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MODELING AND DERIVING POROUS MEDIA STOKES-POISSON-NERNST-PLANCK EQUATIONS BY A MULTI-SCALE APPROACH*

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Abstract. We formulate the basic equations modeling solid-electrolyte composites without surface reactions. From these equations we achieve by the two-scale convergence method homogenized Nernst-Planck-Poisson equations. Moreover, we extend the system by including Stokes flow. Again, the two-scale convergence allows the rigorous justification of the resulting homogenized and nonlinearly coupled overall system. So called "material tensors" naturally arise by the upscaling and replace the commonly used porosity parameter from engineering. The upscaled equations derived here capture more accurately porous structures by including the microscopic geometry in a systematic way. To the author's best knowledge, this seems to be the first approach which derives the Stokes-Poisson-Nernst-Planck system being governed by porous materials and hence serves as a basis for additional specifications in the future.

Key words. Two-scale convergence, Stokes-Poisson-Nernst-Planck equations, porous materials, Darcy's law, periodic homogenization.

AMS subject classifications. 35B27, 35K55, 35Q35, 35Q92, 76M50.

1. Introduction

The presence of electrolytes in porous structures is a highly interdisciplinary field and of general interest. An accurate mathematical description and reliable numerical approximations are the key to future optimization of systems which advantageously want to use the interplay of different scales. We mention some emerging applications for which the subsequent derivations are of importance.

Desalination: A process for desalting water can be based on periodic sorption and desorption of ions on the extensive surfaces of porous materials. It is the adsorption of the electrolyte here which is responsible for the desalting. For the principle ideas we refer to [22]. The reference [51] is a report on research conducted on Capacitive Deionization Technology (CDT) as an alternative to the more conventional membrane desalination technologies like reverse osmosis and electrodialysis. A process for the capacitive deionization of water with a stack of carbon aerogel electrodes is studied in [16]. Unlike ion exchange — one of the more conventional deionization processes — no chemicals are required for regeneration of the system studied in [16]. Electricity is used instead. The design and mathematical optimization of efficient desalination devices is an upcoming task and can be addressed by the new formulation subsequently derived.

Biological nanopores: The interaction of a cell with the extracellular environment through the membrane is important for the cell behavior and cellular function. The lipid bilayer of cell membranes constitutes a barrier to the passage of charged and polar molecules [41]. The channel proteins, which form narrow hydrophilic pores, primarily allow for the passage of small inorganic ions. The opening and closing of ion channels characteristically depend on the membrane voltage or the binding of selective ligand molecules [19]. Synthetic nanochannels have been fabricated to mimic real biological

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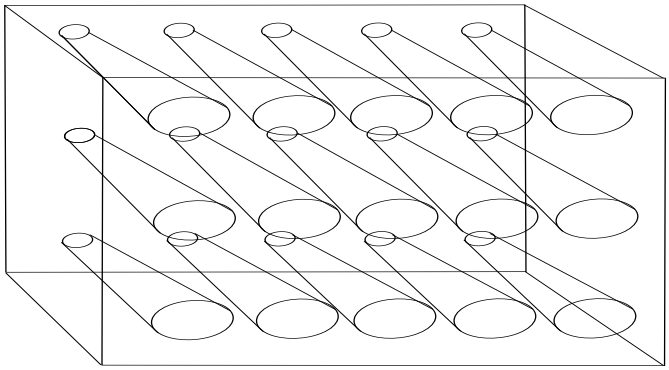

FIG. 1.1. **Array of synthetic nanochannels:** *Optimization of the channel shape allows to mimic real biological nanopores and ion channels.*

nanopores and ion channels [49]. The production techniques and the application of single nanochannels in polymer films with lengths of micrometers and diameter sizes on the nanoscale is presently attracting widespread interest [48]. A recent intriguing finding was that conically shaped nanopores can be put to work as promising sensing elements for small molecules, DNAs, proteins, and yet other substances [26]. An analytical solution of a one-dimensional reduction of a Poisson-Nernst-Planck model for such conical nanopores is considered in [23]. A challenge is the investigation of the influence of an externally applied voltage on different polarity for rectification, being induced by the asymmetry of the nanopore; see Figure 1.1.

Supercapacitors, fuel cells, and batteries: Porous materials are very interesting for energy storage applications [24, 35] because of their large interfacial areas. The Poisson-Nernst-Planck equations are also of interest for fuel cell applications, where for example analytical solutions of Poisson-Boltzmann equations in cylindrical pores are studied [7]. A basic reference on mathematical modeling of electrochemical systems is [34]. In [25], composite electrodes for electrochemical supercapacitors were fabricated by impregnation of the manganese dioxide nanofibers and multiwalled carbon nanotubes (MWCNT) into porous Ni plaque current collectors. A new wave of interest in the application of porous Ni materials is related to the development of electrochemical supercapacitors (ES). ES can complement or replace batteries in electrical energy storage applications when highpower delivery is required. The discovery that ion desolvation occurs in pores smaller than the solvated ions has led to higher capacitance for electrochemical double layer capacitors using carbon electrodes with subnanometer pores, and opened the door to designing high-energy density devices using a variety of electrodes. The Figure 1.2 illustrates the basic principles of a supercapacitor.

Mathematical modeling and simulation will be the key to success in designing tomorrow's high energy and high power devices [46]. Hence, we briefly motivate by an example of carbon aerogel (CA) electrodes the applied nature of the results in this article:

First, we remark that the subsequently achieved results are not restricted to polyaniline (PANI)/CA composite electrode materials. These PANI/CA composites show much better electrochemical performance, high reversibility, and high charge/discharge properties than CA. Via Scanning Microscope Images (SEM) of such materials (see Figure 1.3), the heuristic Y-Algorithm introduced in Section 3

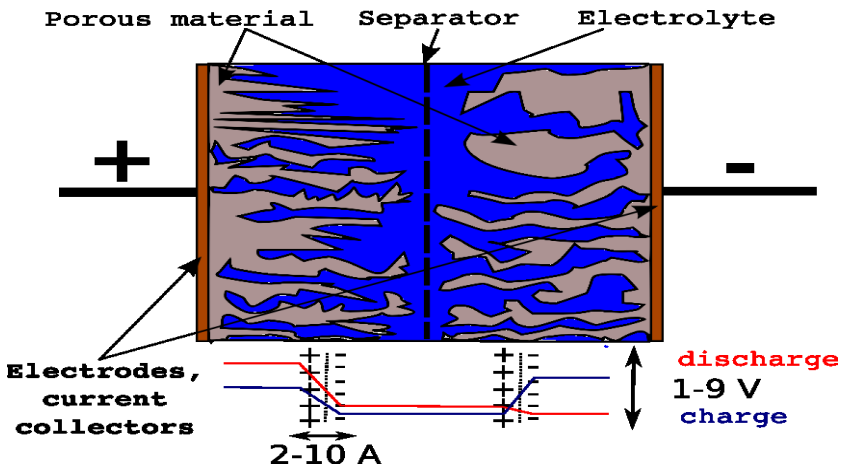

FIG. 1.2. *Supercapacitor as an electrical double-layer capacitor whose electrodes comprise a porous material. The solid porous material in contact with current collectors is permeated with a liquid or solid electrolyte. An electrolyte-permeable separator prevents shorting of the electrodes.*

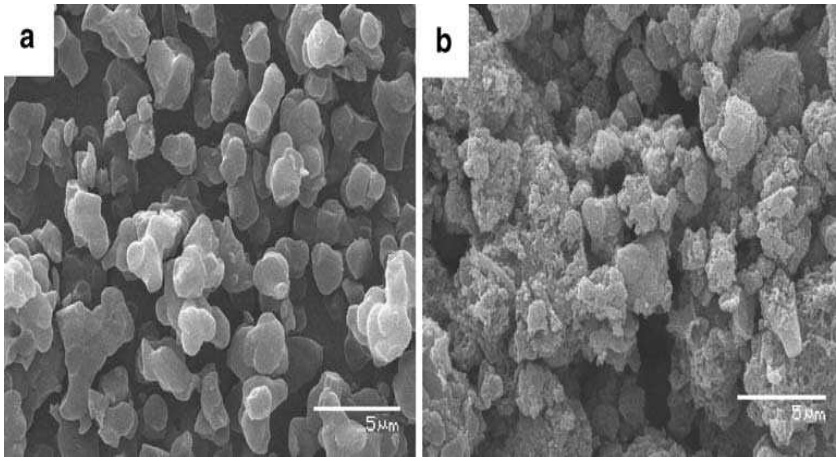

FIG. 1.3. **a)** *SEM of carbon aerogel (CA).* **b)** *SEM of polyaniline (PANI)/ carbon aerogel (CA) composite electrode. Further details can be found in [6].*

allows to compute a periodic reference cell Y. The idea of this cell is motivated in Figure 1.5. The knowledge of the cell Y together with the main Theorem 3.1 defines the Poisson-Nernst-Planck system (or the subsequently stated systems (1.1) and (1.2)-(1.4)) governed by the material microstructure. Such a new formulation allows to systematically account for the pore geometry which determines relevant transport processes in solid-electrolyte composites.

Semiconductors: The Nernst-Planck-Poisson equations serve also as a versatile model to describe the movement of holes and electrons in semiconductors. For a general consideration of semiconductor equations we refer to [27] and [28]. An analytical approach concerning fixed point maps to decouple the nonlinear system is considered in [21]. By the developments of aberration correctors for scanning transmission electron microscopes, the sensitivity to detect and localize single impurity atoms has been greatly improved; see [8]. Today, electron probes with diameters well below 1 $\mathring{A}$ are

available thanks to the improved electron optics. Since a distribution of single dopant or impurity atoms can dramatically alter the properties of semiconductor materials, the porous media Poisson-Nernst-Planck equations could help to improve the design by taking into account such impurities.

The difference in the above applications is mainly induced by boundary conditions. Therefore, the subsequent derivations consider general boundary conditions such that the resulting formulation serves as a basis in the above applications: That means no-flux boundary conditions at the solid-liquid interface for concentrations and continuity conditions for the electric potential at this interface as described in detail in Section 1.2.

First, let us summarize the main results. The Poisson-Nernst-Planck equations, which describe electrolytes in porous materials, have the form

$$\begin{aligned} \theta_2 \partial_t n^+ &= \operatorname{div}\left(\mathbb{S}^0_{11}\nabla n^+ + n^- \mathbb{S}^0_{13}\nabla\phi\right), \\ \theta_2 \partial_t n^- &= \operatorname{div}\left(\mathbb{S}^0_{22}\nabla n^- - n^+ \mathbb{S}^0_{23}\nabla\phi\right), \\ -\operatorname{div}\left(\mathbb{S}^0_{33}(\lambda^2,\alpha)\nabla\phi\right) &= \theta_2\left(n^+ - n^-\right), \end{aligned} \tag{1.1}$$

where the material tensors $\mathbb{S}^0_{ij} \in \mathbb{R}^{N\times N}$ are defined in (3.15). The choice of the subindices arises from the inherent structure of the Poisson-Nernst-Planck system and is advantageously used in Section 1.2. λ is the dimensionless Debye length and α a dimensionless dielectric permittivity. We refer the reader who is not interested in the rigorous derivation of the porous media Stokes-Poisson-Nernst-Planck equations directly to Section 3.1. A more compact representation of the results can be found in Section 3, where also a heuristic Y-Algorithm is introduced. This algorithm allows to determine the reference cell from the microscopic information (as scanning microscope images) of the porous material; see Figure 1.3 for an example. Over such a reference cell Y, the effective material tensors $\mathbb{S}^0_{ij} \in \mathbb{R}^{N\times N}$ are defined.

For the sake of completeness, we also state the extension of (1.1) to the Stokes-Poisson-Nernst-Planck system here. We apply Einstein's summation convention for repeated indices. The Stokes equations transform to well-known Darcy's law in porous structures, i.e.

$$\begin{aligned} \mathrm{v}^k &= \mathrm{k}_{kl}\left(\mathrm{f}^{0,k}_l - \partial_{x_l} p\right), \qquad 1 \le k,l \le N, \\ \operatorname{div}\overline{\mathrm{v}} &= 0. \end{aligned} \tag{1.2}$$

However, the Coulomb force in (1.2) is corrected to $\mathrm{f}^{0,k}_l := -\eta\theta_2\partial_{x_l}\phi\left((n^+ - n^-)\left(1 + \frac{\delta_{kl}}{Y_2}\int_{Y_2}\partial_{y_l}\xi^k_\phi\, dy\right)\right)$, where $\xi^k_\phi := \xi^{44_k}$ is defined by (3.22), η is another dimensionless parameter defined after Equation (1.13), and v^k is the fluid velocity in the porous material characterized by the matrix k_{kl}, i.e.

$$\mathrm{k}_{kl} := \frac{1}{|Y|}\int_{Y_2} \mathrm{w}^k_l\, dy, \tag{1.3}$$

where w^k_l is solution of the reference cell problem (2.16). Finally, we extend the system (1.1) by convective terms to

$$\begin{aligned} \theta_2 \partial_t n^+ &= \operatorname{div}\left(\mathbb{S}^0_{22}(n^+,\overline{\mathrm{v}})\nabla n^+ + n^- \mathbb{S}^0_{24}(n^+,n^-,\overline{\mathrm{v}})\nabla\phi - Pe\,\overline{\mathrm{v}} n^+\right), \\ \theta_2 \partial_t n^- &= \operatorname{div}\left(\mathbb{S}^0_{33}(n^-,\overline{\mathrm{v}})\nabla n^- - n^+ \mathbb{S}^0_{34}(n^+,n^-,\overline{\mathrm{v}})\nabla\phi - Pe\,\overline{\mathrm{v}} n^-\right), \\ -\operatorname{div}\left(\mathbb{S}^0_{44}(\lambda^2,\alpha)\nabla\phi\right) &= \theta_2\left(n^+ - n^-\right), \end{aligned} \tag{1.4}$$

where the tensors $\mathbb{S}^0_{ij}$ are defined in (3.15) and shifted as in Theorem 3.3. Pe is the non-dimensional Péclet number.

The derivation of the effective Stokes-Nernst-Planck-Poisson equations for porous materials bases on the two-scale convergence method [2, 36] for periodic media and a priori estimates derived in [45]. For further details, we refer to Section 3. Next to the applications motivated at the beginning, such a result is also of great numerical interest. In order to accurately resolve the microgeometry, the space discretization usually needs to be much smaller than the microscopic length scale. This leads to numerical problems with a large number of degrees of freedom. The upscaled system derived here prevents such computationally demanding tasks.

In electrochemistry, merely reduced models have been studied so far and the porous structure is described by a porosity parameter only capturing one-dimensional characteristics of pores [35, 15]. In the context of upscaling approaches, formal two-scale expansions for the reduced Poisson-Boltzmann equations or linear formulations regarding Onsager's reciprocity relations have so far been studied to describe electrolytes [4, 30, 32, 37]. Besides these major achievements, the present article seems to be the first approach which rigorously derives upscaled Stokes-Nernst-Planck-Poisson equations for highly heterogeneous structures.

The simple representations (1.1), and (1.2)-(1.4) are motivated in Section 3.1. Unfortunately, analytical solutions for the unknown variables ξ^k_ι for $\iota = n^+, n^-, \phi$ defining the material tensors $\mathbb{S}^0_{ij} \in \mathbb{R}^{N\times N}$ are only available in very symmetric and simplified geometries; see [3, 5]. Moreover, the nonlinear and coupled structure of the porous media correction tensors in (1.4) immediately suggests that we apply efficient numerical strategies to compute $\mathbb{S}^0_{ij}$.

The porous media approximations (1.1)-(1.4) play a relevant role for improving the physical understanding of the influence of the micro-geometry to the macroscopic transport properties. For example, the derived equations allow to refine the relation between tortuosity and the effective coefficients $\mathbb{S}^0_{ij}$. However, the tortuosity is still not consistently defined [13, 47] and of actual interest [29]. The simplest and most intuitive method to estimate the tortuosity τ is the ratio of the length L of the real diffusion path to the shortest distance of its end points Λ, i.e. $\tau := L/\Lambda$.

Another topic of great physical interest are diffusion-dispersion relations. These relations aim to provide so-called effective diffusion tensors for porous materials based on the molecular diffusion constant and a known flow field. Hence, the difference to the tortuosity is that diffusion-dispersion relations also account for fluid flow. The important physical information, which is gained by the derived system (1.4), is that in the Poisson-Nernst-Planck equations the so-called electromigration-dispersion tensors $\mathbb{S}^0_{24}$ and $\mathbb{S}^0_{34}$ also appear. In other words, the effective electrical mobility of the ions is also affected by fluid flow. Finally, we point out that the porous media derivation (1.4) shows a much stronger nonlinear structure than the classical Poisson-Nernst-Planck Equation (1.6).

The article is organized in the following way: In the next Section 1.1, the classical Poisson-Nernst-Planck equations are recalled. We introduce the general framework which allows to derive from the "classical" Poisson-Nernst-Planck equations the corresponding porous media version in Section 1.2. Notation and definitions follow in Section 2. The main results are then given in Section 3. An intuitive representation and simplification of the results is presented in Section 3.1. The homogenized Poisson-Nernst-Planck equations are derived in Section 4 and the extension including Stokes equations is presented in Section 5.

1.1. The "classical" Poisson-Nernst-Planck equations (PNP). The main goal of this article is the derivation of "porous media" Nernst-Planck-Poisson equations (pmPNP); see Section 1.2. In a final step, we include fluid flow for small fluid velocities, i.e. Stokes flow. Before that, we recall the classical Nernst-Planck-Poisson equations (PNP) [10, 19, 34, 40, 43].

The Debye screening length

$$\lambda_D := \left(\frac{\epsilon_f kT}{2e^2\overline{n}}\right)^{\frac{1}{2}} \tag{1.5}$$

is the characteristic parameter which essentially influences the physical behavior. With ϵ_f we denote the dielectric constant of the electrolyte and $\overline{n}$ is a suitable reference salt concentration. The dimensionless number λ is the quotient $\lambda := \frac{\lambda_D}{\ell}$ where ℓ is a suitable length scale of the considered system. Further, the electrostatic potential ϕ is the reduced variable $\phi := \frac{e\Phi}{kT}$. The mobility coefficients are related to the diffusion coefficients via the Einstein relation $D_{kl} = kTM_{kl}$. With our choice of energy scale, this dimensionless Einstein relation reduces to $D_{kl} = M_{kl}$. We shall neglect fluid flow in this section and assume that all the ions have the same diffusion constant for simplicity. The spatial coordinates become dimensionless with the macroscopic length scale ℓ. Further, we scale the time by the diffusion time scale $\tau_D := \frac{\ell^2}{D}$. In these units, the thickness of the boundary layer over which the concentration of positive and negative ions $n^\pm$ varies rapidly is $O(\lambda)$. For a binary symmetric electrolyte, i.e. for ionic valences $z_+ = -z_- = 1$, and for isotropic diffusion coefficents $D\delta_{kl} = D_{kl}$, where δ_{kl} is the Kronecker delta function, the dimensionless Poisson-Nernst-Planck equations read

$$\begin{aligned} \partial_t n^\pm &= \operatorname{div}\left(\nabla n^\pm \pm n^\pm \nabla\phi\right), \\ -\lambda^2\Delta\phi &= n^+ - n^-. \end{aligned} \tag{1.6}$$

Often, one defines dimensionless salt and charge concentrations via

$$c := \frac{n^+ + n^-}{2\overline{n}}, \qquad \rho := \frac{n^+ - n^-}{2\overline{n}}, \tag{1.7}$$

where $\overline{n}$ is the average concentration of neutral salt. The Poisson-Nernst-Planck system (1.6) with respect to the physical quantities (1.7) then becomes

$$\begin{aligned} \partial_t \rho &= \operatorname{div}(\nabla\rho + c\nabla\phi), \\ \partial_t c &= \operatorname{div}(\nabla c + \rho\nabla\phi), \\ -\lambda^2\Delta\phi &= \rho. \end{aligned} \tag{1.8}$$

However, we remark that for the upscaling performed in this article, the recommended starting point is system (1.6). The reason is that the charge density ρ can become negative and admits zero on a very general set. This causes major difficulties for the homogenization of (1.8), i.e., in the resulting reference cell problems; see (3.20) and (3.21).

1.2. The porous media Poisson-Nernst-Planck formulation (pmPNP). We study solid-electrolyte composites without Faradaic reactions where either the solid phase represents a high density of heterogeneities or vice versa. The mathematical approach subsequently applied is general enough that the interface between

the solid and the liquid phase may admit arbitrary shapes. The only restriction on this interface is Lipschitz continuity and that it "essentially" touches the boundary, i.e. except on a set of measure zero. Otherwise, specific measure theoretic tools are required to verify the upscaled limit problem. Since this is only relevant in special applications, we keep this "formidable" task as a future goal. An Y-Algorithm is introduced in Section 3. It enables to compute a valid *periodic replacement* (see Definition 2.1) which statistically represents the microstructure. To improve the quality of the approximation, a relative small variance in the shape of the different particles and a high number of reference samples is recommended. The data for the Y-Algorithm can be obtained by Scanning Electron Microscope (SEM) images. In order to improve the porous media approximation, we assume that the heterogeneities are evenly distributed in the material. These are known to be realistic assumptions for a large class of applications even before the use of the Y-Algorithm.

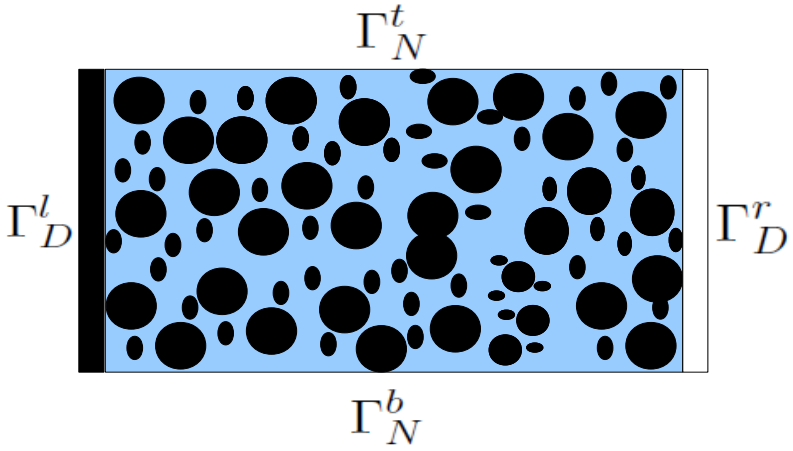

FIG. 1.4. *A porous material, i.e. a solid-electrolyte composite, in the domain* $\Omega=\Omega^s\cup B^s$, *where* Ω^s *is the liquid phase (blue part) and* B^s *the solid phase (black part).* $\Gamma^D:=\Gamma^l\cup\Gamma^r$ *denotes the Dirichlet boundary and* $\Gamma^N:=\Gamma^t\cup\Gamma^b$ *the Neumann boundary, which is also set on the solid-electrolyte interphase* $\partial\Omega^s\setminus\{\Gamma^D\cup\Gamma^N\}$.

A binary symmetric electrolyte occupying a domain Ω for Dirichlet and Neumann boundary conditions, as for example imposed in Figure 1.4, is commonly described by the Nernst-Planck-Poisson system (1.6) and is here advantageously written in the following compact form

$$\begin{aligned}
\mathbf{D}_t\mathbf{u}-\boldsymbol{\Delta}_{\mathbb{S}}\mathbf{u}&=\mathbf{I}(\mathbf{u}), && \text{for } (\mathbf{t},\mathbf{x})\in\boldsymbol{\Omega}_T:=[\Omega_T,\Omega_T,\Omega_T]',\\
\mathbf{u}(0,x)&=\mathbf{h}, && \text{in } \boldsymbol{\Omega}:=[\Omega,\Omega,\Omega]',\\
\mathbf{u}&=\mathbf{g}_l, && \text{on } \boldsymbol{\Gamma}_T^l:=[\Gamma_T^l,\Gamma_T^l,\Gamma_T^l]',\\
\mathbf{u}&=\mathbf{g}_r, && \text{on } \boldsymbol{\Gamma}_T^r:=[\Gamma_T^l,\Gamma_T^l,\Gamma_T^l]',\\
(\mathbb{S}(\mathbf{u})\boldsymbol{\nabla}_{\mathbf{n}}\mathbf{u})^i:=s_{ij}(\mathbf{u})\nabla_n^j\mathrm{u}^j&=0, && \text{on } \boldsymbol{\Gamma}_T^N:=\partial\boldsymbol{\Omega}_T\setminus\boldsymbol{\Gamma}_T^D, \qquad \text{for } i=1,2,3,
\end{aligned} \tag{1.9}$$

where $\mathbf{x}:=[x,x,x]'$ with $x\in\Omega\subset\mathbb{R}^N$ corresponds to the coordinate field for each component of the field vector $\mathbf{u}$ and $\mathbf{t}:=[t,t,t]'$ with $t\in]0,T[$ for any $T\in\mathbb{R}_+$ is the accordingly defined time field. We further use the convention $\Omega_T:=]0,T[\times\Omega$. The notation $\boldsymbol{\Omega}_T$ is necessary, since the components of the field vector $\mathbf{u}$ are defined on different domains Ω in the porous media setting later on, i.e. either on the whole domain Ω

or only on the electrolyte phase Ω^s. We further denote $\mathbf{\Delta}_{\mathbb{S}}\mathbf{u} := \mathbf{div}\,(\mathbb{S}(\mathbf{u})\mathbf{\nabla}\mathbf{u})$ with $\mathbb{S}(\mathbf{u}) := \{s_{i_k j_l}(\mathbf{u})\}_{\substack{1\le i,j\le d \\ 1\le k,l\le N}}$ for $1\le i,j\le 3$, $1\le k,l\le N$, and $s_{i_k j_l}(\mathbf{u}) = s_{ij}(\mathbf{u})\delta_{kl}$ with δ_{kl} the Kronecker symbol, $\nabla_n := \overline{\mathrm{n}}\cdot\nabla$ with $\overline{\mathrm{n}}$ the normal vector pointing outward of Ω, $\mathbf{\Gamma}_T^D := [\Gamma_T^D, \Gamma_T^D, \Gamma_T^D]'$ with $\Gamma_T^D := \Gamma_T^l \cup \Gamma_T^r$ and $\mathbf{\Gamma}_T^N$, $\mathbf{\Gamma}_T^\iota$ for $\iota = r,l$ are correspondingly defined, and

$$\mathbf{D_t} := \begin{bmatrix} \partial_t & 0 & 0 \\ 0 & \partial_t & 0 \\ 0 & 0 & 0 \end{bmatrix}, \qquad \{s_{ij}(\mathbf{u})\}_{1\le i,j\le 3} := \begin{bmatrix} 1 & 0 & n^- \\ 0 & 1 & -n^+ \\ 0 & 0 & \lambda^2 \end{bmatrix}, \qquad \mathbf{\nabla} := \mathbb{I}\nabla := \begin{bmatrix} \nabla & 0 & 0 \\ 0 & \nabla & 0 \\ 0 & 0 & \nabla \end{bmatrix},$$
$$\mathbf{div} := \mathbb{I}\mathrm{div} := \begin{bmatrix} \mathrm{div} & 0 & 0 \\ 0 & \mathrm{div} & 0 \\ 0 & 0 & \mathrm{div} \end{bmatrix}, \qquad \mathbf{u} := [n^+, n^-, \Phi]', \qquad \mathbf{I}(\mathbf{u}) := [0, 0, n^+ - n^-]',$$
$$\mathbf{g}_l := [n_l^+, n_l^-, \phi_l]', \qquad \mathbf{g}_r := [n_r^+, n_r^-, \phi_r]', \qquad \mathbf{h} := [\mathrm{h}^1, \mathrm{h}^2, 0]'. \tag{1.10}$$

Hence, $\mathbf{\nabla_n}$ is the canonical extension of ∇_n to field vectors. We call the tensor $\mathbb{S}(\mathbf{u}) := \{s_{ij}(\mathbf{u})\}_{1\le i,j\le 3}$, used in (1.9) and defined in (1.10), the *material tensor*. One recognizes that we use isotropic diffusion constants for the ions $n^\pm$ for simplicity. But the extension to the anisotropic case is straightforward. The compact notation in (1.9) provides the convenient setting to derive the effective/averaged material tensor $\mathbb{S}^0$ for general solid-electrolyte composites. It prevents the reader from getting lost by repeating every single technical step in the upscaling procedure for each field component. The applied notation is also useful for implementational aspects by using block matrices which are a new feature in Alberta 3.0 [44]. The dimensionless classical Nernst-Planck-Poisson formulation and a corresponding formal asymptotic analysis can be found for example in [10]. For an overview of electrohydrodynamics/electrodiffusion, we refer to the books [14, 43].

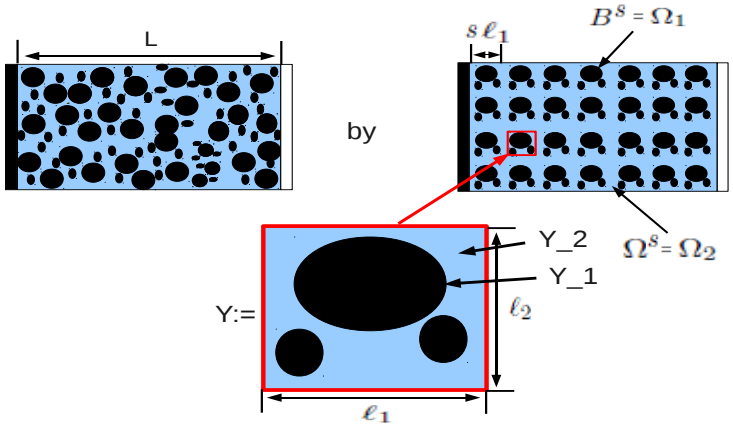

FIG. 1.5. **Top left:** *General porous material on the domain* Ω. **Top right:** *Periodic replacement by a reference cell* Y *capturing the material property by statistical evaluation of the two-phase material as for example by the Y-Algorithm, see Section 3.* **Bottom:** *Reference cell* Y *representing the microscale.*

Our main interest is the macroscopic behavior of a composite material occupying a domain Ω as depicted in Figure 1.4. Suppose that the heterogeneities, i.e. the size of the reference cell Y (see Figure 1.5), are very small with respect to the size of Ω

and that they are evenly distributed. This is a realistic assumption for a large class of applications. From a mathematical point of view, one can model this distribution by supposing that it is a periodic one. In fact, to reduce the approximation error, we suggest to first compute the averaged pore structure of a suitable periodic replacement, see the Y-Algorithm in Section 3. The periodicity can be represented by a small parameter s and hence we replace Ω_2 by Ω^s and Ω_1 by $B^s := \Omega \setminus \Omega^s$ respectively. We assume that the solid domain B^s is a smooth connected open set in $\Omega \subset \mathbb{R}^N$. But we conjecture that the connectedness can be neglected and therefore we consider also more general situations as for example in the Figures 1.4 and 1.5. Let the intersection $I := \partial\Omega^s \cap \partial B^s$ be a smooth interface. Further, we suppose that we are given a reference period Y, in which the reference heterogeneities are defined, see Figure 1.5. The heterogeneities in Ω are periodic of period sY and their size is of order s. The components $\mathrm{u}^1 (= n^+$ in $\Omega^s)$ and $\mathrm{u}^2 (= n^-$ in $\Omega^s)$ have to be solved only in the domain of the liquid phase which is the perforated domain $\Omega^s = \Omega \setminus B^s$ and are extended by zero in B^s. The two-scale convergence method prevents the use of any sophistitcated extensions (apart from the trivial extension by zero in B^s); see [2]. As a consequence, the material tensor $\mathbb{S}$ from $(1.9)_2$ depends now on s, i.e.

$$\left\{ s^s_{i_k j_l}(\mathbf{x}, \mathbf{u}_s) \right\}_{1 \le i,j \le 3} := \begin{bmatrix} 1 & 0 & n_s^- \\ 0 & 1 & -n_s^+ \\ 0 & 0 & \kappa(x/s) \end{bmatrix} \delta_{kl}, \quad \text{for } 1 \le k,l \le N, \tag{1.11}$$

where $\kappa(x) := \lambda^2 \chi_{\Omega^s}(x) + \alpha \chi_{B^s}(x)$ with λ the dimensionless Debye length $\frac{\lambda_D}{\ell}$ (see (1.5)) of the Nernst-Planck-Poisson system (1.6) and ℓ is the characteristic length of the system, $\alpha = \frac{\epsilon_m}{\epsilon_f}$ is the dimensionless dielectric permittivity where ϵ_m and ϵ_f are the dielectric permittivities of the solid phase and liquid phase respectively. Hence, the problem (1.9) reads now in the periodic setting as follows

$$\begin{aligned}
\mathbf{D}_t \mathbf{u}_s - \mathbf{div}\,(\mathbb{S}^s(\mathbf{u}_s)\boldsymbol{\nabla}\mathbf{u}_s) &= \mathbf{I}(\mathbf{u}_s), && \text{in } \boldsymbol{\Omega}^s_T := [\Omega^s_T, \Omega^s_T, \Omega_T]', \\
\mathbf{u}_s(0,x) &= \mathbf{h}_s, && \text{in } \boldsymbol{\Omega}^s := [\Omega^s, \Omega^s, \Omega]', \\
\mathbb{S}^s(\mathbf{u}_s)\boldsymbol{\nabla}_{\mathbf{n}}\mathbf{u}_s &= \mathbf{0}, && \text{on } \boldsymbol{\Gamma}^N_T, \\
\mathbf{u}_s &= \mathbf{g}_\iota, && \text{on } \boldsymbol{\Gamma}^\iota_T, \qquad \iota = l, r, \\
(\mathbb{S}^s(\mathbf{u}_s)\boldsymbol{\nabla}_{\mathbf{n}}\mathbf{u}_s)\mathbf{f}_i &= 0, && \text{on } \partial\Omega^s_T \setminus \left\{ \Gamma^D_T \cup \Gamma^N_T \right\}, \quad \text{for } i = 1,2, \\
(\mathbb{S}^s(\mathbf{u}_s)\boldsymbol{\nabla}_{\mathbf{n}}\mathbf{u}_s)\mathbf{f}_3\big|_{\Omega^s_T} &= (\mathbb{S}^s(\mathbf{u}_s)\boldsymbol{\nabla}_{\mathbf{n}}\mathbf{u}_s)\mathbf{f}_3\big|_{B^s_T}, && \text{on } \partial\Omega^s_T \setminus \left\{ \Gamma^D_T \cup \Gamma^N_T \right\}, \\
\mathrm{u}^3_s\big|_{\Omega^s_T} &= \mathrm{u}^3_s\big|_{B^s_T}, && \text{on } \partial\Omega^s_T \setminus \left\{ \Gamma^D_T \cup \Gamma^N_T \right\},
\end{aligned} \tag{1.12}$$

where $\mathbf{f}_i := [\delta_{i1}, \delta_{i2}, \delta_{i3}]'$ for $i = 1,2,3$ and the Kronecker delta δ_{ij}. From (1.12) it follows that the flux with respect to $\mathbf{u}$ is in general not differentiable. This motivates to study (1.12) in the sense of weak solutions. Moreover, the main difficulty and difference of this work to many other articles about homogenization is the nonlinear structure which prevents the material tensor $\mathbb{S}^s(\mathbf{u}_s)$ to be a strongly elliptic operator. This is the main reason why we apply the two-scale convergence [2, 36] and restrict ourselves to the periodic case instead of using the H-convergence [33, 38] which allows to handle non-periodic situations.

Finally, we extend the Nernst-Planck-Poisson system (1.12) by including fluid flow for small velocities and/or small length scales. Since this implies a small Reynolds number, i.e. $Re := \frac{\rho_f \ell V}{\mu} \to 0$ for $V \to 0$ and/or $\ell \to 0$, a viscous incompressible fluid

can then be described by the quasi-stationary Stokes equations

$$\begin{aligned} -\Delta \overline{\mathrm{v}}_s + \nabla p_s &= -\eta \left(n_s^+ - n_s^-\right) \nabla \phi_s, && \text{in } \Omega_T, \\ \operatorname{div} \overline{\mathrm{v}}_s &= 0, && \text{in } \Omega_T, \\ \overline{\mathrm{v}}_s &= \overline{0}, && \text{on } \partial\Omega_T^s \setminus \Gamma_T^D, \end{aligned} \tag{1.13}$$

where $\overline{\mathrm{v}}_s$ is the dimensionless solution $\overline{\mathrm{v}}_s := \frac{\overline{v}_s}{V}$ of (1.13) with respect to Ω^s is extended by zero in $B^s = \Omega \setminus \Omega^s$. The dimensionless paramter $\eta := \frac{2\overline{n}kT\ell}{V\mu}$, which can be called "Coulomb intensity" or "electro-osmotic Péclet number", consists of the mean fluid velocity V, the dynamic viscosity μ and the average concentration of neutral salt $\overline{n}$. Instead of using a dimensionless Reynolds number for the Stokes equations, i.e. $Re_{St} := \frac{\rho_f V \ell}{\mu}$, we define a dimensionless pressure $p_s := \frac{\tilde{p}_s \ell}{V\mu}$. This pressure p_s is also an appropriate extension such that the pair $(\overline{\mathrm{v}}_s, p_s)$ solves (1.13). By coupling (1.13) with the periodic formulation of the Poisson-Nernst-Planck Equation (1.12), we need the dimensionless Péclet number $Pe := \frac{\ell V}{D}$. Then, the Nernst-Planck-Poisson system (1.12) has to be complemented by a convective term and corresponding boundary conditions in the following way:

$$\begin{aligned} \mathbf{D}_t \mathbf{u}_s - \mathbf{div}\left(\mathbb{S}^s(\mathbf{u}_s)\boldsymbol{\nabla}\mathbf{u}_s - \mathbf{b}^s(\mathbf{u}_s)\mathbf{u}_s\right) &= \mathbf{I}(\mathbf{u}_s), && \text{in } \boldsymbol{\Omega}_T^s, \quad \operatorname{div}\overline{\mathrm{u}}_s^1 = 0, \quad \text{in } \Omega_T, \\ \mathbf{u}_s(0,x) &= \mathbf{h}_s, && \text{in } \boldsymbol{\Omega}^s, \\ \mathbb{S}^s(\mathbf{u}_s)\boldsymbol{\nabla}_{\mathbf{n}}\mathbf{u}_s &= \mathbf{0}, && \text{on } \boldsymbol{\Gamma}_T^N, \\ \\ \mathbf{u}_s &= \mathbf{g}_\iota, && \text{on } \boldsymbol{\Gamma}_T^\iota, \quad \iota = l,r, \\ \overline{\mathrm{u}}_s^1 &= \overline{0}, && \text{on } \partial\Omega_T^s \setminus \Gamma_T^D, \\ (\mathbb{S}^s(\mathbf{u}_s)\boldsymbol{\nabla}_{\mathbf{n}}\mathbf{u}_s)\mathbf{f}_i &= 0, && \text{on } \partial\Omega_T^s \setminus \left\{\Gamma_T^D \cup \Gamma_T^N\right\}, \quad \text{for } i = 2,3, \\ (\mathbb{S}^s(\mathbf{u}_s)\boldsymbol{\nabla}_{\mathbf{n}}\mathbf{u}_s)\mathbf{f}_4\big|_{\Omega^s} &= (\mathbb{S}^s(\mathbf{u}_s)\boldsymbol{\nabla}_{\mathbf{n}}\mathbf{u}_s)\mathbf{f}_4\big|_{B^s}, && \text{on } \partial\Omega_T \setminus \left\{\Gamma_T^D \cup \Gamma_T^N\right\}, \\ \mathrm{u}_s^4\big|_{\Omega^s} &= \mathrm{u}_s^4\big|_{B^s}, && \text{on } \partial\Omega_T \setminus \left\{\Gamma_T^D \cup \Gamma_T^N\right\}, \end{aligned} \tag{1.14}$$

where $\mathbf{u}_s := [\overline{\mathrm{v}}_s, n_s^+, n_s^-, \Phi_s]'$, $\mathbf{b}^s(\mathbf{u}_s) := Pe\,[\overline{0}, \overline{\mathrm{u}}_s^1, \overline{\mathrm{u}}_s^1, \overline{0}]'$,
$\mathbf{I}(\mathbf{u}_s) := \left[-\nabla p_s - \eta \mathrm{u}_s^2 \nabla \mathrm{u}_s^4, 0, 0, \mathrm{u}_s^2 - \mathrm{u}_s^3\right]'$, $\mathbf{h}_s := \left[\overline{0}, \mathrm{h}_s^2, \mathrm{h}_s^3, 0\right]'$,

$$\mathbf{D}_t := \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & \partial_t & 0 & 0 \\ 0 & 0 & \partial_t & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \quad \text{and} \qquad \mathbb{S}^s(\mathbf{u}_s) := \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & \mathrm{u}_s^2 \\ 0 & 0 & 1 & -\mathrm{u}_s^1 \\ 0 & 0 & 0 & \kappa \end{bmatrix}, \tag{1.15}$$

for $\boldsymbol{\Omega}_T^s$ and $\boldsymbol{\Gamma}_T^\iota$ with $\iota = N,l,r$ defined correspondingly as in (1.12) by taking into account that $\overline{\mathrm{u}}^1$ is defined on whole Ω_T; see (1.13). One could also include the term $\overline{\mathrm{f}}_s := -\eta\left(\mathrm{u}_s^2 - \mathrm{u}_s^3\right)\nabla \mathrm{u}_s^4$ in the material tensor $\mathbb{S}$ but then we cannot directly use the established results for the Stokes equations; see Section 2.3.

2. Preliminaries

2.1. Definitions, norms, and notation. To simplify the notation, we introduce the following convention for fields containing physical quantities and spatial vectors. We use a field of dimension d_L, where d denotes the number of field components and L the spacial dimension of each component such that

$$\mathbf{u}(t,x) := \left[\overline{\mathrm{u}}^1(t,x), \overline{\mathrm{u}}^2(t,x), \ldots, \overline{\mathrm{u}}^d(t,x)\right]' \in \mathbb{R}^{d_L}, \tag{2.1}$$

where $\overline{\mathrm{u}}^i \in \mathbb{R}^L$ for any $d, L \in \mathbb{N}_{>0}$. In this article, L is either 1 or the space dimension $1 \leq N \leq 3$. d is 3 for the Poisson-Nernst-Planck system. However, for the Stokes-Poisson-Nernst-Planck equations, we write $\mathbf{u} \in \mathbb{R}^N \times \mathbb{R}^{3_1}$, since the fluid velocity is a vectorial component. For the fields we use the indices i or j and their spatial components are indicated by subindices k or l. Moreover, let us define the algebraic conventions for $L=1$, i.e. for $\mathbf{u}, \mathbf{v} \in \mathbb{R}^{3_1}$, and for $L=N$, i.e. for $\boldsymbol{\xi}, \boldsymbol{\zeta} \in \mathbb{R}^{3_N}$, as follows:

$$\begin{aligned} \mathbf{uv} &:= \left[\mathrm{u}^1\mathrm{v}^1, \mathrm{u}^2\mathrm{v}^2, \mathrm{u}^3\mathrm{v}^3\right]', \\ \boldsymbol{\xi\zeta} &:= \left[\xi^{1_k}\zeta^{1_k}, \xi^{2_k}\zeta^{2_k}, \xi^{3_k}\zeta^{3_k}\right]' \in \mathbb{R}^{3_1}, \end{aligned} \tag{2.2}$$

where we use summation over repeated indices. The multiplication rules (2.2) are canonically extended to fields of the form $\mathbf{u}(\mathbf{t}, \mathbf{x}) \in \mathbb{R}^N \times \mathbb{R}^{3_1}$. Let us also introduce the canonical norms for the fields (2.1). We denote a field whose components are in $L^2(\Omega)$ by $\mathbf{L}^2(\boldsymbol{\Omega})$ supplemented with the canonical norm

$$\|\mathbf{v}\| := \left[\left\|\mathrm{v}^1\right\|, \left\|\mathrm{v}^2\right\|, \left\|\mathrm{v}^3\right\|\right]'. \tag{2.3}$$

In the same way, we write $\mathbf{H}^1(\boldsymbol{\Omega})$ for the space of fields whose components are in $H^1(\Omega)$ and assign the following norm for any $\mathbf{v} \in \mathbf{H}^1(\boldsymbol{\Omega})$, i.e.

$$\|\mathbf{v}\|_{\mathbf{H}^1} := \left[\left\|\mathrm{v}^1\right\| + \left\|\nabla \mathrm{v}^1\right\|, \left\|\mathrm{v}^2\right\| + \left\|\nabla \mathrm{v}^2\right\|, \left\|\mathrm{v}^3\right\| + \left\|\nabla \mathrm{v}^3\right\|\right]'. \tag{2.4}$$

By $\mathbf{C}^s(\boldsymbol{\Omega})$ we denote the space of fields $\boldsymbol{\phi} := \left[\phi^1, \phi^2, \phi^3\right]'$ with $\phi^i \in C^s(\Omega)$ for $i = 1,2,3$ and $0 \leq s \leq \infty$. This notation is canonically extended to time, i.e. $\mathbf{C}^s(\mathbf{[0,T[})$.

We introduce the coordinate $y := \frac{x}{s}$ for the microscale where x is the corresponding macroscale.

Occasionally, we abbreviate integrals as follows:

$$\begin{aligned} \int_Y f(y)\, dy &:= (f,1)_Y, \\ \int_0^T \int_\Omega f(t,x)\, dx dt &:= (f,1)_{T,\Omega}. \end{aligned} \tag{2.5}$$

Let us give some basic definitions.

DEFINITION 2.1. *We call Ω^s a* periodic replacement*, which corresponds to the phase $\Omega_2 \subset \Omega$ of a bounded domain $\Omega \subset \mathbb{R}^N$ with Lipschitz boundary $\partial\Omega$, by representing the phase $\Omega_1 := \Omega \setminus \Omega_2$ by $s(Y_1 + r\ell_k \bar{e}_k)$, where $r \in \mathbb{Z}$, $k \in \{1, \ldots, N\}$, $s > 0$ small, and $Y_1 \subset Y := [0, \ell_1] \times [0, \ell_2] \times \cdots \times [0, \ell_N]$ is closed such that $\mathbb{R}^N \setminus \cup_{r \in \mathbb{Z}} (Y_1 + r\ell_k \bar{e}_k)$ is open. Assume that the set $Y_2 := Y \setminus Y_1$ can be represented as the finite union of Lipschitz domains Q_j, $j = 1, \ldots, q$, i.e. $Y_2 := \cup_{j=1}^q Q_j$, and we only represent those sets Ω_1 from Ω by $s(Y_1 + r\ell_k \bar{e}_k)$, $r \in \mathbb{Z}$ for which $\operatorname{dist}(\partial\Omega, s(Y_1 + r\ell_k \bar{e}_k)) \geq k_0 s$, where k_0 is constant and independent of $s > 0$.*

REMARK 2.1. In the Definition 2.1, Ω_1 corresponds to B^s and Ω_2 to Ω^s; see Figure 1.5.

DEFINITION 2.2. *Let $\alpha, \beta \in \mathbb{R}$, such that $0 < \alpha < \beta$. We denote by $M(\alpha, \beta, \mathcal{O})$ the set of the $N \times N$ matrices $A = (a_{ij})_{1 \leq i,j \leq N} \in (L^\infty(\mathcal{O}))^{N \times N}$ such that*

$$\begin{cases} \quad i) & \left(A(x)\overline{\lambda}, \overline{\lambda}\right) \geq \alpha \left|\overline{\lambda}\right|^2, \\ \quad ii) & \left|A(x)\overline{\lambda}\right| \leq \beta \left|\overline{\lambda}\right|, \end{cases} \tag{2.6}$$

for any $\overline{\lambda}\in\mathbb{R}^N$ *and a.e. in* $\mathcal{O}$. *The set* $\mathcal{O}$ *denotes an open set in* $\mathbb{R}^N$. *The canonical extension to the context of fields (2.1) is achieved by replacing* A *by* $\mathbb{S}\in\mathbb{R}^{3_N\times 3_N}$, *i.e.* $\mathbb{S}\in(L^\infty(\mathcal{O}))^{N\times N}$, *such that the set of* $\mathbb{S}$, *which satisfies (2.6) for* $\boldsymbol{\lambda}\in\mathbb{R}^{3_N}$ *instead of* $\overline{\lambda}\in\mathbb{R}^N$, *is denoted by* $\mathbf{M}(\alpha,\beta,\mathcal{O})$.

DEFINITION 2.3. *Let* Ω *be a bounded open set of* $\mathbb{R}^N$ *and* f *a function in* $L^1(\Omega)$. *The* mean value *of* f *over* Ω *is the real number* $\mathcal{M}_\Omega(f)$ *given by*

$$\mathcal{M}_\Omega(f):=\frac{1}{|\Omega|}\int_\Omega f(y)\,dy.$$

Let us consider periodic functions in Sobolev spaces.

DEFINITION 2.4. *Let* $C^\infty_{per}(Y)$ *be the subset of* $C^\infty(\mathbb{R}^N)$ *of* Y*-periodic functions. We denote by* $H^1_{per}(Y)$ *the closure of* $C^\infty_{per}(Y)$ *in the* H^1*-norm.*

We use the following notation for periodic Sobolev spaces of fields:

$$\begin{aligned}&\mathbf{H}^1_{per}(Y):=H^1_{per}(Y,\mathbb{R}^{3_1}),\\&\mathbf{W}_{per}(Y):=W_{per}(Y,\mathbb{R}^{3_1}):=\left\{\mathbf{v}\in H^1_{per}(Y,\mathbb{R}^{3_1})\big|\mathcal{M}_Y(\mathbf{v})=\mathbf{0}\right\}.\end{aligned}\tag{2.7}$$

In the following, we introduce the notation for the two-scale convergence.

DEFINITION 2.5. *A sequence* $u_s(x)\in L^2(\Omega)$ *such that*

$$\|u_s\|\le C,$$

two-scale converges *to a function* $u(x,y)\in L^2(\Omega\times Y)$ *if for any* $\varphi(x)\in C^\infty_0(\Omega)$ *and* $\Phi(y)\in C^\infty_{per}(Y)$,

$$\int_\Omega u_s(x)\varphi(x)\Phi(x/s)\,dx\quad\to\quad\frac{1}{|Y|}\int_{\Omega\times Y}u(x,y)\varphi(x)\Phi(y)\,dxdy,$$

as $s\to 0$. *In this case, we write*

$$u_s(x)\quad\overset{2}{\to}\quad u(x,y),\quad \text{as } s\to 0.$$

2.2. Review of basic a priori estimates. The analysis in [45] provides necessary results as a priori estimates and existence of solutions for the periodic problems (1.12) and (1.14). That means, the periodic case in $\mathbf{\Omega}^s$ is covered by an immediate adaptation of the results from [45] derived for the homogeneous case $\mathbf{\Omega}$. For the sake of completeness, we restate the definition of a weak solution with respect to the periodic formulation (1.14).

DEFINITION 2.2. *We call* $\mathbf{u}_s=[\overline{\mathrm{v}}_s,n_s^+,n_s^-,\phi_s]'$ *a weak solution of (1.14), if*

(i) it satisfies, uniformly in s,

$$\begin{aligned}&\overline{\mathrm{v}}_s\in L^2(0,T;H^1(\mathrm{div},\Omega^s)),\\&n_s^\pm\in L^2(0,T;H^1(\Omega^s))\cap L^\infty(]0,T[\times\Omega^s)\cap W^{1,\frac{5}{6}}(0,T;(H^1(\Omega^s))^*),\\&\phi_s\in L^2(0,T;H^1(\Omega^s))\cap L^\infty(0,T;H^1(\Omega^s)),\end{aligned}$$

(ii) it solves (1.14) in the distributional sense for the initial conditions

$$n_0^{\pm} \in L^{\infty}(\Omega^s) \qquad \text{and} \qquad n_0^{\pm} \geq \delta > 0 \qquad \text{a.e. in } \Omega^s.$$

We briefly recall the basic ideas and results here. First, we begin with the positivity of $n_s^{\pm}$. This is an immediate consequence after verifying the non-negativity of $n_s^{\pm} - \delta$ as in [45, Lemma 1] for the adapted relation $n_s^{\pm} - \delta = [n_s^{\pm}]_{\delta}^{+} + [n_s^{\pm}]_{\delta}^{-}$, where $[n_s^{\pm}]_{\delta}^{+} := \max\{n_s^{\pm} - \delta, 0\}$ and $[n_s^{\pm}]_{\delta}^{-} := \min\{n_s^{\pm} - \delta, 0\}$.

The uniform L^{∞}-bounds for $n^{\pm}$ (see [45, Lemma 4]) are achieved again by the Moser iteration [31]. By proceeding as in [45, Section 3.2], we obtain the uniform bounds

$$\begin{aligned} \mathrm{u}_s^3 &\in H^1(\Omega_T), \\ \mathrm{u}_s^i &\in L^{\infty}(\Omega_T) \qquad \text{for all } i = 1,2, \\ \mathrm{u}_s^i &\in L^{\infty}(0,T;L^2(\Omega)) \cap L^2(0,T;H^1(\Omega)) \qquad \text{for all } i = 1,2, \end{aligned} \tag{2.8}$$

where u_s^i is extended by zero in B^s. One can also estimate the time derivative $\partial_t \mathrm{u}_s^i$ uniformly in s for $i = 1,2$ (or shifted indices $i = 2,3$ after including fluid flow), i.e. $\|\partial_t \mathrm{u}_s^i\|_{(W^{1,2})^*}^{6/5} \leq C$ by a direct adaptation of the proof in [45, Lemma 6]. Hence, by Aubin-Lion's compactness theorem we get the strong convergence

$$\mathrm{u}_s^i \quad \to \quad \mathrm{u}^i \qquad \text{in } L^2(0,T;L^2(\Omega)) \qquad \text{for } s \to 0 \text{ and } i = 1,2. \tag{2.9}$$

The bounds (2.8) and the strong convergence (2.9) are correspondingly valid for shifted indices in the case of the system (1.14). Finally, the existence of weak solutions for the problems (1.14) and (1.15) is a consequence of Schauder's fixed point theorem and we refer the interested reader to [45, Section 3.3].

Finally, we motivate uniform a priori estimates for the fluid velocity $\overline{\mathrm{v}}_s$ which is a solution of

$$\begin{aligned} -\Delta \overline{\mathrm{v}}_s + \nabla p_s &= -\eta \left(n_s^+ - n_s^- \right) \nabla \phi_s \qquad \text{in } \Omega^s, \\ \operatorname{div} \overline{\mathrm{v}}_s &= 0 \qquad \text{in } \Omega^s. \end{aligned} \tag{2.10}$$

Since $\{\kappa \delta_{kl}\}_{1 \leq k,l \leq N}$ is strongly elliptic, the electrostatic potential $\mathrm{u}^4 = \phi_s$ in Equation $(1.15)_1$ satisfies the estimate

$$\min_{\{\lambda^2,\alpha\}} \|\nabla \phi_s\| \leq Cs, \tag{2.11}$$

after using $(2.8)_2$ together with Poincaré's inequality in Ω^s, i.e.

$$\|u\|_{L^2(\Omega^s)} \leq sC \|\nabla u\|_{L^2(\Omega^s)} \qquad \text{for any } u \in H_0^1(\Omega^s). \tag{2.12}$$

If we replace $\overline{\mathrm{v}}_s$ in (2.10) by $\overline{\mathrm{u}}_s := \frac{\overline{\mathrm{v}}_s}{s^2}$, we can derive the following uniform bound

$$\|\nabla \overline{\mathrm{u}}_s\| \leq C, \tag{2.13}$$

which again implies by Poincaré's inequality (2.12) the usual estimate

$$\|\overline{\mathrm{u}}_s\| + s \|\nabla \overline{\mathrm{u}}_s\| \leq C. \tag{2.14}$$

We skip the estimates for the pressure in a porous medium, since they require a suitable restriction operator from $H_0^1(\Omega)$ into $H_0^1(\Omega^s)$. For further details concerning the derivation of Darcy's law, we refer the interested reader to [1, 19].

2.3. The homogenized Stokes equations: Darcy's law. The Stokes problem in the periodic formulation reads

$$\begin{aligned} -\Delta \overline{\mathrm{v}}_s + \nabla p_s &= \overline{\mathrm{f}}_s, && \text{in } \Omega^s, \\ \operatorname{div} \overline{\mathrm{v}}_s &= 0, && \text{in } \Omega^s, \\ \overline{\mathrm{v}}_s &= \overline{0}, && \text{on } \partial\Omega^s. \end{aligned} \tag{2.15}$$

We are interested in the limit problem for $(p_s, \overline{\mathrm{v}}_s)$ as $s \to 0$. Therefore, we first consider the following auxiliary problem on the periodic cell $Y_2 := Y \setminus Y_1$:

$$\begin{aligned} -\Delta \overline{\mathrm{w}}^k + \nabla_y q^k + \overline{\mathrm{e}}_k &= \overline{0}, && \text{in } Y_2, \\ \operatorname{div}_y \overline{\mathrm{w}}^k &= 0, && \text{in } Y_2, \\ \overline{\mathrm{w}}^k &= 0, && \text{on } \partial Y_1 \cap \partial Y_2, \\ \overline{\mathrm{w}}^k, q^k & && \text{are } Y\text{-periodic with respect to } y_1, \dots, y_N, \end{aligned} \tag{2.16}$$

where $\overline{\mathrm{e}}_1, \dots, \overline{\mathrm{e}}_N$ are the canonical basis functions in $\mathbb{R}^N$. For example by using the two-scale convegence tool, as it is applied later on for the problem (1.12), the following passage to the limit from the Stokes problem in a porous medium to Darcy's law in a homogeneous medium is verified for example in [20] and given here without proof for convenience of the reader.

THEOREM 2.6. *Let $\overline{\mathrm{v}}_s$ be a solution of (2.15) extended by zero to $\Omega \setminus \Omega^s$. For all $s > 0$ there exists an extension p_s of the pressure to $\Omega \setminus \Omega^s$ such that $\frac{\overline{\mathrm{v}}_s}{s^2} \rightharpoonup \overline{\mathrm{v}}_0$ weakly in $L^2(\Omega)$ and $p_s \to p_0$ strongly in $L^2(\Omega)$, where $(p_0, \overline{\mathrm{v}}_0)$ is a solution of the problem*

$$\begin{aligned} \mathrm{v}_0^k &= \mathrm{k}_{kl} \left(\mathrm{f}^l - \partial_{x_l} p_0 \right), && \textit{in } \Omega, \\ \operatorname{div} \overline{\mathrm{v}}_0 &= 0, && \textit{in } \Omega, \\ (\overline{\mathrm{v}}_0, \overline{\nu}) &= 0, && \textit{on } \partial\Omega, \end{aligned} \tag{2.17}$$

and v_0^k is the k-th component of the vector-valued function $\overline{\mathrm{v}}_0$, and $\overline{\nu}$ is the outward normal to $\partial\Omega$ and the matrix k_{kl} is called the Darcy matrix and defined by

$$\mathrm{k}_{kl} := \frac{1}{|Y|} \int_{Y_2} \mathrm{w}_l^k \, dy, \tag{2.18}$$

for solutions w_l^k of (2.16) with index l denoting the l-th component of the vector $\overline{\mathrm{w}}^k$.

3. Main results

From Section 2, we know that the basic system (1.9) that the problem (1.12) and (1.14) are well-posed.

We introduce the auxiliary problem on the reference cell Y^i, which is defined by

$$Y^i := \begin{cases} Y_2, & \text{if } i = 1,2 \\ Y, & \text{else} \end{cases}, \tag{3.1}$$

and has a Lipschitz continuous interface $\partial Y_1 \cap \partial Y_2$, i.e.

$$\begin{aligned} -\partial_{y_k} \left(s_{i_k j_l}(y) \partial_{y_l} \xi^{i j_r}(y) + s_{i_k j_r}(y) \right) &= 0, && \text{in } Y^i, \\ \left(s_{i_k j_l}(y) \partial_{y_l} \xi^{i j_r}(y) + s_{i_k j_r}(y) \right) \mathrm{n}_I^{i_k} &= 0, && \text{on } I := \partial Y_1 \cap \partial Y_2, \qquad i = 1,2, \\ \xi^{3 j_r}\big|_{Y_1} &= \xi^{3 j_r}\big|_{Y_2}, && \text{on } I, \\ s_{3_k j_l}(y) \partial_{y_l} \xi^{3 j_r}\big|_{Y_1} &= s_{3_k j_l}(y) \partial_{y_l} \xi^{3 j_r}\big|_{Y_2}, && \text{on } I, \end{aligned} \tag{3.2}$$

where $\overline{\mathrm{n}}_I^i$ is the normal on $I:=\partial Y_1\cap\partial Y_2$ pointing into Y_1, $1\leq i,j\leq 3$, $1\leq k,l,r\leq N$, $\underline{\xi}^{ij_r}$ is Y-periodic, and $\mathcal{M}_Y(\underline{\xi}^{ij_r})=0$ where $\underline{\xi}^{ij_r}$ is the extension by zero of ξ^{ij_r} on $Y\setminus Y^i$. We remember that $Y_1,Y_2\subset Y$ are subsets introduced in Definition 2.1 and depicted in Figure 1.5. In order to give $(3.2)_1$ and $(3.2)_2$ a proper meaning, we consider the elliptic problem (3.2) in a weak sense. Hence, the well-posedness follows by standard theory of elliptic equations [18].

The following Theorem verifies the convergence of the periodic problem (1.12) to a corresponding homogenized description. It uses a priori estimates derived in [45] and summarized in Section 2.2 for convenience of the reader.

THEOREM 3.1. *Let $\mathbf{u}_s=\mathrm{u}_s^i\mathbf{f}_i$ be a weak solution, extended by zero in $\Omega\setminus\Omega^s$ for $i=1,2$, of (1.12) in the sense of Definition 2.2 for $\overline{\mathrm{v}}_s=\overline{0}$ and let ξ^{ij_r} solve (3.2) in the distributional sense. We assume a bounded $\Omega\subset\mathbb{R}^N$ with $\partial\Omega$ Lipschitz continuous such that $\partial\Omega=\Gamma^D\cup\Gamma^N$ where Γ^D and Γ^N are two disjoint subsets and Γ^D is of positive measure. Moreover, we require that the solid domain B^s is a smooth connected open set in $\Omega\subset\mathbb{R}^N$. Let $\mathbf{h}_s,\mathbf{g}_l,\mathbf{g}_r\in\mathbf{L}^\infty(]0,T[^3;\mathbf{W}^{1,\infty}(\Omega))$. Then, for $s\to 0$, there exists a subsequence $\mathbf{u}_s(\mathbf{t},\mathbf{x})$ (not relabeled) such that*

$$
\begin{aligned}
\nabla\mathrm{u}_s^3 &\overset{*}{\rightharpoonup} \nabla\mathrm{u}^3 \quad \text{in} \quad L^\infty(0,T;H^1(\Omega)),\\
\mathrm{u}_s^i &\rightharpoonup \mathrm{u}^i \quad \text{in} \quad L^2(0,T;H^1(\Omega))\cap W^{1,\frac{6}{5}}(0,T;(H^1(\Omega))^*) \quad \text{for} \quad i=1,2,\\
\mathrm{u}_s^i &\overset{*}{\rightharpoonup} \mathrm{u}^i \quad \text{in} \quad L^\infty(0,T;L^\infty(\Omega)) \quad \text{for} \quad i=1,2,\\
\mathrm{u}_s^i &\to \mathrm{u}^i \quad \text{in} \quad L^2(0,T;L^2(\Omega)) \quad \text{for} \quad i=1,2,\\
\mathbf{u}_s(\mathbf{t},\mathbf{x}) &\overset{2}{\to} \mathbf{u}(\mathbf{t},\mathbf{x})\boldsymbol{\chi}_{Y_2}(\mathbf{y}),\\
\boldsymbol{\nabla}\mathbf{u}_s(\mathbf{t},\mathbf{x}) &\overset{2}{\to} \big\{\boldsymbol{\nabla}_x\mathbf{u}(\mathbf{t},\mathbf{x})+\boldsymbol{\nabla}_y\mathbf{u}_1(\mathbf{t},\mathbf{x},\mathbf{y})\big\}\boldsymbol{\chi}_{Y_2}(\mathbf{y}),
\end{aligned}
\tag{3.3}
$$

where $\mathrm{u}_1^j(t,x,y):=\xi^{ij_k}(t,y)\nabla_{x_k}\mathrm{u}^j(t,x)\in L^2(0,T;L^2(\Omega;H^1_{per}(Y)))$,
$\boldsymbol{\chi}_{Y_2}(\mathbf{y}):=[\chi_{Y_2}(y),\chi_{Y_2}(y),1]'$ and $\mathbf{u}\in\mathbf{L}^\infty(]0,T[^3;\mathbf{L}^2(\boldsymbol{\Omega}))\cap\mathbf{L}^2(]0,T[^3;\mathbf{H}^1(\boldsymbol{\Omega}))$ is the solution of the following limit problem:

$$
\begin{aligned}
\theta_2\mathbf{D}_\mathbf{t}\mathbf{u}-\mathbf{div}\left(\mathbb{S}^0\boldsymbol{\nabla}\mathbf{u}\right)&=\mathbf{I}(\mathbf{u}), && \text{in } \boldsymbol{\Omega}_T,\\
\mathbf{u}(\mathbf{0},\mathbf{x})&=\mathbf{h}_s, && \text{in } \boldsymbol{\Omega},\\
\mathbf{u}&=\mathbf{g}_\iota, && \text{on } \boldsymbol{\Gamma}_T^\iota, \qquad \iota=l,r,\\
\mathbb{S}^0\boldsymbol{\nabla}_\mathbf{n}\mathbf{u}&=\mathbf{0}, && \text{on } \boldsymbol{\Gamma}_T^N,
\end{aligned}
\tag{3.4}
$$

where $\mathbb{S}^0$ is defined for ξ^{ij_l} from (3.2) by

$$
\mathbb{S}^0:=\left\{s^0_{i_kj_l}\right\}_{i_kj_l}:=\theta_2\left\{\mathcal{M}_{Y_2}\left(s_{i_kj_l}(y)\right)+\mathcal{M}_{Y_2}\left(s_{i_kj_r}(y)\partial_{y_r}\xi^{ij_l}\right)\right\}_{i_kj_l},
\tag{3.5}
$$

and $\mathbf{I}(\mathbf{u}):=[0,0,\theta_2\left(\mathrm{u}^1-\mathrm{u}^2\right)]'$.

REMARK 3.2. The Theorem 3.1 only provides the convergence of a subsequence. In order to have convergence of the entire sequence $\mathbf{u}_s$, one needs to verify uniqueness of the problem (3.4). We motivate that for (3.4), uniqueness can be obtained by a Gronwall argument. However, in the subsequent extension to Stokes flow (Theorem 3.3), uniqueness follows not easily due to the additional nonlinearity $\mathbb{S}^0(\mathbf{u})$ in (3.8). Compare also (1.1) with (1.4) in this context.

In the following, we extend the result of Theorem (3.1) to the Stokes-Nernst-Planck-Poisson system (1.14). Therefore, we first have to adapt the auxiliary problem

(3.2) in the following way: We shift the indices $1\le i,j\le 3$ by $+1$ in the auxiliary problem (3.2). The cases $i=j=1$ are covered by (2.16) and Theorem (2.6). More precisely, we introduce the auxiliary problem on the reference cell Y^i defined by (3.1) for shifted indices i with Lipschitz continuous interface $\partial Y_1\cap\partial Y_2$, i.e.

$$\begin{aligned}
&-\partial_{y_k}\left(s_{i_kj_l}(y,\mathbf{u})\partial_{y_l}\xi^{ij_r}(y)+s_{i_kj_r}(y,\mathbf{u})+(\mathrm{b}^{i_k})^0(\mathbf{u})\mathrm{u}^{i_k}\right)=0, && \text{in } Y^i,\\
(\text{for } i=1,2)\qquad &\left(s_{i_kj_l}(y,\mathbf{u})\partial_{y_l}\xi^{ij_r}(y)+s_{i_kj_r}(y,\mathbf{u})+(\mathrm{b}^{i_k})^0(\mathbf{u})\mathrm{u}^{i_k}\right)\mathrm{n}_I^{i_k}=0, && \text{on } I,\\
&\xi^{3j_r}\big|_{Y_1}=\xi^{3j_r}\big|_{Y_2}, && \text{on } I,\\
&s_{3_kj_l}(y,\mathbf{u})\partial_{y_l}\xi^{3j_r}\big|_{Y_1}=s_{3_kj_l}(y,\mathbf{u})\partial_{y_l}\xi^{3j_r}\big|_{Y_2}, && \text{on } I,
\end{aligned}\tag{3.6}$$

where $\overline{\mathrm{n}}_I^i$ is the normal on $\partial Y_1\cap\partial Y_2$ pointing into Y_1, $2\le i,j\le 4$, $1\le k,l,r\le N$, ξ^{ij_r} is Y-periodic and $\mathcal{M}_Y(\xi^{ij_r})=0$. We point out that (3.6) has a weak solution $\xi^{ij_r}(y)$ by standard theory of elliptic equations [18].

THEOREM 3.3. *Let $\mathbf{u}_s=\mathrm{u}_s^i\mathbf{f}_i$ be a weak solution, extended by zero in $B^s:=\Omega\setminus\Omega^s$ for $i=1,2,3$, of (1.14) in the sense of Definition 2.2 and let ξ^{ij_r} solve (3.6) in the distributional sense. We assume a bounded $\Omega\subset\mathbb{R}^N$ with $\partial\Omega$ Lipschitz continuous such that $\partial\Omega=\Gamma^D\cup\Gamma^N$ where Γ^D and Γ^N are two disjoint subsets and Γ^D is of positive measure. Moreover, we require that the solid domain B^s is a smooth connected open set in $\Omega\subset\mathbb{R}^N$. Let $\mathbf{h}_s,\mathbf{g}_l,\mathbf{g}_r\in\mathbf{L}^\infty([0,T[^4;\mathbf{W}^{1,\infty}(\Omega))$. Then, for $s\to 0$, there exists a subsequence $\mathbf{u}_s(\mathbf{t},\mathbf{x})$ (not relabeled) such that*

$$\begin{aligned}
\nabla\mathrm{u}_s^4 &\overset{*}{\rightharpoonup} \nabla\mathrm{u}^4 && \text{in} && L^\infty(0,T;H^1(\Omega)),\\
\mathrm{u}_s^i &\rightharpoonup \mathrm{u}^i && \text{in} && L^2(0,T;H^1(\Omega))\cap W^{1,\frac{6}{5}}(0,T;(H^1(\Omega))^*) \quad \text{for} \quad i=2,3,\\
\mathrm{u}_s^i &\overset{*}{\rightharpoonup} \mathrm{u}^i && \text{in} && L^\infty(0,T;L^\infty(\Omega)) \quad \text{for} \quad i=2,3,\\
\mathrm{u}_s^i &\to \mathrm{u}^i && \text{in} && L^2(0,T;L^2(\Omega)) \quad \text{for} \quad i=2,3,\\
\mathrm{u}_s^i(t,x) &\overset{2}{\to} \mathrm{u}^i(t,x)\chi_{Y_2}(y) && \text{where } \mathrm{u}^i\in L^2(0,T;H^1(\Omega)) && \text{for} \quad i=2,3,4,\\
\nabla\mathrm{u}_s^i(t,x) &\overset{2}{\to} \left\{\nabla_x\mathrm{u}^i(t,x)+\nabla_y\mathrm{u}_1^i(t,x,y)\right\}\chi_{Y_2}(y) && && \text{for} \quad i=2,3,4,\\
\frac{\overline{\mathrm{u}}_s^1}{s^2} &\rightharpoonup \overline{\mathrm{u}}^1 && \text{in} && L^2(\Omega),\\
p_s &\rightharpoonup p && \text{in} && L^2(\Omega),
\end{aligned}\tag{3.7}$$

where $\mathbf{u}_1(\mathbf{t},\mathbf{x},\mathbf{y})\in\mathbf{L}^2(]0,T[^4;\mathbf{L}^2(\mathbf{\Omega},\mathbf{H}^1_{per}(Y)))$ and $\mathbf{u}(\mathbf{t},\mathbf{x})$ is the solution of the following limit problem

$$\begin{aligned}
\theta_2\mathbf{D_t}\mathbf{u}-\mathbf{div}\left(\mathbb{S}^0(\mathbf{u})\boldsymbol{\nabla}\mathbf{u}\right)+\mathbf{b}^0(\mathbf{u})\boldsymbol{\nabla}\mathbf{u}&=\mathbf{I}(\mathbf{u}), && \text{in } \mathbf{\Omega}_T, \quad \mathrm{div}\overline{\mathrm{u}}^1=0 \quad \text{in } \Omega_T,\\
\mathbf{u}(\mathbf{0},\mathbf{x})&=\mathbf{h}_s, && \text{in } \mathbf{\Omega},\\
\mathbf{u}&=\mathbf{g}_\iota, && \text{on } \mathbf{\Gamma}_T^\iota, \quad \iota=l,r,\\
\left(\overline{\mathrm{u}}^1,\overline{\nu}\right)&=0, && \text{on } \Gamma_T^N,\\
\mathbb{S}^0(\mathbf{u})\boldsymbol{\nabla}_\mathbf{n}\mathbf{u}&=\mathbf{0}, && \text{on } \mathbf{\Gamma}_T^N,
\end{aligned}\tag{3.8}$$

where $\overline{\nu}$ is the outward pointing normal on Γ_T^N, $\mathbb{S}^0(\mathbf{u})$ is given by (3.5) for $2\le i,j\le 4$ and

$$s_{i1}^0(\mathbf{u})=s_{1j}^0(\mathbf{u})=:0, \qquad \text{for} \quad i,j=1,2,\ldots,4,$$

and the convective term $\mathbf{b}^0(\mathbf{u})$ *and the right-hand side* $\mathbf{I}(\mathbf{u})$ *are given by*

$$\begin{aligned}
(\mathrm{b}^{i_k})^0(\mathbf{u}) &:= \mathrm{u}^{1_k} Pe, && \text{for } i=2,3, \text{ and } 1\le k\le N,\\
(\mathrm{b}^{i_k})^0(\mathbf{u}) &:= 0, && \text{for } i=1,4, \text{ and } 1\le k\le N,\\
\mathbf{I}(\mathbf{u}) &:= \left[\left\{-\mathrm{u}^{1_k}+\mathrm{k}_{kl}\left(\mathrm{f}_l^0(\mathbf{u})-\partial_{x_l}p\right)\right\}_{1\le k\le N},0,0,\theta_2\left(\mathrm{u}^2-\mathrm{u}^3\right)\right]',
\end{aligned}$$

with $\mathrm{f}_l^0(\mathbf{u}) := -\eta\theta_2\left(\mathrm{u}^2-\mathrm{u}^3\right)\partial_{x_l}\mathrm{u}^4\left(1+\delta_{kl}\mathcal{M}_{Y_2}\left(\partial_{y_l}\xi^{44_k}\right)\right)$ *for* $1\le l\le N$.

To improve the quality of the upscaled equations with respect to experiments, we propose the following simple algorithm to determine the right reference cell Y containing all the necessary information about the microstructure. The basic idea of the algorithm is to statistically determine a probability density which differs the two phases solid and liquid. Hence, we average out the randomness in the material such that we do not have to solve corresponding stochastic partial differential equations with random coefficients. To successfully apply the following algorithm, it is useful to have characteristic, evenly distributed (close to periodic) solid particles in the material.

Y-Algorithm: (2D)

1. *For the considered solid-electolyte composite determine for each solid particle* $1\le i\le P$ *of the same phase* (Ω_1) *the maximal diameter in the* x*-direction, i.e.* d_i^x*, and the maximal diameter in the* z*-direction, i.e.* d_i^z*. Moreover, denote the corresponding averages over all particles by* $\underline{d}_m^x := \frac{1}{P}\sum_{i=1}^P d_i^x$ *(respectively* $\underline{d}_m^z := \frac{1}{P}\sum_{i=1}^P d_i^z$*), where* P *is the total number of particles.*
2. *Compute the number of reference cells in the* x*-direction and in the* z*-direction for the periodic replacement:*

$$n^x := \frac{L^x}{\underline{d}_m^x} \qquad\qquad n^z := \frac{L^z}{\underline{d}_m^z},$$

where L^x *(respectively* L^z*) is the length of the electrode in the* x*-direction (respectively in the* z*-direction).*

3. *Determine the size of the reference cell: Set*

$$i^x := [n^x] \le n^x, \qquad i^z := [n^z] \le n^z,$$

where the operator $[\cdot]$ *takes the integer value of its argument. Hence, with* $\ell_1 := \frac{L^x}{i^x}$ *and* $\ell_2 := \frac{L^z}{i^z}$ *we get*

$$Y := [0,\ell_1]\times[0,\ell_2].$$

5. *Create a probability density on the unit cell* Y*: Therefore, we scan the electrode with respect to the reference cell* Y *by setting the solid phase* Ω_1 *to "*1*" and the liquid phase* Ω_2 *to "*0*". The probability density is then obtained by taking the mean value with respect to the number of reference cells covering the domain of the solid-electrolyte composite.*
6. *Construct the reference cell* Y*: With the probability density* $p(x,z)$ *from 5, we then define the reference cell (for the periodic replacement) by the assignment*

$$(x,z) := \begin{cases} \text{“solid”}, & p(x,z)\ge\frac{1}{2},\\ \text{“interface”}, & p(x,z)=\frac{1}{2},\\ \text{“liquid”}, & p(x,z)<\frac{1}{2}. \end{cases}$$

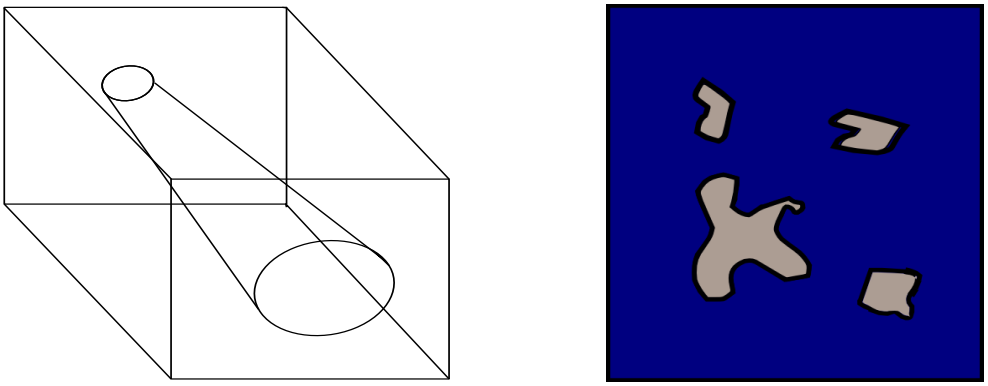

FIG. 3.1. **Left:** *Reference cell induced by a material with conical pores as depicted in Figure 1.1 and with a three-dimensional extension of the Y-Algorithm.* **Right:** *A priori guess of the characteristic reference cell (blue: electrolyte, grey: solid phase) obtained by the Y-Algorithm for the SEM image in Figure 1.3* **a)**.

The above Y-Algorithm only considers the two-dimensional case for illustrative purposes. But an extenison to higher dimensions is straightforward. Moreover, the number of cells determined in Step 2 of the Y-Algorithm, i.e. $\#Y := n^x n^z = \frac{L^x L^z}{s^2 \ell_1 \ell_2}$, allows to compute the scaling factor s, whose smallness is an indicator for the accurateness of the homogenized descriptions, that means

$$s = \sqrt{\frac{L^x L^z}{\ell_1 \ell_2} \frac{1}{\#Y}}. \tag{3.9}$$

As a consequence, we can now determine by Equation (3.9) from experimentally measured (SEM images) and by the Y-Algorithm handled data how accurate our homogenized approximation is. The knowledge of s in practice allows to characterize the approximation error done by using the results stated in the Theorem 3.1 and 3.3.

REMARK 3.4.

1) Instead of introducing random coefficients in the upscaled Nernst-Planck-Poisson equations and then solving the corresponding stochastic partial differential equation by taking the expectation over a sufficiently large sample, we get rid of the stochastic influence by computing in advance the mean/expectation of the material randomness. This approach prevents to solve a computationally expensive problem.

2) By applying statistical tools to the results obtained by the above Y-Algorithm one can even further characterize the quality of the periodic approximation by parameters as the standard deviation, the variance or the mean value for example.

Finally, we motivate the application of the Y-Algorithm with examples presented in the introduction (Section 1). The heterogeneities induced by the conical pores (see Figure 1.1) induce the obvious reference cell Y as shown in Figure 3.1, left.

3.1. An intuitive representation and simplification of the results. For the reader who is only interested in the application of the previous results, we rewrite the expressions (3.2), (3.4), and (3.5) in a more intuitive but less compact form here.

To this end, we determine seperately the correctors corresponding to the equations accessed via the parameter $i = 1,2,3$ in (1.12). We introduce the following suggestive

notations for the correctors, i.e.

$$\xi^r_{n^+} := \xi^{11_r}, \qquad \xi^r_{n^+,\phi} := \xi^{13_r}, \qquad \xi^r_{n^-} := \xi^{22_r}, \qquad \xi^r_{n^-,\phi} := \xi^{23_r}, \qquad \xi^r_{\phi} := \xi^{33_r}, \tag{3.10}$$

for $1 \leq r \leq N$. First, we rewrite the equations providing the correctors $\xi^r_{n^+}$ and $\xi^r_{n^+,\phi}$ required for the equation of the charge density ($i=1$). By further setting $j=1$, we end up with the corrector function $\xi^r_{n^+} := \xi^{11_r}$. More precisely, the variable $\xi^r_{n^+}$ fulfills

$$\begin{cases} -\partial_{y_k}\left(\delta_{kl}\partial_{y_l}\xi^r_{n^+} + \delta_{kr}\right) = 0 & \text{in } Y_2, \\ \left(\delta_{kl}\partial_{y_l}\xi^r_{n^+} + \delta_{kr}\right)\mathrm{n}_I^{1_k} = 0 & \text{on } I, \\ \underline{\xi}^r_{n^+} \quad Y-\text{periodic} \quad \text{and} \quad \mathcal{M}_Y(\underline{\xi}^r_{n^+}) = 0, \end{cases} \tag{3.11}$$

where $\underline{\xi}^r_{n^+}$ denotes the extension by zero of $\xi^r_{n^+}$ to the whole reference cell Y. One immediately recognizes that $\xi^r_{n^+} = \xi^r_{n^-} = \xi^r_{n^+,\phi} = \xi^r_{n^-,\phi}$, since the corresponding reference cell problems are equal. We remark that problem (3.11) can be solved analytically only for very symmetric geometries. For example, if Y_2 represents a straight channel, then in the two-dimensional case the resulting correction tensors have the intuitive form

$$\mathbb{S}^0_{1_k1_l} = \mathbb{S}^0_{2_k2_l} = \mathbb{S}^0_{1_k3_l} = \mathbb{S}^0_{2_k3_l} = \begin{bmatrix} p & 0 \\ 0 & 0 \end{bmatrix} \delta_{kl}, \tag{3.12}$$

where $p := \frac{|Y_2|}{|Y|}$ and $1 \leq k,l \leq N$; see [3].

Hence, we are left with the case $i=3$ providing the corrector function ξ^r_ϕ for the macroscopic Poisson equation. The corresponding corrector problem is

$$\begin{cases} -\partial_{y_k}\left(\kappa(y)\delta_{kl}\partial_{y_l}\xi^r_\phi\right) = \partial_{y_k}\left(\kappa(y)\delta_{kr}\right) & \text{in} \quad Y, \\ \xi^r_\phi \quad Y-\text{periodic} \quad \text{and} \quad \mathcal{M}_Y(\xi^r_\phi) = 0. \end{cases} \tag{3.13}$$

The solutions $\xi^r_{n^+} = \xi^r_{n^-}, \xi^r_{n^+,\phi} = \xi^r_{n^-,\phi}$ and ξ^r_ϕ of (3.11) and (3.13) allow to represent the upscaled material tensor (3.5) by

$$s^0_{i_kj_l}(\mathbf{u}) := \begin{bmatrix} s^0_{1_k1_l} & 0 & \mathrm{u}^2 s^0_{1_k3_l} \\ 0 & s^0_{2_k2_l} & -\mathrm{u}^1 s^0_{2_k3_l} \\ 0 & 0 & s^0_{3_k3_l} \end{bmatrix}, \tag{3.14}$$

where

$$\begin{aligned} s^0_{1_k1_l} &= \frac{1}{|Y|}\int_{Y_2}\left(\partial_{y_r}\xi^l_{n^+}\right)dy\delta_{rl}\delta_{kl} + \theta_2\delta_{kl}, \\ s^0_{2_k2_l} &= \frac{1}{|Y|}\int_{Y_2}\left(\partial_{y_r}\xi^l_{n^-}\right)dy\delta_{rl}\delta_{kl} + \theta_2\delta_{kl}, \\ s^0_{3_k3_l} &= \lambda^2\frac{1}{|Y|}\int_{Y_2}\left(\partial_{y_r}\xi^l_{\phi}\right)dy\delta_{rl}\delta_{kl} \\ &\quad + \alpha\frac{1}{|Y|}\int_{Y_1}\left(\partial_{y_r}\xi^l_{\phi}\right)dy\delta_{rl}\delta_{kl} + \theta_2\lambda^2\delta_{kl} + \theta_1\alpha\delta_{kl}, \\ s^0_{1_k3_l} &= \frac{1}{|Y|}\int_{Y_2}\left(\partial_{y_r}\xi^l_{n^+,\phi}\right)dy\delta_{rl}\delta_{kl} + \theta_2\delta_{kl}, \\ s^0_{2_k3_l} &= \frac{1}{|Y|}\int_{Y_2}\left(\partial_{y_r}\xi^l_{n^-,\phi}\right)dy\delta_{rl}\delta_{kl} + \theta_2\delta_{kl}, \\ \theta_1 &= \frac{|Y_1|}{|Y|}, \qquad \text{and} \qquad \theta_2 = \frac{|Y_2|}{|Y|} \qquad \text{with} \qquad \theta_1 + \theta_2 = 1. \end{aligned} \tag{3.15}$$

We recall that $\delta_{kr}=\delta_{kl}\delta_{rl}$. The nice property of the material tensor (3.14) is that it provides flux relations with respect to a porous material whose characteristic geometry is determined by the elementary cell Y (see Figure 1.5) and the equations (3.11)-(3.13). Hence, for $1\leq k,l\leq N$, these relations can be written with (3.15) in the following way

$$\begin{bmatrix} s^0_{1_k1_l} & 0 & n^- s^0_{1_k3_l} \\ 0 & s^0_{2_k2_l} & -n^+ s^0_{2_k3_l} \\ 0 & 0 & s^0_{3_k3_l} \end{bmatrix} \begin{bmatrix} \partial_{x_k} n^+ \\ \partial_{x_k} n^- \\ \partial_{x_k}\phi \end{bmatrix} = \begin{bmatrix} (\bar{j}_{n^+})_k \\ (\bar{j}_{n^-})_k \\ (\bar{j}_\phi)_k \end{bmatrix}. \tag{3.16}$$

Finally, with the variables introduced in (3.14), the "porous media" Poisson-Nernst-Planck equations can be written as (1.1), i.e.

$$\begin{aligned} \theta_2\partial_t n^+ &= \operatorname{div}\left(\mathbb{S}^0_{11}\nabla n^+ + n^-\mathbb{S}^0_{13}\nabla\phi\right), \\ \theta_2\partial_t n^- &= \operatorname{div}\left(\mathbb{S}^0_{22}\nabla n^- - n^+\mathbb{S}^0_{23}\nabla\phi\right), \\ -\operatorname{div}\left(\mathbb{S}^0_{33}\nabla\phi\right) &= \theta_2\left(n^+ - n^-\right), \end{aligned} \tag{3.17}$$

where the material tensors $\mathbb{S}^0_{ij}$ in 3.17 are defined by

$$\begin{aligned} &\mathbb{S}^0_{11} := \left\{s^0_{1_k1_l}\right\}_{kl} \qquad \mathbb{S}^0_{22} := \left\{s^0_{2_k2_l}\right\}_{kl} \qquad \mathbb{S}^0_{33} := \left\{s^0_{3_k3_l}\right\}_{kl} \\ &\mathbb{S}^0_{13} := \left\{s^0_{1_k3_l}\right\}_{kl} \qquad \mathbb{S}^0_{23} := \left\{s^0_{2_k3_l}\right\}_{kl}. \end{aligned} \tag{3.18}$$

Herewith, the extension to the porous media Stokes-Nernst-Planck-Poisson equations (1.2)-(1.4) is straightforward. The corrector function $\xi^r_{n^+}$ for the diffusion term in the equation for the concentration of positive ions $(3.17)_1$ satisfies the following reference cell problem:

$$\begin{cases} -\partial_{y_k}\left(\delta_{kl}\partial_{y_l}\xi^r_{n^+} + \delta_{kr} + \mathrm{v}^k n^+\right) = 0 & \text{in } Y_2, \\ \left(\delta_{kl}\partial_{y_l}\xi^r_{n^+} + \delta_{kr} + \mathrm{v}^k n^+\right)\mathrm{n}^{1_l}_I = 0 & \text{on } I := \partial Y_1 \cap \partial Y_2, \\ \underline{\xi}^r_{n^+} \quad Y-\text{periodic} \quad \text{and} \quad \mathcal{M}_Y(\underline{\xi}^r_{n^+}) = 0. \end{cases} \tag{3.19}$$

The corrector $\xi^r_{n^-}$ for the negative ion density satisfies the same reference cell problem (3.19) after replacing n^+ by n^-. Further, the function $\xi^r_{n^+,\phi}$ fulfills, after extension to fluid flow, the following problem:

$$\begin{cases} -\partial_{y_k}\left(n^-\delta_{kl}\partial_{y_l}\xi^r_{n^+,\phi} + n^-\delta_{kr} + \mathrm{v}^k n^+\right) = 0 & \text{in } Y_2, \\ \left(n^-\delta_{kl}\partial_{y_l}\xi^r_{n^+,\phi} + n^-\delta_{kr} + \mathrm{v}^k n^+\right)\mathrm{n}^{1_k}_I = 0 & \text{on } I, \\ \underline{\xi}^r_{n^+,\phi} \quad Y-\text{periodic} \quad \text{and} \quad \mathcal{M}_Y(\underline{\xi}^r_{n^+,\phi}) = 0. \end{cases} \tag{3.20}$$

The corresponding corrector function $\xi^r_{n^-,\phi}$ is obtained after replacing n^- by $-n^+$ in (3.20), i.e.

$$\begin{cases} -\partial_{y_k}\left(n^+\delta_{kl}\partial_{y_l}\xi^r_{n^-,\phi} + n^+\delta_{kr} - \mathrm{v}^k n^-\right) = 0 & \text{in } Y_2, \\ \left(n^+\delta_{kl}\partial_{y_l}\xi^r_{n^-,\phi} + n^+\delta_{kr} - \mathrm{v}^k n^-\right)\mathrm{n}^{1_k}_I = 0 & \text{on } I, \\ \underline{\xi}^r_{n^-,\phi} \quad Y-\text{periodic} \quad \text{and} \quad \mathcal{M}_Y(\underline{\xi}^r_{n^-,\phi}) = 0. \end{cases} \tag{3.21}$$

Finally, the macroscopic corrector function ξ^r_ϕ of the electrostatic potential satisfies, in view of $(3.6)_3$ and $(3.6)_4$, the following equations:

$$\begin{cases} -\partial_{y_k}\left(\kappa(y)\delta_{kl}\partial_{y_l}\xi^r_\phi\right) = \partial_{y_k}\left(\kappa(y)\delta_{kr}\right) & \text{in} \quad Y, \\ \xi^r_\phi \quad Y-\text{periodic} \quad \text{and} \quad \mathcal{M}_Y(\xi^r_\phi) = 0. \end{cases} \tag{3.22}$$

The material tensor $S^0_{i_kj_l}$ is still defined by (3.14) and the corresponding components (3.15) for shifted indices i,j as already indicated in Theorem 3.3. Finally, the porous media approximation of the Stokes-Poisson-Nernst-Planck equations becomes (1.2) and (1.4).

4. Proof of Theorem 3.1: The two-scale convergence method

Up to the two-scale convergences, all convergence properties in (3.3) follow from (2.8) and (2.9). Therefore, we verify in the following first the two-scale relation and pass to the limit $s\to 0$ at the end.

Step 1: (*Derivation of the reference cell problem*) Let $\mathbf{u}^s$ be a weak solution in the sense of Definition 2.2 satisfying the integral identity

$$(\mathbf{D_t u}_s,\mathbf{v})+(\mathbb{S}^s(\mathbf{u}_s)\boldsymbol{\nabla}\mathbf{u}_s,\boldsymbol{\nabla}\mathbf{v})=(\mathbf{I}(\mathbf{u}_s),\mathbf{v}),\qquad \forall\mathbf{v}\in\mathbf{V}^{1,2}(\boldsymbol{\Omega}). \tag{4.1}$$

Take $\mathbf{v}(\mathbf{t},\mathbf{x}):=s\boldsymbol{\psi}(\mathbf{x})\boldsymbol{\Psi}(\mathbf{x}/s)\boldsymbol{\eta}(\mathbf{t})$, where $\boldsymbol{\psi}\in\mathbf{C}^\infty(\boldsymbol{\Omega})$ and $\boldsymbol{\Psi}(\mathbf{y})$ is smooth and 1-periodic with respect to $\mathbf{y}$. Moreover, $\Psi^i(y)=0$ if $y\in Y\setminus Y_2$ for $i=1,2$ and $\eta^i(\mathbf{t})\in C^1(]0,T[)$ with $\eta^i(T)=0$ for $i=1,2$. Then,

$$\begin{aligned}&-s(\mathbf{u}_s,\boldsymbol{\psi}\boldsymbol{\Psi}\mathbf{D_t}\boldsymbol{\eta}(\mathbf{t}))_{T,\Omega}+(\mathbb{S}^s(\mathbf{u}_s)\boldsymbol{\nabla}\mathbf{u}_s,\boldsymbol{\nabla}_y\boldsymbol{\Psi}\boldsymbol{\psi}\boldsymbol{\eta}(\mathbf{t}))_{T,\Omega}\\&\quad+s(\mathbb{S}^s(\mathbf{u}_s)\boldsymbol{\nabla}\mathbf{u}_s,\boldsymbol{\Psi}\boldsymbol{\nabla}_x\boldsymbol{\psi}\boldsymbol{\eta}(\mathbf{t}))_{T,\Omega}=s(\mathbf{I}(\mathbf{u}),\boldsymbol{\psi}\boldsymbol{\Psi}\boldsymbol{\eta}(\mathbf{t}))_{T,\Omega}-s(\mathbf{u}_s(\mathbf{0},\cdot),\boldsymbol{\psi}\boldsymbol{\Psi}\boldsymbol{\eta}(\mathbf{0}))_{T,\Omega}.\end{aligned} \tag{4.2}$$

Since the solution $\mathbf{u}^s$ to the problem (1.12) satisfies the uniform estimate $\|\mathbf{u}^s\|_{\mathbf{H}^1}\le C$ with $C>0$, we can choose a subsequence of $\mathbf{u}^s$ by [2, Theorem 0.1, Proposition 1.14] such that

$$\begin{aligned}\mathbf{u}_s(\cdot,\mathbf{x}) &\overset{2}{\to} \mathbf{u}(\cdot,\mathbf{x})\boldsymbol{\chi}_{Y_2}(\mathbf{y}),\\ \boldsymbol{\nabla}_x\mathbf{u}_s(\cdot,\mathbf{x}) &\overset{2}{\to} (\boldsymbol{\nabla}_x\mathbf{u}(\cdot,\mathbf{x})+\boldsymbol{\nabla}_y\mathbf{u}_1(\cdot,\mathbf{x},\mathbf{y}))\boldsymbol{\chi}_{Y_2}(\mathbf{y}),\end{aligned} \tag{4.3}$$

for a non-relabeled subsequence $s\to 0$ where $\boldsymbol{\chi}_{Y_2}(\mathbf{y}):=[\chi_{Y_2}(y),\chi_{Y_2}(y),1]'$ and $\mathbf{u}_1(\cdot,\mathbf{x},\mathbf{y})$ is a function in $\mathbf{]0,T[}\oplus[\boldsymbol{\Omega}\times\mathbf{Y}]$ of class $\mathbf{L^2}(]\mathbf{0,T}[;\mathbf{L^2}(\boldsymbol{\Omega},\mathbf{H^1_{per}}(\mathbf{Y})))$. Now we pass to the limit in the problem (4.2) as $s\to 0$. Hence,

$$\begin{aligned}s(\mathbf{u}_s,\boldsymbol{\psi}\boldsymbol{\Psi}\mathbf{D_t}\boldsymbol{\eta})_{T,\Omega} &\overset{s\to 0}{\to} \mathbf{0},\\ s(\mathbf{I}(\mathbf{u}_s),\boldsymbol{\psi}\boldsymbol{\Psi}\boldsymbol{\eta})_{T,\Omega} &\overset{s\to 0}{\to} \mathbf{0},\end{aligned} \tag{4.4}$$

by (4.3). Since the second term in (4.2) is nonlinear, we make the following decomposition:

$$\begin{aligned}&\big(s^s_{ij}(\mathbf{u}_s)\nabla_x(\mathbf{u}_s)^j,\nabla_y\Psi^i(y)\psi^i(x)\eta^i(t)\big)_{T,\Omega}=\big(\nabla \mathrm{u}^1_s,\nabla_y\Psi^1(y)\psi^1(x)\eta^1(t)\big)_{T,\Omega}\mathbf{f}_1\\&+\big(\nabla \mathrm{u}^2_s,\nabla_y\Psi^2(y)\psi^2(x)\eta^2(t)\big)_{T,\Omega}\mathbf{f}_2+\kappa(y)\big(\nabla \mathrm{u}^3_s,\nabla_y\Psi^3(y)\psi^3(x)\eta^3(t)\big)_{T,\Omega}\mathbf{f}_3\\&+\big(\mathrm{u}^2_s\nabla \mathrm{u}^3_s,\nabla_y\Psi^1(y)\psi^1(x)\eta^1(t)\big)_{T,\Omega}\mathbf{f}_1+\big(\mathrm{u}^1_s\nabla_x \mathrm{u}^3_s,\nabla_y\Psi^2(y)\psi^2(x)\eta(t)\big)_{T,\Omega}\mathbf{f}_2,\end{aligned} \tag{4.5}$$

where $\mathbf{f}_i$ are the canonical basis functions in $\mathbb{R}^{3_1}$ and $\kappa(y):=\lambda^2\chi_{B^s}(y)+\alpha\chi_{\Omega^s}(y)$. In the first three terms of (4.5), we can immediately pass to the limit due to [2, Theorem 0.1, Proposition 1.14]. For the last two terms in (4.5) we apply the strong convergence for u^1_s and u^2_s and property $(4.3)_2$ in order to pass to the limit. Hence, (4.5) satisfies, as $s\to 0$,

$$\begin{aligned}&(\mathbb{S}^s(\mathbf{x},\mathbf{u}_s)\boldsymbol{\nabla}_x\mathbf{u}_s,\boldsymbol{\nabla}_y\boldsymbol{\Psi}(\mathbf{y})\boldsymbol{\psi}(\mathbf{x})\boldsymbol{\eta}(\mathbf{t}))_{T,\Omega}\\&\quad\overset{s\to 0}{\to}\quad\frac{1}{|Y|}(\mathbb{S}(\mathbf{y},\mathbf{u})\{\boldsymbol{\nabla}_x\mathbf{u}+\boldsymbol{\nabla}_y\mathbf{u}_1\}\boldsymbol{\chi}_{Y_2},\boldsymbol{\nabla}_y\boldsymbol{\Psi}(\mathbf{y})\boldsymbol{\psi}(\mathbf{x})\boldsymbol{\eta}(\mathbf{t}))_{T,Y,\Omega}.\end{aligned} \tag{4.6}$$

Due to (4.4) and (4.6) we find in the limit $s\to 0$ the following problem:

$$(\mathbb{S}(\mathbf{y},\mathbf{u})\boldsymbol{\nabla}_y\mathbf{u}_1\boldsymbol{\chi}_{Y_2},\boldsymbol{\nabla}_y\boldsymbol{\Psi})_Y=-(\mathbb{S}(\mathbf{y},\mathbf{u})\boldsymbol{\nabla}_x\mathbf{u}\boldsymbol{\chi}_{Y_2},\boldsymbol{\nabla}_y\boldsymbol{\Psi})_Y,\qquad\forall\boldsymbol{\Psi}\in\mathbf{H}^1_{per}(\mathbf{Y}),$$

since $\boldsymbol{\psi}$ and $\boldsymbol{\eta}$ were arbitrary, where $\mathbf{x}\in\boldsymbol{\Omega}$ and $\mathbf{t}\in]\mathbf{0},\mathbf{T}[$ are regarded as parameters. Let $\xi^{ij_r}(y)\in H^1_{per}(Y)$ be a solution to the following problem: Find $\xi^{ij_r}(y)\in H^1_{per}(Y)$ such that

$$\begin{aligned}&\Big(s_{i_kj_l}(\mathbf{y},\mathbf{u})\nabla_{y_l}\xi^{ij_r}(y)\chi^j_{Y_2},\nabla_{y_k}\Psi^i(y)\Big)_Y\\&\quad=-\Big(s_{i_kj_r}(\mathbf{y},\mathbf{u})\chi^j_{Y_2},\nabla_{y_k}\Psi^i(y)\Big)_Y,\qquad\forall\Psi^i\in H^1_{per}(Y).\end{aligned}\tag{4.7}$$

Via the definition of $s_{i_kj_l}(\mathbf{y},\mathbf{u})$, it becomes immediately clear that (4.7) is well-posed by Lax-Milgram's theorem. With (4.7), the function $\mathbf{u}_1(\mathbf{x},\mathbf{y})$ can be represented in the form

$$\mathrm{u}^i_1(x,y)=\xi^{ij_r}(y)\nabla_{x_r}\mathrm{u}^j(x).\tag{4.8}$$

Step 2: (*Passing to the limit* $s\to 0$) In the integral identity (4.1) we take a test function $\mathbf{v}:=\boldsymbol{\psi}(\mathbf{x})\boldsymbol{\eta}(\mathbf{t})$ independent of $\mathbf{y}$ and s where $\boldsymbol{\psi}\in\mathbf{H}^1(\boldsymbol{\Omega})$ and $\eta^i\in C^1(]0,T[)$ with $\eta^i(T)=0$ for $i=1,2$. After integrating the first term by parts, we can pass to the limit as $s\to 0$ (not relabeled) by using [2, Theorem 0.1, Proposition 1.14] and the same considerations as for (4.6). We obtain the identity

$$\begin{aligned}&-\theta_2(\mathbf{u},\boldsymbol{\psi}\mathbf{D_t}\boldsymbol{\eta})_{T,\Omega}+\frac{1}{|Y|}(\mathbb{S}(\mathbf{y},\mathbf{u})\{\boldsymbol{\nabla}_x\mathbf{u}+\boldsymbol{\nabla}_y\mathbf{u}_1(\mathbf{x},\mathbf{y})\}\boldsymbol{\chi}_{Y_2},\boldsymbol{\nabla}_x\boldsymbol{\psi}(\mathbf{x})\boldsymbol{\eta}(\mathbf{t}))_{T,Y,\Omega}\\&\qquad=(\mathbf{I}(\mathbf{u}),\boldsymbol{\psi}\boldsymbol{\eta}(\mathbf{t}))_{T,\Omega}-(\mathbf{h},\boldsymbol{\psi}\boldsymbol{\eta}(\mathbf{0}))_{T,\Omega}.\end{aligned}\tag{4.9}$$

Substituting the representation (4.8) for $\mathbf{u}_1$ in (4.9) and changing the order of integration (first with respect to $\mathbf{y}$ and then with respect to $\mathbf{x}$), for $r\in\mathbb{N}$ and $1\le r\le 3$ we find

$$\begin{aligned}&-\theta_2(\mathbf{u},\boldsymbol{\psi}\mathbf{D_t}\boldsymbol{\eta})_{T,\Omega}+\frac{1}{|Y|}\left(\left\{s_{i_kj_l}(\mathbf{y},\mathbf{u})+s_{i_kj_r}(\mathbf{y},\mathbf{u})\partial_{y_r}\xi^{ij_l}\right\}\partial_{x_l}\mathrm{u}^j,\partial_{x_k}\phi^i\eta^i(t)\right)_{T,Y_2,\Omega}\delta_{ir}\mathbf{f}_r\\&\qquad=(\mathbf{I}(\mathbf{u}),\boldsymbol{\psi}\boldsymbol{\eta})_{T,\Omega}-(\mathbf{h},\boldsymbol{\psi}\boldsymbol{\eta}(0))_{T,\Omega},\end{aligned}\tag{4.10}$$

where we used

$$\nabla_{y_l}\mathrm{u}^i_1=\partial_{y_r}(\partial_{y_l}y_r)\,\mathrm{u}^i_1=\delta_{lr}\partial_{y_r}\mathrm{u}^i_1=\delta_{lr}\partial_{y_r}\xi^{ij_l}\partial_{x_l}\mathrm{u}^j.\tag{4.11}$$

Denoting

$$\mathbb{S}^0(\mathbf{u}):=\left\{s^0_{i_kj_l}(\mathbf{u})\right\}_{i_kj_l}:=\left\{\frac{1}{|Y|}\left(\left\{s_{i_kj_l}(\mathbf{y},\mathbf{u})+s_{i_kj_r}(\mathbf{y},\mathbf{u}),\partial_{y_r}\xi^{ij_l}(y)\right\}\right)_{Y_2}\right\}_{i_kj_l},\tag{4.12}$$

we conclude that $\mathbf{u}(\mathbf{t},\mathbf{x})$ satisfies the homogenized boundary value problem in the sense of the integral identity

$$-\theta_2(\mathbf{u},\boldsymbol{\psi}\mathbf{D_t}\boldsymbol{\eta})_{T,\Omega}+\left(\mathbb{S}^0(\mathbf{u})\boldsymbol{\nabla}\mathbf{u},\boldsymbol{\nabla}\boldsymbol{\psi}\boldsymbol{\eta}\right)_{T,\Omega}=(\mathbf{I}(\mathbf{u}),\mathbf{v})_{T,\Omega}-(\mathbf{h},\boldsymbol{\psi}\boldsymbol{\eta}(\mathbf{0}))_{T,\Omega}.\tag{4.13}$$

Now, rewriting (4.13) with $\boldsymbol{\eta}\in\mathbf{C}^\infty_0([\mathbf{0},\mathbf{T}[)$ we see that $\mathbf{u}$ satisfies $(3.4)_1$ in the sense of distributions and by density also in the weak sense.

5. Proof of Theorem 3.3

In the following, we only consider the convergence with respect to the new terms. We follow the proof in Section 4.

Step 1: (*Derivation of the reference cell problem*) Let $\mathbf{u}^s$ be a weak solution in the sense of Definition 2.2 satisfying the integral identity

$$(\mathbf{D_t u}_s,\mathbf{v})+(\mathbb{S}^s(\mathbf{u}_s)\boldsymbol{\nabla}\mathbf{u}_s,\boldsymbol{\nabla}\mathbf{v})+(\mathbf{b}^s(\mathbf{u}_s)\mathbf{u}_s,\boldsymbol{\nabla}\mathbf{v})=(\mathbf{I}(\mathbf{u}_s),\mathbf{v}),\qquad \forall\mathbf{v}\in\mathbf{H}^1(\boldsymbol{\Omega}),\quad (5.1)$$

where we used the fact that $\mathbf{b}^s(\mathbf{u}_s)=\mathbf{0}$ on $\partial\boldsymbol{\Omega}_T$. Take $\mathbf{v}(\mathbf{t},\mathbf{x}):=s\boldsymbol{\psi}(\mathbf{x})\boldsymbol{\Psi}(\mathbf{x}/s)\boldsymbol{\eta}(\mathbf{t})$, where $\boldsymbol{\psi}\in\mathbf{C}^\infty(\boldsymbol{\Omega})$ and $\boldsymbol{\Psi}(\mathbf{y})$ is smooth and 1-periodic with respect to $\mathbf{y}$ and $\boldsymbol{\eta}(\mathbf{t})\in\mathbf{C}^1(]\mathbf{0},\mathbf{T}[)$ with $\eta^i(T)=0$ for $i=2,3,4$. This induces for the convective term $(\mathbf{b}^s(\mathbf{u}_s)\mathbf{u}_s,\boldsymbol{\nabla}\mathbf{v})$ the following relation:

$$\begin{aligned}s(\mathbf{b}^s(\mathbf{u}_s)\mathbf{u}_s,\boldsymbol{\nabla}(\boldsymbol{\psi}(\mathbf{x})\boldsymbol{\Psi}(\mathbf{x}/s))\boldsymbol{\eta}(\mathbf{t}))_{T,\Omega}&=(\mathbf{b}^s(\mathbf{u}_s)\mathbf{u}_s,\boldsymbol{\psi}(\mathbf{x})\boldsymbol{\nabla}_y\boldsymbol{\Psi}(\mathbf{y})\boldsymbol{\eta}(\mathbf{t}))_{T,\Omega}\\&\quad+s(\mathbf{b}^s(\mathbf{u}_s)\mathbf{u}_s,\boldsymbol{\nabla}\boldsymbol{\psi}(\mathbf{x})\boldsymbol{\Psi}(\mathbf{y})\boldsymbol{\eta}(\mathbf{t}))_{T,\Omega}.\end{aligned}\quad (5.2)$$

In view of the strong convergence (2.9), we can now pass to the limit $s\to 0$ such that

$$(\mathbf{b}^s(\mathbf{u}_s)\mathbf{u}_s,\boldsymbol{\psi}(\mathbf{x})\boldsymbol{\nabla}_y\boldsymbol{\Psi}(\mathbf{y})\boldsymbol{\eta}(\mathbf{t}))_{T,\Omega}\to\frac{1}{|Y|}\big(\mathbf{b}^0(\mathbf{u})\mathbf{u},\boldsymbol{\psi}(\mathbf{x})\boldsymbol{\nabla}_y\boldsymbol{\Psi}(\mathbf{y})\boldsymbol{\eta}(\mathbf{t})\big)_{T,Y,\Omega}.\quad (5.3)$$

By (5.3), we obtain the relevant extension of the reference cell problem (4.7) for the case including fluid flow, i.e. for $2\le i\le 4$ and $2\le j\le 4$ we have

$$\begin{aligned}\big(s_{i_kj_l}(\mathbf{y},\mathbf{u})\nabla_{y_l}\xi^{ij_r}(y),\nabla_{y_k}\Psi^i(y)\big)_Y&=-\big(s_{i_kj_r}(\mathbf{y},\mathbf{u}),\nabla_{y_k}\Psi^i(y)\big)_Y\\&\quad-\big((\mathrm{b}^{i_k})^0(\mathbf{u})\mathbf{u},\nabla_{y_k}\Psi^i(y)\big)_Y,\qquad\forall\Psi^i\in H^1_{per}(Y).\end{aligned}\quad (5.4)$$

The situation for Stokes flow ($i=1,j=1$) is treated in the usual way such that we immediately end up with the reference cell problem (2.16), except for the right-hand side $\mathbf{I}(\mathbf{u}_s)$; see (5.8) in Step 2 below.

Step 2: (*Passing to the limit* $s\to 0$) Before we start with the limit, let us give the appropriate integral formulation of the Stokes-Nernst-Planck-Poisson problem, i.e.

$$-(\mathbf{u}_s,\boldsymbol{\psi}\mathbf{D_t}\boldsymbol{\tau})_{T,\Omega}+(\mathbb{S}^s(\mathbf{u}_s)\boldsymbol{\nabla}\mathbf{u}_s,\boldsymbol{\nabla}\boldsymbol{\psi}\boldsymbol{\tau})_{T,\Omega}+(\mathbf{b}^s(\mathbf{u}_s)\mathbf{u}_s,\boldsymbol{\nabla}\boldsymbol{\psi}\boldsymbol{\tau})_{T,\Omega}=(\mathbf{I}(\mathbf{u}_s),\boldsymbol{\psi}\boldsymbol{\tau})_{T,\Omega},\quad (5.5)$$

where we have chosen the test function $\mathbf{v}:=\boldsymbol{\psi}\boldsymbol{\tau}$ for $\boldsymbol{\psi}\in\mathbf{H}^1(\boldsymbol{\Omega})$ and $\boldsymbol{\tau}\in\mathbf{C}^1(]\mathbf{0},\mathbf{T}[)$ with $\tau^i(T)=0$ for $i=1,2,3$ in the system (5.5). We recall that the test function ψ^1 satisfies $\psi^1(x,y)\in[C_0^\infty(\Omega;C^\infty_{per}(Y))]^N$ with $\psi^1(x,y)=0$ in $\Omega\times Y_1$, thus $\psi^1(x,x/s)\in[H_0^1(\Omega^s)]^N$. Furthermore, $\psi^1(x,y)$ satisfies the incompressibility conditions

$$\begin{aligned}\mathrm{div}_y\psi^1(x,y)&=0\qquad\text{in }\Omega\times Y,\\ \mathrm{div}_x\left[\int_Y\psi^1(x,y)\,dy\right]&=0\qquad\text{in }\Omega.\end{aligned}\quad (5.6)$$

For details about the derivation of Darcy's law we refer to [1, 20]. It leaves to consider the last two terms in (5.5) for passing to the limit as $s\to 0$. Let us start with the convective term. Due to strong convergence (2.9) of u_s^i in $L^2(\Omega)$ for $i=2,3$, we have

$$(\mathbf{b}^s(\mathbf{u}_s)\mathbf{u}_s,\boldsymbol{\nabla}\boldsymbol{\psi}\boldsymbol{\tau})_{T,\Omega}\quad\overset{s\to0}{\to}\quad\frac{1}{|Y|}\big(\mathbf{b}^0(\mathbf{u})\mathbf{u},\boldsymbol{\nabla}\boldsymbol{\psi}\boldsymbol{\tau}\big)_{T,Y,\Omega},\quad (5.7)$$

where $\mathbf{b}^0(\cdot) := \mathbf{b}^s(\cdot)$. To treat the right-hand side, we first rewrite it by

$$(\mathbf{I}(\mathbf{u}_s), \boldsymbol{\psi\tau})_{T,\Omega} = \mathbf{f}_1 \left(\left\{ -\nabla p_s - \eta \left(\mathrm{u}_s^2 - \mathrm{u}_s^3 \right) \nabla \mathrm{u}_s^4 \right\}, \psi^1 \tau^1 \right)_{T,\Omega} + \mathbf{f}_4 \left(\left(\mathrm{u}_s^2 - \mathrm{u}_s^3 \right), \psi^4 \tau^4 \right)_{T,\Omega}. \tag{5.8}$$

Since the term with $\mathbf{f}_1$ is not just an independent external force, we also need to pass to the limit in this term. By applying the two-scale convergence property $(4.3)_2$, we get

$$\eta \left(\left(\mathrm{u}_s^2 - \mathrm{u}_s^3 \right) \nabla \mathrm{u}_s^4, \psi^1 \tau^1 \right)_{T,\Omega} \xrightarrow{2} \frac{\eta}{|Y|} \left(\left(\mathrm{u}^2 - \mathrm{u}^3 \right) \left\{ \nabla \mathrm{u}^4 + \nabla_y \mathrm{u}_1^4 \right\} \chi_{Y_2}, \psi^1 \tau^1 \right)_{T,Y,\Omega}. \tag{5.9}$$

In fact, that means that the force $\bar{\mathrm{f}}$ in $(2.17)_1$ becomes $\mathrm{f}_k^0(\mathbf{u}) := -\eta \left(\mathrm{u}^2 - \mathrm{u}^3 \right) \frac{1}{|Y|} \left(1 + \delta_{kl} \partial_{y_l} \xi^{44_k}, 1 \right)_{Y_2} \partial_{x_k} \mathrm{u}^4$, and hence with Darcy's law $(2.17)_1$ and (2.18), the right-hand side reads in the limit as

$$\mathbf{I}(\mathbf{u}) := \left[\left\{ -\mathrm{v}^k + \mathrm{k}_{kl} \left(\mathrm{f}_0^l(\mathbf{u}) - \partial_{x_l} p \right) \right\}_{1 \le k \le N}, 0, 0, \theta_2 \left(\mathrm{u}^2 - \mathrm{u}^3 \right) \right]'. \tag{5.10}$$

The Equation (5.10) indicates that we have to redefine the material tensor $\mathbb{S}(\mathbf{u})$ by shifting the coefficients $1 \le i, j \le 3$ by $+1$ and by setting

$$s_{i1}^0 = s_{1j}^0 := 0, \qquad \text{for } i, j = 1, 2, \ldots, 4. \tag{5.11}$$

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