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 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 proposed approach is valid at the low-frequency regime, where capillary pressure perturbations can be safely neglected. 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.

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 these 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 a 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); Allégre et al (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 electromagnetic/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 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.

2 Electromagnetic and mechanical 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. This will not hold for $s_w = 0$, situation that will not be addressed in this work. This means that the air never gets in contact with the solid grains. For very low water saturation 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

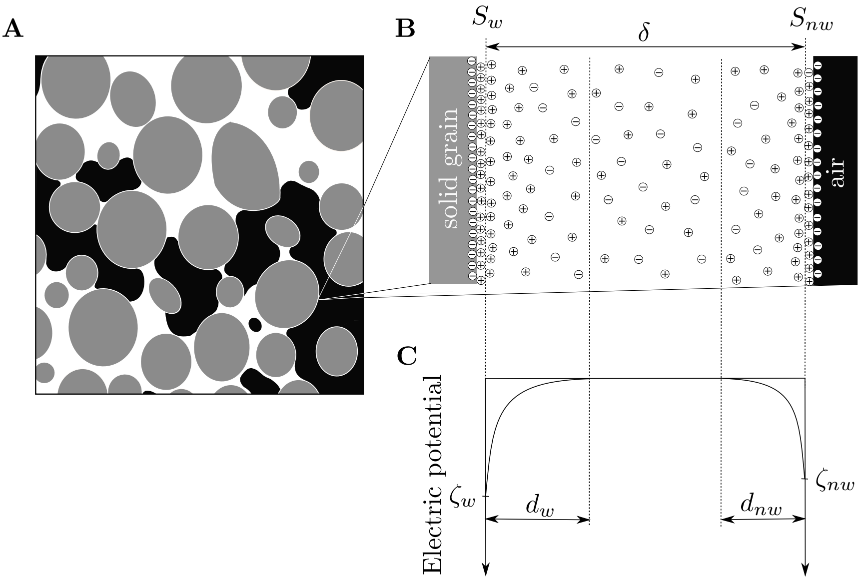

Fig. 1 **A**. Representation of partially-saturated porous rock (adapted from Culligan et al (2004)). Solid grains, water (wetting phase) and air (non-wetting phase) are represented in gray, white and black, respectively, **B**. Amplified view of a thin water film of thickness δ. The charge distribution 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 free ion distributions within the electrolyte are conceptualized following the same approach given by Pride (1994). The *electric double layer* structure is assumed to be present in both contact surfaces, so there will be two *shear* *planes*; S_w between solid and wetting-phase, and S_{nw} between wetting and non-wetting phases.

Both the solid and the non-wetting phase are assumed to be electrically insulating while the wetting fluid 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 and is given by

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

where $\dot{\boldsymbol{u}}_{\boldsymbol{w}}$ is the wetting fluid velocity, kT is the thermal energy, ez_l is the net charge and sign of each species-l ion, N_l is the density and b_l the mobility.

The boundary conditions on the surface S_w are

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

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

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

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

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

where $\boldsymbol{n}$ is the unit vector normal to S_w, directed from wetting phase to solid, $\dot{\boldsymbol{u}}_{\boldsymbol{s}}$ is the velocity of the solid ($= \dot{\boldsymbol{u}}_{\boldsymbol{w}}$ on S_w) and Q_w is the free charge per unit area of the wetting adsorbed layer. 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 we need to close the system with 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 and the second one represents the deviation in the field produced by a harmonic perturbation. Both Q^0_w and Q^0_{nw} are assumed to be uniform over the corresponding surfaces, and as a consequence $\boldsymbol{E^0_w}$ and N^0_l will be the only nonzero static fields (Pride, 1994). Solving Eqs. (6), (7), (8) and (13) for the static case it is possible to show that the electric potential near a shear plane can be approximated by an exponential distribution

$$\Phi^0(\chi) = \zeta e^{-\chi/d}, \tag{27}$$

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

$$\frac{1}{d^2} = \sum_{l=1}^{L} \frac{(ez_l)^2 \mathcal{N}_l}{\epsilon_0 \kappa_w kT}, \tag{28}$$

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

$$\Phi_w^0(\chi) = \zeta_w e^{-\chi/d_w} \quad \text{and} \quad \Phi_{nw}^0(\chi) = \zeta_{nw} e^{-\chi/d_{nw}}, \tag{29}$$

with their corresponding electric fields $\boldsymbol{E^0_{w,(w)}} = -\nabla\Phi_w^0$ and $\boldsymbol{E^0_{w,(nw)}} = -\nabla\Phi_{nw}^0$. 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

$$Q_w^0 \simeq 2d_w \sum_{l=1}^{L} ez_l \mathcal{N}_{l,(w)} e^{-\frac{ez_l\zeta_w}{2kT}} \quad \text{and} \quad Q_{nw}^0 \simeq 2d_{nw} \sum_{l=1}^{L} ez_l \mathcal{N}_{l,(nw)} e^{-\frac{ez_l\zeta_{nw}}{2kT}}. \tag{30}$$

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

$$\frac{1}{d_w^2} = \sum_{l=1}^{L} \frac{(ez_l)^2 \mathcal{N}_{l,(w)}}{\epsilon_0 \kappa_w kT} \quad \text{and} \quad \frac{1}{d_{nw}^2} = \sum_{l=1}^{L} \frac{(ez_l)^2 \mathcal{N}_{l,(nw)}}{\epsilon_0 \kappa_w kT}. \tag{31}$$

Now we need to state the equations governing the disturbances. Preserving only the linear contributions, we obtain

$$\nabla \cdot \boldsymbol{b_s} = 0, \tag{32}$$

$$\nabla \cdot \boldsymbol{d_s} = 0, \tag{33}$$

$$\nabla \times \boldsymbol{e_s} = i\omega \boldsymbol{b_s}, \tag{34}$$

$$\nabla \times \boldsymbol{h_s} = -i\omega \boldsymbol{d_s}, \tag{35}$$

$$\nabla \cdot \boldsymbol{b_w} = 0, \tag{36}$$

$$\nabla \cdot \boldsymbol{d_w} = \sum_{l=1}^{L} e z_l n_l, \tag{37}$$

$$\nabla \times \boldsymbol{e_w} = i\omega \boldsymbol{b_w}, \tag{38}$$

$$\nabla \times \boldsymbol{h_w} = -i\omega \boldsymbol{d_w} + \boldsymbol{j_w}, \tag{39}$$

$$\nabla \cdot \boldsymbol{b_{nw}} = 0, \tag{40}$$

$$\nabla \cdot \boldsymbol{d_{nw}} = 0, \tag{41}$$

$$\nabla \times \boldsymbol{e_{nw}} = i\omega \boldsymbol{b_{nw}}, \tag{42}$$

$$\nabla \times \boldsymbol{h_{nw}} = -i\omega \boldsymbol{d_{nw}}, \tag{43}$$

where

$$\boldsymbol{j_w} = \sum_{l=1}^{L} e z_l \left[-kT b_l \nabla n_l + e z_l b_l \left(N_l^0 \boldsymbol{e_w} + n_l \boldsymbol{E_w^0} \right) + N_l^0 \dot{\boldsymbol{u}}_{\boldsymbol{w}} \right]. \tag{44}$$

The boundary conditions on S_w are

$$\boldsymbol{n} \cdot (\boldsymbol{b_s} - \boldsymbol{b_w}) = 0, \tag{45}$$

$$\boldsymbol{n} \cdot (\boldsymbol{d_s} - \boldsymbol{d_w}) = 0, \tag{46}$$

$$\boldsymbol{n} \times (\boldsymbol{e_s} - \boldsymbol{e_w}) = 0, \tag{47}$$

$$\boldsymbol{n} \times (\boldsymbol{h_s} - \boldsymbol{h_w}) = Q_w^0 \dot{\boldsymbol{u}}_{\boldsymbol{s}}, \tag{48}$$

$$\boldsymbol{n} \cdot \boldsymbol{j_w} = 0, \tag{49}$$

and on S_{nw} we have

$$\boldsymbol{n} \cdot (\boldsymbol{b_{nw}} - \boldsymbol{b_w}) = 0, \tag{50}$$

$$\boldsymbol{n} \cdot (\boldsymbol{d_{nw}} - \boldsymbol{d_w}) = 0, \tag{51}$$

$$\boldsymbol{n} \times (\boldsymbol{e_{nw}} - \boldsymbol{e_w}) = 0, \tag{52}$$

$$\boldsymbol{n} \times (\boldsymbol{h_{nw}} - \boldsymbol{h_w}) = Q_{nw}^0 \dot{\boldsymbol{u}}_{\boldsymbol{nw}}, \tag{53}$$

$$\boldsymbol{n} \cdot \boldsymbol{j_w} = 0. \tag{54}$$

The mechanical equations governing the conservation of linear momentum of the solid and both fluid phases are

$$-i\omega\rho_s \dot{\boldsymbol{u}}_{\boldsymbol{s}} = \nabla \cdot \boldsymbol{\tau_s}, \tag{55}$$

$$-i\omega\rho_w \dot{\boldsymbol{u}}_{\boldsymbol{w}} = \nabla \cdot \boldsymbol{\tau_w} + \sum_{l=1}^{L} e z_l \left(N_l^0 \boldsymbol{e_w} + n_l \boldsymbol{E_w^0} \right), \tag{56}$$

$$-i\omega\rho_{nw} \dot{\boldsymbol{u}}_{\boldsymbol{nw}} = \nabla \cdot \boldsymbol{\tau_{nw}}, \tag{57}$$

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

$$\boldsymbol{\tau_s} = K_s \nabla \cdot \boldsymbol{u_s} \mathbf{I} + G_s \left(\nabla \boldsymbol{u_s} + \nabla \boldsymbol{u_s^T} - \frac{2}{3} \nabla \cdot \boldsymbol{u_s} \mathbf{I} \right), \tag{58}$$

$$\boldsymbol{\tau_w} = K_w \nabla \cdot \boldsymbol{u_w} \mathbf{I} - i\omega\eta_w \left(\nabla \boldsymbol{u_w} + \nabla \boldsymbol{u_w^T} - \frac{2}{3} \nabla \cdot \boldsymbol{u_w} \mathbf{I} \right), \tag{59}$$

$$\boldsymbol{\tau_{nw}} = K_{nw} \nabla \cdot \boldsymbol{u_{nw}} \mathbf{I} - i\omega\eta_{nw} \left(\nabla \boldsymbol{u_{nw}} + \nabla \boldsymbol{u_{nw}^T} - \frac{2}{3} \nabla \cdot \boldsymbol{u_{nw}} \mathbf{I} \right). \tag{60}$$

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

$$\boldsymbol{n} \cdot (\boldsymbol{\tau_s} - \boldsymbol{\tau_w}) = -Q_w^0 \boldsymbol{e_s}, \tag{61}$$

$$\boldsymbol{u_s} - \boldsymbol{u_w} = 0, \tag{62}$$

and on S_{nw}

$$\boldsymbol{n} \cdot (\boldsymbol{\tau_{nw}} - \boldsymbol{\tau_w}) = -Q_{nw}^0 \boldsymbol{e_{nw}}, \tag{63}$$

$$\boldsymbol{u_{nw}} - \boldsymbol{u_w} = 0. \tag{64}$$

3 Volume average of the governing equations

In this section the volume-averaging procedure given in Pride (1994) is applied. Let V_A be the averaging volume. Assuming the volume average of a microscopic field $\boldsymbol{a_\xi}$ associated with the ξth phase is given by

$$\langle \boldsymbol{a_\xi} \rangle = \frac{1}{V_A} \int_{V_\xi} \boldsymbol{a_\xi} dV, \tag{65}$$

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

$$\langle \nabla \boldsymbol{a_\xi} \rangle = \nabla \langle \boldsymbol{a_\xi} \rangle + \frac{1}{V_A} \int_{S_\xi} \boldsymbol{n_\xi} \boldsymbol{a_\xi} dS, \tag{66}$$

$$\langle \nabla \cdot \boldsymbol{a_\xi} \rangle = \nabla \cdot \langle \boldsymbol{a_\xi} \rangle + \frac{1}{V_A} \int_{S_\xi} \boldsymbol{n_\xi} \cdot \boldsymbol{a_\xi} dS, \tag{67}$$

$$\langle \nabla \times \boldsymbol{a_\xi} \rangle = \nabla \times \langle \boldsymbol{a_\xi} \rangle + \frac{1}{V_A} \int_{S_\xi} \boldsymbol{n_\xi} \times \boldsymbol{a_\xi} dS, \tag{68}$$

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

$$\boldsymbol{n_w} = \boldsymbol{n}, \tag{69}$$

$$\boldsymbol{n_s} = -\boldsymbol{n}, \tag{70}$$

$$\boldsymbol{n_{nw}} = -\boldsymbol{n}, \tag{71}$$

with $\boldsymbol{n}$ directed from the wetting-phase to the solid or from the wetting-phase to the non-wetting phase. It will be useful to define two other averages related to $\langle \boldsymbol{a_\xi} \rangle$, the *phase average* and *total average*, which are respectively given by

$$\boldsymbol{\bar{a}_\xi} = \langle \nabla \boldsymbol{a_\xi} \rangle / \varphi_\xi, \tag{72}$$

$$\boldsymbol{\bar{A}} = \sum_\xi \varphi_\xi \boldsymbol{\bar{a}_\xi}, \tag{73}$$

where $\varphi_\xi = V_\xi / V_A$ is the volume fraction of the ξth phase.

The electromagnetic equations governing the disturbances [Eqs.(32)-(44)] are now averaged following the same procedure given in Pride (1994) and neglecting the ion-number-density deviations n_l. As a result one obtains:

$$\nabla \cdot \bar{\boldsymbol{B}} = 0, \tag{74}$$

$$\nabla \cdot \bar{\boldsymbol{D}} = 0, \tag{75}$$

$$\nabla \times \bar{\boldsymbol{E}} = i\omega \bar{\boldsymbol{B}}. \tag{76}$$

$$\nabla \times \bar{\boldsymbol{H}} = -i\omega \bar{\boldsymbol{D}} + \bar{\boldsymbol{J}}. \tag{77}$$

with the current density given by:

$$\bar{\boldsymbol{J}} = s_w \phi \left[\boldsymbol{J_c} + \boldsymbol{J_s} \right], \tag{78}$$

where

$$\boldsymbol{J_c} = \frac{1}{V_w} \int_{V_w} \left(\sum_{l=1}^{L} (ez_l)^2 b_l N_l^0 \right) \boldsymbol{e_w} dV, \tag{79}$$

$$\boldsymbol{J_s} = \frac{1}{V_w} \int_{V_w} \left(\sum_{l=1}^{L} ez_l N_l^0 \right) \boldsymbol{v} dV, \tag{80}$$

$$\boldsymbol{v} = \dot{\boldsymbol{u}}_{\boldsymbol{w}} - \dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}}, \tag{81}$$

being $\dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}}$ the phase-averaged velocity of the solid phase. The current $\boldsymbol{J_c}$ is the *macroscopic conduction current density* and $\boldsymbol{J_s}$ is the *macroscopic streaming current density.*

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

$$\sigma_w = \sum_{l=1}^{L} (ez_l)^2 b_l \mathcal{N}_l = \sum_{l=1}^{L} (ez_l)^2 b_l (\mathcal{N}_{l,(w)} + \mathcal{N}_{l,(nw)}), \tag{82}$$

then, the conduction current can be written as follows

$$\boldsymbol{J_c} = \frac{\sigma_w}{V_w}\int_{V_w} \boldsymbol{e_w} dV + \frac{1}{V_w}\int_{S_w} dS \int_0^D \left(\sum_{l=1}^{L}(ez_l)^2 b_l (N^0_{l,(w)} - \mathcal{N}_{l,(w)})\right)\boldsymbol{e_w} d\chi$$
$$+\frac{1}{V_w}\int_{S_{nw}} dS \int_0^D \left(\sum_{l=1}^{L}(ez_l)^2 b_l (N^0_{l,(nw)} - \mathcal{N}_{l,(nw)})\right)\boldsymbol{e_w} d\chi. \quad (83)$$

The variable χ measures the normal distance from the surfaces S_w and S_{nw} 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.

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

$$\boldsymbol{J_s} = \frac{1}{V_w}\int_{V_w}\left(\sum_{l=1}^{L} ez_l N^0_{l,(w)}\right)\boldsymbol{v} dV + \frac{1}{V_w}\int_{V_w}\left(\sum_{l=1}^{L} ez_l N^0_{l,(nw)}\right)\boldsymbol{v} dV. \quad (84)$$

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

$$\boldsymbol{J_s} = \frac{\epsilon_0\kappa_w}{V_w}\int_{V_w}\left(\nabla\cdot\boldsymbol{E^0_{w,(w)}}\right)\boldsymbol{v} dV + \frac{\epsilon_0\kappa_w}{V_w}\int_{V_w}\left(\nabla\cdot\boldsymbol{E^0_{w,(nw)}}\right)\boldsymbol{v} dV, \quad (85)$$

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

$$\boldsymbol{J_s} = \frac{\epsilon_0\kappa_w}{V_w}\int_{S_w} dS \int_0^D \nabla\Phi^0_w \cdot \nabla\boldsymbol{v} d\chi + \frac{\epsilon_0\kappa_w}{V_w}\int_{S_{nw}} dS \int_0^D \nabla\Phi^0_{nw} \cdot \nabla\boldsymbol{v} d\chi, \quad (86)$$

The integrals appearing in Eq. (83) and Eq. (86) 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 $\boldsymbol{d_\xi}$ yields

$$\bar{\boldsymbol{D}} = \epsilon_0\left[\kappa_s(1-\phi)\bar{\boldsymbol{e}}_{\boldsymbol{s}} + \kappa_w s_w \phi \bar{\boldsymbol{e}}_{\boldsymbol{w}} + \kappa_{nw}(1-s_w)\phi\bar{\boldsymbol{e}}_{\boldsymbol{nw}}\right]. \quad (87)$$

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

$$\bar{\boldsymbol{B}} = \mu_0 \bar{\boldsymbol{H}}. \tag{88}$$

Taking the volume average of mechanical equations (55)-(57) we respectively obtain

$$-i\omega\rho_s \langle \dot{\boldsymbol{u}}_{\boldsymbol{s}} \rangle = \nabla \cdot \langle \boldsymbol{\tau}_{\boldsymbol{s}} \rangle - \frac{1}{V_A}\int_{S_w} \boldsymbol{n}\cdot\boldsymbol{\tau}_{\boldsymbol{s}} dS, \tag{89}$$

$$\begin{aligned} -i\omega\rho_w \langle \dot{\boldsymbol{u}}_{\boldsymbol{w}} \rangle = \nabla \cdot \langle \boldsymbol{\tau}_{\boldsymbol{w}} \rangle + \frac{1}{V_A}\int_{S_w} \boldsymbol{n}\cdot\boldsymbol{\tau}_{\boldsymbol{w}} dS + \frac{1}{V_A}\int_{S_{nw}} \boldsymbol{n}\cdot\boldsymbol{\tau}_{\boldsymbol{w}} dS \\ + \frac{1}{V_A}\int_{V_A} \sum_{l=1}^{L} e z_l \left(N_l^0 \boldsymbol{e}_{\boldsymbol{f}} + n_l \boldsymbol{E}^{\boldsymbol{0}}_{\boldsymbol{w}} \right) dV, \end{aligned} \tag{90}$$

$$-i\omega\rho_{nw} \langle \dot{\boldsymbol{u}}_{\boldsymbol{nw}} \rangle = \nabla \cdot \langle \boldsymbol{\tau}_{\boldsymbol{nw}} \rangle - \frac{1}{V_A}\int_{S_{nw}} \boldsymbol{n}\cdot\boldsymbol{\tau}_{\boldsymbol{nw}} dS, \tag{91}$$

Adding (89), (90) and (91), applying the BC's (61) and (63), the definition of the phase average and neglecting the ion-number-density deviations n_l, we get

$$\begin{aligned} -i\omega \left[(1-\phi)\rho_s \dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}} + s_w\phi\rho_w \dot{\bar{\boldsymbol{u}}}_{\boldsymbol{w}} + (1-s_w)\phi\rho_{nw} \dot{\bar{\boldsymbol{u}}}_{\boldsymbol{nw}}) \right] = \\ \nabla \cdot \left[(1-\phi)\bar{\boldsymbol{\tau}}_{\boldsymbol{s}} + s_w\phi\bar{\boldsymbol{\tau}}_{\boldsymbol{w}} + (1-s_w)\phi\bar{\boldsymbol{\tau}}_{\boldsymbol{nw}}) \right] \end{aligned} \tag{92}$$

If we define:

$$\dot{\bar{\boldsymbol{w}}}_{\boldsymbol{w}} = s_w\phi \left(\dot{\bar{\boldsymbol{u}}}_{\boldsymbol{w}} - \dot{\bar{\boldsymbol{u}}}_s \right), \tag{93}$$

$$\dot{\bar{\boldsymbol{w}}}_{\boldsymbol{nw}} = (1-s_w)\phi \left(\dot{\bar{\boldsymbol{u}}}_{\boldsymbol{nw}} - \dot{\bar{\boldsymbol{u}}}_s \right), \tag{94}$$

$$\bar{\boldsymbol{\tau}}_{\boldsymbol{B}} = (1-\phi)\bar{\boldsymbol{\tau}}_{\boldsymbol{s}} + s_w\phi\bar{\boldsymbol{\tau}}_{\boldsymbol{w}} + (1-s_w)\phi\bar{\boldsymbol{\tau}}_{\boldsymbol{nw}}, \tag{95}$$

$$\rho_B = (1-\phi)\boldsymbol{\rho}_{\boldsymbol{s}} + s_w\phi\boldsymbol{\rho}_{\boldsymbol{w}} + (1-s_w)\phi\boldsymbol{\rho}_{\boldsymbol{nw}}, \tag{96}$$

we can then write:

$$\nabla\bar{\boldsymbol{\tau}}_{\boldsymbol{B}} = -i\omega\left[\rho_B\dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}} + \rho_w\dot{\bar{\boldsymbol{w}}}_{\boldsymbol{w}} + \rho_{nw}\dot{\bar{\boldsymbol{w}}}_{\boldsymbol{nw}}\right], \tag{97}$$

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

$$\rho_f\bar{\boldsymbol{w}}_{\boldsymbol{f}} = \rho_w\bar{\boldsymbol{w}}_{\boldsymbol{w}} + \rho_{nw}\bar{\boldsymbol{w}}_{\boldsymbol{nw}}, \tag{98}$$

where $\rho_f = s_w\rho_w + (1-s_w)\rho_{nw}$. Then Eq. (97) is written

$$\nabla\bar{\boldsymbol{\tau}}_{\boldsymbol{B}} = -i\omega\left[\rho_B\dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}} + \rho_f\dot{\bar{\boldsymbol{w}}}_{\boldsymbol{f}}\right], \tag{99}$$

The averaging of the fluid equations (90) and (91) 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)

$$\bar{\boldsymbol{\tau}}_{\boldsymbol{B}} = (K_c\nabla\cdot\bar{\boldsymbol{u}}_{\boldsymbol{s}} + C\nabla\cdot\bar{\boldsymbol{w}}_f)\mathbf{I} + G\left(\nabla\bar{\boldsymbol{u}}_{\boldsymbol{s}} + \nabla\bar{\boldsymbol{u}}_{\boldsymbol{s}}^T - \frac{2}{3}\nabla\cdot\bar{\boldsymbol{u}}_{\boldsymbol{s}}\mathbf{I}\right), \tag{100}$$

$$-\bar{p} = C\nabla\cdot\bar{\boldsymbol{u}}_{\boldsymbol{s}} + M\nabla\cdot\bar{\boldsymbol{w}}_{\boldsymbol{f}}, \tag{101}$$

where

$$K_c = \frac{K_m + \phi K_f + (1-\phi)K_s\Delta}{1+\Delta}, \tag{102}$$

$$C = \frac{K_f + K_s\Delta}{1+\Delta}, \tag{103}$$

$$M = \frac{1}{\phi}\frac{K_f}{1+\Delta}. \tag{104}$$

in this expressions,

$$\Delta = \frac{K_f}{\phi K_s^2}\left[(1-\phi)K_s - K_m\right], \tag{105}$$

and K_m and G in Eq.(100) 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., $K_f = (s_w/K_w + (1-s_w)/K_{nw})^{-1}$.

It is worth to mention that the capillary pressure perturbations can induce predictable mechanical effects, as pointed out by Santos et al (1990b); Albers (2009). However, these effects are strongly attenuated for frequencies below $\sim$ 100 KHz, and therefore the "effective fluid" approximation employed here as a consequence of neglecting the capillary pressure perturbations, is indeed a fairly good approximation (Berryman et al, 1988; Pride et al, 1992).

4 Boundary-value problems

As mentioned before, to complete the averaging procedure we need to solve the integrals appearing in the various derived expressions. 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. Assume that a macroscopic potential difference and a macroscopic pressure difference exist between the two faces. The macroscopic fields normal to the disk face will then be given by the corresponding difference divided by H. Let z be the direction normal to the disk. The potential or pressure differences will be assumed as the boundary values for the corresponding pore-scale fields. We assume with Pride (1994) that $\boldsymbol{e}_{\boldsymbol{\xi}} = -\nabla \varphi_\xi$. Then

$$\hat{\boldsymbol{z}} \cdot \bar{\boldsymbol{E}} = -\frac{\Delta \phi}{H}, \tag{106}$$

where

$$\Delta \phi = \varphi_\xi(H) - \varphi_\xi(0), \quad \xi = s, w, nw, \tag{107}$$

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

4.2 Pore-scale electric fields

As was demonstrated in Pride (1994) the ion-number-density deviations $n_{l,(w)}$ can be neglected whenever the following two conditions are met: (1) The electric double layer at the solid-electrolyte contact is much thinner than the grain sizes, and (2) a large dielectric contrast exists between the grains and the electrolyte. Under these assumptions, the electric-field in the fluid produced by the double layer at the solid-wetting interface verifies

$$\boldsymbol{e}_{\boldsymbol{w},\boldsymbol{(w)}}(\boldsymbol{r}) = -\nabla \Gamma_w(\boldsymbol{r}) \frac{\Delta \phi}{H}. \tag{108}$$

where the field Γ_w possess units of length and is defined to satisfy

$$\nabla^2 \Gamma_w = 0, \tag{109}$$

$$\boldsymbol{n} \cdot \nabla \Gamma_w = 0 \quad \text{on} \quad S_w, \tag{110}$$

$$\Gamma_w = \begin{cases} H & \text{on} \quad z = H, \\ 0 & \text{on} \quad z = 0. \end{cases} \tag{111}$$

Considering now the electric double layer at S_{nw} it is possible to get, under the same assumptions as before

$$\boldsymbol{e}_{\boldsymbol{w},(\boldsymbol{nw})}(\boldsymbol{r}) = -\nabla\Gamma_{nw}(\boldsymbol{r})\frac{\Delta\phi}{H}, \tag{112}$$

where

$$\nabla^2\Gamma_{nw} = 0, \tag{113}$$

$$\boldsymbol{n}_{\boldsymbol{nw}} \cdot \nabla\Gamma_{nw} = 0 \quad \text{on} \;\; S_{nw}, \tag{114}$$

$$\Gamma_{nw} = \begin{cases} H & \text{on} \;\; z = H, \\ 0 & \text{on} \;\; z = 0. \end{cases} \tag{115}$$

The last result will be valid for all frequencies and for large dielectric contrasts between the non-wetting phase and the electrolyte.

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

$$\begin{aligned} \bar{\boldsymbol{e}}_{\boldsymbol{w}} &= -\frac{1}{V_w}\int_{V_w} \nabla\phi_w dV \\ &= -\frac{1}{V_w}\left[s_w\phi AH\hat{\boldsymbol{z}} + \int_{S_w} \boldsymbol{n}\Gamma_w(\boldsymbol{r})dS + \int_{S_{nw}} \boldsymbol{n}\Gamma_{nw}(\boldsymbol{r})dS\right]\frac{\Delta\phi}{H}, \end{aligned} \tag{116}$$

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

$$\bar{\boldsymbol{e}}_{\boldsymbol{w}} = \left[1 + \frac{\hat{\boldsymbol{z}}}{V_w}\int_{S_w} \boldsymbol{n}\Gamma_w(\boldsymbol{r})dS - \frac{\hat{\boldsymbol{z}}}{V_w}\int_{S_{nw}} \boldsymbol{n}_{\boldsymbol{nw}}\Gamma_{nw}(\boldsymbol{r})dS\right]\bar{\boldsymbol{E}}, \tag{117}$$

which can be written as

$$\bar{\boldsymbol{e}}_{\boldsymbol{w}} = \left[1 - \frac{V_p}{V_w} + \frac{V_p}{V_w}\left\{1 + \frac{\hat{\boldsymbol{z}}}{V_p}\int_{S_w} \boldsymbol{n}\Gamma_w(\boldsymbol{r})dS\right\}\right.$$

$$+\frac{V_{nw}}{V_w}-\frac{V_{nw}}{V_w}\left\{1+\frac{\hat{\boldsymbol{z}}}{V_{nw}}\int_{S_{nw}}\boldsymbol{n_{nw}}\Gamma_{nw}(\boldsymbol{r})dS\right\}\Bigg]\bar{\boldsymbol{E}}, \tag{118}$$

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

$$\frac{1}{\alpha_\infty}=1+\frac{\hat{\boldsymbol{z}}}{V_p}\int_{S_w}\boldsymbol{n}\Gamma_w(\boldsymbol{r})dS, \quad \frac{1}{\alpha_{\infty,nw}}=1+\frac{\hat{\boldsymbol{z}}}{V_{nw}}\int_{S_{nw}}\boldsymbol{n_{nw}}\Gamma_{nw}(\boldsymbol{r})dS, \tag{119}$$

then,

$$\bar{\boldsymbol{e}}_{\boldsymbol{w}}=\left[\frac{1}{s_w}\frac{1}{\alpha_\infty}-\frac{(1-s_w)}{s_w}\frac{1}{\alpha_{\infty,nw}}\right]\bar{\boldsymbol{E}}=\frac{1}{\tilde{\alpha}_{\infty,w}}\bar{\boldsymbol{E}}. \tag{120}$$

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

$$\bar{\boldsymbol{e}}_{\boldsymbol{s}}=-\frac{1}{V_s}\int_{V_s}\nabla\varphi_s dV=-\frac{1}{V_s}\left[(1-\phi)A\Delta\phi\hat{\boldsymbol{z}}+\int_{S_w}\boldsymbol{n_s}\varphi_s dS\right]. \tag{121}$$

Because $\varphi_s=\varphi_w$ at S_w (Pride, 1994)

$$\begin{aligned}\bar{\boldsymbol{e}}_{\boldsymbol{s}}=-\frac{1}{V_s}\int_{V_s}\nabla\varphi_s dV&=-\frac{1}{V_s}\left[(1-\phi)A\Delta\phi\hat{\boldsymbol{z}}-\int_{S_w}\boldsymbol{n}\varphi_w dS\right]\\&=\left[1-\frac{\hat{\boldsymbol{z}}}{V_s}\int_{S_w}\boldsymbol{n}\Gamma_w(\boldsymbol{r})dS\right]\bar{\boldsymbol{E}},\end{aligned} \tag{122}$$

then

$$\bar{\boldsymbol{e}}_{\boldsymbol{s}}=\left[1+\frac{V_p}{V_s}-\frac{V_p}{V_s}\left\{1+\frac{\hat{\boldsymbol{z}}}{V_p}\int_{S_w}\boldsymbol{n}\Gamma_w(\boldsymbol{r})dS\right\}\right]\bar{\boldsymbol{E}}, \tag{123}$$

or

$$\bar{\boldsymbol{e}}_{\boldsymbol{s}}=\left[\frac{1}{(1-\phi)}-\frac{\phi}{(1-\phi)}\left\{1+\frac{\hat{\boldsymbol{z}}}{V_p}\int_{S_w}\boldsymbol{n}\Gamma_w(\boldsymbol{r})dS\right\}\right]\bar{\boldsymbol{E}}. \tag{124}$$

Using the definition of α_∞ we get

$$\bar{\boldsymbol{e}}_{\boldsymbol{s}} = \left[\frac{1}{(1-\phi)} - \frac{\phi}{(1-\phi)}\frac{1}{\alpha_\infty}\right]\bar{\boldsymbol{E}} = \frac{1}{\tilde{\alpha}_{\infty,s}}\bar{\boldsymbol{E}}. \tag{125}$$

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

$$\begin{aligned}\bar{\boldsymbol{e}}_{\boldsymbol{nw}} = -\frac{1}{V_{nw}}\int_{V_{nw}} \nabla\varphi_{nw} dV &= -\frac{1}{V_{nw}}\left[(1-s_w)\phi A\Delta\phi\hat{\boldsymbol{z}} + \int_{S_{nw}} \boldsymbol{n}_{\boldsymbol{nw}}\varphi_w dS\right] \\ &= \left[1 + \frac{\hat{\boldsymbol{z}}}{V_{nw}}\int_{S_{nw}} \boldsymbol{n}_{\boldsymbol{nw}}\Gamma_{nw}(\boldsymbol{r}) dS\right]\bar{\boldsymbol{E}}. \end{aligned} \tag{126}$$

Then

$$\bar{\boldsymbol{e}}_{\boldsymbol{nw}} = \frac{1}{\alpha_{\infty,nw}}\bar{\boldsymbol{E}}. \tag{127}$$

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. (87):

$$\bar{\boldsymbol{D}} = \epsilon_0 \left[\frac{\kappa_s(1-\phi)}{\tilde{\alpha}_{\infty,s}} + \frac{\kappa_w s_w \phi}{\tilde{\alpha}_{\infty,w}} + \frac{\kappa_{nw}(1-s_w)\phi}{\alpha_{\infty,nw}}\right]\bar{\boldsymbol{E}}. \tag{128}$$

This last equation, together with Eq.(88) complete the volume averaged expressions for the electromagnetic constitutive relations.

4.3 Pore-scale flow fields

Let us start recalling Eq.(56) for the wetting-fluid flow at the pore-scale. Neglecting n_l this equation can be written as

$$-i\omega\rho_w \dot{\boldsymbol{u}}_{\boldsymbol{w}} = \nabla\cdot\boldsymbol{\tau}_{\boldsymbol{w}} + \left(\sum_{l=1}^{L} e z_l N_l^0\right)\boldsymbol{e}_{\boldsymbol{w}}, \tag{129}$$

which using $\boldsymbol{v}$ reads

$$-i\omega\rho_w\boldsymbol{v} = \nabla\cdot\boldsymbol{\tau_w} + i\omega\rho_w\dot{\hat{\boldsymbol{u}}}_{\boldsymbol{s}} + \left(\sum_{l=1}^{L} ez_l N_l^0\right)\boldsymbol{e_w}. \tag{130}$$

Assuming that the relative flow is incompressible and defining $\nabla p = \nabla p_w - i\omega\rho_w\dot{\hat{\boldsymbol{u}}}_{\boldsymbol{s}}$, we can state the following boundary-value problem

$$\eta_w\nabla^2\boldsymbol{v} + i\omega\rho_w\boldsymbol{v} = \nabla p - \left(\sum_{l=1}^{L} ez_l N_l^0\right)\boldsymbol{e_w}, \tag{131}$$

$$\nabla\cdot\boldsymbol{v} = 0, \tag{132}$$

$$\boldsymbol{v} = 0 \qquad \text{on } S_w \text{ and } S_{nw}, \tag{133}$$

$$p = \begin{cases} \Delta P = \hat{\boldsymbol{z}}\cdot\left(\nabla\bar{p}_w - i\omega\rho_w\dot{\hat{\boldsymbol{u}}}_{\boldsymbol{s}}\right)H, & z = H, \\ 0, \quad z = 0. \end{cases} \tag{134}$$

Following Pride (1994), the solution for $\boldsymbol{v}$ and p can be separated into mechanically and electrically induced contributions.

$$\boldsymbol{v} = \boldsymbol{v_m} + \boldsymbol{v_e}, \tag{135}$$

$$p = p_m + p_e, \tag{136}$$

where m stands for fields induced by pressure gradients, while e stands for fields induced by electric potential gradients.

Proceeding as Pride (1994) it is possible to show that the electrical contribution for $\boldsymbol{v_e}$ in the low frequency regime will be given by

$$\boldsymbol{v_{e0}} = -\frac{\epsilon_0\kappa_w}{\eta_w}\left(\Phi_w^0 - \zeta_w\right)\nabla\Gamma_w\frac{\Delta\phi}{H} - \frac{\epsilon_0\kappa_w}{\eta_w}\left(\Phi_{nw}^0 - \zeta_{nw}\right)\nabla\Gamma_{nw}\frac{\Delta\phi}{H}. \tag{137}$$

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

$$\boldsymbol{v}_{\boldsymbol{e0,(w)}} = -\frac{\epsilon_0 \kappa_w}{\eta_w} \left(\Phi_w^0 - \zeta_w \right) \nabla \Gamma_w \frac{\Delta \phi}{H}, \tag{138}$$

and

$$\boldsymbol{v}_{\boldsymbol{e0,(nw)}} = -\frac{\epsilon_0 \kappa_w}{\eta_w} \left(\Phi_{nw}^0 - \zeta_{nw} \right) \nabla \Gamma_{nw} \frac{\Delta \phi}{H}. \tag{139}$$

Following Pride (1994) the mechanical contributions at the low frequency regime are given by

$$\boldsymbol{v}_{\boldsymbol{m0}}(\boldsymbol{r}) = \frac{\boldsymbol{g}(\boldsymbol{r})}{\eta_w} \frac{\Delta P}{H}, \tag{140}$$

and

$$p_{m0}(\boldsymbol{r}) = h(\boldsymbol{r}) \frac{\Delta P}{H}, \tag{141}$$

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

$$\nabla^2 \boldsymbol{g} = \nabla h, \tag{142}$$

$$\nabla \cdot h = 0, \tag{143}$$

$$\boldsymbol{g} = 0, \quad \text{on} \quad S_w \cup S_{nw} = \partial V_w, \tag{144}$$

$$h = \begin{cases} H, & z = H, \\ 0, & z = 0. \end{cases} \tag{145}$$

Now we proceed to volume average the non-wetting fluid flow Eq. (57). If we define the relative non-wetting solid-phase flow vector $\boldsymbol{v}_{\boldsymbol{nw}} = \dot{\boldsymbol{u}}_{\boldsymbol{nw}} - \dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}}$ we may write:

$$-i\omega \rho_{nw} \boldsymbol{v}_{\boldsymbol{nw}} = \nabla \cdot \boldsymbol{\tau}_{\boldsymbol{nw}} + i\omega \rho_{nw} \dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}}. \tag{146}$$

Again, if we assume that the local relative flow is incompressible and defining $\nabla p = \nabla p_{nw} - i\omega\rho_{nw}\dot{\hat{\boldsymbol{u}}}_{\boldsymbol{s}}$, the following boundary-value problem can be stated

$$\eta_{nw}\nabla^2\boldsymbol{v_{nw}} + i\omega\rho_{nw}\boldsymbol{v_{nw}} = \nabla p, \tag{147}$$

$$\nabla \cdot \boldsymbol{v_{nw}} = 0, \tag{148}$$

$$\boldsymbol{v_{nw}} = 0 \qquad \text{on} \quad S_{nw} = \partial V_{nw}, \tag{149}$$

$$p = \begin{cases} \Delta P = \hat{\boldsymbol{z}} \cdot \left(\nabla \bar{p}_{nw} - i\omega\rho_{nw}\dot{\hat{\boldsymbol{u}}}_{\boldsymbol{s}}\right) H, & z = H, \\ 0, \quad z = 0. \end{cases} \tag{150}$$

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

$$\nabla^2\boldsymbol{v_{nw}} = \frac{\nabla p}{\eta_{nw}}, \tag{151}$$

$$\nabla \cdot \boldsymbol{v_{nw}} = 0, \tag{152}$$

$$\boldsymbol{v_{nw}} = 0, \quad \text{on} \quad S_{nw} = \partial V_{nw}, \tag{153}$$

$$p = \begin{cases} \Delta P, & z = H, \\ 0, & z = 0. \end{cases} \tag{154}$$

The solution to this boundary-value problem is given by

$$\boldsymbol{v_{nw0}}(\boldsymbol{r}) = \frac{\boldsymbol{g_{nw}}(\boldsymbol{r})}{\eta_{nw}}\frac{\Delta P}{H}, \tag{155}$$

and

$$p_0(\boldsymbol{r}) = h_{nw}(\boldsymbol{r})\frac{\Delta P}{H}, \tag{156}$$

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

$$\nabla^2 \boldsymbol{g_{nw}} = \nabla h_{nw}, \tag{157}$$

$$\nabla \cdot h_{nw} = 0, \tag{158}$$

$$\boldsymbol{g_{nw}} = 0, \quad \text{on} \quad S_{nw} = \partial V_{nw}, \tag{159}$$

$$h_{nw} = \begin{cases} H, & z = H, \\ 0, & z = 0. \end{cases} \tag{160}$$

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 $\boldsymbol{e_{w,(w)}}$ and $\boldsymbol{e_{w,(nw)}}$ in Eq.(83) we obtain

$$\begin{aligned}
&\boldsymbol{J_c} = \frac{\sigma_w}{\tilde{\alpha}_{\infty,w}} \bar{\boldsymbol{E}} \\
&-\frac{1}{V_w}\int_{S_w} \nabla\Gamma_w(\boldsymbol{r})dS \int_0^D \left(\sum_{l=1}^{L}(ez_l)^2 b_l (N^0_{l,(w)} - \mathcal{N}_{l,(w)})\right) \frac{\Delta\phi}{H} d\chi \\
&-\frac{1}{V_w}\int_{S_{nw}} \nabla\Gamma_{nw}(\boldsymbol{r})dS \int_0^D \left(\sum_{l=1}^{L}(ez_l)^2 b_l (N^0_{l,(nw)} - \mathcal{N}_{l,(nw)})\right) \frac{\Delta\phi}{H} d\chi.
\end{aligned} \tag{161}$$

Now if we set, as in (Pride, 1994):

$$\frac{2}{\Lambda} = \frac{\alpha_\infty}{V_p} \int_{S_w} \hat{\boldsymbol{z}} \cdot \nabla\Gamma_w(\boldsymbol{r})dS, \tag{162}$$

$$\frac{2}{\Lambda_{nw}} = \frac{\alpha_{\infty,nw}}{V_{nw}} \int_{S_{nw}} \hat{\boldsymbol{z}} \cdot \nabla\Gamma_{nw}(\boldsymbol{r})dS, \tag{163}$$

and

$$C_{em,(w)} = \int_0^D \left(\sum_{l=1}^{L} (ez_l)^2 b_l (N^0_{l,(w)} - \mathcal{N}_{l,(w)}) \right) d\chi, \tag{164}$$

$$C_{em,(nw)} = \int_0^D \left(\sum_{l=1}^{L} (ez_l)^2 b_l (N^0_{l,(nw)} - \mathcal{N}_{l,(nw)}) \right) d\chi, \tag{165}$$

then, we have:

$$\boldsymbol{J_c} = \left[\frac{\sigma_w}{\tilde{\alpha}_{\infty,w}} + \frac{2C_{em,(w)}}{s_w \alpha_\infty \Lambda} + \frac{(1-s_w)}{s_w} \frac{2C_{em,(nw)}}{\alpha_{\infty,nw}\Lambda_{nw}} \right] \bar{\boldsymbol{E}}. \tag{166}$$

Parameters Λ and Λ_{nw} are a measure of the weighted volume-to-surface ratio of the pore-space and non-wetting fluids respectively. As such, they have units of length. The latter depends, of course, 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

$$C_{em,(w)} \simeq 2d_w \sum_{l=1}^{L} (ez_l)^2 b_l \mathcal{N}_{l,(w)} \left(e^{-\frac{ez_l \zeta_w}{2kT}} - 1 \right), \tag{167}$$

$$C_{em,(nw)} \simeq 2d_{nw} \sum_{l=1}^{L} (ez_l)^2 b_l \mathcal{N}_{l,(nw)} \left(e^{-\frac{ez_l \zeta_{nw}}{2kT}} - 1 \right). \tag{168}$$

5.2 Streaming current density $\boldsymbol{J_s}$

Consider the average streaming current density given by Eq. (86):

$$\boldsymbol{J_s} = \frac{\epsilon_0 \kappa_w}{V_w} \int_{S_w} dS \int_0^D \nabla\Phi^0_w \cdot \nabla\boldsymbol{v} d\chi + \frac{\epsilon_0 \kappa_w}{V_w} \int_{S_{nw}} dS \int_0^D \nabla\Phi^0_{nw} \cdot \nabla\boldsymbol{v} d\chi, \tag{169}$$

where $\nabla\Phi^0_\xi \cdot \nabla\boldsymbol{v} = (\partial\Phi^0_\xi/\partial\chi)(\partial\boldsymbol{v}/\partial\chi)$, $\xi = w, nw$. 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 (138) and (139) in the first and second integrals of (169), respectively, we obtain

$$\boldsymbol{J_{se}} = -\frac{(\epsilon_0\kappa_w)^2}{\eta_w V_w}\left[\int_{S_w}\nabla\Gamma_w dS\int_0^D(\nabla\Phi_w^0)^2 d\chi\frac{\Delta\phi}{H}\right.$$
$$\left.+\int_{S_{nw}}\nabla\Gamma_{nw} dS\int_0^D(\nabla\Phi_{nw}^0)^2 d\chi\frac{\Delta\phi}{H}\right]. \quad (170)$$

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

$$\boldsymbol{J_{se}} = \frac{(\epsilon_0\kappa_w)^2}{\eta_w}\left[\frac{2}{s_w\alpha_\infty\Lambda}\int_0^D(\nabla\Phi_w^0)^2 d\chi + \frac{2(1-s_w)}{s_w\alpha_{\infty,nw}\Lambda_{nw}}\int_0^D(\nabla\Phi_{nw}^0)^2 d\chi\right]\bar{\boldsymbol{E}}, \quad (171)$$

or

$$\boldsymbol{J_{se}} = \left[\frac{2C_{os,(w)}}{s_w\alpha_\infty\Lambda} + \frac{2(1-s_w)C_{os,(nw)}}{s_w\alpha_{\infty,nw}\Lambda_{nw}}\right]\bar{\boldsymbol{E}}, \quad (172)$$

where

$$C_{os,(w)} = \frac{(\epsilon_0\kappa_w)^2}{\eta_w}\int_0^D(\nabla\Phi_w^0)^2 d\chi, \quad (173)$$

$$C_{os,(nw)} = \frac{(\epsilon_0\kappa_w)^2}{\eta_w}\int_0^D(\nabla\Phi_{nw}^0)^2 d\chi. \quad (174)$$

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, in the low-frequency approximation, as

$$C_{os,(w)} = \frac{(\epsilon_0\kappa_w)^2}{\eta_w}\left\{\frac{4kTd_w}{\epsilon_0\kappa_w}\sum_{l=1}^{L}\mathcal{N}_{l,(w)}\left[e^{-\frac{ez_l\zeta_w}{2kT}}-1\right]\right\}, \quad (175)$$

$$C_{os,(nw)} = \frac{(\epsilon_0\kappa_w)^2}{\eta_w}\left\{\frac{4kTd_{nw}}{\epsilon_0\kappa_w}\sum_{l=1}^{L}\mathcal{N}_{l,(nw)}\left[e^{-\frac{ez_l\zeta_{nw}}{2kT}}-1\right]\right\}. \quad (176)$$

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

$$\nabla\Phi_\xi^0 \cdot \nabla\boldsymbol{v_m} = \nabla\cdot(\Phi_\xi^0\nabla\boldsymbol{v_m}) - \Phi_\xi^0\nabla^2\boldsymbol{v_m} \tag{177}$$

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

$$\begin{aligned}\boldsymbol{J_{sm}} &= \frac{\epsilon_0\kappa_w}{V_w}\int_{S_w} dS\int_0^D \nabla\cdot(\Phi_w^0\nabla\boldsymbol{v_m}) - \Phi_w^0\nabla^2\boldsymbol{v_m}d\chi\\ &+\frac{\epsilon_0\kappa_w}{V_w}\int_{S_{nw}} dS\int_0^D \nabla\cdot(\Phi_{nw}^0\nabla\boldsymbol{v_m}) - \Phi_{nw}^0\nabla^2\boldsymbol{v_m}d\chi,\end{aligned} \tag{178}$$

then

$$\begin{aligned}\boldsymbol{J_{sm}} &= \frac{\epsilon_0\kappa_w\zeta_w}{V_w}\int_{S_w} \boldsymbol{n}\cdot\nabla\boldsymbol{v_m} - \left(\int_0^D \frac{\Phi_w^0}{\zeta_w}d\chi\right)\nabla^2\boldsymbol{v_m}dS\\ &+\frac{\epsilon_0\kappa_w\zeta_{nw}}{V_w}\int_{S_{nw}} \boldsymbol{n}\cdot\nabla\boldsymbol{v_m} - \left(\int_0^D \frac{\Phi_{nw}^0}{\zeta_{nw}}d\chi\right)\nabla^2\boldsymbol{v_m}dS,\end{aligned} \tag{179}$$

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

$$\tilde{d}_\xi = \int_0^D \frac{\Phi_\xi^0(\chi)}{\zeta_\xi}d\chi, \qquad \xi = w, nw, \tag{180}$$

we can write

$$\begin{aligned}\boldsymbol{J_{sm}} &= \frac{\epsilon_0\kappa_w\zeta_w}{V_w}\int_{S_w}\left(\boldsymbol{n}\cdot\nabla\boldsymbol{v_m} - \tilde{d}_w\nabla^2\boldsymbol{v_m}\right)dS\\ &+\frac{\epsilon_0\kappa_w\zeta_{nw}}{V_w}\int_{S_{nw}}\left(\boldsymbol{n}\cdot\nabla\boldsymbol{v_m} - \tilde{d}_{nw}\nabla^2\boldsymbol{v_m}\right)dS,\end{aligned} \tag{181}$$

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

$$\boldsymbol{J_{sm0}} = -\left[\frac{\epsilon_0\kappa_w\zeta_w}{\eta_w}\frac{\hat{\boldsymbol{z}}}{V_w}\cdot\int_{S_w}\left(\boldsymbol{n}\cdot\nabla\boldsymbol{g}-\tilde{d}_w\nabla h\right)dS\right]\left(-\nabla\bar{p}_w+i\omega\rho_w\dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}}\right)$$
$$-\left[\frac{\epsilon_0\kappa_w\zeta_{nw}}{\eta_w}\frac{\hat{\boldsymbol{z}}}{V_w}\cdot\int_{S_{nw}}\left(\boldsymbol{n}\cdot\nabla\boldsymbol{g}-\tilde{d}_{nw}\nabla h\right)dS\right]\left(-\nabla\bar{p}_w+i\omega\rho_w\dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}}\right). \quad (182)$$

Then, multiplying by $s_w\phi$ we get

$$s_w\phi\boldsymbol{J_{sm0}} = L_{m0}\left(-\nabla\bar{p}_w+i\omega\rho_w\dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}}\right), \quad (183)$$

where

$$L_{m0} = -\phi\frac{\epsilon_0\kappa_w\zeta_w}{\eta_w}\frac{\hat{\boldsymbol{z}}}{V_p}\cdot\int_{S_w}\left(\boldsymbol{n}\cdot\nabla\boldsymbol{g}-\tilde{d}_w\nabla h\right)dS$$
$$-\phi(1-s_w)\frac{\epsilon_0\kappa_w\zeta_{nw}}{\eta_w}\frac{\hat{\boldsymbol{z}}}{V_{nw}}\cdot\int_{S_{nw}}\left(\boldsymbol{n}\cdot\nabla\boldsymbol{g}-\tilde{d}_{nw}\nabla h\right)dS. \quad (184)$$

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 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. (184) 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,

$$\bar{\boldsymbol{v}}_{\boldsymbol{m0}} = \frac{1}{V_w}\int_{V_w}\boldsymbol{v_{m0}}(\boldsymbol{r})dV = \frac{1}{\eta_w}\left(-\frac{1}{V_w}\int_{V_w}\hat{\boldsymbol{z}}\cdot\boldsymbol{g}dV\right)\left(-\nabla\bar{p}_w+i\omega\rho_w\dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}}\right), \quad (185)$$

then,

$$s_w\phi\bar{\boldsymbol{v}}_{\boldsymbol{m0}} = \frac{1}{\eta_w}\left(-\frac{1}{V_A}\int_{V_w}\hat{\boldsymbol{z}}\cdot\boldsymbol{g}dV\right)\left(-\nabla\bar{p}_w + i\omega\rho_w\dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}}\right), \tag{186}$$

or,

$$s_w\phi\bar{\boldsymbol{v}}_{\boldsymbol{m0}} = \frac{k_{0,w}}{\eta_w}\left(-\nabla\bar{p}_w + i\omega\rho_w\dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}}\right), \tag{187}$$

where

$$k_{0,w} = -\frac{1}{V_A}\int_{V_w}\hat{\boldsymbol{z}}\cdot\boldsymbol{g}dV. \tag{188}$$

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

Next, the low-frequency electrically induced flow is integrated

$$\begin{aligned}\bar{\boldsymbol{v}}_{\boldsymbol{e0}} = \frac{1}{V_w}\int_{V_w}\boldsymbol{v}_{\boldsymbol{e0}}dV = \frac{\epsilon_0\kappa_w}{\eta_w}\frac{\hat{\boldsymbol{z}}}{V_w}\cdot\Bigg[\int_{V_w}\left(\Phi_w^0-\zeta_w\right)\nabla\Gamma_w dV \\ + \int_{V_w}\left(\Phi_{nw}^0-\zeta_{nw}\right)\nabla\Gamma_{nw}dV\Bigg]\bar{\boldsymbol{E}}.\end{aligned} \tag{189}$$

Performing the integration and multiplying by $s_w\phi$ the following expression is obtained

$$s_w\phi\bar{\boldsymbol{v}}_{\boldsymbol{e0}} = L_{e0}\bar{\boldsymbol{E}}, \tag{190}$$

where

$$\begin{aligned}L_{e0} = -\phi\frac{\epsilon_0\kappa_w}{\eta_w}\Bigg\{\zeta_w\left[\frac{1}{\alpha_\infty}-(1-s_w)-\frac{2\tilde{d}_w}{\alpha_\infty\Lambda}\right] \\ + \zeta_{nw}\left[1-\frac{(1-s_w)}{\alpha_{\infty,nw}}-\frac{2\tilde{d}_{nw}(1-s_w)}{\alpha_{\infty,nw}\Lambda_{nw}}\right]\Bigg\}.\end{aligned} \tag{191}$$

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.(166) and (172) we have

$$s_w \phi (\boldsymbol{J_{ce}} + \boldsymbol{J_{se}}) = \sigma \bar{\boldsymbol{E}}, \tag{192}$$

where

$$\sigma = \left[\frac{s_w \phi \sigma_w}{\tilde{\alpha}_{\infty,w}} + \frac{2\phi (C_{em,(w)} + C_{os,(w)})}{\alpha_\infty \Lambda} + (1 - s_w) \frac{2\phi (C_{em,(nw)} + C_{os,(nw)})}{\alpha_{\infty,nw} \Lambda_{nw}} \right], \tag{193}$$

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. (155)

$$\begin{aligned} \bar{\boldsymbol{v}}_{\boldsymbol{nw0}} &= \frac{1}{V_{nw}} \int_{V_{nw}} \boldsymbol{v}_{\boldsymbol{nw0}}(\boldsymbol{r}) dV = \\ & \frac{1}{\eta_{nw}} \left(-\frac{1}{V_{nw}} \int_{V_{nw}} \hat{\boldsymbol{z}} \cdot \boldsymbol{g_{nw}} dV \right) \left(-\nabla \bar{p}_{nw} + i\omega \rho_{nw} \dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}} \right), \end{aligned} \tag{194}$$

then,

$$(1 - s_w)\phi \bar{\boldsymbol{v}}_{\boldsymbol{nw0}} = \frac{1}{\eta_{nw}} \left(-\frac{1}{V_A} \int_{V_{nw}} \hat{\boldsymbol{z}} \cdot \boldsymbol{g_{nw}} dV \right) \left(-\nabla \bar{p}_{nw} + i\omega \rho_{nw} \dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}} \right), \tag{195}$$

or,

$$(1 - s_w)\phi \bar{\boldsymbol{v}}_{\boldsymbol{nw0}} = \frac{k_{0,nw}}{\eta_{nw}} \left(-\nabla \bar{p}_{nw} + i\omega \rho_{nw} \dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}} \right), \tag{196}$$

where

$$k_{0,nw} = -\frac{1}{V_A} \int_{V_{nw}} \hat{\boldsymbol{z}} \cdot \boldsymbol{g_{nw}} dV, \tag{197}$$

is the DC permeability of the non-wetting phase.

5.4 Summary of this section

By adding Eqs.(187) and (190) we have

$$s_w \phi \bar{\boldsymbol{v}}_{\boldsymbol{0}} = s_w \phi (\bar{\boldsymbol{v}}_{\boldsymbol{m0}} + \bar{\boldsymbol{v}}_{\boldsymbol{e0}}) = \frac{k_{0,w}}{\eta_w} \left(-\nabla \bar{p}_w + i\omega \rho_w \dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}} \right) + L_{e0} \bar{\boldsymbol{E}}, \tag{198}$$

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:

$$-i\omega \bar{\boldsymbol{w}}_{\boldsymbol{w}} = L_{e0} \bar{\boldsymbol{E}} + \frac{k_{0,w}}{\eta_w} \left(-\nabla \bar{p}_w + i\omega \rho_w \dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}} \right), \tag{199}$$

with L_{e0} given by (191) and $k_{0,w}$ by (197). From Eq. (196), 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

$$-i\omega \bar{\boldsymbol{w}}_{\boldsymbol{nw}} = \frac{k_{0,nw}}{\eta_{nw}} \left(-\nabla \bar{p}_{nw} + i\omega \rho_{nw} \dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}} \right). \tag{200}$$

Adding (183) and (192) we have the final expression for the second transport equation:

$$\bar{\boldsymbol{J}} = \sigma \bar{\boldsymbol{E}} + L_{m0} \left(-\nabla \bar{p}_w + i\omega \rho_w \dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}} \right), \tag{201}$$

with L_{m0} given by (184) and σ by (193).

Finally, Onsager reciprocity $L_{e0} = L_{m0}$ can be demonstrated in the same way as Pride (1994), by considering for each one of these coefficients the contribution from each double layer separately.

In previous works Li et al (1995); Pengra et al (1999) employing the steady flow version of the transport equations in saturated conditions, postulated that the validity of Onsager's reciprocal relation for the electrofiltration and electroosmotic coupling coefficients, that is $L_{m0} = L_{e0}$, implies that there exists a relationship between fluid conductivity and permeability. They were able to confirm their theoretical predictions in the laboratory by means of a low-frequency AC technique measuring the electrokinetic response of brine saturated rocks or glass beads samples. Additionally, it is known that the four conductances in the transport equations must satisfy certain inequalities derived from thermodynamic laws (Demirel, 2007). Because of these facts, parameters appearing in L_{m0} and L_{e0} won't be susceptible of being arbitrarily chosen.

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 (193), 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. 98), Eqs. (199) and (200) can be placed in Eq. (98), which divided by ρ_f reads

$$\begin{aligned} -i\omega\bar{\boldsymbol{w}}_{\boldsymbol{f}} = \frac{\rho_w}{\rho_f} L_0^{ps} \bar{\boldsymbol{E}} - \left[\frac{\rho_w}{\rho_f} \frac{k_{0,w}}{\eta_w} + \frac{\rho_{nw}}{\rho_f} \frac{k_{0,nw}}{\eta_{nw}} \right] \nabla \bar{p} \\ + i\omega \left[\frac{\rho_w^2}{\rho_f} \frac{k_{0,w}}{\eta_w} + \frac{\rho_{nw}^2}{\rho_f} \frac{k_{0,nw}}{\eta_{nw}} \right] \dot{\bar{\boldsymbol{u}}}_{\boldsymbol{s}}. \end{aligned} \tag{202}$$

Also, it is worthwhile to remark here that at $p_c = 0$, the mechanical constitutive relations given by (100) and (101) will hold. Removing all the overbars appearing in the averaged variables, from (76), (77), (88), (99), (100), (101), (128), (201) and (202) we get:

$$\nabla \times \boldsymbol{E} = i\omega \boldsymbol{B}, \tag{203}$$

$$\nabla \times \boldsymbol{H} = -i\omega \boldsymbol{D} + \boldsymbol{J}, \tag{204}$$

$$\nabla \boldsymbol{\tau_B} = \omega^2 \left[\rho_B \boldsymbol{u_s} + \rho_f \boldsymbol{w_f}\right], \tag{205}$$

$$\boldsymbol{J} = \sigma^{ps} \boldsymbol{E} + L_0^{ps} \left(-\nabla p + \omega^2 \rho_w \boldsymbol{u_s}\right), \tag{206}$$

$$\begin{aligned} -i\omega \boldsymbol{w_f} = \frac{\rho_w}{\rho_f} L_0^{ps} \boldsymbol{E} - \left[\frac{\rho_w}{\rho_f}\frac{k_{0,w}}{\eta_w} + \frac{\rho_{nw}}{\rho_f}\frac{k_{0,nw}}{\eta_{nw}}\right] \nabla p \\ +\omega^2 \left[\frac{\rho_w^2}{\rho_f}\frac{k_{0,w}}{\eta_w} + \frac{\rho_{nw}^2}{\rho_f}\frac{k_{0,nw}}{\eta_{nw}}\right] \boldsymbol{u_s}, \end{aligned} \tag{207}$$

$$\boldsymbol{D} = \epsilon_0 \left[\frac{\kappa_s(1-\phi)}{\tilde{\alpha}_{\infty,s}} + \frac{\kappa_w s_w \phi}{\tilde{\alpha}_{\infty,w}} + \frac{\kappa_{nw}(1-s_w)\phi}{\alpha_{\infty,nw}}\right] \boldsymbol{E}, \tag{208}$$

$$\boldsymbol{B} = \mu_0 \boldsymbol{H}, \tag{209}$$

$$\boldsymbol{\tau_B} = (K_c \nabla \cdot \boldsymbol{u_s} + C\nabla \cdot \boldsymbol{w_f})\mathbf{I} + G\left(\nabla \boldsymbol{u_s} + \nabla \boldsymbol{u_s}^T - \frac{2}{3}\nabla \cdot \boldsymbol{u_s}\mathbf{I}\right), \tag{210}$$

$$-p = C\nabla \cdot \boldsymbol{u_s} + M\nabla \cdot \boldsymbol{w_f}, \tag{211}$$

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

$$\begin{aligned} L_0^{ps} = -\phi \frac{\epsilon_0 \kappa_w}{\eta_w} \Bigg\{ \zeta_w \left[\frac{1}{\alpha_\infty} - (1-s_w) - \frac{2\tilde{d}_w}{\alpha_\infty \Lambda}\right] \\ +\zeta_{nw}\left[1 - \frac{(1-s_w)}{\alpha_{\infty,nw}} - \frac{2\tilde{d}_{nw}(1-s_w)}{\alpha_{\infty,nw}\Lambda_{nw}}\right]\Bigg\}, \end{aligned} \tag{212}$$

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

$$\sigma^{ps} = \left[\frac{s_w \phi \sigma_w}{\tilde{\alpha}_{\infty,w}} + \frac{2\phi(C_{em,(w)} + C_{os,(w)})}{\alpha_\infty \Lambda} + (1-s_w)\frac{2\phi(C_{em,(nw)} + C_{os,(nw)})}{\alpha_{\infty,nw}\Lambda_{nw}}\right]. \tag{213}$$

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. (120) and (125) we respectively have

$$\lim_{s_w \to 1} \frac{1}{\tilde{\alpha}_{\infty,w}} = \frac{1}{\alpha_\infty} \quad \text{and} \quad \frac{1}{\tilde{\alpha}_{\infty,s}} = \frac{1}{(1-\phi)} - \frac{\phi}{(1-\phi)} \frac{1}{\alpha_\infty}, \tag{214}$$

in the fully water saturation case, the final equations (203)-(211) are identical to Pride (1994, Eqs. 248-256) as expected. Note that if the frequencies are low enough that it is safe to neglect the inertial terms in Eqs. (205)-(207), 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

$$\boldsymbol{E} = -\nabla\Phi. \tag{215}$$

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

$$\nabla \cdot \boldsymbol{J} = 0, \tag{216}$$

$$\nabla \cdot (\dot{\boldsymbol{w}}_{\boldsymbol{w}} + \dot{\boldsymbol{w}}_{\boldsymbol{nw}}) = 0, \tag{217}$$

$$\boldsymbol{J} = -\sigma^{ps} \nabla \Phi - L_0^{ps} \nabla p_w, \tag{218}$$

$$\dot{\boldsymbol{w}}_{\boldsymbol{w}} = -L_0^{ps} \nabla \Phi - \frac{k_{0,w}}{\eta_w} \nabla p_w, \tag{219}$$

$$\dot{\boldsymbol{w}}_{\boldsymbol{nw}} = -\frac{k_{0,nw}}{\eta_{nw}} \nabla p_{nw}, \tag{220}$$

$$p_c = p_{nw} - p_w. \tag{221}$$

Note that Eqs. (216) and (217) state the conservation of charges and flow, respectively. Also notice that the capillary relation Eq. (221) 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 where quasistatic perturbations are applied to the porous rock, Eqs. (215) and (216) can still be considered to be valid (Haines and Pride, 2006; Monachesi et al, 2015; Rosas-Carbajal et al, 2020). However, Eq. (217) no longer holds, and should be replaced by a set of constitutive relations appropriate for the case where $p_c \neq 0$ (see for example Santos et al (1990a)). 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. (217) should be replaced by

$\dot{p} = -M\nabla \cdot \dot{\boldsymbol{w}}_{\boldsymbol{f}}$ and the quasistatic equations can be written as

$$\nabla \cdot \boldsymbol{J} = 0, \tag{222}$$

$$\nabla \cdot \dot{\boldsymbol{w}}_{\boldsymbol{f}} = -\frac{\dot{p}}{M}, \tag{223}$$

$$\boldsymbol{J} = -\sigma^{ps}\nabla\Phi - L_0^{ps}\nabla p, \tag{224}$$

$$\dot{\boldsymbol{w}}_{\boldsymbol{f}} = \frac{\rho_w}{\rho_f}L_0^{ps}\nabla\Phi - \left[\frac{\rho_w}{\rho_f}\frac{k_{0,w}}{\eta_w} + \frac{\rho_{nw}}{\rho_f}\frac{k_{0,nw}}{\eta_{nw}}\right]\nabla p. \tag{225}$$

In the case of full water saturation, following the same procedure as before, it is easy to show that Eqs. (222)-(225) 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 $\boldsymbol{w}_{\boldsymbol{nw}} = 0$). 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):

$$\nabla \cdot \boldsymbol{J} = 0, \tag{226}$$

$$\nabla \cdot \dot{\boldsymbol{w}}_{\boldsymbol{w}} = 0, \tag{227}$$

$$\boldsymbol{J} = -\sigma^{ps}\nabla\Phi + L_0^{ps}\nabla p_c, \tag{228}$$

$$\dot{\boldsymbol{w}}_{\boldsymbol{w}} = -L_0^{ps}\nabla\Phi + \frac{k_{0,w}}{\eta_w}\nabla p_c. \tag{229}$$

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. (226)-(229) are coincident with Pride (1994, Eqs. 258-261).

If quasistatic perturbations and highly consolidated rocks are considered in this capillary flow regime, Eq. (227) should be replaced by $\dot{p}_c = \tilde{M}\nabla \cdot \dot{\boldsymbol{w}}_{\boldsymbol{w}}$, where

$$\tilde{M} = \frac{K_w}{s_w\phi + \frac{K_w}{K_s^2}\left[(1-\phi)K_s - K_m\right]}. \tag{230}$$

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 A).

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 hypotheses on deriving the governing equations for coupled electromagnetic/acoustic wave propagation are 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 partially-saturated porous rock. We've also shown that in the limit of full 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 Mechanical constitutive relations in the case of stagnant non-wetting fluid

If the non-wetting fluid is assumed to 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. (60). Following Pride et al (1992), taking into account that the wetting-fluid occupies a volume $s_w\phi$ we obtain

$$\boldsymbol{\tau_B} = (\tilde{K}_c \nabla \cdot \boldsymbol{u_s} + \tilde{C} \nabla \cdot \boldsymbol{w_w})\mathbf{I} + G\left(\nabla \boldsymbol{u_s} + \nabla \boldsymbol{u_s}^T - \frac{2}{3}\nabla \cdot \boldsymbol{u_s}\mathbf{I}\right), \quad \text{(A1)}$$

$$p_c = \tilde{C}\nabla \cdot \boldsymbol{u_s} + \tilde{M}\nabla \cdot \boldsymbol{w_w}, \quad \text{(A2)}$$

where

$$\tilde{K}_c = \frac{K_m + s_w\phi K_w + \left[(1-\phi) + 2s_w\phi\right] K_s\tilde{\Delta}}{1+\Delta}, \quad \text{(A3)}$$

$$\tilde{C} = \frac{K_w + K_s\tilde{\Delta}}{1+\tilde{\Delta}}, \quad \text{(A4)}$$

$$\tilde{M} = \frac{1}{s_w\phi}\frac{K_w}{1+\tilde{\Delta}}. \quad \text{(A5)}$$

In these expressions,

$$\tilde{\Delta} = \frac{K_w}{s_w\phi K_s^2}\left[(1-\phi)K_s - K_m\right]. \quad \text{(A6)}$$

From Eq. (A2), if the solid displacement is negligible, then taking the first time derivative we have $\dot{p}_c = \tilde{M}\nabla \cdot \dot{\boldsymbol{w}}_{\boldsymbol{w}}$.