Appendix of  $\mathbb{R}^d$* .
- <sup>26</sup>Allaire, G.: Homogenization of the Stokes Flow in a Connected Porous Medium, *Asymptotic Analysis*, **2** (1989), 203-222.
- <sup>27</sup>Allaire, G.: One-Phase Newtonian Flow, in *Homogenization and Porous Media*, ed. U.Hornung, Springer, New-York, (1997), 45-68.
- <sup>28</sup>Allaire, G.: Homogenization and two-scale convergence, *SIAM J. Math. Anal.*, **23** (1992), 1482-1518.
- <sup>29</sup>Nguetseng, G.: A general convergence result for a functional related to the theory of homogenization, *SIAM J. Math. Anal.* **20**(3), 608-623 (1989).
- <sup>30</sup>Lions J.-L.: *Some methods in the mathematical analysis of systems and their controls*. Science Press, Beijing, Gordon and Breach, New York, (1981).
- <sup>31</sup>Allaire, G.: Homogenization of the unsteady Stokes equations in porous media, in "Progress in partial differential equations: calculus of variations, applications" Pitman Research Notes in Mathematics Series **267**, 109-123, C. Bandle et al. eds, Longman Higher Education, New York (1992).