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Role of non-ideality for the ion transport in porous media: Derivation of the macroscopic equations using upscaling

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HIGHLIGHTS

- Upscaling of the MSA model of non-ideal transport through a rigid porous medium.
- O'Brien's semi-linearization and analytic study of the equilibrium solutions.
- Solving a variant of the Poisson–Boltzmann equation coupled with algebraic equations.
- Rigorous homogenization and proof of the Onsager properties.
- Numerical comparisons with the ideal case.

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ABSTRACT

This paper is devoted to the homogenization (or upscaling) of a system of partial differential equations describing the non-ideal transport of a N-component electrolyte in a dilute Newtonian solvent through a rigid porous medium. Realistic non-ideal effects are taken into account by an approach based on the mean spherical approximation (MSA) model which takes into account finite size ions and screening effects. We first consider equilibrium solutions in the absence of external forces. In such a case, the velocity and diffusive fluxes vanish and the equilibrium electrostatic potential is the solution of a variant of the Poisson–Boltzmann equation coupled with algebraic equations. Contrary to the ideal case, this nonlinear equation has no monotone structure. However, based on invariant region estimates for the Poisson–Boltzmann equation and for small characteristic value of the solute packing fraction, we prove existence of at least one solution. To our knowledge this existence result is new at this level of generality. When the motion is governed by a small static electric field and a small hydrodynamic force, we generalize O'Brien's argument to deduce a linearized model. Our second main result is the rigorous homogenization of these linearized equations and the proof that the effective tensor satisfies Onsager properties, namely is symmetric positive definite. We eventually make numerical comparisons with the ideal case. Our numerical results show that the MSA model confirms qualitatively the conclusions obtained using the ideal model but there are quantitative differences arising that can be important at high charge or high concentrations.

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1. Introduction

The quasi-static transport of an electrolyte through an electrically charged porous medium is an important and well-known multiscale problem in geosciences and porous materials modeling. An N-component electrolyte is a dilute solution of N species of charged particles, or ions, in a fluid which saturates a rigid charged porous medium [1]. The macroscopic dynamics of such a system is controlled by several phenomena. First the global hydrodynamic flow, which is commonly modeled by Darcy's law depends on the geometry of the pores and also on the charge distributions of the system. Second, the migration of ions because of an electric field can be quantified by the conductivity of the system. Third, the diffusion motion of the ions is modified by the interaction with the surfaces, but also by the interactions between the solute particles. Lastly, electrokinetic phenomena are due to the **electric double layer** (EDL) which is formed as a result of the interaction of the electrolyte solution which neutralizes the charge of the solid phase at the pore solid–liquid interface. Thus, an external electric field can generate a so-called electro-osmotic flow and reciprocally, when a global hydrodynamic flow is applied, an induced streaming potential is created in the system.

The EDL can be split into several parts, depending on the strength of the electrostatic coupling. There is a condensed layer of ions of typical size l_G for which the attraction energy with the surface $e\Sigma/\mathcal{E}l_G$ (with Σ the surface charge and e the elementary charge) is much more than the thermal energy k_BT (with k_B Boltzmann's constant and T the temperature). The corresponding characteristic length $l_G = \mathcal{E}k_BT/\Sigma e$ (Gouy length) is typically less than one nanometer. Consequently, the layer of heavily adsorbed ions practically depends on the molecular nature of the interface and it is generally known as the **Stern layer**. After the Stern layer the **electrostatic diffuse layer** or **Debye's layer** is formed, where the ion density varies. The EDL is the union of Stern and diffuse layers. The thickness of the diffuse layer is predicted by the Debye length λ_D which depends on the electrolyte concentration. For low to moderate electrolyte concentrations λ_D is in the nanometric range. Outside Debye's layer, in the remaining bulk fluid, the solvent can be considered as electrically neutral.

The large majority of theoretical works are concerned with a simple (so-called **ideal**) model for which the departure of ideality of ions are neglected (see later in this introduction a precise definition of ideality). Thus the macroscopic descriptions of charged porous media such as the ones using finite element methods [2], homogenization approaches [3] or lattice-Boltzmann methods [4] are commonly based on the Poisson–Nernst–Planck formalism for which the local activity coefficients of ions are neglected and the transport properties are modeled solely from the mobility at infinite dilution. In addition, the boundary condition for the electrostatic interaction between the two phases is very often simplified by replacing the bare surface charge Σ, which corresponds to the chemistry of the system, by surface potential Ψ. Its boundary value at the no slip plane is known as the zeta potential ζ. In fact, it is rather the surface charge density Σ, proportional to the normal derivative of Ψ, than ζ, which is the relevant parameter (this is confirmed by an asymptotic analysis in [5]).

A few studies do not model the details of the EDL. Under the presence of an external electric field $\mathbf{E}$, the charged fluid may acquire a plug electro-osmotic flow velocity which is proportional to $\mathbf{E}\zeta$ and given by the so-called Smoluchowski's formula. In the case of porous media with large pores, the electro-osmotic effects are modeled by introducing an effective slip velocity at the solid–liquid interfaces, which comes from the Smoluchowski formula. In this setting, the effective behavior of the charge transport through spatially periodic porous media was studied by Edwards in [6], using the volume averaging method. These methods for which the transport beyond the EDL is uncoupled from the one in the EDL are not valid for numerous systems, such as clays because the characteristic pore size is also of the order of the EDL size (a few hundreds of nanometers or even less). Therefore Debye's layer fills largely the pores and its effect cannot anymore be modeled by an effective slip boundary condition at the liquid–solid interface.

In the present paper, we consider continuum equations (such as the Navier–Stokes or the Fick equations) as the right model for the description of porous media at the pore scale where the EDL phenomena and the pore geometry interact. The typical length scale for which these continuous approach are valid is confirmed to be both experimentally (see e.g. [7]) and theoretically [8,9] close to 1 nanometer. Therefore, we consider continuum equations at the microscopic level and, more precisely, we couple the incompressible Stokes equations for the fluid with the electrokinetic model made of a global electrostatic equation and one convection–diffusion equation for each type of ions.

The most original ingredient of the model is the treatment of the departure from ideality. Electrolyte solutions are not ideal anymore as far as the ion concentration is not dilute [10]. Typically simple 1–1 electrolyte, such as NaCl in water have an activity coefficient which is close to 0.6 at molar concentrations (while it is equal to 1 by definition in the ideal case) and the non-ideality effects is even more important for the transport coefficients [11,12]. Thus any ideal model can only be in semi-quantitative agreement with a more rigorous model if departure from ideality are neglected. In the present article, we use a new approach based on the Mean Spherical Approximation (MSA), for which the ions are considered to be charged hard spheres [13,14]. This model is able to describe the properties of the solutions up to molar concentrations. In addition, a generalization of the Fuoss–Onsager theory based on the Smoluchowski equation has been developed [15,16,11,17,18,12] by taking into account this model, and it is possible to predict the various transport coefficients of bulk electrolyte solutions up to molar concentrations. This MSA transport equations extend the well known Debye–Hückel–Onsager limiting law to the domain of concentrated solutions. They have also been proved to be valid [19] for confined solutions in the case of clays by comparing their predictions to molecular and Brownian dynamics simulations.

A more detailed, mathematically oriented, presentation of the fundamental concepts of electro-osmotic flow in nanochannels can be found in the book [20] by Karniadakis et al., pages 447–470, from which we borrow the notations and definitions in this introduction. We now describe precisely our stationary model, describing at the pore scale the electro-chemical interactions of an N-component electrolyte in a dilute Newtonian solvent. All quantities are given in **SI units**. We start with the following mass conservation laws

$$\operatorname{div}\left(\mathbf{j}_i + \mathbf{u}n_i\right) = 0 \quad \text{in } \Omega_p,\ i = 1, \dots, N, \tag{1}$$

where Ω_p is the pore space of the porous medium Ω, i denotes the solute species, $\mathbf{u}$ is the hydrodynamic velocity and n_i is the ith species concentration. For each species i, $\mathbf{u}n_i$ is its convective flux and $\mathbf{j}_i$ its migration–diffusion flux.

The solute velocity is given by the incompressible Stokes equations with a forcing term made of an exterior hydrodynamical force $\mathbf{f}$ and of the electric force applied to the fluid thanks to the charged species

$$\eta\Delta\mathbf{u} = \mathbf{f} + \nabla p + e\sum_{j=1}^{N} z_j n_j \nabla\Psi \quad \text{in } \Omega_p, \tag{2}$$

$$\operatorname{div}\mathbf{u} = 0 \quad \text{in } \Omega_p, \tag{3}$$

$$\mathbf{u} = 0 \quad \text{on } \partial\Omega_p \setminus \partial\Omega, \tag{4}$$

where $\eta > 0$ is the shear viscosity, p is the pressure, e is the elementary charge, z_i is the charge number of the species i and Ψ is the electrostatic potential. The pore space boundary is $\partial\Omega_p$ while $\partial\Omega$ is the outer boundary of the porous medium Ω. On the fluid/solid boundaries $\partial\Omega_p \setminus \partial\Omega$ we assume the no-slip boundary condition (4). For simplicity, we shall assume that Ω is a rectangular domain with periodic boundary conditions on $\partial\Omega$. Furthermore, in order to perform a homogenization process, we assume that the pore distribution is periodic in Ω_p.

We assume that all valencies z_j are different. If not, we lump together different ions with the same valency. Of course, for physical reasons, all valencies z_j are integers. We rank them by increasing order and we assume that they are both anions and cations, namely positive and negative valencies,

$$z_1 < z_2 < \cdots < z_N, \qquad z_1 < 0 < z_N, \tag{5}$$

and we denote by j^+ and j^- the sets of positive and negative valencies.

The migration–diffusion flux $\mathbf{j}_i$ is given by the following linear relationship

$$\mathbf{j}_i = -\sum_{j=1}^{N} L_{ij}(n_1, \dots, n_N)\big(\nabla\mu_j + z_j e\nabla\Psi\big), \quad i = 1, \dots, N, \tag{6}$$

where $L_{ij}(n_1, \dots, n_N)$ is the Onsager coefficient between i and j and μ_j is the chemical potential of the species j given by

$$\mu_j = \mu_j^0 + k_B T \ln n_j + k_B T \ln \gamma_j(n_1, \dots, n_N), \quad j = 1, \dots, N, \tag{7}$$

with γ_j being the **activity coefficient** of the species j, k_B is the Boltzmann constant, μ_j^0 is the standard chemical potential expressed at infinite dilution and T is the absolute temperature. The sum of all fluxes $\mathbf{j}_i$ is not zero because the solvent is not considered here and $\mathbf{j}_i$ is a particle flux. The Onsager tensor L_{ij} is made of the linear Onsager coefficients between the species i and j. It is symmetric and positive definite. Furthermore, on the fluid/solid interfaces a no-flux condition holds true

$$\mathbf{j}_i \cdot \nu = 0 \quad \partial\Omega_p \setminus \partial\Omega, \quad i = 1, \dots, N. \tag{8}$$

The electrostatic potential is calculated from the Poisson equation with the electric charge density as bulk source term

$$\mathcal{E}\Delta\Psi = -e\sum_{j=1}^{N} z_j n_j \quad \text{in } \Omega_p, \tag{9}$$

where $\mathcal{E} = \mathcal{E}_0\mathcal{E}_r$ is the dielectric constant of the solvent. The surface charge Σ is assumed to be given at the pores boundaries, namely the boundary condition reads

$$\mathcal{E}\nabla\Psi \cdot \nu = -\Sigma \quad \text{on } \partial\Omega_p \setminus \partial\Omega, \tag{10}$$

where ν is the unit exterior normal to Ω_p.

The activity coefficients γ_i and the Onsager coefficients L_{ij} depend on the electrolyte. At infinite dilution the solution can be considered **ideal** and we have $\gamma_i = 1$ and $L_{ij} = \delta_{ij} n_i D_i^0/(k_B T)$, where $D_i^0 > 0$ is the diffusion coefficient of species i at infinite dilution. At finite concentration, these expressions which correspond to the Poisson–Nernst–Planck equations are not valid anymore. **Non-ideal effects** modify the ion transport and they are to be taken into account if quantitative description of the system is required. Different models can be used. Here we choose the **Mean Spherical Approximation (MSA)** in simplified form [11] which is valid if the diameters of the ions are not too different. The activity coefficients read

$$\ln\gamma_j = -\frac{L_B \Gamma z_j^2}{1 + \Gamma\sigma_j} + \ln\gamma^{HS}, \quad j = 1, \dots, N, \tag{11}$$

where σ_j is the jth ion diameter, L_B is the Bjerrum length given by $L_B = e^2/(4\pi\mathcal{E}k_B T)$, γ^{HS} is the hard sphere term defined by (13), and Γ is the **MSA screening parameter** defined by

$$\Gamma^2 = \pi L_B \sum_{k=1}^{N} \frac{n_k z_k^2}{(1 + \Gamma\sigma_k)^2}. \tag{12}$$

For dilute solutions, i.e., when all n_j are small, we have

$$2\Gamma \approx \kappa = \frac{1}{\lambda_D} \quad \text{with } \lambda_D = \sqrt{\frac{\mathcal{E}k_B T}{e^2 \sum_{k=1}^{N} n_k z_k^2}},$$

where λ_D is the Debye length. Thus, $1/2\Gamma$ generalizes λ_D at finite concentration and it represents the size of the ionic spheres when the ion diameters σ_i are different from zero. (In the sequel we shall use a slightly different definition of the Debye length, relying on the notion of characteristic concentration, see Table 1.) In (11) γ^{HS} is the hard sphere term which is independent of the type of species and is given by

$$\ln\gamma^{HS} = p(\xi) \equiv \xi\frac{8 - 9\xi + 3\xi^2}{(1 - \xi)^3}, \quad \text{with } \xi = \frac{\pi}{6}\sum_{k=1}^{N} n_k\sigma_k^3, \tag{13}$$

where ξ is the solute packing fraction.

The Onsager coefficients L_{ij} are given by

$$L_{ij}(n_1, \dots, n_N) = n_i\left(\frac{D_i^0}{k_B T}\delta_{ij} + \mathbf{\Omega}_{ij}\right)\left(1 + \mathcal{R}_{ij}\right), \qquad i, j = 1, \dots, N, \tag{14}$$

where $\mathbf{\Omega}_{ij} = \mathbf{\Omega}_{ij}^c + \mathbf{\Omega}_{ij}^{HS}$ stands for the hydrodynamic interactions in the MSA formalism and there is no summation for repeated indices in (14). It is divided into two terms: the Coulombic part is

$$\mathbf{\Omega}_{ij}^c = -\frac{1}{3\eta}\frac{z_i z_j L_B n_j}{(1 + \Gamma\sigma_i)(1 + \Gamma\sigma_j)\left(\Gamma + \sum_{k=1}^{N} n_k \frac{\pi L_B z_k^2 \sigma_k}{(1 + \Gamma\sigma_k)^2}\right)}, \tag{15}$$

and the hard sphere part is

$$\mathbf{\Omega}_{ij}^{HS} = -\frac{\left(\sigma_i + \sigma_j\right)^2}{12\eta} n_j \frac{1 - \tilde{X}_3/5 + (\tilde{X}_3)^2/10}{1 + 2\tilde{X}_3}, \tag{16}$$

with

$$\tilde{X}_3 = \frac{\pi}{6}\sum_{i=1}^{N} n_i \frac{3X_1X_2 + X_3X_0}{4X_0^2} \quad \text{and} \quad X_k = \frac{\pi}{6}\sum_{i=1}^{N} n_i\sigma_i^k. \tag{17}$$

In (14) $\mathcal{R}_{ij}$ is the electrostatic relaxation term given by

$$\mathcal{R}_{ij} = \frac{\kappa_q^2 e^2 z_i z_j}{3\mathcal{E}k_B T(\sigma_i + \sigma_j)(1 + \Gamma\sigma_i)(1 + \Gamma\sigma_j)} \times \frac{1 - e^{-2\kappa_q(\sigma_i + \sigma_j)}}{\kappa_q^2 + 2\Gamma\kappa_q + 2\Gamma^2 - 2\pi L_B \sum_{k=1}^{N} n_k \frac{z_k^2 e^{-\kappa_q\sigma_k}}{(1 + \Gamma\sigma_k)^2}} \tag{18}$$

where $\kappa_q > 0$ is defined by

$$\kappa_q^2 = \frac{e^2}{\mathcal{E}k_B T}\frac{\sum_{i=1}^{N} n_i z_i^2 D_i^0}{\sum_{i=1}^{N} D_i^0}. \tag{19}$$

All these coefficients γ_j, Γ, $\mathbf{\Omega}_{ij}$, $\mathcal{R}_{ij}$ are varying in space since they are functions of the concentrations n_j. The $N \times N$ tensor (L_{ij}) is easily

Table 1
Data description.

	Quantity	Characteristic value
e	Electron charge	1.6e−19 C (Coulomb)
D_i^0	Diffusivity of the *i*th species	$D_i^0 \in (1.333, 2.032)$e−09 m^2/s
k_B	Boltzmann constant	1.38e−23 J/K
n_c	Characteristic concentration	$(6.02\;10^{24}, 6.02\;10^{26})$ particles/m^3
T	Temperature	293°K (Kelvin)
$\mathcal{E}$	Dielectric constant	6.93e−10 C/(mV)
η	Dynamic viscosity	1e−3 kg/(ms)
ℓ	Pore size	5e−9 m
λ_D	Debye's length	$\sqrt{\mathcal{E}k_BT/(e^2n_c)} \in (0.042, 0.42)$ nm
z_j	*j*th electrolyte valence	Given integer
Σ	Surface charge density	0.129 C/m^2 (clays)
f	Given applied force	N/m^3
σ_j	*j*th hard sphere diameter	2e−10 m
Ψ_c	Characteristic electrokinetic potential	0.02527 V (Volt)
L_B	Bjerrum length	7.3e−10 m

seen to be symmetric. However, to be coined "Onsager tensor" it should be positive too, which is not obvious from the above formulas. The reason is that they are only approximations for not too large concentrations. Nevertheless, when the concentrations n_j are small, all entries L_{ij} are first order perturbations of the ideal values $\delta_{ij}n_iD_i^0/(k_BT)$ and thus the Onsager tensor is positive at first order. The various parameters appearing in (1)–(19) are defined in Table 1.

As already said we consider a rectangular domain $\Omega = \prod_{k=1}^{d}(0, L_k)^d$ ($d = 2, 3$ is the space dimension), $L_k > 0$ and at the outer boundary $\partial\Omega$ we set

$$\Psi + \Psi^{ext}(x), \quad n_i, \mathbf{u} \text{ and } p \text{ are } \Omega\text{-periodic.} \tag{20}$$

The applied exterior potential $\Psi^{ext}(x)$ can typically be linear, equal to $\mathbf{E}\cdot x$, where $\mathbf{E}$ is an imposed electrical field. Note that the applied exterior force **f** in the Stokes equation (2) can also be interpreted as some imposed pressure drop or gravity force. Due to the complexity of the geometry and of the equations, it is necessary for engineering applications to upscale the system (1)–(10) and to replace the flow equations with a Darcy type law, including electro-osmotic effects.

It is a common practice to assume that the porous medium has a periodic microstructure. For such media, and in the ideal case, formal two-scale asymptotic analysis of system (1)–(10) has been performed in many previous papers. Many of these works rely on a preliminary linearization of the problem which is first due to O'Brien et al. [21]. Let us mention in particular the work of Looker and Carnie in [22] that we rigorously justify in [23] and for which we provided numerical experiments in [24]. Other relevant references include [2,25–29,3,30–38].

Our goal here is to generalize these works for the non-ideal MSA model. More specifically, we extend our previous works [23,24] and provide the homogenized system for a linearized version of (1)–(10) in a rigid periodic porous medium (the linearization is performed around a so-called equilibrium solution which satisfies the full nonlinear system (1)–(10) with vanishing fluxes). The homogenized system is an elliptic system of $(N + 1)$ equations

$$-\mathrm{div}_x\mathcal{M}\nabla(p^0, \{\mu_j\}_{1\le j\le N}) = \mathcal{S} \quad \text{in } \Omega,$$

where p^0 is the pressure, μ_j the chemical potential of the jth species, $\mathcal{M}$ the Onsager homogenized tensor and $\mathcal{S}$ a source term. The $(N + 1)$ equations express the conservation of mass for the fluid and the N species. More details will be given in Section 5.

In Section 2 we provide a dimensionless version of system (1)–(10). We also explain in Lemma 1 how the ideal case can be recovered from the non-ideal MSA model in the limit of small characteristic value of the solute packing fraction. Section 3 is concerned with the definition of so-called equilibrium solutions when the external forces are vanishing (but not the surface charge Σ). Computing these equilibrium solutions amounts to solve a MSA variant of the nonlinear Poisson–Boltzmann equation for the potential. Existence of a solution to such a Poisson–Boltzmann equation is established in Section 6 under a smallness assumption for a characteristic value of the solute packing fraction. To our knowledge this existence result is the first one at this level of generality. Let us mention nevertheless that, in a slightly simpler setting (two species only and a linear approximation of $p(\xi)$) and with a different method (based on a saddle point approach in the two variables Ψ and $\{n_j\}$), a previous existence result was obtained in [39]. In Section 4 we give a linearized version of system (1)–(10). We generalize the seminal work of O'Brien et al. [21], which was devoted to the ideal case, to the present setting of the MSA model. Under the assumption that all ions have the same diameter σ_j we establish in Proposition 11 and Lemma 12 that the linearized model is well-posed and that its solution satisfies uniform a priori estimates. This property is crucial for homogenization of the linearized model which is performed in Section 5. Following our work [23] in the ideal case, we rigorously obtained the homogenized problem in Theorem 14 and derive precise formulas for the effective tensor in Proposition 15. Furthermore we prove that the so called **Onsager relation** (see e.g. [40]) is satisfied, namely the full homogenized tensor $\mathcal{M}$ is symmetric positive definite.

Eventually Section 7 is devoted to a numerical study of the obtained homogenized coefficients, including their sensitivities to various physical parameters and a systematic comparison with the ideal case.

2. Non-dimensional form

Before studying its homogenization, we need a **dimensionless** form of Eqs. (1)–(10). We follow the same approach as in our previous works [23,24]. The known data are the characteristic pore size ℓ, the characteristic domain size L, the surface charge density Σ (having the characteristic value Σ_c), the static electrical potential Ψ^{ext} and the applied fluid force **f**. As usual, we introduce a small parameter ε which is the ratio between the pore size and the medium size, $\varepsilon = \ell/L \ll 1$.

We are interested in characteristic concentrations n_c taking on typical values in the range $(10^{-2}, 1)$ in Mole/liter, that is $(6.02 \times 10^{24}, 6.02 \times 10^{26})$ particles per m^3. From Table 1, we write $\lambda_D = \sqrt{\mathcal{E}k_BT/(e^2n_c)}$ and we find out that λ_D varies in the range $(0.042, 0.42)$ nm.

Following [20], we introduce the characteristic potential $\zeta = k_BT/e$ and the parameter β related to the Debye–Hückel parameter

$\kappa = 1/\lambda_D$, as follows

$$\beta = \left(\frac{\ell}{\lambda_D}\right)^2. \tag{21}$$

Next we rescale the space variable by setting $x' = x/L$ and $\Omega' = \Omega/L = \prod_{k=1}^{d}(0, L_k')^d$ (we shall drop the primes for simplicity in the sequel). The rescaled dimensions L_k' are assumed to be independent of ε. Similarly, the pore space becomes $\Omega^\varepsilon = \Omega_p/L$ which is a periodically perforated domain with period ε. Still following [20], we define other characteristic quantities

$$\Gamma_c = \sqrt{\pi L_B n_c}, \qquad p_c = n_c k_B T, \qquad u_c = \varepsilon^2 \frac{k_B T n_c L}{\eta},$$

where Γ_c, in terms of n_c, is deduced from (12), p_c is a pressure equilibrating the electrokinetic forces in (2) and u_c is the velocity corresponding to a Poiseuille flow in a tube of diameter ℓ, length L and pressure drop p_c. We also introduce adimensionalized forcing terms

$$\Psi^{ext,*} = \frac{e\Psi^{ext}}{k_B T}, \qquad \mathbf{f}^* = \frac{\mathbf{f}L}{p_c}, \qquad \Sigma^* = \frac{\Sigma}{\Sigma_c}, \qquad N_\sigma = \frac{e\Sigma_c \ell}{\mathcal{E} k_B T},$$

and adimensionalized unknowns

$$\Gamma^\varepsilon = \frac{\Gamma}{\Gamma_c}, \qquad p^\varepsilon = \frac{p}{p_c}, \qquad \mathbf{u}^\varepsilon = \frac{\mathbf{u}}{u_c}, \qquad \Psi^\varepsilon = \frac{e\Psi}{k_B T},$$

$$n_j^\varepsilon = \frac{n_j}{n_c}, \qquad \mathbf{j}_j^\varepsilon = \frac{\mathbf{j}_j L}{n_c D_j^0}.$$

The dimensionless equations for hydrodynamical and electrostatic parts are thus

$$\varepsilon^2 \Delta \mathbf{u}^\varepsilon - \nabla p^\varepsilon = \mathbf{f}^* + \sum_{j=1}^{N} z_j n_j^\varepsilon(x) \nabla \Psi^\varepsilon \quad \text{in } \Omega^\varepsilon, \tag{22}$$

$$\mathbf{u}^\varepsilon = 0 \quad \text{on } \partial\Omega^\varepsilon \setminus \partial\Omega, \qquad \operatorname{div} \mathbf{u}^\varepsilon = 0 \quad \text{in } \Omega^\varepsilon, \tag{23}$$

$$-\varepsilon^2 \Delta \Psi^\varepsilon = \beta \sum_{j=1}^{N} z_j n_j^\varepsilon(x) \quad \text{in } \Omega^\varepsilon; \tag{24}$$

$$\varepsilon \nabla \Psi^\varepsilon \cdot \nu = -N_\sigma \Sigma^* \quad \text{on } \partial\Omega^\varepsilon \setminus \partial\Omega, \tag{25}$$

$$(\Psi^\varepsilon + \Psi^{ext,*}), \quad \mathbf{u}^\varepsilon \text{ and } p^\varepsilon \text{ are } \Omega\text{-periodic in } x. \tag{26}$$

(Recall that $\Omega = \prod_{k=1}^{d}(0, L_k)^d$ so that periodic boundary conditions make sense for such a rectangular domain.) Furthermore, from (11) and (12) we define

$$\gamma_j^\varepsilon = \gamma_\varepsilon^{HS} \exp\left\{-\frac{L_B \Gamma^\varepsilon \Gamma_c z_j^2}{(1 + \Gamma^\varepsilon \Gamma_c \sigma_j)}\right\} \qquad \text{and}$$
$$(\Gamma^\varepsilon)^2 = \sum_{k=1}^{N} \frac{n_k^\varepsilon z_k^2}{(1 + \Gamma_c \Gamma^\varepsilon \sigma_k)^2}. \tag{27}$$

The solute packing fraction ξ is already an adimensionalized quantity (taking values in the range (0, 1)). However, introducing a characteristic value ξ_c we can adimensionalize its formula (13) as

$$\xi_c = \frac{\pi}{6} n_c \sigma_c^3, \qquad \xi = \xi_c \sum_{k=1}^{N} n_k^\varepsilon \left(\frac{\sigma_k}{\sigma_c}\right)^3, \tag{28}$$

where σ_c is the characteristic ion diameter. We note that $\Gamma_c \in (0.117, 1.17)\, 10^9\ \text{m}^{-1}$, $\Gamma_c \sigma_c \in (0.023, 0.23)$, $L_B \Gamma_c \in (0.0857, 0.857)$ and $\xi_c \in (0.252, 25.2)\, 10^{-4}$ which is a small parameter. Concerning $\mathbf{\Omega}_{ij}^c$ which has to be compared with $D_i^0/(k_B T)$, we find out that

$$L_B n_c k_B T/(3\eta \Gamma_c D_i^0) = \Gamma_c k_B T/(3\pi \eta D_i^0) \in (0.005415, 0.5415),$$

while $\mathbf{\Omega}_{ij}^{HS}$ is slightly smaller and $\mathcal{R}_{ij}$ looks negligible. Concerning the transport term, the Peclet number for the jth species is

$$\text{Pe}_j = \frac{u_c L}{D_j^0} = \frac{\ell^2 k_B T n_c}{\eta D_j^0} \in (0.01085, 1.085).$$

After these considerations we obtain the dimensionless form of Eq. (1):

$$\operatorname{div}\left(\mathbf{j}_i^\varepsilon + \text{Pe}_i n_i^\varepsilon \mathbf{u}^\varepsilon\right) = 0 \quad \text{in } \Omega^\varepsilon, i = 1, \dots, N, \tag{29}$$

$$\mathbf{j}_i^\varepsilon \cdot \nu = 0 \quad \text{on } \partial\Omega^\varepsilon \setminus \partial\Omega,\ i = 1, \dots, N, \tag{30}$$

$$\mathbf{j}_i^\varepsilon = -\sum_{j=1}^{N} n_i^\varepsilon K_{ij}^\varepsilon \nabla M_j^\varepsilon \quad \text{and} \quad M_j^\varepsilon = \ln\left(n_j^\varepsilon \gamma_j^\varepsilon e^{z_j \Psi^\varepsilon}\right), \tag{31}$$

$$K_{ij}^\varepsilon = \left(\delta_{ij} + \frac{k_B T}{D_i^0} \mathbf{\Omega}_{ij}\right)\left(1 + \mathcal{R}_{ij}\right), \quad i, j = 1, \dots, N. \tag{32}$$

Eventually the porous medium Ω^ε is assumed to be an ε-periodic smooth open subset of $\Omega = \prod_{k=1}^{d}(0, L_k)^d$ and L_k/ε are integers for every k and every ε. It is built from Ω by removing a periodic distributions of solid obstacles which, after rescaling by $1/\varepsilon$, are all similar to the unit obstacle Y_S. More precisely, we consider a smooth partition of the unit periodicity cell $Y = Y_S \cup Y_F$ where Y_S is the solid part and Y_F is the fluid part. The liquid/solid interface is $S = \partial Y_S \setminus \partial Y$. The fluid part is assumed to be a smooth connected open subset (no assumption is made on the solid part). We define $Y_\varepsilon^j = \varepsilon(Y_F + j)$ and $\Omega^\varepsilon = \bigcup_{j \in \mathbb{Z}^d} Y_\varepsilon^j \cap \Omega$.

We also assume a periodic distribution of charges $\Sigma^* \equiv \Sigma^*(x/\varepsilon)$. This will imply that, at equilibrium (in the absence of other forces), the solution of system (22)–(32) is also periodic of period ε.

We recall that the ideal model (see e.g. [20]) corresponds to the following values of the activity coefficient, $\gamma_i = 1$, and of the Onsager tensor $L_{ij} = \delta_{ij} n_i D_i^0/(k_B T)$. In view of our previous dimensional analysis it is interesting to see in which sense the present non-ideal MSA model is close to the ideal case. We shall make this connection in the limit of a small parameter going to zero. More precisely we rely on the characteristic value ξ_c of the solute packing fraction, defined by (28). The smallness of ξ_c (which means a low concentration, weighted by the ion size) will be a crucial assumption in Theorem 2 that establishes the existence of equilibrium solutions to the MSA model. It is therefore a natural parameter to study the limit ideal case. With this goal in mind we introduce two additional dimensionless numbers: Bjerrum's parameter (also called the Landau plasma parameter)

$$bi = \frac{L_B}{\sigma_c}, \tag{33}$$

and the ratio appearing in Stokes' formula for the drag hydrodynamic force

$$S = \frac{k_B T}{\eta D_c^0 \sigma_c}, \tag{34}$$

where D_c^0 is the characteristic value for the diffusivities D_i^0, $1 \le i \le N$. According to the numerical values of Table 1, we assume that

$$bi \quad \text{and} \quad S \quad \text{are of order one.} \tag{35}$$

More precisely, it is enough to assume that bi and S are bounded quantities when ξ_c becomes infinitely small (they can tend to zero too).

Lemma 1. *Under assumption (35), the ideal case is the limit of our non-ideal MSA model for small solute packing fraction ξ_c, namely*

$$K_{ij}^\varepsilon = \delta_{ij} + O(\sqrt{\xi_c}), \quad \textit{and} \quad \ln \gamma_j^\varepsilon = O(\sqrt{\xi_c}). \tag{36}$$

Hence the MSA model is a regular $O(\sqrt{\xi_c})$ perturbation of the idealized model. Theorem 2 in Section 3 gives the equilibrium MSA solution as an $O(\sqrt{\xi_c})$ perturbation of the equilibrium idealized solution. The arguments from Section 6 could be extended to interpret the MSA variant of the Poisson–Boltzmann equation as an $O(\sqrt{\xi_c})$ perturbation of the classical (ideal) Poisson–Boltzmann equation.

Proof. In view of formula (13) we find

$$\ln \gamma^{HS} = O(\xi_c).$$

From its definition (12) and for small ξ_c we deduce that

$$\Gamma = O(\sqrt{L_B n_c}).$$

Using assumption (35), $bi = O(1)$, yields

$$\Gamma\sigma_j = O(\sqrt{bi\xi_c}) = O(\sqrt{\xi_c}) \quad \text{and} \quad \Gamma L_B = O(\sqrt{bi^3\xi_c}) = O(\sqrt{\xi_c}),$$

which implies from (11)

$$-\frac{L_B\Gamma z_j^2}{1+\Gamma\sigma_j} = O(\sqrt{\xi_c}) \quad \text{and thus} \quad \ln \gamma_j = O(\sqrt{\xi_c}).$$

Turning to the Onsager coefficients, we obtain from (19) that

$$\kappa_q\sigma_c = O(\sqrt{L_B n_c}\sigma_c) = O(\sqrt{\xi_c}),$$

which implies after some algebra that

$$\mathcal{R}_{ij} = O(L_B\kappa_q) = O(\sqrt{\xi_c}).$$

Using the second part of assumption (35), $S = O(1)$, yields

$$\Omega_{ij}^c \frac{k_BT}{D_i^0} = O\left(\frac{k_BT}{\eta D_c^0\sigma_c}\sqrt{bi\xi_c}\right) = O(S\sqrt{bi\xi_c}) = O(\sqrt{\xi_c}).$$

Similarly

$$\Omega_{ij}^{HS} \frac{k_BT}{D_i^0} = O(S\xi_c) = O(\xi_c),$$

which eventually yields

$$L_{ij} = \frac{n_iD_i^0}{k_BT}(\delta_{ij} + O(\sqrt{\xi_c})),$$

from which we infer the conclusion (36). Note that a similar approximation holds for the chemical potential

$$\mu_j = \mu_j^0 + k_BT(\ln n_j + O(\sqrt{\xi_c})). \quad \square$$

3. Equilibrium solution

The goal of this section is to find a so-called **equilibrium solution** of system (22)–(32) when the exterior forces are vanishing $\mathbf{f} = 0$ and $\Psi^{ext} = 0$. However, the surface charge density Σ^* is not assumed to vanish or to be small. This equilibrium solution will be a reference solution around which we shall linearize system (22)–(32) in the next section. Then we perform the homogenization of the (partially) linearized system. We denote by $n_i^{0,\varepsilon}$, $\Psi^{0,\varepsilon}$, $\mathbf{u}^{0,\varepsilon}$, $M_i^{0,\varepsilon}$, $p^{0,\varepsilon}$ the equilibrium quantities.

In the case $\mathbf{f} = 0$ and $\Psi^{ext} = 0$, one can find an equilibrium solution by choosing a zero fluid velocity and taking all diffusion fluxes equal to zero. More precisely, we require

$$\mathbf{u}^{0,\varepsilon} = 0 \quad \text{and} \quad \nabla M_j^{0,\varepsilon} = 0, \tag{37}$$

which obviously implies that $\mathbf{j}_i^{0,\varepsilon} = 0$ and (29)–(30) are satisfied. The Stokes equation (22) shall give the corresponding value of the pressure satisfying

$$\nabla p^{0,\varepsilon}(x) = -\sum_{j=1}^N z_j n_j^{0,\varepsilon}(x)\nabla\Psi^{0,\varepsilon}(x),$$

for which an explicit expression is given below (see (47)). From $\nabla M_j^{0,\varepsilon} = 0$ and (31) we deduce that there exist constants $n_j^0(\infty) > 0$ and $\gamma_j^0(\infty) > 0$ such that

$$n_j^{0,\varepsilon}(x) = n_j^0(\infty)\gamma_j^0(\infty)\frac{\exp\{-z_j\Psi^{0,\varepsilon}(x)\}}{\gamma_j^{0,\varepsilon}(x)}. \tag{38}$$

The value $n_j^0(\infty)$ is the reservoir concentration (also called the infinite dilute concentration) which will be later assumed to satisfy the bulk electroneutrality condition for zero potential. The value $\gamma_j^0(\infty)$ is the reservoir activity coefficient which corresponds to the value of $\gamma_j^{0,\varepsilon}$ for zero potential (see (49) below for its precise formula). Before plugging (38) into Poisson equation (24) to obtain the MSA variant of the Poisson–Boltzmann equation for the potential $\Psi^{0,\varepsilon}$, we have to determine the value of the activity coefficient $\gamma_j^{0,\varepsilon}$.

From the first equation of (27) we have

$$\begin{aligned}\gamma_j^{0,\varepsilon} &= \gamma^{HS}(\xi)\exp\left\{-\frac{L_B\Gamma^{0,\varepsilon}\Gamma_c z_j^2}{1+\Gamma^{0,\varepsilon}\Gamma_c\sigma_j}\right\}\\ &= \exp\left\{p(\xi) - \frac{L_B\Gamma^{0,\varepsilon}\Gamma_c z_j^2}{1+\Gamma^{0,\varepsilon}\Gamma_c\sigma_j}\right\},\end{aligned} \tag{39}$$

where, for $\xi \in [0, 1)$, $p(\xi)$ is a polynomial defined by (13) and, recalling definition (28) of the characteristic value ξ_c, the solute packing fraction ξ is

$$\xi = \xi_c\sum_{j=1}^N n_j^{0,\varepsilon}\left(\frac{\sigma_j}{\sigma_c}\right)^3. \tag{40}$$

The second equation of (27) gives a formula for the MSA screening parameter

$$(\Gamma^{0,\varepsilon})^2 = \sum_{k=1}^N \frac{n_k^{0,\varepsilon}z_k^2}{(1+\Gamma_c\Gamma^{0,\varepsilon}\sigma_k)^2}. \tag{41}$$

Let us explain how to solve the algebraic Eqs. (38)–(41).

Combining (38)–(40), for given potential $\Psi^{0,\varepsilon}$ and screening parameter $\Gamma^{0,\varepsilon}$, the solute packing fraction ξ is a solution of the algebraic equation

$$\begin{aligned}\xi &= \exp\{-p(\xi)\}\xi_c\sum_{j=1}^N\left(\frac{\sigma_j}{\sigma_c}\right)^3 n_j^0(\infty)\gamma_j^0(\infty)\\ &\quad\times\exp\left\{-z_j\Psi^{0,\varepsilon} + \frac{L_B\Gamma^{0,\varepsilon}\Gamma_c z_j^2}{1+\Gamma^{0,\varepsilon}\Gamma_c\sigma_j}\right\}.\end{aligned} \tag{42}$$

Once we know $\xi \equiv \xi(\Psi^{0,\varepsilon}, \Gamma^{0,\varepsilon})$, solution of (42), combining (38) and (41), $\Gamma^{0,\varepsilon}$ is a solution of the following algebraic equation, depending on $\Psi^{0,\varepsilon}$,

$$\begin{aligned}(\Gamma^{0,\varepsilon})^2 &= \sum_{j=1}^N n_j^0(\infty)\gamma_j^0(\infty)\frac{z_j^2}{(1+\Gamma^{0,\varepsilon}\Gamma_c\sigma_j)^2}\\ &\quad\times\exp\left\{-z_j\Psi^{0,\varepsilon} + \frac{L_B\Gamma^{0,\varepsilon}\Gamma_c z_j^2}{1+\Gamma^{0,\varepsilon}\Gamma_c\sigma_j} - p\left(\xi(\Psi^{0,\varepsilon}, \Gamma^{0,\varepsilon})\right)\right\}.\end{aligned} \tag{43}$$

All in all, solving the two algebraic equations (42) and (43) yields the values $\Gamma^{0,\varepsilon}(\Psi^{0,\varepsilon})$ and $\tilde{\xi}(\Psi^{0,\varepsilon}) \equiv \xi\left(\Psi^{0,\varepsilon}, \Gamma^{0,\varepsilon}(\Psi^{0,\varepsilon})\right)$ (see Section 6 for a precise statement).

Then the electrostatic equation (24) reduces to the following MSA variant of the Poisson–Boltzmann equation which is a nonlinear partial differential equation for the sole unknown $\Psi^{0,\varepsilon}$

$$\begin{cases} -\varepsilon^2 \Delta \Psi^{0,\varepsilon} = \beta \displaystyle\sum_{j=1}^{N} z_j n_j^0(\infty)\gamma_j^0(\infty) \\ \quad \times \exp\left\{-z_j\Psi^{0,\varepsilon} + \dfrac{L_B\Gamma^{0,\varepsilon}(\Psi^{0,\varepsilon})\Gamma_c z_j^2}{1+\Gamma^{0,\varepsilon}(\Psi^{0,\varepsilon})\Gamma_c\sigma_j} - p(\tilde{\xi}(\Psi^{0,\varepsilon}))\right\} \\ \quad \text{in } \Omega^\varepsilon, \\ \varepsilon\nabla\Psi^{0,\varepsilon}\cdot\nu = -N_\sigma\Sigma^* \quad \text{on } \partial\Omega^\varepsilon\setminus\partial\Omega,\ \Psi^{0,\varepsilon} \text{ is } \Omega\text{-periodic.} \end{cases} \tag{44}$$

In Section 6 (see Theorem 24) we shall prove the following existence result. Unfortunately we are unable to prove uniqueness.

Theorem 2. *Assuming that the surface charge distribution Σ^* belongs to $L^\infty(\partial\Omega^\varepsilon)$, that the ions are not too small, namely*

$$L_B < (6+4\sqrt{2}) \min_{1\le j\le N} \frac{\sigma_j}{z_j^2} \quad \text{with } 6+4\sqrt{2} \approx 11.656854, \tag{45}$$

and that the characteristic value ξ_c is small enough, there exists at least one solution of (44) $\Psi^{0,\varepsilon} \in H^1(\Omega^\varepsilon)\cap L^\infty(\Omega^\varepsilon)$.

Introducing the primitive $E_j(\Psi)$ of

$$E_j'(\Psi) = z_j n_j^0(\infty)\gamma_j^0(\infty) \times \exp\left\{-z_j\Psi + \frac{L_B\Gamma^{0,\varepsilon}(\Psi)\Gamma_c z_j^2}{1+\Gamma^{0,\varepsilon}(\Psi)\Gamma_c\sigma_j} - p(\tilde{\xi}(\Psi))\right\}, \tag{46}$$

the equilibrium pressure in Stokes equations (corresponding to a zero velocity) is given (up to an additive constant) by

$$p^{0,\varepsilon} = \sum_{j=1}^{N} E_j(\Psi^{0,\varepsilon}). \tag{47}$$

Remark 3. In the ideal case, i.e., when $\gamma_j^{0,\varepsilon} = 1$, the function $E_j(\Psi^{0,\varepsilon})$ defined by (46) is simply equal to $n_j^{0,\varepsilon} = n_j^0(\infty)\exp\{-z_j\Psi^{0,\varepsilon}\}$.

From a physical point of view, it is desired that the solution of (44) vanishes, i.e., $\Psi^{0,\varepsilon} = 0$, when the surface charges are null, i.e., $\Sigma^* = 0$. Therefore, following the literature, we impose the **bulk electroneutrality condition**

$$\sum_{j=1}^{N} E_j'(0) = -\sum_{j=1}^{N} z_j n_j^0(\infty)\gamma_j^0(\infty) \times \exp\left\{\frac{L_B\Gamma^{0,\varepsilon}(0)\Gamma_c z_j^2}{1+\Gamma^{0,\varepsilon}(0)\Gamma_c\sigma_j} - p(\tilde{\xi}(0))\right\} = 0, \tag{48}$$

where $\Gamma^{0,\varepsilon}(0)$ is the solution of (43) for $\Psi^{0,\varepsilon} = 0$.

Defining the equilibrium activity coefficient by

$$\gamma_j^0(\infty) = \exp\left\{p(\tilde{\xi}(0)) - \frac{L_B\Gamma^{0,\varepsilon}(0)\Gamma_c z_j^2}{1+\Gamma^{0,\varepsilon}(0)\Gamma_c\sigma_j}\right\}, \tag{49}$$

the bulk electroneutrality condition (48) reduces to its usual form

$$\sum_{j=1}^{N} z_j n_j^0(\infty) = 0.$$

Formula (49) is an implicit algebraic equation for $\gamma_j^0(\infty)$ since $\tilde{\xi}(0)$ and $\Gamma^{0,\varepsilon}(0)$ depend themselves on the $\gamma_k^0(\infty)$'s. The next lemma proves that it is a well-posed equation.

Lemma 4. *There always exists a unique solution $\gamma_j^0(\infty)$ of the algebraic equation (49).*

Proof. Assume that there exists $\gamma_j^0(\infty)$ satisfying (49) and plug this formula in (43). It yields

$$\left(\Gamma^{0,\varepsilon}(0)\right)^2 = \sum_{j=1}^{N} \frac{n_j^0(\infty) z_j^2}{(1+\Gamma^{0,\varepsilon}(0)\Gamma_c\sigma_j)^2},$$

which admits a unique solution $\Gamma^{0,\varepsilon}(0) > 0$ since the left hand side is strictly increasing and the right hand side is decreasing. On the same token, using (49) in (42) leads to

$$\tilde{\xi}(0) = \xi_c \sum_{j=1}^{N} \left(\frac{\sigma_j}{\sigma_c}\right)^3 n_j^0(\infty).$$

We have thus found explicit values for $\Gamma^{0,\varepsilon}(0)$ and $\tilde{\xi}(0)$ which do not depend on the $\gamma_k^0(\infty)$'s. Using them in (49) gives its unique solution $\gamma_j^0(\infty)$. □

Remark 5. From the proof of Lemma 4 it is clear that $\Gamma^{0,\varepsilon}(0)$ does not depend on ξ_c, while $\tilde{\xi}(0) = O(\xi_c)$, which implies that $\gamma_j^0(\infty) = O(1)$ for small ξ_c.

Remark 6. The bulk electroneutrality condition (48) is not a restriction. Actually all our results hold under the much weaker assumption (5) that all valencies z_j do not have the same sign. Indeed, if (48) is not satisfied, we can make a change of variables in the Poisson–Boltzmann equation (44), defining a new potential $\tilde{\Psi}^{0,\varepsilon} = \Psi^{0,\varepsilon} + C$ where C is a constant reference potential. Since the function

$$C \to \Phi(C) = \sum_{j=1}^{N} z_j n_j^0(\infty)\gamma_j^0(\infty) \times \exp\left\{-z_j C + \frac{L_B\Gamma^{0,\varepsilon}(C)\Gamma_c z_j^2}{1+\Gamma^{0,\varepsilon}(C)\Gamma_c\sigma_j} - p(\tilde{\xi}(C))\right\}$$

is continuous and admits opposite infinite limits when C tends to ±, there exists at least one value C such that $\Phi(C) = 0$. This change of variables for the potential leaves (43) and (44) invariant if we change the constants $n_j^0(\infty)\gamma_j^0(\infty)$ in new constants

$$\tilde{n}_j^0(\infty)\tilde{\gamma}_j^0(\infty) = n_j^0(\infty)\gamma_j^0(\infty) \times \exp\left\{-z_j C + \frac{L_B\Gamma^{0,\varepsilon}(C)\Gamma_c z_j^2}{1+\Gamma^{0,\varepsilon}(C)\Gamma_c\sigma_j} - \frac{L_B\Gamma^{0,\varepsilon}(0)\Gamma_c z_j^2}{1+\Gamma^{0,\varepsilon}(0)\Gamma_c\sigma_j} - p(\tilde{\xi}(C)) + p(\tilde{\xi}(0))\right\}.$$

These new constants satisfy the bulk electroneutrality condition (48).

4. Linearization

We now proceed to the linearization of electrokinetic Eqs. (22)–(32) around the equilibrium solution computed in Section 3. We therefore assume that the external forces, namely the static electric potential $\Psi^{ext}(x)$ and the hydrodynamic force $\mathbf{f}(x)$, are small. However, the surface charge density Σ^* on the pore walls is not assumed to be small since it is part of the equilibrium problem studied in Section 3. Such a linearization process is classical in the ideal case (see the seminal paper [21] by O'Brien et al.) but it is new and slightly more complicated for the MSA model. For small exterior forces, we write the perturbed electrokinetic unknowns as

$$n_i^\varepsilon(x) = n_i^{0,\varepsilon}(x) + \delta n_i^\varepsilon(x), \qquad \Psi^\varepsilon(x) = \Psi^{0,\varepsilon}(x) + \delta\Psi^\varepsilon(x),$$
$$\mathbf{u}^\varepsilon(x) = \mathbf{u}^{0,\varepsilon}(x) + \delta\mathbf{u}^\varepsilon(x), \qquad p^\varepsilon(x) = p^{0,\varepsilon}(x) + \delta p^\varepsilon(x),$$

where $n_i^{0,\varepsilon}$, $\Psi^{0,\varepsilon}$, $\mathbf{u}^{0,\varepsilon}$, $p^{0,\varepsilon}$ are the equilibrium quantities, corresponding to $\mathbf{f} = 0$ and $\Psi^{ext} = 0$. The δ prefix indicates a perturbation. Since the equilibrium velocity vanishes $\mathbf{u}^{0,\varepsilon} = 0$, we identify in the sequel $\mathbf{u}^\varepsilon = \delta\mathbf{u}^\varepsilon$.

Motivated by the form of the Boltzmann equilibrium distribution and the calculation of $n_i^{0,\varepsilon}$, we follow the lead of [21] and introduce a so-called ionic potential Φ_i^ε which is defined in terms of n_i^ε by

$$n_i^\varepsilon(x)\gamma_i^\varepsilon(x) = n_i^0(\infty)\gamma_j^0(\infty) \times \exp\{-z_i(\Psi^\varepsilon(x) + \Phi_i^\varepsilon(x) + \Psi^{ext,*}(x))\}, \tag{50}$$

where

$$\gamma_i^\varepsilon = \exp\left\{p(\xi) - \frac{L_B\Gamma^\varepsilon\Gamma_c z_i^2}{1+\Gamma^\varepsilon\Gamma_c\sigma_i}\right\} \quad \text{and} \quad (\Gamma^\varepsilon)^2 = \sum_{k=1}^N \frac{n_k^\varepsilon z_k^2}{(1+\Gamma^\varepsilon\Gamma_c\sigma_k)^2}, \tag{51}$$

with

$$p(\xi) = \xi\frac{8-9\xi+3\xi^2}{(1-\xi)^3} \quad \text{and} \quad \xi = \xi_c\sum_{j=1}^N n_j^\varepsilon\left(\frac{\sigma_j}{\sigma_c}\right)^3.$$

Since $\Phi_i^{0,\varepsilon} = 0$ by virtue of formula (38) for $n_i^{0,\varepsilon}$, we identify $\delta\Phi_i^\varepsilon$ with Φ_i^ε.

Lemma 7. *The linearization of* (50)–(51) *yields*

$$\delta n_i^\varepsilon(x) = \sum_{k=1}^N z_k\alpha_{i,k}^{0,\varepsilon}(x)\Big(\delta\Psi^\varepsilon(x) + \Phi_k^\varepsilon(x) + \Psi^{ext,*}(x)\Big), \tag{52}$$

with

$$\begin{aligned}\alpha_{i,k}^{0,\varepsilon} &= -n_i^{0,\varepsilon}\delta_{ik} + B^{0,\varepsilon}n_i^{0,\varepsilon}n_k^{0,\varepsilon}\sigma_k^3 - \frac{L_B\Gamma_c}{A^{0,\varepsilon}}n_i^{0,\varepsilon}n_k^{0,\varepsilon}\\ &\quad\times\left(\frac{z_i^2}{(1+\Gamma^{0,\varepsilon}\Gamma_c\sigma_i)^2} - B^{0,\varepsilon}C^{0,\varepsilon}\right)\\ &\quad\times\left(\frac{z_k^2}{(1+\Gamma^{0,\varepsilon}\Gamma_c\sigma_k)^2} - B^{0,\varepsilon}D^{0,\varepsilon}\sigma_k^3\right),\end{aligned} \tag{53}$$

where

$$B^{0,\varepsilon} = \frac{\frac{\pi}{6}n_c p'(\xi)}{1+\xi p'(\xi)}, \qquad C^{0,\varepsilon} = \sum_{k=1}^N \frac{z_k^2\sigma_k^3 n_k^{0,\varepsilon}}{(1+\Gamma^{0,\varepsilon}\Gamma_c\sigma_k)^2},$$
$$D^{0,\varepsilon} = \sum_{k=1}^N \frac{z_k^2 n_k^{0,\varepsilon}}{(1+\Gamma^{0,\varepsilon}\Gamma_c\sigma_k)^2}$$

and

$$\begin{aligned}A^{0,\varepsilon} &= 2\Gamma^{0,\varepsilon} + 2\Gamma_c\sum_{k=1}^N\frac{n_k^{0,\varepsilon}z_k^2\sigma_k}{(1+\Gamma^{0,\varepsilon}\Gamma_c\sigma_k)^3}\\ &\quad - L_B\Gamma_c\sum_{k=1}^N\frac{n_k^{0,\varepsilon}z_k^4}{(1+\Gamma^{0,\varepsilon}\Gamma_c\sigma_k)^4}\\ &\quad + L_B\Gamma_c B^{0,\varepsilon}C^{0,\varepsilon}\sum_{k=1}^N\frac{n_k^{0,\varepsilon}z_k^2}{(1+\Gamma^{0,\varepsilon}\Gamma_c\sigma_k)^2}.\end{aligned}$$

Under assumption (45) *of* Theorem 2 *the coefficient $A^{0,\varepsilon}$ is positive.*

Furthermore, at equilibrium, if we consider $n_i^{0,\varepsilon}$ as a function of $\Psi^{0,\varepsilon}$, we have

$$\frac{dn_i^{0,\varepsilon}}{d\Psi^{0,\varepsilon}} = \sum_{k=1}^N z_k\alpha_{i,k}^{0,\varepsilon}. \tag{54}$$

If all ions have the same diameter ($\sigma_k = \sigma_i$ for all i, k), then the coefficients $\alpha_{i,k}^{0,\varepsilon} = \alpha_{k,i}^{0,\varepsilon}$ are symmetric.

Remark 8. At equilibrium, the concentrations $n_i^{0,\varepsilon}$, as well as the screening parameter $\Gamma^{0,\varepsilon}$, depend only on $\Psi^{0,\varepsilon}$ through the algebraic equations (38)–(41). However, outside equilibrium the concentrations n_i^ε and the screening parameter Γ^ε depend through (50)–(51) on the entire family $(\delta\Psi^\varepsilon + \Phi_k^\varepsilon + \Psi^{ext,*})$, $1 \le k \le N$.

Proof. Linearizing (50) leads to

$$\begin{aligned}\delta n_i^\varepsilon &= \frac{-\delta\gamma_i^\varepsilon}{(\gamma_i^{0,\varepsilon})^2}n_i^0(\infty)\gamma_j^0(\infty)\exp\{-z_i\Psi^{0,\varepsilon}\}\\ &\quad - \frac{z_i n_i^0(\infty)\gamma_j^0(\infty)}{\gamma_i^{0,\varepsilon}}\exp\{-z_i\Psi^{0,\varepsilon}\}\Big(\delta\Psi^\varepsilon + \Phi_i^\varepsilon + \Psi^{ext,*}\Big)\end{aligned}$$

which is equivalent to

$$\delta n_i^\varepsilon = \frac{-\delta\gamma_i^\varepsilon}{\gamma_i^{0,\varepsilon}}n_i^{0,\varepsilon} - z_i n_i^{0,\varepsilon}\Big(\delta\Psi^\varepsilon + \Phi_i^\varepsilon + \Psi^{ext,*}\Big). \tag{55}$$

Linearization of the first equation of (51) yields

$$\frac{\delta\gamma_i^\varepsilon}{\gamma_i^{0,\varepsilon}} = p'(\xi)\delta\xi - \frac{L_B\Gamma_c z_i^2}{(1+\Gamma^{0,\varepsilon}\Gamma_c\sigma_i)^2}\delta\Gamma^\varepsilon$$
$$\text{with } \delta\xi = \frac{\pi}{6}n_c\sum_{k=1}^N\sigma_k^3\delta n_k^\varepsilon. \tag{56}$$

Multiplying (55) by σ_i^3 and (56) by $\sigma_i^3 n_i^{0,\varepsilon}$, then summing up to eliminate $\delta\gamma_i^\varepsilon/\gamma_i^{0,\varepsilon}$, gives

$$\begin{aligned}&\left(\sum_{k=1}^N\sigma_k^3\delta n_k^\varepsilon\right)\left(1 + \frac{\pi}{6}n_c p'(\xi)\sum_{k=1}^N\sigma_k^3 n_k^{0,\varepsilon}\right)\\ &\quad = -\sum_{k=1}^N\sigma_k^3 z_k n_k^{0,\varepsilon}\Big(\delta\Psi^\varepsilon + \Phi_k^\varepsilon + \Psi^{ext,*}\Big)\\ &\qquad + \delta\Gamma^\varepsilon\sum_{k=1}^N\frac{L_B\Gamma_c z_k^2\sigma_k^3 n_k^{0,\varepsilon}}{(1+\Gamma^{0,\varepsilon}\Gamma_c\sigma_k)^2},\end{aligned}$$

from which, together with (55), we deduce

$$\begin{aligned}\delta n_i^\varepsilon(x) &= -z_i n_i^{0,\varepsilon}(x)\Big(\delta\Psi^\varepsilon(x) + \Phi_i^\varepsilon(x) + \Psi^{ext,*}(x)\Big)\\ &\quad + \frac{L_B\Gamma_c z_i^2 n_i^{0,\varepsilon}(x)}{(1+\Gamma^{0,\varepsilon}(x)\Gamma_c\sigma_i)^2}\delta\Gamma^\varepsilon(x)\\ &\quad + B^{0,\varepsilon}n_i^{0,\varepsilon}(x)\sum_{k=1}^N\sigma_k^3 z_k n_k^{0,\varepsilon}(x)\\ &\quad \times\Big(\delta\Psi^\varepsilon(x) + \Phi_k^\varepsilon(x) + \Psi^{ext,*}(x)\Big)\\ &\quad - B^{0,\varepsilon}C^{0,\varepsilon}n_i^{0,\varepsilon}(x)L_B\Gamma_c\delta\Gamma^\varepsilon(x).\end{aligned} \tag{57}$$

Next, we linearize the second formula of (51) to obtain

$$2\Gamma^{0,\varepsilon}\delta\Gamma^\varepsilon = \sum_{k=1}^N\left(\frac{z_k^2\delta n_k^\varepsilon}{(1+\Gamma^{0,\varepsilon}\Gamma_c\sigma_k)^2} - \frac{2n_k^{0,\varepsilon}z_k^2\sigma_k\Gamma_c}{(1+\Gamma^{0,\varepsilon}\Gamma_c\sigma_k)^3}\delta\Gamma^\varepsilon\right).$$

Combining it with (57) leads to

$$
\begin{aligned}
A^{0,\varepsilon}(x)\,\delta\Gamma^{\varepsilon}(x) = &-\sum_{k=1}^{N}\frac{n_k^{0,\varepsilon}(x)z_k^3}{(1+\Gamma^{0,\varepsilon}(x)\Gamma_c\sigma_k)^2}\\
&\times\left(\delta\Psi^{\varepsilon}(x)+\Phi_k^{\varepsilon}(x)+\Psi^{ext,*}(x)\right)\\
&+B^{0,\varepsilon}(x)D^{0,\varepsilon}(x)\sum_{k=1}^{N}n_k^{0,\varepsilon}(x)z_k\sigma_k^3\\
&\times\left(\delta\Psi^{\varepsilon}(x)+\Phi_k^{\varepsilon}(x)+\Psi^{ext,*}(x)\right).
\end{aligned}
\tag{58}
$$

Eventually, plugging (58) into (57) yields (52) and (53).

Since we divide by $A^{0,\varepsilon}$ we check that it does not vanish in some range of the physical parameters. Using definition (51) of $(\Gamma^{0,\varepsilon})^2$ in the equality $2\Gamma^{0,\varepsilon} = 2(\Gamma^{0,\varepsilon})^2/\Gamma^{0,\varepsilon}$ allows us to rewrite the coefficient $A^{0,\varepsilon}$ as

$$
\begin{aligned}
A^{0,\varepsilon}(x) = \Gamma_c&\sum_{k=1}^{N}\frac{n_k^{0,\varepsilon}z_k^2}{(1+\Gamma^{0,\varepsilon}\Gamma_c\sigma_k)^2}\\
\times&\left(\frac{2}{\Gamma^{0,\varepsilon}\Gamma_c}+\frac{2\sigma_k}{(1+\Gamma^{0,\varepsilon}\Gamma_c\sigma_k)}-\frac{L_B z_k^2}{(1+\Gamma^{0,\varepsilon}\Gamma_c\sigma_k)^2}\right)\\
+&L_B\Gamma_c B^{0,\varepsilon}C^{0,\varepsilon}\sum_{k=1}^{N}\frac{n_k^{0,\varepsilon}z_k^2}{(1+\Gamma^{0,\varepsilon}\Gamma_c\sigma_k)^2},
\end{aligned}
$$

where each term in the sum of the first line is positive under the same condition (45) and same proof as in Lemma 18.

The computation leading to (54) is completely similar. Finally, the symmetry relation $\alpha_{i,k}^{0,\varepsilon} = \alpha_{k,i}^{0,\varepsilon}$ is obvious from formula (53) when $\sigma_k = \sigma_i$ for all i, k. □

Remark 9. In the ideal case, $\gamma_i^{\varepsilon} \equiv 1$, Lemma 7 simplifies a lot since $\alpha_{i,k}^{0,\varepsilon} = -n_i^{0,\varepsilon}\delta_{ik}$ which implies there is no coupling between the various ionic potentials in the definition of a single species concentration.

Thanks to the definition (50) of the ionic potential, the linearization of the convection–diffusion equation (29) is easy because the diffusive flux simplifies as

$$
M_j^{\varepsilon} = \ln\left(n_j^{\varepsilon}\gamma_j^{\varepsilon}e^{z_j\Psi^{\varepsilon}}\right) = \ln\left(n_j^0(\infty)\gamma_j^0(\infty)\right) - z_j(\Phi_j^{\varepsilon}+\Psi^{ext,*}).
$$

Furthermore, the equilibrium solution satisfies $\nabla M_j^{0,\varepsilon} = 0$, which implies

$$
\operatorname{div}\left(\sum_{j=1}^{N}n_i^{0,\varepsilon}K_{ij}^{0,\varepsilon}z_j\nabla(\Phi_j^{\varepsilon}+\Psi^{ext,*})+\mathrm{Pe}_i n_i^{0,\varepsilon}\mathbf{u}^{\varepsilon}\right) = 0 \quad \text{in } \Omega^{\varepsilon} \tag{59}
$$

$$
K_{ij}^{0,\varepsilon} = \left(\frac{D_i^0}{k_B T}\delta_{ij}+\Omega_{ij}^0\right)\left(1+\mathcal{R}_{ij}^0\right), \quad i,j=1,\ldots,N. \tag{60}
$$

The linearization of the Stokes equation (22) is more tricky. We first get

$$
\varepsilon^2\Delta\mathbf{u}^{\varepsilon} - \nabla\delta p^{\varepsilon} = \mathbf{f}^* + \sum_{j=1}^{N}z_j\left(\delta n_j^{\varepsilon}\nabla\Psi^{0,\varepsilon}+n_j^{0,\varepsilon}\nabla\delta\Psi^{\varepsilon}\right) \quad \text{in } \Omega^{\varepsilon}, \tag{61}
$$

$$
\operatorname{div}\mathbf{u}^{\varepsilon} = 0 \quad \text{in } \Omega^{\varepsilon}, \quad \mathbf{u}^{\varepsilon} = 0 \quad \text{on } \partial\Omega^{\varepsilon}\setminus\partial\Omega.
$$

We rewrite the sum on the right hand side of (61) as

$$
\nabla\left(\sum_{j=1}^{N}z_j n_j^{0,\varepsilon}\delta\Psi^{\varepsilon}\right)+S^{\varepsilon}
$$

$$
\text{with } S^{\varepsilon} = \sum_{j=1}^{N}z_j\left(\delta n_j^{\varepsilon}\nabla\Psi^{0,\varepsilon}-\delta\Psi^{\varepsilon}\nabla n_j^{0,\varepsilon}\right). \tag{62}
$$

Since $\nabla n_j^{0,\varepsilon} = \frac{dn_j^{0,\varepsilon}}{d\Psi^{0,\varepsilon}}\nabla\Psi^{0,\varepsilon}$ at equilibrium, from Lemma 7 we deduce

$$
\begin{aligned}
S^{\varepsilon} &= \sum_{j,k=1}^{N}z_j\left(z_k\alpha_{j,k}^{0,\varepsilon}\left(\delta\Psi^{\varepsilon}+\Phi_k^{\varepsilon}+\Psi^{ext,*}\right)-z_k\alpha_{j,k}^{0,\varepsilon}\delta\Psi^{\varepsilon}\right)\nabla\Psi^{0,\varepsilon}\\
&= \sum_{j,k=1}^{N}z_j z_k\alpha_{j,k}^{0,\varepsilon}\left(\Phi_k^{\varepsilon}+\Psi^{ext,*}\right)\nabla\Psi^{0,\varepsilon}
\end{aligned}
\tag{63}
$$

If all ions have the same diameter, the coefficients $\alpha_{j,k}^{0,\varepsilon}$ are symmetric, i.e. $\alpha_{j,k}^{0,\varepsilon} = \alpha_{k,j}^{0,\varepsilon}$, so we deduce

$$
\begin{aligned}
S^{\varepsilon} &= \sum_{k=1}^{N}z_k\frac{dn_k^{0,\varepsilon}}{d\Psi^{0,\varepsilon}}\left(\Phi_k^{\varepsilon}+\Psi^{ext,*}\right)\nabla\Psi^{0,\varepsilon}\\
&= \sum_{k=1}^{N}z_k\left(\Phi_k^{\varepsilon}+\Psi^{ext,*}\right)\nabla n_k^{0,\varepsilon}.
\end{aligned}
$$

Thus, we rewrite (61) as

$$
\varepsilon^2\Delta\mathbf{u}^{\varepsilon} - \nabla P^{\varepsilon} = \mathbf{f}^* - \sum_{j=1}^{N}z_j n_j^{0,\varepsilon}\nabla\left(\Phi_j^{\varepsilon}+\Psi^{ext,*}\right), \tag{64}
$$

where the new pressure P^{ε} is defined by

$$
P^{\varepsilon} = \delta p^{\varepsilon} + \sum_{j=1}^{N}z_j n_j^{0,\varepsilon}\left(\delta\Psi^{\varepsilon}+\Phi_j^{\varepsilon}+\Psi^{ext,*}\right).
$$

Remark 10. When the ion diameters are different, we can merely introduce nonlinear functions F_j (defined by their derivatives) such that

$$
S^{\varepsilon} = \sum_{j=1}^{N}z_j\left(\Phi_j^{\varepsilon}+\Psi^{ext,*}\right)\nabla\left(F_j(\Psi^{0,\varepsilon})\right).
$$

In general it is not clear whether $F_j = n_j$.

Of course, one can deduce a linearized equation for $\delta\Psi^{\varepsilon}$ from the non-linear Poisson equation (24) too. But, since $\delta\Psi^{\varepsilon}$ does not enter the previous equations (upon redefining the pressure P^{ε}), it is **decoupled** from the main unknowns $\mathbf{u}^{\varepsilon}$, P^{ε} and Φ_i^{ε}. Therefore it is not necessary to write its equation in detail.

To summarize, we have just proved the following result.

Proposition 11. *Assume that all ions have the same diameter. The linearized system, around the equilibrium solution of Section 3, of the electrokinetic equations (22)–(32) is*

$$
\varepsilon^2\Delta\mathbf{u}^{\varepsilon} - \nabla P^{\varepsilon} = \mathbf{f}^* - \sum_{j=1}^{N}z_j n_j^{0,\varepsilon}\nabla\left(\Phi_j^{\varepsilon}+\Psi^{ext,*}\right) \quad \text{in } \Omega^{\varepsilon}, \tag{65}
$$

$$
\operatorname{div}\mathbf{u}^{\varepsilon} = 0 \quad \text{in } \Omega^{\varepsilon}, \qquad \mathbf{u}^{\varepsilon} = 0 \quad \text{on } \partial\Omega^{\varepsilon}\setminus\partial\Omega, \tag{66}
$$

$$
\begin{aligned}
&\operatorname{div} n_i^{0,\varepsilon}\left(\sum_{j=1}^{N}K_{ij}^{0,\varepsilon}z_j\nabla(\Phi_j^{\varepsilon}+\Psi^{ext,*})+Pe_i\mathbf{u}^{\varepsilon}\right) = 0\\
&\quad\text{in } \Omega^{\varepsilon},\ i=1,\ldots,N,
\end{aligned}
\tag{67}
$$

$$
\sum_{j=1}^{N}K_{ij}^{0,\varepsilon}z_j\nabla(\Phi_j^{\varepsilon}+\Psi^{ext,*})\cdot\nu = 0 \quad \text{on } \partial\Omega^{\varepsilon}\setminus\partial\Omega, \tag{68}
$$

$$
\mathbf{u}^{\varepsilon}, P^{\varepsilon}, \Phi_j^{\varepsilon} \quad \text{are } \Omega\text{-periodic}, \tag{69}
$$

where the coefficients $n_j^{0,\varepsilon}$ and $K_{ij}^{0,\varepsilon}$ (defined by (60)) are evaluated at equilibrium.

This is the system of equations that we are going to homogenize in the next sections. It is the extension to the non-ideal case of a similar ideal system previously studied in [23,24,2,25,27–29,34,22]. The mathematical structure of system (65)–(69) is essentially the same as in the ideal case. The only difference is the coupling of the diffusion equations through the tensor $K_{ij}^{0,\varepsilon}$. Note that the tensor $K_{ij}^{0,\varepsilon}$ is related to the original Onsager tensor L_{ij}, defined in (14): upon adimensionalization and evaluation at equilibrium, L_{ij} becomes $L_{ij}^{0,\varepsilon} = n_i^{0,\varepsilon} K_{ij}^{0,\varepsilon} D_i^0/(k_B T)$. In particular, the tensor $L_{ij}^{0,\varepsilon}$ inherits from the symmetry of L_{ij} (it is thus symmetric positive definite).

Next, we establish the variational formulation of (65)–(69) and prove that it admits a unique solution. The functional spaces related to the velocity field are

$$W^\varepsilon = \{\mathbf{v} \in H^1(\Omega^\varepsilon)^d, \mathbf{v} = 0 \text{ on } \partial\Omega^\varepsilon \setminus \partial\Omega, \Omega\text{-periodic in } x\}$$

and

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

The variational formulation of (65)–(69) is: find $\mathbf{u}^\varepsilon \in H^\varepsilon$ and $\{\Phi_j^\varepsilon\}_{j=1,\dots,N} \in H^1(\Omega^\varepsilon)^N$, Φ_j^ε being Ω-periodic, such that, for any test functions $\mathbf{v} \in H^\varepsilon$ and $\{\phi_j\}_{j=1,\dots,N} \in H^1(\Omega^\varepsilon)^N$, ϕ_j being Ω-periodic,

$$a\left((\mathbf{u}^\varepsilon, \{\Phi_j^\varepsilon\}), (\mathbf{v}, \{\phi_j\})\right) = \langle \mathcal{L}, (\mathbf{v}, \{\phi_j\})\rangle,$$

where the bilinear form a and the linear form $\mathcal{L}$ are defined by

$$\begin{aligned} a\left((\mathbf{u}^\varepsilon, \{\Phi_j^\varepsilon\}), (\mathbf{v}, \{\phi_j\})\right) &:= \varepsilon^2 \int_{\Omega^\varepsilon} \nabla \mathbf{u}^\varepsilon : \nabla \mathbf{v}\, dx \\ &+ \sum_{i,j=1}^N \frac{z_i z_j}{\mathrm{Pe}_i} \int_{\Omega^\varepsilon} n_i^{0,\varepsilon} K_{ij}^{0,\varepsilon} \nabla \Phi_j^\varepsilon \cdot \nabla \phi_i\, dx \\ &+ \sum_{j=1}^N z_j \int_{\Omega^\varepsilon} n_j^{0,\varepsilon} \left(\mathbf{u}^\varepsilon \cdot \nabla \phi_j - \mathbf{v} \cdot \nabla \Phi_j^\varepsilon\right) dx \\ \langle \mathcal{L}, (\mathbf{v}, \{\phi_j\})\rangle &:= \sum_{j=1}^N z_j \int_{\Omega^\varepsilon} n_j^{0,\varepsilon} \mathbf{E}^* \cdot \mathbf{v}\, dx \\ &- \sum_{i,j=1}^N \frac{z_i z_j}{\mathrm{Pe}_i} \int_{\Omega^\varepsilon} n_i^{0,\varepsilon} K_{ij}^{0,\varepsilon} \mathbf{E}^* \cdot \nabla \phi_i\, dx - \int_{\Omega^\varepsilon} \mathbf{f}^* \cdot \mathbf{v}\, dx, \end{aligned} \tag{70}$$

where, for simplicity, we denote by $\mathbf{E}^*$ the electric field corresponding to the potential $\Psi^{ext,*}$, i.e., $\mathbf{E}^*(x) = \nabla \Psi^{ext,*}(x)$.

Lemma 12. *For sufficiently small values of $n_c > 0$ and $\xi_c > 0$, and under assumption (45), there exists a unique solution of (65)–(69), $\mathbf{u}^\varepsilon \in H^\varepsilon$ and $\{\Phi_j^\varepsilon\}_{j=1,\dots,N} \in H^1(\Omega^\varepsilon)^N$, Φ_j^ε being Ω-periodic. Furthermore, there exists a positive constant C, independent of ε, such that*

$$\begin{aligned} &\|\mathbf{u}^\varepsilon\|_{L^2(\Omega^\varepsilon)^d} + \varepsilon \|\nabla \mathbf{u}^\varepsilon\|_{L^2(\Omega^\varepsilon)^{d^2}} + \max_{1\le j\le N} \|\Phi_j^\varepsilon\|_{H^1(\Omega^\varepsilon)} \\ &\quad \le C\left(\|\mathbf{E}^*\|_{L^2(\Omega)^d} + \|\mathbf{f}^*\|_{L^2(\Omega)^d}\right). \end{aligned} \tag{71}$$

Proof. Assumption (45) and small $\xi_c > 0$ imply that the potential $\Psi^{0,\varepsilon}$ is bounded in $L^\infty(\Omega^\varepsilon)$ (see Theorem 24). The same holds true for ξ and $\Gamma^{0,\varepsilon}$ which are algebraic functions of $\Psi^{0,\varepsilon}$. Thus, the concentrations $n_j^{0,\varepsilon}$, defined by (109) are uniformly positive and bounded in $L^\infty(\Omega^\varepsilon)$. Due to the structure of $\mathbf{\Omega}_{ij}^c$, $\mathbf{\Omega}_{ij}^{HS}$ and $\mathcal{R}_{ij}$, these coefficients, evaluated at equilibrium, are arbitrary small in $L^\infty(\Omega^\varepsilon)$ for small n_c. Consequently, the tensor $K_{ij}^{0,\varepsilon}$ is positive definite (as a perturbation of the identity) and the bilinear form a is coercive for $n_c \le n_c^{\mathrm{cr}}$. The rest of the proof, including the a priori estimates, is similar to the ideal case, studied in [23], where we had $K_{ij}^{0,\varepsilon} = \delta_{ij}$. □

5. Homogenization

In Sections 3 and 4 we did not use our assumption that the porous medium and the surface charge distribution are ε-periodic (see the end of Section 2). Our further analysis relies crucially on this ε-periodicity hypothesis. Theorem 2 gives the existence of a solution to the Poisson–Boltzmann equation (44) but not its uniqueness. Nevertheless, we can define a particular solution of (44), which is ε-periodic,

$$\Psi^{0,\varepsilon}(x) = \Psi^0\left(\frac{x}{\varepsilon}\right), \tag{72}$$

where $\Psi^0(y)$ is a solution of the unit cell Poisson–Boltzmann equation

$$\begin{cases} -\Delta_y \Psi^0(y) = \beta \displaystyle\sum_{j=1}^N z_j n_j^0(y) & \text{in } Y_F, \\ \nabla_y \Psi^0 \cdot \nu = -N_\sigma \Sigma^*(y) & \text{on } \partial Y_F \setminus \partial Y, \\ y \to \Psi^0(y) \ \text{ is 1-periodic,} & \\ n_j^0(y) = n_j^0(\infty)\gamma_j^0(\infty) \dfrac{\exp\{-z_j \Psi^0(y)\}}{\gamma_j^0(y)}, & \end{cases} \tag{73}$$

with the activity coefficient defined by

$$\gamma_j^0(y) = \gamma^{HS}(y) \exp\left\{-\frac{L_B \Gamma^0(y) \Gamma_c z_j^2}{(1 + \Gamma^0(y)\Gamma_c \sigma_j)}\right\} \quad \text{and}$$

$$(\Gamma^0(y))^2 = \sum_{k=1}^N \frac{n_k^0(y) z_k^2}{(1 + \Gamma_c \Gamma^0(y) \sigma_k)^2},$$

and

$$\gamma^{HS} = \exp\{p(\xi)\} \quad \text{with } p(\xi) = \xi \frac{8 - 9\xi + 3\xi^2}{(1-\xi)^3} \text{ and}$$

$$\xi(y) = \frac{\pi n_c}{6} \sum_{k=1}^N n_k^0(y) \sigma_k^3.$$

The formal two-scale asymptotic expansion method [41–43] can be applied to system (65)–(69) as in the ideal case studied by [22,3,30,31,33,23] and [24]. Introducing the fast variable $y = x/\varepsilon$, it assumes that the solution of (65)–(69) is given by

$$\begin{cases} \mathbf{u}^\varepsilon(x) = \mathbf{u}^0(x, x/\varepsilon) + \varepsilon \mathbf{u}^1(x, x/\varepsilon) + \cdots, \\ P^\varepsilon(x) = p^0(x) + \varepsilon p^1(x, x/\varepsilon) + \cdots, \\ \Phi_j^\varepsilon(x) = \Phi_j^0(x) + \varepsilon \Phi_j^1(x, x/\varepsilon) + \cdots. \end{cases} \tag{74}$$

We then plug this ansatz in Eqs. (65)–(69) and use the chain-rule lemma for a function $\phi(x, \frac{x}{\varepsilon})$

$$\nabla\left(\phi\left(x, \frac{x}{\varepsilon}\right)\right) = \left(\nabla_x \phi + \frac{1}{\varepsilon}\nabla_y \phi\right)\left(x, \frac{x}{\varepsilon}\right).$$

Identifying the various powers of ε we obtain a cascade of equations from which we retain only the first ones that constitute the following two-scale homogenized problem. This type of calculation is classical and we do not reproduce it here. It can be made rigorous thanks to the notion of two-scale convergence [44,45].

Proposition 13. *From each bounded sequence $\{w^\varepsilon\}$ in $L^2(\Omega^\varepsilon)$ one can extract a subsequence which two-scale converges to a limit $w \in L^2(\Omega \times Y_F)$ in the sense that*

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

for any $\varphi \in L^2\left(\Omega; C_{\mathrm{per}}(Y)\right)$ ("per" denotes 1-periodicity).

For sequences of functions w^ε defined in the perforated domain Ω^ε and satisfying uniform in εH^1-bounds, it is well-known [42] that one can build extensions to the entire domain Ω satisfying the same uniform bounds. We implicitly assume such extensions in the theorem below but do not give details which are classical and may be found in [23].

Theorem 14. *Under the assumptions of Lemma 12 the solution of (65)–(69) converges in the following sense*

$$\begin{aligned}
&\mathbf{u}^\varepsilon \to \mathbf{u}^0(x,y) \quad \textit{in the two-scale sense}\\
&\varepsilon\nabla\mathbf{u}^\varepsilon \to \nabla_y\mathbf{u}^0(x,y) \quad \textit{in the two-scale sense}\\
&P^\varepsilon \to p^0(x) \quad \textit{strongly in } L^2(\Omega)\\
&\Phi_j^\varepsilon \to \Phi_j^0(x) \quad \textit{weakly in } H^1(\Omega) \textit{ and strongly in } L^2(\Omega)\\
&\nabla\Phi_j^\varepsilon \to \nabla_x\Phi_j^0(x) + \nabla_y\Phi_j^1(x,y) \quad \textit{in the two-scale sense}
\end{aligned}$$

where $(\mathbf{u}^0, p^0) \in L^2(\Omega; H^1_{per}(Y)^d) \times L^2_0(\Omega)$ *and* $\{\Phi_j^0, \Phi_j^1\}_{j=1,\dots,N} \in \left(H^1(\Omega) \times L^2(\Omega; H^1_{per}(Y))\right)^N$ *is the unique solution of the two-scale homogenized problem*

$$\begin{aligned}
&-\Delta_y\mathbf{u}^0(x,y) + \nabla_y p^1(x,y) = -\nabla_x p^0(x) - \mathbf{f}^*(x)\\
&\quad + \sum_{j=1}^N z_j n_j^0(y)\left(\nabla_x\Phi_j^0(x) + \nabla_y\Phi_j^1(x,y) + \mathbf{E}^*(x)\right) \quad \text{in } \Omega \times Y_F,
\end{aligned} \tag{75}$$

$$\operatorname{div}_y\mathbf{u}^0(x,y) = 0 \quad \text{in } \Omega \times Y_F, \qquad \mathbf{u}^0(x,y) = 0 \quad \text{on } \Omega \times S, \tag{76}$$

$$\operatorname{div}_x\left(\int_{Y_F}\mathbf{u}^0(x,y)\,dy\right) = 0 \quad \text{in } \Omega, \tag{77}$$

$$\begin{aligned}
&-\operatorname{div}_y n_i^0(y)\Bigg(\sum_{j=1}^N K_{ij}(y) z_j\big(\nabla_y\Phi_j^1(x,y) + \nabla_x\Phi_j^0(x)\\
&\quad + \mathbf{E}^*(x)\big) + Pe_i\mathbf{u}^0(x,y)\Bigg) = 0 \quad \text{in } \Omega \times Y_F,
\end{aligned} \tag{78}$$

$$\sum_{j=1}^N K_{ij}(y) z_j\big(\nabla_y\Phi_j^1 + \nabla_x\Phi_j^0 + \mathbf{E}^*\big)\cdot\nu(y) = 0 \quad \text{on } \Omega \times S, \tag{79}$$

$$\begin{aligned}
&-\operatorname{div}_x\int_{Y_F} n_i^0(y)\Bigg(\sum_{j=1}^N K_{ij}(y) z_j\big(\nabla_y\Phi_j^1(x,y) + \nabla_x\Phi_j^0(x) + \mathbf{E}^*(x)\big)\\
&\quad + Pe_i\mathbf{u}^0(x,y)\Bigg)\,dy = 0 \quad \text{in } \Omega,
\end{aligned} \tag{80}$$

$$\Phi_i^0, \int_{Y_F}\mathbf{u}^0\,dy \ \textit{ and } \ p^0 \textit{ being } \Omega\textit{-periodic in } x, \tag{81}$$

with periodic boundary conditions on the unit cell Y_F *for all functions depending on* y *and* $S = \partial Y_S \setminus \partial Y$.

The limit problem introduced in Theorem 14 is called the two-scale and two-pressure homogenized problem, following the terminology of [42,46]. It features two incompressibility constraints (76) and (77) which are exactly dual to the two pressures $p^0(x)$ and $p^1(x,y)$ which are their corresponding Lagrange multipliers. Remark that Eqs. (75), (76) and (78) are just the leading order terms in the ansatz of the original equations. On the other hand, Eqs. (77) and (80) are averages on the unit cell Y_F of the next order terms in the ansatz. For example, (77) is deduced from

$$\operatorname{div}_y\mathbf{u}^1(x,y) + \operatorname{div}_x\mathbf{u}^0(x,y) = 0 \quad \text{in } \Omega \times Y_F$$

by averaging on Y_F, recalling that $\mathbf{u}^1(x,y) = 0$ on $\Omega \times S$.

Proof. The proof of convergence and the derivation of the homogenized system is completely similar to the proof of Theorem 1 in [23] which holds in the ideal case. The only point which deserves to be made precise here is the well-posedness of the two-scale homogenized problem.

Following section 3.1.2 in [47], we introduce the functional space for the velocities

$$V = \{\mathbf{u}^0(x,y) \in L^2_{per}\left(\Omega; H^1_{per}(Y_F)^d\right) \text{ satisfying (76)–(77)}\},$$

which is known to be orthogonal in $L^2_{per}\left(\Omega; H^1_{per}(Y_F)^d\right)$ to the space of gradients of the form $\nabla_x q(x) + \nabla_y q_1(x,y)$ with $q(x) \in H^1_{per}(\Omega)/\mathbb{R}$ and $q_1(x,y) \in L^2_{per}\left(\Omega; L^2_{per}(Y_F)/\mathbb{R}\right)$. We define the functional space $X = V \times H^1_{per}(\Omega)/\mathbb{R} \times L^2_{per}(\Omega; H^1_{per}(Y_F)^d/\mathbb{R})$ and the variational formulation of (75)–(81) is to find $(\mathbf{u}^0, \{\Phi_j^0, \Phi_j^1\}) \in X$ such that, for any test functions $(\mathbf{v}, \{\phi_j^0, \phi_j^1\}) \in X$,

$$a\left((\mathbf{u}^0, \{\Phi_j^0, \Phi_j^1\}), (\mathbf{v}, \{\phi_j^0, \phi_j^1\})\right) = \langle\mathcal{L}, (\mathbf{v}, \{\phi_j^0, \phi_j^1\})\rangle, \tag{82}$$

where the bilinear form a and the linear form $\mathcal{L}$ are defined by

$$\begin{aligned}
&a\left((\mathbf{u}^0, \{\Phi_j^0, \Phi_j^1\}), (\mathbf{v}, \{\phi_j^0, \phi_j^1\})\right) := \int_\Omega\int_{Y_F}\nabla_y\mathbf{u}^0 : \nabla\mathbf{v}\,dx\,dy\\
&\quad + \sum_{i,j=1}^N \frac{z_i z_j}{\mathrm{Pe}_i}\int_\Omega\int_{Y_F} n_i^0 K_{ij}(\nabla_x\Phi_j^0 + \nabla_y\Phi_j^1)\cdot(\nabla_x\phi_j^0 + \nabla_y\phi_j^1)\,dx\,dy\\
&\quad + \sum_{j=1}^N z_j\int_\Omega\int_{Y_F} n_j^0\big(\mathbf{u}^0\cdot(\nabla_x\phi_j^0 + \nabla_y\phi_j^1)\\
&\quad - \mathbf{v}\cdot(\nabla_x\Phi_j^0 + \nabla_y\Phi_j^1)\big)\,dx\,dy
\end{aligned} \tag{83}$$

and

$$\begin{aligned}
\langle\mathcal{L}, (\mathbf{v}, \{\phi_j\})\rangle &:= \sum_{j=1}^N z_j\int_\Omega\int_{Y_F} n_j^0\mathbf{E}^*\cdot\mathbf{v}\,dx\,dy - \int_\Omega\int_{Y_F}\mathbf{f}^*\cdot\mathbf{v}\,dx\,dy\\
&\quad - \sum_{i,j=1}^N \frac{z_i z_j}{\mathrm{Pe}_i}\int_\Omega\int_{Y_F} n_i^0 K_{ij}\mathbf{E}^*\cdot(\nabla_x\phi_j^0 + \nabla_y\phi_j^1)\,dx\,dy,
\end{aligned}$$

We apply the Lax–Milgram lemma to prove the existence and the uniqueness of the solution in X of (82). The only point which requires to be checked is the coercivity of the bilinear form. We take $\mathbf{v} = \mathbf{u}^0$, $\phi_j^0 = \Phi_j^0$ and $\phi_j^1 = \Phi_j^1$ as the test functions in (82).

We define a local diffusion tensor

$$\tilde{K}(y) = \left(\frac{z_i z_j}{\mathrm{Pe}_i}K_{ij}(y) n_i^0(y)\right)_{1\le i,j\le N} = \left(\frac{k_B T}{u_c L} z_i z_j L_{ij}(y)\right)_{1\le i,j\le N}, \tag{84}$$

which is symmetric since (L_{ij}) is symmetric too. As already remarked in the proof of Lemma 12, $\tilde{K}$ is uniformly coercive for small enough $n_c > 0$ and $\xi_c > 0$. Therefore, the second integral on the right hand side of (83) is positive. The third integral, being skew-symmetric, vanishes, which proves the coercivity of a. □

Of course, one should extract from (75)–(81) the macroscopic homogenized problem, which requires to separate the fast and slow scale. In the ideal case, Looker and Carnie in [22] proposed a first approach which was further improved in [23] and [24].

The main idea is to recognize in the two-scale homogenized problem (75)–(81) that there are two different macroscopic fluxes, namely $(\nabla_x p^0(x) + \mathbf{f}^*(x))$ and $\{\nabla_x\Phi_j^0(x) + \mathbf{E}^*(x)\}_{1\le j\le N}$. Therefore we introduce two family of cell problems, indexed by $k \in \{1,\dots,d\}$ for each component of these fluxes. We denote by $\{\mathbf{e}^k\}_{1\le k\le d}$ the canonical basis of $\mathbb{R}^d$.

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

$$-\Delta_y \mathbf{v}^{0,k}(y) + \nabla_y \pi^{0,k}(y) = \mathbf{e}^k + \sum_{j=1}^{N} z_j n_j^0(y) \nabla_y \theta_j^{0,k}(y) \quad \text{in } Y_F \tag{85}$$

$$\mathrm{div}_y \mathbf{v}^{0,k}(y) = 0 \quad \text{in } Y_F, \qquad \mathbf{v}^{0,k}(y) = 0 \quad \text{on } S, \tag{86}$$

$$-\mathrm{div}_y n_i^0(y) \left(\sum_{j=1}^{N} K_{ij}(y) z_j \nabla_y \theta_j^{0,k}(y) + \mathrm{Pe}_i \mathbf{v}^{0,k}(y) \right) = 0 \quad \text{in } Y_F \tag{87}$$

$$\sum_{j=1}^{N} K_{ij}(y) z_j \nabla_y \theta_j^{0,k}(y) \cdot \nu = 0 \quad \text{on } S. \tag{88}$$

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

$$-\Delta_y \mathbf{v}^{l,k}(y) + \nabla_y \pi^{l,k}(y) = \sum_{j=1}^{N} z_j n_j^0(y) (\delta_{lj} \mathbf{e}^k + \nabla_y \theta_j^{l,k}(y)) \quad \text{in } Y_F \tag{89}$$

$$\mathrm{div}_y \mathbf{v}^{l,k}(y) = 0 \quad \text{in } Y_F, \qquad \mathbf{v}^{l,k}(y) = 0 \quad \text{on } S, \tag{90}$$

$$-\mathrm{div}_y n_i^0(y) \left(\sum_{j=1}^{N} K_{ij}(y) z_j \big(\delta_{lj} \mathbf{e}^k + \nabla_y \theta_j^{l,k}(y) \big) + \mathrm{Pe}_i \mathbf{v}^{l,k}(y) \right) = 0 \quad \text{in } Y_F \tag{91}$$

$$\sum_{j=1}^{N} K_{ij}(y) z_j \big(\delta_{lj} \mathbf{e}^k + \nabla_y \theta_j^{l,k}(y) \big) \cdot \nu = 0 \quad \text{on } S, \tag{92}$$

where δ_{ij} is the Kronecker symbol. As usual the cell problems are complemented with periodic boundary conditions.

Then, we can decompose the solution of (75)–(81) as

$$\mathbf{u}^0(x, y) = \sum_{k=1}^{d} \left(-\mathbf{v}^{0,k}(y) \left(\frac{\partial p^0}{\partial x_k} + f_k^* \right)(x) + \sum_{i=1}^{N} \mathbf{v}^{i,k}(y) \left(E_k^* + \frac{\partial \Phi_i^0}{\partial x_k} \right)(x) \right) \tag{93}$$

$$p^1(x, y) = \sum_{k=1}^{d} \left(-\pi^{0,k}(y) \left(\frac{\partial p^0}{\partial x_k} + f_k^* \right)(x) + \sum_{i=1}^{N} \pi^{i,k}(y) \left(E_k^* + \frac{\partial \Phi_i^0}{\partial x_k} \right)(x) \right) \tag{94}$$

$$\Phi_j^1(x, y) = \sum_{k=1}^{d} \left(-\theta_j^{0,k}(y) \left(\frac{\partial p^0}{\partial x_k} + f_k^* \right)(x) + \sum_{i=1}^{N} \theta_j^{i,k}(y) \left(E_k^* + \frac{\partial \Phi_i^0}{\partial x_k} \right)(x) \right). \tag{95}$$

We average (93)–(95) in order to get a purely macroscopic homogenized problem. We define the homogenized quantities: first, the electro-chemical potential

$$\mu_j(x) = -z_j (\Phi_j^0(x) + \Psi^{ext,*}(x)), \tag{96}$$

then, the ionic flux of the jth species

$$\mathbf{j}_j(x) = \frac{1}{|Y_F|} \int_{Y_F} n_j^0(y) \left(\sum_{l=1}^{N} K_{jl}(y) \frac{z_l}{\mathrm{Pe}_j} \big(\nabla_y \Phi_l^1(x, y) + \nabla_x \Phi_l^0(x) + \mathbf{E}^*(x) \big) + \mathbf{u}^0 \right) dy, \tag{97}$$

and finally the filtration velocity

$$\mathbf{u}(x) = \frac{1}{|Y_F|} \int_{Y_F} \mathbf{u}^0(x, y) \, dy. \tag{98}$$

From (93)–(95) we deduce the homogenized or upscaled equations for the above effective fields.

Proposition 15. *Introducing the flux $\mathcal{J}(x) = (\mathbf{u}, \{\mathbf{j}_j\}_{1 \le j \le N})$ and the gradient $\mathcal{F}(x) = (\nabla_x p^0, \{\nabla_x \mu_j\}_{1 \le j \le N})$, the macroscopic equations are*

$$\mathrm{div}_x \mathcal{J} = 0 \quad \text{in } \Omega, \tag{99}$$

$$\mathcal{J} = -\mathcal{M}\mathcal{F} - \mathcal{M}(\mathbf{f}^*, \{0\}), \tag{100}$$

with a homogenized tensor $\mathcal{M}$ defined by

$$\mathcal{M} = \begin{pmatrix} \mathbb{K} & \dfrac{\mathbb{J}_1}{z_1} & \cdots & \dfrac{\mathbb{J}_N}{z_N} \\ \mathbb{L}_1 & \dfrac{\mathbb{D}_{11}}{z_1} & \cdots & \dfrac{\mathbb{D}_{1N}}{z_N} \\ \vdots & \vdots & \ddots & \vdots \\ \mathbb{L}_N & \dfrac{\mathbb{D}_{N1}}{z_1} & \cdots & \dfrac{\mathbb{D}_{NN}}{z_N} \end{pmatrix}, \tag{101}$$

and complemented with periodic boundary conditions for p^0 and $\{\Phi_j^0\}_{1 \le j \le N}$. The matrices $\mathbb{J}_i$, $\mathbb{K}$, $\mathbb{D}_{ji}$ and $\mathbb{L}_j$ are defined by their entries

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

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

$$\{\mathbb{D}_{ji}\}_{lk} = \frac{1}{|Y_F|} \int_{Y_F} n_j^0(y) \times \left(\mathbf{v}^{i,k}(y) + \sum_{m=1}^{N} K_{jm}(y) \frac{z_m}{\mathrm{Pe}_j} \left(\delta_{im} \mathbf{e}^k + \nabla_y \theta_m^{i,k}(y) \right) \right) \cdot \mathbf{e}^l \, dy,$$

$$\{\mathbb{L}_j\}_{lk} = \frac{1}{|Y_F|} \int_{Y_F} n_j^0(y) \left(\mathbf{v}^{0,k}(y) + \sum_{m=1}^{N} K_{jm}(y) \frac{z_m}{\mathrm{Pe}_j} \nabla_y \theta_m^{0,k}(y) \right) \cdot \mathbf{e}^l \, dy.$$

Furthermore, $\mathcal{M}$ is symmetric positive definite, which implies that the homogenized equations (99)–(100) have a unique solution.

Remark 16. The symmetry of $\mathcal{M}$ is equivalent to the famous Onsager's reciprocal relations. In the ideal case, the symmetry of the tensor $\mathcal{M}$ was proved in [22,23].

Proof. The conservation law (99) is just a rewriting of (77) and (80). The constitutive equation (100) is an immediate consequence of the definition (97) and (98) of the homogenized fluxes, taking into account the decomposition (93)–(95).

We now prove that $\mathcal{M}$ is positive definite. For any collection of vectors $\lambda^0, \{\lambda^i\}_{1 \le i \le N} \in \mathbb{R}^d$ let us introduce the following linear combinations of the cell solutions

$$\begin{aligned} \mathbf{v}^{\lambda} &= \sum_{k=1}^{d} \left(\lambda_k^0 \mathbf{v}^{0,k} + \sum_{i=1}^{N} \lambda_k^i \mathbf{v}^{i,k} \right), \\ \theta_j^{\lambda} &= \sum_{k=1}^{d} \left(\lambda_k^0 \theta_j^{0,k} + \sum_{i=1}^{N} \lambda_k^i \theta_j^{i,k} \right), \end{aligned} \tag{102}$$

which satisfy

$$-\Delta_y \mathbf{v}^{\lambda}(y) + \nabla_y \pi^{\lambda}(y) = \lambda^0 + \sum_{j=1}^{N} z_j n_j^0(y) \left(\lambda^j + \nabla_y \theta_j^{\lambda}(y) \right) \quad \text{in } Y_F \tag{103}$$

$$\mathrm{div}_y \mathbf{v}^\lambda(y) = 0 \quad \text{in } Y_F, \qquad \mathbf{v}^\lambda(y) = 0 \quad \text{on } S, \tag{104}$$

$$-\mathrm{div}_y \left(n_i^0(y) \left(\sum_{j=1}^N z_j K_{ij} (\lambda^j + \nabla_y \theta_j^\lambda(y)) + \mathrm{Pe}_i \mathbf{v}^\lambda(y) \right) \right) = 0$$
$$\text{in } Y_F \tag{105}$$

$$\sum_{j=1}^N z_j K_{ij} (\lambda^j + \nabla_y \theta_j^\lambda(y)) \cdot \nu = 0 \quad \text{on } S, \tag{106}$$

Multiplying the Stokes equation (103) by $\mathbf{v}^\lambda$, the convection–diffusion equation (105) by θ_j^λ and summing up, we obtain

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

The left hand side of the above equality is positive. This proves the positive definite character of $\mathcal{M}$.

Following a computation of [23] in the ideal case, we prove the symmetry of $\mathcal{M}$. For another set of vectors $\tilde{\lambda}^0, \{\tilde{\lambda}^i\}_{1 \le i \le N} \in \mathbb{R}^d$, we define $\mathbf{v}^{\tilde{\lambda}}$ and $\theta_j^{\tilde{\lambda}}$ by (102). Multiplying the Stokes equation for $\mathbf{v}^\lambda$ by $\mathbf{v}^{\tilde{\lambda}}$ and the convection–diffusion equation for $\theta_j^{\tilde{\lambda}}$ by θ_j^λ (note the skew-symmetry of this computation), then adding the two variational formulations yields

$$\begin{aligned}
&\int_{Y_F} \nabla_y \mathbf{v}^\lambda \cdot \nabla_y \mathbf{v}^{\tilde{\lambda}} \, dy + \sum_{i,j=1}^N \int_{Y_F} \frac{z_i z_j}{\mathrm{Pe}_i} n_i^0 K_{ij} \nabla_y \theta_j^{\tilde{\lambda}} \cdot \nabla_y \theta_j^\lambda \, dy \\
&= \int_{Y_F} \lambda^0 \cdot \mathbf{v}^{\tilde{\lambda}} \, dy + \sum_{j=1}^N \int_{Y_F} z_j n_j^0 \lambda^j \cdot \mathbf{v}^{\tilde{\lambda}} \, dy \\
&\quad - \sum_{i,j=1}^N \int_{Y_F} \frac{z_i z_j}{\mathrm{Pe}_i} n_i^0 K_{ij} \tilde{\lambda}^j \cdot \nabla_y \theta_i^\lambda \, dy.
\end{aligned} \tag{107}$$

The diffusion tensor appearing in the left hand side of (107) is precisely equal to $\tilde{K}$, defined by (84), which is symmetric. Therefore, the left hand side of (107) is symmetric in $\lambda, \tilde{\lambda}$. Exchanging the last term in (107), we deduce by symmetry

$$\begin{aligned}
&\int_{Y_F} \lambda^0 \cdot \mathbf{v}^{\tilde{\lambda}} \, dy + \sum_{j=1}^N \int_{Y_F} z_j n_j^0 \lambda^j \cdot \mathbf{v}^{\tilde{\lambda}} \, dy \\
&\quad + \sum_{i,j=1}^N \int_{Y_F} \frac{z_i z_j}{\mathrm{Pe}_i} n_i^0 K_{ij} \lambda^j \cdot \nabla_y \theta_i^{\tilde{\lambda}} \, dy \\
&= \int_{Y_F} \tilde{\lambda}^0 \cdot \mathbf{v}^\lambda \, dy + \sum_{j=1}^N \int_{Y_F} z_j n_j^0 \tilde{\lambda}^j \cdot \mathbf{v}^\lambda \, dy \\
&\quad + \sum_{i,j=1}^N \int_{Y_F} \frac{z_i z_j}{\mathrm{Pe}_i} n_i^0 K_{ij} \tilde{\lambda}^j \cdot \nabla_y \theta_i^\lambda \, dy,
\end{aligned}$$

which is equivalent to the desired symmetry

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

6. Existence of solutions to the MSA variant of Poisson–Boltzmann equation

The goal of this section is to prove Theorem 2, i.e., the existence of solutions to system (44), the MSA variant of the Poisson–Boltzmann equation. These solutions are the so-called equilibrium solutions computed in Section 3. In a slightly different setting (two species and a linear approximation of $p(\xi)$) and with a different method (based on a saddle point approach in the two variables, potential and concentrations), a previous existence result was obtained in [39].

To simplify the notations we shall drop all ε- or 0-indices. In the same spirit, the pore domain is denoted Ω_p, a subset of the full domain Ω. To simplify we denote by $\partial\Omega_p$ the solid boundary of Ω_p, which should rather be $\partial\Omega_p \setminus \partial\Omega$ since we impose periodic boundary conditions on $\partial\Omega$. With our simplified notations, Theorem 2 is restated below as Theorem 24 and the Poisson–Boltzmann equation reads

$$\begin{cases} -\Delta\Psi = \beta \displaystyle\sum_{j=1}^N z_j n_j(x) & \text{in } \Omega_p, \\ \nabla\Psi \cdot \nu = -N_\sigma \Sigma^* & \text{on } \partial\Omega_p, \ \Psi \text{ is } \Omega\text{-periodic}, \end{cases} \tag{108}$$

where, in view of (38), the equilibrium concentrations are

$$n_j = \frac{n_j^0(\infty)\gamma_j^0(\infty)}{\gamma^{HS}} \exp\left\{ -z_j\Psi + \frac{L_B \Gamma \Gamma_c z_j^2}{1 + \Gamma\Gamma_c\sigma_j} \right\}. \tag{109}$$

We recall that the MSA screening parameter Γ is defined by

$$(\Gamma)^2 = \sum_{j=1}^N \frac{n_j z_j^2}{(1 + \Gamma_c \Gamma \sigma_j)^2} \tag{110}$$

and the hard sphere part of the activation coefficient is given by

$$\gamma^{HS} = \exp\{p(\xi)\} \quad \text{with } p(\xi) = \xi \frac{8 - 9\xi + 3\xi^2}{(1-\xi)^3} \text{ and}$$

$$\xi = \xi_c \sum_{j=1}^N n_j \left(\frac{\sigma_j}{\sigma_c} \right)^3, \tag{111}$$

where $\xi \in [0, 1)$ is the solute packing fraction and ξ_c its characteristic value defined by (28).

Let us now explain our strategy to solve the boundary value problem (108) coupled with the algebraic equations (109)–(111). In a first step (Lemmas 17 and 18) we eliminate the algebraic equations and write a nonlinear boundary value problem (116) for the single unknown Ψ. In a second step we introduce a truncated or "cut-off" problem (120) which is easily solved by a standard energy minimization since the nonlinearity has been truncated. The third and most delicate step is to prove a maximum principle for these truncated solutions (Proposition 23) which, in turn, imply our desired existence result.

In the first step we eliminate ξ as a function of (Ψ, Γ) and then Γ as a function of Ψ. From (42), for given potential Ψ and screening parameter Γ, the solute packing fraction ξ is a solution of the algebraic equation

$$\begin{aligned}
\xi &= \exp\{-p(\xi)\} \xi_c \sum_{j=1}^N \left(\frac{\sigma_j}{\sigma_c} \right)^3 n_j^0(\infty) \gamma_j^0(\infty) \\
&\quad \times \exp\left\{ -z_j\Psi + \frac{L_B \Gamma \Gamma_c z_j^2}{1 + \Gamma\Gamma_c\sigma_j} \right\}.
\end{aligned} \tag{112}$$

Lemma 17. *For given values of Ψ and Γ, there exists a unique solution $\xi \equiv \xi(\Psi, \Gamma) \in [0, 1)$ of (112). Furthermore, this solution depends smoothly on Ψ, Γ and is increasing with Γ.*

Proof. One can check that $p(\xi)$ is an increasing function of ξ on $[0, 1)$ with range $\mathbb{R}^+$ since

$$p'(\xi) = \frac{8 - 2\xi}{(1-\xi)^4}.$$

The existence and the uniqueness follow from the strict decrease of the function $\exp\{-p(\xi)\}$ from 1 to 0, while the left hand side ξ of (112) increases from 0 to 1. Since the function

$$\Gamma \to \frac{L_B \Gamma \Gamma_c z_j^2}{1 + \Gamma \Gamma_c \sigma_j}$$

is increasing, so is the solution ξ of (112) as a function of Γ. $\square$

Once we know $\xi \equiv \xi(\Psi, \Gamma)$, the MSA screening parameter Γ satisfies the following algebraic equation (see (43))

$$(\Gamma)^2 = \sum_{j=1}^{N} n_j^0(\infty) \gamma_j^0(\infty) \frac{z_j^2}{(1 + \Gamma \Gamma_c \sigma_j)^2} \times \exp\left\{ -z_j \Psi + \frac{L_B \Gamma \Gamma_c z_j^2}{1 + \Gamma \Gamma_c \sigma_j} - p\left(\xi(\Psi, \Gamma)\right) \right\}. \qquad (113)$$

We now prove that the algebraic equation (113) admits a unique solution $\Gamma(\Psi)$ under a mild assumption.

Lemma 18. *For any value of Ψ, there always exists at least one solution $\Gamma \equiv \Gamma(\Psi)$ of the algebraic equation (113). Furthermore, under the following assumption on the physical parameters*

$$L_B < (6 + 4\sqrt{2}) \min_{1 \le j \le N} \frac{\sigma_j}{z_j^2} \quad \text{with } 6 + 4\sqrt{2} \approx 11.656854, \qquad (114)$$

the solution $\Gamma(\Psi)$ is unique and is a differentiable function of Ψ.

Proof. Existence of a solution is a consequence of the fact that, as functions of Γ, the left hand side of (113) spans $\mathbb{R}^+$ while the right hand side remains positive and bounded on $\mathbb{R}^+$.

Denote by $F(\Gamma)$ the difference between the left and the right hand sides of (113). Let us show that (114) implies that F is an increasing function on $\mathbb{R}^+$, and, moreover, $F'(\Gamma) > 0$. To this end we use the trick $2\Gamma = 2(\Gamma)^2/\Gamma$ and compute the derivative (see (115) in Box I on next page).

Lemma 17 shows that $\partial\xi/\partial\Gamma > 0$, so the second line of Eq. (115) in Box I is positive. Introducing $x = \Gamma \Gamma_c \sigma_j$, the sign of each term in the sum of the first line of Eq. (115) in Box I is exactly that of the polynomial $P(x) = 4x^2 + (6 - L_B z_j^2/\sigma_j)x + 2$. A simple computation shows that $P(x)$ has no positive roots (and thus is positive for $x \ge 0$) if and only if (114) holds true.

Since, $F(0) < 0$ and $\lim_{+\infty} F(\Gamma) = +\infty$, the inequality $F'(\Gamma) > 0$ yields the existence and the uniqueness of the root Γ such that $F(\Gamma) = 0$. Then, a standard application of the implicit function theorem leads to the differentiable character of $\Gamma(\Psi)$. $\square$

Remark 19. The bound (114) is a sufficient, but not a necessary, condition for uniqueness of the root $\Gamma(\Psi)$, the solution of (113). There are other criteria (not discussed here) which ensure the uniqueness of $\Gamma(\Psi)$. However there are cases when multiple solutions do exist: it is interpreted as a phase transition phenomenon and it was studied, e.g., in [48].

In view of Lemma 18 the solute packing fraction is now a nonlinear function of the potential Ψ that we denote by

$$\tilde{\xi}(\Psi) \equiv \xi\Big(\Psi, \Gamma(\Psi)\Big).$$

As a result of our first step, the electrostatic equation (108) reduces to the following Poisson–Boltzmann equation which is a nonlinear partial differential equation for the sole unknown Ψ

$$\begin{cases} -\Delta\Psi = \beta \displaystyle\sum_{j=1}^{N} z_j n_j^0(\infty)\gamma_j^0(\infty) \\ \qquad \times \exp\left\{ -z_j\Psi + \dfrac{L_B \Gamma(\Psi) \Gamma_c z_j^2}{1 + \Gamma(\Psi)\Gamma_c \sigma_j} - p(\tilde{\xi}(\Psi)) \right\} \quad \text{in } \Omega_p, \\ \nabla\Psi \cdot \nu = -N_\sigma \Sigma^* \quad \text{on } \partial\Omega_p, \ \Psi \text{ is } \Omega\text{-periodic}. \end{cases} \qquad (116)$$

Recall that $N_\sigma > 0$ is a parameter and that $\Sigma^*(x)$ is assumed to be a Ω-periodic function in $L^\infty(\partial\Omega_p)$. Our goal is to prove existence of at least one solution to problem (116). The main difficulty is the non-linearity of the right hand side which is growing exponentially fast at infinity. Recalling definition (46) of $E_j(\Psi)$, the right hand side of (116) is the nonlinear function Φ defined by its derivative

$$\Phi'(\Psi) = \beta \sum_{j=1}^{N} E_j'(\Psi). \qquad (117)$$

In the ideal case, Remark 3 tells us that $E_j(\Psi) = n_j^0(\infty)\exp\{-z_j\Psi\}$. We are thus lead to introduce

$$g(\psi) = \sum_{j=1}^{N} n_j^0(\infty)\gamma_j^0(\infty) \exp\left\{-z_j\psi\right\}, \quad \psi \in \mathbb{R}, \qquad (118)$$

which is a strictly convex function. In the ideal case, we have $\Phi(\Psi) = \beta g(\Psi)$ and the existence and the uniqueness of a solution of (116) are more or less standard thanks to a monotonicity argument (see [49,5]). For the MSA model our strategy of proof is different since Φ is not anymore convex. We rely on a truncation argument, L^∞-bounds and still some monotonicity properties of part of Φ'. Our proof requires a smallness condition on the characteristic value ξ_c.

The second step of our proof introduces a truncation operator at the level $M > 0$ defined, for any function φ, by

$$T_M(\varphi) = \begin{cases} -\dfrac{M}{z_N} & \text{if } \varphi < -\dfrac{M}{z_N}, \\ \varphi & \text{if } -\dfrac{M}{z_N} \le \varphi \le \dfrac{M}{|z_1|}, \\ \dfrac{M}{|z_1|} & \text{if } \varphi > \dfrac{M}{|z_1|}. \end{cases}$$

Note that this truncation is not symmetric since the growth condition at $\pm\infty$ of Φ and g are not symmetric too. We define a "cut-off" function Φ_M by its derivative

$$\Phi_M'(\Psi) = \Phi' \circ T_M(\Psi), \qquad (119)$$

and solve the associated "cut-off" problem

$$\begin{cases} -\Delta\Psi_M = -\Phi_M'(\Psi_M) & \text{in } \Omega_p, \\ \nabla\Psi_M \cdot \nu = -N_\sigma \Sigma^* & \text{on } \partial\Omega_p, \ \Psi_M \text{ is } \Omega\text{-periodic}. \end{cases} \qquad (120)$$

Note that $\Phi_M'(\Psi)$ is a bounded Lipschitz function and its primitive $\Phi_M(\Psi)$ is a coercive C^1-function, with a linear growth at infinity. Therefore, for $\Sigma^* \in L^\infty(\partial\Omega_p)$ and M sufficiently large, the corresponding functional

$$J(\psi) = \frac{1}{2}\int_{\Omega_p} |\nabla\psi|^2 + \int_{\Omega_p} \Phi_M(\psi) + N_\sigma \int_{\partial\Omega_p} \Sigma^*\psi$$

$$F'(\Gamma) = \sum_{j=1}^{N} n_j^0(\infty)\gamma_j^0(\infty)\frac{z_j^2 \exp\left\{-z_j\Psi + \frac{L_B\Gamma\Gamma_c z_j^2}{1+\Gamma\Gamma_c\sigma_j} - p(\xi)\right\}}{(1+\Gamma\Gamma_c\sigma_j)^2}\left(\frac{2}{\Gamma} - \Gamma_c\frac{L_B z_j^2 - 2\sigma_j(1+\Gamma\Gamma_c\sigma_j)}{(1+\Gamma\Gamma_c\sigma_j)^2}\right)$$
$$+ \frac{\partial\xi}{\partial\Gamma}\, p'(\xi)\sum_{j=1}^{N} n_j^0(\infty)\gamma_j^0(\infty)\frac{z_j^2}{(1+\Gamma\Gamma_c\sigma_j)^2}\exp\left\{-z_j\Psi + \frac{L_B\Gamma\Gamma_c z_j^2}{1+\Gamma\Gamma_c\sigma_j} - p(\xi)\right\}. \tag{115}$$

Box I.

is lower semi-continuous with respect to the weak topology of H^1 and coercive on H^1. Then the basic calculus of variations yields existence of at least one solution for problem (120). Furthermore, for smooth domains, Ψ_M belongs to $W^{2,q}(\Omega_p)$ for all $q < +\infty$.

The third step of our proof amounts to prove an L^∞-estimate for Ψ_M such that, for M sufficiently large, it implies $\Phi_M(\Psi_M) = \Phi(\Psi_M)$ and, consequently, existence of at least one solution for problem (116). We start by some simple lemmas giving bounds on the solute packing fraction ξ.

Lemma 20. *Let $p(\xi)$, $\xi \equiv \xi(\Psi, \Gamma)$ and $g(\psi)$ be given by (111), (112) and (118) respectively. Then we have*

$$\mathcal{A}_{\min} g(\Psi) \le \xi e^{p(\xi)} \le \mathcal{A}_{\max} g(\Psi), \tag{121}$$

with

$$\mathcal{A}_{\min} = \xi_c \min_r \left(\frac{\sigma_r}{\sigma_c}\right)^3, \qquad \mathcal{A}_{\max} = \xi_c \max_r \left(\frac{\sigma_r}{\sigma_c}\right)^3 e^{L_B \max_j \frac{z_j^2}{\sigma_j}}.$$

Let ξ_0 be the unique solution of $x\exp\{p(x)\} = \mathcal{A}_{\min} g_m$ where g_m is the minimal value of $g(\psi)$. Then we have

$$\xi_0 \le \xi \le \mathcal{A}_{\max} g(\Psi). \tag{122}$$

Proof. Formula (112) yields

$$\xi \exp\{p(\xi)\} = \xi_c \sum_{j=1}^{N} \left(\frac{\sigma_j}{\sigma_c}\right)^3 n_j^0(\infty)\gamma_j^0(\infty)$$
$$\times \exp\left\{-z_j\Psi + \frac{L_B\Gamma\Gamma_c z_j^2}{1+\Gamma\Gamma_c\sigma_j}\right\}.$$

Since

$$0 < \frac{L_B\Gamma\Gamma_c z_j^2}{1+\Gamma\Gamma_c\sigma_j} \le L_B \max_j \frac{z_j^2}{\sigma_j},$$

we deduce the bound (121). The other bound (122) is then a consequence of the fact that $p(\xi) \ge 0$ and $\xi \to \xi e^{p(\xi)}$ is increasing. □

For the sequel it is important to find a bound for ξ which is independent of ξ_c, small as we wish, at least for large values of the potential Ψ.

Lemma 21. *Let $\xi \equiv \xi(\Psi, \Gamma)$ be the unique solution of (112). There exists a threshold $0 < \xi^{\mathrm{cr}} < 1$ such that, for any number $q \ge 1$, there exist positive values $\xi_{\min}, \xi_{\max} > 0$ such that, for any characteristic value $0 < \xi_c < \xi^{\mathrm{cr}}/q$,*

$$\xi \ge \xi_{\min} \quad \text{if } \Psi < \frac{-1}{z_N}\log\frac{1}{q\xi_c},$$
$$\xi \ge \xi_{\max} \quad \text{if } \Psi > \frac{1}{|z_1|}\log\frac{1}{q\xi_c}.$$

Remark 22. The point in Lemma 21 is that the lower bounds $\xi_{\min}, \xi_{\max} > 0$ are independent of ξ_c (but they depend on q), on the contrary of ξ_0 in Lemma 20. In the proof of Proposition 23 the number q will be chosen as $O(1)$ with respect to ξ_c.

Proof. We improve the lower bound for Eq. (113) when the potential is very negative $\Psi < (\log(q\xi_c))/z_N$. From (121) we deduce for small ξ_c

$$\xi e^{p(\xi)} \ge \mathcal{A}_{\min} g(\Psi) = n_N^0(\infty)\gamma_N^0(\infty)\min_r\left(\frac{\sigma_r}{\sigma_c}\right)^3$$
$$\times \frac{\xi_c}{q\xi_c}\left(1 + O(\xi_c^{1-z_{N-1}/z_N})\right)$$
$$\ge \frac{1}{2q} n_N^0(\infty)\gamma_N^0(\infty)\min_r\left(\frac{\sigma_r}{\sigma_c}\right)^3 = O(1),$$

where the lower bound is independent of ξ_c. The conclusion follows by defining $\xi_{\min}$ as the unique solution of

$$\xi_{\min} e^{p(\xi_{\min})} = \frac{1}{2q} n_N^0(\infty)\gamma_N^0(\infty)\min_r\left(\frac{\sigma_r}{\sigma_c}\right)^3.$$

Note that $\xi_{\min}$ is uniformly bounded away from 0 for small ξ_c since $\gamma_N^0(\infty) = O(1)$ by virtue of Remark 5.

The proof of the estimate for large values $\Psi > (\log(q\xi_c))/z_1$ is analogous. □

Now the upper bound in Lemma 20 implies that for $\xi = \xi(\Psi, \Gamma)$ we have

$$\frac{\xi_{\min}}{g(\Psi)\xi_c \max_r(\frac{\sigma_r}{\sigma_c})^3} e^{-L_B \max_j \frac{z_j^2}{\sigma_j}} \le e^{-p(\xi)}, \quad \text{for } \Psi < \frac{-1}{z_N}\log\frac{1}{q\xi_c}. \tag{123}$$

Indeed, by (121) and Lemma 21

$$e^{-p(\xi)} \ge \frac{\xi}{\mathcal{A}_{\max} g(\Psi)} \ge \frac{\xi_{\min}}{g(\Psi)\xi_c \max_r\left(\frac{\sigma_r}{\sigma_c}\right)^3} e^{-L_B \max_j \frac{z_j^2}{\sigma_j}}.$$

For the purpose of comparison we introduce the following auxiliary Neumann problem

$$\begin{cases} -\Delta U = \dfrac{1}{|\Omega_p|}\displaystyle\int_{\partial\Omega_p} N_\sigma \Sigma^*\, dS & \text{in } \Omega_p, \\ \nabla U \cdot \nu = -N_\sigma \Sigma^* & \text{on } \partial\Omega_p, \\ U \text{ is } \Omega\text{-periodic}, & \displaystyle\int_{\Omega_p} U(x)\, dx = 0. \end{cases} \tag{124}$$

Remark that (124) admits a solution $U \in H^1_\#(\Omega_p)$ since the bulk and surface source terms are in equilibrium. Furthermore, the zero average condition of the solution gives its uniqueness. It is known that U is continuous and achieves its minimum and maximum in $\overline{\Omega}_p$. Define

$$\overline{\sigma} = \frac{1}{|\Omega_p|}\int_{\partial\Omega_p} N_\sigma \Sigma^*\, dS, \qquad U_{\min} = \min_{x\in\overline{\Omega}_p} U(x) \quad \text{and}$$
$$U_{\max} = \max_{x\in\overline{\Omega}_p} U(x).$$

Then our L^∞-bound reads as follows.

Proposition 23. *Let Ψ_M be a solution for the cut-off problem (120) and take*

$$M = \log \frac{1}{\xi_c}.$$

Under assumption (114), there exists a critical value $\xi^{\mathrm{cr}} > 0$ such that, for any $\xi_c \in (0, \xi^{\mathrm{cr}})$, the solution Ψ_M of (120) satisfies the following bounds

$$-\frac{M}{z_N} \le \Psi_M(x) \le \frac{M}{|z_1|}. \tag{125}$$

Proof. We write the variational formulation for $\Psi_M - U$ for any smooth Ω-periodic function φ. Taking into account the definition $\Phi'_M(\Psi_M) = \Phi'(T_M(\Psi_M))$, it reads

$$\begin{aligned}
&\int_{\Omega_p} \nabla(\Psi_M - U)\cdot\nabla\varphi\,dx - \beta\sum_{j=1}^N z_j n_j^0(\infty)\gamma_j{}^0(\infty)\\
&\quad\times\int_{\Omega_p}\left(e^{-z_j T_M(\Psi_M)} - e^{-z_j T_M(U-C)}\right)\\
&\quad\times e^{L_B \frac{z_j^2 \Gamma_c \Gamma(T_M(\Psi_M))}{1+\Gamma_c\Gamma(T_M(\Psi_M))\sigma_j} - p(\xi(T_M(\Psi_M)))}\varphi\,dx\\
&\quad+\int_{\Omega_p}\left(-\beta\sum_{j=1}^N z_j n_j^0(\infty)\gamma_j{}^0(\infty)e^{-z_j T_M(U-C)}\right.\\
&\quad\left.\times e^{L_B \frac{z_j^2 \Gamma_c \Gamma(T_M(\Psi_M))}{1+\Gamma_c\Gamma(T_M(\Psi_M))\sigma_j} - p(\xi(T_M(\Psi_M)))} + \overline{\sigma}\right)\varphi\,dx = 0.
\end{aligned}\tag{126}$$

We take $\varphi(x) = (\Psi_M(x) - U(x) + C)^-$, where C is a constant to be determined and, as usual, the function $f^- = \min(f, 0)$ is the negative part of f. The first term in (126) is thus non-negative.

By monotonicity of $v \to -z_j \exp\{-z_j T_M(v)\}$ the second term of (126) is non-negative. To prove that the third one is non-negative too (which would imply that $\varphi \equiv 0$), it remains to choose C in such a way that the coefficient Q in front of φ in the third term is non-positive.

For a given number $q \ge 1$ (to be defined later, independent of ξ_c) we define constants

$$\tilde{M} = \log\frac{1}{q\xi_c} \le M = \log\frac{1}{\xi_c}$$

and we choose $C = U_{\max} + \tilde{M}/z_N$. Since $\varphi \neq 0$ if and only if $\Psi_M < U - C$, we restrict the following computation to these negative values of Ψ_M. In such a case, we have $\Psi_M < \frac{-1}{z_N}\log\frac{1}{q\xi_c}$ (the same is true for $T_M(\Psi_M)$) so we can apply (123) from Lemma 21. Then, since $-M/z_N \le T_M(U - C) \le -\tilde{M}/z_N$, we bound the coefficient Q (decomposing the indices in j^- for negative valencies and j^+ for positive ones)

$$\begin{aligned}
Q &= \overline{\sigma} - \beta\sum_{j=1}^N z_j n_j^0(\infty)\gamma_j{}^0(\infty)e^{-z_j T_M(U-C)}\\
&\qquad\times e^{L_B \frac{z_j^2 \Gamma_c \Gamma(T_M(\Psi_M))}{1+\Gamma_c\Gamma(T_M(\Psi_M))\sigma_j} - p(\xi(T_M(\Psi_M)))}\\
&\le \overline{\sigma} - \beta\sum_{j\in j^-} z_j n_j^0(\infty)\gamma_j{}^0(\infty)e^{L_B \max_j \frac{z_j^2}{\sigma_j}}\\
&\quad - \beta\sum_{j\in j^+} z_j n_j^0(\infty)\gamma_j{}^0(\infty)e^{z_j\tilde{M}/z_N}e^{-p(\xi(T_M(\Psi_M)))}
\end{aligned}$$

$$\begin{aligned}
&\underbrace{\le}_{\text{using (123)}} \overline{\sigma} - \beta\sum_{j\in j^-} z_j n_j^0(\infty)\gamma_j{}^0(\infty)e^{L_B \max_j \frac{z_j^2}{\sigma_j}}\\
&\quad - \beta\sum_{j\in j^+} z_j n_j^0(\infty)\gamma_j{}^0(\infty)\frac{\xi_{\min}e^{z_j\tilde{M}/z_N}e^{-L_B\max_j\frac{z_j^2}{\sigma_j}}}{g(T_M(\Psi_M))\xi_c\max_r(\frac{\sigma_r}{\sigma_c})^3}.
\end{aligned}\tag{127}$$

Next, for small ξ_c (i.e. very negative values of Ψ_M), the function $g(T_M(\Psi_M))$ is decreasing (and equivalent to $n_N^0(\infty)e^{-z_N T_M(\Psi_M)}$ at $-\infty$)

$$g(T_M(\Psi_M)) \le g(-M/z_N).$$

Thus

$$\begin{aligned}
&\sum_{j\in j^+} z_j n_j^0(\infty)\gamma_j{}^0(\infty)\frac{e^{z_j\tilde{M}/z_N}}{g(T_M(\Psi_M))}\\
&\quad\ge\frac{1}{g(-M/z_N)}\sum_{j\in j^+} z_j n_j^0(\infty)\gamma_j{}^0(\infty)e^{z_j\tilde{M}/z_N}\\
&\quad\ge z_N\frac{\xi_c(1+o(1))}{q\xi_c(1+o(1))} = \frac{z_N}{q}(1+o(1)).
\end{aligned}\tag{128}$$

We insert inequality (128) into the last term in (127) which yields

$$\begin{aligned}
Q &\le \overline{\sigma} - \beta\sum_{j\in j^-} z_j n_j^0(\infty)\gamma_j{}^0(\infty)e^{L_B \max_j \frac{z_j^2}{\sigma_j}}\\
&\quad - \beta\frac{z_N\xi_{\min}}{q\xi_c\max_r(\frac{\sigma_r}{\sigma_c})^3}e^{-L_B\max_j\frac{z_j^2}{\sigma_j}}(1+o(1)).
\end{aligned}\tag{129}$$

Then, recalling that $\xi_{\min}$ and $\gamma_j{}^0(\infty)$ are $O(1)$ for small ξ_c, it follows that, for given $q \ge 1$, there exists $\xi^{\mathrm{cr}} < 1$ such that, for any $0 < \xi_c \le \xi^{\mathrm{cr}}$, the expression on the right hand side of (129) is negative.

Now we conclude that $\varphi = (\Psi_M - U + C)^- = 0$, which implies $\psi_M \ge U - U_{\max} - \frac{1}{z_N}\log\frac{1}{q\xi_c}$. Choosing q sufficiently large so that $\frac{1}{z_N}\log q \ge U_{\max} - U_{\min}$, we deduce the lower bound $\psi_M \ge -M/z_N$ in (125).

An analogous calculation gives the upper bound in (125) and the proposition is proved. □

As a conclusion of our three steps of the proof, we can state the final result which is Theorem 2, stated in the simplified notations of this section.

Theorem 24. *Let $\Sigma^* \in L^\infty(\partial\Omega_p)$. Under assumption (114) and for small enough $\xi_c \in (0, \xi^{\mathrm{cr}})$, there exists a solution of the Poisson–Boltzmann problem (116), $\Psi \in H^1(\Omega_p)\cap L^\infty(\Omega_p)$. In particular, n_j satisfies a uniform lower bound $n_j(x) \ge C > 0$ in Ω_p.*

Proof. Proposition 23 implies that $T_M(\Psi_M) = \Psi_M$, so $\Phi'_M(\Psi_M) = \Phi'(\Psi_M)$, which proves that Ψ_M solves the original Poisson–Boltzmann problem (116). □

Remark 25. Note that the assumption (114) and ξ_c small enough are completely independent of the scaling of the domain Ω_p and thus of ε. Therefore, Theorem 24 applies uniformly with respect to ε in the porous medium Ω_ε, as stated in Theorem 2.

Remark 26. Of course, further regularity of Ψ can be obtained by standard elliptic regularity in (116). For example, assuming $\Sigma^* \in C^\infty(\partial\Omega_p)$, the right hand side of Eq. (116) is bounded and using the smoothness of the geometry, we conclude that $\Psi \in W^{2,q}(\Omega_p)$ for every $q < +\infty$. By bootstrapping, we obtain that $\Psi \in C^\infty(\overline{\Omega_p})$.

7. Numerical results

We perform two-dimensional numerical computations with the **FreeFem++** package [50]. The goal of this section is to compute the effective coefficients constituting the Onsager homogenized tensor (101), to study their variations in terms of some physical parameters (concentration, pore size and porosity) and to make comparisons with the ideal case studied in [24] in a realistic model of porous media. We use the same unit cell geometries and complete the same test cases as in [24]. It corresponds to a simple model of geological montmorillonite clays.

The linearization of the electrokinetic equations (see Section 4) allows us to decouple the computation of the electrostatic potential from those of the cell problems.

In a first step, we compute the solution Ψ^0 of the nonlinear Poisson–Boltzmann equation (73) with the associated hard sphere term γ^{HS} and MSA screening parameter Γ, from which we infer the activity coefficients γ_j^0 and the concentrations n_j^0.

Second, knowing the n_j^0's, and thus the MSA screening parameter Γ, we compute the hydrodynamic interaction terms Ω_{ij} (15)–(16) and the electrostatic relaxation terms $\mathcal{R}_{ij}$ (18). In turn it yields the value of the tensor K_{ij} given by (60). The concentrations n_j^0 and the tensor K_{ij} play the role of coefficients in the cell problems (85)–(88) and (90)–(92). Thus, we can now compute their solutions which are used to evaluate the various entries of the effective tensor (101) according to the formula from Proposition 15. In all figures we plot the adimensionalized entries of the effective tensors (101). However, when the concentrations are involved, we plot them in their physical units, namely we use the dimensional quantity

$$n_j^*(\infty) = n_c\, n_j^0(\infty). \tag{130}$$

For large pores (compared to the Debye length) the electrostatic potential is varying as a boundary layer close to the solid boundaries. In such a case, the mesh is refined close to those boundaries (see e.g. Fig. 1). The total number of degrees of freedom is around 18 000 (depending on the infinite dilution concentration $n_j^*(\infty)$).

The nonlinear Poisson–Boltzmann equation (73) is solved with Lagrange P2 finite elements and a combination of a Newton–Raphson algorithm and a double fixed point algorithm. The Newton–Raphson algorithm is used to solve the Poisson–Boltzmann equation at fixed values of the MSA coefficients γ^{HS} and Γ. The double fixed point algorithm is performed on these values of γ^{HS} and Γ. It starts with the initial values $\gamma^{HS} = 1$ and $\Gamma = 0$ which correspond to the ideal case.

Let $n = 1, 2, \ldots, n_{\text{final}}$ be the iteration number of the first level of the fixed point algorithm (the outer loop) which update the electrokinetic potential from the previous value $\Psi^{(n-1)}$ to the new value $\Psi^{(n)}$, keeping $\gamma^{HS}_{(n-1)}$ fixed. We first solve the Poisson–Boltzmann equation with these initial values and a MSA screening parameter initialized to $\Gamma^{(n-1)}_{(0)}$. Let us note $\Gamma^{(n-1)}_{(k-1)}$ the generic term at iteration k. Here, the iteration number $k = 1, 2, \ldots, k_{\text{final}}$ refers to the second level (inner loop) of the double fixed point algorithm. It yields the electrokinetic potential $\Psi^{(n-1)}_{(k-1)}$ and, through (41), the new $\Gamma^{(n-1)}_{(k)}$ value which allows us to iterate in k. The inner iterations are stopped when the wished accuracy is reached at $k = k_{\text{final}}$.

From this new electrokinetic potential $\Psi^{(n-1)}_{(k_{\text{final}})}$, we determine the species concentrations and, through (13), the solute packing fraction $\xi^{(n-1)}$. At this stage, a new hard sphere term $\gamma^{HS}_{(n)}$ is defined and we start a new iteration of the outer loop. The outer loop is broken when the wished accuracy is reached at $n = n_{\text{final}}$.

All the following computations are ran for an aqueous solution of NaCl at 298 K (Kelvin), where species $j = 1$ is the cation Na$^+$ ($z_1 = 1$) with diffusivity $D_1^0 = 13.33\text{e}{-10}\ \text{m}^2/\text{s}$ and species $j = 2$ the anion Cl$^-$ ($z_2 = -1$) with $D_2^0 = 20.32\text{e}{-10}\ \text{m}^2/\text{s}$ (note that this is the opposite convention of the previous sections where $z_1 < 0 < z_2$). The hard sphere diameters of the two species are considered equal to $3.3e{-10}$ m. This model of NaCl electrolyte solution is able to reproduce both the equilibrium (activity coefficients, osmotic pressure) and the transport coefficients (conductivity, Hittorf transference number [51], self and mutual diffusion coefficient of the electrolyte) up to molar concentrations. The infinite dilution concentrations of the species are considered equal, $n_1^0(\infty) = n_2^0(\infty)$, and the characteristic concentration is $n_c = 0.1$ mol/l.

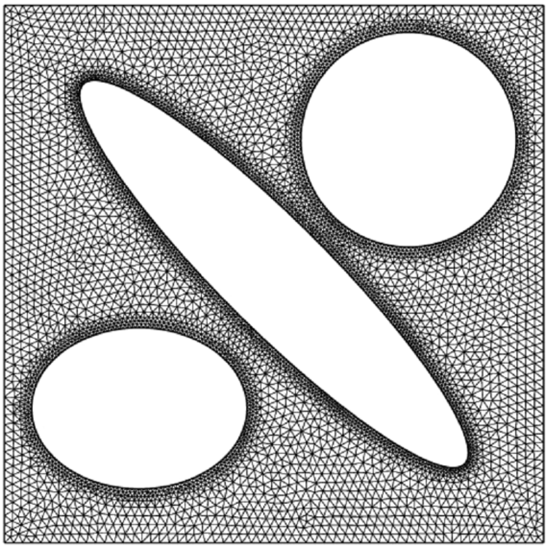

Fig. 1. Mesh for a periodicity cell with ellipsoidal inclusions (porosity is equal to 0.62).

The dynamic viscosity η is equal to 0.89e−3 kg/(ms). Instead of using the formula of Table 1 for defining the Debye length, we use the following definition (as in the introduction)

$$\lambda_D = \sqrt{\frac{\mathcal{E} k_B T}{e^2 \sum_{j=1}^{N} n_j z_j^2}},$$

which differs by a factor of $\sqrt{2}$ in the present case of two monovalent ions. Other physical values are to be found in Table 1. Following [24] two model geometries are considered. The first one features ellipsoid solid inclusions (see Fig. 1), for which we perform variations of concentrations from 10^{-3} to 1 mol/l and variations of the pore size ($3 \le \ell \le 50$ nm). The second one is a rectangular model (see Fig. 2) which allows us to perform porosity variation.

7.1. Variation of the concentration

Here we consider the geometry with ellipsoidal inclusions (Fig. 1). We vary the infinite dilution concentrations $n_j^0(\infty)$ in the range $(10^{-2}, 10)$ or, equivalently through (130), the dimensional infinite dilution concentrations $n_j^*(\infty)$ vary from 10^{-3} to 1 mol/l. The pore size is $\ell = 50$ nm. Varying proportionally all values of $n_j^0(\infty)$ is equivalent to varying the parameter β in the Poisson–Boltzmann equation (73).

As can be checked in Fig. 3, except for very small concentrations, the cell-average of the concentrations $|Y_F|^{-1} \int_{Y_F} n_j(y)\, dy$ is almost equal to the infinite dilution concentrations $n_j^0(\infty)$. This is clear in the ideal case, but in the MSA case the cell-average of the concentrations is slightly smaller than the infinite dilution

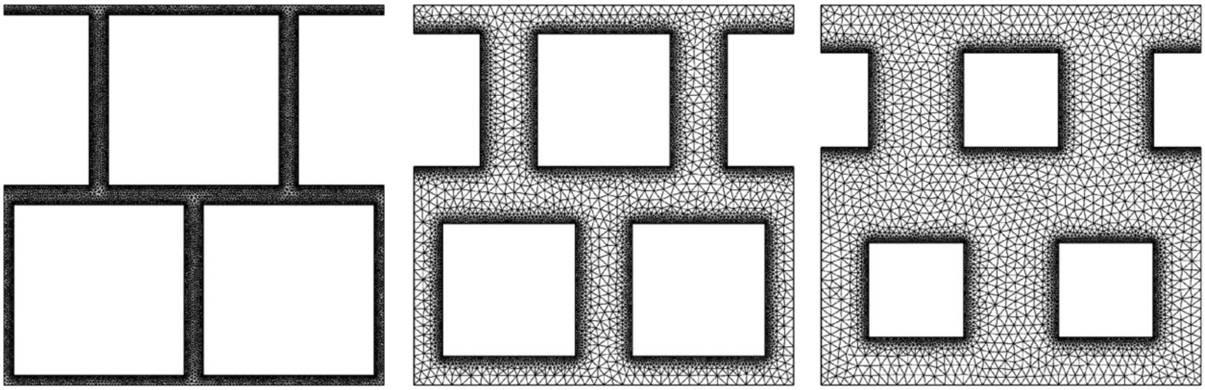

Fig. 2. Meshes for three different porosities (0.19, 0.51 and 0.75) of a periodic cell with rectangular inclusions.

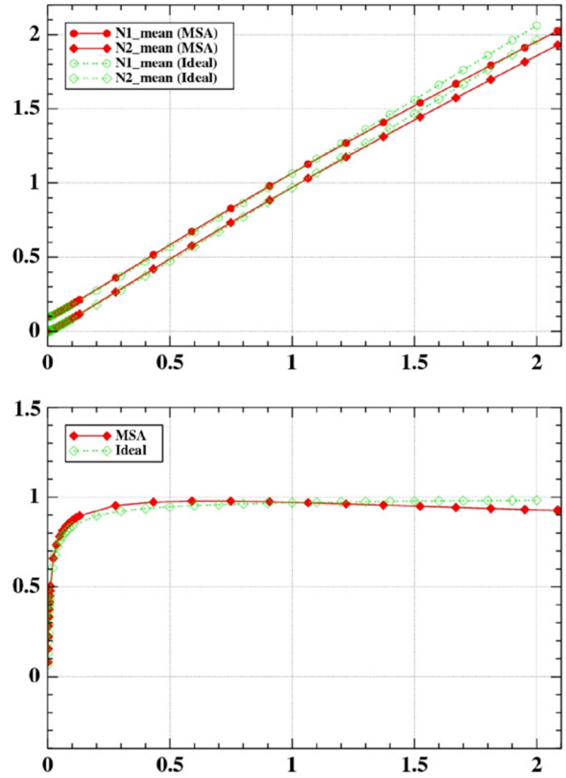

Fig. 3. Averaged cell concentrations $Nj\_mean = |Y_F|^{-1} \int_{Y_F} n_j(y)\,dy$ (top) and rescaled averaged cell anion concentration $N2\_mean/n_2^0(\infty)$ (bottom) as a function of the dimensional (mol/l) infinite dilution concentrations $n_j^*(\infty)$.

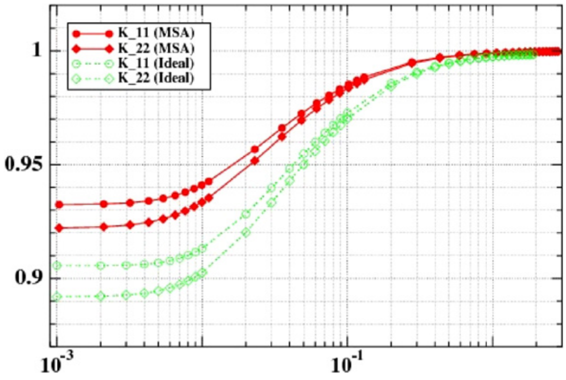

Fig. 4. Diagonal entries of the relative permeability tensor, $\mathbb{K}_{11}$ and $\mathbb{K}_{22}$, as functions of the dimensional (mol/l) infinite dilution concentrations $n_j^*(\infty)$.

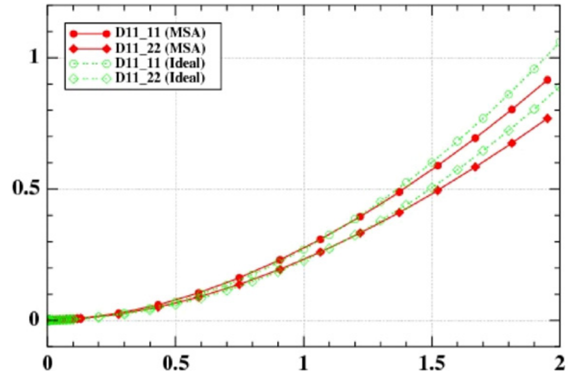

Fig. 5. Entries of the electrodiffusion tensor $\mathbb{D}_{11}$ for the cation, as functions of the dimensional (mol/l) infinite dilution concentrations $n_j^*(\infty)$.

concentrations for large concentrations. It is a manifestation of the packing effect which forbids the boundary layer to be too thin in the MSA setting. The behavior of Fig. 3 (bottom) which represents the Donnan effect was expected. For small dilutions the MSA concentration is higher than the ideal one because the electrolyte is in the attractive electrostatic regime so that there is a tendency of incorporating anions. It is the opposite for large dilutions: the electrolyte is in the repulsive hard sphere regime and the excluded volumes expel the anions.

Since the permeability tensor $\mathbb{K}$ depends on the pore size ℓ, we renormalize its entries by dividing them by the corresponding ones for a pure filtration problem (computed through the usual Stokes cell problems [42]). The resulting relative permeability coefficients are plotted in Fig. 4: the smaller the infinite dilution concentration, the smaller the permeability. We clearly see an asymptotic limit of the relative permeability tensor not only for high concentrations but also for low concentrations. In the latter regime, the hydrodynamic flux is reduced: the electrostatic attraction of the counterions with respect to the surface slows down the fluid motion. This effect is not negligible because the Debye layer is important. The MSA model differs from the ideal case. The curve is qualitatively the same but the electrostatic reduction of the Darcy flow is more important. Non-ideality diminishes the mobility of the counterions at the vicinity of the surface so that the electrostatic interactions in the double layers are more pronounced.

The entries of the electrodiffusion tensor $\mathbb{D}_{11}$ for the cation are plotted in Fig. 5. A similar behavior is obtained for the other tensor $\mathbb{D}_{22}$ for the anion. As expected the flux increases with the infinite dilution concentration $n_j^*(\infty)$. It is not a linear law because even at low concentration there are still counterions; they do not appear to be very mobile, though. The cross-diffusion tensor $\mathbb{D}_{12}$

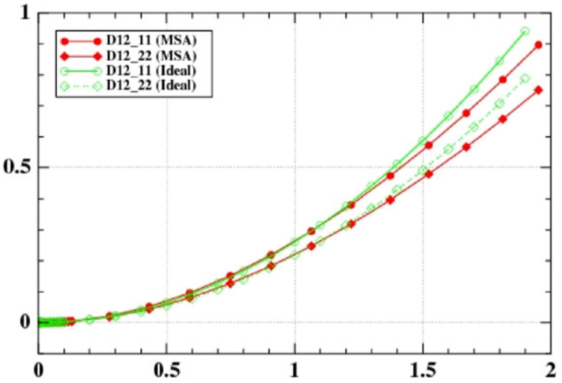

Fig. 6. Diagonal entries of the cross-diffusion tensor $\mathbb{D}_{12}$, as functions of the dimensional (mol/l) infinite dilution concentrations $n_j^*(\infty)$.

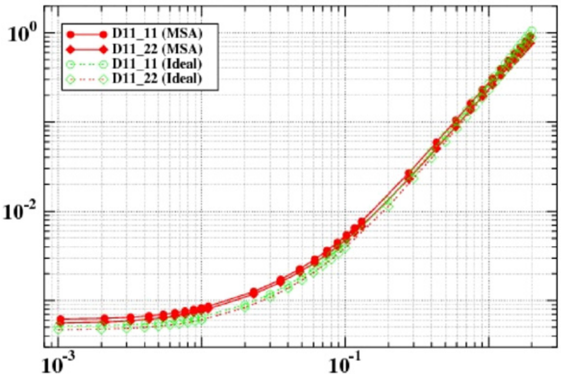

Fig. 7. Diagonal entries of the electrodiffusion tensor $\mathbb{D}_{11}$ as functions of the dimensional (mol/l) infinite dilution concentrations $n_j^*(\infty)$ (log–log plot).

is displayed in Fig. 6: for large concentrations it is of the same order of magnitude than the species diffusion tensors $\mathbb{D}_{11}$ and $\mathbb{D}_{22}$, because of the strong electrostatic interactions between the ions. In all cases, the MSA model is close to the ideal one: it is only for large concentrations that the values of the electrodiffusion tensor are different, and smaller, for MSA compared to ideal. There are probably compensating effects: same charge correlations increase diffusion but this effect is somewhat counterbalanced by opposite charge correlations that slow down the diffusion process. Non-ideal effects could be more important in the case of further quantities such as the electric conductivity for which cross effects are additive.

The log–log plot of Fig. 7 (where the slope of the curve is approximately 2) shows that the electrodiffusion tensors $\mathbb{D}_{ji}$ behaves quadratically as a function of $n_j^*(\infty)$ when $n_j^*(\infty)$ becomes large. This asymptotic analysis can be made rigorous in the ideal case. At low salt concentration, correlation effects (*i.e.* non-ideality) enhance slightly diffusion. In this regime, there are no counterions. So the relaxation effect is purely repulsive and diffusion is enhanced [52]. At high concentration, the co-ion concentration is not negligible and there is a classical electrostatic relaxation friction.

The coupling tensors $\mathbb{L}_1$ and $\mathbb{L}_2$ are plotted in Fig. 8. The coupling is, of course, maximal for large concentrations but the coupling tensor $\mathbb{L}_1$ for the cation does not vanish for very small infinite dilution concentrations since the cell-average of the cation concentration has a non-zero limit (required to compensate the negative surface charge) as can be checked in Fig. 3. The differences between the ideal and MSA models are very limited in this logarithmic plot.

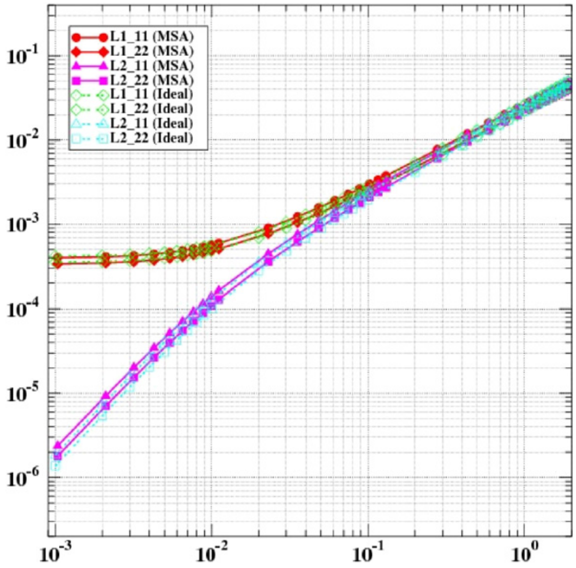

Fig. 8. Diagonal entries of the coupling tensors $\mathbb{L}_1$ and $\mathbb{L}_2$, as functions of the dimensional (mol/l) infinite dilution concentrations $n_j^*(\infty)$ (log–log plot).

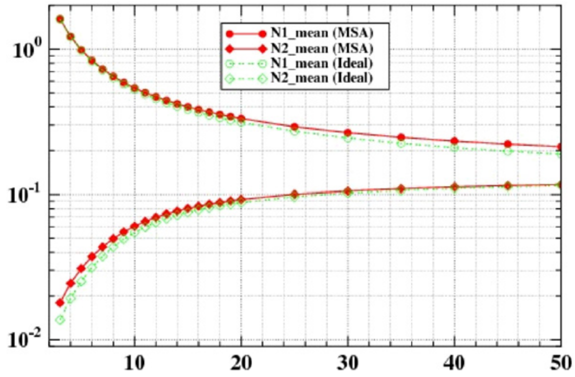

Fig. 9. Averaged cell concentration $Nj\_mean = |Y_F|^{-1} \int_{Y_F} n_j(y)\,dy$ versus pore size ℓ (nm).

7.2. Variation of pore size

We keep the same geometry with ellipsoidal inclusions (Fig. 1) but we now vary the pore size ℓ, which is equivalent to vary the parameter β, defined by (21), in the Poisson–Boltzmann equation (73). It thus changes the values of the concentrations $n_j^0(y)$ which play the role of coefficients in the cell problems (85)–(88) and (89)–(92). This is the only modification which is brought into the cell problems. We emphasize that varying the pore size does not change the geometry of the unit cell, but simply changes the coefficients of the cell problems.

The dimensional infinite dilution concentration $n_1^*(\infty) = n_2^*(\infty)$ is 10^{-1} mol/l which yields a value 0.7678 for the infinite dilute activity coefficients $\gamma_0^1(\infty) = \gamma_0^2(\infty)$.

In Fig. 9 we plot the cell-average of the concentrations $|Y_F|^{-1} \int_{Y_F} n_j(y)\,dy$ as functions of the pore size ℓ. Qualitatively, there is a close agreement between the ideal and MSA cases, as can be checked on this logarithmic plot. Yet, the departure from ideality is not negligible. For small pore size the Donnan effect, which corresponds to the anion concentration, is typically 40% higher than its value in the ideal case. When the pore size goes to infinity the averaged concentrations should converge to the infinite dilution concentrations.

In Fig. 10 we plot the relative permeability coefficients with respect to the ones of the Stokes problem. As was already observed

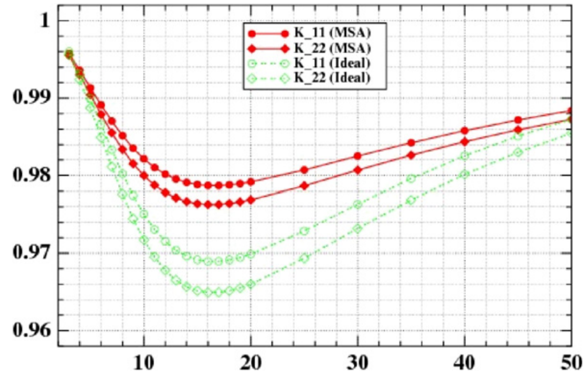

Fig. 10. Relative permeability coefficients $\mathbb{K}_{11}$ and $\mathbb{K}_{22}$ versus pore size ℓ (nm).

in [24], the variation is not monotone and there is a minimum for a pore size of roughly 20 nm. This effect is less pronounced for the MSA model but the location of the ℓ value where the minimum is attained is not affected. This is the signature of a transition from a bulk diffusion regime for small pores to a surface diffusion regime (caused by large boundaries) at large pores. Globally, the counterions reduce the hydrodynamic flow because of the attraction with the surface, but this relaxation effect is less important at very large or very small pore size ℓ. More precisely, if the pore size becomes very large, the electrostatic screening is important, as already mentioned. Thus the domain of attraction becomes very small and the lowering of the hydrodynamic flow is reduced: the permeability is increased. On the other hand, for very small pores, the counterion profile becomes more and more uniform. Consequently, there is no screening, but the hydrodynamic flow does not modify a lot the counterion distribution, since it is globally uniform and the resulting electrostatic slowdown becomes less important. The departures from ideality modeled by the MSA globally reduce the total variation of the permeability tensor because the mobility of the ions in the Debye layer is weaker and their dynamics influence less the Darcy flow.

7.3. Variation of the porosity

Eventually we investigate the influence of the porosity on the effective tensors. To this end we rely on the rectangular geometry where we vary the size of the inclusions (see Fig. 2). The infinite dilution concentration is fixed at $n_j^0(\infty) = 1$, or $n_j^*(\infty) = 0.1$ mol/l. The porosity is defined as $|Y_F|/|Y|$ and takes the successive values of 0.19, 0.36, 0.51, 0.64, 0.75 in our computations. Note that the porosity is independent of the pore size ℓ which is defined as the characteristic size of the entire periodicity cell, i.e., the union of its fluid and solid parts. In Fig. 11 we plot the cell-average of the concentrations $|Y_F|^{-1}\int_{Y_F} n_j(y)\,dy$ as functions of the porosity. They are almost identical between the ideal and MSA cases. When the porosity goes to 1, meaning that there are no more solid charged walls, the averaged concentrations should become equal, respecting the global electroneutrality. In Fig. 12 we check that the permeability tensor is increasing with porosity, as expected. The same happens for the electrodiffusion tensor $\mathbb{D}_{22}$ for the anion in Fig. 14. More surprising is the behavior of the electrodiffusion tensor $\mathbb{D}_{11}$ for the cation in Fig. 13: again there is a minimum value attained for a 0.35 value of the porosity. This may be explained again by a transition from a bulk diffusion regime for large porosities to a surface diffusion regime (caused by the charged boundaries) for small porosities.

The departures from ideality are found to be very important. They multiply the magnitude of diffusion by a factor of two, especially at low porosities for which the amount of anions is low.

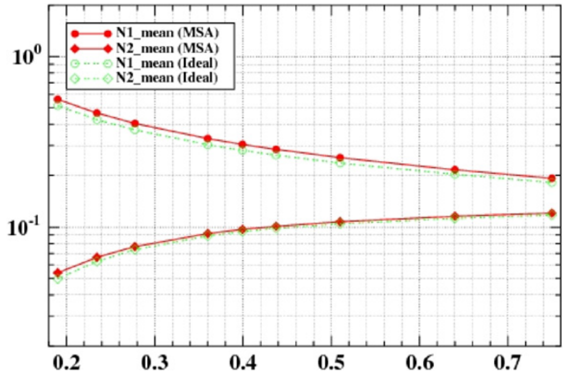

Fig. 11. Averaged cell concentration $Nj\_mean = |Y_F|^{-1}\int_{Y_F} n_j(y)\,dy$ versus porosity ($n_j^*(\infty) = 0.1$ mol/l).

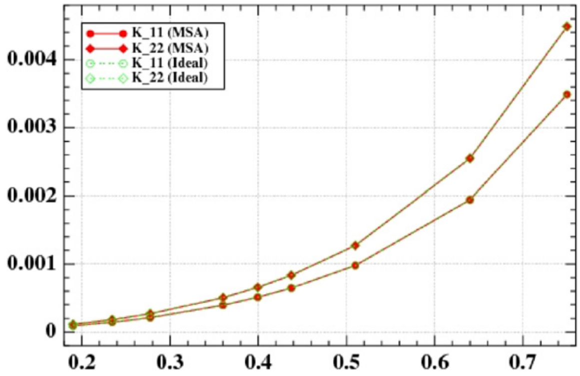

Fig. 12. Permeability tensor $\mathbb{K}$ versus porosity ($n_j^*(\infty) = 0.1$ mol/l).

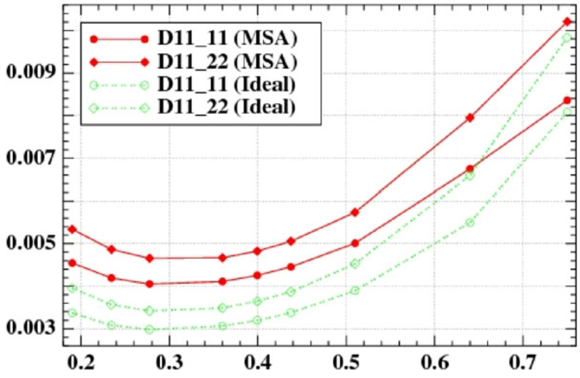

Fig. 13. Electrodiffusion tensor $\mathbb{D}_{11}$ for the cation versus porosity ($n_j^*(\infty) = 0.1$ mol/l).

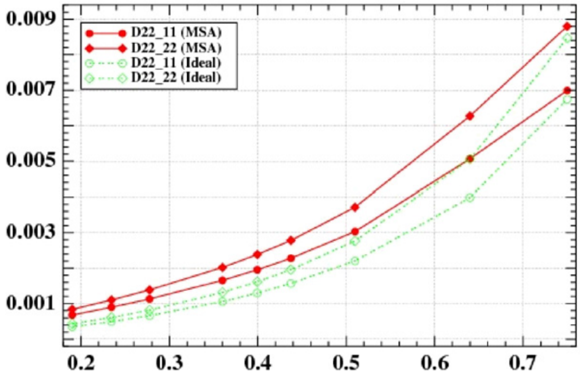

Fig. 14. Electrodiffusion tensor $\mathbb{D}_{22}$ for the anion versus porosity ($n_j^*(\infty) = 0.1$ mol/l).

It corresponds to the case for which the relaxation effect is purely repulsive. A similar trend is obtained for the anion but the diffusion coefficient is much lower at low porosities: anions are expelled from the surface and they cannot have surface diffusion so that their transport properties are globally reduced.

8. Conclusion

We presented the homogenization (or upscaling) of the transport properties for a N-component electrolyte solution confined in a charged rigid porous medium. Contrary to what is commonly supposed in this domain the departures from ideality are properly taken into account thanks to a MSA-transport model, both for the equilibrium properties (activity coefficients γ_j) and for the transport quantities (Onsager coefficients L_{ij}). These non-ideal effects are expected to be significant in most of the applications for which the electrolyte concentrations are typically molar. In the case of the equilibrium solution (in absence of external forces, apart from the surface charges on the solid wall), we prove the existence of (at least) one solution for small solute packing fractions (which corresponds to the validity of the MSA approach).

When a (small) external electric field is applied or when a (small) hydrodynamic or chemical potential gradient occurs, a rigorous homogenization procedure yields (at the linear response regime) the homogenized macroscopic laws. The effective Onsager tensor takes into account the departure from ideality, but it is still symmetric and positive definite. The significance of non-ideality has been studied by applying the results to a model of porous media (typically geological clays) for simple dissociated 1–1 electrolytes in water. It is shown that non-ideality only slightly modifies the qualitative aspects, but it can strongly modify the quantitative values, depending on the homogenized quantities.

For the equilibrium properties, it enhances the ion concentrations at low external concentration (because electrostatic attraction is predominant) and it reduces them at the opposite limit. The relative permeability tensor is increased but, in any case, it is close to the reference value calculated with a neutral solution. The differences for the coupled diffusions and ion electrodiffusions depend on the concentrations and on the species. Similarly to bulk diffusion, the non-ideality can have an impact of the order of 50% for molar concentrations. Nevertheless, for some cases, there are compensating effects. It should be noted that for the model we considered the charges (ions, solid phase) were relatively low so that the differences should be magnified for highly charged media with higher valency electrolytes and higher concentrations. In that case, the result could be completely different because of the possibility of ion pairing that can change the sign of the ion charge. Nevertheless, the (relatively) simple MSA-transport theory we presented is not valid anymore in that case so that a realistic quantitative description of such complex media would require further developments.

To conclude, we showed that non-ideality can actually be important for the description of porous media. Since most of the existing effective theories for concentrated systems are based on ideal models which neglect the departure from ideality, the parameters that can be measured thanks to these approaches may be wrongly estimated. In that case, they cannot be considered as robust structural quantities of the system: they are effective parameters that depend on the experimental conditions.

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