

# HOMOGENIZATION OF THE POISSON-NERNST-PLANCK EQUATIONS FOR ION TRANSPORT IN CHARGED POROUS MEDIA \*

MARKUS SCHMUCK<sup>†</sup> AND MARTIN Z. BAZANT<sup>‡</sup>

**Abstract.** Effective Poisson-Nernst-Planck (PNP) equations are derived for macroscopic ion transport in charged porous media. Homogenization analysis is performed for a two-component periodic composite consisting of a dilute electrolyte continuum (described by standard PNP equations) and a continuous dielectric matrix, which is impermeable to the ions and carries a given surface charge. Three new features arise in the upscaled equations: (i) the effective ionic diffusivities and mobilities become tensors, related to the microstructure; (ii) the effective permittivity is also a tensor, depending on the electrolyte/matrix permittivity ratio and the ratio of the Debye screening length to mean pore size; and (iii) the surface charge per volume appears as a continuous “background charge density”. The coefficient tensors in the macroscopic PNP equations can be calculated from periodic reference cell problem, and several examples are considered. For an insulating solid matrix, all gradients are corrected by a single tortuosity tensor, and the Einstein relation holds at the macroscopic scale, which is not generally the case for a polarizable matrix. In the limit of thin double layers, Poisson’s equation is replaced by macroscopic electroneutrality (balancing ionic and surface charges). The general form of the macroscopic PNP equations may also hold for concentrated solution theories, based on the local-density and mean-field approximations. These results have broad applicability to ion transport in porous electrodes, separators, membranes, ion-exchange resins, soils, porous rocks, and biological tissues.

**Key words.** diffusion, electromigration, porous media, membranes, Poisson-Nernst-Planck equations, homogenization

**AMS subject classifications.**

**1. Introduction.** The theory of electrochemical transport in free solutions is well developed [56, 64, 68], but in many practical situations, ions move through porous microstructures with internal surface charge. Important examples in biology include nerve impulse propagation in the porous intracellular matrix of an axon [84], selective ion transport through protein-based ion channels in cell membranes [29, 67], and the electroporation of porous tissues for drug delivery and medical diagnostics [83]. In chemical engineering, the selective transport of ions and charged particles through membranes, gels and porous media is widely used for particle separations [33], desalination and ion exchange [38, 64], characterization of porous rocks [69], energy conversion in fuel cells [60] and energy storage in batteries [55] and electrochemical supercapacitors [26]. Analogous nanoscale transport phenomena are also beginning to be exploited in microfluidic devices [20, 75], which involve artificial porous structures with precisely controlled geometries and surface properties.

In *microscopic* continuum models of electrolytes, the ionic fluxes are given by the Nernst-Planck equations describing diffusion and electromigration in the mean electric field, which is determined self-consistently from the mean ionic charge density via Poisson’s equation. The resulting Poisson-Nernst-Planck (PNP) system has been studied extensively for the past century in the dilute solution approximation, not only for electrolytes [8, 10, 30], but also for semiconductors, where electrons and holes

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<sup>†</sup>Departments of Chemical Engineering and Mathematics, Imperial College, London, UK

<sup>‡</sup>Departments of Chemical Engineering and Mathematics, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

behave like anions and cations, respectively [52]. The dilute-solution PNP equations can be derived rigorously from stochastic Langevin equations for the motion of point-like ions [54].

Recently, a variety of modified PNP equations for concentrated solutions have been developed to describe strong interactions of finite-sized ions with charged surfaces at the nanoscale, as reviewed by [11]. Hard-sphere density functional theory [34, 35] and simpler mean-field models [43, 61] have been used to modify the Nernst-Planck equations for ionic fluxes to account for steric hindrance. Poisson’s equation has also been modified to account for electrostatic correlations [12, 22, 36, 70], explicit treatment of solvent dipoles [44] and solvation energy variations due to nonuniform permittivity [82]. All of these developments improve the microscopic description of ion transport close to charged surfaces, but our focus here is on the homogenization of such models over a charged microstructure to derive effective PNP equations valid at the *macroscopic* scale.

There is a long history of heuristic models for macroscopic ion transport in charged membranes and porous media, dating back at least to the 1930s [80]. A classical concept in membrane science, which we place on a rigorous footing below for general porous media, is the notion of a fixed “background charge” entering Poisson’s equation, due to the volume-averaged surface charge of the porous medium [38]. In nanoporous membranes, the double layers are thick compared to the pore thickness, so that there are only small variations in diffuse ionic charge between the fixed surface or molecular charges. For most porous media, however, the double layers are assumed to be thin, leaving the pore spaces to be mostly filled with neutral solution, and Poisson’s equation is replaced by electroneutrality, without accounting for the background charge. In electrochemistry, this is a fundamental assumption of “porous electrode theory” (PET), introduced by Newman and Tobias [57], which postulates electroneutrality within the pores and effective Nernst-Planck equations of the same form as in the bulk solution, except for an empirical tortuosity factor multiplying the ionic diffusivities. This approach has been applied extensively to batteries [27, 45, 55, 56]. The nonlinear effects of double layer charging [10] have also recently been incorporated into PET to model capacitive desalination and energy storage [13, 15]. The assumptions of PET have been tested against large-scale numerical solutions of the microscopic transport equations in certain cases of realistic microstructures [31, 32], but mathematical derivations are still needed to predict the form of the macroscopic equations and to provide a systematic method to calculate their coefficients. This is the goal of the present work.

We are not aware of any prior attempts to rigorously homogenize the PNP equations in charged porous microstructures, in spite of the many important applications listed above. Some formal derivations of PET have suggested such connections [13, 45], but without treating diffuse charge explicitly or relating macroscopic coefficients to the microstructure. For neutral species, the homogenization of linear diffusion over porous microstructures is well developed, and rigorous bounds are available for the effective macroscopic diffusivity tensor over all possible microstructures [81]. Homogenization methods have also been applied to simplified models of ion transport, but not the full nonlinear PNP equations. Moyne and Murad [53] assume a Boltzmann equilibrium distribution of ions in a binary electrolyte at the pore scale and perform a homogenization analysis to derive effective equations for deformable porous media. Looker and Carnie [48] make the same approximation of microscopic Boltzmann equilibrium and derive symmetric Onsager relations for linear response, without stating

the general effective equations at the macroscopic scale. Allaire et al. [3] revisit the derivation of Looker and Carnie [48] using two-scale convergence methods developed by Nguetseng [58] and Allaire [1] (as we also use here) and prove the positive definiteness of the Onsager tensor, but they make explicit use of an electroneutrality assumption. Although these studies simplify the treatment of diffuse charge in the pores, they do account for fluid flow coupled to ion transport. This leads to many complex electrokinetic phenomena in porous media and membranes [39], whose macroscopic mathematical description has been developed for decades [17, 38, 72, 77, 85], albeit without the aid of rigorous homogenization methods that connect the microstructure to the macroscopic transport coefficients.

In this article, we derive porous-media PNP equations for charged microstructures using two-scale homogenization methods. We extend the analysis of [74] for the PNP-Stokes equations in uncharged dielectric porous media to account for the crucial, nonlinear influence of surface charge on the pore walls, although we neglect fluid flow. In the limit of thin double layers for isotropic media, our effective equations have the same classical form as those recently used by [28, 37, 50, 65, 78] for nanochannels, where the potential is determined implicitly by macroscopic electroneutrality, including not only the ions, but also the surface charge. Helfferich [38] credits Oel [59] with the formal justification of this approximation for charged porous media with thin double layers. Here, we derive more general PNP equations, valid for any double layer thickness, which preserve the form of Poisson's equation with a modified effective permittivity, where the electric field is produced by the total charge density. Our mathematical approach also provides a systematic means to calculate the tensorial coefficients in the macroscopic equations for a given microstructure.

The article is organized as follows. We begin in Section 2 by recalling the PNP equations for homogeneous bulk solutions, and we summarize our results for porous-media PNP equations in section 3. We summarize the mathematical derivation using the two-scale convergence method in Section 4. In section 5, we briefly discuss the effective diffusivity and mobility tensors and investigate the validity of Einstein's relation between them. We illustrate our results for straight channels in Section 6 and irregular channels in Section 7. We discuss definitions of tortuosity in Section 8 and derive the general ambipolar diffusion equation for a binary electrolyte in a charged porous medium in section 9, following Mani and Bazant [49]. In Sections 10 and 11, we take the limits of thin and thick double layers in the porous-media PNP equations, respectively. In Section 12, we perform a simple microstructural optimization of the effective conductivity of a symmetric binary electrolyte for the case of parallel straight channels. In Section 13, we conclude by discussing possible extensions and applications of our homogenized PNP equations.

## 2. Poisson-Nernst-Planck equations for homogeneous media .

**2.1. Dilute solution theory .** For simplicity, in this article we will perform most of our analysis for dilute, completely dissociated  $z : z$  electrolytes, focusing on their appropriate mathematical description in charged porous materials. We emphasize, however, that our results are by no means limited to symmetric binary electrolytes and can be easily extended to multicomponent, asymmetric electrolytes. We adopt well studied mathematical framework for dilute binary electrolytes [10, 11, 25, 42, 43, 61], which can also be used to describe general concentrated solutions (below) The concentrations of the ions  $c^\pm(x, t)$  evolve according to mass con-

servation laws

$$\partial_t c^\pm = -\operatorname{div} \left( -c^\pm M_\pm \nabla \mu_\pm \right), \quad (2.1)$$

where the classical Nernst-Planck fluxes (in parentheses) can be expressed in terms of the gradients of the ionic chemical potentials, given by dilute solution theory,

$$\mu_\pm = kT \ln c^\pm + z_\pm e \phi. \quad (2.2)$$

For electrolytes (but not semiconductors) it is customary to neglect homogeneous generation and recombination reactions, since charge transfer reactions tend to occur at interfaces. The variable  $\phi$  is the electrostatic potential, which describes the Coulomb interaction in a mean-field approximation. The coefficients  $D_\pm$  are the (tracer) diffusivities of the two ionic species. The mobilities,  $M_\pm$ , which give the drift velocity in response to an applied force, are then obtained by the Einstein relation  $M_\pm = \frac{D_\pm}{kT}$ . The total mean ionic charge density  $\rho$  controls the spatial variation of the potential  $\phi$  through Poisson's equation,

$$-\epsilon_s \Delta \phi = \rho := ze(c^+ - c^-), \quad (2.3)$$

where  $\epsilon_s$  is the dielectric permittivity of the solution (roughly equal to that of the solvent), assumed to be a constant. The essence of the mean-field approximation is that each ion drifts in response to the electric field self-consistently produced by the mean charge density. For simplicity, we will mainly restrict ourselves to the case of a common diffusivity  $D = D_+ = D_-$  and mobility  $M = M_+ = M_-$ .

In preparation for analyzing the full, nonlinear problem in a porous medium, we cast the equations in a dimensionless form using  $\ell$  as the reference length scale and  $t_D = \ell^2/D$  as the reference time scale. We use the thermal voltage  $\frac{kT}{e}$  as a scale for the electric potential. We introduce the reduced variables

$$\tilde{c}^+ = \frac{c^+}{\bar{c}}, \quad \tilde{c}^- = \frac{c^-}{\bar{c}}, \quad \tilde{\phi} = \frac{ze\phi}{kT}, \quad \tilde{x} = \frac{x}{\ell}, \quad \tilde{t} = \frac{t}{t_D}, \quad \tilde{\nabla} = \ell \nabla, \quad (2.4)$$

where  $\bar{c}$  a reference concentration of ions, such as the nominal salt concentration of a quasi-neutral bulk electrolyte prior to its perfusion in the porous medium. The reference solution could be removed, or maintained in contact with the porous medium as a reservoir of ions at the reference concentration. We thus arrive at dimensionless Poisson-Nernst-Planck equations containing only the dimensionless parameter  $\epsilon = \frac{\lambda_D}{\ell}$ ,

$$\begin{aligned} \partial_{\tilde{t}} \tilde{c}^+ &= \operatorname{div} \left( \tilde{\nabla} \tilde{c}^+ + \tilde{c}^- \tilde{\nabla} \tilde{\phi} \right), \\ \partial_{\tilde{t}} \tilde{c}^- &= \operatorname{div} \left( \tilde{\nabla} \tilde{c}^- - \tilde{c}^+ \tilde{\nabla} \tilde{\phi} \right), \\ -\epsilon^2 \tilde{\Delta} \tilde{\phi} &= \tilde{c}^+ - \tilde{c}^-, \end{aligned} \quad (2.5)$$

where  $\lambda_D$  is the Debye screening length of the reference solution, defined by  $\lambda_D := \left( \frac{\epsilon_s kT}{2e^2 \bar{c}} \right)^{1/2}$  for a symmetric binary electrolyte.

In the subsequent sections, we also work with the dimensionless charge density  $\tilde{\rho}$  and total ion concentration  $\tilde{c}$ , which are defined by

$$\tilde{c} = \frac{c^+ + c^-}{2\bar{c}}, \quad \tilde{\rho} = \frac{c^+ - c^-}{2\bar{c}}, \quad (2.6)$$

respectively [8, 10]. In terms of these dimensionless variables (2.6), the PNP equations take an elegant symmetric form,

$$\begin{aligned}\partial_{\tilde{t}}\tilde{c} &= \tilde{\text{div}}\left(\tilde{\nabla}\tilde{c} + \tilde{\rho}\tilde{\nabla}\tilde{\phi}\right), \\ \partial_{\tilde{t}}\tilde{\rho} &= \tilde{\text{div}}\left(\tilde{\nabla}\tilde{\rho} + \tilde{c}\tilde{\nabla}\tilde{\phi}\right), \\ -\epsilon^2\tilde{\Delta}\tilde{\phi} &= \tilde{\rho}.\end{aligned}\tag{2.7}$$

This formulation is not only mathematically convenient, but also provides physical insight by distinguishing between dynamical phenomena involving diffuse charge, such as capacitive charge storage and surface conduction, and those involving neutral salt transport, such as bulk diffusion, surface diffusion and capacitive desalination [10, 13, 24, 25, 61]. This formulation is also useful in the analysis of Frumkin double-layer effects on Faradaic electron-transfer reaction kinetics [8, 15, 16].

In our analysis below, we shall use dimensionless equations and drop the tilde accents for ease of notation.

**2.2. Concentrated solution theories .** In a concentrated solution, various physical effects contribute an excess chemical potential of an ion,  $\mu_i^{ex}$ , beyond that of a dilute solution (2.2),

$$\mu_i = kT\ln c^i + z_i e\phi + \mu_i^{ex} = kT\ln(\gamma_i c^i) + z_i e\phi\tag{2.8}$$

where we also define the molar activity coefficient  $\gamma_i = \exp(\mu_i^{ex}/kT)$ , and the diffusivity and mobility may also contain nonlinear modifications [11]. The excess chemical potential is generally a non-local functional of the ion concentrations and potential, which can be treated using statistical density functional theory [34] or the weighted-density approximation [47], leading to integro-differential equations. In the local-density approximation (LDA), the excess chemical potential depends only pointwise on the ion concentrations, and the model leads to partial differential equations. The LDA becomes exact in a uniform bulk solution, but it is also widely used in the presence of strong concentration gradients, although not always maintaining accuracy. Classical concentrated solution theory [56] assumes a neutral bulk solution, and the concentration-dependence of the activity coefficient and diffusivity are left for empirical fitting to experimental data. Alternatively, concentrated solution models can be derived from various microscopic physical assumptions, as in charged hard-sphere or lattice-gas models [11].

### 3. Homogenized Poisson-Nernst-Planck equations for porous media.

**3.1. Microscopic model.** Our derivation begins with a periodic representation of the microstructure and uses a formal two-scale convergence method to derive effective equations valid at scales much larger than the geometrical period, as sketched in Figure 3.1. Schmuck [74] recently applied this approach to derive effective PNP equations for ion transport with convection in uncharged porous media. The extension to fluid flow for the full nonlinear PNP equations in a charged microstructure is still lacking a consistent derivation, as pointed out in [73]. Indeed, the classical theory of electrokinetic phenomena in porous media (e.g. streaming potential, electro-osmotic flow, diffusio-osmosis) assumes linear response to small perturbations [39], but it has only recently been understood that many nonlinear electrokinetic phenomena, such as second-kind electro-osmotic flows [46, 79], induced-charge electro-osmotic flows [9],

deionization shocks [49, 50], and surface-driven over-limiting current [28], can arise due to the coupling between ion transport and surface charge in microstructures. Hence, we neglect flow, but we allow for a fixed surface charge density on the solid or molecular matrix. In the following sections, we emphasize physical implications and provide some illustrative examples.

Suppose that the heterogeneities, i.e. the size of the pores defined by a reference cell  $Y$ , as for example in Figure 6.1 left (in 2D), are very small with respect to the size of the porous medium denoted by  $\Omega \subset \mathbb{R}^d$ ,  $1 \leq d \leq 3$ , 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, one can first compute the averaged pore structure of a suitable periodic replacement by a so-called Y-Algorithm, see [74]. The periodicity can be represented by a small parameter  $r$  and hence the porous subset  $\Omega^p$  of  $\Omega$  is then denoted by  $\Omega_r^p$  and correspondingly the solid subset  $\Omega^s$  by  $\Omega_r^s := \Omega \setminus \Omega_r^p$ . For the moment, we assume that the solid-electrolyte interface  $I_r := \partial\Omega_r^p \cap \partial\Omega_r^s$  is smooth. Further, we suppose that we are given a reference period  $Y$ , in which the reference heterogeneities are defined, see Figure 6.1 left (in 2D) respectively Figure 6.1 right (in 3D). The pores in  $\Omega$  are periodic of period  $rY$  and their size is of order  $r$ . The concentration densities  $c^\pm$  have to be solved only in the domain of the liquid phase which is the perforated domain  $\Omega_r^p = \Omega \setminus \Omega_r^s$ . Then, for the scaling parameter  $r > 0$ , the positive ion density  $c_r^+$ , negative ion density  $c_r^-$ , and the electrostatic potential  $\phi_r$  are governed by the equations

$$\text{(micro PNP)} \quad \begin{cases} \partial_t c_r^+ = \operatorname{div}(\nabla c_r^+ + c_r^- \nabla \phi_r) & \text{in } \Omega_r^p, \\ \partial_t c_r^- = \operatorname{div}(\nabla c_r^- - c_r^+ \nabla \phi_r) & \text{in } \Omega_r^p, \\ -\operatorname{div}(\varepsilon(x/r) \nabla \phi_r) = c_r^+ - c_r^- & \text{in } \Omega := \Omega_r^p \cup \Omega_r^s, \end{cases} \quad (3.1)$$

where  $\varepsilon(x) := \epsilon^2 \chi_{\Omega_r^p}(x) + \alpha \chi_{\Omega_r^s}(x)$ ,  $\epsilon := \frac{\lambda_D}{\ell}$  the dimensionless Debye length, and  $\alpha := \frac{\varepsilon_s}{\varepsilon_p}$  the dimensionless electric permittivity of the solid material  $\varepsilon_s$  scaled to that of the pore phase  $\varepsilon_p$ . The system (3.1) is completed by the boundary conditions

$$\begin{aligned} \nabla_n c_r^+ + c_r^- \nabla_n \phi_r &= 0 & \text{on } I_r := \partial\Omega_r^p \cap \partial\Omega_r^s, \\ \nabla_n c_r^- - c_r^+ \nabla_n \phi_r &= 0 & \text{on } I_r, \\ -\varepsilon(x/r) \nabla_n \phi_r &= \sigma_s(x/r) & \text{on } I_r, \end{aligned} \quad (3.2)$$

where  $\sigma_s(x/r)$  is a periodic surface charge density. Since we describe the solid-electrolyte composite by macroscopic respectively continuous variables, we do not model the surface charge by a jump boundary condition. In Figure 3.1, we illustrate the periodic formulation (3.1)–(3.2), which allows to introduce a periodic reference cell  $Y := Y^p \cup Y^s$  capturing the pore geometry.

**3.2. Macroscopic approximation .** A formal application of the two-scale convergence allows to derive the following upscaled equations describing electrolytes in porous media for fixed surface charge. The basic idea is an asymptotic approximation of the form

$$\begin{aligned} c_r^\pm(t, x) &\approx (1 + r \delta_{c^\pm}^l(x/r) \partial_{x_i} + \mathcal{O}(r^2)) c_0^\pm(t, x), \\ \phi_r(t, x) &\approx (1 + r \delta_\phi^l(x/r) \partial_{x_i} + \mathcal{O}(r^2)) \phi_0(t, x), \end{aligned} \quad (3.3)$$

where Einstein's summation convention is applied over repeated indices and the microscopic variable  $y = x/r \in Y$  is used. We point out that the series in (3.3) are

**Macro scale:  $(x_1, x_2)$**

**Micro scale:  $(y_1, y_2)$**

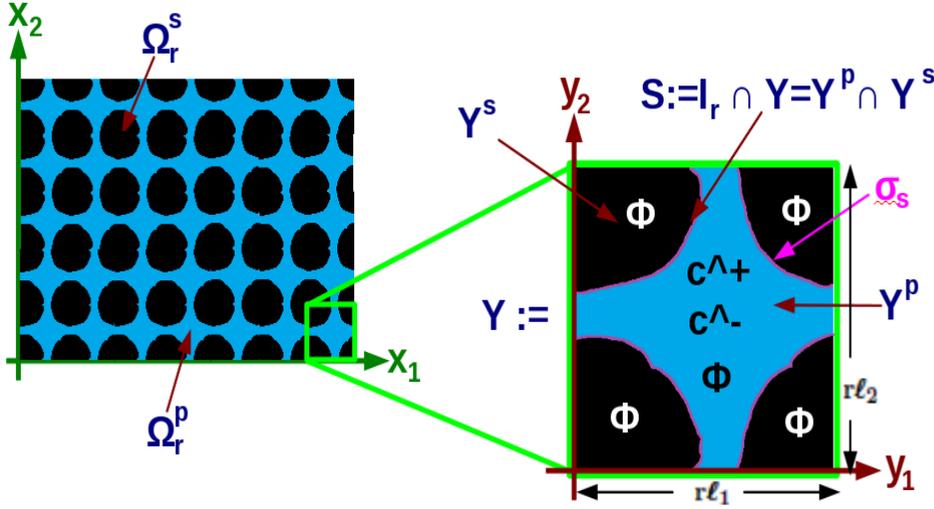


FIGURE 3.1. **Left, macro scale:** Domain  $\Omega := \Omega_r^p \cup \Omega_r^s$  with the solid-liquid interface  $I_r := \partial\Omega_r^p \cap \partial\Omega_r^s$ . **Right, micro scale:** Reference cell  $Y := Y^p \cup Y^s := [0, \ell_1] \times [0, \ell_2]$  with solid-liquid interface  $S := Y^p \cap Y^s = I_r \cap Y$ . The micro scale is obtained by rescaling the macro scale with the parameter  $r$  which measures the characteristic size of the heterogeneities. The upscaling or averaging process then consists in passing to the limit  $r \rightarrow 0$ , i.e. the electrolyte and the solid phase are homogeneously mixed under keeping the corresponding volume fractions constant.

not necessarily convergent. By  $Y$  we denote the reference cell which captures the geometric and interfacial information of the microstructure.

It is important to stress that we use dimensionless length and time variables (2.4) scaled to the characteristic length and time scales for diffusion across a reference cell at the scale of individual pores. This is convenient for homogenization and allows us to vary the Debye length relative to the mean pore size (below). In applications of the macroscopic PNP equations obtained by homogenization, however, it is better to rescale length and time according to the scales of bulk diffusion across  $r^{-1} \gg 1$  reference cells over a length  $L = \ell/r$  in terms of the following macroscopic dimensionless variables:

$$\bar{\epsilon} = \frac{\lambda_D}{L} = r\epsilon, \quad \bar{x} = \frac{x}{L} = r\tilde{x}, \quad \bar{\nabla} = L\nabla = r^{-1}\tilde{\nabla}, \quad \bar{t} = \frac{tD}{L^2} = r^2\tilde{t} \quad (3.4)$$

This rescaling will be useful below when we consider the limit of thick double layers compared to the pore size ( $\epsilon \ll 1$ ), which could be thin ( $\bar{\epsilon} \ll 1$ ) or thick ( $\bar{\epsilon} \gg 1$ ) at the macroscopic geometrical scale.

Without further details, we directly state here the main result which extends the derivations in [74] to the case of charged porous materials. We further generalize [74] under local thermodynamic equilibrium as achieved in [73]. The following definition guarantees the well-posedness of the effective porous media approximation subsequently presented. It can also be justified on both physical and mathematical grounds by the assumed separation of the macroscopic and microscopic length scales, analogous to the quasi-equilibrium approximation for thin double layers.

DEFINITION 1. (Local thermodynamic equilibrium in dilute solutions) *We say that for dilute solutions the reference cells  $Y$  are in local thermodynamic equilibrium if and only if,*

$$\mu_0^i := \log c^i(t, x) + z_i \phi(t, x) = \text{const.} \quad \text{in } x/s = y \in Y, \quad (3.5)$$

where  $\mu_0^i$  denotes a constant value of the chemical potential of positive ( $i = +$ ) and negative ( $i = -$ ) ion densities and  $z_{\pm} := \pm 1$ . The locally constant potential  $\mu_0^i$  can assume different values in different reference cells.

REMARK 1. *We emphasize that the equilibrium condition (3.5) specifically accounts for dilute solutions. For the more general concentrated solution theory, a corresponding equilibrium is defined in (2.8).*

Under local thermodynamic equilibrium, the effective positive ion density  $c^+$ , effective concentration of negative ions  $c^-$ , and the effective electric potential  $\phi$  are determined by

$$\text{(macro PNP)} \quad \begin{cases} p \partial_t c^+ = \text{div} \left( \hat{D} \nabla c^+ + c^- \hat{M} \nabla \phi \right), & \text{in } \Omega, \\ p \partial_t c^- = \text{div} \left( \hat{D} \nabla c^- - c^+ \hat{M} \nabla \phi \right), & \text{in } \Omega, \\ -\text{div} (\hat{\varepsilon}(\epsilon, \alpha) \nabla \phi) = p(c^+ - c^-) + \rho_s, & \text{in } \Omega, \end{cases} \quad (3.6)$$

where  $\rho_s := \frac{1}{|Y|} \int_{\partial Y_1 \cap \partial Y_2} \sigma_s d\sigma(y)$  is the total surface charge per volume (which plays the role of the “background charge” in classical membrane and semiconductor models),  $\alpha := \frac{\epsilon_s}{\epsilon_p}$  is the permittivity ratio,  $\epsilon := \sqrt{\frac{\epsilon_p k T}{2 e^2 C_0}} / \ell$  is the dimensionless Debye length (measuring the thickness of the double layers), and the different tensors  $\hat{D} := \{d_{kl}\}_{1 \leq k, l \leq d}$ ,  $\hat{M} := \{m_{kl}\}_{1 \leq k, l \leq d}$ , and  $\hat{\varepsilon}(\epsilon, \alpha) := \{\varepsilon_{kl}(\epsilon, \alpha)\}_{1 \leq k, l \leq d}$  are defined by

$$\begin{aligned} d_{kl} &= \frac{1}{|Y|} \int_{Y^s} \{ \delta_{kl} - \delta_{kj} \partial_{y_j} \xi^{ii}(y) \} dy \quad \text{for } i = 1, 2, \\ m_{kl} &= \frac{1}{|Y|} \int_{Y^s} \{ \delta_{kl} - \delta_{kj} \partial_{y_j} \xi^{33i}(y) \} dy \quad \text{for } i = 1, 2, \\ \varepsilon_{kl}(\epsilon, \alpha) &= \frac{\lambda^2}{|Y|} \int_{Y^s} \{ \delta_{kl} - \delta_{kj} \partial_{y_j} \xi^{33i}(y) \} dy + \frac{\alpha}{|Y|} \int_{Y \setminus Y^s} \{ \delta_{kl} - \delta_{kj} \partial_{y_j} \xi^{33i}(y) \} dy. \end{aligned} \quad (3.7)$$

The corrector functions  $\xi^{ii_r}$  solve for  $i = 1, 2, 3$  and  $1 \leq r \leq d$  the reference cell problems

$$\left\{ \begin{array}{ll} -\Delta_y (\xi^{ii_r} - y_r) = -\Delta_y (\xi^{33_r} - y_r) & \text{in } Y^s, \\ (-\nabla_y (\xi^{ii_r} - y_r) + \nabla_y (\xi^{33_r} - y_r)) \cdot \mathbf{n}_I = 0 & \text{on } I := \partial Y^s, \\ \xi^{ii_r} \text{ is } Y^s\text{-periodic and } \mathcal{M}_{Y^s}(\xi^{ii_r}) = 0, & \\ -\text{div}_y (\hat{\varepsilon}(y) \nabla_y (\xi^{33_r} - y_r)) = 0 & \text{in } Y, \\ \xi^{33_r} \text{ is } Y\text{-periodic and } \mathcal{M}(\xi^{33_r}) = 0. & \end{array} \right. \quad (3.8)$$

As a consequence of (3.8), it holds  $\xi^{11_r} = \xi^{22_r}$ . The quantity  $\partial Y^s$  denotes the boundary of the solid phase in the reference cell  $Y = Y^s \cup Y^p$  and is part of the interface  $I$  on the domain  $\Omega$ , see for example Figure 6.1 left. The subset  $Y^s$  denotes the solid phase (black in Figure 3.1) and  $Y^p$  the electrolyte phase (blue in Figure

3.1). Furthermore, the effective tensors (3.7)<sub>1</sub>–(3.7)<sub>2</sub> contain relevant macroscopic corrections defined by the microscopic pore structure. We remark that the corrector  $\varepsilon_{kl}(\epsilon, \alpha)$  for the Poisson equation (3.6)<sub>3</sub> is equal to  $\hat{D}_{kl}$  defined in (3.7)<sub>1</sub>, if and only if we assume that the electric field only exists in the electrolyte phase. Such an assumption is equivalent to the limit  $\alpha \rightarrow 0$ , see Section (3.6). The correction tensor  $\hat{D}_{kl}$  can only be motivated analytically in the case of straight channels, see Section 6 and [5]. Already for perturbed straight channels, a numerical approach is required to solve the reference cell problem (3.8). We refer to Section 7 and [6] for further details.

Finally, we motivate that the assumption of local thermodynamic equilibrium (3.5) guarantees solvability of the reference cell problem (3.8). As demonstrated in [73], (3.8)<sub>1</sub> is obtained as the  $\mathcal{O}(r^{-1})$ -order problem for an asymptotic expansion (3.3). That means, for arbitrary smooth test functions  $\Psi^i$ ,  $i = 1, 2$ , we first obtain

$$\sum_{k,l=1}^N \left\{ \left( (\delta_{kl} \partial_{y_l} \xi^{i i_r}, \partial_{y_k} \Psi^i)_{Y^s} - (\delta_{kr}, \partial_{y_k} \Psi^i)_{Y^s} \right) \partial_{x_r} c^i + \left( (c^i \delta_{kl} \partial_{y_l} \xi^{33r}, \partial_{y_k} \Psi^i)_{Y^s} - (c^i \delta_{kr}, \partial_{y_k} \Psi^i)_{Y^s} \right) z_i \partial_{x_r} \phi \right\} = 0 \quad \text{for } i = 1, 2, \quad (3.9)$$

where  $c^1 = c^+$ ,  $c^2 = c^-$ ,  $z_1 = +1$ , and  $z_2 = -1$ . The notation  $(u, v)_D := \int_D uv \, dx$  denotes the scalar product in  $L^2(D)$ -sense with  $D = Y^s$ . In classical homogenization theory, one can immediately cancel out macroscopic quantities like  $\partial_{x_r} c^i$ . This is here not possible due to the additional gradient of the electric potential  $\partial_{x_r} \phi$ . Since we do not exactly know when  $\partial_{x_r} c^i(x, t)$  becomes zero, we cannot immediately apply Lax-Milgram's theorem or the Fredholm alternative in order to guarantee solvability of (3.9). But under the local equilibrium assumption (3.5), we are able to remove the macroscopic quantities  $\partial_{x_r} c^i$  and  $z_i \partial_{x_r} \phi$  such that we end up with equation (3.8)<sub>1</sub>. Solvability of (3.8)<sub>1</sub> then immediately follows via Lax-Milgram's theorem.

**3.3. Einstein relations.** The upscaled PNP equations indicate that Einstein's relation between diffusion  $D$  and mobility  $M$  coefficient, i.e.,  $M = \frac{D}{kT}$ , does not hold with respect to the porous media correction tensors  $\hat{D}$  and  $\hat{M}$ . At first, this seems to be physically inconsistent, since we seem to lose the gradient flow structure (2.1) and a Boltzmann distribution for ion densities in equilibrium.

However, we point out that the tensors  $\hat{D}$  and  $\hat{M}$  are corrections to  $\nabla c^\pm$  and  $\nabla \phi$ , respectively, and not to diffusion and mobility coefficients. This important fact then motivates to define the mean field approximations

$$\begin{aligned} \overline{\nabla c^\pm} &:= \hat{D} \nabla c^\pm, \\ \overline{\nabla \phi} &:= \hat{M} \nabla \phi. \end{aligned} \quad (3.10)$$

It is immediately clear that the Einstein relation holds for the quantities (3.10), i.e.,  $kT D_\pm \overline{\nabla c^\pm} + M_\pm \overline{\nabla \phi} = M_\pm \overline{\nabla \mu}$  in dimensional variables. Moreover, via (3.10) we can define a mean field gradient of the chemical potential by

$$\overline{\nabla \mu} := \frac{\delta \mu}{\delta c^i} \overline{\nabla c^i} + \frac{\delta \mu}{\delta \phi} \overline{\nabla \phi} = \frac{\delta \mu}{\delta c^i} \hat{D} \nabla c^i + \frac{\delta \mu}{\delta \phi} \hat{M} \nabla \phi, \quad (3.11)$$

such that gradient flow (2.1) becomes,

$$\partial_t c^\pm = -\operatorname{div} \left( -c^\pm M \overline{\nabla \mu_\pm} \right), \quad (3.12)$$

where  $M = M_{\pm} = \frac{D_{\pm}}{kT}$ . We further remark that the mean field approximation (3.11) is only defined for the gradient of the chemical potential. This fact is a direct consequence of the Ansatz (3.3). As a consequence, the chemical potential  $\mu_{\pm}$  remains unchanged and hence Boltzmann's distribution for the ion densities still holds in thermodynamic equilibrium.

**3.4. Material tensor and Onsager relations.** In [74], it is shown that the definitions (3.7)<sub>1</sub>–(3.7)<sub>3</sub> allow to introduce a so-called effective material tensor

$$\hat{S}_{i_k j_l}(\mathbf{Q}) := \begin{bmatrix} \hat{D}_{kl} & 0 & Q^2 \hat{M}_{kl} \\ 0 & \hat{D}_{kl} & -Q^1 \hat{M}_{kl} \\ 0 & 0 & \hat{\epsilon}_{kl}(\epsilon, \alpha) \end{bmatrix}, \quad (3.13)$$

which allows to write (3.6) for the field vector  $\mathbf{Q} := [c^+, c^-, \phi]'$  and the right-hand side  $\mathbf{I}(\mathbf{Q}) := [0, 0, Q^1 - Q^2]'$  by

$$\partial_t \mathbf{Q} + \operatorname{div} \left( \hat{S}(\mathbf{Q}) \nabla \mathbf{Q} \right) = \mathbf{I}(\mathbf{Q}), \quad (3.14)$$

where  $\partial_t$  is the operator

$$\partial_t := \begin{bmatrix} \partial_t & 0 & 0 \\ 0 & \partial_t & 0 \\ 0 & 0 & 0 \end{bmatrix}, \quad (3.15)$$

and also  $\nabla$  and  $\operatorname{div}$  are correspondingly defined.

**REMARK 2.** *Let us point out the special case where the electric field only exists in the electrolyte phase. In such situations, the tensor  $\hat{\epsilon}_{kl}(\epsilon, \alpha)$  in (3.13) can be replaced by  $\epsilon^2 \hat{D}_{kl}$ , see Section (3.6).*

The material tensor (3.13) provides a “nonlinear equivalent” to the Onsager relations for situations apart from thermodynamic equilibrium. It is completely determined by the elementary cell  $Y$  as for example given in Figure 6.1 left (in 2D) and right (in 3D), respectively the equations (3.7)–(3.8). Such a reference cell represents the characteristic geometry of the porous material under consideration. The material tensor  $\hat{S}$  relates the gradients of concentrations and electric potential to their corresponding fluxes  $\mathbf{J} := [J_{c^+}, J_{c^-}, J_{\phi}]'$ , i.e.

$$\mathbf{J} = \hat{S}(\mathbf{Q}) \nabla \mathbf{Q}. \quad (3.16)$$

The classical Onsager reciprocal relations only hold true for a linearized material tensor (3.13). In fact, Allaire et al. [2] rigorously achieve the Onsager relations, first verified in Looker and Carnie [48], for a linearized and time-independent version of ionic transport in contrast to the full nonlinear problem considered here.

Next to the physical information gained by the transport parameters in the tensor (3.13), the effective equations (3.6) also prevent high-dimensional and hence computationally expensive problems. Such computationally demanding situations generally result by solving (2.5) over the real microstructure. In fact, the mesh for such computations is required to be smaller than the characteristic length scale  $r$  of the heterogeneities.

Let us mention that it is not possible to derive (3.6) by volume averaging or the representative volume method (RVM), since the system (2.5) is nonlinear. Moreover, it is not clear what is the right size of the test volumes with respect to which the

gradients and their corresponding fluxes are averaged. Also a possible dependence on a source term and boundary conditions, see (3.2)<sub>3</sub>, cannot be captured by such approaches. These reasons strongly motivate the effective equations (3.6) derived here by homogenization techniques.

**3.5. Reformulation of (3.6) for salt and charge variables.** Finally, we reformulate (3.6) for the physical quantities charge  $\rho$  and salt  $c$ , i.e.

$$\begin{aligned} p\partial_t\rho &= \operatorname{div}\left(\hat{D}\nabla\rho + c\hat{M}\nabla\phi\right), & \text{in } \Omega, \\ p\partial_tc &= \operatorname{div}\left(\hat{D}\nabla c + \rho\hat{M}\nabla\phi\right), & \text{in } \Omega, \\ -\operatorname{div}(\hat{\varepsilon}(\epsilon, \alpha)\nabla\phi) &= p\rho + \rho_s, & \text{in } \Omega, \end{aligned} \quad (3.17)$$

where we call  $\hat{\kappa} := \rho\hat{M}$  the macroscopic conductivity.  $\hat{D}$  and  $\hat{M}$  are microscopic correction tensors which contain the information about the pore geometry.

There is a growing body of recent theoretical and experimental work on ion transport in charged nanopores. If the Debye length is smaller than the pore radius, then continuum models can agree very well with experimental data [65]. The mathematical description of ion transport in various recent models [28, 49, 50, 66, 78] has a similar form as our porous-media PNP system (3.17), but without making any connection between the microstructure and the macroscopic coefficients in the equations. In particular, the hydrodynamic factors  $K_{i,d}$  and  $K_{i,c}$  used in [78] are not systematically derived and not defined by the pore geometry as  $\hat{D}$  and  $\hat{M}$  in (3.7) and (3.8). Moreover, the cross-sectional area averaging developed by [66] and [50] was only applied to straight, symmetric channels.

**3.6. Insulating porous matrix.** As indicated in Remark 2, the porous media correction  $\hat{\varepsilon}(\epsilon, \alpha)$  for the Poisson equation can be reduced to  $\hat{D}$  in the case of an insulating porous material. As a consequence, also  $\hat{M}$  reduces to  $\hat{D}$  and hence the material tensor (3.13) simplifies to

$$\hat{S}_{i_k j_l}(\mathbf{Q}) := \begin{bmatrix} \hat{D}_{kl} & 0 & Q^2\hat{D}_{kl} \\ 0 & \hat{D}_{kl} & -Q^1\hat{D}_{kl} \\ 0 & 0 & \epsilon\hat{D}_{kl} \end{bmatrix}. \quad (3.18)$$

Let us introduce the following coordinate transformation

$$\tilde{x} := \hat{D}^{-1/2}x, \quad (3.19)$$

where components of  $\tilde{x}$  admitting “ $\infty$ ” are subsequently to be treated as parameters. This coordinate transformation can also be interpreted from a more experimental view point, since there is a close relation to tortuosity and diffusivity, see Section 8 for details. With (3.19) the gradient  $\nabla_x$  and the divergence operator  $\operatorname{div}_x$  change with respect to the new coordinates to

$$\nabla_x = \hat{D}^{-1/2}\nabla_{\tilde{x}}, \quad \text{and} \quad \operatorname{div}_x = (\nabla_x)' = \operatorname{div}_{\tilde{x}}\hat{D}^{-1/2}. \quad (3.20)$$

Via (3.20), the tensor (3.18) can be written in this new coordinates  $\tilde{x}$  by

$$\hat{M}_{i_k j_l}(\tilde{\mathbf{Q}}) := \begin{bmatrix} 1 & 0 & \tilde{Q}^2 \\ 0 & 1 & -\tilde{Q}^1 \\ 0 & 0 & 1 \end{bmatrix}, \quad (3.21)$$

where  $\tilde{Q}(t, \hat{D}^{1/2}\tilde{x}) = Q(t, x)$ . Hence, the material tensor (3.18) takes the same form in the new coordinates  $\tilde{x}$  as the classical PNP equations for homogeneous media in the case of an insulating porous matrix. Moreover, the porous media equation (3.14) reads in the new coordinates as

$$\partial_t \tilde{Q} + \operatorname{div}_{\tilde{x}} \left( \hat{M}(\tilde{Q}) \nabla_{\tilde{x}} \tilde{Q} \right) = \mathbf{I}(\tilde{Q}). \quad (3.22)$$

Let us remark that the transformation (3.19) accounts for a finite separation of scales and can be generalized to the case of a continuum of scales by the idea of metric-based upscaling introduced in [62].

**3.7. Concentrated solution theory.** We briefly consider arbitrary chemical potentials (2.8) satisfying the local density approximation, i.e. depending only on local concentrations and the potential. In that case, the gradient flow (2.1) can be accordingly obtained for species  $c^i$  and electric potential  $\phi$ . To this end, we first compute the gradient of the chemical potential (2.2), i.e.

$$\nabla \mu(c^i, \phi) = \frac{\delta \mu}{\delta c^i} \nabla c^i + \frac{\delta \mu}{\delta \phi} \nabla \phi. \quad (3.23)$$

If the first variations  $\frac{\delta \mu}{\delta c^i}$  and  $\frac{\delta \mu}{\delta \phi}$  are linear, then the form of the upscaled equations can be verified as in Section 4. For nonlinear  $\frac{\delta \mu}{\delta c^i}$  and  $\frac{\delta \mu}{\delta \phi}$ , the multiple-scale method (3.3) allows us to at least formally obtain the structure of the homogenized equations. In light of the explanations after (3.23), we expect that the general porous media formulation for LDA models takes the same basic form

$$p \partial_t c_i := -\operatorname{div} \left( -M_i \overline{\nabla \mu}(c_j, \phi) \right) \quad (3.24)$$

where  $\overline{\nabla \mu}$  is defined as in (3.11) and we allow for a multicomponent electrolyte, as well as (formally) for nonlinearities in the mobilities.

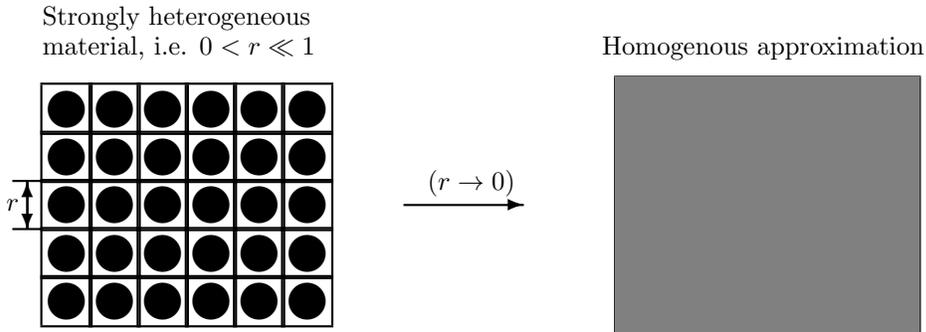


FIGURE 4.1. **Left:** A composite material whose characteristic heterogeneity has the length  $r$ . **Middle:** Passing to the limit  $r \rightarrow 0$  under constant volume fraction between circle and square. **Right:** The limit problem is obtained with the theory of homogenization.

**4. Formal derivation of the upscaled equations by the two-scale convergence method.** In Figure 4.1 we recall the basic idea behind the homogenization method. For the upscaling process, we first write the system (3.1) in the distributional sense. Therefore, we multiply equations (3.1)<sub>1</sub> and (3.1)<sub>2</sub> by a smooth function

$\varphi \in C^\infty(\Omega_r^p)$  and the Poisson equation (3.1)<sub>3</sub> with  $\varphi \in C^\infty(\Omega)$ . After integration over  $\Omega_r^p$  and  $\Omega$ , we end up with the formulation

$$\begin{aligned} (\partial_t c_r^+, \varphi)_{\Omega_r^p} &= (\nabla c_r^+ + c_r \nabla \phi_r, \nabla \varphi)_{\Omega_r^p} + \int_{I_r} \{\nabla \rho_r + c_r \nabla \phi_r\} \varphi \mathbf{n} \, do(x), \\ (\partial_t c_r^-, \varphi)_{\Omega_r^p} &= (\nabla c_r^- + c_r^+ \nabla \phi_r, \nabla \varphi)_{\Omega_r^p} + \int_{I_r} \{\nabla c_r^- + c_r^+ \nabla \phi_r\} \varphi \mathbf{n} \, do(x), \\ -(\varepsilon(x/r) \nabla \phi_r, \nabla \varphi)_\Omega &= (c_r^+ - c_r^-, \varphi)_\Omega - \int_{I_r} \hat{\varepsilon}(x/r) \nabla \phi_r \varphi \mathbf{n} \, do(x). \end{aligned} \quad (4.1)$$

With the boundary conditions (3.2), the system (4.1) reduces to

$$\begin{aligned} (\partial_t c_r^+, \varphi)_{\Omega_r^p} &= (\nabla c_r^+ + c_r^- \nabla \phi_r, \nabla \varphi)_{\Omega_r^p}, \\ (\partial_t c_r^-, \varphi)_{\Omega_r^p} &= (\nabla c_r^- + c_r^+ \nabla \phi_r, \nabla \varphi)_{\Omega_r^p}, \\ -(\varepsilon(x/r) \nabla \phi_r, \nabla \varphi)_\Omega &= (c_r^+ - c_r^-, \varphi)_\Omega + \int_{I_r} \sigma_s \varphi \, do(x). \end{aligned} \quad (4.2)$$

Now, we take the limit  $r \rightarrow 0$  and get the upscaled or homogenized description of (4.2). We recall that the concentrations  $c_r^\pm$  need to be extended to the whole domain  $\Omega$  in (4.2) before one passes to the limit  $r \rightarrow 0$ , as in [74] for the case without surface charge. Hence, it remains to account for the presence of the periodic, surface charge  $\sigma_s(x/r)$  on the boundary  $I_r := \partial\Omega_r^p \cap \partial\Omega_r^s$ . Therefore, we apply the test function  $\varphi_r(x) := \varphi(x) + r\varphi_1(x, \frac{x}{r})$  to (4.2)<sub>3</sub>. Subsequently, we only consider the boundary integral, i.e.,

$$\int_{I_r} \sigma_s(x/r) \varphi_r \, do(x) \rightarrow \frac{1}{|Y|} \int_\Omega \varphi(x) \int_{\partial Y_1 \cap \partial Y_2} \sigma_s(y) \, dx \, do(y). \quad (4.3)$$

Using (4.3) and the limit in the other terms of (4.2)<sub>3</sub>, achieved in [74] (and in a more general context in [73]), finally leads to upscaled Poisson equation (3.6)<sub>3</sub>.

**5. Effective diffusivity and mobility.** In order to get the effective diffusivity tensor  $\mathbb{D}$  and mobility tensor  $\mathbb{M}$ , we need to go back to the dimensional quantities  $C_\pm$ , which represent concentrations of charged species in the considered electrolyte. Since we restrict ourselves to a binary symmetric electrolytes, we only distinguish between positive charged species  $C_+$  and negative ones  $C_-$ . In these variables, the upscaled equations look like

$$\begin{aligned} p \partial_t C_\pm &= \operatorname{div} (\mathbb{D}_\pm \nabla C_\pm \pm ze C_\pm \mathbb{M}_\pm \nabla \Phi), \\ -\operatorname{div} (\hat{\varepsilon}_0(\epsilon_p, \alpha) \nabla \Phi) &= pze (C_+ - C_-) + \rho_s, \end{aligned} \quad (5.1)$$

where we used the definitions

$$\begin{cases} \mathbb{D}_\pm := D_\pm \hat{D}, \\ \mathbb{M}_\pm := M_\pm \hat{M}. \end{cases} \quad (5.2)$$

We recall that the mobility is defined via Einstein's relation by  $M_\pm = \frac{D_\pm}{kT}$ . Hence, the relations (5.2) define the dimensional effective diffusivity tensor  $\mathbb{D}_\pm$  and the dimensional effective mobility tensor  $\mathbb{M}_\pm$ . Furthermore, the equations (5.2) further indicate

that (Nernst-)Einstein's relation is still consistent with the upscaled formulation (5.1). However, since the tensors  $\hat{D}$  and  $\hat{M}$  are corrections to the gradients and not to  $D_{\pm}$  and  $M_{\pm}$ , Einstein's relations do not hold for the effective quantities  $\mathbb{D}_{\pm}$  and  $\mathbb{M}_{\pm}$  see Section 3 (3.3). We also emphasize that the applicability of the Nernst-Einstein equation must not be guaranteed in every situation, see for example the discussion in [56, Section 11.7 and Section 12.5]. There, it is pointed out that the validity of Einstein's relation is valid at infinite dilution, although its failure is related to the approximate nature of the flux of the Poisson-Nernst-Planck equations. But primarily, the validity of the Nernst-Einstein relation rests on the fact that the driving force for both migration and diffusion is the gradient of the electrochemical potential, and the decomposition of this into a concentration term and an electrostatic-potential term is without basic physical significance.

**6. Solving the reference cell problem for straight channels.** For the subsequently studied examples, we additionally suppose that the electric potential  $\phi$  only exists in the electrolyte phase as the salt and charge concentration. This assumption implies that the correction tensor  $\hat{\epsilon}(\epsilon, \alpha)$  becomes  $\epsilon \hat{D}_{kl}$  as motivated in Section 3 (3.6).

*The two-dimensional case:* For simplicity, let us assume the molecular diffusion tensor  $D$  as isotropic,  $D_{ij} = \delta_{ij}$ . Hence, via Einstein's relation, i.e.  $M_{ij} = \frac{\delta_{ij}}{kT}$ , the mobility tensor  $M$  is also isotropic. We consider a reference cell defined by Figure 6.1 left (in 2D). The porous media correction with respect to the diffusion can be written in the two-dimensional case as follows

$$\hat{D} = \begin{bmatrix} \hat{D}_{11} & 0 \\ 0 & \hat{D}_{22} \end{bmatrix}. \quad (6.1)$$

Obviously, in the case considered we have, as in [5],  $\hat{D}_{11} = pD$  and  $\hat{D}_{22} = 0$ . Hence, the porous media Poisson-Nernst-Planck equations (3.6) take the following elegant form

$$\begin{aligned} \partial_t \rho &= \partial_{x_1}^2 \rho + \partial_{x_1} (c \partial_{x_1} \phi) & \text{in } \Omega, \\ \partial_t c &= \partial_{x_1}^2 c + \partial_{x_1} (\rho \partial_{x_1} \phi) & \text{in } \Omega, \\ -p\epsilon \partial_{x_1}^2 \phi &= p\rho + \rho_s & \text{in } \Omega. \end{aligned} \quad (6.2)$$

*The three-dimensional case:* The porous media correction tensor for the diffusion is obtained by the same arguments as in the two-dimensional case, i.e.

$$\hat{D} = \begin{bmatrix} \hat{D}_{11} & 0 & 0 \\ 0 & \hat{D}_{22} & 0 \\ 0 & 0 & \hat{D}_{33} \end{bmatrix}, \quad (6.3)$$

where  $\hat{D}_{11} = \hat{D}_{33} = p$  and  $\hat{D}_{22} = 0$ . A straightforward extension of the straight channel to dimension three is depicted in Figure 6.1 right. As in (6.2), we obtain the following porous media equations for straight channels in the three-dimensional case, i.e.

$$\begin{aligned} \partial_t \rho &= (\partial_{x_1}^2 + \partial_{x_3}^2) \rho + (\partial_{x_1} (c \partial_{x_1} \phi) + \partial_{x_3} (c \partial_{x_3} \phi)) & \text{in } \Omega, \\ \partial_t c &= (\partial_{x_1}^2 + \partial_{x_3}^2) c + (\partial_{x_1} (\rho \partial_{x_1} \phi) + \partial_{x_3} (\rho \partial_{x_3} \phi)) & \text{in } \Omega, \\ -p\epsilon (\partial_{x_1}^2 + \partial_{x_3}^2) \phi &= p\rho + \rho_s & \text{in } \Omega. \end{aligned} \quad (6.4)$$

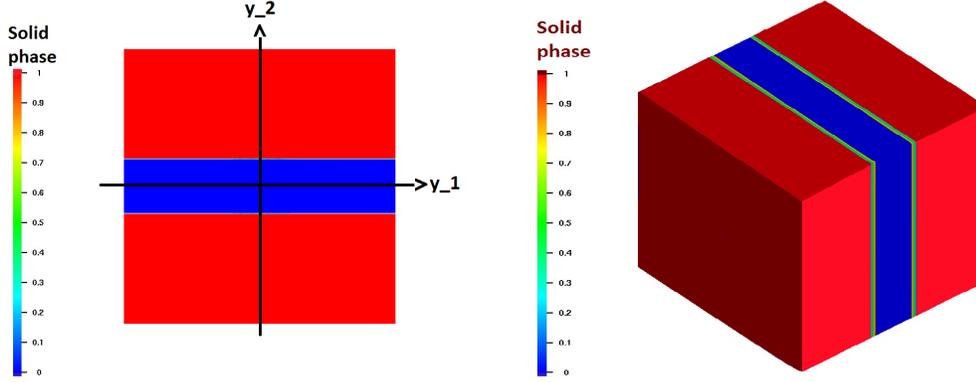


FIGURE 6.1. **Example of straight channels:** Left: *Two-dimensional case.* (pore phase is red) Right: *Three-dimensional case.*

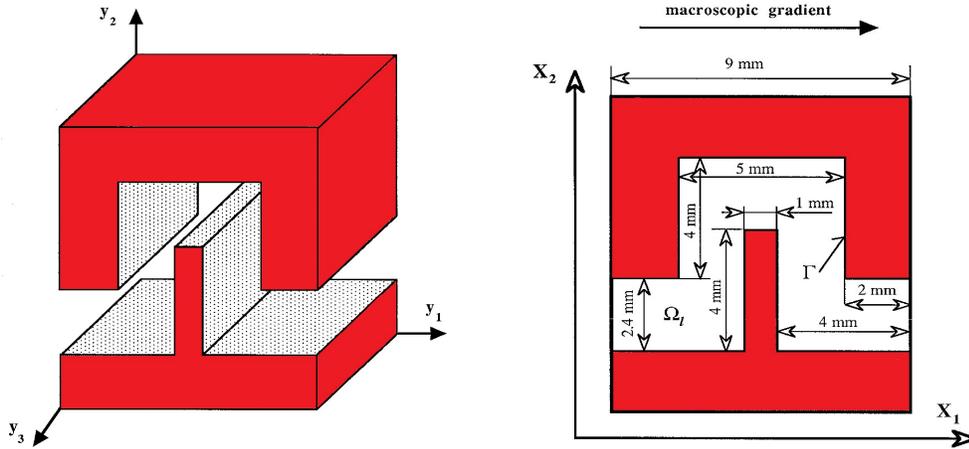


FIGURE 7.1. **Perturbed straight channels in 3D,** see [6]: Left: *Reference cell geometry.* Right: *Cross-section of the period.*

**7. Solving the reference cell problem for perturbed straight channels (3D).** In difference to straight channels, the case of perturbed straight channels requires the numerical calculation of the components  $d_{ii}$  for  $i = 1, 3$  of the effective diffusion tensor  $\mathbb{D}$ . However, the component  $d_{22}$  is 0 as in (6.3). For details about the numerics, we refer to [6] and state immediately the computational results here, i.e.

$$\hat{\mathbb{D}} = p \begin{bmatrix} 0.3833 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}. \quad (7.1)$$

Hence, with (7.1) the porous media approximation (6.4) immediately changes in case of perturbed channels as depicted in Figure 7.1 to the following system of equations

$$\begin{aligned} \partial_t \rho &= (0.3833 \partial_{x_1}^2 + \partial_{x_3}^2) \rho + (\partial_{x_1} (0.3833 c \partial_{x_1} \phi) + \partial_{x_3} (c \partial_{x_3} \phi)) & \text{in } \Omega, \\ \partial_t c &= (0.3833 \partial_{x_1}^2 + \partial_{x_3}^2) c + (\partial_{x_1} (0.3833 \rho \partial_{x_1} \phi) + \partial_{x_3} (\rho \partial_{x_3} \phi)) & \text{in } \Omega, \\ -p \epsilon (0.3833 \partial_{x_1}^2 + \partial_{x_3}^2) \phi &= p \rho + \rho_s & \text{in } \Omega. \end{aligned} \quad (7.2)$$

Let us now compare system (7.2) for perturbed straight channels with the straight channel example (6.4). One immediately recognizes that the porosity parameter  $p$  doesn't affect the ion density equations. Further, it is apparent that longer fluid paths modify these ion concentration equations accordingly. This fact is connected to the study of the tortuosity, which is the topic of the next section.

**8. Discussion of tortuosity and effective diffusivity.** In the following, we motivate that homogenization allows to validate current tortuosity relations and to give directions towards refinements of such relations. The explicit examples from the Sections 6 and 7 allow to systematically understand the influence of the geometric structure to the tortuosity. Sometimes, people introduce a so-called diffusibility  $Q$  which relates the molecular diffusion constant  $D_f$  to the effective diffusion constant  $D_p$  of a porous medium, i.e.

$$D_p = QD_f. \quad (8.1)$$

The expressions for  $Q$  available in literature can be divided into three classes, see Brakel et al. [19]: (1) empirical correlations, (2) semi-empirical equations based on a pore model, and (3) theoretical expressions.

(1) The empirical correlations express  $Q$  as a function of the porosity  $p$ , i.e.  $Q = f(p)$ . (2) If  $Q$  is defined by the special class of functions  $f(p) = \gamma p^\mu$ . The term  $p^\mu$  is generally said to account for the influence of the smaller cross sectional surface available for diffusion. (3) The theoretical expressions for  $Q$  have been derived for dispersed solids in the form of spheres.

But, let us first give a historical overview. In any porous system, the presence of solid particles/material causes the diffusion paths of species to deviate from straight lines. Consequently, the diffusion coefficients of species must be corrected. One tries to capture this deviation from straight lines in a porous medium by a term called tortuosity, whose suitable definition is still an actual research topic. This is also motivated by the following considerations.

By theory and dimensional reasoning, Petersen [63] suggests that the diffusion coefficient is scaled with tortuosity as follows

$$D_p = \frac{D_f}{\tau^2}, \quad (8.2)$$

which implies for the diffusibility  $Q = 1/\tau^2$ . A similar relationship is introduced by Aris [4] and Satterfield [71], i.e.

$$D_p = \frac{p}{\tau} D_f, \quad (8.3)$$

and hence  $Q = p/\tau$ . The simplest and most intuitive method to estimate the tortuosity  $\tau$  (in the one-dimensional case) is the ratio of the length of the curve  $L_\gamma$  to the shortest distance of its end points  $L_{ab}$ , i.e.

$$\tau := \frac{L_\gamma}{L_{ab}}. \quad (8.4)$$

In Brakel et al. [19], they consider a slight generalization of (8.2) by introducing a constrictivity parameter  $d := \left(\frac{D_p}{pD_f}\right)_{\tau=1}$ , which accounts for the fact that the cross section of a segment varies over its length. Hence, (8.2) changes to

$$D_p = \frac{pd}{\tau^2} D_f, \quad (8.5)$$

sucht that  $Q = \frac{pd}{\tau^2}$ .

Further, Brakel et al. [19] argue that for porous materials a function of the kind  $Q = f(p)$  does not exist. Moreover, they emphasize that the pragmatic value of the available  $Q - p$  relations is not very great. Recently, also Shen and Chen [76] give a critical review of the current impact of tortuosity on diffusion. Therefore, we motivate our discussion and study of  $Q$  in this section by suggesting a theoretically obtained  $Q$  with the help of homogenization theory. The diffusivity  $Q$  could turn out as a relevant parameter to compare empirical measurements with theoretically obtained effective quantities.

Up to this end, we first extend the above relations to tensorial versions, i.e. we denote by  $\hat{D}_p$  the effective diffusion tensor in a porous environment and by  $\hat{D}_f := \{D\delta_{ij}\}_{ij}$  the molecular diffusion tensor in free space.  $\delta_{ij}$  denotes the Kronecker delta function. First, we extend (8.2) to

$$\hat{\tau} := \left( \frac{\hat{D}_f}{\hat{D}_p} \right)^{1/2}, \quad (8.6)$$

where  $\hat{D}_p := D\hat{D}$  and the diffusion corrector  $\hat{D}$  is obtained by homogenization in (3.7)<sub>1</sub>. The quotient in (8.6) is understood as a division of each component if and only if both, the corresponding nominator  $\hat{D}_f$  and the denominator  $\hat{D}_p$  are different from zero. Instead of this restriction, we could also allow for a tortuosity  $\hat{\tau}$  with components admitting “ $\infty$ ”. We point out that the tensorial relation (8.6) also implies a tensorial diffusivity, i.e.  $\hat{Q} = 1/\hat{\tau}^2$ .

Another very interesting interpretation of (8.6) is possible in the case of an insulating porous matrix, see Section 3.6. The tortuosity  $\hat{\tau}$  in (8.6) corresponds to the coordinate transformation (3.19), i.e.  $\tilde{x} = \hat{\tau}x$ .

In view of (8.3) and (8.5), we motivate further the extensions of (8.3) to

$$\hat{\tau} := \frac{p\hat{D}_f}{\hat{D}_p}, \quad (8.7)$$

with corresponding  $\hat{Q} = p/\hat{\tau}$  and

$$\hat{\tau} := \left( \frac{pd_{ij}\hat{D}_f}{\hat{D}_p} \right)^{1/2}, \quad (8.8)$$

with  $\hat{Q} = p\hat{d}/\hat{\tau}^2$ .

Let us apply definition (8.6) to the examples from Sections 6 and 7. In the case of straight channels, see Figure 6.1 on the right-hand side, the definition (8.6) implies the following tortuosity tensor

$$\hat{\tau} = \begin{bmatrix} 1/\sqrt{p} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1/\sqrt{p} \end{bmatrix}. \quad (8.9)$$

We point out that the porosity  $p$  with respect to straight channels corresponds to the channel height on the unit reference cell. Let us compare (8.9) with the intuitive definition (8.4). If we apply definition (8.4) in a straightforward manner, then  $\tau = 1$ .

However, it is not clear for straight channels, which path  $L_\gamma$  is reasonable. Let us check for example the average

$$L_\gamma = \frac{1}{N} \sum_{i=1}^N L_{\gamma_i}. \quad (8.10)$$

With (8.10), we get  $\tau = L_\gamma$  where  $L_\gamma = \frac{1}{3} \left( \sqrt{1+p^2} + 1 + (1+p) \right)$  for the path lengths  $\gamma_1 := L_{ab} = 1$ ,  $\gamma_2 := L_{ab} + p = 1+p$  where the porosity  $p$  is the channel height, and  $\gamma_3 := \sqrt{1+p^2}$  the diameter. But due to Boudreau [18, Section 2], the tortuosity must approach unity for  $p \rightarrow 1$ . This is violated by definition (8.4) together with (8.10) since  $\tau = 1 + \frac{\sqrt{2}}{3}$  with (8.10). But the tortuosity (8.9) defined via the homogenization process perfectly satisfies this condition, see [18, Section 2]. Accordingly, in the case of perturbed straight channels as considered in Section 7, the tortuosity tensor (8.6) becomes

$$\hat{\tau} = \begin{bmatrix} 1/\sqrt{0.3833p} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1/\sqrt{p} \end{bmatrix}. \quad (8.11)$$

One immediately recognizes that  $\hat{\tau}_{11}$  in (8.11) is  $> 1$  in the limit  $p \rightarrow 1$ . Hence Boudreau [18, Section 2] doesn't hold. This contradiction requires caution by using definitions (8.2) and (8.6). Next, we examine the definition (8.7) which becomes for the case of straight channels

$$\hat{\tau} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}. \quad (8.12)$$

A comparison of (8.12) with (8.4) shows perfect agreement, i.e.  $(\tau_{(8.12)})_{11} = 1 = \tau_{(8.4)}$ . However, in the case of perturbed straight channels, we depend on the numerical accuracy. Since the mesh in [6] is not very fine, we cannot necessarily expect equality. In fact, we obtain  $(\tau_{(8.12)})_{11} = 2.6$  and  $\tau_{(8.4)} = \frac{4.4+1}{9} = 1.9$ . However, this discrepancy also motivates the critical statements of [19, 76] about the pragmatic value of tortuosity as mentioned above. We leave the investigation of the definition (8.8) to the interested reader, since the definition of the constrictivity parameter in [19] is a delicate point and again a new source for modeling errors.

As a conclusion of this discussion, we motivate that homogenization theory allows to derive effective equations which do not require a questionable tortuosity or diffusivity parameter. Moreover, the correction tensors obtained by the two-scale convergence method provide a tool to check available tortuosity or diffusivity definitions and might provide directions how to improve their consistency.

**9. Ambipolar diffusion equation for a binary electrolyte.** Motivated by the considerations in Mani and Bazant [49] by volume-averaging, we study here the same problem with the help of homogenization theory. The advantage relies on the fact that we are able to accurately treat the nonlinear terms. Up to now, there exists no general rule how to upscale the nonlinear terms by volume-averaging approaches.

Hence, we extend the porous media approximation (3.6) to a dilute, asymmetric binary electrolyte ( $i = +, -$ ) with arbitrary ionic charges,  $q_\pm = \pm z_\pm e$  in this section.

For simplicity, we assume constant diffusivities  $D_{\pm}$  in the microstructure and denote the corresponding upscaled diffusivities and mobilities by  $\mathbb{D}_{\pm} = D_{\pm}\hat{\mathbb{D}}$  and  $\mathbb{M}_{\pm} = M_{\pm}\hat{\mathbb{D}}$ . Without loss of generality, we consider a negative surface charge, i.e.,  $\rho_s < 0$ . Moreover, we work in the context of an insulating porous matrix such that the porous media correction tensors satisfy  $\hat{\mathbb{D}} = \hat{\mathbb{M}} = \hat{\varepsilon}$ , see Section 3 (3.6). We simplify now the Poisson-Nernst-Planck system by applying the usual conventions

$$\begin{aligned} 0 &= pe(z_+C_+ - z_-C_-) + \rho_s, \\ pc &= p(z_+C_+ + z_-C_-) + \frac{\rho_s}{e}, \end{aligned} \quad (9.1)$$

where the first relation expresses quasi-neutrality for the case of surface charge. This assumption naturally arises here in view of the derived effective equations (3.17) for fixed surface charge. However, in [51, 66, 78] such a neutrality condition has been suggested by purely physical reasoning. Furthermore, we will not make use of the Nernst-Einstein equation between the diffusivity tensors  $\mathbb{D}_{\pm} = D_{\pm}\hat{\mathbb{D}}$  and mobility tensors  $\mathbb{M}_{\pm} = M_{\pm}\hat{\mathbb{D}}$ . Hence, the ambipolar diffusion equation derived under such assumptions takes the form

$$p\partial_t c = \bar{D}\operatorname{div}(\hat{\mathbb{D}}\nabla c) - \frac{\bar{z}}{e}\operatorname{div}(\rho_s\hat{\mathbb{D}}\nabla\hat{\phi}) - \frac{D_+\bar{z}}{kTez_+M_+}\operatorname{div}(\hat{\mathbb{D}}\nabla\rho_s), \quad (9.2)$$

where we used relations

$$\bar{D} := \frac{z_+M_+D_- + z_-M_-D_+}{z_+M_+ + z_-M_-} \quad \text{and} \quad \bar{z} := \frac{2z_+z_-M_+M_-kT}{z_+D_-M_+ + z_-D_+M_-}. \quad (9.3)$$

We remember that  $\hat{\mathbb{D}}$  is defined as (3.7)<sub>1</sub>.

The correction tensors  $\hat{\mathbb{D}}$  for straight channels (in Section 6) and for perturbed straight channels (in Section 7) allow to accordingly rewrite the ambipolar diffusion equation (9.2), which describes a porous material for a surface charge density  $\sigma_s$ . In view of the volume-averaged straight channels studied in [49], we only consider in the following the example from Section 6. With (6.1), the equation (9.2) immediately takes the form

$$\partial_t c = \bar{D}\partial_{x_1}^2 c - \frac{\bar{z}}{e}\partial_{x_1}(\rho_s\partial_{x_1}\hat{\phi}) - \frac{D_+\bar{z}}{kTez_+M_+}\partial_{x_1}^2\rho_s. \quad (9.4)$$

An interesting remark regarding (9.4) is that the porosity parameter  $p$  cancels out.

**10. Thin double layers at the pore scale .** Recently, Mani et al. [50] developed a "simple model" describing the propagation of salt gradients in a microchannel with parallel walls during the passage of constant current through a nano channel junction. The basic idea in the derivation is depth averaging across the channel thickness, assuming that the electrical double layers are thin ( $\epsilon \ll 1$ ) and confined to near-wall regions. Similar area-averaged models for nano channels with thin double layers have also been developed by [28, 66, 78]. Recently, the thin-double-layer formulation for microchannels was (formally) extended to porous media by Mani and Bazant [49] by including the surface charge as a homogeneous background charge in the electroneutrality condition. In this limit, the (weakly) charged porous medium behaves like a "bad membrane", whose ion concentrations can be significantly depleted and enriched by the passage of current, since only a small fraction of the ions are involved in screening the surface charge.

A systematic extension of these results to general porous media requires more involved techniques to accurately treat the nonlinear terms in (3.6). At this point, the results from Section 3 are necessary to properly describe material transport in highly heterogeneous media, based on homogenization theory to derive effective Poisson-Nernst-Planck equations (3.6). A further advantage is that the system (3.6) is not restricted to a special geometry and rather can be adapted for general porous structures by the tensors  $\hat{D}$ . In the case of straight channels, the correction tensor  $\hat{D}$  can be analytically obtained, as in Section 6, although for more complicated geometries, such as the irregular channels considered in Section 7, the correction tensor  $\hat{D}$  must be calculated numerically.

In order to describe situations with thin electrical double layers compared to the mean pore size, we consider the limit  $\epsilon = \lambda_D/\ell \rightarrow 0$  in (3.6). In the general case of a polarizable solid matrix, one immediately sees that the limit  $\epsilon \rightarrow 0$ , does not reduce the complexity of the macroscopic formulation, when we apply this limit in the system (5.1) and set  $\epsilon = 0$  in  $\hat{\epsilon}(\epsilon, \alpha)$ . However, if we pass to the joint limit  $\epsilon, \alpha \rightarrow 0$ , where the solid matrix is electrically insulating, then the porous media Poisson-Nernst-Planck system behaves almost like the classical PNP for  $\epsilon \rightarrow 0$ , since we obtain the following leading order bulk approximation for salt density  $c$ , charge density  $\rho$ , and electric potential  $\phi$ , i.e.

$$\begin{aligned} 0 &= \operatorname{div} \left( c \hat{D} \nabla \phi \right), \\ p \partial_t c &= \operatorname{div} \left( \hat{D} \nabla c \right) - \operatorname{div} \left( \frac{\rho_s}{p} \hat{D} \nabla \phi \right), \\ 0 &= p \rho + \rho_s. \end{aligned} \tag{10.1}$$

The first equation expresses charge conservation in the quasi-neutral bulk solution by setting the divergence of the current to zero. The second equation expresses total salt conservation. This description of bulk electrolytes with thin double layers is very well known and forms the basis for classical theories of electrochemical transport, based on the assumption of quasi-electroneutrality *in the electrolyte*  $\rho = 0$ , see Newman and Thomas-Alyea [56]. The third equation, however, is different and expresses quasi-electroneutrality of the entire porous composite, including not only the diffuse ionic charge  $\rho$ , but also the *homogenized surface charge*  $\rho_s$ . Naively, one might expect such a relation to hold for thick double layers, but this is not necessarily the case, as shown in the next section.

Instead, the macroscopic electroneutrality condition, Equation (10.1), generally holds in the limit of *thin* double layers in charged porous media, as proposed by Mani and Bazant [49]. Physically, the reason is that the counter-ions screening the surface charge in a thin double layer provide an extra surface conductivity, proportional to the total diffuse double-layer charge, which is acted on by the same tangential electric field as in the nearby bulk solution. If the double layers were not thin, the electric field would be strongly perturbed by the diffuse charge throughout the pore, and the extra counter ions could not be viewed as simply providing extra conductivity for bulk ion transport.

We briefly mention some simple cases of the thin-double-layer limit. In the case of straight channels from Section 6, the reduced porous media approximation becomes

in the two-dimensional case

$$\begin{aligned} 0 &= p\partial_{x_1}(c\partial_{x_1}\phi), \\ p\partial_t c &= p\partial_{x_1}^2 c - \partial_{x_1}(\rho_s\partial_{x_1}\phi), \\ \rho &= -\frac{\rho_s}{p}. \end{aligned} \quad (10.2)$$

With the considerations in Section 6, a corresponding extension to the three-dimensional case is straightforward. Note that, although we have written the thin double-layer equations using the reference cell length and time scales 2.4), they have the same form at the macroscopic length and time scales 3.4.

## 11. Thick double layers at the pore scale .

**11.1. Membrane limit .** Next we consider the limit of thick double layers,  $\epsilon = \lambda_D/\ell \ll 1$ , taken after the homogenization limit  $r \rightarrow 0$ . We first consider the "membrane limit" where the Debye length is much larger than the mean pore size, but much smaller than the macroscopic geometrical scale,  $\bar{\epsilon} = \epsilon r = \lambda_D/L \ll 1$ . Again, the upscaled equations take a simple form if the electric potential only exists in the solid phase, i.e.,  $\alpha \rightarrow 0$ . In that case, the macroscopic PNP equations (3.6) take the following form at leading order for thick double layers at the pore scale:

$$-\bar{\nabla} \cdot (\bar{\epsilon}^2 \hat{\mathbf{D}} \bar{\nabla} \phi) = p(c^+ - c^-) + \rho_s \quad \text{in } \Omega. \quad (11.1)$$

$$p\partial_{\bar{t}} c^\pm = \bar{\nabla} \cdot (\hat{\mathbf{D}} \bar{\nabla} c^\pm \pm c^\pm \hat{\mathbf{D}} \bar{\nabla} \phi) \quad \text{in } \Omega, \quad (11.2)$$

where we have rescaled to the macroscopic length and time scales (3.4). Aside from the geometrical tensor  $\hat{\mathbf{D}}$ , this form of the macroscopic PNP equations (11.1)-(11.2) reduces to a standard mathematical model for diffuse charge in membranes [14, 16] and doped semiconductors [52]. As a result of the thick double layer limit over the pores, such materials act as "good membranes" and maintain roughly uniform conductivity outside the double layers, which are typically thin at the geometrical scale.

**11.2. Thin-film limit .** For very thin porous films, we can also consider the limit where the double layer thickness is much larger than the macroscopic length scale,  $\bar{\epsilon} = \lambda_D/L \gg 1$ . For such thin films, Poisson's equation is replaced by

$$\bar{\nabla} \cdot (\hat{\mathbf{D}} \bar{\nabla} \phi) = 0 \quad (11.3)$$

In this limit, the macroscopic electric field  $-\bar{\nabla}\phi$ , which drives electromigration of the ions, satisfies Poisson equation for an *uncharged* dielectric material with anisotropic permittivity. Mathematically, from Eq. (11.1) we see that local electric field variations are very small,  $\bar{\nabla} \cdot (\hat{\mathbf{D}} \bar{\nabla} \phi) = O(\bar{\epsilon}^{-2})$ , and show no significant effect from diffuse charge fluctuations, which are corresponding small within the pores. It can be shown that a similar thick-double-layer, thin-film approximation (11.2) also holds true for the case where the electric potential is additionally defined in a polarizable solid matrix.

A useful feature of this limit is that the potential satisfies Laplace's equation (11.2)<sub>2</sub> (in transformed coordinates, as noted above), which is decoupled from the ion transport problem. The resulting electric field acts like an external potential flow on the ions, leading to an advection-diffusion equation for the concentration profiles

(11.2)<sub>1</sub>. This is also a common approximation in gel electrophoresis, where it can also be justified for charged tracer particles outside thin macroscopic double layers ( $\bar{\epsilon} \ll 1$ ), where the total conductivity is dominated by the fixed gel charge, according to the general thick double layer formulation (11.2). In two dimensions, this problem has an elegant mathematical structure in steady state, amenable to solution by conformal mapping [7, 23], which could be useful for this class of ion transport problems in charged porous media.

**12. Optimizing the conductivity for parallel straight channels.** We are interested in the effective conductivity  $\hat{\sigma}(x)$  of a binary symmetric electrolyte occupying the domain  $\Omega$  with corresponding surface  $\partial\Omega$ . The domain  $\Omega$  is assumed to be a porous medium with porosity  $p$ . For simplicity, we first consider the pores to be straight (cylindrical) channels and the case of an insulating porous matrix, that means  $\hat{D} = \hat{M} = \hat{\epsilon}$ , see Section 3 (3.6). For a current density  $\bar{J}$  together with the electrostatic equations  $\text{div } \bar{J} = 0$  and  $\text{rot } \bar{E} = 0$ , where  $\bar{E} = \nabla\phi$ , we obtain

$$\text{div}(\hat{\sigma}\nabla\phi) = 0, \quad (12.1)$$

the constitutive relation  $\bar{J} = \hat{\sigma}\bar{E}$  entered. The upscaled Poisson-Nernst-Planck equations provide the current density  $\bar{J}$  for a binary symmetric electrolyte, i.e.

$$\bar{J} := \hat{D}\nabla\rho + c\hat{D}\nabla\phi. \quad (12.2)$$

In order to determine  $\hat{\sigma}$  in (12.1), we replace  $\rho$  in (12.2) by the Poisson equation (3.6)<sub>3</sub> with  $\epsilon^2\hat{D}$  instead of  $\hat{\epsilon}_{kl}(\epsilon, \alpha)$  as explained in Remark 2. We obtain

$$\begin{aligned} \bar{J} &= -\hat{D}\nabla\left(\text{div}\left(\frac{\epsilon^2}{p}\hat{D}\nabla\phi\right) + \frac{\rho_s}{p}\right) + c\hat{D}\nabla\phi, \\ &= -\frac{1}{p}\hat{D}^2\nabla\left(\epsilon^2\Delta\phi + \frac{\rho_s}{p}\right) + c\hat{D}\nabla\phi. \end{aligned} \quad (12.3)$$

The structure of equation (12.3) motivates to consider the eigenvalue problem for the Laplace operator, i.e.

$$\begin{cases} -\Delta_y u_i(y) + \theta_i u_i(y) = 0 & \text{in } Y^p, \\ u_i(y) = 0 & \text{on } \partial Y^p \cap \partial Y^s. \end{cases} \quad (12.4)$$

We remark that it is not immediately clear what kind of boundary conditions are required in (12.4). The boundary condition (12.4)<sub>2</sub> has the advantage that it gives a lower bound [21, 40] on the first eigenvalue  $\theta_i$  in (12.4) for the geometry defined by the pore phase  $Y^p$ . We point out that instead of using the macroscopic Laplace operator  $\Delta_x$ , we apply the microscopic Laplace operator  $\Delta_y = s^2\Delta_x$  on the pore phase of the reference cell  $Y^p$ . Hence, the eigenvalue  $\theta$  depends on the pore geometry which is the striking point for our optimization goal. Since the self-adjoint eigenvalue problem (12.4) is a regular Sturm-Liouville problem, we can use its solutions  $\{u_i\}_i$  to generate an orthonormal basis in  $L^2(\Omega)$ . Thus, for any function  $f \in L^2(\Omega)$  we have

$$f = \sum_i^\infty \langle f, u_i \rangle u_i, \quad (12.5)$$

where equality is in the sense of  $L^2$ .

Now, we can choose  $\hat{D}$  as in Section 6 for straight channels, if we additionally assume that the electrostatic potential only exists in the electrolyte phase. Hence, after choosing  $f = \partial_{x_1}\phi$ , the relation (12.3) becomes

$$J^1 = p \sum_i^\infty \left( \frac{\epsilon^2}{s^2} \Delta_y + c \right) \langle \partial_{x_1}\phi, u_i \rangle u_i - \partial_{x_1}\rho_s, \quad (12.6)$$

where equality holds again in the  $L^2$ -sense. We can now approximate (12.6) by only considering the first eigenvalue  $\theta_1$  of (12.4). That means, we obtain

$$J^1 \approx p \left( \frac{\epsilon^2}{s^2} \theta_1 + c \right) \langle \partial_{x_1}\phi, u_1 \rangle u_1 - \partial_{x_1}\rho_s. \quad (12.7)$$

As a consequence, the conductivity  $\hat{\sigma}$  can be approximated by

$$\sigma_{11} \approx p \left( \frac{\epsilon^2}{s^2} \theta_1 + c \right). \quad (12.8)$$

That means, optimization of the conductivity in direction of the straight pores is achieved by increasing  $\epsilon$  and  $\theta_1$  for given  $p$ ,  $c$  and  $s$ . With the help of Cheeger's number  $h(\Omega^p)$ , we obtain an additional tool to optimize the conductivity with respect to the geometry. In fact, it holds due to Cheeger [21] and Kawohl and Fridman [40]

$$\theta_1 \geq \left( \frac{h(\Omega^p)}{2} \right)^2. \quad (12.9)$$

*Example 1: (Square)* For a square  $S_a := [-a, a]^2$ , Cheeger's number can be determined explicitly by  $h(S_a) = \frac{4-\pi}{(4-2\sqrt{\pi})a}$ . Moreover, we know that the first eigenvalue is  $\theta_1(S_1) = 2\pi^2$ . This indicates that the lower bound given by estimate (12.9) is not too sharp. However, it allows at least to obtain first insights for possible directions towards optimization of the conductivity (12.8).

*Example 2: (Rectangle)* For a rectangle  $R_{a,b} := [-a, a] \times [-b, b]$ , one immediately gets the following Cheeger constant, see [41],

$$h(R_{a,b}) = \frac{4-\pi}{a+b-\sqrt{(a-b)^2+\pi ab}}. \quad (12.10)$$

Hence, in order to optimize the conductivity (12.8) for a rectangle shaped pore  $R_{a,b}$ , we have to maximize  $h(R_{a,b})$  what is equivalent to the minimization of  $a$  and  $b$ . If we assume that we are given a porous material of characteristic length  $b = l$ , then it immediately follows that  $h$  is maximal after minimizing the channel height  $a > 0$ .

**13. Conclusion .** We have applied a systematic, formal homogenization procedure for the Poisson-Nernst-Planck equations (3.1) for ion transport in charge porous media. The resulting upscaled macroscopic equations (3.6) have a similar form as the microscopic equations, except for two fundamental modifications: (i) The ionic diffusivities and mobilities, as well as the effective medium permittivity, become tensorial coefficients, which are explicitly connected to the microstructure by solving the periodic reference cell problem, and (ii) the total surface charge per volume appears as an extra ‘‘background charge’’ in the upscaled Poisson equation. The porous-medium PNP equations may find many applications in electrochemical and biological systems

involving ion transport in charged porous media, where effects of fluid flow can be neglected. Simplified equations for the limits of thin or thick double layers may also be appropriate in many cases.

There are many interesting avenues for future work, building on these results. There is a substantial literature on rigorous bounds and approximations for the effective diffusivity or conductivity of a composite medium [81], related to solutions of Laplace's equation with flux matching interfacial conditions. It would be challenging and useful to derive analogous mathematical bounds and approximations for the effective diffusivities and mobilities of ions in a charged composite medium, which appear as tensorial coefficients in our porous-medium PNP equations. One might expect analogs of the Wiener bounds for anisotropic composites to hold for striped microstructures and analogs of the Hashin-Shtrikman bounds for isotropic microstructures to hold for space-filling random sphere packings, although the appearance of an internal length scale for electrostatic interactions (the Debye screening length) complicates such simple geometrical constructions.

It would also be valuable to find simple ways to approximate the solution to the reference-cell problem and thus derive simplified expressions for the tensorial diffusivities and mobilities. In the limit of thin double layers, this could be done using surface conservation laws, which are effective boundary conditions on the neutral solution obtained by singular perturbation methods [25]. In the opposite limit of thick double layers, regular perturbation methods might be applied to capture effects of diffuse charge variations in the microstructure.

We close by emphasizing the open challenge of deriving effective ion transport equations in more general situations using homogenization theory. We have already commented on the extension to concentrated solution theories based on the local density approximation (for chemical interactions) and the mean-field approximation (for electrostatics) [11]. Going beyond these approximations in the microscopic equations can lead to non-local Nernst-Planck integral equations [34, 35] or higher-order Poisson equations [12, 22, 36, 70], whose upscaled form remains to be determined. Perhaps even more challenging, and more important for many applications, would be to predict the effects of fluid flow on the homogenized PNP equations, coupled to the Navier-Stokes equations with electrostatic body forces.

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