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A Two-Scale Model for Coupled Electro-Chemo-Mechanical Phenomena and Onsager's Reciprocity Relations in Expansive Clays: I Homogenization Analysis

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Abstract. The macroscopic model governing coupled electro-chemo-mechanical phenomena in expansive clays is revisited within a rigorous homogenization procedure applied to the microscopic governing equations which describe the local interaction between charged clay particles and a binary monovalent aqueous electrolyte solution. The up-scaling of the microscopic electro-hydro-dynamics leads to a two-scale approach wherein the macroscopic model appears governed by a fully coupled form of Onsager's reciprocity relations, mass conservation equations and a modified Terzaghi's effective stress principle. In addition, the two-scale approach provides microscopic representations for the effective coefficients which are exploited herein to obtain further insight in the constitutive behavior of the electrochemical parameters and the swelling pressure. Among other effects, we show that these microscopic closure relations are mainly dictated by the spatial variability of a microscale electric potential which satisfies a local version of the Poisson–Boltzmann problem in a periodic unit cell, The proposed framework allows to address various relevant still open issues regarding the constitutive behavior of swelling systems, Among them we give particular emphasis on the analysis of the influence of the fluctuation and distortion of the electrical double layer upon the magnitude of the electrochemical coefficients and the precise local conditions for the validity of the symmetry of Onsager's relations.

Key words: swelling clay, homogenization, closure problems, Onsager's relations, Poisson–Boltzmann, electro-osmosis, chemico-osmosis, electro-migration, distortion of the double-layer, modified Terzaghi's principle, disjoining (swelling) pressure, streaming current, Hartmann number.

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1. Introduction

Swelling porous media such as 2-1 lattice clays, hydrophilic polymers, shales, corneal endothelium and connective biological tissues are ubiquitous in almost all aspects of life. For example swelling clays play a critical role in the quality of fresh water and in the distribution of plants and nutrients in the earth's crust. The electro-chemical mechanisms of water adsorption by smectites are of utmost importance in determining the ability of soils to transport and supply water. Clay swelling (or collapse) is of widespread relevance in geotechnical and geoenvironmental fields. Owing to the presence of binding agents for pollutants together with the low hydraulic conductivity, plastic character and self-sealing capacity, bentonitic clays have been suggested appropriate engineered barriers against environmental pollution to prevent the migration of pollutants. Compacted soil liners have been used as earthen barriers to prevent leakage of contaminated water from leachates to the subsurface environment. In the context of petroleum technology swelling plays a crucial role in the stability of boreholes drilled through clay-rich rocks such as shales. The ionic content of the pore fluid affects the tendency of the shale to swell when brought into contact with fresh water in particular using environmental acceptable water-based drilling muds. Swelling is also a concern to the civil engineer because volume changes in expansive clays may reduce the stability of landslopes and can produce ground movement capable of causing severe damage to foundations, highways and runways. Electrokinetic phenomena near charged surfaces have other numerous technological applications such as in the remediation of contaminated soils, in the design of artificial membranes with high ion-exchange capacity, in filtration processes and in the development of efficient drug delivery substrates. The physiological states of soft connective tissues (articular cartilage and intervertebral disk) are partially swollen and exhibit prestresses which play an important role in the load bearing characteristics of articulating joints. As such, it is imperative that any macroscopic model describing the complex electro-chemo-mechanical interaction inherent to this type of system contains the appropriate constitutive relations.

Expansive materials have in common a structure that can be loosely identified as a mixture of macromolecules (polymers, clay particles, proteoglycans), whose characteristic length lies in the colloidal range ($\approx 1\ \mu$m), and a solvent (water, hydrocarbons). The solvent is either adsorbed to the macromolecules in the form of an electrolyte solution with partially or totally dissociated ionic species, or in bulk (free of any adsorptive force). For simplicity we henceforth restrict our discussion to clay-water-electrolyte systems. The reader will be aware, however, that the approach developed herein can also be applied to most colloidal systems.

The minerals of the smectite group are mostly colloidal aluminosilicates. A typical 2:1 smectite such as montmorillonite has a platy morphology of extremely small size composed of two structural units; a sheet of alumina octahedra sandwiched between two sheets of silica tetrahedra. The result of this arrangement is a flat composite layer exhibiting tremendous surface area with the flakes forming structural channels with a tendency to bind water. Crystal imperfections and isomorphous substitutions of higher valence ions with lower valence ions in the smectitic minerals render a surface charge imbalance which is compensated by the adsorption of oppositely charged ions (counter-ions) forming the diffusive electrical double layer (e.d.l.). In this picture, ion concentration gradients in the counterion cloud and charge distribution in the liquid are ruled by the electrochemical interactions with the static charges on the dielectric mineral surfaces (Newman, 1973; Van Olphen, 1977; Hunter, 1981; Lyklema, 1993). In addition, the imbalance of ions between the electrolyte solution and the surrounding bulk fluid is primarily responsible for many macroscopically observed electrochemical and electrokinetic coupled phenomena such as electro-osmosis, chemico-osmosis, streaming potentials, streaming current, electromigration and electroviscous effects (see, e.g., Lyklema, 1993; Mitchell, 1993).

The microscopic electro-chemical interactions in colloidal systems are now well understood. For instance, electro-osmotic flows characterized by fluid movement induced by an applied electric field are described by an additional body force of Coulomb type in the Stokes equations of motion (Eringen and Maugin, 1989). Streaming currents arise from the convective transport of the counterion charge cloud induced by a pressure gradient and can be described by further manipulating the Nernst–Planck equations governing the convective and diffusive (Fickian and electro-migration) motion of the ions (see, e.g., Coelho *et al.*, 1996). Streaming (electric) potentials arise from the enforcement of the constraint of zero electric current in an open-circuit (Gu *et al.*, 1998). Electro-migration and electrophoresis are the movement of the mobile ions and charged particles driven by spatial variability of the macroscopic electric potential. To conserve charge the electromigration movement occurs in the opposite direction of the streaming current and can be described by a back (conduction) current which acts to slow down the movement of the counter-ions of the diffuse double layer. In the steady-state configuration characterized by an open-circuit picture, the conduction current balances the streaming current and leads to the condition of zero net current (Yang and Li, 1998). Owing to the viscous drag interaction the reverse force exerted on the ions is transferred to the solvent molecules resulting in electroosmotic flow opposing the pressure gradient driven flow. These two competing mechanisms result in the appearance of the so-called electroviscous retardation effect which is manifested as an increase in the viscosity of the electrolyte solution (usually termed apparent viscosity) compared to its classical bulk phase value when nonionic species are suspended in the aqueous phase (see, e.g., Hunter, 1981; Ren *et al.*, 2001).

The development of ionic atmospheres around the clay minerals also leads to the appearance of electro-chemical stresses in the clay matrix which are responsible for the expansion/shrinking of the clay lattice. When water comes in contact with a mass of clay crystals, it penetrates between the layers and forces them apart. When hydration progresses the crystals may expand several times their original thickness. Derjaguin and coworkers (1987) described the lyophilic interaction between fluid and substrate in terms of a disjoining pressure, defined as an excess in the fluid pressure normal to the solid surface relative to the surrounding bulk phase. For long-range interactions, where hydration and steric effects are neglected, swelling is dominated by electrostatic forces arising from the overlapping between the ionic double layers (Derjaguin *et al.*, 1987; Israelachvili, 1991; Mitchell, 1993). At the macroscale (the homogenized microscale) this electro-chemical stress has been identified with the swelling pressure (the averaged Derjaguin's disjoining pressure) which has been experimentally evaluated by measuring the overburden pressure excess that must be applied to a well-ordered arrangement of parallel particles to prevent further uptake of water (see Low, 1987).

At the microscale electro-chemical effects are governed by the electrohydrodynamics coupled with Nernst–Planck equations and the Poisson–Boltzmann problem which govern the fluid movement, transport of mobile charges and electric potential distribution in the electrolyte solution (see Gross and Osterlé, 1968; Fair and Osterlé, 1971; Melcher, 1981; Sasidhar and Ruckenstein, 1981, 1982; Sherwood, 1992; Macevoy and Avellaneda, 1997; Yang and Li, 1998; Revil, 1999). Boundary conditions on the particle–fluid interface couple the eletrochemical effects in the fluid with the deformation and stress analysis in the solid phase. At the macroscale the highly heterogeneous microstructural solid–fluid interactions are represented in an averaged fashion with the clay and adsorbed fluid treated as overlaying continua forming the clay clusters or aggregates with averaged properties defined at every point in the domain occupied by the mixture (Bennethum *et al.*, 2000; Bennethum and Cushman, 2002). Under near-equilibrium conditions, the averaged fluid flow, overall flux of ions and electric current are linearly coupled with the gradients of head, concentration and electric potential through Onsager's reciprocity relations (see, e.g., Lai *et al.*,1991; Yeung and Mitchell, 1993; Heidug and Wong, 1996; Huyghe and Janssen, 1997; Gu *et al.*, 1998, 1998). The Onsager's coefficients reflect (in an averaged fashion) the microscopic electro-hydrochemical interactions in the electrolyte solution. The macroscopic reciprocity relations are coupled with a modified form of Terzaghi's effective stress principle which incorporates an extra component accounting for swelling. More precisely, this principle states that, in addition to the well-known purely mechanical stresses (contact stresses and pore pressure), an additional physico-chemical component containing the net repulsive (R) and attractive (A) forces (commonly denoted by ($R - A$)) also plays a crucial role in the expansion/shrinking of the clay matrix (see Lambe, 1960; Sridharan and Rao, 1973; Hueckel, 1992). In the case where the repulsive force is ruled by electro-chemical effects, R is nothing but the averaged counterpart of the electrostatic component of Derjaguin's disjoining pressure governing osmotic swelling (see Achari *et al.*, 1999).

Despite a large number of publications on the development of phenomenological models for swelling media (see, e.g., Smiles and Rosenthal, 1968; Philip, 1969; Kim *et al.*, 1992) and applications of Thermodynamics of Irreversible Processes and Onsager's reciprocity relations to the macroscopic modelling of coupled electro-chemo-mechanical phenomena (see, e.g., Lai *et al.*, 1991; Yeung and Mitchell, 1993; Heidug and Wong, 1996; Huyghe and Janssen, 1997), still limited accomplishments have been achieved toward the incorporation of the clay morphology and local e.d.l. properties in the macroscopic model. As mixture theoretic approaches are directly conducted at the macroscale, the complex microstructural solid–fluid interactions are overlooked and the magnitude of the electrokinetic coefficients is obtained based on experimental evidence or by solving inverse problems through optimization processes. On the other hand it has been advocated that the clay microstructure plays a paramount importance in many macroscopic observed physico-chemical and electro-chemical phenomena. For instance, it is well known that the swelling pressure is strongly dictated by particle orientation and anisotropy (Anandarajah, 1997).

Historically, attempts at correlating the morphology of the medium with the magnitude of the effective coefficients began by considering idealized microstructures with the porous system composed by a bundle of capillary tubes. In this context Gross and Osterlé (1968), Fair and Osterlé (1971), Sherwood (1992) and Szymczyk *et al.* (1999) have established the first correlations between the macroscopic Onsager's coefficients and the microscopic electro-hydrodynamics. In this over-simplified parallel particle arrangement, local fluctuations in pressure and concentration in the direction orthogonal to the particle surface are neglected. Further, under equilibrium conditions between the electrolyte solution and an outer saline bath, Dormieux *et al.* (2003) established correlations between a macroscopic equilibrium thermodynamical approach and micromechanics aiming at providing microscopic representations for the effective parameters in general microgeometries. Still under thermodynamical equilibrium constraint, Murad and Moyne (2002) proposed a homogenization procedure based on two-scale asymptotic expansions to up-scale the micromechanical picture of charged clay particles saturated by an electrolyte solution. The up-scaling led to a modified form of Terzaghi's decomposition containing an additional swelling stress tensor term which incorporates the macroscopic effect of the disjoining forces. The microscopic representation of this electro-chemical component includes a deviatoric part and suggests a tensorial generalization of the swelling pressure. By solving numerically the closure problem for constant salinity the constitutive dependence of the swelling stress tensor on particle separation has been computed in a two-dimensional periodic unit cell (see Murad and Moyne, 2002 for details). Further, the homogenization technique has been generalized in Moyne and Murad (2003) to accommodate local nonequilibrium macroscopic phenomena related to fluid flow and ion transport in general microstructures. Moreover in Moyne and Murad (2002) the technique proposed in Moyne and Murad (2003) has been combined with a suitable decomposition of the total electric potential leading to the appearance of the streaming potential (Sasidhar and Ruckenstein, 1981, 1982; Bike and Prieve, 1992). The approach proposed in Moyne and Murad (2002) provided a more realistic macroscopic picture of the swelling clay wherein phenomena such as electro-osmosis and electro-migration naturally appear in the homogenized forms of the convection-diffusion equations and Darcy's law as components driven by streaming potential gradients (see Moyne and Murad, 2002 for details).

In the homogenization technique proposed in Moyne and Murad (2002), a small order of magnitude of the Péclet number was adopted. In addition, the microscopic closure problems for the electro-chemo-mechanical effective parameters were solved for small electric potentials with the Poisson Boltzmann problem replaced by its linearized Debye–Huckel approximation (Hunter, 1994; Van Olphen, 1997). Here we remove these restrictions. We show that when adopting a more realistic higher order of magnitude for the Péclet number, the homogenization technique is capable of capturing important microscopic features inherent to the dynamical interactions between the advection of the ions and charge cloud and incorporating them in the closure relations for the effective Onsager's parameters. These features have been overlooked by the previous formulations and are mainly related to perturbations in ion dispersivities and conductivities for fluid flow induced by the distortion of the charge clouds along with their restoring relaxation effect (see Sherwood, 1980). Our development shows that these relaxation phenomena are essential features ruled by the magnitude of the Péclet number which may play a paramount importance in the constitutive behavior of the effective electro-chemical parameters.

In order to illustrate the importance of bridging electro-kinetic phenomena at two different scales and to motivate the development of our two-scale formulation, below we highlight still unresolved issues associated with the constitutive behavior of swelling systems Which will be addressed herein.

(i) *Influence of local fluctuations in the electro-chemical potential of the ions on the symmetry of Onsager's reciprocity relations.* The Onsager's matrix is postulated to be symmetric provided a local reversibility assumption is postulated (de Groot and Mazur, 1962; Prigogine, 1967). Hence, an open question remains how to incorporate local nonequilibrium phenomena, associated with fluctuations in the electro-chemical potential of the ions, in the magnitude of Onsager's coefficients.

(ii) *Role of the e.d.l. thickness in the magnitude of the Onsager's parameters.* The magnitude of the conductivity for electro-osmotic flow (electro-osmotic permeability) differs somewhat in the cases of microstructure characterized by thin e.d.l.s with large electrokinetic distance (the ratio of the channel width to the e.d.l. thickness) and narrow channels when the e.d.l.s overlap and span the entire micro-pore space. For thin e.d.l.s the electro-osmotic permeability is solely dictated by the zeta potential (the electric potential in the interface between the diffusion and compact years of fixed and mobile charges) through the well-known Smoluchowski model (see Newman, 1973; Hunter, 1981; Coelho *et al.*, 1996; Shang, 1997). In addition a secondary component arising from the interaction between e.d.1.s in the case of small electrokinetic distances also plays an important role in the magnitude of the electro-osmotic permeability (Hunter, 1981). Szymczyk *et al.* (1999) have proposed correction factors to extend Smoluchowski's model to incorporate this secondary effect. Hence, the relative roles of primary and secondary effects when considering random cell geometries and their influence upon the magnitude on the electro-osmotic permeability are crucial issues which need to be properly addressed.

(iii) *Influence of the distortion of the e.d.l. on the macroscopic fluid movement and ion transport.* As mentioned before the distortion of the mobile portion of the e.d.l. induced by the advection velocity of the electrolyte solution and its capacity to restore its equilibrium configuration result in a strong retardation drag force acting on the fluid flow and ion transport (see Sherwood, 1980; Hinch and Sherwood, 1983). This ion relaxation effect alters the diffusivity of the counterions, the conductivity for fluid flow and the electrophoretic mobility of ionized macromolecules (Allison, 1996) and needs to be accurately incorporated in the model.

(iv) *Relation between microscopic Derjaguin's disjoining pressure and macroscopic Low's swelling Pressure.* The constitutive behavior of the electro-chemical stresses induced in the solid phase has not been treated in an unified manner. In particular, some discrepancies between the constitutive relation of the swelling pressure and its microscale disjoining pressure counterpart (Derjaguin *et al.*, 1987) have been observed. Although this latter microscopic quantity includes both chemico-osmotic and Maxwell stresses (Derjaguin *et al.*, 1987; Dahnert and Huster, 1999), the dependence of the swelling pressure on salt concentration has not incorporated similar effects, being commonly identified with the macroscopic Donnan osmotic pressure (see, e.g., Barbour and Fredlund, 1989). The same observation also applies to the controversial aspects of the averaged stress partitioning mechanisms in the solid matrix within a modified form of Terzaghi's effective stress principle. Although the macroscopic repulsive force R in the modified Terzaghi's effective stress principle has been identified with the averaged disjoining pressure calculated via e.d.l. theory (Achari *et al.*, 1999), a similar quantity, referred to as chemical-expansion stress, has been thermodynamically introduced within the context of mixture theory to describe the expansion of charged hydrated biological tissues (Gu *et al.*, 1988, 1988). Unlike the disjoining pressure, the constitutive law for the chemical-expansion stress depends exponentially on ion concentration (Lai *et al.*, 1991). Hence one may observe that the constitutive response of the extra electro-chemical component in Terzaghi's decomposition remains controversial.

(v) *Role of the electro-chemical compressibility in mass conservation.* In a similar fashion to the Biot-Willis (1957) coupling parameter (α) which incorporates the effect of rock compressibility in both Terzaghi's principle and overall mass balance, the role and constitutive behavior of the electro-chemical compressibility parameter (see, e.g., Barbour and Fredlund, 1989; Mitchell, 1993) along with its relation with the swelling/disjoining pressure have not been addressed in a unified manner.

Other peculiar phenomena in swelling systems include polarization of the e.d.l. (Rathore and Horvath, 1997; Lee *et al.*, 2000) electro-osmosis of second kind (Mishchuk, 1998), extended Nernst–Planck model for non-ideal ionic solutions (Samson and Marchand, 1999), dynamic Stern layer and surface conduction (Rubio-Hernndez *et al.*, 1998; Sherwood *et al.*, 2000). Although the microscopic modeling of these phenomena have been discussed in the literature, the development of an accurate up-scaling procedure to quantity macroscopically these effects remains an open issue.

The proper addressing of the aforementioned issues enhances the robustness and accuracy of the two-scale model and provide a more realistic portrait of the swelling medium. The goal of this contribution is to accomplish this task. To this end we adopt the homogenization procedure based on asymptotic expansions but, unlike (Moyne and Murad, 2002) neither we assume a small Péclet number nor make use of the Debye–Hueckel linearized approximation to represent the nonlinear Poisson–Boltzmann problem. A notable consequence of our up-scaling procedure are the new closure problems for the effective electro-chemical parameters which contain new microscopic relaxation phenomena. The numerical solution of these closure problems provide further insight in the development of an accurate theory of constitution of colloidal systems and are presented in a companion paper (Moyne and Murad (2006)) for a particular microstructure of the clay.

An outline of the paper is as follows. In Section 2 we present the microscopic model. In Section 3 we rephrase the micro-model in terms of alternative bulk variables, which are more appropriate for the enforcement of boundary conditions. In Section 4 we present the homogenization procedures for derivation of the macroscopic model along with the new closure problems. Finally, in Section 5 we rephrase the macro-model in an alternative form based on Onsager's reciprocity relations.

2. Microscopic Model

At the microscale we consider a two-phase system composed of colloidal Na-montmorillonite particles uniformly charged on the surface saturated by a continuum dielectric aqueous solution containing symmetric 1:1 completely dissociated monovalent electrolytes Na^+ and Cl^-. The solvent is considered a dilute solution with the ions treated as point charges so that hydration and steric effects associated with size effects are neglected. Denoting Ω_f and Ω_s the microscopic domains occupied by the fluid and solid and Γ the common interface, we present the coupled microscopic model governing fluid flow, ion transport, electric potential distribution and particle deformation.

2.1. ELECTROSTATICS

Let $\{c_+, c_-\}$ and $\{\Phi, \boldsymbol{E}\}$ be the pairs of molar concentrations of cations/anions and electric potential/electric field, respectively. In classical electrostatics Φ and $\boldsymbol{E}$ are governed by the Poisson problem (see, e.g., Landau and Lifchitz, 1960)

$$\begin{aligned} &\tilde{\varepsilon}\tilde{\varepsilon}_0 \nabla . \boldsymbol{E} = q, \\ &\boldsymbol{E} = -\nabla \Phi, \quad \text{in } \Omega_\mathrm{f}, \end{aligned} \tag{2.1}$$

where $\tilde{\varepsilon}_0$ and $\tilde{\varepsilon}$ are the permittivity of the free space and the relative dielectric constant of the solvent (assumed constant) and q is the net charge density. Denote F the Faraday constant and z the valence ($z = z_+ = -z_- = 1$ for symmetrical monovalent electrolytes) and define q by the product between the molar charge and the concentration difference between cations and anions, i.e. $q \equiv F(c_+ - c_-)$. Hence we have

$$\Delta\Phi = -\frac{q}{\tilde{\varepsilon}\tilde{\varepsilon}_0} = -\frac{F}{\tilde{\varepsilon}\tilde{\varepsilon}_0}(c_+ - c_-). \tag{2.2}$$

2.2. MODIFIED STOKES PROBLEM

The appearance of the product between net charge density and electric field gives rise to the electroosmotic movement of the aqueous electrolyte solution. The electric field exerts a force on the charge cloud which is transferred to the solvent molecules by viscous interactions leading to an electrokinetic coupling between flow and charge transport. This effect is modeled by an additional body force of Coulomb type $q\boldsymbol{E}$ in the fluid (Eringen and Maugin, 1989; Lyklema, 1993). Thus, assuming the fluid incompressible and Newtonian and neglecting gravity, the creeping viscous flow of the electrolyte solution is governed by the modified Stokes problem

$$\mu_{\mathrm{f}}\Delta\mathbf{v} - \nabla p = -q\boldsymbol{E} = q\nabla\Phi, \tag{2.3}$$

$$\nabla\cdot\mathbf{v} = 0, \quad \text{in } \Omega_{\mathrm{f}}, \tag{2.4}$$

where μ_{f}, $\mathbf{v}$ and p are the viscosity, velocity and thermodynamic pressure of the liquid. The above momentum balance can also be rephrased in terms of the Cauchy stress tensor of the electrolyte solution $\boldsymbol{\sigma}_{\mathrm{f}}$ as

$$\begin{aligned} &\nabla\cdot\boldsymbol{\sigma}_{\mathrm{f}} = 0, \quad \text{in} \quad \Omega_{\mathrm{f}}, \\ &\boldsymbol{\sigma}_{\mathrm{f}} = -p\boldsymbol{I} + 2\mu_{\mathrm{f}}\boldsymbol{\mathcal{E}}(\mathbf{v}) + \boldsymbol{\tau}_{\mathbf{M}}, \end{aligned} \tag{2.5}$$

where $\boldsymbol{I}$ is the unit tensor, $\boldsymbol{\mathcal{E}}(\mathbf{v})$ the symmetrical part of $\nabla\mathbf{v}$ and $\boldsymbol{\tau}_{\mathbf{M}}$ the Maxwell stress tensor (Landau and Lifchitz, 1960)

$$\boldsymbol{\tau}_{\mathbf{M}} \equiv \frac{\tilde{\varepsilon}\tilde{\varepsilon}_0}{2}(2\boldsymbol{E}\otimes\boldsymbol{E} - E^2\boldsymbol{I}) \tag{2.6}$$

with $\otimes$ denoting the tensorial product between vectors. From (2.1) and (2.6) one may easily note that $\nabla\cdot\boldsymbol{\tau}_{\mathbf{M}} = q\boldsymbol{E}$.

2.3. MOVEMENT OF THE IONS

Denoting t the characteristic time associated to the movement of the ionic species and $\boldsymbol{J}_+$ and $\boldsymbol{J}_-$ their molar fluxes, the mass conservations of cations and anions read

$$\frac{\partial c_\pm}{\partial t} + \nabla\cdot\boldsymbol{J}_\pm = 0, \quad \text{in } \Omega_{\mathrm{f}}. \tag{2.7}$$

The notation ± aims at representing the two mass balances in a single set. The constitutive relations for $\boldsymbol{J}_\pm$ reflect their convective–diffusive nature and are represented by the Nernst–Planck relations (Lyklema, 1993; Samson *et al.*, 1999). Denoting μ_+ and μ_- the molar electrochemical potentials of cations and anions, under the dilute solution approximation, where the activity coefficients of the ions are equal to the unity, they are given as (see e.g., Callen, 1985; Lyklema 1993; Dormieux *et al.*, 1995)

$$\mu_\pm \equiv \bar{\mu}_\pm \pm \boldsymbol{F}\Phi + RT \, \log c_\pm, \tag{2.8}$$

where T is the absolute temperature, R the universal ideal gas constant and $\bar{\mu}_\pm$ is the reference value for the chemical potential depending on T and p. Assuming that the temperature is constant and neglecting the effect of pressure on the magnitude of $\mu_\pm$, the reference quantities $\bar{\mu}_\pm$ are treated as constants. Denoting $\mathcal{D}_\pm$ the binary water–ions diffusion coefficients and $\bar{\Phi} = F\Phi/RT$ the dimensionless electric potential, the Nernst–Planck equations read

$$J_\pm = c_\pm \mathbf{v} - \frac{D_\pm c_\pm}{RT} \nabla \mu_\pm = c_\pm \mathbf{v} - \mathcal{D}_\pm (\nabla c_\pm \pm c_\pm \nabla \bar{\Phi}). \tag{2.9}$$

In addition to the advection component induced by the fluid velocity, the last two terms in the r.h.s. show ion diffusion governed by the sum of Fickian and electromigration components which govern the movement of the ions under concentration and electric potential gradients respectively. Using (2.9) in (2.7) we obtain the modified convection–diffusion equations governing ion transport

$$\frac{\partial c_\pm}{\partial t} + \nabla \cdot (c_\pm \mathbf{v}) = \nabla \cdot \left[\mathcal{D}_\pm (\nabla c_\pm \pm c_\pm \nabla \bar{\Phi})\right]. \tag{2.10}$$

2.4. DEFORMATION OF SOLID PARTICLES

Assume that the clay particles are linear elastic and isotropic with Lamé constants λ_s and μ_s. Denoting $\mathbf{u}$ and $\boldsymbol{\sigma}_s$ the displacement and stress tensor of the solid, the classical elasticity problem reads

$$\nabla \cdot \boldsymbol{\sigma}_s = 0, \quad \text{in } \Omega_s, \tag{2.11}$$

$$\boldsymbol{\sigma}_s = \lambda_s \nabla \cdot \mathbf{u} \boldsymbol{I} + 2\mu_s \boldsymbol{\mathcal{E}}(\mathbf{u}). \tag{2.12}$$

2.5. CHARGE CONSERVATION IN THE SOLID PHASE

To close the set of microscopic equations it remains to write mass conservations for the fixed charges in the solid–fluid interface Γ. To avoid the complexities associated with surface-averaging interfacial balance equations (Gray and Hassanizadeh, 1989; Ochoa-Tapia *et al.*, 1993), we assume that the electrical charges in the solid phase are volumetrically distributed within a small layer in the vicinity of Γ. Charge transport in the solid occurs solely due to the advection induced by the velocity $\partial \mathbf{u}/\partial t$. Whence, denoting the concentrations and fluxes in the solid phase by the superscript 's' we have

$$\frac{\partial c^{\mathrm{s}}_{\pm}}{\partial t} + \nabla \cdot \boldsymbol{J}^{\mathrm{s}}_{\pm} = 0 \quad \text{with} \quad \boldsymbol{J}^{\mathrm{s}}_{\pm} = c^{\mathrm{s}}_{\pm} \frac{\partial \mathbf{u}}{\partial t} \quad \text{in } \Omega_{\mathrm{s}}. \tag{2.13}$$

2.6. BOUNDARY CONDITIONS

Denote $\boldsymbol{n}$ the unit normal exterior to Ω_{f} and let $\sigma < 0$ be the fixed surface charge of the solid particles. Considering Γ an impervious solid–fluid interface, together with the no-slip condition, continuity of the normal component of the stress tensor and the relation between the electric field and surface charge density we have the boundary conditions

$$\begin{aligned} &\mathcal{D}_{\pm}\left(\nabla c_{\pm} \pm c_{\pm} \nabla \bar{\Phi}\right) \cdot \boldsymbol{n} = 0, \quad \mathbf{v} = \frac{\partial \mathbf{u}}{\partial t} \quad \text{on } \Gamma, \\ &\boldsymbol{\sigma}_{\mathrm{s}} \boldsymbol{n} = \boldsymbol{\sigma}_{\mathrm{f}} \boldsymbol{n}, \quad \tilde{\varepsilon}\tilde{\varepsilon}_0 \boldsymbol{E} \cdot \boldsymbol{n} = -\sigma, \end{aligned} \tag{2.14}$$

where σ and q are related through the overall electroneutrality condition

$$\int_{\Omega_{\mathrm{f}}} q \,\mathrm{d}\Omega_{\mathrm{f}} = \tilde{\varepsilon}\tilde{\varepsilon}_0 \int_{\Omega_{\mathrm{f}}} \nabla \cdot \boldsymbol{E} \,\mathrm{d}\Omega_{\mathrm{f}} = \tilde{\varepsilon}\tilde{\varepsilon}_0 \int_{\Gamma} \boldsymbol{E} \cdot \boldsymbol{n} \,\mathrm{d}\Gamma = -\int_{\Gamma} \sigma \,\mathrm{d}\Gamma. \tag{2.15}$$

The microscopic model consists in solving (2.2)–(2.4), (2.10) for the unknowns $\{\Phi, \mathbf{v}, p, c_{\pm}\}$ in Ω_{f} coupled with (2.11)–(2.13) for $\{\mathbf{u}, \boldsymbol{\sigma}, c^{\mathrm{s}}_{\pm}\}$ in Ω_{s} along with boundary conditions (2.14) on Γ and initial conditions. Finally, using (2.5) in (2.14)(c) one may note that swelling at the microscale is incorporated in the traction boundary condition for the stress tensor through the chemico and electro components in the fluid stress $\boldsymbol{\sigma}_{\mathrm{f}}$. The former is included in the thermodynamic pressure p, which incorporates the Donnan osmotic pressure (see Section 4.1), whereas the latter is lumped in the Maxwell stress tensor $\boldsymbol{\tau}_{\mathbf{M}}$.

3. Alternative Microscale Bulk Formulation

As pointed out by Moyne and Murad (2002, 2003) the above microscopic model is not formulated in a natural manner for application of a macroscopization procedure. To illustrate this conjecture we simply recall the classical e.d.l. properties when the electrolyte solution is at thermodynamic equilibrium with an outer bulk fluid (Newman, 1973; Van Olphen, 1977; Hunter, 1994). In this simple micromechanical picture, for a given bulk concentration of the non-ionic species in the outer fluid c_b, the ion concentrations ($c_\pm$) vary strongly across the micro-pore space according to Boltzmann distributions resulting from the equality between the electrochemical potentials (Dormieux *et al.*, 1995). In addition, the thermodynamic pressure (p) is the sum of the pressure of the bulk fluid (p_b) and the Donnan osmotic pressure (π), which for dilute solutions is classically defined in terms of the Van't Hoff relation (Huyghe, 1997). Further, under flow conditions, the total electric potential (Φ) incorporates a component purely associated with the e.d.l. (φ) and the so-called streaming potential (ψ_b), which is a non-equilibrium quantity that develops in the bulk fluid in order to fulfill the condition of zero electric current under the open-circuit assumption (Yang and Li, 1998). Hence, $c_\pm, p$ and Φ are discontinuous across the interface with an outer saline bath and therefore such variables do not play the role of primary unknowns controlled through interface conditions. This suggests a change of primary variables by replacing $\{\Phi, p, c_\pm\}$ by their corresponding 'bulk' counterparts $\{\psi_\mathrm{b}, p_\mathrm{b}, c_\mathrm{b}\}$, to whom boundary conditions can naturally be enforced. It should be noted that for thin double layers the bulk properties are nothing but the properties away from the particle surface. Conversely, when the e.d.l.s span the entire micropores, bulk properties become 'hidden' or 'fictitious' quantities (see Moyne and Murad, 2002) and their pointwise characterization requires the more elaborate analysis developed next.

In the notation that follows, a bulk variable is denoted by the subscript 'b' to distinguish from the corresponding quantity inherent to the electrolyte solution. In order to define pointwisely local bulk properties to the domain Ω_f occupied by the electrolyte solution, we follow Newman (1973) who characterizes a bulk medium by the absence of a net charge density ($q_\mathrm{b} \equiv F(c_{\mathrm{b}+} - c_{\mathrm{b}-}) = 0$) or by the equality in concentrations ($c_{\mathrm{b}+} = c_{\mathrm{b}-}) = c_\mathrm{b}$). This characterization is equivalent to fulfilling the electroneutrality condition (2.15) pointwisely rather than globally. We then adapt Newman's conjecture to our microscopic picture by defining a fictitious bulk solution in Ω_f as a medium satisfying the electroneutrality condition locally with suspended species at local thermodynamical equilibrium with cations and anions. As addressed before, rather than treated as a neutral fluid, the enforcement of the electroneutrality condition pointwisely under the open-circuit condition is tied up to the appearance in the bulk medium of the streaming potential component of Φ (Sasidhar and Ruckenstein, 1981, 1982; Bike and Prieve, 1992; Yang and Li, 1998). Thus, to define mathematically thermodynamic porperties associated with fictitious bulk solution we begin by making use of the decomposition proposed in Sasidhar and Ruckenstein (1981, 1982) and Bike and Prieve (1992) which splits the contributions to the electric potentital Φ purely arising from the e.d.l. and those induced by non-equilibrium fluid flow giving rise to the streaming potential. Therefore, we begin by decomposing Φ in the form:

$$\Phi = \varphi + \psi_{\mathrm{b}}. \tag{3.1}$$

As mentioned before, to characterize φ and ψ_{b}, the former aims at representing a potential which varies across the pore domain, purely related to double layer effects, whereas the latter component is selected to play a similar role of the streaming potential under the open-circuit assumption. We then define the electrochemical potential of the species in the bulk fluid ($\mu_{\mathrm{b}\pm}$) by setting $c_{\mathrm{b}+} = c_{\mathrm{b}-} = c_{\mathrm{b}}$ and $\Phi = \psi_{\mathrm{b}}$ in definition (2.8) for $\mu_\pm$ which leads to $\mu_{\mathrm{b}\pm} \equiv \bar{\mu}_\pm \pm F\psi_{\mathrm{b}} + RT \log c_{\mathrm{b}}$. This local characterization is based on neglecting the e.d.l. potential φ and the net charge density q_{b} in a bulk fluid (recall that $c_{\mathrm{b}+} = c_{\mathrm{b}-}$). Further, the condition of thermodynamical equilibrium between the species in the electrolyte solution and in the apparent bulk fluid is governed by the equality between the chemical potentials $\mu_{\mathrm{b}\pm} \equiv \mu_\pm$. Introducing the dimensionless potentials $\bar{\varphi} \equiv F\varphi/RT$ and $\bar{\psi}_{\mathrm{b}} \equiv F\psi_{\mathrm{b}}/RT$ and using (2.8) this yields

$$\mu_{\mathrm{b}\pm} \equiv \bar{\mu}_\pm \pm F\psi_{\mathrm{b}} + RT \log c_{\mathrm{b}} = \mu_\pm = \bar{\mu}_\pm \pm F\Phi + RT \log c_\pm$$

in which when combined with (3.1) leads to the following generalized Boltzmann distributions:

$$c_\pm = c_{\mathrm{b}} \exp(\mp\bar{\Phi} \pm \bar{\psi}_{\mathrm{b}}) = c_{\mathrm{b}} \exp(\mp\bar{\varphi}), \tag{3.2}$$

$$q = F(c_+ - c_-) = -2Fc_{\mathrm{b}} \sinh \bar{\varphi}. \tag{3.3}$$

Thus, given $c_\pm$ and $\bar{\varphi}$ one may envisage (3.2) as a local characterization of c_{b}. Using (3.1) and (3.3) in (2.2) results in the following alternative form of the Poisson problem:

$$\Delta(\bar{\varphi} + \bar{\psi}_{\mathrm{b}}) = -\frac{Fq}{RT\tilde{\varepsilon}\tilde{\varepsilon}_0} = \frac{2F^2 c_{\mathrm{b}}}{RT\tilde{\varepsilon}\tilde{\varepsilon}_0} \sinh \bar{\varphi}, \tag{3.4}$$

$$\boldsymbol{E} = -\frac{RT}{F}(\nabla\bar{\varphi} + \bar{\psi}_{\mathrm{b}}). \tag{3.5}$$

It should be noted that in the particular case of absence of fluid flow and ion transport, when the electrolyte solution is at equilibrium which an outer saline bath of concentration c_{eq}, the classical Poisson–Boltzmann equation is recovered from our results by simply setting $\bar{\psi}_{\mathrm{b}}$ = constant, $\bar{\Phi} = \bar{\varphi}$ and $c_{\mathrm{b}} = c_{\mathrm{eq}}$.

We now rephrase the convection–diffusion equations in terms of the unknowns c_{b} and $\bar{\psi}_{\mathrm{b}}$ associated with the apparent bulk fluid. Using (3.2) and (3.1) in (2.10) we have

$$\frac{\partial}{\partial t}(\exp(\mp\bar{\varphi})c_{\mathrm{b}}) + \nabla\cdot(\exp(\mp\bar{\varphi})c_{\mathrm{b}}\mathbf{v}) = \nabla\cdot[\mathcal{D}_\pm \exp(\mp\bar{\varphi})(\nabla c_{\mathrm{b}} \pm c_{\mathrm{b}}\nabla\bar{\psi}_{\mathrm{b}})]. \tag{3.6}$$

It should be noted that the replacement of the unknowns $\{c_+, c_-\}$ by $\{c_\text{b}, \bar{\psi}_\text{b}\}$ results in the appearance of the additional ion-exchange capacity terms $(\exp(\mp\bar{\varphi}))$ in the convection–diffusion equations. Such coefficient is much larger for the counterions owing to their higher storage capacity in the e.d.l. (recall that $\bar{\varphi} < 0$).

We now proceed by characterizing the local bulk fluid pressure p_b. To this end we adopt an entirely analogous procedure to the one used to define c_b. Likewise $c_\pm$ and $\bar{\Phi}$, at equilibrium, the thermodynamic pressure p varies across the fluid domain as it incorporates the contributions of the bulk phase pressure of the outer solution p_b and the Donnan osmotic pressure π, which for dilute solutions is classically defined in terms of the Van't Hoff relation $\pi = RT(c_+ + c_- - 2c_\text{b})$ (Donnan, 1924; Huyghe and Janssen, 1997). Thus, a decomposition similar to (3.1) can be adopted for p and interpreted as a pointwise characterization for p_b in Ω_f. We then consider the case of thermodynamic equilibrium where $\mathbf{v} = 0$ and $\psi_\text{b} =$ cte. Using (3.1) we rewrite (2.3) as $\nabla p = -q\nabla\Phi = -q\nabla(\varphi + \psi_\text{b}) = -q\nabla\varphi = -\nabla(\int_0^\varphi q(\varphi)\mathrm{d}\varphi)$. This suggests that the body force in the r.h.s. plays the role of an osmotic pressure which raises the magnitude of p compared to its bulk phase value p_b. Hence, we define the local apparent bulk phase pressure as $p_\text{b} \equiv p + \int_0^\varphi q\,\mathrm{d}\varphi$. We then show that the above definition is equivalent to subtracting the osmotic pressure π from p. In fact, using (3.2) and (3.3) in the above definition gives

$$\begin{aligned} p_\text{b} &\equiv p + \int_0^\varphi q\,\mathrm{d}\varphi = p - 2Fc_\text{b}\int_0^\varphi \sinh\bar{\varphi}\;\mathrm{d}\varphi \\ &= p - 2RTc_\text{b}(\cosh\bar{\varphi} - 1) = p - RT(c_+ + c_- - 2c_\text{b}) = p - \pi, \end{aligned} \tag{3.7}$$

which shows the desired result. Thus, likewise the bulk concentration c_b, the reference unknown p_b plays the role of the pressure of a bulk fluid constructed locally at equilibrium with the electrolyte solution (this pressure has been also termed solvent pressure by Sasidhar and Ruckenstein, 1982). Further using (3.7) in (2.5) the Cauchy stress tensor of the fluid is given by

$$\boldsymbol{\sigma}_\text{f} = -(p_\text{b} + 2RTc_\text{b}(\cosh\;\bar{\varphi} - 1))\boldsymbol{I} + \boldsymbol{\tau}_\text{M} + 2\mu_\text{f}\boldsymbol{\mathcal{E}}(\mathbf{v}).$$

Finally, using (3.1), (3.3) and (3.7), in terms of the driving forces $\{\nabla p_\text{b}, \nabla c_\text{b}, \nabla\bar{\psi}_\text{b}\}$ reflecting the hydraulic, chemico-osmotic and electro-osmotic components of the flow, the modified Stokes problem (2.3) can be rewritten as

$$\begin{aligned} &\mu_\text{f}\Delta\mathbf{v} - \nabla p_\text{b} - 2RT(\cosh\bar{\varphi} - 1)\nabla c_\text{b} \\ &\quad = 2RTc_\text{b}\sinh\bar{\varphi}\nabla\bar{\varphi} + \frac{qRT}{F}\nabla(\bar{\varphi} + \bar{\psi}_\text{b}) \\ &\quad = 2RTc_\text{b}\sinh\bar{\varphi}\nabla\bar{\varphi} - 2RTc_\text{b}\sinh\bar{\varphi}\nabla(\bar{\varphi} + \bar{\psi}_\text{b}) \\ &\quad = -2RTc_\text{b}\sinh\bar{\varphi}\nabla\bar{\psi}_\text{b}. \end{aligned} \tag{3.8}$$

Note that, in a similar fashion to (3.6), when rephrasing the Stokes problem in terms of bulk quantities, additional coefficients containing the e.d.l. potential $\bar{\varphi}$ appear incorporating the interaction between the chemico-osmotic and electro-osmotic components of the flow and the charge cloud.

Finally, denoting δ^{ij} the Kronecker delta symbol and $\mathbf{c}_{\rm s}$ the fourth-order elastic modulus tensor of the solid phase with components $c^{ijkl}=\lambda_{\rm s}\delta^{ij}\delta^{kl}+\mu_{\rm s}(\delta^{ik}\delta^{jl}+\delta^{il}\delta^{jk})$, by rephrasing the boundary conditions in (2.14) in terms of bulk variables gives

$$\begin{aligned}
&\mathcal{D}_{\pm}\exp(\mp\bar{\varphi})(\nabla c_{\rm b}\pm c_{\rm b}\nabla\bar{\psi}_{\rm b})\cdot\boldsymbol{n}=0, \quad \nabla(\bar{\varphi}+\bar{\psi}_{\rm b})\cdot\boldsymbol{n}=\frac{\sigma F}{\tilde{\varepsilon}\tilde{\varepsilon}_0 RT}, \quad \text{on } \Gamma,\\
&[-(p_{\rm b}+2RTc_{\rm b}(\cosh\bar{\varphi}-1))\boldsymbol{I}+\boldsymbol{\tau}_{\rm M}+2\mu_{\rm f}\boldsymbol{\mathcal{E}}(\mathbf{v})]\boldsymbol{n}=\boldsymbol{c}_{\rm s}\boldsymbol{\mathcal{E}}(\mathbf{u})\boldsymbol{n},
\end{aligned}$$

where (3.5) has been used. Our alternative microscopic bulk formulation is now well posed. In $\Omega_{\rm f}$ it consists of solving Equations (2.4), (3.4), (3.6) (for + and −) and (3.8) for the unknowns $\{\mathbf{v}, p_{\rm b}, \bar{\varphi}, \bar{\psi}_{\rm b}, c_{\rm b}\}$. After solving for these quantities, the 'true' variables of the electrolyte solution $\{\Phi, c_{+}, c_{-}, p\}$ can be computed within a post-processing using (3.1), (3.2) and (3.7).

4. Homogenization

In this section we make use of the homogenization technique to derive effective equations governing macroscopic coupled electro-chemo-mechanical phenomena. Following the usual procedure described in, e.g., Sanchez–Palencia (1980), two characteristic length scales are introduced; a microscopic scale associated with the dimensions of the cell (l) and a macroscopic length scale (L) characteristic of the dimensions of the clay aggregates. A perturbation parameter ϵ is defined by the ratio ℓ/L. By invoking the scale separation assumption, ℓ is considered small compared to L so that $\epsilon\ll 1$. The ϵ-model consists of properly scaled equations posed in the macroscopic domain Ω^{ϵ}, considered the union of nonoverlapping disjoint fluid and solid subdomains $\Omega^{\epsilon}_{\rm f}$ and $\Omega^{\epsilon}_{\rm s}$, along with scaled boundary conditions on the common interface Γ^{ϵ}. The fluid and solid subdomains are given by the union of adjacent cell domains $Y^{\epsilon}_{\rm f}$ and $Y^{\epsilon}_{\rm s}$, respectively, whereas the interface Γ^{ϵ} is given by the union of solid–fluid boundaries within each cell $\partial Y^{e}_{\rm fs}$. Each Y^{ϵ} is congruent to a standard unitary closed set Y which characterizes the period of the microstructure. Within this reference unit cell, $Y_{\rm s}$ and $Y_{\rm f}$ designate the disjoint open sets occupied by the clay particles and electrolyte respectively whereas the common boundary is denoted by $\partial Y_{\rm fs}$. Our starting point, $\epsilon=1$, corresponds to our microscopic model. The basic problem is to investigate the asymptotics of the solution as $\epsilon\to 0$ and obtain the homogenized limit as the scale of the inhomogeneity decays.

In our subsequent analysis we also make use of the classical spatial and time averaging theorems (Whitaker, 1999; Slattery, 1999). Designate $\langle\cdot\rangle_\epsilon \equiv |Y^\epsilon|^{-1}\int_{Y^\epsilon_\alpha}\cdot\,\mathrm{d}Y_\alpha(\alpha=\mathrm{f},\mathrm{s})$ the volume average operator over the α-portion of the cell Y^ϵ. Further, denote f^ϵ and $\boldsymbol{g}^\epsilon$ general scalar and vectorial functions defined in Y^ϵ_{f} and let the interfacial velocity be given by $\partial\mathbf{u}^\epsilon/\partial t$. Using the no-slip condition (2.14)(b) we have

$$\begin{aligned}\left\langle\frac{\partial f^\epsilon}{\partial t}\right\rangle_\epsilon &= \frac{\partial\langle f^\epsilon\rangle_\epsilon}{\partial t} - \frac{1}{|Y^\epsilon|}\int_{\partial Y^\epsilon_{\mathrm{fs}}} f^\epsilon\frac{\partial\mathbf{u}^\epsilon}{\partial t}\cdot\boldsymbol{n}\ \mathrm{d}\Gamma = \frac{\partial\langle f^\epsilon\rangle_\epsilon}{\partial t} - \frac{1}{|Y^\epsilon|}\int_{\partial Y^\epsilon_{\mathrm{fs}}} f^\epsilon\mathbf{v}^\epsilon\cdot\boldsymbol{n}\ \mathrm{d}\Gamma,\\ \langle\boldsymbol{\nabla}\cdot\boldsymbol{g}^\epsilon\rangle_\epsilon &= \boldsymbol{\nabla}\cdot\langle\boldsymbol{g}^\epsilon\rangle_\epsilon + \frac{1}{|Y^\epsilon|}\int_{\partial Y^\epsilon_{\mathrm{fs}}}\boldsymbol{g}^\epsilon\cdot\boldsymbol{n}\ \mathrm{d}\Gamma.\end{aligned}\tag{4.1}$$

4.1. SCALING ANALYSIS OF THE MICROSCOPIC MODEL

Following the procedure proposed by Auriault (1991), begin by estimating the dimensionless quantities which characterize the local description. To this end we normalize the unknowns with respect to their reference values denoted herein by the subscript 'ref'. To estimate the order of magnitude of the dimensionless numbers involved we begin by selecting the reference characteristic length ℓ_{ref} of the order of the macroscopic medium, i.e. $\ell_{\mathrm{ref}} \equiv L$ such that the macroscopic length L is used to normalize the spatial differential operators. The microscopic length ℓ associated with the dimensions of the cell is selected as a typical length scale to which e.d.l. effects become pronounced. We then choose $\ell = 2\ell_{\mathrm{D}}^{\mathrm{ref}}$ where $\ell_{\mathrm{D}}^{\mathrm{ref}} \equiv (\tilde{\varepsilon}\tilde{\varepsilon}_0 RT/2F^2 c_{\mathrm{ref}})^{1/2}$ is the Debye's length (Van Olphen, 1977; Hunter, 1981). In parallel particle arrangements, typical of classical e.d.l. theory, $\ell_{\mathrm{D}}^{\mathrm{ref}}$ is commonly interpreted as half of the particle distance where swelling due to the overlapping between the e.d.l.s becomes meaningful. Further, the time scale is normalized with respect to $t_{\mathrm{ref}} = L^2/\mathcal{D}_\pm$.

Dividing each variable by the corresponding reference value defines a dimensionless quantity which is denoted by the superscript * (e.g. $\_p^* \equiv p/p_{\mathrm{ref}}$). Denoting Φ_{ref} the reference value for φ and ψ_{b} also define $\bar{\Phi}_{\mathrm{ref}} \equiv F\Phi_{\mathrm{ref}}/RT$. By rephrasing the governing equations in the fluid domain along with the boundary conditions in terms of dimensionless unknowns we obtain

$$\begin{aligned}&\Delta_{**}(\varphi^* + \psi_{\mathrm{b}}^*) = \frac{c_{\mathrm{b}}^*}{N_{\mathrm{L}}}\sinh(\bar{\Phi}_{\mathrm{ref}}\varphi^*), \qquad E^* = -E_{\mathrm{L}}\boldsymbol{\nabla}_*(\varphi^* + \psi_{\mathrm{b}}^*), \quad \text{in } \Omega_{\mathrm{f}},\\ &Q_{\mathrm{L}}^{-1}\Delta_{**}\mathbf{v}^* = \boldsymbol{\nabla}_* p_{\mathrm{b}}^* + M_1\left[\left(\cosh\left(\bar{\Phi}_{\mathrm{ref}}\varphi^*\right) - 1\right)\boldsymbol{\nabla}_* c_{\mathrm{b}}^* - c_{\mathrm{b}}^*\sinh\left(\bar{\Phi}_{\mathrm{ref}}\varphi^*\right)\bar{\Phi}_{\mathrm{ref}}\boldsymbol{\nabla}_*\psi_{\mathrm{b}}^*\right],\\ &\frac{\partial}{\partial t^*}\left[\exp\left(\mp\bar{\Phi}_{\mathrm{ref}}\varphi^*\right)c_{\mathrm{b}}^*\right] + Pe_{\mathrm{L}}\boldsymbol{\nabla}_*\cdot\left[\exp\left(\mp\bar{\Phi}_{\mathrm{ref}}\varphi^*\right)c_{\mathrm{b}}^*\mathbf{v}^*\right]\\ &\quad = \boldsymbol{\nabla}_*\cdot\left[\exp\left(\mp\bar{\Phi}_{\mathrm{ref}}\varphi^*\right)\left(\nabla_* c_{\mathrm{b}}^* \pm c_{\mathrm{b}}^*\boldsymbol{\nabla}_*\left(\bar{\Phi}_{\mathrm{ref}}\psi_{\mathrm{b}}^*\right)\right)\right]\end{aligned}$$

and

$$B_{\mathrm{L}}\nabla_*(\varphi^*+\psi_{\mathrm{b}}^*)\cdot\boldsymbol{n}=1,\quad \mathbf{v}^*=U_{\mathrm{L}}\frac{\partial\mathbf{u}^*}{\partial t},\quad \left(\nabla_*c_{\mathrm{b}}^*\pm c_{\mathrm{b}}^*\bar{\Phi}_{\mathrm{ref}}\nabla_*\psi_{\mathrm{b}}^*\right)\cdot\boldsymbol{n}=0,$$
$$-\left\{\left[p_{\mathrm{b}}^*+M_1\left(\cosh\left(\bar{\Phi}_{\mathrm{ref}}\varphi^*\right)-1\right)\right]\boldsymbol{I}+0.5M_2\boldsymbol{\tau}_{\mathbf{M}}^*+2Q_L^{-1}\boldsymbol{\mathcal{E}}_*(\mathbf{v}^*)\right\}\boldsymbol{n}=\boldsymbol{M}_3\boldsymbol{\mathcal{E}}_*(\mathbf{u}^*)\boldsymbol{n},\ \text{ on } \Gamma,$$

where the superscript * denotes spatial derivative with respect to a dimensionless coordinate ($z^*=z/L$). Further, denoting $C_{\mathrm{ref}}^E=\tilde{\varepsilon}\tilde{\varepsilon}_0E_{\mathrm{ref}}^2$ the reference value for the Maxwell stress tensor, the above dimensionless quantities are defined as

$$N_{\mathrm{L}}=\bar{\Phi}_{\mathrm{ref}}\left(\frac{\ell_{\mathrm{D}}^{\mathrm{ref}}}{L}\right)^2,\qquad E_{\mathrm{L}}=\frac{\Phi_{\mathrm{ref}}}{E_{\mathrm{ref}}L},\qquad Q_{\mathrm{L}}=\frac{p_{\mathrm{ref}}L}{\mu_{\mathrm{f}}v_{\mathrm{ref}}},\qquad M_1=\frac{2RTc_{\mathrm{ref}}}{p_{\mathrm{ref}}},$$
$$Pe_{\mathrm{L}}=\frac{v_{\mathrm{ref}}L}{\mathcal{D}_\pm},\quad B_{\mathrm{L}}=\frac{\tilde{\varepsilon}\tilde{\varepsilon}_0\Phi_{\mathrm{ref}}}{L\sigma},\quad U_{\mathrm{L}}=\frac{u_{\mathrm{ref}}D_\pm}{v_{\mathrm{ref}}L^2},\quad M_2=\frac{C_{\mathrm{ref}}^E}{p_{\mathrm{ref}}},\quad M_3=\frac{\boldsymbol{c}_su_{\mathrm{ref}}}{p_{\mathrm{ref}}L}.$$

To establish the order of magnitude of the above numbers in powers of ϵ we begin by estimating the classical number Q_{L} which quantifies the ratio between a macroscopic pressure gradient and viscous forces in the Stokes problem (Auriault, 1990). To this end we choose the order of magnitude of the reference velocity v_{ref} and pressure p_{ref} based on classical dimensional analysis of Darcy's law which shows $v_{\mathrm{ref}}=\ell^2p_{\mathrm{ref}}/\mu_{\mathrm{f}}L$ (Auriault, 1991). This yields $Q_{\mathrm{L}}=\mathcal{O}(\epsilon^{-2})$. The parameter Pe_{L} is the classical macroscopic Péclet number which measures the ratio between convective and diffusive effects. Here, unlike Moyne and Murad (2002), we consider the case where macroscopic convective and diffusive effects are of the same order of magnitude such that $Pe_{\mathrm{L}}=\mathcal{O}(1)$. The choice of the reference electric field E_{ref} is based on boundary condition (2.14)(d) which suggests $E_{\mathrm{ref}}\equiv\sigma/\tilde{\varepsilon}\tilde{\varepsilon}_0$ and implies $B_{\mathrm{L}}=E_{\mathrm{L}}$. As the characteristic length for electrical effects to become pronnounced is the Debye's length, we entail the reference values for the electric potential and electric field in the form $\Phi_{\mathrm{ref}}=\ell_{\mathrm{D}}^{\mathrm{ref}}E_{\mathrm{ref}}$. This yields $B_{\mathrm{L}}=E_{\mathrm{L}}=\ell_{\mathrm{D}}^{\mathrm{ref}}/L=\mathcal{O}(\epsilon)$, $\Phi_{\mathrm{ref}}=\ell_{\mathrm{D}}^{\mathrm{ref}}\sigma/(\tilde{\varepsilon}\tilde{\varepsilon}_0)$ and $\bar{\Phi}_{\mathrm{ref}}=F\ell_{\mathrm{D}}^{\mathrm{ref}}\sigma/(\tilde{\varepsilon}\tilde{\varepsilon}_0RT)$. To fulfill the electroneutrality condition (2.15) ion concentrations vary over a distance of $\mathcal{O}(\ell_{\mathrm{D}}^{\mathrm{ref}})$ from the particle surface to counterbalance the surface charge σ. Whence we choose the reference concentration $c_{\mathrm{ref}}=\sigma/2F\ell_{\mathrm{D}}^{\mathrm{ref}}$ (the factor 1/2 is simply a convenience) which yields $\bar{\Phi}_{\mathrm{ref}}=2F^2c_{\mathrm{ref}}\ell_{\mathrm{D}}^{\mathrm{ref}^2}/(\tilde{\varepsilon}\tilde{\varepsilon}_0RT)$. Recalling the definition $(\ell_{\mathrm{D}}^{\mathrm{ref}})^2=\tilde{\varepsilon}\tilde{\varepsilon}_0RT/2F^2c_{\mathrm{ref}}$, we then obtain $\bar{\Phi}_{\mathrm{ref}}=1$, $\Phi_{\mathrm{ref}}=RT/F$, $E_{\mathrm{ref}}=RT/(F\ell_{\mathrm{D}}^{\mathrm{ref}})$ and $N_{\mathrm{L}}=(\ell_{\mathrm{D}}^{\mathrm{ref}}/L)^2=\mathcal{O}(\epsilon^2)$. The reference pressure p_{ref} is selected of the same order of the osmotic pressure, $p_{\mathrm{ref}}=2RTc_{\mathrm{ref}}$, so that $M_1=1$ and $M_2=\tilde{\varepsilon}\tilde{\varepsilon}_0E_{\mathrm{ref}}^2/2RTc_{\mathrm{ref}}=F\ell_{\mathrm{D}}^{\mathrm{ref}}E_{\mathrm{ref}}/RT=F\Phi_{\mathrm{ref}}/RT=\bar{\Phi}_{\mathrm{ref}}=1$. Denoting c^{ijkl} the components of the fourth-order elastic tensor $\boldsymbol{c}_{\mathrm{s}}$ and $\bar{c}=\max c^{ijkl}$ we choose $u_{\mathrm{ref}}=\mathcal{O}(L)$ and $\sigma_{\mathrm{sref}}\equiv\bar{c}u_{\mathrm{ref}}/L$ of the same order of p_{ref} such that $M_3=\mathcal{O}(1)$. Finally, since $U_{\mathrm{L}}=u_{\mathrm{ref}}/(Pe_{\mathrm{L}}L)$ using the estimates for the

Péclet number we have $U_L=\mathcal{O}(1)$. To summarize, we have $M_1=M_2=1$ along with the estimates

$$
\begin{aligned}
&N_{\mathrm{L}}=\mathcal{O}(\epsilon^2), \quad E_{\mathrm{L}}=\mathcal{O}(\epsilon), \quad Q_{\mathrm{L}}=\mathcal{O}(\epsilon^{-2}), \quad Pe_{\mathrm{L}}=\mathcal{O}(1)\\
&B_{\mathrm{L}}=\mathcal{O}(\epsilon), \qquad U_{\mathrm{L}}=\mathcal{O}(1), \qquad M_3=\mathcal{O}(1).
\end{aligned}
\tag{4.2}
$$

In addition, the Hartmann number H, introduced by Sherwood (1980), is defined as

$$
H\equiv\frac{\tilde{\varepsilon}\tilde{\varepsilon}_0\Phi_{\mathrm{ref}}^2}{\mathcal{D}\pm\mu_{\mathrm{f}}}=\frac{M_1N_{\mathrm{L}}Pe_{\mathrm{L}}}{Q_{\mathrm{L}}^{-1}}=\frac{N_{\mathrm{L}}Pe_{\mathrm{L}}}{Q_{\mathrm{L}}^{-1}}=\mathcal{O}(1).
\tag{4.3}
$$

From (4.3) one may observe that H governs the ratio between the product $N_{\mathrm{L}}Pe_{\mathrm{L}}$ which quantifies the perturbation in the electrical forces acting in the liquid induced by the distortion of the charge cloud due to advection and the number Q_{L}^{-1}, which measures the intensity of the viscous forces to restore equilibrium (Sherwood, 1980). When the Hartmann number is small, as in the cases of high viscosity, small Péclet number, or low electric potentials, typical of the Debye–Hueckel approximation of Poisson–Boltzmann ($|\varphi|\leqslant 25\,\mathrm{mV}$), the ionic atmosphere around the clay particles restores instantaneously to its equilibrium configuration and the above non-equilibrium relaxation phenomena is neglected (see Sherwood, 1980 for details). As we shall illustrate in our subsequent development, the estimates Pe_{L} and H of $\mathcal{O}(1)$ adopted herein are capable of capturing the influence of the distortion of the charge cloud on the macroscopic forms of Darcy's law and modified convection–diffusion governing ion transport.

Making use of the estimates (4.2), the alternative bulk formulation of Section 3 is rephrased below with a ϵ^n factor to indicate the order of magnitude of each term. We then have in Ω_{f}

$$
\begin{aligned}
&\epsilon^2\Delta(\bar{\varphi}+\bar{\psi}_{\mathrm{b}})=\frac{2F^2c_b}{RT\tilde{\varepsilon}\tilde{\varepsilon}_0}\sinh\bar{\varphi}, \quad \boldsymbol{E}=-\frac{\epsilon RT}{F}\nabla(\bar{\varphi}+\bar{\psi}_{\mathrm{b}}), \;\; c_{\pm}=c_{\mathrm{b}}\exp(\mp\bar{\varphi}),\\
&\pi=2RTc_{\mathrm{b}}(\cosh\bar{\varphi}-1), \quad \nabla\cdot\boldsymbol{\sigma}_{\mathrm{f}}=0,\\
&\boldsymbol{\sigma}_{\mathrm{f}}=-(p_{\mathrm{b}}+\pi)\boldsymbol{I}+\frac{\tilde{\varepsilon}\tilde{\varepsilon}_0}{2}(2\boldsymbol{E}\otimes\boldsymbol{E}-E^2\boldsymbol{I})+2\epsilon^2\mu_{\mathrm{f}}\boldsymbol{\mathcal{E}}(\mathbf{v}),\\
&\nabla\cdot\mathbf{v}=0, \quad \epsilon^2\mu_{\mathrm{f}}\Delta\mathbf{v}=\nabla p_{\mathrm{b}}+2RT(\cosh\bar{\varphi}-1)\nabla c_{\mathrm{b}}-2RTc_{\mathrm{b}}\sinh\bar{\varphi}\nabla\bar{\psi}_{\mathrm{b}},\\
&\frac{\partial}{\partial t}(\exp(\mp\bar{\varphi})c_{\mathrm{b}})+\nabla\cdot(\exp(\mp\bar{\varphi})c_{\mathrm{b}}\mathbf{v})=\nabla\cdot\left[\mathcal{D}_{\pm}\exp(\mp\bar{\varphi})(\nabla c_{\mathrm{b}}\pm c_{\mathrm{b}}\nabla\bar{\psi}_{\mathrm{b}})\right]\\
&\qquad=\nabla\cdot\left[\mathcal{D}_{\pm}\exp(\mp(\bar{\varphi}+\bar{\psi}_{\mathrm{b}}))\nabla(c_{\mathrm{b}}\exp(\pm\bar{\psi}_{\mathrm{b}}))\right],
\end{aligned}
\tag{4.4}
$$

whereas in Ω_s

$$
\begin{aligned}
&\nabla\cdot\boldsymbol{\sigma}_{\mathrm{s}}=0, \quad \boldsymbol{\sigma}_{\mathrm{s}}=\boldsymbol{c}_{\mathrm{s}}\boldsymbol{\mathcal{E}}(\mathbf{u}),\\
&\frac{\partial c_{\pm}^{\mathrm{s}}}{\partial t}+\nabla\cdot\left(c_{\pm}^{\mathrm{s}}\frac{\partial\mathbf{u}}{\partial t}\right)=0.
\end{aligned}
\tag{4.5}
$$

and on the fluid–solid interface Γ

$$\frac{\epsilon RT}{F}\nabla(\bar{\varphi}+\bar{\psi}_{\mathrm{b}})\cdot\boldsymbol{n}=\frac{\sigma}{\tilde{\varepsilon}\tilde{\varepsilon}_0},\quad \mathbf{v}=\frac{\partial\mathbf{u}}{\partial t},\quad -\mathcal{D}_{\pm}\exp(\mp\bar{\varphi})(\nabla c_{\mathrm{b}}\pm c_{\mathrm{b}}\nabla\bar{\psi}_{\mathrm{b}})\cdot\boldsymbol{n}=0,$$

$$\boldsymbol{\sigma}_{\mathrm{f}}\mathbf{n}=[-(p_{\mathrm{b}}+2RTc_{\mathrm{b}}(\cosh\bar{\varphi}-1))\boldsymbol{I}+\frac{\tilde{\varepsilon}\tilde{\varepsilon}_0}{2}(2\boldsymbol{E}\otimes\boldsymbol{E}-E^2\boldsymbol{I})+2\varepsilon^2\mu_{\mathrm{f}}\boldsymbol{\mathcal{E}}(\mathbf{v})]\boldsymbol{n}=\boldsymbol{\sigma}_{\mathrm{s}}\boldsymbol{n}$$
$$=\mathbf{c}_{\mathrm{s}}\epsilon(\mathbf{u})\boldsymbol{n}.$$

Finally we also consider the scaling analysis of the averaging relations (4.1). Designating $\langle\cdot\rangle\equiv|Y|^{-1}\int_{Y_\alpha}\cdot\mathrm{d}Y_\alpha(\alpha=\mathrm{f,s})$ the volume average operator over the α-portion of the unit cell Y and recalling that the ratio between volume and area of the periodic cell scales with $\mathcal{O}(\epsilon^3)/\mathcal{O}(\epsilon^2)$, we have $|Y^\epsilon|/|\partial Y^\epsilon_{\mathrm{fs}}|$ of $\mathcal{O}(\epsilon)$ which implies

$$\left\langle\frac{\partial f}{\partial t}\right\rangle=\frac{\partial\langle f\rangle}{\partial t}-\frac{1}{\epsilon|Y|}\int_{\partial Y_{\mathrm{fs}}}f\mathbf{v}\cdot\boldsymbol{n}\ \mathrm{d}\Gamma, \tag{4.6}$$

$$\langle\nabla\cdot\boldsymbol{g}\rangle=\nabla\cdot\langle\boldsymbol{g}\rangle+\frac{1}{\epsilon|Y|}\int_{\partial Y_{\mathrm{fs}}}\boldsymbol{g}\cdot\boldsymbol{n}\ \mathrm{d}\Gamma. \tag{4.7}$$

4.2. MATCHED ASYMPTOTIC EXPANSIONS

In the formal homogenization process based on asymptotic developments we consider each point described by two coordinates. The macroscopic position vector $\boldsymbol{x}$, which describes the location in the macroscopic domain Ω, and the microscopic coordinate $\boldsymbol{y}$, of the same order of magnitude of the Debye's length (l_{D}), which locates a point in Y. Up to a translation, $\boldsymbol{x}$ and $\boldsymbol{y}$ are related by $\boldsymbol{x}=\epsilon\boldsymbol{y}$. Following the usual framework, consider each unknown depending on both coordinates in the form $f=f(\boldsymbol{x},\boldsymbol{y})$ and postulate two-scale asymptotic expansions in terms of the small parameter ϵ for the set θ^ϵ of unknowns $\{\mathbf{u},\boldsymbol{\sigma}_{\mathrm{s}},c^{\mathrm{s}}_{\pm}\}$ and $\{\bar{\Phi},\bar{\varphi},\bar{\psi}_{\mathrm{b}},\boldsymbol{E},c_{\pm},c_{\mathrm{b}},\mu_{\pm},\mu_{\mathrm{b}\pm},\pi,\boldsymbol{\sigma}_{\mathrm{f}},p_{\mathrm{b}},\mathbf{v},\boldsymbol{\tau}_{\mathbf{M}}\}$ in the form:

$$\theta^\epsilon(\boldsymbol{x},\boldsymbol{y})=\theta^0(\boldsymbol{x},\boldsymbol{y})+\epsilon\theta^2(x,y)+\epsilon^2\theta^2(x,y)+\cdots$$

with the coefficients θ^i, spatially periodic in $\mathbf{y}$ over the unit cell $Y=Y_{\mathrm{f}}\cup Y_{\mathrm{s}}$. By the chain rule the operator ∂/∂_x is replaced by $\partial/\partial_x+\epsilon^{-1}\partial/\partial_y$ with ∂_x and ∂_y denoting the gradients with respect to $\boldsymbol{x}$ and $\boldsymbol{y}$. The perturbation approach consists in inserting the ansatz in the above microscopic model and solve the initial/boundary-value problems which arise at the successive orders of ϵ. For the fluid in Y_{f} we have

$$\tilde{\varepsilon}\tilde{\varepsilon}_0\Delta_{yy}(\bar{\varphi}^0+\bar{\psi}^0_{\mathrm{b}})=\frac{2F^2c^0_{\mathrm{b}}}{RT}\sinh\bar{\varphi}^0,\quad \mathbf{E}^0=-\frac{RT}{F}\nabla_y(\bar{\varphi}^0+\bar{\psi}^0_{\mathrm{b}}),$$
$$c^0_{\pm}=c^0_{\mathrm{b}}\exp(\mp\bar{\varphi}^0), \tag{4.8}$$

$$\mu^0_\pm = \bar{\mu}_\pm + RT(\pm\bar{\psi}^0_\mathrm{b} + \log\, c^0_\mathrm{b}), \quad \mu^1_\pm = \frac{RT}{c^0_\mathrm{b}}(\pm c^0_\mathrm{b}\bar{\psi}^1_\mathrm{b} + c^1_\mathrm{b}),$$
$$\bar{\Phi}^0 = \bar{\varphi}^0 + \bar{\psi}^0_\mathrm{b}, \tag{4.9}$$

$$\nabla_y \cdot \mathbf{v}^0 = 0, \quad \nabla_x \cdot \mathbf{v}^0 + \nabla_y \cdot \mathbf{v}^1 = 0, \tag{4.10}$$

$$\nabla_y \cdot \sigma^0_\mathrm{f} = 0, \quad \nabla_x \cdot \sigma^0_\mathrm{f} + \nabla_\mathbf{y} \cdot \sigma^1_\mathrm{f} = 0, \quad \sigma^0_\mathrm{f} = -(p^0_\mathrm{b} + \pi^0)\boldsymbol{I} + \boldsymbol{\tau}^0_\mathbf{M}, \tag{4.11}$$

$$p^0 = p^0_\mathrm{b} + \pi^0, \quad \pi^0 = 2RTc^0_\mathrm{b}(\cosh\bar{\varphi}^0 - 1),$$
$$\boldsymbol{\tau}^0_\mathbf{M} = \frac{\tilde{\varepsilon}\tilde{\varepsilon}_0}{2}\left(2\boldsymbol{E}^0 \otimes \boldsymbol{E}^0 - (E^0)^2\boldsymbol{I}\right), \tag{4.12}$$

$$\nabla_y p^0_\mathrm{b} + 2RT(\cosh\bar{\varphi}^0 - 1)\nabla_y c^0_\mathrm{b} - 2RTc^0_\mathrm{b}\,\sinh\bar{\varphi}^0\nabla_y\bar{\psi}^0_\mathrm{b} = 0, \tag{4.13}$$

$$\mu_\mathrm{f}\Delta_{yy}\mathbf{v}^0 = \nabla_x p^0_\mathrm{b} + \nabla_y p^1_\mathrm{b} + 2RT(\cosh\bar{\varphi}^0 - 1)(\nabla_x c^0_\mathrm{b} + \nabla_y c^1_\mathrm{b}) -$$
$$-2RTc^0_\mathrm{b}\,\sinh\bar{\varphi}^0(\nabla_x\bar{\psi}^0_\mathrm{b} + \nabla_y\bar{\psi}^1_\mathrm{b}), \tag{4.14}$$

$$\nabla_y \cdot [\mathcal{D}_\pm \exp(\mp\bar{\varphi}^0)(\nabla_y c^0_\mathrm{b} \pm c^0_\mathrm{b}\nabla_y\bar{\psi}^0_\mathrm{b})]$$
$$= \nabla_y \cdot [\mathcal{D}_\pm \exp(\mp(\bar{\varphi}^0 + \bar{\psi}^0_\mathrm{b}))\nabla_y(c^0_\mathrm{b}\,\exp(\pm\bar{\psi}^0_\mathrm{b}))] = 0, \tag{4.15}$$

$$\nabla_y \cdot [\exp(\mp\bar{\varphi}^0)c^0_\mathrm{b}\mathbf{v}^0] = \nabla_y \cdot [\mathcal{D}_\pm \exp(\mp\bar{\varphi}^0)(\nabla_x c^0_\mathrm{b} \pm c^0_\mathrm{b}\nabla_x\bar{\psi}^0_\mathrm{b} +$$
$$+\nabla_y c^1_\mathrm{b} \pm c^0_\mathrm{b}\nabla_y\bar{\psi}^1_\mathrm{b})], \tag{4.16}$$

$$\frac{\partial}{\partial t}[c^0_\mathrm{b}\ \exp(\mp\bar{\varphi}^0)] + \nabla_x \cdot [c^0_\mathrm{b}\ \exp(\mp\bar{\varphi}^0)\mathbf{v}^0] +$$
$$+\nabla_y \cdot [\exp\ (\mp\bar{\varphi}^0)(c^1_\mathrm{b}\mathbf{v}^0 \mp c^0_\mathrm{b}\bar{\varphi}^1\mathbf{v}^0 + c^0_\mathrm{b}\mathbf{v}^1)]$$
$$= \nabla_x \cdot [\mathcal{D}_\pm \exp(\mp\bar{\varphi}^0)(\nabla_y c^1_\mathrm{b} \pm c^0_\mathrm{b}\nabla_y\bar{\psi}^1_\mathrm{b} + \nabla_x c^0_\mathrm{b} \pm c^0_\mathrm{b}\nabla_x\bar{\psi}^0_\mathrm{b})] +$$
$$+\nabla_y \cdot \{\mathcal{D}_\pm \exp(\mp\bar{\varphi}^0)[\nabla_y c^2_\mathrm{b} + \nabla_x c^1_\mathrm{b} \pm c^0_\mathrm{b}(\nabla_y\bar{\psi}^2_\mathrm{b} + \nabla_x\bar{\psi}^1_\mathrm{b}) \pm$$
$$\pm c^1_\mathrm{b}(\nabla_y\bar{\psi}^1_\mathrm{b} + \nabla_x\bar{\psi}^0_\mathrm{b}) \mp \bar{\varphi}^1(\nabla_y c^1_\mathrm{b} + \nabla_x c^0_\mathrm{b} \pm c^0_\mathrm{b}(\nabla_y\bar{\psi}^1_\mathrm{b} + \nabla_x\bar{\psi}^0_\mathrm{b}))]\}. \tag{4.17}$$

For the clay particles in Y_s we have

$$\nabla_y \cdot (\boldsymbol{c}_\mathrm{s}\boldsymbol{\mathcal{E}}_y(\mathbf{u}^0)) = 0, \quad \nabla_y \cdot [\boldsymbol{c}_\mathrm{s}(\boldsymbol{\mathcal{E}}_y(\mathbf{u}^1) + \boldsymbol{\mathcal{E}}_x(\mathbf{u}^0)] = 0, \tag{4.18}$$

$$\nabla_x \cdot \boldsymbol{\sigma}^0_\mathrm{s} + \nabla_y \cdot \boldsymbol{\sigma}^1_\mathrm{s} = 0, \quad \boldsymbol{\sigma}^0_\mathrm{s} = \boldsymbol{c}_\mathrm{s}(\boldsymbol{\mathcal{E}}_x(\mathbf{u}^0) + \boldsymbol{\mathcal{E}}_y(\mathbf{u}^1)), \tag{4.19}$$

$$\frac{\partial c^{\mathrm{s}0}_\pm}{\partial t} + \nabla_x \cdot \left(c^{\mathrm{s}0}_\pm \frac{\partial \mathbf{u}^0}{\partial t}\right) + \nabla_y \cdot \left(c^{\mathrm{s}1}_\pm \frac{\partial \mathbf{u}^0}{\partial t} + c^{\mathrm{s}0}_\pm \frac{\partial \mathbf{u}^1}{\partial t}\right) = 0 \tag{4.20}$$

and the parametrized boundary conditions on ∂Y_fs read as

$$\nabla_y(\bar{\varphi}^0+\bar{\psi}_{\mathrm{b}}^0)\cdot\boldsymbol{n}=\frac{\sigma F}{\tilde{\varepsilon}\tilde{\varepsilon}_0 RT},\quad \mathbf{v}^0=\frac{\partial\mathbf{u}^0}{\partial t},\quad \mathbf{v}^1=\frac{\partial\mathbf{u}^1}{\partial t},\tag{4.21}$$

$$\boldsymbol{c}_{\mathrm{s}}(\boldsymbol{\mathcal{E}}_y(\mathbf{u}^0))\boldsymbol{n}=0,\quad \boldsymbol{\sigma}_{\mathrm{s}}^1\boldsymbol{n}=\boldsymbol{\sigma}_{\mathrm{f}}^1\boldsymbol{n},\tag{4.22}$$

$$(-(p_{\mathrm{b}}^0+2RTc_{\mathrm{b}}^0(\cosh\bar{\varphi}^0-1))\boldsymbol{I}+\boldsymbol{\tau}_{\mathbf{M}}^0)\boldsymbol{n}=\boldsymbol{c}_{\mathrm{s}}(\boldsymbol{\mathcal{E}}_x(\mathbf{u}^0)+\boldsymbol{\mathcal{E}}_y(\mathbf{u}^1))\boldsymbol{n},\tag{4.23}$$

$$\mathcal{D}_{\pm}\exp(\mp(\bar{\varphi}^0+\bar{\psi}_{\mathrm{b}}^0))\nabla_y(c_{\mathrm{b}}^0\exp(\pm\bar{\psi}_{\mathrm{b}}^0))\cdot\boldsymbol{n}=0,\tag{4.24}$$

$$-\mathcal{D}_{\pm}\exp(\mp\bar{\varphi}^0)[\nabla_x c_{\mathrm{b}}^0\pm c_{\mathrm{b}}^0\nabla_x\bar{\psi}_{\mathrm{b}}^0+\nabla_y c_{\mathrm{b}}^1\pm c_{\mathrm{b}}^0\nabla_y\bar{\psi}_{\mathrm{b}}^1]\cdot\boldsymbol{n}=0,\tag{4.25}$$

$$\begin{aligned}&-\mathcal{D}_{\pm}\exp(\mp\bar{\varphi}^0)[\nabla_y c_{\mathrm{b}}^2+\nabla_x c_{\mathrm{b}}^1\pm c_{\mathrm{b}}^0(\nabla_y\bar{\psi}_{\mathrm{b}}^2+\nabla_x\bar{\psi}_{\mathrm{b}}^1)\pm c_{\mathrm{b}}^1(\nabla_y\bar{\psi}_{\mathrm{b}}^1+\nabla_x\bar{\psi}_{\mathrm{b}}^0)\mp\\&\mp\bar{\varphi}^1(\nabla_y c_{\mathrm{b}}^1+\nabla_x c_{\mathrm{b}}^0\pm c_{\mathrm{b}}^0(\nabla_y\bar{\psi}_{\mathrm{b}}^1+\nabla_x\bar{\psi}_{\mathrm{b}}^0))]\cdot\boldsymbol{n}=0.\end{aligned}\tag{4.26}$$

Finally considering the perturbation expansions of (4.6) and (4.7) and noting that $\nabla_y\cdot\langle\boldsymbol{g}^1\rangle=0$ we have

$$\left\langle\frac{\partial f}{\partial t}\right\rangle=\frac{\partial\langle f^0\rangle}{\partial t}-\frac{1}{|Y|}\int_{\partial Y_{\mathrm{fs}}}(\varepsilon^{-1}f^0\mathbf{v}^0+f^1\mathbf{v}^0+f^0\mathbf{v}^1)\cdot\boldsymbol{n}\;\mathrm{d}\Gamma+\mathcal{O}(\varepsilon),\tag{4.27}$$

$$\langle\nabla\cdot\boldsymbol{g}\rangle=\nabla_x\cdot\langle\boldsymbol{g}^0\rangle+\frac{1}{|Y|}\int_{\partial Y_{\mathrm{fs}}}(\varepsilon^{-1}\boldsymbol{g}^0+\boldsymbol{g}^1)\cdot\boldsymbol{n}\,\mathrm{d}\Gamma+\mathcal{O}(\varepsilon).\tag{4.28}$$

By choosing $\boldsymbol{g}=f\mathbf{v}$ so that $\boldsymbol{g}^0=f^0\mathbf{v}^0$ and $\boldsymbol{g}^1=f^1\mathbf{v}^0+f^0\mathbf{v}^1$, after adding (4.27) and (4.28) we have the expansion

$$\left\langle\frac{\partial f}{\partial t}+\nabla\cdot(f\mathbf{v})\right\rangle=\frac{\partial\langle f^0\rangle}{\partial t}+\nabla_x\cdot\langle f^0\mathbf{v}^0\rangle+\mathcal{O}(\varepsilon).\tag{4.29}$$

At $\mathcal{O}(\epsilon^0)$ Equations (4.28) and (4.29) can be written as

$$\langle\nabla_x\cdot\boldsymbol{g}^0\rangle+\langle\nabla_y\cdot\boldsymbol{g}^1\rangle=\nabla_x\cdot\langle\boldsymbol{g}^0\rangle+\frac{1}{|Y|}\int_{\partial Y_{\mathrm{fs}}}\boldsymbol{g}^1\cdot\boldsymbol{n}\,\mathrm{d}\Gamma,\tag{4.30}$$

$$\left\langle\frac{\partial f^0}{\partial t}\right\rangle+\langle\nabla_x\cdot(f^0\mathbf{v}^0)\rangle+\langle\nabla_y\cdot(f^1\mathbf{v}^0+f^0\mathbf{v}^1)\rangle=\frac{\partial\langle f^0\rangle}{\partial t}\nabla_x\cdot\langle f^0\mathbf{v}^0\rangle.\tag{4.31}$$

4.2.1. *Nonoscillatory Variables*

We begin by collecting our set of 'slow' variables which are independent of the fast coordinate $\boldsymbol{y}$. Begin by noting that variables such as $\mathbf{u}^0$ and $c_{\mathrm{b}}^0\exp(\pm\bar{\psi}_{\mathrm{b}}^0)$ satisfy the Neumann problems given by (4.18)(a) and (4.15) together with the boundary conditions (4.22)(a) and (4.24) whose solution are the rigid motions $\mathbf{u}^0(\boldsymbol{x},\boldsymbol{y},t)=\mathbf{u}^0(\boldsymbol{x},t)$ and $c_{\mathrm{b}}^0\exp(\pm\bar{\psi}_{\mathrm{b}}^0)\,(\boldsymbol{x},\boldsymbol{y},t)=c_b^0\exp(\pm\bar{\psi}_{\mathrm{b}}^0)(\boldsymbol{x},t)$. Further, taking the product of this last result for cations and anions furnish $c_{\mathrm{b}}^0(\boldsymbol{x},\boldsymbol{y},t)=c_{\mathrm{b}}^0(\boldsymbol{x},t)$ and $\bar{\psi}_{\mathrm{b}}^0(\boldsymbol{x},\boldsymbol{y},t)=\bar{\psi}_{\mathrm{b}}^0(\boldsymbol{x},t)$. Using this result in (4.9)(a) give $\mu^0_\pm(\boldsymbol{x},\boldsymbol{y},t)=\mu^0_\pm(\boldsymbol{x},t)$. Finally using these results in (4.13) also implies $\nabla_y p^0_\mathrm{b}=0$ and $p^0_\mathrm{b}(\boldsymbol{x},\boldsymbol{y},t)=p^0_\mathrm{b}(\boldsymbol{x},t)$. Therefore, our set of 'slow' variables is $\{\mathbf{u}^0, c^0_\mathrm{b}, \bar{\psi}^0_\mathrm{b}, \mu^0_\pm, p^0_\mathrm{b}\}$.

4.2.2. *Local Poisson–Boltzmann*

Since $\bar{\psi}^0_\mathrm{b}$ is independent of the fast coordinate $\boldsymbol{y}$, from(4.8)(b), we have $\boldsymbol{E}^0=-RTF^{-1}\nabla_y\bar{\varphi}^0$ and the Poisson equation (4.8)(a) along with boundary condition (4.21)(a) lead to the local Poisson–Boltzmann problem for $\bar{\varphi}^0$

$$\begin{aligned}\Delta_{yy}\bar{\varphi}^0 &= \frac{1}{(l^0_D)^2}\sinh\bar{\varphi}^0 \quad \text{in } Y_\mathrm{f},\\ \nabla_y\bar{\varphi}^0\cdot\boldsymbol{n} &= \frac{F\sigma}{RT\tilde{\varepsilon}\tilde{\varepsilon}_0} \quad \text{on } \partial Y_\mathrm{f}\end{aligned} \tag{4.32}$$

with $l^0_\mathrm{D} \equiv (\tilde{\varepsilon}\tilde{\varepsilon}_0 RT/2F^2c^0_\mathrm{b})^{1/2}$ denoting the zeroth-order Debye's length. Defining the averaged charge density $q^0_* = F\langle c^0_+ - c^0_-\rangle$, by averaging the Boltzmann distributions (4.8)(c) we obtain $q^0_*=-2Fc^0_\mathrm{b}\langle\sinh\bar{\varphi}^0\rangle$. Moreover, the local version of the electroneutrality condition (2.15) reads

$$q^0_*=-\frac{2Fc^0_\mathrm{b}}{|Y|}\int_{Y_\mathrm{f}}\sinh\bar{\varphi}^0\,\mathrm{d}Y=-\frac{1}{|Y|}\int_{\partial Y_\mathrm{fs}}\sigma\,\mathrm{d}\Gamma. \tag{4.33}$$

An important consequence of (4.32) is the extension of the Poisson–Boltzmann problem to the nonequilibrium case provided $\bar{\Phi}^0$ is replaced by the relative potential $\bar{\varphi}^0$. Thus, the spatial distribution $\bar{\psi}^0_b(\boldsymbol{x},t)$ assigns reference values for the electric potential to which the excess $\bar{\varphi}^0=\bar{\Phi}^0-\bar{\psi}^0_\mathrm{b}$ plays the role of a potential purely associated with e.d.l. effects. Whence, the influence of nonequilibrium effects upon the e.d.l. (e.g., distortion induced by convection effects (Sherwood,1980; Hinch and Sherwood, 1983)) tends to decay as $\epsilon\to 0$ and consequently, at $\mathcal{O}(\epsilon^0)$ the potential $\bar{\varphi}^0$ behaves as a classical e.d.l. potential. Another essential feature underlying (4.32) is the fact that the Poisson–Boltzmann problem does not survive at the macroscale. This arises from the scaling factor ϵ^2 in the Poisson problem (4.4)(a) which 'shrinks' the homogenized equation as $\epsilon\to 0$. Thus, $\bar{\varphi}^0$ and $\boldsymbol{E}^0$ are highly oscillatory quantities which depend strongly on $\boldsymbol{y}$. Notably this fact is consistent with the e.d.l. results at equilibrium where these quantities vary across the pore fluid domain (Newman, 1973; Van Olphen, 1977; Hunter, 1994).

If we admit that the electrical charges in the solid phase are equivalent to the surface charge σ, by defining the averaged net density in solid phase as $q^{s0}_*=F(\langle c^{s0}_+-c^{s0}_-\rangle)$ we have

$$q^{s0}_*=\frac{F}{|Y|}\int_{Y_\mathrm{s}}(c^{s0}_+-c^{s0}_-)\mathrm{d}Y=-\frac{1}{|Y|}\int_{\partial Y_\mathrm{fs}}\sigma\,\mathrm{d}\Gamma. \tag{4.34}$$

4.2.3. *Closure Relations for c_{b}^1 and $\bar{\psi}_{\mathrm{b}}^1$*

To derive the homogenized forms of the convection–diffusion equations governing ion transport and Darcy's law for the fluid, we begin by invoking the closure problems (4.16) and (4.25). Using (4.10) (a) and recalling that c_{b}^0 and $\bar{\psi}_{\mathrm{b}}^0$ are independent of $\boldsymbol{y}$ we have the local problems for $\{c_{\mathrm{b}}^1, \bar{\psi}_b^1\}$

$$\begin{aligned}
&\nabla_y \cdot \left[\mathcal{D}_\pm \exp(\mp\bar{\varphi}^0)(\nabla_x c_{\mathrm{b}}^0 \pm c_{\mathrm{b}}^0 \nabla_x \bar{\psi}_{\mathrm{b}}^0 + \nabla_y c_{\mathrm{b}}^1 \pm c_{\mathrm{b}}^0 \nabla_y \bar{\psi}_{\mathrm{b}}^1)\right] \\
&\quad = \mp c_{\mathrm{b}}^0 \exp(\mp\bar{\varphi}^0)\mathbf{v}^0 \cdot \nabla_y \bar{\varphi}^0, \quad \text{in} \quad Y_{\mathrm{f}} \qquad (4.35)\\
&-\mathcal{D}_\pm \exp(\mp\bar{\varphi}^0)[\nabla_x c_{\mathrm{b}}^0 \pm c_{\mathrm{b}}^0 \nabla_x \bar{\psi}_{\mathrm{b}}^0 + \nabla_y c_{\mathrm{b}}^1 \pm c_{\mathrm{b}}^0 \nabla_y \bar{\psi}_{\mathrm{b}}^1] \cdot \boldsymbol{n} = 0, \quad \text{on} \quad \partial Y_{\mathrm{fs}}.
\end{aligned}$$

As the solution of the above Neumann problem is given up to a rigid motion $\hat{c}^\pm(\boldsymbol{x}, t)$, to maintain the periodicity and ensure the compatibility condition, we rephrase it in a translated frame $\boldsymbol{y}'$ linked to the solid, i.e. $\boldsymbol{y}' = \boldsymbol{y} - \mathbf{u}^0(\boldsymbol{x}, t)$ so that $\nabla_y c_{\mathrm{b}}^1 = \nabla_{y'} c_{\mathrm{b}}^1$ and the r.h.s. of (4.35) is replaced by $\mp c_{\mathrm{b}}^0 \exp(\mp\bar{\varphi}^0)(\mathbf{v}^0 - \partial\mathbf{u}^0/\partial t) \cdot \nabla_y \bar{\varphi}^0 = \pm c_{\mathrm{b}}^0 \nabla_y \cdot (\exp(\mp\bar{\varphi}^0)(\mathbf{v}^0 - \partial\mathbf{u}^0/\partial t))$ (using the incompressibility condition (4.10(a)). Note that, by invoking the divergence theorem and the nonslip condition (4.21)(b) the average of this latter term vanishes and thus the compatibility condition is fulfilled. As we shall illustrate next, the above change of frame does not alter the closure problems for the effective parameters as they appear influenced by $\nabla_y c_{\mathrm{b}}^1$ rather than c_{b}^1.

By a classical superposition argument, the solution of (4.35) can be represented as

$$c_{\mathrm{b}}^1 \pm c_{\mathrm{b}}^0 \bar{\psi}_{\mathrm{b}}^1 = \chi^\pm c_{\mathrm{b}}^0 + \boldsymbol{f}^\pm \left(\nabla_x c_{\mathrm{b}}^0 \pm c_{\mathrm{b}}^0 \nabla_x \bar{\psi}_{\mathrm{b}}^0\right) + \hat{c}^\pm(\mathbf{x}, \mathbf{t}), \qquad (4.36)$$

where $\chi^\pm$ and $\boldsymbol{f}^\pm$ are auxiliary scalar and vectorial Y-periodical functions satisfying the cell problems

$$\begin{aligned}
&\nabla_y \cdot [\mathcal{D}_\pm \exp(\mp\bar{\varphi}^0)\nabla_y \chi^\pm] = \mp \exp(\mp\bar{\varphi}^0)\left(\mathbf{v}^0 - \frac{\partial \mathbf{u}^0}{\partial t}\right) \cdot \nabla_y \bar{\varphi}^0 \quad \text{in } Y_{\mathrm{f}}, \quad (4.37)\\
&-\mathcal{D}_\pm \exp(\mp\bar{\varphi}^0)\nabla_y \chi^\pm \cdot \boldsymbol{n} = 0 \quad \text{on } \partial Y_{\mathrm{fs}}
\end{aligned}$$

and

$$\begin{aligned}
&\nabla_y \cdot [\mathcal{D}_\pm \exp(\mp\bar{\varphi}^0)(\nabla_y \boldsymbol{f}^\pm + \boldsymbol{I})] = 0 \quad \text{in } Y_f, \qquad (4.38)\\
&-\mathcal{D}_\pm \exp(\mp\bar{\varphi}^0)(\boldsymbol{I} + \nabla_y \boldsymbol{f}^\pm) \cdot \boldsymbol{n} = 0 \quad \text{on } \partial Y_{\mathrm{fs}}.
\end{aligned}$$

When comparing the above closure problems with the ones derived in the homogenization of convection–diffusion equations of nonionic species (Auriault and Adler, 1995) and those obtained by Moyne and Murad (2002) adopting the lower order estimate $Pe = \mathcal{O}(\epsilon)$, one may observe two essential differences. The local cell problems (4.38) for $\boldsymbol{f}^\pm$ are essentially the same of the ones derived in Auriault and Adler (1995) with the exception of the appearance of the capacity coefficients ($\exp(\pm\bar{\varphi}^0)$). Since the

Poisson–Boltzmann equation (4.32) entails the dependence of $\bar{\varphi}^0$ on salinity through the Debye's length, this yields an extra dependence of $\boldsymbol{f}^{\pm}$ on c_{b}^0 for ionic species. In addition, the cell problems (4.37) for $\chi^{\pm}$ are new and represent and $\mathcal{O}(Pe)$-fluctuation of the ion atmosphere due to convection effects. We remark that (4.37) has also been postulated by Sherwood (1980) (considering the Hartmann number of $\mathcal{O}(1)$) who introduced the relaxation potentials $\chi^{\pm}$ to account for this nonequilibrium effect.

Finally by adding and subtracting (4.36) over cations and anions we obtain the closure relations for c_{b}^1 and $\bar{\psi}_{\mathrm{b}}^1$

$$2c_{\mathrm{b}}^1 = (\chi^+ + \chi^-)c_{\mathrm{b}}^0 + (\boldsymbol{f}^+ + \boldsymbol{f}^-)\nabla_x c_{\mathrm{b}}^0 + (\boldsymbol{f}^+ - \boldsymbol{f}^-)c_{\mathrm{b}}^0 \nabla_x \bar{\psi}_{\mathrm{b}}^0 + g(\boldsymbol{x}, t), \tag{4.39}$$

$$2c_{\mathrm{b}}^0 \bar{\psi}_{\mathrm{b}}^1 = (\chi^+ - \chi^-)c_{\mathrm{b}}^0 + (\boldsymbol{f}^+ - \boldsymbol{f}^-)\nabla_x c_{\mathrm{b}}^0 + (\boldsymbol{f}^+ + \boldsymbol{f}^-)c_{\mathrm{b}}^0 \nabla_x \bar{\psi}_{\mathrm{b}}^0 + h(x, t). \tag{4.40}$$

4.2.4. *Darcy's Law*

To derive macroscopic Darcy's law governing the motion of the electrolyte solution we use the closure relations (4.39) and (4.40) in the zeroth-order Stokes problem (4.14). Together with the incompressibility condition (4.10)(a), (4.37) and boundary conditions (4.21)(b) we obtain the following extended Stokes problem formulated in terms of $\{\mathbf{v}^0, p_{\mathrm{b}}^1, \chi^{\pm}\}$:

$$\begin{aligned}
&\mu_{\mathrm{f}} \Delta_{yy} \mathbf{v}^0 - \nabla_y p_{\mathrm{b}}^1 - A \nabla_y \chi^+ - B \nabla_y \chi^- = \nabla_x p_{\mathrm{b}}^0 + \boldsymbol{F} \nabla_x c_{\mathrm{b}}^0 + \boldsymbol{G} \nabla_x \bar{\psi}_{\mathrm{b}}^0, \qquad (4.41)\\
&\nabla_y \cdot \mathbf{v}^0 = 0 \quad \text{in } Y_{\mathrm{f}},\\
&\nabla_y \cdot [\mathcal{D}_{\pm} \exp\left(\mp\bar{\varphi}^0\right) \nabla_y \chi^{\pm}] = \mp \exp\left(\mp\bar{\varphi}^0\right) \left(\mathbf{v}^0 - \frac{\partial \mathbf{u}^0}{\partial t}\right) \cdot \nabla_y \bar{\varphi}^0,\\
&\nabla_y \chi^{\pm} \cdot \boldsymbol{n} = 0, \quad \mathbf{v}^0 = \frac{\partial \mathbf{u}^0}{\partial t} \quad \text{on } \partial Y_{\mathrm{fs}}
\end{aligned}$$

with

$$\boldsymbol{F} = RT\left[2\left(\cosh\bar{\varphi}^0 - 1\right)\boldsymbol{I} + \left(\exp(-\bar{\varphi}^0) - 1\right)\nabla_y \boldsymbol{f}^+ + \left(\exp(+\bar{\varphi}^0) - 1\right)\nabla_y \boldsymbol{f}^-\right], \tag{4.42}$$

$$\boldsymbol{G} = RTc_{\mathrm{b}}^0\left[-2\sinh\bar{\varphi}^0 \boldsymbol{I} + \left(\exp(-\bar{\varphi}^0) - 1\right)\nabla_y \boldsymbol{f}^+ - \left(\exp(+\bar{\varphi}^0) - 1\right)\nabla_y \boldsymbol{f}^-\right], \tag{4.43}$$

$$A = RTc_{\mathrm{b}}^0\left(\exp(-\bar{\varphi}^0) - 1\right), \quad B = RTc_{\mathrm{b}}^0\left(\exp(+\bar{\varphi}^0) - 1\right).$$

The above problem contains new relevant physical information which can be explored to obtain further insight in the still open issues regarding the magnitude of the macroscopic conductivities. The source terms in the r.h.s. show that in addition to a bulk phase pressure gradient, flow is also induced by gradients in concentration (chemico-osmotic effect) and macroscale electric potential (electro-osmotic effect). This result reproduces the well-known mechanisms driving flow of electrolyte solutions in microchannels composed of parallel walls (see Gross and Osterlé, 1968; Fair and Osterlé, 1991; Sherwood, 1992; Szymczyk *et al.*, 1999). Moreover, one may note the appearance of the gradient of the characteristic relaxation potentials $\chi^{\pm}$ which incorporates the interaction force between fluid motion and the distortion of the charge cloud (Sherwood, 1980) when $(\mathbf{v}^0 - \partial\mathbf{u}/\partial t)$ is not orthogonal to $\nabla_y\bar{\varphi}^0$ (as one may observe from the r.h.s. of (4.37)). This dynamical effect, parametrized by $\mathcal{O}(Pe)$, plays the role of an additional electro-chemical drag force acting in the fluid, when the e.d.l restores its equilibrium configuration after being perturbed by the fluid velocity. It should be noted that in the particular case of parallel particles, the e.d.l.s develop normal to the clay surface and orthogonal to the fluid velocity. This implies that the r.h.s. of (4.37) vanishes leading to $\nabla_y\chi^{\pm} = 0$ and consequently to a classical Stokes problem in terms of $\{\mathbf{v}^0, p_{\mathrm{b}}^1\}$ with flow driven by $\{\nabla_x p_{\mathrm{b}}^0, \nabla_x c_{\mathrm{b}}^0, \nabla_x \bar{\psi}_{\mathrm{b}}^0\}$. Moreover, by invoking Moyne and Murad (2002) the reader may verify that the same simplification is verified adopting the lower order estimate $Pe = \mathcal{O}(\epsilon)$. Thus, the appearance of the dynamical drag force involving the relaxation functions $\nabla_y\chi^{\pm}$ is tied up directly to the estimate $Pe = \mathcal{O}(1)$ combined with microgeometries composed of nonparallel particles.

To derive Darcy's law from the above Stokes problem we decompose the velocity, pressure fluctuation and relaxation potentials into their hydraulic, chemico-osmotic and electro-osmotic components

$$\mathbf{v}^0 = \mathbf{v}_{\mathrm{p}}^0 + \mathbf{v}_{\mathrm{c}}^0 + \mathbf{v}_{\mathrm{e}}^0, \quad p_{\mathrm{b}}^1 = p_{\mathrm{p}}^1 + p_{\mathrm{c}}^1 + p_{\mathrm{e}}^1, \quad \chi^{\pm} = \chi_{\mathrm{p}}^{\pm} + \chi_{\mathrm{c}}^{\pm} + \chi_{\mathrm{e}}^{\pm}.$$

The four unknowns $\{\mathbf{v}_{\mathrm{p}}^0, p_{\mathrm{p}}^1, \chi_{\mathrm{p}}^{\pm}\}$ satisfy the local modified Stokes problem only driven by a pressure gradient

$$\begin{aligned}
&\mu_{\mathrm{f}}\Delta_{yy}\mathbf{v}_{\mathrm{p}}^0 - \nabla_y p_{\mathrm{p}}^1 - A\nabla_y\chi_{\mathrm{p}}^{+} - B\nabla_y\chi_{\mathrm{p}}^{-} = \nabla_x p_{\mathrm{b}}^0,\\
&\nabla_y\cdot\mathbf{v}_{\mathrm{p}}^0 = 0 \quad \text{in } Y_{\mathrm{f}},\\
&\nabla_y\cdot[\mathcal{D}_{\pm}\exp\left(\mp\bar{\varphi}^0\right)\nabla_y\chi_{\mathrm{p}}^{\pm}] \pm \left(\mathbf{v}_{\mathrm{p}}^0 - \frac{\partial\mathbf{u}^0}{\partial t}\right)\cdot\exp\left(\mp\bar{\varphi}^0\right)\nabla_y\bar{\varphi}^0 = 0,\\
&\mathbf{v}_{\mathrm{p}}^0 = \frac{\partial\mathbf{u}^0}{\partial t}, \quad \nabla_y\chi_{\mathrm{p}}^{\pm}\cdot\boldsymbol{n} = 0 \quad \text{on } \partial Y_{\mathrm{fs}},
\end{aligned}$$

whereas the chemico and electro-osmotic components satisfy

$$\begin{aligned}
&\mu_{\mathrm{f}}\Delta_{yy}\mathbf{v}_{\mathrm{c}}^0 - \nabla_y p_{\mathrm{c}}^1 - A\nabla_y\chi_{\mathrm{c}}^{+} - B\nabla_y\chi_{\mathrm{c}}^{-} = \boldsymbol{F}\nabla_x c_{\mathrm{b}}^0,\\
&\nabla_y\cdot\mathbf{v}_{\mathrm{c}}^0 = 0 \quad \text{in } Y_{\mathrm{f}},\\
&\nabla_y\cdot[\mathcal{D}_{\pm}\exp\left(\mp\bar{\varphi}^0\right)\nabla_y\chi_{\mathrm{c}}^{\pm}] \pm \mathbf{v}_{\mathrm{c}}^0\cdot\exp\left(\mp\bar{\varphi}^0\right)\nabla_y\bar{\varphi}^0 = 0,\\
&\mathbf{v}_{\mathrm{c}}^0 = 0, \quad \nabla_y\chi_{\mathrm{c}}^{\pm}\cdot\boldsymbol{n} = 0 \quad \text{on } \partial Y_{\mathrm{fs}}
\end{aligned}$$

and

$$\begin{aligned}
&\mu_{\mathrm{f}}\Delta_{yy}\mathbf{v}_{\mathrm{e}}^{0}-\nabla_{y}p_{\mathrm{e}}^{1}-A\nabla_{y}\chi_{\mathrm{e}}^{+}-B\nabla_{y}\chi_{\mathrm{e}}^{-}=\boldsymbol{G}\nabla_{x}\bar{\psi}_{\mathrm{b}}^{0},\\
&\nabla_{y}\cdot\mathbf{v}_{\mathrm{e}}^{0}=0\quad\text{in } Y_{\mathrm{f}},\\
&\nabla_{y}\cdot[\mathcal{D}_{\pm}\exp\left(\mp\bar{\varphi}^{0}\right)\nabla_{y}\chi_{\mathrm{e}}^{\pm}]\pm\mathbf{v}_{\mathrm{e}}^{0}\cdot\exp\left(\mp\bar{\varphi}^{0}\right)\nabla_{y}\bar{\varphi}^{0}=0,\\
&\mathbf{v}_{\mathrm{e}}^{0}=0,\quad\nabla_{y}\chi_{\mathrm{e}}^{\pm}\cdot\boldsymbol{n}=0\quad\text{on }\partial Y_{\mathrm{fs}}.
\end{aligned}$$

Denoting $\{e^{j}\}(j=1,2,3)$ an orthonormal basis, define the set of periodic characteristic tensorial functions $\{\boldsymbol{\kappa}_{\mathrm{p}},\boldsymbol{\kappa}_{\mathrm{c}},\boldsymbol{\kappa}_{\mathrm{e}}\}$ and vectorial quantities $\{\boldsymbol{g}_{\mathrm{p}},\boldsymbol{g}_{\mathrm{c}},\boldsymbol{g}_{\mathrm{e}},\boldsymbol{h}_{\mathrm{p}}^{\pm},\boldsymbol{h}_{\mathrm{c}}^{\pm},\boldsymbol{h}_{\mathrm{e}}^{\pm}\}$ with components $\{\boldsymbol{\kappa}_{\mathrm{p}}^{j},\boldsymbol{\kappa}_{\mathrm{c}}^{j},\boldsymbol{\kappa}_{\mathrm{e}}^{j}\}$ (vectors) and $\{g_{\mathrm{p}}^{j},g_{\mathrm{c}}^{j},g_{\mathrm{e}}^{j},h_{\mathrm{p}}^{\pm j},h_{c}^{\pm j},h_{\mathrm{e}}^{\pm j}\}$ (scalars) satisfying the following canonical problems:

$$\begin{aligned}
&\mu_{\mathrm{f}}\Delta_{yy}\boldsymbol{\kappa}_{\mathrm{p}}^{j}-\nabla_{y}g_{\mathrm{p}}^{j}-A\nabla_{y}h_{\mathrm{p}}^{+j}-B\nabla_{y}h_{\mathrm{p}}^{-j}=-\boldsymbol{e}^{j},\\
&\nabla_{y}\cdot\boldsymbol{\kappa}_{\mathrm{p}}^{j}=0\quad\text{in } Y_{\mathrm{f}},\quad j=1,2,3,\\
&\nabla_{y}\cdot[\mathcal{D}_{\pm}\exp\left(\mp\bar{\varphi}^{0}\right)\nabla_{y}h_{\mathrm{p}}^{\pm j}]\pm\boldsymbol{\kappa}_{\mathrm{p}}^{j}\cdot\exp\left(\mp\bar{\varphi}^{0}\right)\nabla_{y}\bar{\varphi}^{0}=0,\\
&\boldsymbol{\kappa}_{\mathrm{p}}^{j}=0,\quad\nabla_{y}h_{\mathrm{p}}^{\pm j}\cdot\boldsymbol{n}=0\quad\text{on }\partial Y_{\mathrm{fs}}
\end{aligned}\tag{4.44}$$

along with

$$\begin{aligned}
&\mu_{\mathrm{f}}\Delta_{yy}\boldsymbol{\kappa}_{\mathrm{c}}^{j}-\nabla_{y}g_{\mathrm{c}}^{j}-A\nabla_{y}h_{\mathrm{c}}^{+j}-B\nabla_{y}h_{\mathrm{c}}^{-j}=-\boldsymbol{F}\boldsymbol{e}^{j},\\
&\nabla_{y}\cdot\boldsymbol{\kappa}_{\mathrm{c}}^{j}=0\quad\text{in } Y_{\mathrm{f}},\quad j=1,2,3,\\
&\nabla_{y}\cdot[\mathcal{D}_{\pm}\exp\left(\mp\bar{\varphi}^{0}\right)\nabla_{y}h_{\mathrm{c}}^{\pm j}]\pm\boldsymbol{\kappa}_{\mathrm{c}}^{j}\cdot\exp\left(\mp\bar{\varphi}^{0}\right)\nabla_{y}\bar{\varphi}^{0}=0,\\
&\boldsymbol{\kappa}_{\mathrm{c}}^{j}=0,\quad\nabla_{y}h_{\mathrm{c}}^{\pm j}\cdot\boldsymbol{n}=0\quad\text{on }\partial Y_{\mathrm{fs}}
\end{aligned}\tag{4.45}$$

and

$$\begin{aligned}
&\mu_{\mathrm{f}}\Delta_{yy}\boldsymbol{\kappa}_{\mathrm{e}}^{j}-\nabla_{y}g_{\mathrm{e}}^{j}-A\nabla_{y}h_{\mathrm{e}}^{+j}-B\nabla_{y}h_{\mathrm{e}}^{-j}=-\boldsymbol{G}\boldsymbol{e}^{j},\\
&\nabla_{y}\cdot\boldsymbol{\kappa}_{\mathrm{e}}^{j}=0\quad\text{in } Y_{\mathrm{f}},\quad j=1,2,3,\\
&\nabla_{y}\cdot[\mathcal{D}_{\pm}\exp\left(\mp\bar{\varphi}^{0}\right)\nabla_{y}h_{\mathrm{e}}^{\pm j}]\pm\boldsymbol{\kappa}_{\mathrm{e}}^{j}\cdot\exp\left(\mp\bar{\varphi}^{0}\right)\nabla_{y}\bar{\varphi}^{0}=0,\\
&\boldsymbol{\kappa}_{\mathrm{e}}^{j}=0,\quad\nabla_{y}h_{\mathrm{e}}^{\pm j}\cdot\boldsymbol{n}=0\quad\text{on }\partial Y_{\mathrm{fs}}.
\end{aligned}\tag{4.46}$$

Thus, exploiting the linearity between the above local problems we arrive at the decompositions

$$\begin{aligned}
&\mathbf{v}_{\mathrm{p}}^{0}-\frac{\partial\mathbf{u}^{0}}{\partial t}=-\boldsymbol{\kappa}_{\mathrm{p}}\nabla_{x}p_{\mathrm{b}}^{0},\qquad &&\mathbf{v}_{\mathrm{c}}^{0}=-\boldsymbol{\kappa}_{\mathrm{c}}\nabla_{x}c_{\mathrm{b}}^{0},\qquad &&\mathbf{v}_{\mathrm{e}}^{0}=-\boldsymbol{\kappa}_{\mathrm{e}}\nabla_{x}\bar{\psi}_{\mathrm{b}}^{0},\\
&p_{\mathrm{p}}^{1}=\boldsymbol{g}_{\mathrm{p}}\cdot\nabla_{x}p_{\mathrm{b}}^{0}, &&p_{\mathrm{c}}^{1}=\boldsymbol{g}_{\mathrm{c}}\cdot\nabla_{x}c_{\mathrm{b}}^{0}, &&p_{\mathrm{e}}^{1}=\boldsymbol{g}_{\mathrm{e}}\cdot\nabla_{x}\bar{\psi}_{\mathrm{b}}^{0},\\
&\chi_{\mathrm{p}}^{\pm}=\boldsymbol{h}_{\mathrm{p}}^{\pm}\cdot\nabla_{x}p_{\mathrm{b}}^{0}, &&\chi_{\mathrm{c}}^{\pm}=\boldsymbol{h}_{\mathrm{c}}^{\pm}\cdot\nabla_{x}c_{\mathrm{b}}^{0}, &&\chi_{\mathrm{e}}^{\pm}=\boldsymbol{h}_{\mathrm{e}}^{\pm}\cdot\nabla_{x}\bar{\psi}_{\mathrm{b}}^{0}.
\end{aligned}\tag{4.47}$$

Combining the above result for $\mathbf{v}_{i}^{0}(i=\mathrm{p},\mathrm{c},\mathrm{e})$ with the decomposition $\mathbf{v}^{0}=\mathbf{v}_{\mathrm{p}}^{0}+\mathbf{v}_{\mathrm{c}}^{0}+\mathbf{v}_{\mathrm{e}}^{0}$ we obtain

$$\mathbf{v}^{0}-\frac{\partial\mathbf{u}^{0}}{\partial t}=-\boldsymbol{\kappa}_{\mathrm{p}}\nabla_{x}p_{\mathrm{b}}^{0}-\boldsymbol{\kappa}_{\mathrm{c}}\nabla_{x}c_{\mathrm{b}}^{0}-\boldsymbol{\kappa}_{\mathrm{e}}\nabla_{x}\bar{\psi}_{\mathrm{b}}^{0}.\tag{4.48}$$

By averaging (4.47) we also have

$$\begin{aligned}
&\left\langle \mathbf{v}_{\mathrm{p}}^{0} - \frac{\partial \mathbf{u}^{0}}{\partial t} \right\rangle = -\boldsymbol{K}_{\mathrm{P}} \nabla_{x} p_{\mathrm{b}}^{0}, \quad \text{with } \boldsymbol{K}_{\mathrm{P}} \equiv \langle \boldsymbol{\kappa}_{\mathrm{p}} \rangle \\
&\langle \mathbf{v}_{\mathrm{c}}^{0} \rangle = -\boldsymbol{K}_{\mathrm{C}} \nabla_{x} c_{\mathrm{b}}^{0}, \quad \text{with } \boldsymbol{K}_{\mathrm{C}} \equiv \langle \boldsymbol{\kappa}_{\mathrm{c}} \rangle, \\
&\langle \mathbf{v}_{\mathrm{e}}^{0} \rangle = -\boldsymbol{K}_{\mathrm{E}} \nabla_{x} \bar{\psi}_{\mathrm{b}}^{0}, \quad \text{with } \boldsymbol{K}_{\mathrm{E}} \equiv \langle \boldsymbol{\kappa}_{\mathrm{e}} \rangle.
\end{aligned} \tag{4.49}$$

Defining the Darcian velocity $\mathbf{v}_{\mathrm{D}}^{0} \equiv \langle \mathbf{v}^{0} - \partial \mathbf{u}^{0}/\partial t \rangle$ we have from (4.48) and (4.49)

$$\mathbf{v}_{\mathrm{D}}^{0} = -\boldsymbol{K}_{\mathrm{P}} \nabla_{x} p_{\mathrm{b}}^{0} - \boldsymbol{K}_{\mathrm{C}} \nabla_{x} c_{\mathrm{b}}^{0} - \boldsymbol{K}_{\mathrm{E}} \nabla_{x} \bar{\psi}_{\mathrm{b}}^{0}. \tag{4.50}$$

The above result resembles in form Darcy's law derived in Gu *et al.* (1998) and Huyghe and Janssen (1997), within the context of the Thermodynamics of Irreversible Processes, and Moyne and Murad (2002) within the framework of homogenization adopting the estimate $Pe = \mathcal{O}(\epsilon)$. Nevertheless, by invoking the new closure problems (4.44)–(4.46), one may observe crucial differences in the interpretation of the conductivities appearing in (4.50). For example, the first term in the r.h.s. of Darcy's law quantifies the hydraulic component of the flow driven by the bulk phase pressure gradient. However, in contrast to the classical viscous and geometric interpretation of hydraulic conductivity, the coefficient $\boldsymbol{K}_{\mathrm{P}}$ in (4.50) also incorporates the additional electrical drag induced by the distortion of the e.d.l. appearing quantified by the terms involving the relaxation potentials $h_{\mathrm{p}}^{\pm j}$ in (4.44). Hence, we envisage $\boldsymbol{K}_{\mathrm{P}}$ as a generalized tensor which incorporates the classical viscous drag with the solid particles and an electro-viscous effect associated with the perturbations in the fluid flow due to the fluctuation of the charge cloud.

The two other driving forces in the r.h.s. of (4.50) are nothing but the chemico-osmotic and electro-osmotic components of the flow driven by concentration and electric potential gradients (Lai *et al.*, 1991; Huyghe and Janssen, 1997; Gu *et al.*, 1998). In a similar fashion to $\boldsymbol{K}_{\mathrm{P}}$, the magnitude of the chemico-osmotic and electro-osmotic permeabilities $\boldsymbol{K}_{\mathrm{C}}$ and $\boldsymbol{K}_{\mathrm{E}}$ are strongly influenced by the relaxation potentials $h_{\mathrm{c}}^{\pm}$ and $h_{\mathrm{e}}^{\pm}$ associated with the deformation of the ion atmosphere. The reader shall verify that such perturbation disappears under the assumption $Pe_{\mathrm{L}} \leqslant \mathcal{O}(\epsilon)$ (Moyne and Murad, 2002).

Finally we remark the information concerning the influence of the fluctuating concentration c_{b}^{1} (through the characteristic functions $\chi^{\pm}$ and $\boldsymbol{f}^{\pm}$ in (4.36)) on the magnitude of the conductivities in Darcy's law. In particular, from (4.42) and (4.43), one may note that the functions $\boldsymbol{F}$ and $\boldsymbol{G}$ are hierarchically governed by leading components associated with the distribution of the electric potential across the pore space (first terms in the r.h.s. of (4.42) and (4.43)) and additional fluctuating contributions due to the gradient of the characteristic functions $\boldsymbol{f}^{\pm}$. The reader may verify invoking Moyne and Murad (2002, 2006) that for parallel particles the contribution of $\nabla_y \boldsymbol{f}^{\pm}$ and $\nabla_y \chi^{\pm}$ to the axial velocity and permeabilities in (4.41)–(4.43) vanish and consequently the closure problems (4.44)–(4.46) reduce to classical Stokes type problems with $\boldsymbol{F}$ and $\boldsymbol{G}$ solely given by the first term in the r.h.s of (4.42) and (4.43).

4.2.5. *Macroscopic Movement of the Ions*

We now proceed by deriving the homogenized form of the modified convection–diffusion equation. Integrating (4.17) over Y, using (4.31) for the l.h.s. with the choices

$$f^0 = c_{\mathrm{b}}^0 \exp(\mp\bar{\varphi}^0), \quad f^1 = \exp(\mp\bar{\varphi}^0)(c_{\mathrm{b}}^1 \mp c_{\mathrm{b}}^0 \bar{\varphi}^1),$$

we obtain at $\mathcal{O}(\epsilon^0)$

$$\begin{aligned}
&\left\langle \frac{\partial}{\partial t}\left(c_{\mathrm{b}}^0 \exp(\pm\bar{\varphi}^0)\right)\right\rangle + \left\langle \nabla_x \cdot \left(c_{\mathrm{b}}^0 \exp(\pm\bar{\varphi}^0)\mathbf{v}^0\right)\right\rangle + \\
&\quad + \left\langle \nabla_y \cdot \left[\exp\left(\mp\bar{\varphi}^0\right)\left(c_{\mathrm{b}}^1 \mathbf{v}^0 \mp c_{\mathrm{b}}^0 \bar{\varphi}^1 \mathbf{v}^0 + c_{\mathrm{b}}^0 \mathbf{v}^1\right)\right]\right\rangle \\
&= \frac{\partial}{\partial t}\left\langle c_{\mathrm{b}}^0 \exp(\pm\bar{\varphi}^0)\right\rangle + \nabla_x \cdot \left\langle c_{\mathrm{b}}^0 \exp(\pm\bar{\varphi}^0)\mathbf{v}^0\right\rangle.
\end{aligned} \tag{4.51}$$

Further by averaging the r.h.s. of (4.17), using (4.30) with the choices

$$\boldsymbol{g}^0 = \mathcal{D}_{\pm} \exp\left(\mp\bar{\varphi}^0\right)\left(\nabla_y c_{\mathrm{b}}^1 \pm c_{\mathrm{b}}^0 \nabla_y \bar{\psi}_{\mathrm{b}}^1 + \nabla_x c_{\mathrm{b}}^0 \pm c_{\mathrm{b}}^0 \nabla_x \bar{\psi}_{\mathrm{b}}^0\right)$$

and

$$\begin{aligned}
\boldsymbol{g}^1 = \mathcal{D}_{\pm} \exp\left(\mp\bar{\varphi}^0\right)&\left[\nabla_y c_{\mathrm{b}}^2 + \nabla_x c_{\mathrm{b}}^1 \pm c_{\mathrm{b}}^0\left(\nabla_y \bar{\psi}_{\mathrm{b}}^2 + \nabla_x \bar{\psi}_{\mathrm{b}}^1\right) \pm c_{\mathrm{b}}^1\left(\nabla_y \bar{\psi}_{\mathrm{b}}^1 + \nabla_x \bar{\psi}_{\mathrm{b}}^0\right) \pm\right. \\
&\left. \pm\bar{\varphi}^1\left(\nabla_y c_{\mathrm{b}}^1 + \nabla_x c_{\mathrm{b}}^0 \pm c_{\mathrm{b}}^0\left(\nabla_y \bar{\psi}_{\mathrm{b}}^1 + \nabla_x \bar{\psi}_{\mathrm{b}}^0\right)\right)\right]
\end{aligned}$$

and using the boundary condition (4.26) we obtain

$$\begin{aligned}
&\nabla_x \cdot \left[\mathcal{D}_{\pm}\left\langle \exp(\mp\bar{\varphi}^0)\left(\nabla_y c_{\mathrm{b}}^1 \pm c_{\mathrm{b}}^0 \nabla_y \bar{\psi}_{\mathrm{b}}^1 + \nabla_x c_{\mathrm{b}}^0 \pm c_{\mathrm{b}}^0 \nabla_x \bar{\psi}_{\mathrm{b}}^0\right)\right\rangle\right] + \\
&\quad + \left\langle \nabla_y \cdot \left[\mathcal{D}_{\pm} \exp(\mp\bar{\varphi}^0)\left(\nabla_y c_{\mathrm{b}}^2 + \nabla_x c_{\mathrm{b}}^1 \pm c_{\mathrm{b}}^0\left(\nabla_y \bar{\psi}_{\mathrm{b}}^2 + \nabla_x \bar{\psi}_{\mathrm{b}}^1\right) \pm\right.\right.\right. \\
&\quad \left.\left.\left. \pm c_{\mathrm{b}}^1\left(\nabla_y \bar{\psi}_{\mathrm{b}}^1 + \nabla_x \bar{\psi}_{\mathrm{b}}^0\right)\right) \pm \bar{\varphi}^1\left(\nabla_y c_{\mathrm{b}}^1 + \nabla_x c_{\mathrm{b}}^0 \pm c_{\mathrm{b}}^0\left(\nabla_y \bar{\psi}_{\mathrm{b}}^1 + \nabla_x \bar{\psi}_{\mathrm{b}}^1\right)\right)\right]\right\rangle \\
&= \nabla_x \cdot \left[\mathcal{D}_{\pm}\left\langle \exp(\mp\bar{\varphi}^0)\left(\nabla_y c_{\mathrm{b}}^1 \pm c_{\mathrm{b}}^0 \nabla_y \bar{\psi}_{\mathrm{b}}^1\right)\right\rangle + \right. \\
&\quad \left. + \mathcal{D}_{\pm}\left\langle \exp(\mp\bar{\varphi}^0)\right\rangle\left(\nabla_x c_{\mathrm{b}}^0 \pm c_{\mathrm{b}}^0 \nabla_x \bar{\psi}_{\mathrm{b}}^0\right)\right].
\end{aligned} \tag{4.52}$$

Thus, equating (4.51) and (4.52) gives

$$\begin{aligned}&\frac{\partial}{\partial t}\left(\left\langle\exp(\mp\bar{\varphi}^0)\right\rangle c_{\mathrm{b}}^0\right)+\nabla_x\cdot\left(\left\langle\exp(\mp\bar{\varphi}^0)\mathbf{v}^0\right\rangle c_{\mathrm{b}}^0\right)\\ &\quad=\nabla_x\cdot\left[\mathcal{D}_\pm\left\langle\exp(\mp\bar{\varphi}^0)\left(\nabla_y c_{\mathrm{b}}^1\pm c_{\mathrm{b}}^0\nabla_y\bar{\psi}_{\mathrm{b}}^1\right)\right\rangle+\right.\\ &\qquad\qquad\left.+\mathcal{D}_\pm\left\langle\exp(\mp\bar{\varphi}^0)\right\rangle\left(\nabla_x c_{\mathrm{b}}^0\pm c_{\mathrm{b}}^0\nabla_x\bar{\psi}_{\mathrm{b}}^0\right)\right].\end{aligned}$$

Hence, denoting $\langle.\rangle^\alpha\equiv|Y_\alpha|^{-1}\int_{Y_\alpha}\cdot\mathrm{d}Y_\alpha(\alpha=\mathrm{f},\mathrm{s})$ the intrinsic volume average operator over the α-portion of the unit cell and $n_\alpha\equiv|Y_\alpha|/|Y|(\alpha=\mathrm{f},\mathrm{s})$ the volume fraction of the α-phase, using the closure relations (4.36) for $c_{\mathrm{b}}^1\pm c_{\mathrm{b}}^0\psi_{\mathrm{b}}^1$ we obtain

$$\begin{aligned}&\frac{\partial}{\partial t}\left(n_{\mathrm{f}}\left\langle\exp(\mp\bar{\varphi}^0)\right\rangle^{\mathrm{f}}c_{\mathrm{b}}^0\right)+\nabla_x\cdot\left(n_{\mathrm{f}}\left\langle\exp(\mp\bar{\varphi}^0)(\mathbf{v}^0-\mathcal{D}_\pm\nabla_y\chi^\pm)\right\rangle^{\mathrm{f}}c_{\mathrm{b}}^0\right)\\ &\quad=\nabla_x\cdot\left[n_{\mathrm{f}}\mathcal{D}_\pm\left\langle\exp(\mp\bar{\varphi}^0)(\boldsymbol{I}+\nabla_y\boldsymbol{f}^\pm)\right\rangle^{\mathrm{f}}\left(\nabla_x c_{\mathrm{b}}^0\pm c_{\mathrm{b}}^0\nabla_x\bar{\psi}_{\mathrm{b}}^0\right)\right].\end{aligned}$$

Finally making use of the decomposition $\chi^\pm=\chi_{\mathrm{p}}^\pm+\chi_{\mathrm{c}}^\pm+\chi_{\mathrm{e}}^\pm$ and the closure relations for $\chi_i^\pm(i=\mathrm{p},\mathrm{c},\mathrm{e})$ in (4.47) in the above result we obtain

$$\begin{aligned}&\frac{\partial}{\partial t}\left(n_{\mathrm{f}}G_\pm c_{\mathrm{b}}^0\right)+\nabla_x\cdot\boldsymbol{J}_\pm^0=0\\ &\text{with }\boldsymbol{J}_\pm^0\equiv G_\pm c_{\mathrm{b}}^0\mathbf{v}_\pm^0-n_{\mathrm{f}}\left(\boldsymbol{D}_\pm^{\mathrm{c}}\nabla_x c_{\mathrm{b}}^0\pm\boldsymbol{D}_\pm^{\mathrm{e}}c_{\mathrm{b}}^0\nabla_x\bar{\psi}_{\mathrm{b}}^0+\boldsymbol{D}_\pm^{\mathrm{p}}\nabla_x p_{\mathrm{b}}^0\right)\end{aligned}\tag{4.53}$$

denoting the homogenized flux of cations and anions and

$$\begin{aligned}&G_\pm=\left\langle\exp\left(\mp\bar{\varphi}^0\right)\right\rangle^f,\quad G_\pm\mathbf{v}_\pm^0=\left\langle\exp\left(\mp\bar{\varphi}^0\right)\mathbf{v}^0\right\rangle,\quad \boldsymbol{D}_\pm^{\mathrm{p}}=\mathcal{D}_\pm\left\langle\exp\left(\mp\bar{\varphi}^0\right)\nabla_y\boldsymbol{h}_{\mathrm{p}}^\pm\right\rangle^f,\\ &\boldsymbol{D}_\pm^{\boldsymbol{I}}=\mathcal{D}_\pm\left\langle\exp\left(\mp\bar{\varphi}^0\right)\left(\boldsymbol{I}+\nabla_y\boldsymbol{f}^\pm+c_{\mathrm{b}}^0\nabla_y\boldsymbol{h}_{\boldsymbol{I}}^\pm\right)\right\rangle^{\mathrm{f}},\quad \boldsymbol{I}=\mathrm{c},\mathrm{e}.\end{aligned}\tag{4.54}$$

Equation (4.53) is our homogenized form of the Nernst–Planck equation governing the macroscopic movement of the charged species. When comparing this form and the local cell representations (4.54) with the corresponding well-known results for nonionic species (e.g. Auriault and Adler, 1995) one may observe some essential differences. We remark particularly the appearance of the up-scaled coefficients $G_\pm$ which incorporate the averaged storage capacity owing to the ion exchange capacity with the e.d.l.; the convection of the ions induced by the averaged velocities $\mathbf{v}_\pm^0$ which differ from $\langle\mathbf{v}^0\rangle$ due to the disturbance in the advection caused by the charge cloud; and the strong dependence of the diffusion coefficients $\boldsymbol{D}_\pm^{\boldsymbol{I}}(\boldsymbol{I}=\mathrm{p},\mathrm{c},\mathrm{e})$ on the relative electrical potential $\bar{\varphi}^0$ and consequently on concentrations through the local Poisson–Boltzmann problem (4.32). In addition, the influence of the local fluctuation in concentration c_{b}^1 on the diffusivities appears manifested through the characteristic functions $\boldsymbol{f}^\pm$ (which also appear in the case of nonionic species (Auriault and Adler, 1995) and $\boldsymbol{h}_{\boldsymbol{I}}^{\pm}$. The effect of this latter $\mathcal{O}(Pe)$-function is restricted to ionic species and is tied up to the perturbations in the diffusivities caused by the fluctuations in the charge cloud induced by advection effects.

Finally, adopting an entirely analogous procedure in the macroscopization of the purely advection equation (4.20) governing ion movement in the solid phase, we obtain a result similar to (4.53). In terms of the averaged concentrations $\langle c_{\pm}^{s0}\rangle$ (rather than writing in terms of bulk concentrations) we obtain, after dropping the diffusive component of the flux

$$\frac{\partial}{\partial t}\langle c_{\pm}^{s0}\rangle + \nabla_x \cdot \langle \boldsymbol{J}_{\pm}^{s0}\rangle = 0 \quad \text{with} \quad \boldsymbol{J}_{\pm}^{s0} = c_{\pm}^{s0}\frac{\partial \mathbf{u}^0}{\partial t}. \tag{4.55}$$

4.2.6. *Modified Terzaghi's Decomposition*

To derive the modified Terzaghi's effective principle we average the fluid and solid momentum balances (4.11)(b) and (4.19)(a). Using the divergence theorem, boundary condition (4.22)(b) and the periodicity we obtain the overall momentum balance

$$\nabla_x \cdot \boldsymbol{\sigma}_{\mathrm{T}}^0 = 0, \quad \text{where} \quad \boldsymbol{\sigma}_{\mathrm{T}}^0 \equiv \langle \boldsymbol{\sigma}_{\mathrm{f}}^0\rangle + \langle \boldsymbol{\sigma}_{\mathrm{s}}^0\rangle \tag{4.56}$$

is the overall stress tensor of the mixture. The modified Terzaghi's effective stress principle can be obtained by considering the homogenized constitutive laws for $\langle \boldsymbol{\sigma}_{\mathrm{f}}^0\rangle$ and $\langle \boldsymbol{\sigma}_{\mathrm{s}}^0\rangle$. To this end we rephrase the Neumann problem (4.18)(b) and (4.23) for $\mathbf{u}^1$ as

$$\begin{aligned} &\nabla_y \cdot (\boldsymbol{c}_{\mathrm{s}}\boldsymbol{\mathcal{E}}_y(\mathbf{u}^1)) = 0 \quad \text{in } Y_{\mathrm{s}} \\ &-\left[p_{\mathrm{b}}^0(\boldsymbol{x},t)\boldsymbol{I} + \Pi_{\mathrm{d}}^0(\boldsymbol{x},\boldsymbol{y},t)\right]\boldsymbol{n} = \boldsymbol{c}_{\mathrm{s}}[\boldsymbol{\mathcal{E}}_x(\mathbf{u}^0(\boldsymbol{x},t)) + \boldsymbol{\mathcal{E}}_y(\mathbf{u}^1)]\boldsymbol{n} \quad \text{on } \partial Y_{\mathrm{fs}}, \end{aligned} \tag{4.57}$$

where Π_{d}^0 is a disjoining stress tensor which incorporates the Donnan osmotic pressure π^0 and Maxwell stresses $\boldsymbol{\tau}_{\mathbf{M}}^0$

$$\Pi_{\mathrm{d}}^0 = \pi^0\boldsymbol{I} - \boldsymbol{\tau}_{\mathbf{M}}^0 = 2RTc_{\mathrm{b}}^0(\cosh\bar{\varphi}^0 - 1)\boldsymbol{I} - \boldsymbol{\tau}_{\mathbf{M}}^0. \tag{4.58}$$

Equations (4.57) and (4.58) provide relevant information on the local stress analysis of charged particles. When comparing the closure problem (4.57) for $\mathbf{u}^1$ with the similar Neumann problem which appears in the homogenization derivation of Biot's equations of poroelasticity (see, e.g., Auriault and Sanchez–Palencia, 1977; Auriault, 1990; Terada *et al.*, 1998), the novelty is the appearance of the disjoining tensor Π_{d}^0 which incorporates the influence of electro-chemical effects on the traction boundary condition. We remark that for parallel particles, the component of Π_{d}^0 normal to the clay surface is nothing but the electrostatic component of the disjoining pressure (Derjaguin *et al.*, 1987; Dahnert and Huster, 1999). For a more detailed discussion on this issue (see Moyne and Murad 2002, 2003).

By linearity we have

$$\mathbf{u}^1(\boldsymbol{x},\boldsymbol{y},t)=\boldsymbol{\zeta}(\boldsymbol{y})p_{\mathrm{b}}^0(\boldsymbol{x},t)+\boldsymbol{\xi}(\boldsymbol{y})\boldsymbol{\mathcal{E}}_x(\mathbf{u}^0(\boldsymbol{x},t))+\mathbf{u}_\pi^1(\boldsymbol{x},\boldsymbol{y},t)+\hat{\mathbf{u}}(\boldsymbol{x},t). \quad (4.59)$$

The canonical cell problems for the third-order tensor $\boldsymbol{\xi}$ and the vector $\boldsymbol{\zeta}$ are classical (Auriault 1990; Terada *et al.*, 1998; Lydzba and Shao, 2000).

$$\begin{aligned}&\nabla_y\cdot(\boldsymbol{c}_{\mathrm{s}}\boldsymbol{\mathcal{E}}_y(\boldsymbol{\xi}))=0 \quad \text{in } Y_{\mathrm{s}}, \qquad \nabla_y\cdot(\boldsymbol{c}_{\mathrm{s}}\boldsymbol{\mathcal{E}}_y(\boldsymbol{\zeta}))=0 \quad \text{in } Y_{\mathrm{s}},\\ &(\boldsymbol{c}_{\mathrm{s}}\boldsymbol{\mathcal{E}}_y(\boldsymbol{\xi}))\boldsymbol{n}=-\boldsymbol{c}_{\mathrm{s}}\boldsymbol{II}\boldsymbol{n} \quad \text{on } \partial Y_{\mathrm{fs}}, \qquad (\boldsymbol{c}_{\mathrm{s}}\boldsymbol{\mathcal{E}}_y(\boldsymbol{\zeta}))\boldsymbol{n}=-\boldsymbol{I}\boldsymbol{n} \quad \text{on } \partial Y_{\mathrm{fs}}\end{aligned}$$

where $\boldsymbol{II}$ denotes the unity fourth-order tensor with components $\delta^{ij}\delta^{kl}$. The novelty in (4.59) is the appearance of the electro-chemical component $\mathbf{u}_\pi^1$ which corresponds to the particle displacement component due to the traction induced by the disjoining tensor $\boldsymbol{\Pi}_{\mathrm{d}}^0$

$$\begin{aligned}&\nabla_y\cdot\left(\boldsymbol{c}_{\mathrm{s}}\boldsymbol{\mathcal{E}}_y\left(\mathbf{u}_\pi^1\right)\right)=0 \quad \text{in } Y_{\mathrm{s}},\\ &(\boldsymbol{c}_{\mathrm{s}}\boldsymbol{\mathcal{E}}_y(\mathbf{u}_\pi^1))\boldsymbol{n}=-\boldsymbol{\Pi}_{\mathrm{d}}^0\boldsymbol{n} \quad \text{on } \partial Y_{\mathrm{fs}}.\end{aligned} \quad (4.60)$$

Denoting $\boldsymbol{C}_{\mathrm{s}}\equiv\langle\boldsymbol{c}_{\mathrm{s}}(\boldsymbol{II}+\boldsymbol{\mathcal{E}}_y(\boldsymbol{\xi}))$ the macroscopic elastic modulus (fourth-rank tensor), by averaging the constitutive equation (4.19)(b) for σ_{s}^0 and using (4.59) we obtain

$$\left\langle\boldsymbol{\sigma}_{\mathrm{s}}^0\right\rangle=\boldsymbol{C}_{\mathrm{s}}\boldsymbol{\mathcal{E}}_x\left(\mathbf{u}^0\right)+\langle\boldsymbol{c}_{\mathrm{s}}\boldsymbol{\mathcal{E}}_x(\boldsymbol{\zeta})\rangle p_{\mathrm{b}}^0+\langle\boldsymbol{c}_{\mathrm{s}}\boldsymbol{\mathcal{E}}_y(\mathbf{u}_\pi^1)\rangle. \quad (4.61)$$

By averaging the constitutive equation for $\boldsymbol{\sigma}_{\mathrm{f}}^0$ (4.11)(c) and using (4.58) we get $\left\langle\boldsymbol{\sigma}_{\mathrm{f}}^0\right\rangle=-n_{\mathrm{f}}p_{\mathrm{b}}^0\boldsymbol{I}-\left\langle\boldsymbol{\Pi}_{\mathrm{d}}^0\right\rangle$. Using this result in definition (4.56) along with (4.61) we obtain

$$\boldsymbol{\sigma}_{\mathrm{T}}^0=-\boldsymbol{\alpha}p_{\mathrm{b}}^0+\boldsymbol{C}_{\mathrm{s}}\boldsymbol{\mathcal{E}}_x(\mathbf{u}^0)-\boldsymbol{\Pi}^0, \quad (4.62)$$

where $\boldsymbol{\alpha}\equiv n_{\mathrm{f}}\boldsymbol{I}-\langle\boldsymbol{c}_{\mathrm{s}}\boldsymbol{\mathcal{E}}_y(\boldsymbol{\zeta})\rangle$ is the Biot–Willis coefficient (Biot and Willis, 1957) and

$$\boldsymbol{\Pi}^0=\left\langle\boldsymbol{\Pi}_{\mathrm{d}}^0\right\rangle+n_{\mathrm{s}}\boldsymbol{\Pi}_{\mathrm{S}}^0 \quad \text{with} \quad \boldsymbol{\Pi}_{\mathrm{S}}^0\equiv-\left\langle\boldsymbol{c}_{\mathrm{s}}\boldsymbol{\mathcal{E}}_y(\mathbf{u}_\pi^1)\right\rangle^{\mathrm{s}} \quad (4.63)$$

with $n_{\mathrm{s}}=1-n_{\mathrm{f}}$ the volume fraction of the solid (recall that $\langle\cdot\rangle=n_{\mathrm{s}}\langle\cdot\rangle^{\mathrm{s}}$). Equation (4.62) reproduces the modified form of Terzaghi's decomposition derived in Murad and Moyne (2002) and Moyne and Murad (2002) under the assumption $Pe=\mathcal{O}(\epsilon)$. This suggests that the closure relation for $\boldsymbol{\Pi}_{\mathrm{S}}^0$ is independent of the estimate adopted for the Péclet number. Thus, in addition to the pore pressure p_{b}^0 and contact stresses $\boldsymbol{C}_{\mathrm{s}}\boldsymbol{\mathcal{E}}_x(\mathbf{u}^0)$, the above result shows the appearance of the electro-chemical tensor $\boldsymbol{\Pi}^0$ incorporating the influence of electro-chemical effects upon the overall stresses of the clay clusters $\boldsymbol{\sigma}_{\mathrm{T}}^0$. From (4.63) this quantity is decomposed into the averaged counterpart of $\boldsymbol{\Pi}_{\mathrm{d}}^0$ (which from (4.58) is the sum of chemico-osmotic and Maxwell stresses) and the additional component $\boldsymbol{\Pi}_{\mathrm{S}}^0$, which consists of electro-chemical stresses in the solid particles owing to the traction boundary condition induced by $\boldsymbol{\Pi}_{\mathrm{d}}^{0}$ in (4.60). Since $\boldsymbol{\Pi}_{\mathrm{S}}^{0}$ represents a stress acting effectively in the solid phase, it may be viewed as the electro-chemical component directly responsible for the expansion of the aggregates. Whence, following the terminology of Moyne and Murad (2002) and Murad and Moyne (2000), we refer to this quantity as a *swelling stress tensor* which plays the role of a tensorial generalization of Low's swelling pressure to incorporate deviatoric effects. Likewise the other effective electro-chemical parameters, $\boldsymbol{\Pi}_{\mathrm{S}}^{0}$ depends in a non-linear fashion on c_{b}^{0} and on cell microgeometry (see Murad and Moyne, 2002).

The above modified Terzaghi's decomposition resembles in form some heuristic effective stress principles for clays (see, e.g., Lambe, 1960; Sridharan and Rao, 1973). Historically, physicochemical forces have heuristically been modeled at the macroscale through the addition of a term to Terzaghi's principle which measures the effect of net repulsive ($R\boldsymbol{I}$) and attractive ($A\boldsymbol{I}$) forces between particles. This stress is commonly denoted by $(R-A)\boldsymbol{I}$ (see Sridharan and Rao, 1973). The electro-static component of R has been controversially associated with different macroscopic quantities. Barbour and Fredlund (1989) and Mitchell (1993) have identified it with the averaged Donnan osmotic pressure whereas Achari *et al.* (1999) have postulated the equality between R and the averaged disjoining pressure calculated via classical Gouy–Chapmann e.d.l. theory in a parallel particle arrangement (see Newman, 1973; Van Olphen, 1979; Hunter, 1994). Moreover, within the framework of mixture theory, a similar form of (4.62) has been postulated to describe the mechanics of charged hydrated biological tissues. Likewise, an extra physico-chemical component, referred to as chemical-expansion stress (T_c), is thermodynamically introduced and included in the original form of Terzaghi's principle (see, e.g., Lai *et al.*, 1991). The mixture theory approach suggests a constitutive law for the chemical-expansion stress depending exponentially on ion concentration (Lai *et al.*, 1991). The microscopic representation (4.63) consists of a first rational attempt to overcome the discrepancies between the different macroscopic versions of the constitutive law for $\boldsymbol{\Pi}_{\mathrm{S}}^{0}$. By solving numerically the local cell problems (4.63) and (4.60) in random cell geometries one may accurately derive the constitutive behavior of the swelling stress tensor. Finally, it should be noted that for microstructural arrangements composed of parallel particles, $\boldsymbol{\Pi}_{\mathrm{S}}^{0}$ reduces to a scalar component normal to the clay surface. Such component has been identified with Low's swelling pressure (Low, 1987), given by the averaging of the disjoining pressure (see Moyne and Murad, 2002, 2006).

4.2.7. *Overall Mass Balance*

We now derive the overall macroscopic mass balance. By averaging (4.10)(b), using boundary condition (4.21)(c) together with the closure equation

(4.59) and the divergence theorem we get

$$\begin{aligned}\left\langle\nabla_x\cdot\mathbf{v}^0\right\rangle &= -\left\langle\nabla_y\cdot\mathbf{v}^1\right\rangle = -\frac{1}{|Y|}\int_\Gamma \mathbf{v}^1\cdot\boldsymbol{n}\,\mathrm{d}\Gamma = -\frac{1}{|Y|}\int_\Gamma \frac{\partial\mathbf{u}^1}{\partial t}\cdot\boldsymbol{n}\,\mathrm{d}\Gamma\\ &= \left\langle\nabla_y\cdot\frac{\partial\mathbf{u}^1}{\partial t}\right\rangle = \langle\nabla_y\cdot\boldsymbol{\xi}\rangle : \frac{\partial}{\partial t}\boldsymbol{\mathcal{E}}_x(\mathbf{u}^0) + \langle\nabla_y\cdot\boldsymbol{\zeta}\rangle\frac{\partial p_{\mathrm{b}}^0}{\partial t} + \left\langle\nabla_y\cdot\frac{\partial\mathbf{u}_\pi^1}{\partial t}\right\rangle\end{aligned}$$

with $\mathbf{A}:\mathbf{B}$ denoting the classical inner product between tensors $(A^{ij}B^{ij})$. By rewriting the above result in terms of the Darcian velocity $\mathbf{v}_{\mathrm{D}}^0$ we obtain

$$\nabla_x\cdot\mathbf{v}_{\mathrm{D}}^0 + \boldsymbol{\alpha}^* : \frac{\partial}{\partial t}\boldsymbol{\mathcal{E}}_x(\mathbf{u}^0) = \beta\frac{\partial p_{\mathrm{b}}^0}{\partial t} + \frac{\partial\gamma_\pi}{\partial t},$$

where $\alpha^*\equiv n_{\mathrm{f}}\boldsymbol{I} - \langle\nabla_y\cdot\boldsymbol{\xi}\rangle$, $\beta\equiv\langle\nabla_y\cdot\boldsymbol{\zeta}\rangle$, and $\gamma_\pi = \langle\nabla_y\cdot\mathbf{u}_\pi^1\rangle$. Using the analysis presented in Auriault (1997) one can show the classical relation $\boldsymbol{\alpha}^*\equiv n_{\mathrm{f}}\boldsymbol{I} - \langle \boldsymbol{c}_{\mathrm{s}}\boldsymbol{\mathcal{E}}_y(\boldsymbol{\zeta})\rangle = \boldsymbol{\alpha}$ a commonly adopted in Biot's theory of poroelasticity. In addition to the mechanical compressibilities α and β which appear in the theory of poroelasticity, one may also observe the appearance of the extra electro-chemical component $\partial\gamma_\pi/\partial t$ quantifying the microscopic compressibility of the particles under the traction induced by the disjoining tensor $\boldsymbol{\Pi}_{\mathrm{d}}^0$ in (4.60). This electro-chemical component has been introduced in the context of equilibrium thermodynamics by Mitchell (1993) and Barbour and Fredlund (1989). Unlike the mechanical coefficients α and β, the electro-chemical compressibility exhibits nonlinear dependence on c_{b}^0. The reader may verify that the case of microscopically incompressible particles we have $\alpha=1$ and $\beta=\gamma_\pi=0$.

4.2.8. *Mass Balance of the Fluid Phase*

To close the system it remains to derive a mass balance for the fluid phase to compute the porosity n_{f}. To this end we set $f^0=1$ and $f^1=0$ in (4.31) and make use of (4.10)(b) to obtain

$$\frac{\partial n_{\mathrm{f}}}{\partial t} + \nabla_x\cdot\left\langle\mathbf{v}^0\right\rangle = 0.$$

By rewriting the above result in terms of the Darcy velocity $\mathbf{v}_{\mathrm{D}}^0 = \left\langle\mathbf{v}^0 - \partial\mathbf{u}^0/\partial t\right\rangle$ and neglecting the convective effects induced by $\partial\mathbf{u}^0(\boldsymbol{x},t)/\partial t$ we obtain, at $\mathcal{O}(\epsilon^0)$

$$\frac{\partial n_{\mathrm{f}}}{\partial t} + \nabla_x\cdot\mathbf{v}_{\mathrm{D}}^0 + n_{\mathrm{f}}\nabla_x\cdot\frac{\partial\mathbf{u}^0}{\partial t} = 0.$$

4.3. SUMMARY OF THE TWO-SCALE MODEL

Let $\{\boldsymbol{\zeta},\boldsymbol{\xi}\}$ be the set of aforementioned coefficients depending only on cell geometry. Further let $\{\boldsymbol{f}^{\pm},\boldsymbol{\kappa}_{\mathrm{p}},\boldsymbol{\kappa}_{\mathrm{c}},\boldsymbol{\kappa}_{\mathrm{e}},\boldsymbol{h}_{\mathrm{p}}^{\pm},\boldsymbol{h}_{\mathrm{c}}^{\pm},\boldsymbol{h}_{\mathrm{e}}^{\pm}\}$ be the set of characteristic functions depending on both microgeometry and $c_{\rm b}^0(\boldsymbol{x}, t)$. The two-scale model consists in finding the macroscopic variables $\{\boldsymbol{\sigma}_{\rm T}^0, \mathbf{u}^0, p_{\rm b}^0, \mathbf{v}_{\rm D}^0, c_{\rm b}^0, \bar{\psi}_{\rm b}^0, \boldsymbol{J}_{\pm}^0, n_{\rm f}\}$ satisfying

$$
\begin{aligned}
&\nabla_x \cdot \boldsymbol{\sigma}_{\rm T}^0 = 0,\\
&\boldsymbol{\sigma}_{\rm T}^0 = -\boldsymbol{\alpha} p_{\rm b}^0 + \boldsymbol{C}_{\rm s}\boldsymbol{\mathcal{E}}_x(\mathbf{u}^0) - \boldsymbol{\Pi}^0,\\
&\mathbf{v}_{\rm D}^0 = -\boldsymbol{K}_{\rm P}\nabla_x p_{\rm b}^0 - \boldsymbol{K}_{\rm C}\nabla_x c_{\rm b}^0 - \boldsymbol{K}_{\rm E}\nabla_x \bar{\psi}_{\rm b}^0,\\
&\nabla_x \cdot \mathbf{v}_{\rm D}^0 + \boldsymbol{\alpha} : \frac{\partial}{\partial t}\boldsymbol{\mathcal{E}}_x(\mathbf{u}^0) = \beta \frac{\partial p_{\rm b}^0}{\partial t} + \frac{\partial \gamma_\pi}{\partial t},\\
&\frac{\partial}{\partial t}\left(n_{\rm f} G_{\pm} c_{\rm b}^0\right) + \nabla_x \cdot \boldsymbol{J}_{\pm}^0 = 0,\\
&\boldsymbol{J}_{\pm}^0 = G_{\pm} c_{\rm b}^0 \mathbf{v}_{\pm}^0 - n_{\rm f}\left(\boldsymbol{D}_{\pm}^{\rm c}\nabla_x c_{\rm b}^0 \pm \boldsymbol{D}_{\pm}^{\rm e} c_{\rm b}^0 \nabla_x \bar{\psi}_{\rm b}^0 + \boldsymbol{D}_{\pm}^{\rm p}\nabla_x p_{\rm b}^0\right),\\
&\frac{\partial n_{\rm f}}{\partial t} + \nabla_x \cdot \mathbf{v}_{\rm D}^0 + n_{\rm f}\nabla_x \cdot \frac{\partial \mathbf{u}^0}{\partial t} = 0 \quad \text{in } \Omega,
\end{aligned}
$$

where the components $\left\{\boldsymbol{\alpha}, \boldsymbol{C}_{\rm s}, \boldsymbol{\Pi}^0, \boldsymbol{K}_{\rm P}, \boldsymbol{K}_{\rm C}, \boldsymbol{K}_{\rm E}, \beta, \gamma_\pi, \boldsymbol{D}_{\pm}^{\rm p}, \boldsymbol{D}_{\pm}^{\rm c}, \boldsymbol{D}_{\pm}^{\rm e}, G_{\pm}, \mathbf{v}_{\pm}^0\right\}$ admit the following microscopic representations in the unit cell Y:

$$
\begin{aligned}
&\boldsymbol{\Pi}^0 = \langle \boldsymbol{\Pi}_{\rm d}^0 \rangle + n_{\rm s}\boldsymbol{\Pi}_{\rm S}^0, \quad \boldsymbol{\Pi}_{\rm S}^0 = -\left\langle \boldsymbol{c}_{\rm s}\boldsymbol{\mathcal{E}}_y\left(\mathbf{u}_\pi^1\right)\right\rangle^{\rm s}, \quad \boldsymbol{C}_{\rm s} = \langle \boldsymbol{c}_{\rm s}(\boldsymbol{I}\boldsymbol{I} + \boldsymbol{\mathcal{E}}_y(\boldsymbol{\xi}))\rangle,\\
&\boldsymbol{\alpha} = n_{\rm f}\boldsymbol{I} - \langle \boldsymbol{c}_{\rm s}\boldsymbol{\mathcal{E}}_y(\boldsymbol{\zeta})\rangle = n_{\rm f}\boldsymbol{I} - \langle \nabla_y \cdot \boldsymbol{\xi}\rangle, \quad \beta \equiv \langle \nabla_y \cdot \boldsymbol{\zeta}\rangle,\\
&\boldsymbol{K}_{\rm P} = \langle \boldsymbol{\kappa}_{\rm p}\rangle, \quad \boldsymbol{K}_{\rm C} = \langle \boldsymbol{\kappa}_{\rm c}\rangle, \quad \boldsymbol{K}_{\rm E} = \langle \boldsymbol{\kappa}_{\rm e}\rangle, \quad \gamma_\pi = \langle \nabla_y \cdot \mathbf{u}_\pi^1\rangle,\\
&\boldsymbol{D}_{\pm}^{\boldsymbol{I}} = \mathcal{D}_{\pm}\left\langle \exp\left(\mp\bar{\varphi}^0\right)\left(\boldsymbol{I} + \nabla_y \boldsymbol{f}^{\pm} + c_{\rm b}^0 \nabla_y \boldsymbol{h}_{\boldsymbol{I}}^{\pm}\right)\right\rangle^{\rm f}, \quad \boldsymbol{I} = {\rm c, e},\\
&\boldsymbol{D}_{\pm}^{\rm p} = \mathcal{D}_{\pm}\left\langle \exp(\mp\bar{\varphi}^0)\nabla_y \boldsymbol{h}_{\rm p}^{\pm}\right\rangle^{f}, \quad G_{\pm} = \left\langle \exp(\mp\bar{\varphi}^0)\right\rangle^{\rm f}, \quad G_{\pm}\mathbf{v}_{\pm}^0 = \left\langle \exp\left(\mp\bar{\varphi}^0\right)\mathbf{v}^0\right\rangle
\end{aligned}
\tag{4.64}
$$

with the set of local variables $\{\boldsymbol{\Pi}_{\rm d}^0, \bar{\varphi}^0, \boldsymbol{E}^0, \mathbf{u}_\pi^1\}$ given as

$$
\begin{aligned}
&\boldsymbol{\Pi}_{\rm d}^0 = \pi^0 \boldsymbol{I} - \boldsymbol{\tau}_{\mathbf{M}}^0, \quad \pi^0 = 2RTc_{\rm b}^0(\cosh\bar{\varphi}^0 - 1), \boldsymbol{\tau}_{\mathbf{M}}^0 = \frac{\tilde{\varepsilon}\tilde{\varepsilon}_0}{2}\left(2\boldsymbol{E}^0 \otimes \boldsymbol{E}^0 - (E^0)^2\boldsymbol{I}\right),\\
&\mathbf{v}^0 - \frac{\partial \mathbf{u}^0}{\partial t} = -\boldsymbol{\kappa}_{\rm p}\nabla_x p_{\rm b}^0 - \boldsymbol{\kappa}_{\rm c}\nabla_x c_{\rm b}^0 - \boldsymbol{\kappa}_{\rm e}\nabla_x \bar{\psi}_{\rm b}^0
\end{aligned}
$$

and

$$
\begin{array}{l|l}
\tilde{\varepsilon}\tilde{\varepsilon}_0 \Delta_{yy}\bar{\varphi}^0 = \frac{2F^2 c_{\rm b}^0}{RT}\sinh\bar{\varphi}^0 & \nabla_y \cdot (\boldsymbol{c}_{\rm s}\boldsymbol{\mathcal{E}}_y(\mathbf{u}_\pi^1)) = 0 \quad \text{in } Y_{\rm s},\\
\boldsymbol{E}^0 = -RTF^{-1}\nabla_y \bar{\varphi}^0 \quad \text{in } Y_{\rm f} & (\boldsymbol{c}_{\rm s}\boldsymbol{\mathcal{E}}_y(\mathbf{u}_\pi^1))\boldsymbol{n} = \boldsymbol{\Pi}_{\rm d}^0 \boldsymbol{n} \quad \text{on } \partial Y_{\rm fs}.\\
\tilde{\varepsilon}\tilde{\varepsilon}_0 \boldsymbol{E}^0 \cdot \boldsymbol{n} = -\sigma \quad \text{on } \partial Y_{\rm fs} &
\end{array}
$$

The above system is supplemented by initial and boundary conditions on the macroscopic boundary of the swelling medium. Finally, after solving for $\{c_{\rm b}^0, p_{\rm b}^0, \bar{\psi}_{\rm b}^0, \bar{\varphi}^0\}$, the averaged ion concentrations, fluid thermodynamic pressure and total electric potential can be recovered within a post-processing approach considering the averaged forms of (4.8)(c), (4.9)(c) and (4.12)(a). We then have

$$\langle c_{\pm}^0\rangle^{\mathrm{f}} = c_{\mathrm{b}}^0 \left\langle \exp\left(\mp\bar{\varphi}^0\right)\right\rangle^{f}, \quad \left\langle p^0\right\rangle^{\mathrm{f}} = p_{\mathrm{b}}^0 + 2RTc_{\mathrm{b}}^0\left(\langle\cosh\,\bar{\varphi}^0\rangle^{\mathrm{f}} - 1\right),$$
$$\left\langle\bar{\Phi}^0\right\rangle^{\mathrm{f}} = \left\langle\bar{\varphi}^0\right\rangle^{\mathrm{f}} + \bar{\psi}_{\mathrm{b}}^0.$$

5. Alternative Formulation: Onsager's Reciprocity Relations

The two-scale model can also be rephrased in a more appropriate formulation resembling in form the macroscopic model derived within the framework of the Thermodynamics of irreversible Processes based on Onsager's reciprocity relations (de Groot and Mazur, 1962; Prigogine, 1967). To this end we proceed by rewriting the homogenized convection-diffusion equations (4.53) in terms of the total flux of species $\boldsymbol{J}^0$, the electric current $\boldsymbol{I}_{\mathrm{e}}^0$ and the averaged net charge density q_*^0 given by

$$\boldsymbol{J}^0 + n_{\mathrm{f}} G_{\mathrm{c}} c_{\mathrm{b}}^0 \frac{\partial \mathbf{u}^0}{\partial t} \equiv \boldsymbol{J}_+^0 + \boldsymbol{J}_-^0; \qquad \boldsymbol{I}_{\mathrm{e}}^0 + F n_{\mathrm{f}} G_{\mathrm{s}} c_{\mathrm{b}}^0 \frac{\partial \mathbf{u}^0}{\partial t} \equiv F(\boldsymbol{J}_+^0 - \boldsymbol{J}_-^0);$$
$$q_*^0 = -2Fc_{\mathrm{b}}^0\left\langle\sinh\,\bar{\varphi}^0\right\rangle,$$

where (4.33) has been used. By adding and subtracting (4.53) over cations and anions we obtain

$$\frac{\partial}{\partial t}\left(n_{\mathrm{f}} G_{\mathrm{c}} c_{\mathrm{b}}^0\right) = -\nabla_x \cdot \left(n_{\mathrm{f}} G_{\mathrm{c}} c_{\mathrm{b}}^0 \frac{\partial \mathbf{u}^0}{\partial t} + \boldsymbol{J}^0,\right)$$
$$F\frac{\partial}{\partial t}\left(n_{\mathrm{f}} G_{\mathrm{s}} c_{\mathrm{b}}^0\right) = \frac{\partial q_*^0}{\partial t} = -\nabla \cdot \left(F n_{\mathrm{f}} G_{\mathrm{s}} c_{\mathrm{b}}^0 \frac{\partial \mathbf{u}^0}{\partial t} + \boldsymbol{I}_{\mathrm{e}}^0\right). \tag{5.1}$$

with

$$\boldsymbol{J}^0 \equiv G_{\mathrm{c}} c_{\mathrm{b}}^0 \mathbf{v}_{\mathrm{c}}^0 - n_{\mathrm{f}}\left(\boldsymbol{D}_*^{\mathrm{c}} \nabla_x c_{\mathrm{b}}^0 + \boldsymbol{\Delta}_*^{\mathrm{e}} c_{\mathrm{b}}^0 \nabla_x \bar{\psi}_{\mathrm{b}}^0 + \boldsymbol{D}_*^{\mathrm{p}} \nabla_x p_{\mathrm{b}}^0\right),$$
$$\boldsymbol{I}_{\mathrm{e}}^0 \equiv F G_{\mathrm{s}} c_{\mathrm{b}}^0 \mathbf{v}_{\mathrm{s}}^0 - n_{\mathrm{f}} F\left(\boldsymbol{\Delta}_*^{\mathrm{c}} \nabla_x c_{\mathrm{b}}^0 + \boldsymbol{D}_*^{\mathrm{e}} c_{\mathrm{b}}^0 \nabla_x \bar{\psi}_{\mathrm{b}}^0 + \boldsymbol{\Delta}_*^{\mathrm{p}} \nabla_x p_{\mathrm{b}}^0\right) \tag{5.2}$$

and the set of overall electric capacities and diffusion coefficients given as

$$G_{\mathrm{c}} = G_+ + G_- = 2\langle\cosh\bar{\varphi}^0\rangle^{\mathrm{f}}; \quad G_{\mathrm{s}} = G_+ - G_- = -2\langle\sinh\bar{\varphi}^0\rangle^{f}; \tag{5.3}$$

$$G_{\mathrm{c}}\mathbf{v}_{\mathrm{ch}}^0 = G_+\left(\mathbf{v}_+^0 - n_{\mathrm{f}}\frac{\partial \mathbf{u}^0}{\partial t}\right) + G_-\left(\mathbf{v}_-^0 - n_{\mathrm{f}}\frac{\partial \mathbf{u}^0}{\partial t}\right) = 2\left\langle\cosh\bar{\varphi}^0\left(\mathbf{v}^0 - \frac{\partial \mathbf{u}^0}{\partial t}\right)\right\rangle;$$
$$G_{\mathrm{s}}\mathbf{v}_{\mathrm{sh}}^0 = G_+\left(\mathbf{v}_+^0 - n_{\mathrm{f}}\frac{\partial \mathbf{u}^0}{\partial t}\right) - G_-\left(\mathbf{v}_-^0 - n_{\mathrm{f}}\frac{\partial \mathbf{u}^0}{\partial t}\right) = -2\left\langle\sinh\bar{\varphi}^0\left(\mathbf{v}^0 - \frac{\partial \mathbf{u}^0}{\partial t}\right)\right\rangle; \tag{5.4}$$

$$\boldsymbol{D}_*^{\boldsymbol{I}} = \boldsymbol{D}_+^{\boldsymbol{I}} + \boldsymbol{D}_-^{\boldsymbol{I}}, \quad \boldsymbol{\Delta}_*^{\boldsymbol{I}} = \boldsymbol{D}_+^{\boldsymbol{I}} - \boldsymbol{D}_-^{\boldsymbol{I}}, \quad \boldsymbol{I} = \mathrm{p, c, e}. \tag{5.5}$$

In order to embed the constitutive relations for $\{\mathbf{v}_{\mathrm{D}}^0, \boldsymbol{J}_{\mathrm{c}}^0, \boldsymbol{I}_{\mathrm{e}}^0\}$ in the framework of Onsager's reciprocity relations, we remove the purely advective component of nonionic species $2c_{\mathrm{b}}^{0}\mathbf{v}_{\mathrm{D}}^{0}$ from $\boldsymbol{J}^{0}$ and define the diffusive flux $\boldsymbol{J}_{\mathrm{c}}^{0}$ in the sense of Onsager in the form

$$\boldsymbol{J}_{\mathrm{c}}^{0} \equiv \boldsymbol{J}^{0} - 2c_{\mathrm{b}}^{0}\mathbf{v}_{\mathrm{D}}^{0} = c_{\mathrm{b}}^{0}\left(G_{\mathrm{c}}\mathbf{v}_{\mathrm{c}}^{0} - 2\langle\mathbf{v}^{0}\rangle\right) - n_{\mathrm{f}}\left(\boldsymbol{D}_{*}^{\mathrm{c}}\nabla_{x}c_{\mathrm{b}}^{0} + \boldsymbol{\Delta}_{*}^{\mathrm{e}}c_{\mathrm{b}}^{0}\nabla_{x}\bar{\psi}_{\mathrm{b}}^{0} + \boldsymbol{D}_{*}^{\mathrm{p}}\nabla_{x}p_{\mathrm{b}}^{0}\right). \tag{5.6}$$

Unlike $\boldsymbol{J}^{0}$, the flux $\boldsymbol{J}_{\mathrm{c}}^{0}$ only incorporates the fluctuation in the advection velocity $(G_{\mathrm{c}}\mathbf{v}_{\mathrm{c}}^{0} - 2\mathbf{v}_{\mathrm{D}}^{0})$ resulting from the interaction with the e.d.l. In the absence of e.d.l. effects $(\sinh\bar{\varphi} = 0, \cosh\bar{\varphi}^{1} = 1, G_{\mathrm{s}} = 0, G_{\mathrm{c}} = 2, \mathbf{v}_{\mathrm{c}}^{0} = \langle\mathbf{v}^{0} - \partial\mathbf{u}^{0}/\partial t\rangle = \mathbf{v}_{\mathrm{D}}^{0})$, the advective parts of $\boldsymbol{J}_{\mathrm{c}}^{0}$ and $\boldsymbol{I}_{\mathrm{e}}^{0}$ vanish and the constitutive laws of these fluxes become purely diffusive.

Using (4.50), (4.48) and (5.4) in (5.2) and (5.6) we have

$$\begin{aligned}\boldsymbol{J}_{\mathrm{c}}^{0} = &-\left(2c_{\mathrm{b}}^{0}\langle\kappa_{\mathrm{p}}(\cosh\bar{\varphi}^{0} - 1)\rangle + n_{\mathrm{f}}\boldsymbol{D}_{*}^{\mathrm{p}}\right)\nabla_{x}p_{\mathrm{b}}^{0} - \left(2c_{\mathrm{b}}^{0}\langle\kappa_{\mathrm{c}}(\cosh\bar{\varphi}^{0} - 1)\rangle +\right.\\ &\left.+n_{\mathrm{f}}\boldsymbol{D}_{*}^{\mathrm{c}}\right)\nabla_{x}c_{\mathrm{b}}^{0} - c_{\mathrm{b}}^{0}\left(2\langle\kappa_{\mathrm{e}}(\cosh\bar{\varphi}^{0} - 1)\rangle + n_{\mathrm{f}}\boldsymbol{\Delta}_{*}^{\mathrm{e}}\right)\nabla_{x}\bar{\psi}_{\mathrm{b}}^{0},\end{aligned} \tag{5.7}$$

$$\begin{aligned}\boldsymbol{I}_{\mathrm{e}}^{0} = &-F\left(-2c_{\mathrm{b}}^{0}\langle\kappa_{\mathrm{p}}\sinh\bar{\varphi}^{0}\rangle + n_{\mathrm{f}}\boldsymbol{\Delta}_{*}^{\mathrm{p}}\right)\nabla_{x}p_{\mathrm{b}}^{0} - F\left(-2c_{\mathrm{b}}^{0}\langle\kappa_{\mathrm{c}}\sinh\bar{\varphi}^{0}\rangle + n_{\mathrm{f}}\boldsymbol{\Delta}_{*}^{\mathrm{c}}\right)\nabla_{x}c_{\mathrm{b}}^{0} -\\ &-F\left(2c_{\mathrm{b}}^{0}\langle\kappa_{\mathrm{e}}\sinh\bar{\varphi}^{0}\rangle + n_{\mathrm{f}}\boldsymbol{D}_{*}^{\mathrm{e}}\right)\nabla_{x}\bar{\psi}_{\mathrm{b}}^{0}.\end{aligned} \tag{5.8}$$

Hence, replacing $\nabla_{x}\bar{\psi}_{\mathrm{b}}^{0}$ by $\nabla_{x}\psi_{\mathrm{b}}^{0}$ and $\nabla_{x}c_{\mathrm{b}}^{0}$ by $\nabla_{x}\mu_{\mathrm{b}}^{0} = RT\nabla_{x}\ln c_{\mathrm{b}}^{0}$ (commonly referred to as gradient of the Nernst potential Gu *et al.*, 1998) from (4.50), (5.7) and (5.8) the three fluxes $\{\mathbf{v}_{\mathrm{D}}^{0}, \boldsymbol{J}_{\mathrm{c}}^{0}, \boldsymbol{I}_{\mathrm{e}}^{0}\}$ appear conjugated (in the thermodynamical sense) with the three driving forces $\{\nabla_{x}p_{\mathrm{b}}^{0}, \nabla_{x}\mu_{\mathrm{b}}^{0}, \nabla_{x}\psi_{\mathrm{b}}^{0}\}$ in the form:

$$\begin{pmatrix}\mathbf{v}_{\mathrm{D}}^{0}\\ \boldsymbol{J}_{\mathrm{c}}^{0}\\ \boldsymbol{I}_{\mathrm{e}}^{0}\end{pmatrix} = -\begin{pmatrix}\boldsymbol{L}_{\mathrm{PP}} & \boldsymbol{L}_{\mathrm{PC}} & \boldsymbol{L}_{\mathrm{PE}}\\ \boldsymbol{L}_{\mathrm{CP}} & \boldsymbol{L}_{\mathrm{CC}} & \boldsymbol{L}_{\mathrm{CE}}\\ \boldsymbol{L}_{\mathrm{EP}} & \boldsymbol{L}_{\mathrm{EC}} & \boldsymbol{L}_{\mathrm{EE}}\end{pmatrix}\begin{pmatrix}\nabla_{x}p_{\mathrm{b}}^{0}\\ RT\nabla_{x}\ln c_{\mathrm{b}}^{0}\\ \nabla_{x}\psi_{\mathrm{b}}^{0}\end{pmatrix}$$

with

$$\boldsymbol{L}_{\mathrm{PP}} = \boldsymbol{K}_{\mathrm{P}}, \qquad \boldsymbol{L}_{\mathrm{PC}} = \frac{c_{\mathrm{b}}^{0}\boldsymbol{K}_{\mathrm{C}}}{RT}, \qquad \boldsymbol{L}_{\mathrm{PE}}\frac{F\boldsymbol{K}_{\mathrm{E}}}{RT}, \tag{5.9}$$

$$\boldsymbol{L}_{\mathrm{CP}} = \left(2c_{\mathrm{b}}^{0}\left\langle\boldsymbol{\kappa}_{\mathrm{p}}(\cosh\bar{\varphi}^{0} - 1)\right\rangle + n_{\mathrm{f}}\boldsymbol{D}_{*}^{\mathrm{p}}\right), \quad \boldsymbol{L}_{\mathrm{CC}} = \frac{c_{\mathrm{b}}^{0}}{RT}\left(2c_{\mathrm{b}}^{0}\left\langle\boldsymbol{\kappa}_{\mathrm{c}}(\cosh\bar{\varphi}^{0} - 1)\right\rangle + n_{\mathrm{f}}\boldsymbol{D}_{*}^{\mathrm{c}}\right),$$

$$\boldsymbol{L}_{\mathrm{CE}} = \frac{Fc_{\mathrm{b}}^{0}}{RT}\left(2\left\langle\boldsymbol{\kappa}_{\mathrm{e}}(\cosh\bar{\varphi}^{0} - 1)\right\rangle + n_{\mathrm{f}}\boldsymbol{\Delta}_{*}^{\mathrm{e}}\right), \quad \boldsymbol{L}_{\mathrm{EP}} = F\left(-2c_{\mathrm{b}}^{0}\left\langle\boldsymbol{\kappa}_{\mathrm{p}}\sinh\bar{\varphi}^{0}\right\rangle + n_{\mathrm{f}}\boldsymbol{\Delta}_{*}^{\mathrm{p}}\right),$$

$$\boldsymbol{L}_{\mathrm{EC}} = \frac{Fc_{\mathrm{b}}^{0}}{RT}\left(-2c_{\mathrm{b}}^{0}\left\langle\boldsymbol{\kappa}_{\mathrm{c}}\sinh\bar{\varphi}^{0}\right\rangle + n_{\mathrm{f}}\boldsymbol{\Delta}_{*}^{\mathrm{c}}\right), \quad \boldsymbol{L}_{\mathrm{EE}} = \frac{F^{2}c_{\mathrm{b}}^{0}}{RT}\left(-2\left\langle\boldsymbol{\kappa}_{\mathrm{e}}\sinh\bar{\varphi}^{0}\right\rangle + n_{\mathrm{f}}\boldsymbol{D}_{*}^{\mathrm{e}}\right).$$

The above equations are nothing but Onsager's reciprocity relations. The coefficients $\boldsymbol{L}_{\mathrm{EE}}$ and $\boldsymbol{L}_{\mathrm{EP}}$ are commonly referred to as the electric conductivity in Ohm's law and the streaming current parameter which reflects electric current driven by hydraulic gradients (Lyklema, 1993). By establishing a direct correlation between the magnitude of the Onsager's coefficients and the microscopic electro-chemical behavior of the electrolyte solution, the closure problems in (5.9) bridge the gap between the macroscopic Thermodynamics of Irreversible Processes and microscopic Colloid Science of electrolyte solutions.

5.1. ALTERNATIVE FORM OF THE ELECTRONEUTRALITY CONDITION

By rephrasing the purely advective transport equation of the species in the solid phase (4.55) in terms of the averaged net charge density $q_*^{s0} \equiv F\langle c_+^{s0} - c_-^{s0}\rangle$ we obtain

$$\frac{\partial q_*^{s0}}{\partial t} + \nabla_x \cdot \left(q_*^{s0} \frac{\partial \mathbf{u}^0}{\partial t} \right) = 0.$$

Defining the surface averaging $\langle\sigma\rangle^{fs} \equiv |\partial Y_{fs}|^{-1} \int_{\partial Y_{fs}} \sigma \, d\Gamma$ and the surface volume fraction $n_{f_s} = |\partial Y_{fs}|/|Y|$, by combining the above result with (4.34) gives

$$\frac{\partial}{\partial t}\left(n_{fs}\langle\sigma\rangle^{fs}\right) + \nabla_x \cdot \left(n_{fs}\langle\sigma\rangle^{fs} \frac{\partial \mathbf{u}^0}{\partial t} \right) = 0. \tag{5.10}$$

The above result is nothing but the macroscopic conservation of the fixed charges in the solid–fluid interface (see Gray and Hassanizadeh (1989), Hassanizadeh and Gray (1990) for derivation within a surface averaging procedure). Finally, using (5.4) and the electroneutrality condition (4.33) to replace the term $n_{fs}\langle\sigma\rangle^{fs}$ in (5.10), along with the definition of the capacity G_s, we arrive at

$$\frac{\partial}{\partial t}\left(n_f G_s c_b^0\right) + \nabla_x \cdot \left(n_f G_s c_b^0 \frac{\partial \mathbf{u}^0}{\partial t} \right) = 0$$

in which when combined with the conservation of charge (5.1) gives

$$\nabla_x \cdot \mathbf{I}_e^0 = 0.$$

5.2. SUMMARY OF THE ALTERNATIVE FORMULATION BASED ON ONSAGER'S RECIPROCITY RELATIONS

The alternative two-scale model consists in finding the macroscopic variables $\{\boldsymbol{\sigma}_T^0, \mathbf{u}^0, p_b^0, c_b^0, \psi_b^0, \mathbf{v}_D^0, \boldsymbol{J}_c^0, \boldsymbol{I}_e^0, n_f\}$ satisfying

$$\nabla_x \cdot \boldsymbol{\sigma}_T^0 = 0,$$
$$\boldsymbol{\sigma}_T^0 = -\boldsymbol{\alpha} p_b^0 + \boldsymbol{C}_s \boldsymbol{\mathcal{E}}_x(\mathbf{u}^0) - \boldsymbol{\Pi}^0,$$
$$\nabla_x \cdot \mathbf{v}_D^0 + \boldsymbol{\alpha} : \frac{\partial}{\partial t}\boldsymbol{\mathcal{E}}_x(\mathbf{u}^0) = \beta \frac{\partial p_b^0}{\partial t} + \frac{\partial \gamma_\pi}{\partial t},$$

$$\begin{aligned}
&\frac{\partial n_{\mathrm{f}}}{\partial t}+\boldsymbol{\nabla}_x.\mathbf{v}_D^0+n_f\boldsymbol{\nabla}_x.\frac{\partial u^0}{\partial t}=0,\\
&\frac{\partial}{\partial t}(n_{\mathrm{f}}G_{\mathrm{c}}c_{\mathrm{b}}^0)+\boldsymbol{\nabla}_x\cdot\left(2c_{\mathrm{b}}^0\mathbf{v}_{\mathrm{D}}^0+n_{\mathrm{f}}G_{\mathrm{c}}c_{\mathrm{b}}^0\frac{\partial\mathbf{u}^0}{\partial t}+\boldsymbol{J}_{\mathrm{c}}^0\right)=0,\\
&\boldsymbol{\nabla}_x\cdot\boldsymbol{I}_{\mathrm{e}}^0=0,\quad \text{in }\Omega,\\
&\mathbf{v}_{\mathrm{D}}^0=-\boldsymbol{L}_{\mathrm{PP}}\boldsymbol{\nabla}_x p_{\mathrm{b}}^0-RT\boldsymbol{L}_{\mathrm{PC}}\boldsymbol{\nabla}_x\ln c_{\mathrm{b}}^0-\boldsymbol{L}_{\mathrm{PE}}\boldsymbol{\nabla}_x\psi_{\mathrm{b}}^0,\\
&\boldsymbol{J}_{\mathrm{c}}^0=-\boldsymbol{L}_{\mathrm{CP}}\boldsymbol{\nabla}_x p_{\mathrm{b}}^0-RT\boldsymbol{L}_{\mathrm{CC}}\boldsymbol{\nabla}_x\ln c_{\mathrm{b}}^0-\boldsymbol{L}_{\mathrm{CE}}\boldsymbol{\nabla}_x\psi_{\mathrm{b}}^0,\\
&\boldsymbol{I}_{\mathrm{e}}^0=-\boldsymbol{L}_{\mathrm{EP}}\boldsymbol{\nabla}_x p_{\mathrm{b}}^0-RT\boldsymbol{L}_{\mathrm{EC}}\boldsymbol{\nabla}_x\ln c_{\mathrm{b}}^0-\boldsymbol{L}_{\mathrm{EE}}\boldsymbol{\nabla}_x\psi_{\mathrm{b}}^0
\end{aligned}$$

with the coefficients $\{\alpha, \boldsymbol{C}_{\mathrm{s}}, \boldsymbol{\Pi}^0, \beta, \gamma_\pi\}$ admitting the aforementioned microscopic representations (4.64), the electric capacities $\{G_{\mathrm{c}}, G_{\mathrm{s}}\}$ given by (5.3)(a) and (5.4)(a) and the Onsager's coefficients $\boldsymbol{L}_{IJ}(I, J = \mathrm{P, C, E}\}$ microscopically represented by the set of equations in (5.9).

5.3. REMARKS ON THE SYMMETRY OF ONSAGER'S RELATIONS

The microscopic representations (5.9) for the Onsager's parameters can be further exploited to establish the precise microscopic conditions for the validity of the symmetry of the matrix L_{IJ}. In what follows we show that if the electro-chemical potentials of the ions do not fluctuate in the micropores, $(\boldsymbol{\nabla}_y\mu_\pm^1=0)$, then the Onsager's matrix is symmetric. To show this conjecture we use this assumption in (4.9)(b) and in the closure relation (4.36). For $c_{\mathrm{b}}^0=c_{\mathrm{b}}^0(\boldsymbol{x},t)$ and $\bar{\psi}_{\mathrm{b}}^0=\bar{\psi}_{\mathrm{b}}^0(\boldsymbol{x},t)$ this yields

$$0=\frac{c_{\mathrm{b}}}{RT}\boldsymbol{\nabla}_y\mu_\pm^1=\boldsymbol{\nabla}_y c_b^1\pm c_{\mathrm{b}}^0\boldsymbol{\nabla}_y\bar{\psi}_{\mathrm{b}}^1=c_{\mathrm{b}}^0\boldsymbol{\nabla}_y\chi^\pm+(\boldsymbol{\nabla}_x c_b^0\pm c_{\mathrm{b}}^0\boldsymbol{\nabla}_x\bar{\psi}_{\mathrm{b}}^0(\boldsymbol{x},t))\boldsymbol{\nabla}_y\boldsymbol{f}^\pm. \tag{5.11}$$

We shall henceforth denote $\boldsymbol{L}_{IJ}^*(I, J = \mathrm{P, C, E})$ the set of reduced Onsager's parameters which satisfy the microscopic representations (5.9) in conjunction with the local equilibrium constraint (5.11). To exploit further consequences begin by noting that since c_{b}^0 and $\boldsymbol{\nabla}_x c_b^0\pm c_{\mathrm{b}}^0\boldsymbol{\nabla}_x\bar{\psi}_{\mathrm{b}}^0$ may vary independently, (5.11) is only fulfilled under the condition $\boldsymbol{\nabla}_y\chi^\pm=\boldsymbol{\nabla}_y\boldsymbol{f}^\pm=0$. In addition, by invoking the last equation in (4.47) we also have $\boldsymbol{\nabla}_y\boldsymbol{h}_i^\pm=0$ $(i=\mathrm{p, c, e})$. Using this latter result in (4.64), (5.5), (4.42) and (4.43) implies that the coefficients $\boldsymbol{D}_\pm^{\mathrm{p}}$ and $\boldsymbol{\Delta}_\pm^{\mathrm{p}}$ vanish and the other tensors $\boldsymbol{F}, \boldsymbol{G}, \boldsymbol{D}_\pm^I, \boldsymbol{D}_*^I$ and $\boldsymbol{\Delta}_*^I(\mathrm{I}=\mathrm{C, E})$ reduce to multiples of the identity, $\boldsymbol{F}=F_*\boldsymbol{I}, \boldsymbol{G}=G_*\boldsymbol{I}$, $\boldsymbol{D}_\pm^I=D_\pm^I\boldsymbol{I}, \boldsymbol{D}_*^I=D_*^I\boldsymbol{I}$ and $\boldsymbol{\Delta}_*^I=\Delta_*^I$ with

$$F_*=2RT(\cosh\bar{\varphi}^0-1),\qquad G_*=-2RTc_{\mathrm{b}}^0\sinh\bar{\varphi}^0 \tag{5.12}$$

and

$$\begin{aligned}
&D^{\mathrm{c}}_{\pm} = D^{\mathrm{e}}_{\pm} = D_{\pm} = \mathcal{D}_{\pm}\langle \exp(\mp\bar{\varphi}^0)\rangle,\\
&D^{\mathrm{c}}_{*} = D^{\mathrm{e}}_{*} = D_{*} = \mathcal{D}_{+}\langle \exp(-\bar{\varphi}^0)\rangle + \mathcal{D}_{-}\langle \exp(\bar{\varphi}^0)\rangle,\\
&\Delta^{\mathrm{c}}_{*} = \Delta^{\mathrm{e}}_{*} = \Delta_{*} = \mathcal{D}_{+}\langle \exp(-\bar{\varphi}^0)\rangle - \mathcal{D}_{-}\langle \exp(\bar{\varphi}^0)\rangle.
\end{aligned} \tag{5.13}$$

In addition, using the simplifications $h_i^{\pm j} = h_i^{\pm j}(\boldsymbol{x}, t)$ and (5.12) in (4.44)–(4.46) lead to classical Stokes-type problems (resembling in form the one derived in Moyne and Murad (2002), formulated in terms of the reduced unknowns $\{\boldsymbol{\kappa}^j_{\mathrm{p}*}, \boldsymbol{\kappa}^j_{\mathrm{c}*}, \boldsymbol{\kappa}^j_{\mathrm{e}*}\}$ and $\{g^j_{\mathrm{p}*}, g^j_{\mathrm{c}*}, g^j_{\mathrm{e}*}\}$ We then have

$$\begin{aligned}
&\mu_{\mathrm{f}}\Delta_{yy}\boldsymbol{\kappa}^j_{\mathrm{p}*} - \nabla_y g^j_{\mathrm{p}*} = -\boldsymbol{e}^j,\\
&\nabla_y \cdot \boldsymbol{\kappa}^j_{\mathrm{p}*} = 0, \quad j = 1, 2, 3,\\
&\boldsymbol{\kappa}^j_{\mathrm{p}*} = 0 \quad \text{on } \partial Y_{\mathrm{fs}}
\end{aligned} \tag{5.14}$$

and

$$\left.\begin{aligned}
&\mu_{\mathrm{f}}\Delta_{yy}\boldsymbol{\kappa}^j_{\mathrm{c}*} - \nabla_y g^j_{\mathrm{c}*} = -F_*\boldsymbol{e}^j\\
&\nabla_y \cdot \boldsymbol{\kappa}^j_{\mathrm{c}*} = 0\\
&\boldsymbol{\kappa}^j_{\mathrm{c}*} = 0 \quad \text{on } \partial Y_{\mathrm{fs}}
\end{aligned}\right|
\begin{aligned}
&\mu_{\mathrm{f}}\Delta_{yy}\boldsymbol{\kappa}^j_{\mathrm{e}*} - \nabla_y g^j_{\mathrm{e}*} = -G_*\boldsymbol{e}^j,\\
&\nabla_y \cdot \boldsymbol{\kappa}^j_{\mathrm{e}*} = 0, \quad j = 1, 2, 3,\\
&\boldsymbol{\kappa}^j_{\mathrm{e}*} = 0 \quad \text{on } \partial Y_{\mathrm{fs}}.
\end{aligned} \tag{5.15}$$

For $j = 1, 2, 3$, define the reduced tensorial functions $\boldsymbol{\kappa}_i^* = \boldsymbol{\kappa}_i^{*j}$ $(i = \mathrm{p, c, e})$ and the averaged reduced permeabilities $\boldsymbol{K}^*_{\mathrm{P}} = \langle\boldsymbol{\kappa}_{\mathrm{p}*}\rangle$, $\boldsymbol{K}^*_{\mathrm{C}} = \langle\boldsymbol{\kappa}_{\mathrm{c}*}\rangle$ and $\boldsymbol{K}^*_{\mathrm{E}} = \langle\boldsymbol{\kappa}_{\mathrm{e}*}\rangle$. Using (5.13) for the diffusivities, the micromechanical representations (5.9) for the reduced Onsager's coefficients L^*_{IJ} can be rewritten in the simplified form

$$\boldsymbol{L}^*_{\mathrm{PP}} = \boldsymbol{K}^*_{\mathrm{P}}, \quad \boldsymbol{L}^*_{\mathrm{PC}} = \frac{c^0_{\mathrm{b}}\boldsymbol{K}^*_{\mathrm{C}}}{RT}, \quad \boldsymbol{L}^*_{\mathrm{PE}} = \frac{F\boldsymbol{K}_{\mathrm{E}*}}{RT}, \tag{5.16}$$

$$\begin{aligned}
&\boldsymbol{L}^*_{\mathrm{CP}} = 2c^0_{\mathrm{b}}\langle\boldsymbol{\kappa}_{\mathrm{p}*}(\cosh\bar{\varphi}^0 - 1)\rangle, \quad \boldsymbol{L}^*_{\mathrm{CC}} = \frac{c^0_{\mathrm{b}}}{RT}\left(2c^0_{\mathrm{b}}\langle\boldsymbol{\kappa}_{\mathrm{c}*}(\cosh\bar{\varphi}^0 - 1)\rangle, + n_{\mathrm{f}}D_*\boldsymbol{I}\right),\\
&\boldsymbol{L}^*_{\mathrm{CE}} = \frac{Fc^0_{\mathrm{b}}}{RT}\left(2\langle\boldsymbol{\kappa}_{\mathrm{e}*}(\cosh\bar{\varphi}^0 - 1)\rangle + n_{\mathrm{f}}\Delta_*\boldsymbol{I}\right), \quad \boldsymbol{L}^*_{\mathrm{EP}} = -2Fc^0_{\mathrm{b}}\langle\boldsymbol{\kappa}_{\mathrm{p}*}\sinh\bar{\varphi}^0\rangle,\\
&\boldsymbol{L}^*_{\mathrm{EC}} = \frac{Fc^0_{\mathrm{b}}}{RT}\left(-2c^0_{\mathrm{b}}\langle\boldsymbol{\kappa}_{\mathrm{c}*}\sinh\bar{\varphi}^0\rangle + n_{\mathrm{f}}\Delta_*\boldsymbol{I}\right), \quad \boldsymbol{L}^*_{\mathrm{EE}} = \frac{F^2c^0_{\mathrm{b}}}{RT}\left(-2\langle\boldsymbol{\kappa}_{\mathrm{e}*}\sinh\bar{\varphi}^0\rangle + n_{\mathrm{f}}D_*\boldsymbol{I}\right).
\end{aligned}$$

In what follows we begin by showing symmetry of the off-diagonal components $\boldsymbol{L}^*_{\mathrm{IJ}} = \boldsymbol{L}^*_{\mathrm{JI}}$, $\boldsymbol{I} \neq J$. The same arguments of the proof are furthermore adopted to show symmetry of the tensorial components in the diagonal of $\boldsymbol{L}^*_{IJ}$.

5.3.1. *Relation Between L^*_{PE} and L^*_{EP}*

We begin by showing the equality between the reduced electro-osmotic permeability $\boldsymbol{L}^*_{\mathrm{PE}}$ and the streaming current parameter $\boldsymbol{L}^*_{\mathrm{EP}}$. To this end we make use of the usual tensor representation in tensorial products of the orthonormal basis $\boldsymbol{\kappa}_* = \sum_{i=1}^{3} \sum_{j=1}^{3} = \kappa_*^{ij} \boldsymbol{e}^i \otimes \boldsymbol{e}^j$ with components $\kappa_*^{ij} = \boldsymbol{e}^i \cdot \boldsymbol{\kappa}_*^j = \boldsymbol{\kappa}_* \boldsymbol{e}^j \cdot \boldsymbol{e}^i$. We then have from the microscopic representation of $\boldsymbol{L}_{\mathrm{EP}}^*$ in (5.16) along with (5.12)(b) and (5.15)(b)

$$
\begin{aligned}
\boldsymbol{L}_{\mathrm{EP}}^* &= -2Fc_{\mathrm{b}}^0 \langle \boldsymbol{\kappa}_{\mathrm{p}*} \sinh \bar{\varphi}^0 \rangle = \frac{F}{RT} \langle G_* \boldsymbol{I} \boldsymbol{\kappa}_{\mathrm{p}*} \rangle = \frac{F}{RT} \sum_{i=1}^{3} \sum_{j=1}^{3} \langle G_* \boldsymbol{\kappa}_{\mathrm{p}*}^{ij} \rangle \boldsymbol{e}^i \otimes \boldsymbol{e}^j \\
&= \frac{F}{RT} \sum_{i=1}^{3} \sum_{j=1}^{3} \langle G_* \boldsymbol{e}^i \cdot \boldsymbol{\kappa}_{\mathrm{p}*}^j \rangle \boldsymbol{e}^i \otimes \boldsymbol{e}^j \\
&= \frac{F}{RT} \sum_{i=1}^{3} \sum_{j=1}^{3} \left\langle (-\mu_{\mathrm{f}} \Delta_{yy} \boldsymbol{\kappa}_{\mathrm{e}*}^i + \nabla_y g_{\mathrm{e}*}^i) \cdot \boldsymbol{\kappa}_{\mathrm{p}*}^j \right\rangle \boldsymbol{e}^i \otimes \boldsymbol{e}^j. \qquad (5.17)
\end{aligned}
$$

Using the incompressibility and the nonslip conditions in (5.14) along with the periodicity, the coefficients in the last term of the r.h.s. of (5.17) vanish. In fact we have

$$
\begin{aligned}
\langle \nabla_y g_{\mathrm{e}*}^i \cdot \boldsymbol{\kappa}_{\mathrm{p}*}^j \rangle &= \frac{1}{|Y|} \int_{Y_{\mathrm{f}}} \nabla_y g_{\mathrm{e}*}^i \cdot \boldsymbol{\kappa}_{\mathrm{p}*}^j \, \mathrm{d}Y = \frac{1}{|Y|} \int_{Y_{\mathrm{f}}} \nabla_y \cdot (g_{\mathrm{e}*}^i \cdot \boldsymbol{\kappa}_{\mathrm{p}*}^j) \, \mathrm{d}Y \\
&= \frac{1}{|Y|} \int_{\partial Y_{\mathrm{f}}} g_{\mathrm{e}*}^i \boldsymbol{\kappa}_{\mathrm{p}*}^j \cdot n \, \mathrm{d}\Gamma = 0 \quad i, j = 1, 2, 3.
\end{aligned}
$$

Further, denoting L_{EP}^{*ij} the components of L_{EP}^*, using Green's theorem and the above result in (5.17) we obtain for $i, j = 1, 2, 3$

$$
\begin{aligned}
L_{\mathrm{EP}}^{*ij} &= -\frac{F\mu_{\mathrm{f}}}{RT} \left\langle \Delta_{yy} \boldsymbol{\kappa}_{\mathrm{e}*}^i \cdot \boldsymbol{\kappa}_{\mathrm{p}*}^i \right\rangle \\
&= -\frac{F\mu_{\mathrm{f}}}{RT|Y|} \int_{\partial Y_{\mathrm{fs}}} \nabla_{\mathrm{y}} \boldsymbol{\kappa}_{e*}^{\mathrm{i}} \boldsymbol{n} \cdot \boldsymbol{\kappa}_{p*}^{\mathrm{j}} \, \mathrm{d}\Gamma + \frac{F\mu_{\mathrm{f}}}{RT} \left\langle \nabla_y \boldsymbol{\kappa}_{\mathrm{e}*}^i \cdot \nabla_y \boldsymbol{\kappa}_{\mathrm{p}*}^j \right\rangle, \qquad (5.18)
\end{aligned}
$$

where the first term in the r.h.s. vanishes due to the nonslip condition. Hence, again integrating by parts, using the incompressibility and non-slip conditions for $\boldsymbol{\kappa}_{e*}^j$ along with (5.14) we obtain

$$
\begin{aligned}
L_{\mathrm{EP}}^{*ij} &= \frac{F\mu_{\mathrm{f}}}{RT} \langle \nabla_y \boldsymbol{\kappa}_{e*}^i \cdot \nabla_y \boldsymbol{\kappa}_{\mathrm{p}*}^j \rangle = -\frac{F\mu_{\mathrm{f}}}{RT} \langle \Delta_{yy} \boldsymbol{\kappa}_{\mathrm{p}*}^j \cdot \boldsymbol{\kappa}_{\mathrm{e}*}^i \rangle = \frac{F}{RT} \langle (\boldsymbol{e}^j - \nabla_y g_{\mathrm{p}*}^j) \cdot \boldsymbol{\kappa}_{\mathrm{e}*}^i \rangle \\
&= \frac{F}{RT} \langle \boldsymbol{e}^j \cdot \boldsymbol{\kappa}_{\mathrm{e}*}^i - \nabla_y \cdot (g_{\mathrm{p}*}^j \boldsymbol{\kappa}_{\mathrm{e}*}^i) \rangle = \frac{F}{RT} \langle \boldsymbol{e}^j \cdot \boldsymbol{\kappa}_{\mathrm{e}*}^i \rangle = \frac{F}{RT} \langle \boldsymbol{\kappa}_{\mathrm{e}*}^{ji} \rangle = L_{\mathrm{PE}}^{*ji}, \quad i, j = 1, 2, 3,
\end{aligned}
$$

which shows the desired result.

5.3.2. *Relation between L_{CP}^* and L_{PC}^**

The proof of the equality between the other Onsager's parameters follows an entirely analogous procedure. To show the relation between $\mathrm{L}_{\mathrm{CP}}^*$ and $\mathrm{L}_{\mathrm{PC}}^*$ we have

$$
\begin{aligned}
L^*_{\rm CP} &= 2c^0_{\rm b}\big\langle \boldsymbol{\kappa}_{\rm p*}(\cosh\bar{\varphi}^0 - 1)\big\rangle = \frac{c^{\rm b}_0}{RT}\big\langle F_*\boldsymbol{I}\boldsymbol{\kappa}_{\rm p*}\big\rangle = \frac{c^0_{\rm b}}{RT}\sum_{i=1}^{3}\sum_{j=1}^{3}\big\langle F_*\boldsymbol{\kappa}^{ij}_{\rm p*}\big\rangle \boldsymbol{e}^i\otimes\boldsymbol{e}^j\\
&= \frac{c^0_{\rm b}}{RT}\sum_{i=1}^{3}\sum_{j=1}^{3}\big\langle F_*\boldsymbol{e}^i\cdot\boldsymbol{\kappa}^j_{\rm p*}\big\rangle\\
&= \frac{c^0_{\rm b}}{RT}\sum_{i=1}^{3}\sum_{j=1}^{3}\big\langle(-\mu_{\rm f}\Delta_{yy}\boldsymbol{\kappa}^i_{\rm c*} + \nabla_y g^i_{\rm c*})\cdot\boldsymbol{\kappa}^j_{\rm p*}\big\rangle\boldsymbol{e}^i\otimes\boldsymbol{e}^j.
\end{aligned}
\tag{5.19}
$$

By the same aforementioned arguments the coefficients in the last term of the r.h.s. vanish. We then obtain for each component $i, j = 1, 2, 3$

$$
\begin{aligned}
L^{*ij}_{\rm CP} &= -\frac{c^0_b\mu_{\rm f}}{RT}\big\langle\Delta_{yy}\boldsymbol{\kappa}^i_{c*}\cdot\boldsymbol{\kappa}^j_{p*}\big\rangle\\
&= -\frac{c^0_b\mu_{\rm f}}{RT|Y|}\int_{\partial Y_{\rm fs}}\nabla_y\boldsymbol{\kappa}^i_{\rm c*}\boldsymbol{n}\cdot\boldsymbol{\kappa}^j_{\rm p*}\,{\rm d}\Gamma + \frac{c^0_{\rm b}\mu_{\rm f}}{RT}\big\langle\nabla_y\boldsymbol{\kappa}^i_{\rm c*}\cdot\nabla_y\boldsymbol{\kappa}^j_{\rm p*}\big\rangle.
\end{aligned}
\tag{5.20}
$$

Hence, in a analogous manner we obtain

$$
\begin{aligned}
L^{*ij}_{\rm CP} &= \frac{c^0_{\rm b}\mu_{\rm f}}{RT}\Big\langle\nabla_y\boldsymbol{\kappa}^i_{\rm c*}\cdot\nabla_y\boldsymbol{\kappa}^j_{\rm p*}\Big\rangle\\
&= -\frac{c^0_{\rm b}\mu_{\rm f}}{RT}\Big\langle\Delta_{yy}\boldsymbol{\kappa}^j_{\rm p*}\cdot\boldsymbol{\kappa}^i_{\rm c*}\Big\rangle = \frac{c^0_{\rm b}}{RT}\Big\langle(\boldsymbol{e}^j - \nabla_y g^j_{\rm p*})\cdot\boldsymbol{\kappa}^i_{c*}\Big\rangle\\
&= \frac{c^0_{\rm b}}{RT}\Big\langle\boldsymbol{e}^j\cdot\boldsymbol{\kappa}^i_{\rm c*}\Big\rangle = \frac{c^0_{\rm b}}{RT}\Big\langle\boldsymbol{\kappa}^{ji}_{\rm c*}\Big\rangle = L^{*ji}_{\rm PC}, \quad i, j = 1, 2, 3,
\end{aligned}
$$

which shows the conjecture.

5.3.3. *Relation between $L^*_{\rm CE}$ and $L^*_{\rm EC}$*

Likewise, to show the equality between $\boldsymbol{L}^*_{\rm CE}$ and $\boldsymbol{L}^*_{\rm EC}$ we have

$$
\begin{aligned}
\boldsymbol{L}^*_{\rm CE} - \frac{n_{\rm f}Fc^0_{\rm b}\Delta_*}{RT}\boldsymbol{I} &= \frac{2Fc^0_{\rm b}}{RT}\big\langle\boldsymbol{\kappa}_{\rm e*}(\cosh\bar{\varphi}^0 - 1)\big\rangle = \frac{Fc^0_{\rm b}}{R^2T^2}\big\langle F_*\boldsymbol{I}\boldsymbol{\kappa}_{\rm e*}\big\rangle\\
&= \frac{Fc^0_{\rm b}}{R^2T^2}\sum_{i=1}^{3}\sum_{j=1}^{3}\big\langle F_*\kappa^{ij}_{\rm e*}\big\rangle\boldsymbol{e}^i\otimes\boldsymbol{e}^j\\
&= \frac{Fc^0_{\rm b}}{R^2T^2}\sum_{i=1}^{3}\sum_{j=1}^{3}\big\langle F_*\mathbf{e}^i\cdot\boldsymbol{\kappa}^j_{\rm e*}\big\rangle\\
&= \frac{Fc^0_b}{R^2T^2}\sum_{i=1}^{3}\sum_{j=1}^{3}\big\langle(-\mu_{\rm f}\Delta_{yy}\boldsymbol{\kappa}^i_{\rm c*} + \nabla_y g^i_{\rm c*})\cdot\boldsymbol{\kappa}^j_{\rm e*}\big\rangle\boldsymbol{e}^i\otimes\boldsymbol{e}^j.
\end{aligned}
$$

Hence, for $\boldsymbol{I}=\sum_{i=1}^{3}\sum_{j=1}^{3}=\delta^{ij}\boldsymbol{e}^i\otimes\boldsymbol{e}^j$, we have for each component

$$\boldsymbol{L}^{*ij}_{\mathrm{CE}}-\frac{n_{\mathrm{f}}Fc_{\mathrm{b}}^0\Delta_*}{RT}\delta^{ij}=-\frac{Fc_{\mathrm{b}}^0\mu_{\mathrm{f}}}{R^2T^2}\left\langle\Delta_{yy}\boldsymbol{\kappa}^i_{\mathrm{c}*}\cdot\boldsymbol{\kappa}^j_{\mathrm{e}*}\right\rangle=-\frac{Fc_{\mathrm{b}}^0\mu_{\mathrm{f}}}{R^2T^2|Y|}\int_{\delta y_{\mathrm{fs}}}\nabla_y\boldsymbol{\kappa}^i_{\mathrm{c}*}\boldsymbol{n}\cdot\boldsymbol{\kappa}^j_{\mathrm{e}*}\,\mathrm{d}\Gamma+$$
$$+\frac{Fc_{\mathrm{b}}^0\mu_{\mathrm{f}}}{R^2T^2}\left\langle\nabla_y\boldsymbol{\kappa}^i_{\mathrm{c}*}\cdot\nabla_y\boldsymbol{\kappa}^j_{\mathrm{e}*}\right\rangle,\quad i,j=1,2,3.$$

Hence, in a similar fashion we obtain

$$L^{*ij}_{\mathrm{CE}}-\frac{n_{\mathrm{f}}Fc_{b}^0\Delta_*}{RT}\delta^{ij}=\frac{Fc_{\mathrm{b}}^0\mu_{\mathrm{f}}}{R^2T^2}\langle\nabla_y\boldsymbol{\kappa}^i_{\mathrm{c}*}\cdot\nabla_y\boldsymbol{\kappa}^j_{\mathrm{e}*}\rangle=-\frac{Fc_{\mathrm{b}}^0\mu_{\mathrm{f}}}{R^2T^2}\left\langle\Delta_{yy}\boldsymbol{\kappa}^j_{\mathrm{e}*}\cdot\boldsymbol{\kappa}^i_{\mathrm{c}*}\right\rangle$$
$$=\frac{Fc_{\mathrm{b}}^0}{R^2T^2}\left\langle(G_*\boldsymbol{e}^j-\nabla_y g^j_{\mathrm{e}*})\cdot\boldsymbol{\kappa}^i_{\mathrm{c}*}\right\rangle=\frac{Fc_{\mathrm{b}}^0}{R^2T^2}\left\langle G\boldsymbol{e}^j\cdot\boldsymbol{\kappa}^i_{\mathrm{c}*}\right\rangle$$
$$=-\frac{2F\left(c_{\mathrm{b}}^0\right)^2}{RT}\left\langle\sinh\bar{\varphi}^0\cdot\boldsymbol{\kappa}^{ji}_{\mathrm{c}*}\right\rangle=L^{*ji}_{\mathrm{EC}}-\frac{n_{\mathrm{f}}Fc_{\mathrm{b}}^0\Delta_*}{RT}\delta^{ji},\quad i,j=1,2,3,$$

which completes the proof for the off-diagonal components of $\boldsymbol{L}_{\mathrm{IJ}}$.

5.3.4. *Symmetry of L^*_{IJ} for $I=J$*

The complete the proof it remains to show symmetry for the reduced components in the main diagonal $\{\boldsymbol{L}^*_{\mathrm{PP}},\boldsymbol{L}^*_{\mathrm{CC}},\boldsymbol{L}^*_{\mathrm{EE}}\}$. To this end be begin by noting from (5.16) that the symmetry of the hydraulic conductivity $\boldsymbol{K}^*_{\mathrm{P}}$ implies in the same property of $\boldsymbol{L}^*_{\mathrm{PP}}$. To show the same result for $\boldsymbol{L}^*_{\mathrm{CC}}$ we also invoke its microscopic represntation in (5.16) and make use of the same arguments in (5.19) and (5.20) (with $\boldsymbol{\kappa}_{\mathrm{p}*}$ replaced by $\boldsymbol{\kappa}_{\mathrm{c}*}$) to obtain

$$\boldsymbol{L}^*_{\mathrm{CC}}-\frac{c_{\mathrm{b}}^0n_{\mathrm{f}}D_*}{RT}\boldsymbol{I}=\frac{2(c_{\mathrm{b}}^0)^2}{RT}\left\langle\boldsymbol{\kappa}_{\mathrm{c}*}(\cosh\bar{\varphi}^0-1)\right\rangle$$
$$=\frac{(c_{\mathrm{b}}^0)^2}{R^2T^2}\sum_{i=1}^{3}\sum_{j=1}^{3}\left\langle(-\mu_{\mathrm{f}}\Delta_{yy}\boldsymbol{\kappa}^i_{\mathrm{c}*}+\nabla_y g^i_{\mathrm{c}*})\cdot\boldsymbol{\kappa}^j_{\mathrm{c}*}\right\rangle\boldsymbol{e}^i\otimes\boldsymbol{e}^j$$

and

$$\boldsymbol{L}^{*ij}_{\mathrm{CC}}-\frac{c_{\mathrm{b}}^0n_{\mathrm{f}}D_*}{RT}\delta^{ij}=\frac{(c_{\mathrm{b}}^0)^2\mu_{\mathrm{f}}}{R^2T^2}\langle\nabla_y\boldsymbol{\kappa}^i_{\mathrm{c}*}\cdot\nabla_y\boldsymbol{\kappa}^j_{\mathrm{c}*}\rangle$$
$$=\frac{(c_{\mathrm{b}}^0)^2\mu_{\mathrm{f}}}{R^2T^2}\langle\nabla_y\boldsymbol{\kappa}^j_{\mathrm{c}*}\cdot\nabla_y\boldsymbol{\kappa}^i_{\mathrm{c}*}\rangle=L^{*ji}_{\mathrm{CC}}-\frac{c_{b}^0n_{\mathrm{f}}D_*}{RT}\delta^{ij}$$

as expected. Finally, the symmetry of $\boldsymbol{L}^*_{\mathrm{EE}}$ follows using the same arguments. We then have in an analogous fashion using (5.16) and replacing $\boldsymbol{\kappa}_{\mathrm{p}*}$ by $\boldsymbol{\kappa}_{\mathrm{e}*}$ in (5.17) and (5.18)

$$
\begin{aligned}
\boldsymbol{L}^{*}_{\mathrm{EE}} - \frac{F^2 c_{\mathrm{b}}^0 n_{\mathrm{f}} D_*}{RT}\boldsymbol{I} &= -\frac{2F^2 c_{\mathrm{b}}^0}{RT}\langle \boldsymbol{\kappa}_{\mathrm{e}*} \sinh \bar{\varphi}^0 \rangle \\
&= \frac{F^2}{R^2T^2}\sum_{i=1}^{3}\sum_{j=1}^{3}\langle (-\mu_{\mathrm{f}}\Delta_{yy}\boldsymbol{\kappa}^i_{\mathrm{e}*} + \nabla_y g^i_{\mathrm{e}*}) \cdot \boldsymbol{\kappa}^j_{\mathrm{e}*} \rangle \boldsymbol{e}^i \otimes \boldsymbol{e}^j
\end{aligned}
$$

and

$$
\begin{aligned}
L^{*ij}_{EE} - \frac{F^2 c_{\mathrm{b}}^0 n_{\mathrm{f}} D_*}{RT}\delta^{ij} &= \frac{F^2 \mu_{\mathrm{f}}}{R^2T^2}\langle \nabla_y \boldsymbol{\kappa}^i_{\mathrm{e}*} \cdot \nabla_y \boldsymbol{\kappa}^j_{\mathrm{e}*} \rangle \\
&= \frac{F^2 \mu_{\mathrm{f}}}{R^2T^2}\langle \nabla_y \boldsymbol{\kappa}^j_{\mathrm{e}*} \cdot \nabla_y \boldsymbol{\kappa}^i_{\mathrm{e}*} \rangle = L^{*ji}_{\mathrm{EE}} - \frac{F^2 c_{\mathrm{b}}^0 n_{\mathrm{f}} D_*}{RT}\delta^{ij}.
\end{aligned}
$$

The proof is now complete.

5.3.5. *Symmetry, Local Equilibrium and Microstructure*

The relation between the symmetry of Onsager's matrix and the condition of local equilibrium (5.11) validates the conjecture proposed by Prigogine (1967) who postulated a similar claim within the context of the Thermodynamics of Irreversible Processes. Furthermore, an open issue addressed herein is the strong correlation between (5.11) and the clay morphology. As we shall illustrate in the companion paper (Moyne and Murad, 2006) the condition of local equilibrium is fulfilled for microstructures composed of parallel particles of face-to-face contact. In this type of microgeometry, local fluctuations in the electro-chemical potential could only occur in the direction normal to the clay surface. However when the particles are parallel such fluctuations vanish and the effective parameters are solely dictated by the local Poisson–Boltzmann profile of the e.d.l. potential.

6. Conclusion

In this article we have proposed a two-scale model for expansive clays. The model was derived within the framework of homogenization in the up-scaling of the pore-scale description consisting of elastic macromolecules coupled with the electro-hydrodynamics, Nernst–Planck relations and the Poisson–Boltzmann problem governing the fluid movement, ion transport and local electrostatics in the electrolyte solution. After establishing the proper order of magnitude of the dimensionless quantities involved, application of a formal matched asymptotic expansion technique led to a macroscopic model wherein effective electro-chemo-mechanical parameters appear strongly related to the response of the microstructure. The homogenized model consists of Onsager's reciprocity relations coupled with mass and charge conservations and with a modified form of Terzaghi's decomposition incorporating an additional swelling stress tensor component. Among other effects, the magnitude of the effective parameters appears strongly dictated by the microscopic variability of the e.d.l. potential satisfying a local version of the Poisson–Boltzman problem.

The essential feature underlying the two-scale approach proposed herein are the form of the local closure problems obtained for the effective coefficients which can be exploited to obtain further insight in the somewhat obscure constitutive theory of swelling systems. Here such closure relations were used to obtain precise local conditions for the validity of the symmetry of Onsager's reciprocity relations. Further work is in progress to extend the model to swelling clays characterized by two levels of porosity including the inter-phase mass transfer between micro- and macro-pores and toward more realistic elasto-plastic constitutive relations of the solid matrix (Loret *et al.*, 2002, Murad and Cushman, 1997, 2000).

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