Electromagnetic/acoustic coupling in partially-saturated porous rocks: An extension of Pride's theory

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Abstract

In this paper a set of equations governing the electromagnetic/acoustic coupling in partially-saturated porous rocks in the low-frequency regime is derived. The equations are obtained by volume averaging of fundamental electromagnetic and mechanical equations valid at the porescale, following the same procedure as the one developed in the seminal paper of S. Pride for porous media where the fluid electrolyte fully saturates the pore space. In the present approach it is assumed that the porous rock is partially saturated with a wetting-fluid electrolyte

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Suggested Reviewers:	Steve Pride Berkeley Laboratory: E O Lawrence Berkeley National Laboratory srpride@lbl.gov The theory we propose follows the approach of the seminal work by S. Pride (1994). It would not only highly recommended but also a honor for us that the manuscript was reviewed by him.
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Abstract

In this paper a set of equations governing the electromagnetic/acoustic coupling in partially-saturated porous rocks in the low-frequency regime is derived. The equations are obtained by volume averaging of fundamental electromagnetic and mechanical equations valid at the pore-scale, following the same procedure as the one developed in the seminal paper of S. Pride for porous media where the fluid electrolyte fully saturates the pore space. In the present approach it is assumed that the porous rock is partially saturated with a wetting-fluid electrolyte (water) and a non-wetting fluid (air). We also assume that an electromagnetic/mechanical coupling exists at the water-solid and water-air contact surfaces through adsorbed excess charges balanced by mobile ions in the water. The capillary pressure perturbations are assumed to be negligible. The governing equations thus derived are similar to the ones obtained by Pride with the main difference that the various coefficients, including the electrokinetic coupling coefficient and electric conductivity appearing in the transport equations are functions of the water saturation and depend on electrical and topological properties of both electric double layers. Onsager reciprocity is also demonstrated.

Keywords: Electrokinetics, partially-saturated porous media, Electric double layer, Volume Averaging Method

1 Introduction

The phenomenon of seismic-to-electromagnetic energy conversion along with its counterpart have been known for a long time by the geophysical community, as well as the existence of several theoretical models and experiments aiming to describe it, i.e., (Frenkel, 1944; Neev and Yeatts, 1989; Thompson and Gist, 1993). The work of Pride (1994), presenting a closed set of equations modeling the propagation of coupled mechanical and electromagnetic perturbations in an isotropic porous medium saturated with an electrolyte, created a long-standing wave of interest of many research groups around the world. Consequently, laboratory work, field measurements and theoretical developments have followed, enlarging our comprehension of the nature of the involved phenomena and giving rise to further questions. Among them, the issue of extending Pride's theory to account for either partially saturated rocks or rocks fully saturated with immiscible fluids has been studied in several publications. We give here an overview of several of their works, for a more insightful read we suggest the review (Jouniaux and Zyserman, 2016) and the books (Revil et al, 2015; Grobbe et al, 2020).

Haines et al (2007); Dupuis et al (2007) suggested that the full range of saturation has to be considered when performing seismoelectric studies of partially saturated regions, as for example the vadose zone, to get a better understanding of the electrokinetic phenomenon. As a way of testing the dependence of seismoelectric signals on saturation, Bordes et al (2009) showed the absence of coseismic signal on completely dry rocks. Zyserman et al (2010) numerically studied the electroseismic response of an hydrocarbon reservoir considering the presence of gas and oil by proposing an effective fluid approach, but considered the electrokinetic coupling coefficient to be that of the full saturation scenario. An extension to a partially saturated medium was introduced (Warden et al, 2013) based on a) the relation between the electrokinetic coupling coefficient and the streaming potential coefficient and b) different extensions of the latter to partial saturation scenarios existing in the literature. This approach has been employed in several later works, e.g., Zyserman et al (2015) numerically studied the seismoelectric response of a CO_2 geological deposition site, analyzing its dependence on water saturation. Laboratory experiments were performed by Bordes et al (2015) on the seismoelectric response of partially saturated sand using effective fluids in the associated computations of transfer functions. Another model was proposed by Jardani and Revil (2015) for seismoelectric conversions by considering two immiscible fluids taking into account the contribution of the electric double layer at the fluid-fluid interface. Applications for contaminated aquifer and vadose zone were also developed: Munch and Zyserman (2016) numerically modeled the seismoelectric response of an aquifer with different degrees of contamination due to the presence of (D)NAPLs, and Zyserman et al (2017) studied the seismoelectric responses of the vadose zone when considering different soil textures and water saturations. Moreover the first analytic expression for the interface response (IR) studying the SHTE response of a partially saturated medium overlying a fully saturated one was published by Monachesi et al (2018). More recently passive electromagnetic sources have been considered by Zyserman et al (2022) to study the seismic responses of a hydrocarbon reservoir at different oil saturations.

Several authors analyzed the dependence on saturation of the streaming potential coefficient through laboratory studies and theoretical models (Perrier and Morat, 2000; Guichet et al, 2003; Revil and Cerepi, 2004; Linde et al, 2007; Revil et al, 2007; Vinogradov and Jackson, 2011). All these studies lead to a constant or monotonous decreasing behavior of the electric response when the water saturation diminishes. On the other hand, other studies (Jackson, 2010; Allègre et al, 2012; Jougnot et al, 2012; Fiorentino et al, 2017) measured and predicted a non monotonous behavior for a diminishing water saturation; in the first of these works oil was the considered wetting fluid. In the last of these references, as it was previously suggested by Allègre et al (2014, 2015), it was shown through a numerical lattice-Boltzmann procedure that indeed the polarization of the air-water interface does play an important role both in the amplitude of the electrokinetic coupling and in its non monotonic behavior. These results were reaffirmed by the analysis performed by Jouniaux et al (2020) revisiting laboratory data published by different authors.

As a conclusion of the published research to the date, there is a need for models able to explain the electromagnetic/mechanical coupling for partially-saturated porous rocks. There is a clear evidence that the electric double layer effect of the water-air interface must be taken into account in any proposed model.

In this work we derive a set of equations governing the coupled electro-magnetic/acoustic phenomena in partially-saturated porous rocks valid in the low-frequency regime, where the wetting fluid (water) is assumed to be an ideal electrolyte and the non-wetting phase is air. We introduce two main assumptions in our derivation: the first one is the existence of an electrical double layer at the water-air interface (Creux et al, 2007; Yang and Sato, 2001) whose potential does not interact with the one generated by the electric double layer at the rock matrix-water interface. The second assumption is that, in the wave propagation frequency regime the capillary pressure perturbations are negligible, implying that pressure perturbations in both wetting and non-wetting fluids are the same (Berryman et al, 1988; Pride et al, 1992). It is also assumed with Pride (1994) that the porous rock is homogeneous and isotropic at the macroscopic scale and that that local variations in ion concentration are negligible. The presence of the non-wetting phase has a major role in the proposed model, not only because the electromagnetic/mechanical coupling is assumed to exist in both water-solid and water-air surfaces through adsorbed excess charges balanced by mobile ions in the water, but also due to its influence in the emerging electromagnetic and mechanical properties of the medium. As it is shown along this work, the various coefficients thus derived depend on both the relative fraction of water and air and on the topological features of the latter within the porous space. As a corollary, the equations for the flow-regime in partially saturated porous media are derived.

This paper is organized as follows. In Section 2 the pore-scale electromagnetic and mechanical governing equations are written for each one of the three phases, together with the boundary conditions valid at the contact surfaces. The volume-average of the pore-scale equations is performed following Pride (1994) procedure in Section 3. In Section 4 the boundary-value problems at the pore-scale are stated in the thin-disk-volume approach from Pride

(1994), which allows to obtain relations between pore-scale fields with the corresponding macroscopic fields. The volume-average of the transport equations are completed in Section 5, and new expressions for the electrokinetic coupling coefficient and electric conductivity are obtained. The final set of equations is gathered in Section 6, and in Section 7 we offer our concluding remarks. As a support of the various derivations, three appendixes are included. In Appendix B Onsager reciprocity is demonstrated.

2 Governing equations at the pore scale

Let us start with a pore-scale description of the considered scenario. Fig.1A shows a schematic representation of a partially-saturated rock (adapted from Culligan et al (2004)). The solid grains are represented in gray, water in white and air in black. Note that water is assumed to be the wetting phase, and as such, the surface limiting the water volume, S_w, is always the same whatever the water saturation s_w, with the exception of $s_w = 0$ (case that will not be treated here). This means that the air never gets in contact with the solid grains. At most there will be thin films of water surrounding the grains (Culligan et al, 2004). On the other hand, the surface surrounding the non-wetting fluid, S_{nw}, will be different for different water saturation values, and of course it will exist for $s_w < 1$. Fig.1B shows how the free ion distributions within the electrolyte are conceptualized. Following Pride (1994) there is a layer of electrolyte ions and structured water molecules chemically and physically adsorbed to the surface of both the solid and the air. These ions are assumed to be immobile, and constitute the adsorbed layer. The latter has a net excess charge, balanced by the same amount of charge of opposite sign in the adjacent fluid. This region of charge balance is called *diffuse layer*. Both

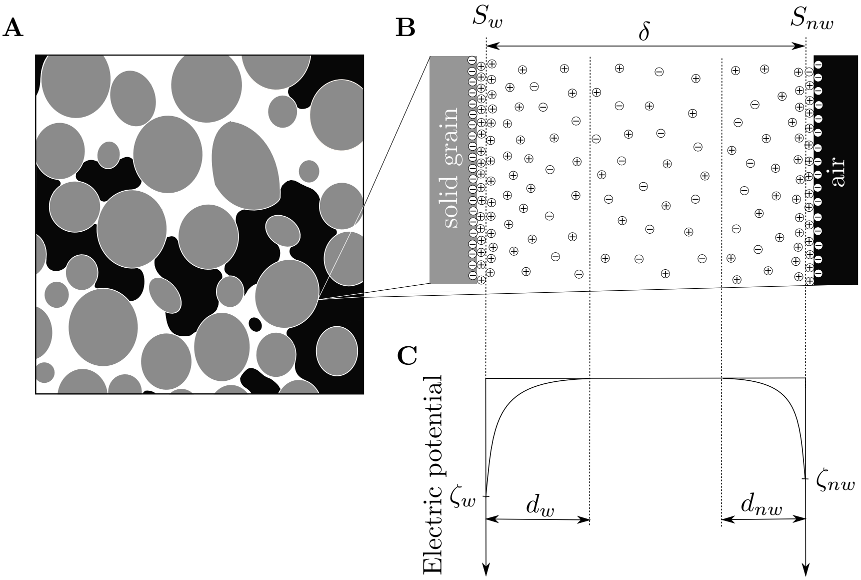

Fig. 1 **A**. Representation of partially-saturated porous rock (adapted from Culligan et al (2004)). Solid grains, water (wetting phase) and air (non-wetting phase) are represented in gray, white and black, respectively, **B**. Amplified view of a thin water film of thickness δ. The charge distribution is represented at both interfaces and the location of the corresponding shear planes are indicated; **C**. The electric potential distribution near each shear plane S_w and S_{nw} is represented, where ζ_w, d_w and ζ_{nw}, d_{nw} are their respective zeta potentials and Debye lengths. The main assumption is that both Debye lengths are much smaller than any geometrical feature of the porous space, including the thickness of the thin water films δ.

the adsorbed and diffuse layers constitute the *electric double layer*. The surface separating the diffuse layer and the adsorbed layer is called *shear plane*. This structure is assumed to be present in both interfaces, so there will be two shear planes; S_w between solid and wetting-phase, and S_{nw} between wetting and non-wetting phases. The adsorbed layers are thin enough to be treated as having negligible volume. Therefore, the physical properties of the adsorbed layers will be included in the description as boundary conditions on the shear planes. These boundary conditions are simply stated as uniform surface charge densities over each shear plane Q^0_w and Q^0_{nw}, and the no-slip flow condition.

2.1 Electromagnetic equations

Both the solid and the non-wetting phase (air) are assumed to be electrically insulating while the wetting fluid (water) is assumed to be an electrolyte with L ionic species. Then, Maxwell's equations can be written as follows: For the solid phase (s)

$$\nabla \cdot \boldsymbol{B_s} = 0, \tag{1}$$

$$\nabla \cdot \boldsymbol{D_s} = 0, \tag{2}$$

$$\nabla \times \boldsymbol{E_s} = -\dot{\boldsymbol{B}}_{\boldsymbol{s}}, \tag{3}$$

$$\nabla \times \boldsymbol{H_s} = \dot{\boldsymbol{D}}_{\boldsymbol{s}}, \tag{4}$$

for the wetting phase (w)

$$\nabla \cdot \boldsymbol{B_w} = 0, \tag{5}$$

$$\nabla \cdot \boldsymbol{D_w} = \sum_{l=1}^{L} e z_l N_l, \tag{6}$$

$$\nabla \times \boldsymbol{E_w} = -\dot{\boldsymbol{B}}_{\boldsymbol{w}}, \tag{7}$$

$$\nabla \times \boldsymbol{H_w} = \dot{\boldsymbol{D}}_{\boldsymbol{w}} + \boldsymbol{J_w}, \tag{8}$$

and for the non-wetting phase (nw)

$$\nabla \cdot \boldsymbol{B_{nw}} = 0, \tag{9}$$

$$\nabla \cdot \boldsymbol{D_{nw}} = 0, \tag{10}$$

$$\nabla \times \boldsymbol{E_{nw}} = -\dot{\boldsymbol{B}}_{\boldsymbol{nw}}, \tag{11}$$

$$\nabla \times \boldsymbol{H_{nw}} = \dot{\boldsymbol{D}}_{\boldsymbol{nw}}. \tag{12}$$

$\boldsymbol{J_w}$ in Eq. (8) represents the ionic-current density. Its main contributions come from diffusion, electromigration and convection of ions (first, second and third terms, respectively),

$$\boldsymbol{J_w} = \sum_{l=1}^{L} ez_l \left[-kTb_l \nabla N_l + ez_l b_l N_l \boldsymbol{E_w} + N_l \boldsymbol{\dot{u}_w} \right], \tag{13}$$

where $\boldsymbol{\dot{u}_w}$ is the wetting fluid velocity. In this expression, kT is the thermal energy, ez_l represents the net charge and sign of each species-l ion, N_l represents the density (number of species-l ions per unit volume) and b_l the mobility.

Eq. (13) strictly holds for an ideal electrolyte (ion concentrations lower than $\simeq$ 1 mol/L). On the other hand, the Lorenz force is assumed to be negligible, and because of the random arrangement of the solid grains, no piezoelectric effects are accounted for Pride (1994). The same will be assumed for the non-wetting phase.

The boundary conditions that hold on the surface S_w are

$$\boldsymbol{n} \cdot (\boldsymbol{B_s} - \boldsymbol{B_w}) = 0, \tag{14}$$

$$\boldsymbol{n} \cdot (\boldsymbol{D_s} - \boldsymbol{D_w}) = Q_w, \tag{15}$$

$$\boldsymbol{n} \times (\boldsymbol{E_s} - \boldsymbol{E_w}) = 0, \tag{16}$$

$$\boldsymbol{n} \times (\boldsymbol{H_s} - \boldsymbol{H_w}) = Q_w \boldsymbol{\dot{u}_s}, \tag{17}$$

$$\boldsymbol{n} \cdot \boldsymbol{J_w} = \dot{Q}_w, \tag{18}$$

$\boldsymbol{n}$ is the unit vector normal to S_w, directed from wetting phase to solid, $\boldsymbol{\dot{u}_s}$ is the velocity of the solid ($= \boldsymbol{\dot{u}_w}$ on S_w) and Q_w is the free charge per unit area of the wetting adsorbed layer. Eq. (18) is a consequence of charge conservation and follows by taking the divergence of Ampere's law and the time derivative of Coulomb's law. In the same way, the boundary conditions on the surface S_{nw} are given by:

$$\boldsymbol{n} \cdot (\boldsymbol{B_{nw}} - \boldsymbol{B_w}) = 0, \tag{19}$$

$$\boldsymbol{n} \cdot (\boldsymbol{D_{nw}} - \boldsymbol{D_w}) = Q_{nw}, \tag{20}$$

$$\boldsymbol{n} \times (\boldsymbol{E_{nw}} - \boldsymbol{E_w}) = 0, \tag{21}$$

$$\boldsymbol{n} \times (\boldsymbol{H_{nw}} - \boldsymbol{H_w}) = Q_{nw}\dot{\boldsymbol{u}}_{\boldsymbol{nw}}, \tag{22}$$

$$\boldsymbol{n} \cdot \boldsymbol{J_w} = \dot{Q}_{nw}, \tag{23}$$

Note that the surface S_{nw} together with S_w constitute the boundary of the volume occupied by the wetting phase, i.e., $\partial V_w = S_w \cup S_{nw}$. Finally, the above equations are closed by the constitutive relations:

$$\boldsymbol{B_\xi} = \mu_0 \boldsymbol{H_\xi}, \tag{24}$$

$$\boldsymbol{D_\xi} = \epsilon_0 \kappa_\xi \boldsymbol{E_\xi}, \tag{25}$$

where μ_0 is the vacuum magnetic permeability, ϵ_0 the vacuum electric permittivity and κ_ξ, $\xi = s, w$, or nw is the corresponding dielectric constant.

Now, the time dependence of any field variable $\boldsymbol{A}$ is written as

$$\boldsymbol{A}(t) = \boldsymbol{A^0} + \mathrm{Re}\left\{\boldsymbol{a}(\omega)e^{-i\omega t}\right\}, \tag{26}$$

where the first term represents the static-equilibrium field prior to disturbance, while the second one represents the deviation in the field due to a time-harmonic perturbation. It will be assumed that no free charge q is induced on the surfaces (note that the free charge q does not include the polarization charge dielectrically induced on the surfaces). Because Q_w^0 and Q_{nw}^0 are assumed to be uniform over the corresponding surfaces, it can be shown using a simple argument based on Stoke's law that $\boldsymbol{E_s^0}$ and $\boldsymbol{E_{nw}^0}$ must be zero (Pride, 1994). The only nonzero static fields are then $\boldsymbol{E_w^0}$ and N_l^0. The equations governing these fields are, from Eqs. (6), (7), (8) and (13)

$$\epsilon_0 \kappa_w \nabla \cdot \boldsymbol{E_w^0} = \sum_{l=1}^{L} e z_l N_l^0, \tag{27}$$

$$\nabla \times \boldsymbol{E_w^0} = 0, \tag{28}$$

$$-kT \nabla N_l^0 + N_l^0 e z_l \boldsymbol{E_w^0} = 0, \tag{29}$$

with the boundary conditions on S_w

$$\epsilon_0 \kappa_w \boldsymbol{n} \cdot \boldsymbol{E_w^0} = Q_w^0, \tag{30}$$

$$\boldsymbol{n} \times \boldsymbol{E_w^0} = 0, \tag{31}$$

and on S_{nw}

$$\epsilon_0 \kappa_w \boldsymbol{n} \cdot \boldsymbol{E_w^0} = Q_{nw}^0, \tag{32}$$

$$\boldsymbol{n} \times \boldsymbol{E_w^0} = 0. \tag{33}$$

Equations (28) and (29) are satisfied by

$$\boldsymbol{E_w^0} = -\nabla \Phi^0, \tag{34}$$

$$N_l^0 = \mathcal{N}_l e^{-\frac{e z_l}{kT} \Phi^0}, \tag{35}$$

where $\mathcal{N}_l$ are the bulk-ionic concentrations. Then, Coulomb's law leads to the Poisson-Boltzmann equation

$$\nabla^2 \Phi^0 = -\sum_{l=1}^{L} \frac{e z_l \mathcal{N}_l}{\epsilon_0 \kappa_w} e^{-\frac{e z_l}{kT} \Phi^0}. \tag{36}$$

The electric potential satisfying this problem completely solves the static case. The potential near a plane wall has, approximately, an exponential distribution given by (Pride, 1994)

$$\Phi^0(\chi) = \zeta e^{-\chi/d}, \tag{37}$$

where χ is a local coordinate for the distance normal to the surface, d is the Debye length, defined as

$$\frac{1}{d^2} = \sum_{l=1}^{L} \frac{(e z_l)^2 \mathcal{N}_l}{\epsilon_0 \kappa_w kT}, \tag{38}$$

and ζ is the zeta potential being the static electric potential at the shear plane (i.e., S_w or S_{nw}). Then, a different solution on each considered surface is expected to be obtained. If the Debye length associated with each shear plane is much smaller than any geometrical feature of the porous medium (even smaller than the thin water films thicknesses), then the electric potential at each shear plane can be treated separately, as two non-interacting electric potentials, as illustrated in Fig.1C. This is just the "thin-double-layer" approximation adopted by Pride (1994), employed here twice. Then we will have

$$\Phi^0_w(\chi) = \zeta_w e^{-\chi/d_w} \quad \text{and} \quad \Phi^0_{nw}(\chi) = \zeta_{nw} e^{-\chi/d_{nw}}, \tag{39}$$

with their corresponding electric fields $\boldsymbol{E^0_{w,(w)}} = -\nabla\Phi^0_w$ and $\boldsymbol{E^0_{w,(nw)}} = -\nabla\Phi^0_{nw}$. The zeta potentials ζ_w and ζ_{nw} are related to the respective charge per unit area of S_w and S_{nw} as follows

$$Q^0_w \simeq 2d_w \sum_{l=1}^{L} ez_l \mathcal{N}_{l,(w)} e^{-\frac{ez_l\zeta_w}{2kT}} \quad \text{and} \quad Q^0_{nw} \simeq 2d_{nw} \sum_{l=1}^{L} ez_l \mathcal{N}_{l,(nw)} e^{-\frac{ez_l\zeta_{nw}}{2kT}}. \tag{40}$$

Note that the bulk-ionic concentrations $\mathcal{N}_{l,(w)}$ and $\mathcal{N}_{l,(nw)}$ must satisfy $\mathcal{N}_l = \mathcal{N}_{l,(w)} + \mathcal{N}_{l,(nw)}$, and the respective Debye lengths are given by

$$\frac{1}{d_w^2} = \sum_{l=1}^{L} \frac{(ez_l)^2\mathcal{N}_{l,(w)}}{\epsilon_0\kappa_w kT} \quad \text{and} \quad \frac{1}{d_{nw}^2} = \sum_{l=1}^{L} \frac{(ez_l)^2\mathcal{N}_{l,(nw)}}{\epsilon_0\kappa_w kT}. \tag{41}$$

Now we need to state the equations governing the time-harmonic disturbances. In order to preserve only the linear contributions, all products of disturbances are neglected. We then obtain

$$\nabla \cdot \boldsymbol{b_s} = 0, \tag{42}$$

$$\nabla \cdot \boldsymbol{d_s} = 0, \tag{43}$$

$$\nabla \times \boldsymbol{e_s} = i\omega \boldsymbol{b_s}, \tag{44}$$

$$\nabla \times \boldsymbol{h_s} = -i\omega \boldsymbol{d_s}, \tag{45}$$

$$\nabla \cdot \boldsymbol{b_w} = 0, \tag{46}$$

$$\nabla \cdot \boldsymbol{d_w} = \sum_{l=1}^{L} ez_l n_l, \tag{47}$$

$$\nabla \times \boldsymbol{e_w} = i\omega \boldsymbol{b_w}, \tag{48}$$

$$\nabla \times \boldsymbol{h_w} = -i\omega \boldsymbol{d_w} + \boldsymbol{j_w}, \tag{49}$$

$$\nabla \cdot \boldsymbol{b_{nw}} = 0, \tag{50}$$

$$\nabla \cdot \boldsymbol{d_{nw}} = 0, \tag{51}$$

$$\nabla \times \boldsymbol{e_{nw}} = i\omega \boldsymbol{b_{nw}}, \tag{52}$$

$$\nabla \times \boldsymbol{h_{nw}} = -i\omega \boldsymbol{d_{nw}}, \tag{53}$$

where

$$\boldsymbol{j_w} = \sum_{l=1}^{L} e z_l \left[-kTb_l \nabla n_l + e z_l b_l \left(N_l^0 \boldsymbol{e_w} + n_l \boldsymbol{E_w^0} \right) + N_l^0 \dot{\boldsymbol{u}}_{\boldsymbol{w}} \right]. \tag{54}$$

The boundary conditions on S_w are

$$\boldsymbol{n} \cdot (\boldsymbol{b_s} - \boldsymbol{b_w}) = 0, \tag{55}$$

$$\boldsymbol{n} \cdot (\boldsymbol{d_s} - \boldsymbol{d_w}) = 0, \tag{56}$$

$$\boldsymbol{n} \times (\boldsymbol{e_s} - \boldsymbol{e_w}) = 0, \tag{57}$$

$$\boldsymbol{n} \times (\boldsymbol{h_s} - \boldsymbol{h_w}) = Q_w^0 \dot{\boldsymbol{u}}_{\boldsymbol{s}}, \tag{58}$$

$$\boldsymbol{n} \cdot \boldsymbol{j_w} = 0, \tag{59}$$

and on S_{nw} we have

$$\boldsymbol{n} \cdot (\boldsymbol{b_{nw}} - \boldsymbol{b_w}) = 0, \tag{60}$$

$$\boldsymbol{n} \cdot (\boldsymbol{d_{nw}} - \boldsymbol{d_w}) = 0, \tag{61}$$

$$\boldsymbol{n} \times (\boldsymbol{e_{nw}} - \boldsymbol{e_w}) = 0, \tag{62}$$

$$\boldsymbol{n} \times (\boldsymbol{h_{nw}} - \boldsymbol{h_w}) = Q_{nw}^0 \dot{\boldsymbol{u}}_{\boldsymbol{nw}}, \tag{63}$$

$$\boldsymbol{n} \cdot \boldsymbol{j_w} = 0, \tag{64}$$

2.2 Mechanical equations

The conservation of linear momentum governs the dynamics of solid and the wetting and non-wetting fluid phases. This law is expressed for time-harmonic disturbances as

$$-i\omega\rho_s\dot{\boldsymbol{u}}_{\boldsymbol{s}} = \nabla \cdot \boldsymbol{\tau}_{\boldsymbol{s}}, \tag{65}$$

$$-i\omega\rho_w\dot{\boldsymbol{u}}_{\boldsymbol{w}} = \nabla \cdot \boldsymbol{\tau}_{\boldsymbol{w}} + \sum_{l=1}^{L} ez_l \left(N_l^0 \boldsymbol{e}_{\boldsymbol{w}} + n_l \boldsymbol{E}_{\boldsymbol{w}}^{\boldsymbol{0}}\right), \tag{66}$$

$$-i\omega\rho_{nw}\dot{\boldsymbol{u}}_{\boldsymbol{nw}} = \nabla \cdot \boldsymbol{\tau}_{\boldsymbol{nw}}, \tag{67}$$

where the solid and wetting-phase and non-wetting stress tensors are respectively given by

$$\boldsymbol{\tau}_{\boldsymbol{s}} = K_s \nabla \cdot \boldsymbol{u}_{\boldsymbol{s}}\mathbf{I} + G_s \left(\nabla \boldsymbol{u}_{\boldsymbol{s}} + \nabla \boldsymbol{u}_{\boldsymbol{s}}^{\boldsymbol{T}} - \frac{2}{3}\nabla \cdot \boldsymbol{u}_{\boldsymbol{s}}\mathbf{I}\right), \tag{68}$$

$$\boldsymbol{\tau}_{\boldsymbol{w}} = K_w \nabla \cdot \boldsymbol{u}_{\boldsymbol{w}}\mathbf{I} - i\omega\eta_w \left(\nabla \boldsymbol{u}_{\boldsymbol{w}} + \nabla \boldsymbol{u}_{\boldsymbol{w}}^{\boldsymbol{T}} - \frac{2}{3}\nabla \cdot \boldsymbol{u}_{\boldsymbol{w}}\mathbf{I}\right), \tag{69}$$

$$\boldsymbol{\tau}_{\boldsymbol{nw}} = K_{nw} \nabla \cdot \boldsymbol{u}_{\boldsymbol{nw}}\mathbf{I} - i\omega\eta_{nw} \left(\nabla \boldsymbol{u}_{\boldsymbol{nw}} + \nabla \boldsymbol{u}_{\boldsymbol{nw}}^{\boldsymbol{T}} - \frac{2}{3}\nabla \cdot \boldsymbol{u}_{\boldsymbol{nw}}\mathbf{I}\right). \tag{70}$$

In the expression for $\boldsymbol{\tau}_{\boldsymbol{s}}$, K_s and G_s are the bulk and shear modulus of the solid phase, while in $\boldsymbol{\tau}_{\boldsymbol{w}}$, K_w is the wetting-phase bulk modulus and η_w its viscosity. The corresponding parameters for the non-wetting phase are $\boldsymbol{\tau}_{\boldsymbol{nw}}$, K_{nw} and η_{nw}. Finally, the boundary conditions on S_w are

$$\boldsymbol{n} \cdot (\boldsymbol{\tau}_{\boldsymbol{s}} - \boldsymbol{\tau}_{\boldsymbol{w}}) = -Q_w^0 \boldsymbol{e}_{\boldsymbol{s}}, \tag{71}$$

$$\boldsymbol{u}_{\boldsymbol{s}} - \boldsymbol{u}_{\boldsymbol{w}} = 0, \tag{72}$$

and on S_{nw}

$$\boldsymbol{n} \cdot (\boldsymbol{\tau_{nw}} - \boldsymbol{\tau_w}) = -Q^0_{nw}\boldsymbol{e_{nw}}, \tag{73}$$

$$\boldsymbol{u_{nw}} - \boldsymbol{u_w} = 0. \tag{74}$$

The right hand side of Eqs. (71) and (73) are the body forces per unit volume acting on the excess charge of the corresponding adsorbed layer. Eqs. (72) and (74) are the no-slip flow conditions on each boundary.

3 Volume average of the governing equations

The pore-scale governing equations will be volume averaged in order to obtain a set of equations valid at a macroscopic scale. Let V_A be the averaging volume, assumed to be larger than the grains dimensions but much smaller than the wavelengths of the applied disturbances. Defining the volume average of a microscopic field $\boldsymbol{a_\xi}$ associated with the ξth phase as

$$\langle \boldsymbol{a_\xi} \rangle = \frac{1}{V_A} \int_{V_\xi} \boldsymbol{a_\xi} dV, \tag{75}$$

where V_ξ is the volume occupied by the ξth phase within V_A, then the following theorems due to Slattery (1967) hold:

$$\langle \nabla \boldsymbol{a_\xi} \rangle = \nabla \langle \boldsymbol{a_\xi} \rangle + \frac{1}{V_A} \int_{S_\xi} \boldsymbol{n_\xi} \boldsymbol{a_\xi} dS, \tag{76}$$

$$\langle \nabla \cdot \boldsymbol{a_\xi} \rangle = \nabla \cdot \langle \boldsymbol{a_\xi} \rangle + \frac{1}{V_A} \int_{S_\xi} \boldsymbol{n_\xi} \cdot \boldsymbol{a_\xi} dS, \tag{77}$$

$$\langle \nabla \times \boldsymbol{a_\xi} \rangle = \nabla \times \langle \boldsymbol{a_\xi} \rangle + \frac{1}{V_A} \int_{S_\xi} \boldsymbol{n_\xi} \times \boldsymbol{a_\xi} dS, \tag{78}$$

where $\boldsymbol{n_\xi}$ is the normal to $S_\xi = \partial V_\xi$, and is defined as

$$\boldsymbol{n_w} = \boldsymbol{n}, \tag{79}$$

$$\boldsymbol{n_s} = -\boldsymbol{n}, \tag{80}$$

$$\boldsymbol{n_{nw}} = -\boldsymbol{n}, \tag{81}$$

with $\boldsymbol{n}$ directed from the wetting-phase to the solid or from the wetting-phase to the non-wetting phase. When applying the averaging theorem to the porous material, it will be assumed that the solid and both fluid phases have homogeneous material properties throughout V_A. Furthermore, it is assumed that macroscopic-material properties vary slowly as V_A is moved over distances the size of V_A or less.

It will be useful to define two other averages related to $\langle \boldsymbol{a_\xi} \rangle$

$$\bar{\boldsymbol{a}}_{\boldsymbol{\xi}} = \langle \nabla \boldsymbol{a_\xi} \rangle / \varphi_\xi, \tag{82}$$

$$\bar{\boldsymbol{A}} = \sum_\xi \langle \nabla \boldsymbol{a_\xi} \rangle = \sum_\xi \varphi_\xi \bar{\boldsymbol{a}}_{\boldsymbol{\xi}}, \tag{83}$$

where φ_ξ is the volume fraction of the ξth phase,

$$\varphi_\xi = \frac{V_\xi}{V_A}, \tag{84}$$

$\bar{\boldsymbol{a}}_{\boldsymbol{\xi}}$ is the *phase average* because it represents the average value within the ξth phase, while $\bar{\boldsymbol{A}}$ is the *total average* because it represents the average value of a given type throughout the complete averaging volume V_A.

3.1 Electromagnetic equations

It is natural to first obtain the volume average of the static fields prior to disturbance. The only non-zero static field is $\boldsymbol{E_w^0} = -\nabla\left(\Phi_w^0 + \Phi_{nw}^0\right)$ whose average is given by

$$\left\langle \boldsymbol{E_w^0} \right\rangle = -\nabla\left\langle \Phi_w^0 \right\rangle - \frac{1}{V_A}\int_{S_w} \boldsymbol{n}\Phi_w^0 dS - \nabla\left\langle \Phi_{nw}^0 \right\rangle - \frac{1}{V_A}\int_{S_{nw}} \boldsymbol{n}\Phi_{nw}^0 dS. \quad (85)$$

Given that $\Phi_w^0(=\zeta_w)$ is assumed to be constant over S_w and the same occurs for $\Phi_{nw}^0(=\zeta_{nw})$ over S_{nw}, the surface integrals vanish. If the material has uniform macroscopic properties so that $\left\langle \Phi_w^0 \right\rangle = \text{const.}$ and $\left\langle \Phi_{nw}^0 \right\rangle = \text{const,}$ then $\left\langle \boldsymbol{E_w^0} \right\rangle = 0$; i.e., the macroscopic static fields average zero. We've assumed then that an electric field is created at each shear plane, $\boldsymbol{E^0_{w,(w)}}$ associated to S_w and $\boldsymbol{E^0_{w,(nw)}}$ associated to S_{nw}. Each of them are responsible for a fraction of the total number of ions within the fluid.

The equations governing the disturbances [Eqs.(42)-(54)] are now averaged in the following manner

1. Volume average is applied;
2. The corresponding result from Slattery's theorem is applied;
3. (3) the solid phase, wetting phase and non-wetting phase equations are added;
4. the boundary conditions (55)-(64) are applied;
5. the relative wetting phase-solid flow vector is introduced,

$$\boldsymbol{v} = \dot{\boldsymbol{u}}_{\boldsymbol{w}} - \dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}}, \quad (86)$$

   where $\dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}}$ is the phase-averaged velocity of the solid phase;

6. the electroneutrality condition prior to disturbances is stated,

$$\sum_{l=1}^{L} ez_l \left\langle N^0_{l,(w)} \right\rangle V_A + Q^0_w S_w = 0, \text{ and } \sum_{l=1}^{L} ez_l \left\langle N^0_{l,(nw)} \right\rangle V_A + Q^0_{nw} S_{nw} = 0. \tag{87}$$

The first corresponds to the electroneutrality statement in the case of S_w and the second the one corresponding to S_{nw}.

As a result one obtains:

$$\nabla \cdot \bar{\boldsymbol{B}} = 0, \tag{88}$$

$$\nabla \cdot \bar{\boldsymbol{D}} = s_w \phi \sum_{l=1}^{L} ez_l \bar{n}_l. \tag{89}$$

$$\nabla \times \bar{\boldsymbol{E}} = i\omega \bar{\boldsymbol{B}}. \tag{90}$$

$$\nabla \times \bar{\boldsymbol{H}} = -i\omega \bar{\boldsymbol{D}} + \bar{\boldsymbol{J}}. \tag{91}$$

with the current density given by:

$$\bar{\boldsymbol{J}} = s_w \phi \left[\boldsymbol{J_d} + \boldsymbol{J_c} + \boldsymbol{J_s} + \boldsymbol{J_n} \right], \tag{92}$$

where

$$\boldsymbol{J_d} = -\sum_{l=1}^{L} ez_l b_l kT \nabla \bar{n}_l, \tag{93}$$

$$\boldsymbol{J_c} = \frac{1}{V_w} \int_{V_w} \left(\sum_{l=1}^{L} (ez_l)^2 b_l N^0_l \right) \boldsymbol{e_w} dV, \tag{94}$$

$$\boldsymbol{J_s} = \frac{1}{V_w} \int_{V_w} \left(\sum_{l=1}^{L} ez_l N^0_l \right) \boldsymbol{v} dV, \tag{95}$$

$$\boldsymbol{J_n} = -\frac{1}{V_w} \sum_{l=1}^{L} ez_l b_l kT \left[\int_{S_w} n_l \boldsymbol{n} dS + \int_{S_{nw}} n_l \boldsymbol{n} dS - \int_{V_w} \frac{\nabla N^0_{l,(w)}}{N^0_{l,(w)}} n_l dV \right]. \tag{96}$$

Note that the total averaged current density has four contributions. Both $\boldsymbol{J_d}$ and $\boldsymbol{J_n}$ contribute to the *diffusion* of current. The current $\boldsymbol{J_c}$ is the *macroscopic conduction current density* and $\boldsymbol{J_s}$ is the *macroscopic streaming current density*. If the considered porous medium is assumed to be homogeneous, then both $\boldsymbol{J_d}$ and $\boldsymbol{J_n}$ are negligible. As was demonstrated in Pride (1994), the local variations in ion-concentration n_l are negligible, which results in the total absence of diffusion currents. As a result, the contributions to the total current density come only from $\boldsymbol{J_c}$ and $\boldsymbol{J_s}$.

If we define the bulk-wetting fluid conductivity and express it as the sum of the contributions of both diffuse layers

$$\sigma_w = \sum_{l=1}^{L} (ez_l)^2 b_l \mathcal{N}_l = \sum_{l=1}^{L} (ez_l)^2 b_l (\mathcal{N}_{l,(w)} + \mathcal{N}_{l,(nw)}), \tag{97}$$

then, the conduction current can be written as follows

$$\begin{aligned}\boldsymbol{J_c} = \frac{\sigma_w}{V_w} \int_{V_w} \boldsymbol{e_w} dV + \frac{1}{V_w} \int_{S_w} dS \int_0^D \left(\sum_{l=1}^{L} (ez_l)^2 b_l (N^0_{l,(w)} - \mathcal{N}_{l,(w)}) \right) \boldsymbol{e_w} d\chi \\ + \frac{1}{V_w} \int_{S_{nw}} dS \int_0^D \left(\sum_{l=1}^{L} (ez_l)^2 b_l (N^0_{l,(nw)} - \mathcal{N}_{l,(nw)}) \right) \boldsymbol{e_w} d\chi. \end{aligned} \tag{98}$$

The variable χ measures the normal distance from the surfaces S_w and S_{nw} (into the wetting fluid) and $D = \max_\xi \{D_\xi\}$, $\xi = w, nw$, where D_ξ represents the distance over which the charge excess $N^0_{l,(\xi)} - \mathcal{N}_{l,(\xi)}$ associated with each diffuse layer is significant (a few Debye lengths). In practice $\boldsymbol{e_w}$ will be assumed as constant across the double layers.

In the same way we can express the streaming current as follows:

$$\boldsymbol{J_s} = \frac{1}{V_w} \int_{V_w} \left(\sum_{l=1}^{L} ez_l N^0_{l,(w)} \right) \boldsymbol{v} dV + \frac{1}{V_w} \int_{V_w} \left(\sum_{l=1}^{L} ez_l N^0_{l,(nw)} \right) \boldsymbol{v} dV. \tag{99}$$

Substituting Coulomb's law for the static field is into the last equation

$$\boldsymbol{J_s} = \frac{\epsilon_0 \kappa_w}{V_w} \int_{V_w} \left(\nabla \cdot \boldsymbol{E^0_{w,(w)}} \right) \boldsymbol{v} dV + \frac{\epsilon_0 \kappa_w}{V_w} \int_{V_w} \left(\nabla \cdot \boldsymbol{E^0_{w,(nw)}} \right) \boldsymbol{v} dV, \tag{100}$$

which for homogeneous media can be approximated as (Pride, 1994)

$$\boldsymbol{J_s} = \frac{\epsilon_0 \kappa_w}{V_w} \int_{S_w} dS \int_0^D \nabla \Phi^0_w \cdot \nabla \boldsymbol{v} d\chi + \frac{\epsilon_0 \kappa_w}{V_w} \int_{S_{nw}} dS \int_0^D \nabla \Phi^0_{nw} \cdot \nabla \boldsymbol{v} d\chi, \tag{101}$$

The integrals appearing in Eq. (98) and Eq. (101) will be solved in the next section, once the fields at the pore-scale are related to their corresponding macroscopic fields.

It remains to average the electromagnetic constitutive laws. Performing this task on $\boldsymbol{d_\xi} = \epsilon_0 \kappa_\xi \boldsymbol{e_\xi}$ yields

$$\bar{\boldsymbol{D}} = \epsilon_0 \left[\kappa_s (1-\phi) \bar{\boldsymbol{e}}_{\boldsymbol{s}} + \kappa_w s_w \phi \bar{\boldsymbol{e}}_{\boldsymbol{w}} + \kappa_{nw} (1-s_w) \phi \bar{\boldsymbol{e}}_{\boldsymbol{nw}} \right]. \tag{102}$$

If we assume that the magnetic susceptibilities are negligible in the three phases, we simply have

$$\bar{\boldsymbol{B}} = \mu_0 \bar{\boldsymbol{H}}. \tag{103}$$

3.2 Averaging the mechanical equations

Taking the volume average of Eqs. (65)-(67) we respectively obtain

$$-i\omega \rho_s \langle \dot{\boldsymbol{u}}_{\boldsymbol{s}} \rangle = \nabla \cdot \langle \boldsymbol{\tau_s} \rangle - \frac{1}{V_A} \int_{S_w} \boldsymbol{n} \cdot \boldsymbol{\tau_s} dS, \tag{104}$$

$$\begin{aligned} -i\omega \rho_w \langle \dot{\boldsymbol{u}}_{\boldsymbol{w}} \rangle = \nabla \cdot \langle \boldsymbol{\tau_w} \rangle + \frac{1}{V_A} \int_{S_w} \boldsymbol{n} \cdot \boldsymbol{\tau_w} dS + \frac{1}{V_A} \int_{S_{nw}} \boldsymbol{n} \cdot \boldsymbol{\tau_w} dS \\ + \frac{1}{V_A} \int_{V_A} \sum_{l=1}^{L} e z_l \left(N_l^0 \boldsymbol{e_f} + n_l \boldsymbol{E^0_w} \right) dV, \end{aligned} \tag{105}$$

$$-i\omega\rho_{nw}\left\langle \dot{\boldsymbol{u}}_{\boldsymbol{nw}}\right\rangle = \nabla\cdot\left\langle \boldsymbol{\tau}_{\boldsymbol{nw}}\right\rangle - \frac{1}{V_A}\int_{S_{nw}} \boldsymbol{n}\cdot\boldsymbol{\tau}_{\boldsymbol{nw}} dS, \tag{106}$$

Adding (104), (105) and (106), applying the BC's (71) and (73) and the definition of the phase average we get

$$\begin{aligned} &-i\omega\left[(1-\phi)\rho_s\dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}} + s_w\phi\rho_w\dot{\bar{\boldsymbol{u}}}_{\boldsymbol{w}} + (1-s_w)\phi\rho_{nw}\dot{\bar{\boldsymbol{u}}}_{\boldsymbol{nw}}\right] = \\ &\nabla\cdot\left[(1-\phi)\bar{\boldsymbol{\tau}}_{\boldsymbol{s}} + s_w\phi\bar{\boldsymbol{\tau}}_{\boldsymbol{w}} + (1-s_w)\phi\bar{\boldsymbol{\tau}}_{\boldsymbol{nw}}\right] + s_w\phi\left(\boldsymbol{f_a} + \boldsymbol{f_d} + \boldsymbol{f_n}\right), \end{aligned} \tag{107}$$

where:

$$\boldsymbol{f_a} = \frac{Q_w^0}{V_w}\int_{S_w} \boldsymbol{e_s} dS + \frac{Q_{nw}^0}{V_w}\int_{S_{nw}} \boldsymbol{e_{nw}} dS, \tag{108}$$

$$\begin{aligned} \boldsymbol{f_d} = \frac{1}{V_w}\int_{V_w}\left(\sum_{l=1}^{L} ez_l N_l^0\right)\boldsymbol{e_w} dV &= \frac{1}{V_w}\int_{V_w}\left(\sum_{l=1}^{L} ez_l N_{l,(w)}^0\right)\boldsymbol{e_w} dV \\ &+ \frac{1}{V_w}\int_{V_w}\left(\sum_{l=1}^{L} ez_l N_{l,(nw)}^0\right)\boldsymbol{e_w} dV, \end{aligned} \tag{109}$$

$$\boldsymbol{f_n} = \frac{1}{V_w}\int_{V_w}\left(\sum_{l=1}^{L} ez_l n_l\right)\boldsymbol{E_w^0} dV. \tag{110}$$

$\boldsymbol{f_a}$ arises from the BC's and accounts for the average force acting on the excess charge of both adsorbed layers and $\boldsymbol{f_d}$ is the average force acting normal to the adsorbed layers due to any induced-charge excesses in the double layers. If we define:

$$\dot{\bar{\boldsymbol{w}}}_{\boldsymbol{w}} = s_w\phi\left(\dot{\bar{\boldsymbol{u}}}_{\boldsymbol{w}} - \dot{\bar{\boldsymbol{u}}}_s\right), \tag{111}$$

$$\dot{\bar{\boldsymbol{w}}}_{\boldsymbol{nw}} = (1-s_w)\phi\left(\dot{\bar{\boldsymbol{u}}}_{\boldsymbol{nw}} - \dot{\bar{\boldsymbol{u}}}_s\right), \tag{112}$$

$$\bar{\boldsymbol{\tau}}_{\boldsymbol{B}} = (1-\phi)\bar{\boldsymbol{\tau}}_{\boldsymbol{s}} + s_w\phi\bar{\boldsymbol{\tau}}_{\boldsymbol{w}} + (1-s_w)\phi\bar{\boldsymbol{\tau}}_{\boldsymbol{nw}}, \tag{113}$$

$$\rho_B = (1-\phi)\boldsymbol{\rho_s} + s_w\phi\boldsymbol{\rho_w} + (1-s_w)\phi\boldsymbol{\rho_{nw}}, \tag{114}$$

we can then write:

$$\nabla \bar{\boldsymbol{\tau}}_{\boldsymbol{B}} = -i\omega \left[\rho_B \dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}} + \rho_w \dot{\bar{\boldsymbol{w}}}_{\boldsymbol{w}} + \rho_{nw} \dot{\bar{\boldsymbol{w}}}_{\boldsymbol{nw}} \right] - s_w \phi \left(\boldsymbol{f_a} + \boldsymbol{f_d} + \boldsymbol{f_n} \right). \quad (115)$$

In Eqs. (111) and (112) the left hand sides are the volume-averaged relative velocity of the wetting and non-wetting phases with respect to that of the solid matrix respectively. As in Pride (1994), it can be shown that $\boldsymbol{f_a} + \boldsymbol{f_d} = 0$ whenever the solid-water and air-water dielectric contrasts are high. This is to say $\kappa_s, \kappa_{nw} \ll \kappa_w$. The force $\boldsymbol{f_n}$ and the current density $\boldsymbol{J_n}$ are negligible under the same assumption, that is, the perturbations in ionic concentration n_l are negligible. Then, Eq.(115) results

$$\nabla \bar{\boldsymbol{\tau}}_{\boldsymbol{B}} = -i\omega \left[\rho_B \dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}} + \rho_w \dot{\bar{\boldsymbol{w}}}_{\boldsymbol{w}} + \rho_{nw} \dot{\bar{\boldsymbol{w}}}_{\boldsymbol{nw}} \right], \quad (116)$$

It is convenient to introduce the *effective fluid filtration* $\bar{\boldsymbol{w}}_{\boldsymbol{f}}$ as

$$\rho_f \bar{\boldsymbol{w}}_{\boldsymbol{f}} = \rho_w \bar{\boldsymbol{w}}_{\boldsymbol{w}} + \rho_{nw} \bar{\boldsymbol{w}}_{\boldsymbol{nw}}, \quad (117)$$

where $\rho_f = s_w \rho_w + (1 - s_w)\rho_{nw}$. Then Eq. (116) is written

$$\nabla \bar{\boldsymbol{\tau}}_{\boldsymbol{B}} = -i\omega \left[\rho_B \dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}} + \rho_f \dot{\bar{\boldsymbol{w}}}_{\boldsymbol{f}} \right], \quad (118)$$

The averaging of the fluid equations (105) and (106) is completed in a different way and is addressed in Section 4.

Finally, the stress-strain relations are volume averaged following Pride et al (1992). Assuming that the capillary pressure perturbations $p_c = p_{nw} - p_w$ are negligible, then $p_w = p_{nw} = p$ and the averaged constitutive relations result

(Berryman et al, 1988; Pride et al, 1992)

$$\bar{\boldsymbol{\tau}}_{\boldsymbol{B}} = (K_c \nabla \cdot \bar{\boldsymbol{u}}_{\boldsymbol{s}} + C \nabla \cdot \bar{\boldsymbol{w}}_f)\mathbf{I} + G\left(\nabla \bar{\boldsymbol{u}}_{\boldsymbol{s}} + \nabla \bar{\boldsymbol{u}}_{\boldsymbol{s}}{}^T - \frac{2}{3}\nabla \cdot \bar{\boldsymbol{u}}_{\boldsymbol{s}}\mathbf{I}\right), \tag{119}$$

$$-\bar{p} = C\nabla \cdot \bar{\boldsymbol{u}}_{\boldsymbol{s}} + M\nabla \cdot \bar{\boldsymbol{w}}_{\boldsymbol{f}}, \tag{120}$$

where

$$K_c = \frac{K_m + \phi K_f + (1-\phi)K_s\Delta}{1+\Delta}, \tag{121}$$

$$C = \frac{K_f + K_s\Delta}{1+\Delta}, \tag{122}$$

$$M = \frac{1}{\phi}\frac{K_f}{1+\Delta}. \tag{123}$$

In these expressions,

$$\Delta = \frac{K_f}{\phi K_s^2}\left[(1-\phi)K_s - K_m\right], \tag{124}$$

and K_m and G in Eq.(119) are the bulk modulus and shear modulus of the solid matrix respectively, and K_f is the effective bulk modulus of the fluid phase, obtained by a Wood mean, i.e., $K_f = (s_w/K_w + (1-s_w)/K_{nw})^{-1}$.

4 Boundary-value problems

As mentioned before, to complete the averaging procedure we need so solve the integrals appearing in the various derived expressions for the macroscopic fields. In order to do so, any pore-scale field needs to be related to macroscopic fields. In this section, we follow Pride's approach by introducing a new disk-shaped averaging volume, where the boundary-value problems governing the pore-scale fields will be stated and solved.

4.1 Volume averaging over a thin disk

Let us consider an imaginary volume with the shape of a thin disk within the porous rock, defined by two large plane-parallel faces of area A separated by a distance H. This volume can be pictured as a circular disk of radius much greater than H. The total volume occupied by the disk will then be AH. Assume that a macroscopic potential difference and a macroscopic pressure difference exist between the two faces. These differences are defined in such a way that when divided by H, the corresponding macroscopic field in the direction normal to the disk face is obtained. Let z be the direction normal to the disk. The potential or pressure differences will be assumed to be the boundary values for the corresponding pore-scale fields. Also, if we assume that the macroscopic electromagnetic disturbances have wavelength much larger than H, we will also have that $\nabla \times \boldsymbol{e_s} = \nabla \times \boldsymbol{e_w} = \nabla \times \boldsymbol{e_{nw}} = 0$ at the pore-scale. This is equivalent to assume that $\boldsymbol{e_s} = -\nabla \varphi_s$, $\boldsymbol{e_w} = -\nabla \varphi_w$ and $\boldsymbol{e_{nw}} = -\nabla \varphi_{nw}$. As a consequence, under this thin-averaging-disk approach we have

$$\hat{\boldsymbol{z}} \cdot \bar{\boldsymbol{E}} = -\frac{\Delta \phi}{H}, \tag{125}$$

where

$$\Delta \phi = \varphi_\xi(H) - \varphi_\xi(0), \quad \xi = s, w, nw, \tag{126}$$

is the potential difference between the two flat faces (Pride, 1994).

4.2 Pore-scale electric fields and ion-number-density deviations

We start by stating the boundary-value problems controlling the electric potentials and ionic-density deviations n_l. As we mentioned before, n_l will be neglected at the end, but the conditions required to make this valid will be stated.

Let us begin by rewriting the current density in the fluid (Eq. 54) but assuming that this current arises from the electric field created at the wetting adsorbed layer (we denote this by the subindex (w)):

$$\boldsymbol{j_{w,(w)}} = \sum_{l=1}^{L} ez_l \Big[-kTb_l \nabla n_{l,(w)} + ez_l b_l \left(-N_l^0 \nabla \varphi_{w,(w)} + n_{l,(w)} \boldsymbol{E^0_{w,(w)}} \right) + N^0_{l,(w)} \dot{\boldsymbol{u}}_{\boldsymbol{w}} \Big]. \tag{127}$$

Now, using the static-equilibrium condition $ez_l N^0_{l,(w)} \boldsymbol{E^0_{w,(w)}} = kT \nabla N^0_{l,(w)}$ and introducing the relative wetting phase-solid flow vector, we obtain

$$\boldsymbol{j_{w,(w)}} = \sum_{l=1}^{L} ez_l N^0_{l,(w)} \left[\boldsymbol{v} - kTb_l \nabla \left(\frac{n_{l,(w)}}{N^0_{l,(w)}} + \frac{ez_l}{kT} \varphi_{w,(w)} \right) \right]. \tag{128}$$

This last expression is used in the conservation of charge

$$\nabla \cdot \boldsymbol{j_{w,(w)}} = i\omega \sum_{l=1}^{L} ez_l n_{l,(w)}. \tag{129}$$

This conservation law holds for an electrolyte of arbitrary specifications. Then we can write for each one of the L ionic species

$$\nabla \cdot \left\{ N^0_{l,(w)} \left[\boldsymbol{v} - kTb_l \nabla \left(\frac{n_{l,(w)}}{N^0_{l,(w)}} + \frac{ez_l}{kT} \varphi_{w,(w)} \right) \right] \right\} = i\omega n_{l,(w)}. \tag{130}$$

Assuming that the wetting-fluid is incompressible at the pore scale ($\nabla \cdot \boldsymbol{v} = 0$) we can write the so-called *ion balance equation* (Pride, 1994)

$$\nabla^2 \left(\frac{n_{l,(w)}}{N^0_{l,(w)}} + \frac{ez_l}{kT} \varphi_{w,(w)} \right) + \frac{i\omega}{b_l kT} \frac{n_{l,(w)}}{N^0_{l,(w)}} = \frac{\nabla N^0_{l,(w)}}{N^0_{l,(w)}} \cdot \left[\frac{\boldsymbol{v}}{b_l kt} - \nabla \left(\frac{n_{l,(w)}}{N^0_{l,(w)}} + \frac{ez_l}{kT} \varphi_{w,(w)} \right) \right]. \tag{131}$$

The ion balance should be complemented with the boundary condition of no ion accumulation on S_w ($\boldsymbol{n} \cdot \boldsymbol{j_{w,(w)}} = 0$ on S_w), which is equivalent to state

$$\boldsymbol{n} \cdot \left(\frac{n_{l,(w)}}{N^0_{l,(w)}} + \frac{ez_l}{kT} \varphi_{w,(w)} \right) = 0, \tag{132}$$

$$\boldsymbol{n} \cdot \boldsymbol{v} = 0, \tag{133}$$

on S_w.

The gradient $\nabla N^0_{l,(w)}$ in the right-hand side of Eq. (131) is everywhere normal to the grain surfaces and is nonzero only in the electric double layer. As it is argued by Pride (1994) for small Debye lengths there will not be normal components of any of both terms between brackets multiplying $\nabla N^0_{l,(w)}$, and thus the right-hand side of Eq. (131) will be zero. Under the thin-double-layer condition and in the low-frequency limit where $\omega \ll b_l kT/r^2$, being r the radius of the pore grains [using typical values one gets $f \ll 200$ Hz (Pride, 1994)] we obtain the following boundary-value problem

$$\psi_{l,(w)} = \frac{n_{l,(w)}}{N^0_{l,(w)}} + \frac{ez_l}{kT} \varphi_{w,(w)} \tag{134}$$

$$\nabla^2 \psi_{l,(w)} = 0, \tag{135}$$

$$\boldsymbol{n} \cdot \nabla \psi_{l,(w)} = 0 \quad \text{on} \quad S_w, \tag{136}$$

and with the boundary conditions at the flat faces of the averaging disk given by

$$\psi_{l,(w)} = \begin{cases} \frac{ez_l}{kT} \Delta\phi & \text{on} \quad z = H \\ 0 & \text{on} \quad z = 0. \end{cases} \tag{137}$$

Note that this last condition states that there exists a macroscopic-electric-potential difference of $\Delta\phi$ between both faces of the averaging disk but that no macroscopic gradients in $n_{l,(w)}$ exist. An equivalent way to write this problem is to express it in terms of a related, purely geometric, field Γ_w possessing units of length and defined to satisfy

$$\nabla^2 \Gamma_w = 0, \tag{138}$$

$$\boldsymbol{n} \cdot \nabla \Gamma_w = 0 \quad \text{on} \quad S_w, \tag{139}$$

$$\Gamma_w = \begin{cases} H & \text{on} \quad z = H, \\ 0 & \text{on} \quad z = 0. \end{cases} \tag{140}$$

Thus, we obtain

$$\frac{n_{l,(w)}(\boldsymbol{r})}{N^0_{l,(w)}} = \frac{ez_l}{kT} \left[\Gamma_w(\boldsymbol{r}) \frac{\Delta\phi}{H} - \varphi_{w,(w)}(\boldsymbol{r}) \right]. \tag{141}$$

Now we consider the boundary-value problem for $\varphi_{w,(w)}$ defined by Coulomb's law

$$\nabla^2 \varphi_{w,(w)} = -\sum_{l=1}^{L} \frac{ez_l}{\epsilon_0 \kappa_w} n_{l,(w)} = -\sum_{l=1}^{L} \frac{(ez_l)^2}{\epsilon_0 \kappa_w kT} N^0_{l,(w)} \left(\Gamma_w \frac{\Delta\phi}{H} - \varphi_{w,(w)} \right), \tag{142}$$

with the the boundary condition on S_w

$$\boldsymbol{n} \cdot \nabla \varphi_{w,(w)} = \frac{\kappa_s}{\kappa_w} \boldsymbol{n} \cdot \nabla \varphi_s, \tag{143}$$

and on the flat faces

$$\varphi_{w,(w)} = \begin{cases} \Delta\phi & \text{on} \quad z = H, \\ 0 & \text{on} \quad z = 0. \end{cases} \tag{144}$$

Note that the boundary condition at S_w contains φ_s, so we need to establish a boundary-value problem for φ_s,

$$\nabla^2 \varphi_s = 0, \tag{145}$$

$$\varphi_s = \varphi_{w,(w)} \quad \text{on} \;\; S_w, \tag{146}$$

$$\varphi_s = \begin{cases} \Delta\phi & \text{on} \;\; z = H, \\ 0 & \text{on} \;\; z = 0. \end{cases} \tag{147}$$

The following expression

$$\varphi^p_{w,(w)} = \Gamma_w \frac{\Delta\phi}{H}. \tag{148}$$

is a particular solution for $\varphi_{w,(w)}$. It satisfies the differential equation but not necessarily the boundary conditions. If the condition $\kappa_s/\kappa_w \ll 1$ holds, so that $\boldsymbol{n} \cdot \nabla\varphi_{w,(w)} \simeq 0$ on S_w, this particular solution is the actual solution. In this case, we then have $n_{l,(w)} \simeq 0$ and the integrals $\boldsymbol{J_n}$ and $\boldsymbol{f_n}$ from the volume averaging vanish. As mentioned by Pride (1994), for a quartz-electrolyte interface, the contrast is $\kappa_s/\kappa_w \simeq 1/20$, and this approximation is appropriate. Then, if the dielectric contrast is large, large polarization-charge densities are induced on those portions of S_w that have $\boldsymbol{n} \cdot \hat{\boldsymbol{z}} \neq 0$. These polarization charges produce local fields that keep $\boldsymbol{n} \cdot \nabla\varphi_s \simeq 0$ everywhere along S_w and, thus, $n_{l,(w)} = 0$ throughout the fluid. The case of small dielectric contrast is assumed not to be present in our study.

As a resume, the neglect of $n_{l,(w)}$ is justified whenever the following two conditions are met (Pride, 1994): (1) The electric double layer must be much thinner than the grain sizes which allows to neglect the right-hand side of the ion balance, and (2) a large dielectric contrast must exist between the grains and the electrolyte.

In conclusion, if $n_{l,(w)}$ are ignored, then *for all the frequencies* the electric-field in the fluid produced by the double layer at the solid-wetting interface is given by

$$\boldsymbol{e_{w,(w)}}(\boldsymbol{r}) = -\nabla\varphi_{w,(w)}(\boldsymbol{r}) = -\nabla\Gamma_w(\boldsymbol{r})\frac{\Delta\phi}{H}. \tag{149}$$

Under the mentioned assumptions, this field can be taken to be constant and tangential to S_w throughout the thin electric double layer.

Following the same procedure but considering the electric double layer at S_{nw} it is possible to get, under the same assumptions as before

$$\boldsymbol{e_{w,(nw)}}(\boldsymbol{r}) = -\nabla\Gamma_{nw}(\boldsymbol{r})\frac{\Delta\phi}{H}, \tag{150}$$

where

$$\nabla^2\Gamma_{nw} = 0, \tag{151}$$

$$\boldsymbol{n_{nw}} \cdot \nabla\Gamma_{nw} = 0 \quad \text{on} \;\; S_{nw}, \tag{152}$$

$$\Gamma_{nw} = \begin{cases} H & \text{on} \;\; z = H, \\ 0 & \text{on} \;\; z = 0. \end{cases} \tag{153}$$

Of course, the last derivation will be valid for all frequencies and for large dielectric contrasts between the non-wetting phase (air) and the electrolyte.

We can now volume-average the electric fields in the disk. Let's start with $\boldsymbol{\bar{e}_w}$:

$$\begin{aligned} \boldsymbol{\bar{e}_w} &= -\frac{1}{V_w}\int_{V_w}\nabla\phi_w dV \\ &= -\frac{1}{V_w}\left[s_w\phi AH\boldsymbol{\hat{z}} + \int_{S_w}\boldsymbol{n}\Gamma_w(\boldsymbol{r})dS + \int_{S_{nw}}\boldsymbol{n}\Gamma_{nw}(\boldsymbol{r})dS\right]\frac{\Delta\phi}{H}, \end{aligned} \tag{154}$$

multiplying by $\hat{\boldsymbol{z}}$ and replacing $-\boldsymbol{n_{nw}} = \boldsymbol{n}$ in the second integral

$$\bar{\boldsymbol{e}}_{\boldsymbol{w}} = \left[1 + \frac{\hat{\boldsymbol{z}}}{V_w} \int_{S_w} \boldsymbol{n} \Gamma_w(\boldsymbol{r}) dS - \frac{\hat{\boldsymbol{z}}}{V_w} \int_{S_{nw}} \boldsymbol{n_{nw}} \Gamma_{nw}(\boldsymbol{r}) dS\right] \bar{\boldsymbol{E}}, \tag{155}$$

which can be written as

$$\begin{aligned} \bar{\boldsymbol{e}}_{\boldsymbol{w}} = \Bigg[& 1 - \frac{V_p}{V_w} + \frac{V_p}{V_w} \left\{1 + \frac{\hat{\boldsymbol{z}}}{V_p} \int_{S_w} \boldsymbol{n} \Gamma_w(\boldsymbol{r}) dS\right\} \\ & + \frac{V_{nw}}{V_w} - \frac{V_{nw}}{V_w} \left\{1 + \frac{\hat{\boldsymbol{z}}}{V_{nw}} \int_{S_{nw}} \boldsymbol{n_{nw}} \Gamma_{nw}(\boldsymbol{r}) dS\right\} \Bigg] \bar{\boldsymbol{E}}, \end{aligned} \tag{156}$$

or, identifying the *tortuosities* of the porous space α_∞ and of the non-wetting phase $\alpha_{\infty,nw}$ as

$$\frac{1}{\alpha_\infty} = 1 + \frac{\hat{\boldsymbol{z}}}{V_p} \int_{S_w} \boldsymbol{n} \Gamma_w(\boldsymbol{r}) dS, \quad \frac{1}{\alpha_{\infty,nw}} = 1 + \frac{\hat{\boldsymbol{z}}}{V_{nw}} \int_{S_{nw}} \boldsymbol{n_{nw}} \Gamma_{nw}(\boldsymbol{r}) dS, \tag{157}$$

then,

$$\bar{\boldsymbol{e}}_{\boldsymbol{w}} = \left[\frac{1}{s_w} \frac{1}{\alpha_\infty} - \frac{(1 - s_w)}{s_w} \frac{1}{\alpha_{\infty,nw}}\right] \bar{\boldsymbol{E}} = \frac{1}{\tilde{\alpha}_{\infty,w}} \bar{\boldsymbol{E}}. \tag{158}$$

At this point we have all the ingredients to compute the macroscopic conduction current, which is completed in the following Section. It remains to compute the constitutive electromagnetic equation relating $\bar{\boldsymbol{D}}$ and $\bar{\boldsymbol{E}}$. To this end, we need to compute $\bar{\boldsymbol{e}}_{\boldsymbol{s}}$ and $\bar{\boldsymbol{e}}_{\boldsymbol{nw}}$. Note that

$$\bar{\boldsymbol{e}}_{\boldsymbol{s}} = -\frac{1}{V_s} \int_{V_s} \nabla \varphi_s dV = -\frac{1}{V_s} \left[(1 - \phi) A \Delta \phi \hat{\boldsymbol{z}} + \int_{S_w} \boldsymbol{n_s} \varphi_s dS\right]. \tag{159}$$

Because $\varphi_s = \varphi_w$ at S_w (see Eq. 146)

$$\bar{\boldsymbol{e}}_{\boldsymbol{s}} = -\frac{1}{V_s} \int_{V_s} \nabla \varphi_s dV = -\frac{1}{V_s} \left[(1 - \phi) A \Delta \phi \hat{\boldsymbol{z}} - \int_{S_w} \boldsymbol{n} \varphi_w dS\right]$$

$$= \left[1 - \frac{\hat{\boldsymbol{z}}}{V_s} \int_{S_w} \boldsymbol{n} \Gamma_w(\boldsymbol{r}) dS \right] \bar{\boldsymbol{E}}, \quad (160)$$

then

$$\bar{\boldsymbol{e}}_{\boldsymbol{s}} = \left[1 + \frac{V_p}{V_s} - \frac{V_p}{V_s} \left\{ 1 + \frac{\hat{\boldsymbol{z}}}{V_p} \int_{S_w} \boldsymbol{n} \Gamma_w(\boldsymbol{r}) dS \right\} \right] \bar{\boldsymbol{E}}, \quad (161)$$

or

$$\bar{\boldsymbol{e}}_{\boldsymbol{s}} = \left[\frac{1}{(1-\phi)} - \frac{\phi}{(1-\phi)} \left\{ 1 + \frac{\hat{\boldsymbol{z}}}{V_p} \int_{S_w} \boldsymbol{n} \Gamma_w(\boldsymbol{r}) dS \right\} \right] \bar{\boldsymbol{E}}. \quad (162)$$

Using the definition of α_∞ we get

$$\bar{\boldsymbol{e}}_{\boldsymbol{s}} = \left[\frac{1}{(1-\phi)} - \frac{\phi}{(1-\phi)} \frac{1}{\alpha_\infty} \right] \bar{\boldsymbol{E}} = \frac{1}{\tilde{\alpha}_{\infty,s}} \bar{\boldsymbol{E}}. \quad (163)$$

Following the same reasoning and under the same hypothesis regarding the dielectric contrast we proceed to compute the field $\bar{\boldsymbol{e}}_{\boldsymbol{nw}}$:

$$\bar{\boldsymbol{e}}_{\boldsymbol{nw}} = -\frac{1}{V_{nw}} \int_{V_{nw}} \nabla \varphi_{nw} dV = -\frac{1}{V_{nw}} \left[(1-s_w)\phi A \Delta\phi \hat{\boldsymbol{z}} + \int_{S_{nw}} \boldsymbol{n}_{\boldsymbol{nw}} \varphi_w dS \right]$$
$$= \left[1 + \frac{\hat{\boldsymbol{z}}}{V_{nw}} \int_{S_{nw}} \boldsymbol{n}_{\boldsymbol{nw}} \Gamma_{nw}(\boldsymbol{r}) dS \right] \bar{\boldsymbol{E}}. \quad (164)$$

Then

$$\bar{\boldsymbol{e}}_{\boldsymbol{nw}} = \frac{1}{\alpha_{\infty,nw}} \bar{\boldsymbol{E}}. \quad (165)$$

It is easy to verify that $\bar{\boldsymbol{E}} = (1-\phi)\bar{\boldsymbol{e}}_{\boldsymbol{s}} + \phi s_w \bar{\boldsymbol{e}}_{\boldsymbol{w}} + \phi(1-s_w)\bar{\boldsymbol{e}}_{\boldsymbol{nw}}$ as expected from the definition of $\bar{\boldsymbol{E}}$.

Replacing the average fields in Eq. (102):

$$\bar{\boldsymbol{D}} = \epsilon_0 \left[\frac{\kappa_s(1-\phi)}{\tilde{\alpha}_{\infty,s}} + \frac{\kappa_w s_w \phi}{\tilde{\alpha}_{\infty,w}} + \frac{\kappa_{nw}(1-s_w)\phi}{\alpha_{\infty,nw}} \right] \bar{\boldsymbol{E}}. \quad (166)$$

This last equation, together with Eq.(103) complete the volume averaged expressions for the electromagnetic constitutive relations.

4.3 Pore-scale flow fields

Let us start recalling Eq.(66), for the wetting-fluid flow at the pore-scale. Neglecting n_l this equation can be written as

$$-i\omega\rho_w \dot{\boldsymbol{u}}_{\boldsymbol{w}} = \nabla \cdot \boldsymbol{\tau}_{\boldsymbol{w}} + \left(\sum_{l=1}^{L} e z_l N_l^0 \right) \boldsymbol{e}_{\boldsymbol{w}}, \tag{167}$$

which using $\boldsymbol{v}$ reads

$$-i\omega\rho_w \boldsymbol{v} = \nabla \cdot \boldsymbol{\tau}_{\boldsymbol{w}} + i\omega\rho_w \dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}} + \left(\sum_{l=1}^{L} e z_l N_l^0 \right) \boldsymbol{e}_{\boldsymbol{w}}. \tag{168}$$

Assuming as in the previous section that the relative flow is incompressible, we can write

$$\nabla \cdot \boldsymbol{\tau}_{\boldsymbol{w}} = -\nabla p_w - \eta_w \nabla \times \nabla \times \boldsymbol{v}, \tag{169}$$

so that

$$-i\omega\rho_w \boldsymbol{v} = -\nabla p_w + i\omega\rho_w \dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}} - \eta_w \nabla \times \nabla \times \boldsymbol{v} + \left(\sum_{l=1}^{L} e z_l N_l^0 \right) \boldsymbol{e}_{\boldsymbol{w}}. \tag{170}$$

Noting that $\nabla \times \nabla \times \boldsymbol{v} = -\nabla^2 \boldsymbol{v}$ and defining $\nabla p = \nabla p_w - i\omega\rho_w \dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}}$, we can state the following boundary-value problem within the averaging disk

$$\eta_w \nabla^2 \boldsymbol{v} + i\omega\rho_w \boldsymbol{v} = \nabla p - \left(\sum_{l=1}^{L} e z_l N_l^0 \right) \boldsymbol{e}_{\boldsymbol{w}}, \tag{171}$$

$$\nabla \cdot \boldsymbol{v} = 0, \tag{172}$$

$$\boldsymbol{v} = 0 \qquad \text{on } S_w \text{ and } S_{nw}, \tag{173}$$

$$p = \begin{cases} \Delta P = \hat{\boldsymbol{z}} \cdot \left(\nabla \bar{p}_w - i\omega\rho_w \dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}} \right) H, & z = H, \\ 0, & z = 0. \end{cases} \tag{174}$$

The solution for $\boldsymbol{v}$ and p can be separated into mechanically and electrically induced contributions.

$$\boldsymbol{v} = \boldsymbol{v_m} + \boldsymbol{v_e}, \tag{175}$$

$$p = p_m + p_e, \tag{176}$$

where m stands for fields induced by pressure gradients $\Delta P/H$, while e stands for fields induced by electric potential gradients $\Delta\phi/H$. If the viscous skin depth is introduced

$$\delta_{\mathrm{sd}} = \sqrt{\frac{\eta_w}{\omega\rho_w}}, \tag{177}$$

the boundary-value problem results in two separate problems:

$$\nabla^2\boldsymbol{v_m} + \frac{i}{\delta_{\mathrm{sd}}^2}\boldsymbol{v_m} = \frac{\nabla p_m}{\eta_w}, \tag{178}$$

$$p_m = \begin{cases} \Delta P, & z = H, \\ 0, & z = 0. \end{cases} \tag{179}$$

and

$$\eta_w\nabla^2\boldsymbol{v_e} + i\omega\rho_w\boldsymbol{v_e} = \nabla p_e - \left(\sum_{l=1}^{L} e z_l N_l^0\right)\boldsymbol{e_w} \tag{180}$$

$$p_e = \begin{cases} 0, & z = H, \\ 0, & z = 0. \end{cases} \tag{181}$$

with the additional conditions $\boldsymbol{v_e} = \boldsymbol{v_m} = 0$ on S_w and S_{nw}, and $\nabla\cdot\boldsymbol{v_e} = \nabla\cdot\boldsymbol{v_m} = 0$ everywhere within the wetting fluid.

Let us deal in a first step with the electrically induced fields. Introducing the fields $\boldsymbol{e_{w,(w)}}$ and $\boldsymbol{e_{w,(nw)}}$ we have

$$\eta_w\nabla^2\boldsymbol{v_e}+i\omega\rho_w\boldsymbol{v_e} = \nabla p_e-\epsilon_0\kappa_w\nabla^2\Phi_w^0\nabla\Gamma_w\frac{\Delta\phi}{H}-\epsilon_0\kappa_w\nabla^2\Phi_{nw}^0\nabla\Gamma_{nw}\frac{\Delta\phi}{H}, \tag{182}$$

$$p_e = \begin{cases} 0, & z = H, \\ 0, & z = 0. \end{cases} \tag{183}$$

Given that the electrical body forces inducing flow only act in the thin double layers and are tangential to S_w and S_{nw} we have that $\boldsymbol{n} \cdot \nabla p_e = 0$ on S_w and S_{nw}. Then $p_e = 0$ everywhere and for all frequencies. In the limit of very low frequencies ($\delta_{\rm sd} \to \infty$), the flow velocity is

$$\boldsymbol{v_{e0}} = -\frac{\epsilon_0 \kappa_w}{\eta_w} \left(\Phi_w^0 - \zeta_w\right) \nabla \Gamma_w \frac{\Delta \phi}{H} - \frac{\epsilon_0 \kappa_w}{\eta_w} \left(\Phi_{nw}^0 - \zeta_{nw}\right) \nabla \Gamma_{nw} \frac{\Delta \phi}{H}. \tag{184}$$

Note that this last equation can be interpreted as the sum of two contributions coming from the electrical effects from both double layers

$$\boldsymbol{v_{e0,(w)}} = -\frac{\epsilon_0 \kappa_w}{\eta_w} \left(\Phi_w^0 - \zeta_w\right) \nabla \Gamma_w \frac{\Delta \phi}{H}, \tag{185}$$

and

$$\boldsymbol{v_{e0,(nw)}} = -\frac{\epsilon_0 \kappa_w}{\eta_w} \left(\Phi_{nw}^0 - \zeta_{nw}\right) \nabla \Gamma_{nw} \frac{\Delta \phi}{H}. \tag{186}$$

These fields are solutions for the following problems

$$\eta_w \nabla^2 \boldsymbol{v_{e,(w)}} = -\epsilon_0 \kappa_w \nabla^2 \Phi_w^0 \nabla \Gamma_w \frac{\Delta \phi}{H} \tag{187}$$

and

$$\eta_w \nabla^2 \boldsymbol{v_{e,(nw)}} = -\epsilon_0 \kappa_w \nabla^2 \Phi_w^0 \nabla \Gamma_w \frac{\Delta \phi}{H}, \tag{188}$$

respectively.

The mechanical induced wetting-fluid flow problem is more difficult because the vorticity is not always confined to thin boundary layers near S_w and S_{nw}. This is controlled by the frequency of the perturbations by whether the inertial term is significant or not. A transition frequency f_t between low and high frequency regimes is estimated as

$$f_t = \frac{\eta_w}{2\pi\rho_w}\frac{\nabla^2 \boldsymbol{v_m}}{\boldsymbol{v_m}} \simeq \frac{\eta_w}{2\pi\rho_w r^2}, \tag{189}$$

where r can be taken as a typical pore radius. For water and $r = 10^{-3}$ m, this gives $f_t \simeq 2000$ Hz. This result holds for any kind of fluid considered, even in the case of low-viscosity fluids like air (Pride, 1994). When $f \ll f_t$ (low frequencies), the vorticity extends throughout the fluid and the inertial term is everywhere negligible. Then, the mechanical problem is written as

$$\nabla^2 \boldsymbol{v_m} = \frac{\nabla p_m}{\eta_w}, \tag{190}$$

$$\nabla \cdot \boldsymbol{v_m} = 0, \tag{191}$$

$$\boldsymbol{v_m} = 0, \quad \text{on} \quad S_w \cup S_{nw} = \partial V_w, \tag{192}$$

$$p_m = \begin{cases} \Delta P, & z = H, \\ 0, & z = 0. \end{cases} \tag{193}$$

The solution to this boundary value problem is given by

$$\boldsymbol{v_{m0}}(\boldsymbol{r}) = \frac{\boldsymbol{g}(\boldsymbol{r})}{\eta_w}\frac{\Delta P}{H}, \tag{194}$$

and

$$p_{m0}(\boldsymbol{r}) = h(\boldsymbol{r})\frac{\Delta P}{H}, \tag{195}$$

where $\boldsymbol{g}(\boldsymbol{r})$ has the units of length squared and $h(\boldsymbol{r})$ has the units of length, and verify:

$$\nabla^2 \boldsymbol{g} = \nabla h, \tag{196}$$

$$\nabla \cdot h = 0, \tag{197}$$

$$\boldsymbol{g} = 0, \quad \text{on} \quad S_w \cup S_{nw} = \partial V_w, \tag{198}$$

$$h = \begin{cases} H, & z = H, \\ 0, & z = 0. \end{cases} \tag{199}$$

In general, $\boldsymbol{n} \cdot \nabla h = -\boldsymbol{n} \cdot \nabla \times \nabla \times \boldsymbol{g} \neq 0$ both on S_w and on S_{nw}. Then, $h \neq \Gamma_w$ and $h \neq \Gamma_{nw}$. However, it is convenient to express h as $h = \Gamma_w + \delta h_w$ when we are close to S_w, or $h = \Gamma_{nw} + \delta h_{nw}$ when we are close to S_{nw}, and δh_ξ, $\xi = w$, nw satisfies

$$\nabla^2 \delta h_\xi = 0, \tag{200}$$

$$\boldsymbol{n} \cdot \nabla \delta h_\xi = -\boldsymbol{n} \cdot \nabla \times \nabla \times \boldsymbol{g} \quad \text{on} \quad S_\xi, \tag{201}$$

$$\delta h_\xi = \begin{cases} 0, & z = H, \\ 0, & z = 0. \end{cases}$$

The source of the δh_ξ field is the rotation of vorticity near the surface S_ξ. Then, using the first expression of h we will be considering the pressure field near S_w and using the second one, the pressure field near S_{nw}. We can write these as follows:

$$\eta_w \nabla^2 \boldsymbol{v_{m,(w)}} = \nabla \left(\delta p_{m,(w)} + \Gamma_w \frac{\Delta P}{H} \right) \tag{202}$$

and

$$\eta_w \nabla^2 \boldsymbol{v_{m,(nw)}} = \nabla \left(\delta p_{m,(nw)} + \Gamma_{nw} \frac{\Delta P}{H} \right), \tag{203}$$

where $\delta p_{m,(\xi)} = \delta h_\xi \Delta P / H$. Given that in both equations the right-hand sides are provided by fields associated with different boundary layers, then we will have two mechanical velocities $\boldsymbol{v_{m,(w)}}$ and $\boldsymbol{v_{m,(nw)}}$. The usefulness of these last expressions will be clear at the end of the following Section.

Now we proceed to volume average the non-wetting fluid flow Eq. (67). If we define the relative non-wetting solid-phase flow vector $\boldsymbol{v_{nw}} = \dot{\boldsymbol{u}}_{\boldsymbol{nw}} - \dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}}$ we may write:

$$- i\omega\rho_{nw}\boldsymbol{v_{nw}} = \nabla \cdot \boldsymbol{\tau_{nw}} + i\omega\rho_{nw}\dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}}. \tag{204}$$

Again, if we assume that the local relative flow is incompressible ($\nabla \cdot \boldsymbol{v_{nw}} = 0$) then:

$$\nabla \cdot \boldsymbol{\tau_{nw}} = -\nabla p_{nw} - \eta_{nw}\nabla \times \nabla \times \boldsymbol{v_{nw}}, \tag{205}$$

from which

$$- i\omega\rho_{nw}\boldsymbol{v_{nw}} = -\nabla p_{nw} + i\omega\rho_{nw}\dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}} - \eta_{nw}\nabla \times \nabla \times \boldsymbol{v_{nw}}. \tag{206}$$

Noting that $\nabla \times \nabla \times \boldsymbol{v_{nw}} = -\nabla^2\boldsymbol{v_{nw}}$ and defining $\nabla p = \nabla p_{nw} - i\omega\rho_{nw}\dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}}$, the following boundary-value problem can be stated within the averaging disk

$$\eta_{nw}\nabla^2\boldsymbol{v_{nw}} + i\omega\rho_{nw}\boldsymbol{v_{nw}} = \nabla p, \tag{207}$$

$$\nabla \cdot \boldsymbol{v_{nw}} = 0, \tag{208}$$

$$\boldsymbol{v_{nw}} = 0 \qquad \text{on} \quad S_{nw} = \partial V_{nw}, \tag{209}$$

$$p = \begin{cases} \Delta P = \hat{\boldsymbol{z}} \cdot \left(\nabla\bar{p}_{nw} - i\omega\rho_{nw}\dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}}\right) H, & z = H, \\ 0, & z = 0. \end{cases} \tag{210}$$

This is a purely mechanical problem, and can be solved in the same way as the wetting-fluid case. First, note that in the low-frequency regime we can write

$$\nabla^2\boldsymbol{v_{nw}} = \frac{\nabla p}{\eta_{nw}}, \tag{211}$$

$$\nabla \cdot \boldsymbol{v_{nw}} = 0, \tag{212}$$

$$\boldsymbol{v_{nw}} = 0, \quad \text{on} \quad S_{nw} = \partial V_{nw}, \tag{213}$$

$$p = \begin{cases} \Delta P, & z = H, \\ 0, & z = 0. \end{cases} \tag{214}$$

The solution to this boundary-value problem is given by

$$\boldsymbol{v_{nw0}}(\boldsymbol{r}) = \frac{\boldsymbol{g_{nw}}(\boldsymbol{r})}{\eta_{nw}} \frac{\Delta P}{H}, \tag{215}$$

and

$$p_0(\boldsymbol{r}) = h_{nw}(\boldsymbol{r}) \frac{\Delta P}{H}, \tag{216}$$

where $\boldsymbol{g_{nw}}(\boldsymbol{r})$ and $h_{nw}(\boldsymbol{r})$ verify:

$$\nabla^2 \boldsymbol{g_{nw}} = \nabla h_{nw}, \tag{217}$$

$$\nabla \cdot h_{nw} = 0, \tag{218}$$

$$\boldsymbol{g_{nw}} = 0, \quad \text{on} \quad S_{nw} = \partial V_{nw}, \tag{219}$$

$$h_{nw} = \begin{cases} H, & z = H, \\ 0, & z = 0. \end{cases} \tag{220}$$

The so-called Stokes-flow geometry fields $\boldsymbol{g}$ and $\boldsymbol{g_{nw}}$ are the only ones needed to establish relations between the various macroscopic-transport coefficients. However, explicit solutions for them are not required, as we will see in the following Section.

At this stage all the low-frequency regime pore scale fields needed to obtain the macroscopic transport coefficients have been obtained so the final transport equations will be computed in the following Section.

5 Transport equations

5.1 Conduction current density $\boldsymbol{J_c}$

Replacing the expressions for the averaged field $\bar{\boldsymbol{e}}_{\boldsymbol{w}}$ and the local fields $\boldsymbol{e}_{\boldsymbol{w},(\boldsymbol{w})}$ and $\boldsymbol{e}_{\boldsymbol{w},(\boldsymbol{nw})}$ in Eq.(98) we obtain

$$\begin{aligned}
\boldsymbol{J_c} &= \frac{\sigma_w}{\tilde{\alpha}_{\infty,w}}\bar{\boldsymbol{E}} \\
&-\frac{1}{V_w}\int_{S_w}\nabla\Gamma_w(\boldsymbol{r})dS\int_0^D\left(\sum_{l=1}^{L}(ez_l)^2 b_l(N^0_{l,(w)}-\mathcal{N}_{l,(w)})\right)\frac{\Delta\phi}{H}d\chi \\
&-\frac{1}{V_w}\int_{S_{nw}}\nabla\Gamma_{nw}(\boldsymbol{r})dS\int_0^D\left(\sum_{l=1}^{L}(ez_l)^2 b_l(N^0_{l,(nw)}-\mathcal{N}_{l,(nw)})\right)\frac{\Delta\phi}{H}d\chi. \quad (221)
\end{aligned}$$

Now, if we define:

$$\frac{2}{\Lambda} = \frac{\alpha_\infty}{V_p}\int_{S_w}\hat{\boldsymbol{z}}\cdot\nabla\Gamma_w(\boldsymbol{r})dS, \quad (222)$$

$$\frac{2}{\Lambda_{nw}} = \frac{\alpha_{\infty,nw}}{V_{nw}}\int_{S_{nw}}\hat{\boldsymbol{z}}\cdot\nabla\Gamma_{nw}(\boldsymbol{r})dS, \quad (223)$$

and

$$C_{em,(w)} = \int_0^D\left(\sum_{l=1}^{L}(ez_l)^2 b_l(N^0_{l,(w)}-\mathcal{N}_{l,(w)})\right)d\chi, \quad (224)$$

$$C_{em,(nw)} = \int_0^D\left(\sum_{l=1}^{L}(ez_l)^2 b_l(N^0_{l,(nw)}-\mathcal{N}_{l,(nw)})\right)d\chi, \quad (225)$$

then, for isotropic media we have:

$$\boldsymbol{J_c} = \left[\frac{\sigma_w}{\tilde{\alpha}_{\infty,w}} + \frac{2C_{em,(w)}}{s_w\alpha_\infty\Lambda} + \frac{(1-s_w)}{s_w}\frac{2C_{em,(nw)}}{\alpha_{\infty,nw}\Lambda_{nw}}\right]\bar{\boldsymbol{E}}. \quad (226)$$

Λ is a fundamental porous material geometry parameter and is a measure of the *weighted volume-to-surface ratio* of the porous media. Therefore it has units of length. Similarly, Λ_{nw} is the corresponding parameter of the non-wetting phase, and of course it will depend on the water saturation s_w. The quantities

$C_{em,(w)}$ and $C_{em,(nw)}$ are the conductances associated with electromigration of double layer ions. Following Pride (1994) the Debye approximation allows to obtain the following expressions

$$C_{em,(w)} \simeq 2d_w \sum_{l=1}^{L} (ez_l)^2 b_l \mathcal{N}_{l,(w)} \left(e^{-\frac{ez_l\zeta_w}{2kT}} - 1 \right), \tag{227}$$

$$C_{em,(nw)} \simeq 2d_{nw} \sum_{l=1}^{L} (ez_l)^2 b_l \mathcal{N}_{l,(nw)} \left(e^{-\frac{ez_l\zeta_{nw}}{2kT}} - 1 \right). \tag{228}$$

5.2 Streaming current density $\boldsymbol{J_s}$

Consider the average streaming current density given by Eq. (101):

$$\boldsymbol{J_s} = \frac{\epsilon_0\kappa_w}{V_w} \int_{S_w} dS \int_0^D \nabla\Phi_w^0 \cdot \nabla \boldsymbol{v} d\chi + \frac{\epsilon_0\kappa_w}{V_w} \int_{S_{nw}} dS \int_0^D \nabla\Phi_{nw}^0 \cdot \nabla \boldsymbol{v} d\chi, \tag{229}$$

where $\nabla\Phi_\xi^0 \cdot \nabla \boldsymbol{v} = (\partial\Phi_\xi^0/\partial\chi)(\partial\boldsymbol{v}/\partial\chi)$, $\xi = w, nw$. Given the separation into an electrically induced field $\boldsymbol{v_e}$ and a mechanically induced field $\boldsymbol{v_m}$, we also have $\boldsymbol{J_s} = \boldsymbol{J_{se}} + \boldsymbol{J_{sm}}$. Focusing on the electrical contribution, replacing the expressions for $\boldsymbol{v_{e0,(w)}}$ and $\boldsymbol{v_{e0,(nw)}}$ from (185) and (186) in the first and second integrals of (229), respectively, we obtain

$$\boldsymbol{J_{se}} = -\frac{(\epsilon_0\kappa_w)^2}{\eta_w V_w} \left[\int_{S_w} \nabla\Gamma_w dS \int_0^D (\nabla\Phi_w^0)^2 d\chi \frac{\Delta\phi}{H} \right. \\ \left. + \int_{S_{nw}} \nabla\Gamma_{nw} dS \int_0^D (\nabla\Phi_{nw}^0)^2 d\chi \frac{\Delta\phi}{H} \right]. \tag{230}$$

Then, from the definitions of Λ and Λ_{nw}, we get

$$\boldsymbol{J_{se}} = \frac{(\epsilon_0\kappa_w)^2}{\eta_w} \left[\frac{2}{s_w\alpha_\infty\Lambda} \int_0^D (\nabla\Phi_w^0)^2 d\chi + \frac{2(1-s_w)}{s_w\alpha_{\infty,nw}\Lambda_{nw}} \int_0^D (\nabla\Phi_{nw}^0)^2 d\chi \right] \bar{\boldsymbol{E}}, \tag{231}$$

or

$$\boldsymbol{J_{se}} = \left[\frac{2C_{os,(w)}}{s_w \alpha_\infty \Lambda} + \frac{2(1-s_w)C_{os,(nw)}}{s_w \alpha_{\infty,nw}\Lambda_{nw}}\right]\bar{\boldsymbol{E}}, \tag{232}$$

where

$$C_{os,(w)} = \frac{(\epsilon_0 \kappa_w)^2}{\eta_w}\int_0^D (\nabla \Phi_w^0)^2 d\chi, \tag{233}$$

$$C_{os,(nw)} = \frac{(\epsilon_0 \kappa_w)^2}{\eta_w}\int_0^D (\nabla \Phi_{nw}^0)^2 d\chi. \tag{234}$$

The parameters $C_{os,(w)}$ and $C_{os,(nw)}$ are the conductances due to electrically induced streaming of the excess double-layer ions. Following Pride (1994) they can be estimated as

$$C_{os,(w)} = \frac{(\epsilon_0 \kappa_w)^2}{\eta_w}\left\{\frac{4kTd_w}{\epsilon_0 \kappa_w}\sum_{l=1}^{L}\mathcal{N}_{l,(w)}\left[e^{-\frac{ez_l\zeta_w}{2kT}}-1\right]+\frac{i^{3/2}}{\delta_{\rm sd}}\zeta_w^2\right\}, \tag{235}$$

$$C_{os,(nw)} = \frac{(\epsilon_0 \kappa_w)^2}{\eta_w}\left\{\frac{4kTd_{nw}}{\epsilon_0 \kappa_w}\sum_{l=1}^{L}\mathcal{N}_{l,(nw)}\left[e^{-\frac{ez_l\zeta_{nw}}{2kT}}-1\right]+\frac{i^{3/2}}{\delta_{\rm sd}}\zeta_{nw}^2\right\}. \tag{236}$$

Note that the second term in these expressions shows a frequency dependence through the skin depth $\delta_{\rm sd}$ (Eq. 177). However, in the low-frequency approximation this term vanishes.

The mechanically induced streaming current density is now derived. Using the following identity

$$\nabla \Phi_\xi^0 \cdot \nabla \boldsymbol{v_m} = \nabla \cdot (\Phi_\xi^0 \nabla \boldsymbol{v_m}) - \Phi_\xi^0 \nabla^2 \boldsymbol{v_m} \tag{237}$$

and the fact that $\nabla^2 \boldsymbol{v_m}$ (unlike $\nabla^2 \boldsymbol{v_e}$) is approximately constant across the thin double layer in comparison with Φ_ξ^0, we have

$$\begin{aligned}\boldsymbol{J_{sm}} &= \frac{\epsilon_0 \kappa_w}{V_w}\int_{S_w} dS \int_0^D \nabla \cdot (\Phi_w^0 \nabla \boldsymbol{v_m}) - \Phi_w^0 \nabla^2 \boldsymbol{v_m} d\chi \\ &+ \frac{\epsilon_0 \kappa_w}{V_w}\int_{S_{nw}} dS \int_0^D \nabla \cdot (\Phi_{nw}^0 \nabla \boldsymbol{v_m}) - \Phi_{nw}^0 \nabla^2 \boldsymbol{v_m} d\chi,\end{aligned} \tag{238}$$

then

$$\boldsymbol{J_{sm}} = \frac{\epsilon_0 \kappa_w \zeta_w}{V_w} \int_{S_w} \boldsymbol{n} \cdot \nabla \boldsymbol{v_m} - \left(\int_0^D \frac{\Phi_w^0}{\zeta_w} d\chi \right) \nabla^2 \boldsymbol{v_m} dS$$
$$+ \frac{\epsilon_0 \kappa_w \zeta_{nw}}{V_w} \int_{S_{nw}} \boldsymbol{n} \cdot \nabla \boldsymbol{v_m} - \left(\int_0^D \frac{\Phi_{nw}^0}{\zeta_{nw}} d\chi \right) \nabla^2 \boldsymbol{v_m} dS, \quad (239)$$

or, introducing $\tilde{d}_w$ and $\tilde{d}_{nw}$ defined as

$$\tilde{d}_\xi = \int_0^D \frac{\Phi_\xi^0(\chi)}{\zeta_\xi} d\chi, \qquad \xi = w, nw, \quad (240)$$

we can write

$$\boldsymbol{J_{sm}} = \frac{\epsilon_0 \kappa_w \zeta_w}{V_w} \int_{S_w} \left(\boldsymbol{n} \cdot \nabla \boldsymbol{v_m} - \tilde{d}_w \nabla^2 \boldsymbol{v_m} \right) dS$$
$$+ \frac{\epsilon_0 \kappa_w \zeta_{nw}}{V_w} \int_{S_{nw}} \left(\boldsymbol{n} \cdot \nabla \boldsymbol{v_m} - \tilde{d}_{nw} \nabla^2 \boldsymbol{v_m} \right) dS, \quad (241)$$

Now, using the expressions for $\boldsymbol{v_{m0}}$:

$$\boldsymbol{J_{sm0}} = - \left[\frac{\epsilon_0 \kappa_w \zeta_w}{\eta_w} \frac{\hat{\boldsymbol{z}}}{V_w} \cdot \int_{S_w} \left(\boldsymbol{n} \cdot \nabla \boldsymbol{g} - \tilde{d}_w \nabla h \right) dS \right] \left(-\nabla \bar{p}_w + i\omega \rho_w \dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}} \right)$$
$$- \left[\frac{\epsilon_0 \kappa_w \zeta_{nw}}{\eta_w} \frac{\hat{\boldsymbol{z}}}{V_w} \cdot \int_{S_{nw}} \left(\boldsymbol{n} \cdot \nabla \boldsymbol{g} - \tilde{d}_{nw} \nabla h \right) dS \right] \left(-\nabla \bar{p}_w + i\omega \rho_w \dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}} \right). \quad (242)$$

Then, multiplying by $s_w \phi$ we get

$$s_w \phi \boldsymbol{J_{sm0}} = L_{m0} \left(-\nabla \bar{p}_w + i\omega \rho_w \dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}} \right), \quad (243)$$

where

$$L_{m0} = -\phi \frac{\epsilon_0 \kappa_w \zeta_w}{\eta_w} \frac{\hat{\boldsymbol{z}}}{V_p} \cdot \int_{S_w} \left(\boldsymbol{n} \cdot \nabla \boldsymbol{g} - \tilde{d}_w \nabla h \right) dS$$
$$-\phi(1 - s_w) \frac{\epsilon_0 \kappa_w \zeta_{nw}}{\eta_w} \frac{\hat{\boldsymbol{z}}}{V_{nw}} \cdot \int_{S_{nw}} \left(\boldsymbol{n} \cdot \nabla \boldsymbol{g} - \tilde{d}_{nw} \nabla h \right) dS. \quad (244)$$

It is important to note here that in the case of full water saturation, the second term in the last equation is identically zero, not only because of the $(1 - s_w)$ factor but also because due to the fact the water-air interface does not exist, i.e., $\zeta_{nw} = 0$. However, the first term will still be present because of the solid-water double layer effects. In this case, Eq. (244) coincides with the L_{m0} coefficient derived by Pride (1994, Eq. 212).

5.3 Relative flows $\bar{\boldsymbol{v}}$ and $\bar{\boldsymbol{v}}_{\boldsymbol{nw}}$

Consider first the mechanically induced wetting-fluid flow. In the limit of low frequencies,

$$\bar{\boldsymbol{v}}_{\boldsymbol{m0}} = \frac{1}{V_w} \int_{V_w} \boldsymbol{v}_{\boldsymbol{m0}}(\boldsymbol{r}) dV = \frac{1}{\eta_w} \left(-\frac{1}{V_w} \int_{V_w} \hat{\boldsymbol{z}} \cdot \boldsymbol{g} dV \right) \left(-\nabla \bar{p}_w + i\omega \rho_w \dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}} \right), \quad (245)$$

then,

$$s_w \phi \bar{\boldsymbol{v}}_{\boldsymbol{m0}} = \frac{1}{\eta_w} \left(-\frac{1}{V_A} \int_{V_w} \hat{\boldsymbol{z}} \cdot \boldsymbol{g} dV \right) \left(-\nabla \bar{p}_w + i\omega \rho_w \dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}} \right), \quad (246)$$

or,

$$s_w \phi \bar{\boldsymbol{v}}_{\boldsymbol{m0}} = \frac{k_{0,w}}{\eta_w} \left(-\nabla \bar{p}_w + i\omega \rho_w \dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}} \right), \quad (247)$$

where

$$k_{0,w} = -\frac{1}{V_A} \int_{V_w} \hat{\boldsymbol{z}} \cdot \boldsymbol{g} dV. \quad (248)$$

The parameter $k_{0,w}$ is the DC permeability of the wetting phase.

Next, the low-frequency electrically induced flow is integrated

$$\bar{\boldsymbol{v}}_{\boldsymbol{e0}} = \frac{1}{V_w}\int_{V_w} \boldsymbol{v}_{\boldsymbol{e0}} dV = \frac{\epsilon_0\kappa_w}{\eta_w}\frac{\hat{\boldsymbol{z}}}{V_w}\cdot\left[\int_{V_w}\left(\Phi_w^0-\zeta_w\right)\nabla\Gamma_w dV \right. \\ \left. + \int_{V_w}\left(\Phi_{nw}^0-\zeta_{nw}\right)\nabla\Gamma_{nw} dV\right]\bar{\boldsymbol{E}}. \tag{249}$$

Performing the integrals and multiplying by $s_w\phi$ the following expression is obtained (see Appendix A)

$$s_w\phi\bar{\boldsymbol{v}}_{\boldsymbol{e0}} = L_{e0}\bar{\boldsymbol{E}}, \tag{250}$$

where

$$L_{e0} = -\phi\frac{\epsilon_0\kappa_w}{\eta_w}\left\{\zeta_w\left[\frac{1}{\alpha_\infty}-(1-s_w)-\frac{2\tilde{d}_w}{\alpha_\infty\Lambda}\right]\right. \\ \left. +\zeta_{nw}\left[1-\frac{(1-s_w)}{\alpha_{\infty,nw}}-\frac{2\tilde{d}_{nw}(1-s_w)}{\alpha_{\infty,nw}\Lambda_{nw}}\right]\right\}. \tag{251}$$

Again, for fully-water saturated porous medium, the second term will not be present, and the first term will coincide with the coefficient L_{e0} derived by Pride (1994, Eq. 227).

Note that from Eqs.(226) and (232) we have

$$s_w\phi(\boldsymbol{J}_{\boldsymbol{ce}}+\boldsymbol{J}_{\boldsymbol{se}}) = \sigma\bar{\boldsymbol{E}}, \tag{252}$$

where

$$\sigma = \left[\frac{s_w\phi\sigma_w}{\tilde{\alpha}_{\infty,w}}+\frac{2\phi(C_{em,(w)}+C_{os,(w)})}{\alpha_\infty\Lambda}+(1-s_w)\frac{2\phi(C_{em,(nw)}+C_{os,(nw)})}{\alpha_{\infty,nw}\Lambda_{nw}}\right], \tag{253}$$

In the limit of full water saturation, the third term in this last equation will not be present. Noting that $\tilde{\alpha}_{\infty,w}$ tends to α_∞ when s_w tends to 1, the electric conductivity will coincide with the corresponding one derived by Pride (1994, Eq. 242).

Finally, let us consider the non-wetting fluid flow average. From Eq. (215)

$$\bar{\boldsymbol{v}}_{\boldsymbol{nw0}} = \frac{1}{V_{nw}} \int_{V_{nw}} \boldsymbol{v}_{\boldsymbol{nw0}}(\boldsymbol{r}) dV = \\ \frac{1}{\eta_{nw}} \left(-\frac{1}{V_{nw}} \int_{V_{nw}} \hat{\boldsymbol{z}} \cdot \boldsymbol{g}_{\boldsymbol{nw}} dV \right) \left(-\nabla \bar{p}_{nw} + i\omega\rho_{nw} \dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}} \right), \tag{254}$$

then,

$$(1-s_w)\phi \bar{\boldsymbol{v}}_{\boldsymbol{nw0}} = \frac{1}{\eta_{nw}} \left(-\frac{1}{V_A} \int_{V_{nw}} \hat{\boldsymbol{z}} \cdot \boldsymbol{g}_{\boldsymbol{nw}} dV \right) \left(-\nabla \bar{p}_{nw} + i\omega\rho_{nw} \dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}} \right), \tag{255}$$

or,

$$(1-s_w)\phi \bar{\boldsymbol{v}}_{\boldsymbol{nw0}} = \frac{k_{0,nw}}{\eta_{nw}} \left(-\nabla \bar{p}_{nw} + i\omega\rho_{nw} \dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}} \right), \tag{256}$$

where

$$k_{0,nw} = -\frac{1}{V_A} \int_{V_{nw}} \hat{\boldsymbol{z}} \cdot \boldsymbol{g}_{\boldsymbol{nw}} dV, \tag{257}$$

is the DC permeability of the non-wetting phase.

5.4 Summary of this section

By adding Eqs.(247) and (250) we have

$$s_w \phi \bar{\boldsymbol{v}}_{\boldsymbol{0}} = s_w \phi (\bar{\boldsymbol{v}}_{\boldsymbol{m0}} + \bar{\boldsymbol{v}}_{\boldsymbol{e0}}) = \frac{k_{0,w}}{\eta_w} \left(-\nabla \bar{p}_w + i\omega\rho_w \dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}} \right) + L_{e0} \bar{\boldsymbol{E}}, \tag{258}$$

and recalling that $-i\omega\bar{\boldsymbol{w}}_{\boldsymbol{w}} = \dot{\bar{\boldsymbol{w}}}_{\boldsymbol{w}} = s_w\phi\bar{\boldsymbol{v}}$ the transport equation for the relative wetting-fluid velocity reads:

$$- i\omega\bar{\boldsymbol{w}}_{\boldsymbol{w}} = L_{e0}\bar{\boldsymbol{E}} + \frac{k_{0,w}}{\eta_w}\left(-\nabla\bar{p}_w + i\omega\rho_w\dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}}\right), \tag{259}$$

with L_{e0} given by (251) and $k_{0,w}$ by (257). From Eq. (256), recalling that $-i\omega\bar{\boldsymbol{w}}_{\boldsymbol{nw}} = (1-s_w)\phi\bar{\boldsymbol{v}}_{\boldsymbol{nw}}$ we can write the equation for the relative non-wetting fluid velocity as

$$- i\omega\bar{\boldsymbol{w}}_{\boldsymbol{nw}} = \frac{k_{0,nw}}{\eta_{nw}}\left(-\nabla\bar{p}_{nw} + i\omega\rho_{nw}\dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}}\right). \tag{260}$$

Adding (243) and (252) we have the final expression for the second transport equation:

$$\bar{\boldsymbol{J}} = \sigma\bar{\boldsymbol{E}} + L_{m0}\left(-\nabla\bar{p}_w + i\omega\rho_w\dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}}\right), \tag{261}$$

with L_{m0} given by (244) and σ by (253).

It remains to show that Onsager reciprocity $L_{e0} = L_{m0}$ is verified. This is addressed in Appendix B.

6 Final equations

6.1 Governing equations for coupled electromagnetic/acoustic wave propagation

In this section, all the derived electromagnetic, mechanical and transport equations are gathered. The so-called electrokinetic coupling coefficient is simply noted by L_0^{ps} in what follows, where the supraindex ps express the fact that the coefficient is valid for a *partially-saturated* porous rock. The same notation is employed for the electric conductivity (253), i.e. σ^{ps}.

Note that under the assumption of negligible perturbations of capillary pressure ($p_c = 0$), both pressure perturbations verify $p_w = p_{nw} = p$. Introducing the effective fluid $\boldsymbol{w_f}$ (Eq. 117), Eqs. (259) and (260) can be placed in Eq. (117), which divided by ρ_f reads

$$-i\omega\bar{\boldsymbol{w}}_{\boldsymbol{f}} = \frac{\rho_w}{\rho_f} L_0^{ps} \bar{\boldsymbol{E}} - \left[\frac{\rho_w}{\rho_f} \frac{k_{0,w}}{\eta_w} + \frac{\rho_{nw}}{\rho_f} \frac{k_{0,nw}}{\eta_{nw}} \right] \nabla \bar{p}$$
$$+ i\omega \left[\frac{\rho_w^2}{\rho_f} \frac{k_{0,w}}{\eta_w} + \frac{\rho_{nw}^2}{\rho_f} \frac{k_{0,nw}}{\eta_{nw}} \right] \dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}}. \tag{262}$$

Also, it is worthwhile to remark here that at $p_c = 0$, the mechanical constitutive relations given by (119) and (120) will hold. Removing all the overbars appearing in the averaged variables, then from (90), (91), (103), (118), (119), (120), (166), (261) and (262) we get:

$$\nabla \times \boldsymbol{E} = i\omega \boldsymbol{B}, \tag{263}$$

$$\nabla \times \boldsymbol{H} = -i\omega \boldsymbol{D} + \boldsymbol{J}, \tag{264}$$

$$\nabla \boldsymbol{\tau_B} = \omega^2 \left[\rho_B \boldsymbol{u_s} + \rho_f \boldsymbol{w_f} \right], \tag{265}$$

$$\boldsymbol{J} = \sigma^{ps} \boldsymbol{E} + L_0^{ps} \left(-\nabla p + \omega^2 \rho_w \boldsymbol{u_s} \right), \tag{266}$$

$$-i\omega \boldsymbol{w_f} = \frac{\rho_w}{\rho_f} L_0^{ps} \boldsymbol{E} - \left[\frac{\rho_w}{\rho_f} \frac{k_{0,w}}{\eta_w} + \frac{\rho_{nw}}{\rho_f} \frac{k_{0,nw}}{\eta_{nw}} \right] \nabla p$$
$$+ \omega^2 \left[\frac{\rho_w^2}{\rho_f} \frac{k_{0,w}}{\eta_w} + \frac{\rho_{nw}^2}{\rho_f} \frac{k_{0,nw}}{\eta_{nw}} \right] \boldsymbol{u_s}, \tag{267}$$

$$\boldsymbol{D} = \epsilon_0 \left[\frac{\kappa_s (1-\phi)}{\tilde{\alpha}_{\infty,s}} + \frac{\kappa_w s_w \phi}{\tilde{\alpha}_{\infty,w}} + \frac{\kappa_{nw}(1-s_w)\phi}{\alpha_{\infty,nw}} \right] \boldsymbol{E}, \tag{268}$$

$$\boldsymbol{B} = \mu_0 \boldsymbol{H}, \tag{269}$$

$$\boldsymbol{\tau_B} = (K_c \nabla \cdot \boldsymbol{u_s} + C \nabla \cdot \boldsymbol{w_f}) \mathbf{I} + G \left(\nabla \boldsymbol{u_s} + \nabla \boldsymbol{u_s}^T - \frac{2}{3} \nabla \cdot \boldsymbol{u_s} \mathbf{I} \right), \tag{270}$$

$$-p = C \nabla \cdot \boldsymbol{u_s} + M \nabla \cdot \boldsymbol{w_f}, \tag{271}$$

where the *partially-saturated electrokinetic coupling coefficient* is given by

$$L_0^{ps} = -\phi \frac{\epsilon_0 \kappa_w}{\eta_w} \left\{ \zeta_w \left[\frac{1}{\alpha_\infty} - (1 - s_w) - \frac{2\tilde{d}_w}{\alpha_\infty \Lambda} \right] \right. \\ \left. + \zeta_{nw} \left[1 - \frac{(1 - s_w)}{\alpha_{\infty,nw}} - \frac{2\tilde{d}_{nw}(1 - s_w)}{\alpha_{\infty,nw}\Lambda_{nw}} \right] \right\}, \quad (272)$$

and the *partially-saturated electric conductivity* is expressed as

$$\sigma^{ps} = \left[\frac{s_w \phi \sigma_w}{\tilde{\alpha}_{\infty,w}} + \frac{2\phi(C_{em,(w)} + C_{os,(w)})}{\alpha_\infty \Lambda} + (1 - s_w) \frac{2\phi(C_{em,(nw)} + C_{os,(nw)})}{\alpha_{\infty,nw}\Lambda_{nw}} \right]. \quad (273)$$

This is the final set of equations governing the coupled electromagnetic/acoustic wave propagation. Note that when $s_w \to 1$, Pride's final equations are recovered: when $s_w \to 1$, then $\rho_f \to \rho_w$, $\boldsymbol{w_f} \to \boldsymbol{w_w}$, $\rho_B \to (1 - \phi)\rho_s + \phi \rho_w$ and $K_f \to K_w$. In this limiting case we also have that $L_0^{ps} \to L_0$ and $\sigma^{ps} \to \sigma$ as was demonstrated in the previous section. Also note that $\kappa_{0,nw} \to 0$ and $\kappa_{0,w} \to \kappa_0$, being κ_0 the DC permeability of the porous medium. Finally, given that from Eqs. (158) and (163) we respectively have

$$\lim_{s_w \to 1} \frac{1}{\tilde{\alpha}_{\infty,w}} = \frac{1}{\alpha_\infty} \quad \text{and} \quad \frac{1}{\tilde{\alpha}_{\infty,s}} = \frac{1}{(1-\phi)} - \frac{\phi}{(1-\phi)} \frac{1}{\alpha_\infty}, \quad (274)$$

in the fully water saturation case, the final equations (263)-(271) are identical to Pride (1994, Eqs. 248-256) as expected. Finally, note that if the frequencies are low enough that it is safe to neglect the inertial terms in Eqs. (265)-(267), we obtain a set of equations valid to deal with electromagnetic/mechanical coupling for the so-called *consolidation* problems in poromechanics (Biot, 1956).

6.2 Governing equations for flow regime

In this section we consider different situations which allow for simplified versions of the governing equations given above, allowing to address problems of electromagnetic/mechanical coupling during fluid flow in partially-saturated porous rocks. Let us start considering that the applied pressure gradients are steady in time, and that we are in a position to consider the Quasi-Stationary Conduction (QSC) approximation of Maxwell's equations (Rapetti and Rousseaux, 2014), that is, we can neglect all explicit time dependence in them. In this case, we can assume that

$$\boldsymbol{E} = -\nabla\Phi. \tag{275}$$

If the solid frame can be assumed to be rigid as it is usual in groundwater flow problems (Bear, 1988), the governing equations reduce to the system

$$\nabla \cdot \boldsymbol{J} = 0, \tag{276}$$

$$\nabla \cdot (\dot{\boldsymbol{w}}_{\boldsymbol{w}} + \dot{\boldsymbol{w}}_{\boldsymbol{nw}}) = 0, \tag{277}$$

$$\boldsymbol{J} = -\sigma^{ps}\nabla\Phi - L_0^{ps}\nabla p_w, \tag{278}$$

$$\dot{\boldsymbol{w}}_{\boldsymbol{w}} = -L_0^{ps}\nabla\Phi - \frac{k_{0,w}}{\eta_w}\nabla p_w, \tag{279}$$

$$\dot{\boldsymbol{w}}_{\boldsymbol{nw}} = -\frac{k_{0,nw}}{\eta_{nw}}\nabla p_{nw}, \tag{280}$$

$$p_c = p_{nw} - p_w. \tag{281}$$

Note that Eqs. (276) and (277) state the conservation of charges and flow, respectively. Also notice that the capillary relation Eq. (281) has to be taken into account. This is usually dealt with by introducing a capillary-pressure function depending on saturation (Bear, 1988). This set of equations describe the coupled electric/mechanic steady two-phase flow in a partially saturated porous rock.

In the case were quasistatic perturbations are applied to the porous rock, Eqs. (275) and (276) can still be considered to be valid (Haines and Pride, 2006; Monachesi et al, 2015; Rosas-Carbajal et al, 2020). However, Eq. (277) no longer holds, and should be replaced by a set of constitutive relations appropriate for the the case where $p_c \neq 0$ (see for example Santos et al (1992)). This case will be addressed in a forthcoming paper.
If, on the other hand, capillary pressure perturbations can be assumed to be zero, and also we are dealing with highly consolidated rocks ($K_m \gg K_f$) such that $\nabla \cdot \boldsymbol{u_s}$ can be neglected, then Eq. (277) should be replaced by $\dot{p} = -M\nabla \cdot \dot{\boldsymbol{w}}_{\boldsymbol{f}}$ and the quasistatic equations can be written as

$$\nabla \cdot \boldsymbol{J} = 0, \tag{282}$$

$$\nabla \cdot \dot{\boldsymbol{w}}_{\boldsymbol{f}} = -\frac{\dot{p}}{M}, \tag{283}$$

$$\boldsymbol{J} = -\sigma^{ps}\nabla\Phi - L_0^{ps}\nabla p, \tag{284}$$

$$\dot{\boldsymbol{w}}_{\boldsymbol{f}} = \frac{\rho_w}{\rho_f}L_0^{ps}\nabla\Phi - \left[\frac{\rho_w}{\rho_f}\frac{k_{0,w}}{\eta_w} + \frac{\rho_{nw}}{\rho_f}\frac{k_{0,nw}}{\eta_{nw}}\right]\nabla p. \tag{285}$$

In the case of full water saturation, following the same procedure as before, it is easy to show that Eqs. (282)-(285) are coincident with the corresponding ones in Pride (1994).

Another particular set of equations is obtained when the non-wetting fluid is assumed to be *stagnant* ($p_{nw} = 0$ and $\boldsymbol{w_{nw}} = 0$). This case finds useful applications in the study of partially-saturated steady water flow in the vadose zone, where the non-wetting phase (air) is in direct contact with the atmosphere. Therefore its pressure perturbations p_{nw} are zero (air at constant atmospheric pressure). Then, for the capillary pressure we have $p_c = -p_w$, which is the reason why this case is also known as *capillary flow* (Perrier and Morat, 2000):

$$\nabla \cdot \boldsymbol{J} = 0, \tag{286}$$

$$\nabla \cdot \dot{\boldsymbol{w}}_{\boldsymbol{w}} = 0, \tag{287}$$

$$\boldsymbol{J} = -\sigma^{ps} \nabla \Phi + L_0^{ps} \nabla p_c, \tag{288}$$

$$\dot{\boldsymbol{w}}_{\boldsymbol{w}} = -L_0^{ps} \nabla \Phi + \frac{k_{0,w}}{\eta_w} \nabla p_c. \tag{289}$$

In some applications, body forces originated in gravity effects play an important role, so they must be included in this set of equations. This is accomplished by simply replacing ∇p_c by $(\nabla p_c + \rho_w \boldsymbol{g})$, where $\boldsymbol{g}$ is the acceleration of gravity. In the case of full water saturation, following the same procedure as above, it is easy to show that Eqs. (286)-(289) are coincident with Pride (1994, Eqs. 258-261).

If quasistatic perturbations and highly consolidated rocks are considered in this capillary flow regime, Eq. (287) should be replaced by $\dot{p}_c = \tilde{M} \nabla \cdot \dot{\boldsymbol{w}}_{\boldsymbol{w}}$, where

$$\tilde{M} = \frac{K_w}{s_w \phi + \frac{K_w}{K_s^2} \left[(1-\phi) K_s - K_m \right]}. \tag{290}$$

This coefficient is obtained upon the volume average of the mechanical constitutive relations in partially-saturated rocks where the non-wetting fluid is assumed stagnant (see Appendix C).

7 Conclusions

We have derived a low-frequency extension of Pride's theory accounting for the case of partially-saturated homogeneous and isotropic porous rocks, where the wetting fluid is assumed to be an ideal electrolyte and the non-wetting fluid is air. The main hypothesis on deriving the governing equations for coupled electromagnetic/acoustic wave propagation were the existence of an additional electric double layer at the water-air interface and that both electric double layers don't interact, which would be the case when the corresponding Debye lengths are smaller than any other geometrical feature of the porous rock. This condition is likely to be met for any saturation condition, with the exception of very low water saturation, where thin-water films could be small enough to make the later hypothesis not valid. Also, both air and solid phases are assumed to be electrical insulators and to have high dielectric contrasts when compared with the wetting phase. Moreover, in our derivation the ion number density perturbations were neglected together with the capillary pressure perturbations in wave propagation frequency regime. For a given value of water saturation, the deduced governing equations show that both the electrokinetic coupling coefficient and the electric conductivity have contributions from the water-air electric double layer and also depend on water saturation and topological properties of the porous partially-saturated porous rock. We've also shown that Onsager reciprocity holds and that in the limit of fully water saturation the final equations coincide with Pride's model, as expected. We have also obtained simplified versions of the proposed governing equations valid for flow regime. The derived electrokinetic coupling L_0^{ps} and electrical conductivity σ^{ps} will allow to model and interpret the experimental observations of the related streaming potential coefficient in unsaturated conditions taking into account the importance of the water/air interface.

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Declarations

Not applicable

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Appendix A Derivation of Eqs. (250) and (251)

From Eq. (249) we can equivalently express

$$\bar{\boldsymbol{v}}_{\boldsymbol{e0}} = \frac{\epsilon_0 \kappa_w}{\eta_w} \frac{\hat{\boldsymbol{z}}}{V_w} \cdot \left[\zeta_w \int_{S_w} \int_0^D \left(\frac{\Phi_w^0}{\zeta_w} - 1 \right) \nabla \Gamma_w d\chi dS \right.$$

$$+\zeta_{nw} \int_{S_{nw}} \int_0^D \left(\frac{\Phi^0_{nw}}{\zeta_{nw}} - 1 \right) \nabla \Gamma_{nw} d\chi dS \Bigg] \bar{\boldsymbol{E}}. \qquad \text{(A1)}$$

Both integrals conforming each term in the last expression can be solved in the same fashion. Let's take the first one:

$$\begin{aligned}
&\frac{\hat{\boldsymbol{z}}}{V_w} \cdot \int_{S_w} \int_0^D \left(\frac{\Phi^0_w}{\zeta_w} - 1 \right) \nabla \Gamma_w d\chi dS \\
&= \frac{\hat{\boldsymbol{z}}}{V_w} \cdot \left[\int_{S_w} \int_0^D \frac{\Phi^0_w}{\zeta_w} \nabla \Gamma_w d\chi dS - \int_{S_w} \int_0^D \nabla \Gamma_w d\chi dS \right] \\
&= \tilde{d}_w \frac{\hat{\boldsymbol{z}}}{V_w} \cdot \int_{S_w} \nabla \Gamma_w dS - \frac{\hat{\boldsymbol{z}}}{V_w} \cdot \int_{V_w} \nabla \Gamma_w d\chi dS \\
&= \tilde{d}_w \frac{\hat{\boldsymbol{z}}}{V_w} \cdot \int_{S_w} \nabla \Gamma_w dS - \frac{\hat{\boldsymbol{z}}}{V_w} \cdot \int_{V_w} \nabla \Gamma_w dV. \qquad \text{(A2)}
\end{aligned}$$

Integrating the last term in (A2) we have that it is equal to

$$= \tilde{d}_w \frac{\hat{\boldsymbol{z}}}{V_w} \cdot \int_{S_w} \nabla \Gamma_w dS - \left[1 + \frac{\hat{\boldsymbol{z}}}{V_w} \cdot \int_{S_w} \boldsymbol{n} \cdot \Gamma_w dS \right]$$

or

$$= \tilde{d}_w \frac{1}{s_w} \frac{1}{V_p} \int_{S_w} \hat{\boldsymbol{z}} \cdot \nabla \Gamma_w dS - \left[1 - \frac{1}{s_w} + \frac{1}{s_w} \left(1 + \frac{\hat{\boldsymbol{z}}}{V_p} \cdot \int_{S_w} \boldsymbol{n} \cdot \Gamma_w dS \right) \right].$$

Using the definitions of α_∞ and Λ

$$= \tilde{d}_w \frac{1}{s_w} \frac{2}{\alpha_\infty \Lambda} - \frac{1}{s_w} \left[\frac{1}{\alpha_\infty} - (1 - s_w) \right],$$

which leads to

$$\frac{\hat{\boldsymbol{z}}}{V_w} \cdot \int_{S_w} \int_0^D \left(\frac{\Phi^0_w}{\zeta_w} - 1 \right) \nabla \Gamma_w d\chi dS$$

$$= -\left\{ \frac{1}{s_w} \left[\frac{1}{\alpha_\infty} - (1 - s_w) \right] - \tilde{d}_w \frac{1}{s_w} \frac{2}{\alpha_\infty \Lambda} \right\}. \tag{A3}$$

Proceeding in the same way with the second term of Eq. (A1) one obtains

$$\begin{aligned} &\frac{\hat{\boldsymbol{z}}}{V_w} \cdot \int_{S_{nw}} \int_0^D \left(\frac{\Phi^0_{nw}}{\zeta_{nw}} - 1 \right) \nabla \Gamma_{nw} d\chi dS \\ &= -\left\{ \frac{1}{s_w} \left[1 - \frac{(1 - s_w)}{\alpha_{\infty,nw}} \right] - \tilde{d}_{nw} \frac{(1 - s_w)}{s_w} \frac{2}{\alpha_{\infty,nw} \Lambda_{nw}} \right\}. \end{aligned} \tag{A4}$$

Introducing the results from Eqs. (A3) and (A4) in (A1) and multiplying by $s_w\phi$, leads to Eqs. (250) and (251).

Appendix B Demonstration of Onsager reciprocity

Note that Eq. (250) can be written by splitting the contribution from each double layer as follows:

$$s_w \phi \bar{\boldsymbol{v}}_{\boldsymbol{e0,(w)}} = L_{e0,(w)} \bar{\boldsymbol{E}}, \quad \text{and} \quad s_w \phi \bar{\boldsymbol{v}}_{\boldsymbol{e0,(nw)}} = L_{e0,(nw)} \bar{\boldsymbol{E}}, \tag{B5}$$

where

$$L_{e0,(w)} = -\phi \frac{\epsilon_0 \kappa_w \zeta_w}{\eta_w} \left[\frac{1}{\alpha_\infty} - (1 - s_w) - \frac{2\tilde{d}_w}{\alpha_\infty \Lambda} \right], \tag{B6}$$

$$L_{e0,(nw)} = -\phi \frac{\epsilon_0 \kappa_w \zeta_{nw}}{\eta_w} \left[1 - \frac{(1 - s_w)}{\alpha_{\infty,nw}} - \frac{2\tilde{d}_{nw}(1 - s_w)}{\alpha_{\infty,nw} \Lambda_{nw}} \right]. \tag{B7}$$

In the same manner Eq. (243) can be written as

$$s_w \phi \boldsymbol{J}_{\boldsymbol{sm0,(w)}} = L_{m0,(w)} \left(-\nabla \bar{p}_w + i\omega \rho_w \dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}} \right),$$

$$s_w \phi \boldsymbol{J_{sm0,(nw)}} = L_{m0,(nw)} \left(-\nabla \bar{p}_w + i\omega\rho_w \dot{\boldsymbol{\hat{u}}}_{\boldsymbol{s}} \right). \tag{B8}$$

where

$$L_{m0,(w)} = -\phi \frac{\epsilon_0 \kappa_w \zeta_w}{\eta_w} \frac{\hat{\boldsymbol{z}}}{V_p} \cdot \int_{S_w} \left(\boldsymbol{n} \cdot \nabla \boldsymbol{g} - \tilde{d}_w \nabla h \right) dS, \tag{B9}$$

$$L_{m0,(nw)} = -\phi(1-s_w) \frac{\epsilon_0 \kappa_w \zeta_{nw}}{\eta_w} \frac{\hat{\boldsymbol{z}}}{V_{nw}} \cdot \int_{S_{nw}} \left(\boldsymbol{n} \cdot \nabla \boldsymbol{g} - \tilde{d}_{nw} \nabla h \right) dS. \tag{B10}$$

In what follows we will show, following Pride's demonstration, that $L_{e0,(w)} = L_{m0,(w)}$ and $L_{e0,(nw)} = L_{m0,(nw)}$, which will allow to conlcude $L_{e0} = L_{m0}$.

Let's start by accounting for the double layer at S_w. From Eq. (202) we have:

$$\eta_w \nabla^2 \boldsymbol{v_{m0,(w)}} = \nabla \left(\delta p_{m,(w)} + \Gamma_w \frac{\Delta P}{H} \right), \tag{B11}$$

where $\delta p_{m,(w)} = 0$ on the disk faces. For the electrically induced flow $\boldsymbol{v_{e0,(w)}}$ we have from (Eq. (187)

$$\eta_w \nabla^2 \boldsymbol{v_{e0,(w)}} = \rho_w^0 \nabla \Gamma_w \frac{\Delta \phi}{H}, \tag{B12}$$

where $p_{e,(w)} = 0$ on the disk faces and $\rho_w^0 = -\epsilon_0 \kappa_w \nabla^2 \Phi_w^0 = \sum_{l=1}^{L} e z_l N_{l,(w)}^0$ is the excess-charge density in the diffuse double layer at S_w. We also have that $\nabla \cdot \boldsymbol{v_{m0,(w)}} = \nabla \cdot \boldsymbol{v_{e0,(w)}} = 0$ everywhere and $\boldsymbol{v_{m0,(w)}} = \boldsymbol{v_{e0,(w)}} = 0$ on S_w.

Multiplying (B11) by $\boldsymbol{v_{e0,(w)}}$ and (B12) by $\boldsymbol{v_{m0,(w)}}$ with the scalar product and taking the difference between both results we get

$$\begin{aligned} &\eta_w \left[\nabla^2 \boldsymbol{v_{m0,(w)}} \cdot \boldsymbol{v_{e0,(w)}} - \nabla^2 \boldsymbol{v_{e0,(w)}} \cdot \boldsymbol{v_{m0,(w)}} \right] - \nabla \delta p_{m,(w)} \\ &= \nabla \cdot \left\{ \Gamma_w \left[\boldsymbol{v_{e0,(w)}} \frac{\Delta P}{H} - \rho_w^0 \boldsymbol{v_{m0,(w)}} \frac{\Delta \phi}{H} \right] \right\} + \Gamma_w \nabla \rho_w^0 \cdot \boldsymbol{v_{m0,(w)}} \frac{\Delta \phi}{H}, \end{aligned} \tag{B13}$$

Now, if the last equation is volume-integrated over the volume occupied by the wetting face in the averaging disk and the divergence theorem is applied, then the left hand side will vanish for homogeneous media, i.e., under the assumption that the fields involved don't undergo significant changes across the disk. The second term on the right hand side will also vanish under the thin-double-layer approximation (Pride, 1994). As a result we have

$$H \int_{z=H} \hat{\boldsymbol{z}} \cdot \left(\boldsymbol{v_{e0,(w)}} \frac{\Delta P}{H} - \rho_w^0 \boldsymbol{v_{m0,(w)}} \frac{\Delta \phi}{H} \right) dS = 0. \tag{B14}$$

On the other hand, from the first of (B5) we can write:

$$\frac{\hat{\boldsymbol{z}}}{V_w} \cdot \int_{V_w} \boldsymbol{v_{e0,(w)}} dV = \hat{\boldsymbol{z}} \cdot \bar{\boldsymbol{v}}_{\boldsymbol{e0,(w)}} = \frac{L_{e0,(w)}}{V_w} \frac{\Delta \phi}{H} \tag{B15}$$

and from Eq. (100) and the first of (B8):

$$\frac{\hat{\boldsymbol{z}}}{V_w} \cdot \int_{V_w} \rho_w^0 v_{m0,(w)} dV = \hat{\boldsymbol{z}} \cdot \bar{\boldsymbol{J}}_{\boldsymbol{sm0,(w)}} = \frac{L_{m0,(w)}}{V_w} \frac{\Delta P}{H}. \tag{B16}$$

Then we can write

$$\begin{aligned}
&\frac{\Delta P}{H} \frac{\Delta \phi}{H} \left(L_{e0,(w)} - L_{m0,(w)} \right) \\
&= \hat{\boldsymbol{z}} \cdot \int_{V_w} \left(\boldsymbol{v_{e0,(w)}} \frac{\Delta P}{H} - \rho_w^0 \boldsymbol{v_{m0,(w)}} \frac{\Delta \phi}{H} \right) dV \\
&= \int_{V_w} \nabla \cdot \left[\hat{\boldsymbol{z}} \left(\boldsymbol{v_{e0,(w)}} \frac{\Delta P}{H} - \rho_w^0 \boldsymbol{v_{m0,(w)}} \frac{\Delta \phi}{H} \right) \right] dV \\
&= H \int_{z=H} \hat{\boldsymbol{z}} \cdot \left(\boldsymbol{v_{e0,(w)}} \frac{\Delta P}{H} - \rho_w^0 \boldsymbol{v_{m0,(w)}} \frac{\Delta \phi}{H} \right) dS.
\end{aligned} \tag{B17}$$

The last expression is zero, as shown before. Then $L_{e0,(w)} = L_{m0,(w)}$. Proceeding in the same way with the fields associated with S_{nw} one obtains

$L_{e0,(nw)} = L_{m0,(nw)}$. Finally, adding both results we obtain $L_{e0} = L_{m0} = L_0^{ps}$, which proves Onsager reciprocity.

Appendix C Mechanical constitutive relations in the case of stagnant non-wetting fluid

If the non-wetting fluid is assumed be stagnant ($p_{nw} = 0$, $\boldsymbol{w_{nw}} = 0$ and $p_w = -p_c$) then the volume average of the stress-strain relations are taken without the consideration of Eq. (70). Following Pride et al (1992), taking into account that the wetting-fluid occupies a volume $s_w\phi$ we obtain

$$\boldsymbol{\tau_B} = (\tilde{K}_c \nabla \cdot \boldsymbol{u_s} + \tilde{C}\nabla \cdot \boldsymbol{w_w})\mathbf{I} + G\left(\nabla \boldsymbol{u_s} + \nabla \boldsymbol{u_s}^T - \frac{2}{3}\nabla \cdot \boldsymbol{u_s}\mathbf{I}\right), \quad \text{(C18)}$$

$$p_c = \tilde{C}\nabla \cdot \boldsymbol{u_s} + \tilde{M}\nabla \cdot \boldsymbol{w_w}, \quad \text{(C19)}$$

where

$$\tilde{K}_c = \frac{K_m + s_w\phi K_w + [(1-\phi) + 2s_w\phi]\, K_s\tilde{\Delta}}{1+\Delta}, \quad \text{(C20)}$$

$$\tilde{C} = \frac{K_w + K_s\tilde{\Delta}}{1+\tilde{\Delta}}, \quad \text{(C21)}$$

$$\tilde{M} = \frac{1}{s_w\phi}\frac{K_w}{1+\tilde{\Delta}}. \quad \text{(C22)}$$

In these expressions,

$$\tilde{\Delta} = \frac{K_w}{s_w\phi K_s^2}\left[(1-\phi)K_s - K_m\right]. \quad \text{(C23)}$$

From Eq. (C19), if the solid displacement is negligible, then taking the first time derivative we have $\dot{p}_c = \tilde{M}\nabla \cdot \dot{\boldsymbol{w}}_{\boldsymbol{w}}$.