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Governing equations for the coupled electromagnetics and acoustics of porous media

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The macroscopic governing equations controlling the coupled electromagnetics and acoustics of porous media are derived here from first principles. The porous material is assumed to consist of a packing of solid grains that is saturated by an electrolyte. A sedimentary rock is an example of such a material. The approach is to volume average the equations known to apply in the fluid and solid phases while allowing for the boundary conditions that exist on the fluid-solid interface. The coupling is due to a layer of excess charge adsorbed to the surfaces of the solid grains that is balanced by mobile ions in the fluid electrolyte; i.e., the coupling is electrokinetic in nature. The derived equations have the form of Maxwell's equations coupled to Biot's equations with coupling occurring in the flux-force (or transport) relations. The frequency-dependent macroscopic-transport coefficients are explicitly obtained and related to each other. Onsager reciprocity is derived and is not simply postulated.

I. INTRODUCTION

This paper is concerned with the macroscopic dynamics of two-phase (fluid and solid) porous media possessing continuously distributed phases. A packing of grains saturated by a fluid is an example of such a material. The term "macroscopic," as used here, means that the wavelengths of the applied disturbances are much greater than the dimensions of the grains. When a macroscopic-mechanical disturbance propagates through such a material, a small amount of relative motion is induced between the fluid and solid phases. This relative flow will carry along the excess ions in the electric double layers near the grain surfaces. Thus, a mechanical wave can act as a current source for macroscopic-electromagnetic disturbances. Similarly, when an electromagnetic disturbance propagates, the electric field will act on the charge excesses of the double layers producing pressure gradients in the fluid and, in principle, macroscopic-mechanical disturbances. Thompson and Gist[1] have made field measurements clearly demonstrating that seismic waves can induce electromagnetic disturbances in saturated sediments in the Earth. It is believed that their observations can be explained by the electrokinetic mechanism mentioned above. In this paper, the equations controlling such behavior will be derived and the coefficients defined.

There has not been much previous work in this direction. In 1944, Frenkel[2] postulated equations that estimated the amount of relative fluid motion induced by a seismic wave. He attempted to allow for flow-induced electric fields by employing, incorrectly, the Helmholtz-Smoluchowski equation. This equation assumes that the total electric current in the porous material, which is a sum of the mechanically driven streaming current (due to convection of double-layer ions) and an electrically driven conduction current, is everywhere zero. Thus, in Frenkel's model, the generated electric field exists only where there is seismically induced relative flow. Correctly, the total current should be present in Ampère's law and the full set of Maxwell's equations utilized. This is the more general result obtained here.

Neev and Yeatts[3] also postulated a set of equations that attempt to model the interaction between mechanical waves and electric fields due to electrokinetics. They also do not allow for the full set of Maxwell's equations which leads them to the erroneous conclusion that mechanical shear waves do not generate electromagnetic disturbances. They only allow for electric fields generated by charge separation. A mechanical shear wave, however, generates a divergence-free (no induced-charge excess) streaming current that will act as a current source in Ampère's law, thus demonstrating the need to use the complete set of Maxwell's equations. Both Neev and Yeatts and Frenkel completely ignore the frequency dependence of their proposed transport laws.

The central problem with both of these cited works is that their equations are not derived from the underlying constituent properties. In this paper, the continuum equations known to apply in the solid grains and fluid electrolyte are volume averaged to obtain the macroscopic-governing equations. The final equations have the form of Maxwell's equations coupled to Biot's[4] equations. The coupling arises naturally from just two postulates: (1) The solid grains have a uniform surface-charge density adsorbed to their surface, and (2) prior to the arrival of a disturbance, the net charge in a volume of the porous material is zero. The definition and frequency dependences of the transport coefficients will be given. Onsager reciprocity will be derived and not simply assumed.

A brief summary of the major assumptions and/or limitations of the derived theory is now given. Only linear disturbances are considered (i.e., those that obey superposition). The fluid is assumed to be an ideal electrolyte, thus restricting salt concentrations to be less than 1 mol/liter. Both the solid grains and all the macroscopic-constitutive laws are assumed to be isotropic. All wave-induced diffusion effects (flux due to wave-induced ion-concentration gradients) are, in the end, ignored. It is demonstrated that two conditions must be fulfilled in order to make this assumption at the pore and grain scale: (1) The dielectric constant of the grains must be much less than that of the electrolyte (say a factor of 10 or more), and (2) the thickness of the double layer should be much less than the radii of curvature of the solid grains. The specific class of porous media that are of primary interest here are water-saturated sediments and sedimentary rocks. For these materials, both of these assumptions are valid. Last, no wave scattering from the individual grains of the porous material will be allowed for. This implies that wavelengths λ are always much greater than grain sizes (e.g., $\lambda \geq 1$ mm). Thus, the largest applied frequency that can be considered (for mechanical waves) is on the order of 10^6 Hz.

The structure of the paper is as follows. In Sec. II, the grain-scale equations and boundary conditions for the fluid and solid phases are stated. In Sec. III, these equations are volume averaged to obtain the macroscopic equations of interest. However, several integrals present in the macroscopic-transport equations require the local electric and fluid-flow fields in the pore space to be related to the macroscopic fields generating them. Thus, in Sec. IV, the boundary-value problems controlling the pore-scale fields are treated and in Sec. V, the remaining integrals evaluated to give the macroscopic-transport coefficients. Last, in Sec. VI, the governing equations are presented in final form and summarized.

II. PORE AND GRAIN-SCALE GOVERNING EQUATIONS

There is assumed to be a layer of electrolyte ions and structured (hydrogen-bonded) water molecules that are chemically and physically adsorbed to the surface of the solid grains. This layer also includes the ionized surface sites present on the grain surfaces. The molecules and ions in this layer are assumed to be immobile. In the lexicon of the electric double layer,[5] this adsorbed layer corresponds to the "Stern layer" or, equivalently, to both the "inner and outer Helmholtz layers." If there is a net excess of charge in the adsorbed layer (the usual situation), it is balanced by an opposite amount of excess mobile ions distributed in the adjacent fluid. This region of fluid balancing the charge of the adsorbed layer is called the "diffuse layer." The adsorbed layer and diffuse layer together constitute the electric double layer. The surface that separates the diffuse layer from the adsorbed layer is called the "shear plane" and will be the surface used to define the fluid-solid interface S_w in what follows (the subscript w stands for the "wall"). The adsorbed layer is so thin (≤ 10 Å) that it cannot be properly treated as a separate phase. Thus, in the continuum description that follows, the physical properties of the adsorbed layer show up as boundary conditions on S_w, namely, as a uniform surface-charge density Q^0 and as the no-slip flow condition.

A. Electromagnetic equations

The solid grains (e.g., quartz) are assumed to be electrically insulating while the fluid electrolyte is assumed to possess L ionic species. Maxwell's equations for the solid and fluid phases take the form, respectively,

$$\nabla \cdot \mathbf{B}_s = 0, \tag{1}$$

$$\nabla \cdot \mathbf{D}_s = 0, \tag{2}$$

$$\nabla \times \mathbf{E}_s = -\dot{\mathbf{B}}_s, \tag{3}$$

$$\nabla \times \mathbf{H}_s = \dot{\mathbf{D}}_s, \tag{4}$$

and

$$\nabla \cdot \mathbf{B}_f = 0, \tag{5}$$

$$\nabla \cdot \mathbf{D}_f = \sum_{\ell=1}^{L} e z_\ell N_\ell, \tag{6}$$

$$\nabla \times \mathbf{E}_f = -\dot{\mathbf{B}}_f, \tag{7}$$

$$\nabla \times \mathbf{H}_f = \dot{\mathbf{D}}_f + \mathbf{J}_f, \tag{8}$$

where $\mathbf{J}_f$ is the ionic-current density and has contributions from the diffusion, electromigration, and convection of ions,

$$\mathbf{J}_f = \sum_{\ell=1}^{L} e z_\ell \left[-kT b_\ell \nabla N_\ell + e z_\ell b_\ell N_\ell \mathbf{E}_f + N_\ell \dot{\mathbf{u}}_f \right]. \tag{9}$$

$\dot{\mathbf{u}}_f$ is the instantaneous fluid velocity (the fluid may be accelerating). The ionic properties are the valences z_ℓ ($e z_\ell$ represents the net charge and sign on each species-ℓ ion), the number densities N_ℓ (the number of species-ℓ ions per unit volume), and the mobilities b_ℓ (units of velocity per unit force). The Einstein-Stokes approximation $b_\ell = 1/(6\pi\eta R_\ell)$, where η is the fluid's shear viscosity and R_ℓ is the effective "ion radius," is often accurate and is quite convenient. The mobilities are related to the ionic diffusivities D_ℓ as $D_\ell = kTb_\ell$. Note that some authors employ an alternative definition of ionic mobility, say, u_ℓ, given by $u_\ell = |e z_\ell| b_\ell$.

The above estimate for the current density is strictly valid only when ions move independently from each other (an ideal electrolyte). By considering the ion-separation distant at which electrostatic-interaction energies become significant compared to the thermal energy kT, it can be concluded that as long as ion concentrations are less than, say, 1 mol/liter, the ideal electrolyte assumption is (at least roughly) valid. Although the fluid has a velocity $\dot{\mathbf{u}}_f$, the Lorentz electric field $\dot{\mathbf{u}}_f \times \mathbf{B}_f$ that should be added to $\mathbf{E}_f$ in the current density is completely negligible if $\mathbf{B}_f$ is associated with the same disturbance that produces $\mathbf{E}_f$; i.e., the fluid velocity is dramatically less than the speed of the electromagnetic disturbance. Alternatively, if $\mathbf{B}_f$ is taken to be the maximum possible value of the Earth's field at the Earth's surface ($\sim 10^{-4}$ T), one has that $|e z_\ell b_\ell \dot{\mathbf{u}}_f \times \mathbf{B}_f| / |\dot{\mathbf{u}}_f|$ is of the order 10^{-12}; i.e., the current generated by the Lorentz force is completely negligible compared to that generated by convection of the free double-layer ions (although, of course, the Lorentz-force current will operate regardless of whether there are charge excesses in the diffuse double layer). Last, although the grains are assumed to be a material like quartz, no piezoelectric effects will be allowed for. This is because the grains of the material are assumed to be oriented at random to one another so that the average polarization of a group of grains is zero.

The boundary conditions that hold on the surface S_w (obtained by volume integrating Maxwell's equations over an infinitesimally thin disk that straddles S_w) are

$$\mathbf{n}\cdot(\mathbf{B}_s-\mathbf{B}_f)=\mathbf{0}, \tag{10}$$

$$\mathbf{n}\cdot(\mathbf{D}_s-\mathbf{D}_f)=Q, \tag{11}$$

$$\mathbf{n}\times(\mathbf{E}_s-\mathbf{E}_f)=\mathbf{0}, \tag{12}$$

$$\mathbf{n}\times(\mathbf{H}_s-\mathbf{H}_f)=Q\dot{\mathbf{u}}_s, \tag{13}$$

$$\mathbf{n}\cdot\mathbf{J}_f=\dot{Q}, \tag{14}$$

where $\mathbf{n}$ is the normal to S_w directed from fluid to solid, $\dot{\mathbf{u}}_s$ is the instantaneous velocity of the solid ($=\dot{\mathbf{u}}_f$ on S_w), and Q is the free charge per unit area of the adsorbed layer. Equation (14) follows, as usual, by taking the divergence of Ampère's law and the time derivative of Coulomb's law (i.e., it is a consequence of charge conservation). The right-hand side of Eq. (12) follows only if the charge of the adsorbed layer is uniformly distributed along S_w. An additional current term could be added to the right-hand side of Eq. (13) if it was assumed that conduction can occur in the adsorbed layer. Although this possibility is ignored here, hydrogen ions may efficiently conduct through the network of hydrogen-bonded water molecules present in the adsorbed layer. This effect can be included in future work.

Last, the above equations are closed by the constitutive laws

$$\mathbf{B}_\xi=\mu_0\mathbf{H}_\xi, \tag{15}$$

$$\mathbf{D}_\xi=\epsilon_0\kappa_\xi\mathbf{E}_\xi, \tag{16}$$

where $\xi=f$ or s and where κ_ξ is the dielectric constant.

All the field variables will now be written in the form

$$Q(t)=Q^0+\mathrm{Re}\{q(\omega)e^{-i\omega t}\}, \tag{17}$$

$$N_\ell(t)=N_\ell^0+\mathrm{Re}\{n_\ell(\omega)e^{-i\omega t}\}, \tag{18}$$

$$\mathbf{E}_f(t)=\mathbf{E}_f^0+\mathrm{Re}\{\mathbf{e}_f(\omega)e^{-i\omega t}\}, \tag{19}$$

and so on. The first term in these expressions represents the static-equilibrium field prior to the arrival of any disturbance, while the second term represents the deviation in the field due to a time-harmonic disturbance. It will be assumed, here, that no free charge q is induced on the surface (note that the free charge q does not include the polarization charge dielectrically induced on the surface). The only way for the free charge of the adsorbed layer to change is if chemical reactions occur and, thus, such chemical reactions are ignored here. It is assumed that no steady currents operate prior to disturbance and that there are no static magnetic fields present. Because Q^0 is assumed to be uniform over the grain surfaces, it can be shown using a simple argument based on Stoke's law that $\mathbf{E}_s^0$ must be zero (the net circulation of $\mathbf{E}_s^0$ around a closed path that runs along the surface of the grain and then passes arbitrarily through the grain must be zero).

The only nonzero static fields are then $\mathbf{E}_f^0$ and N_ℓ^0. The equations governing these fields are [from Eqs. (6)–(9) and (17)–(19)]

$$\epsilon_0\kappa_f\nabla\cdot\mathbf{E}_f^0=\sum_{\ell=1}^{L}ez_\ell N_\ell^0, \tag{20}$$

$$\nabla\times\mathbf{E}_f^0=\mathbf{0}, \tag{21}$$

$$-kT\nabla N_\ell^0+N_\ell^0ez_\ell\mathbf{E}_f^0=\mathbf{0}, \tag{22}$$

with the boundary conditions on S_w,

$$\epsilon_0\kappa_f\mathbf{n}\cdot\mathbf{E}_f^0=Q^0, \tag{23}$$

$$\mathbf{n}\times\mathbf{E}_f^0=\mathbf{0}. \tag{24}$$

The dielectric constant is assumed constant right up to S_w (Ref. 6 shows that there is at most a 1% deviation in κ_f across the diffuse portion of the double layer). Equations (21) and (22) are satisfied by

$$\mathbf{E}_f^0=-\nabla\Phi^0, \tag{25}$$

$$N_\ell^0=\mathcal{N}_\ell\exp\left(-\frac{ez_\ell}{kT}\Phi^0\right), \tag{26}$$

where $\mathcal{N}_\ell$ are the bulk-ionic concentrations. Thus, Coulomb's law leads to the so-called "Poisson-Boltzmann" equation

$$\nabla^2\Phi^0=-\sum_{\ell=1}^{L}\frac{ez_\ell\mathcal{N}_\ell}{\epsilon_0\kappa_f}\exp\left(-\frac{ez_\ell}{kT}\Phi^0\right). \tag{27}$$

The solution to this problem completely solves the static case.

In Appendix A, solutions to the Poisson-Boltzmann equation are considered. The potential near a plane wall has, approximately, an exponential distribution given by

$$\Phi^0=\zeta\exp(-\chi/d), \tag{28}$$

where χ is a local coordinate measuring distance normal to the wall surface, d is called the Debye length and is defined as

$$\frac{1}{d^2}=\sum_{\ell=1}^{L}\frac{(ez_\ell)^2\mathcal{N}_\ell}{\epsilon_0\kappa_f kT}, \tag{29}$$

and ζ is called the zeta potential and is the static electric potential at the shear plane (i.e., the surface S_w). Validity of the simple exponential distribution (the Debye approximation) and the relation between Q^0 and ζ are discussed in Appendix A. Here it is emphasized that the Debye length, which is a measure of the thickness of the diffuse double layer, is much smaller than any geometrical length associated with the porous material. For example, a univalent electrolyte at room temperature gives $d = 3 \times 10^{-10}/\sqrt{C}$ (m), where C is the bulk-electrolyte molarity. In practice, it is uncommon ever to work with electrolyte more dilute (in the pores) than 10^{-4} mol/liter which corresponds to $d \leq 3 \times 10^{-8}$ m. In sedimentary materials, typical sand-grain radii are on the order of 10^{-4} m, while clay particles have characteristic lengths of the order of 10^{-6} m. The point is that for porous media of interest, the double layer can be modeled as being planar relative to the grain surfaces. This "thin-double-layer" approximation will be made throughout the entire analysis.

The time-harmonic disturbances are governed by [from Eqs. (1)–(9) and (17)–(19)]

$$\nabla \cdot \mathbf{b}_s = 0, \tag{30}$$

$$\nabla \cdot \mathbf{d}_s = 0, \tag{31}$$

$$\nabla \times \mathbf{e}_s = i\omega \mathbf{b}_s, \tag{32}$$

$$\nabla \times \mathbf{h}_s = -i\omega \mathbf{d}_s, \tag{33}$$

and

$$\nabla \cdot \mathbf{b}_f = 0, \tag{34}$$

$$\nabla \cdot \mathbf{d}_f = \sum_{\ell=1}^{L} e z_\ell n_\ell, \tag{35}$$

$$\nabla \times \mathbf{e}_f = i\omega \mathbf{b}_f, \tag{36}$$

$$\nabla \times \mathbf{h}_f = -i\omega \mathbf{d}_f + \mathbf{j}_f, \tag{37}$$

where

$$\mathbf{j}_f = \sum_{\ell=1}^{L} e z_\ell \Big[-kTb_\ell \nabla n_\ell + e z_\ell b_\ell \left(N_\ell^0 \mathbf{e}_f + n_\ell \mathbf{E}_f^0 \right) + N_\ell^0 \dot{\mathbf{u}}_f(\omega) \Big]. \tag{38}$$

The notation $\dot{\mathbf{u}}_f(t) = \mathrm{Re}\{\dot{\mathbf{u}}_f(\omega) e^{-i\omega t}\}$ is being employed. Products of disturbances have been neglected in $\mathbf{j}_f$. The neglect of these terms linearizes the equations. The boundary conditions on S_w are

$$\mathbf{n} \cdot (\mathbf{b}_s - \mathbf{b}_f) = 0, \tag{39}$$

$$\mathbf{n} \cdot (\mathbf{d}_s - \mathbf{d}_f) = 0, \tag{40}$$

$$\mathbf{n} \times (\mathbf{e}_s - \mathbf{e}_f) = \mathbf{0}, \tag{41}$$

$$\mathbf{n} \times (\mathbf{h}_s - \mathbf{h}_f) = Q^0 \dot{\mathbf{u}}_s(\omega), \tag{42}$$

$$\mathbf{n} \cdot \mathbf{j}_f = 0. \tag{43}$$

B. Mechanical equations

The conservation of linear momentum governs the dynamics of both the fluid and solid phases and is expressed for time-harmonic disturbances as

$$-i\omega \rho_f \dot{\mathbf{u}}_f = \nabla \cdot \boldsymbol{\tau}_f + \sum_{\ell=1}^{L} e z_\ell \left(N_\ell^0 \mathbf{e}_f + n_\ell \mathbf{E}_f^0 \right), \tag{44}$$

$$-i\omega \rho_s \dot{\mathbf{u}}_s = \nabla \cdot \boldsymbol{\tau}_s. \tag{45}$$

The summation on the right-hand side of the fluid balance is the electrical body force acting on any excess charge (with products of disturbances again neglected). The Lorentz force $\mathbf{j}_f \times \mathbf{B}_f$ has been neglected in the fluid balance for the same reasons that the Lorentz electric field is negligible. The nonlinear convective accelerations $\dot{\mathbf{u}} \cdot \nabla \dot{\mathbf{u}}$ have also been ignored as justified by Pride, Gangi, and Morgan.[7] The fluid and solid stress tensors are given by

$$\boldsymbol{\tau}_f = K_f \nabla \cdot \mathbf{u}_f \mathbf{I} - i\omega\eta \left(\nabla \mathbf{u}_f + \nabla \mathbf{u}_f^{\mathrm{T}} - \frac{2}{3} \nabla \cdot \mathbf{u}_f \mathbf{I} \right), \tag{46}$$

$$\boldsymbol{\tau}_s = K_s \nabla \cdot \mathbf{u}_s \mathbf{I} + G \left(\nabla \mathbf{u}_s + \nabla \mathbf{u}_s^{\mathrm{T}} - \frac{2}{3} \nabla \cdot \mathbf{u}_s \mathbf{I} \right), \tag{47}$$

where $-i\omega \mathbf{u}(\omega) = \dot{\mathbf{u}}(\omega)$. Finally, the boundary conditions on S_w are

$$\mathbf{n} \cdot (\boldsymbol{\tau}_s - \boldsymbol{\tau}_f) = -Q^0 \mathbf{e}_s, \tag{48}$$

$$\mathbf{u}_s - \mathbf{u}_f = 0. \tag{49}$$

The right-hand side of Eq. (48) represents the electrical body force (per unit area) acting on the excess charge of the adsorbed layer.

III. AVERAGING THE GOVERNING EQUATIONS

The above microscopic (i.e., pore and grain scale) equations will now be volume averaged to obtain the macroscopic equations of interest. The averaging volume V_A is assumed to be larger than the grains but much smaller than the wavelengths of the applied disturbances. If the volume average for some microscopic field $\mathbf{a}_\xi$ associated with the ξth phase is defined as

$$\langle \mathbf{a}_\xi \rangle = \frac{1}{V_A} \int_{V_\xi} \mathbf{a}_\xi \, dV, \tag{50}$$

where V_ξ represents the volume of the ξth phase within V_A, then the following theorem due to Slattery[8] is easily established:[7]

$$\langle \nabla \mathbf{a}_\xi \rangle = \nabla \langle \mathbf{a}_\xi \rangle + \frac{1}{V_A} \int_{S_w} \mathbf{n}_\xi \mathbf{a}_\xi \, dS, \tag{51}$$

where $\mathbf{n}_\xi$ is the normal to S_w and is defined as

$$\mathbf{n}_f = \mathbf{n}, \tag{52}$$

$$\mathbf{n}_s = -\mathbf{n}, \tag{53}$$

with $\mathbf{n}$ directed from the fluid to the solid. When applying the averaging theorem to the porous material, it will be assumed that the fluid and solid phases each have homogeneous material properties throughout V_A. Furthermore, it is assumed that macroscopic-material properties such as porosity ϕ ($\equiv V_f/V_A$) vary slowly as V_A is moved over distances the size of V_A or less. Boundary conditions at singular jumps in the macroscopic-material properties are treated as part of another paper.[9]

It is convenient to define two other averages that are simply related to $\langle \mathbf{a}_\xi \rangle$,

$$\bar{\mathbf{a}}_\xi = \langle \mathbf{a}_\xi \rangle / \varphi_\xi, \tag{54}$$

$$\overline{\mathbf{A}} = \sum_\xi \langle \mathbf{a}_\xi \rangle = \sum_\xi \varphi_\xi \bar{\mathbf{a}}_\xi, \tag{55}$$

where φ_ξ is the volume fraction of the ξth phase,

$$\varphi_\xi = V_\xi / V_A; \tag{56}$$

i.e., $\varphi_f = \phi$ (porosity) and $\varphi_s = 1 - \phi$. $\bar{\mathbf{a}}_\xi$ may be called the "phase average" because it represents the average value within the ξth phase, while $\overline{\mathbf{A}}$ may be called the "total average" because it represents the average value of a given field type throughout all of V_A.

A. Averaging the electromagnetic equations

To start with, the static field $\mathbf{E}_f^0 = -\nabla \Phi^0$ is averaged to give

$$\langle \mathbf{E}_f^0 \rangle = -\nabla \langle \Phi^0 \rangle - \frac{1}{V_A} \int_{S_w} \mathbf{n} \Phi^0 \, dS. \tag{57}$$

Because $\Phi^0 (= \zeta)$ is assumed to be constant over S_w, the surface integral vanishes. Thus, if the material has uniform macroscopic properties so that $\langle \Phi^0 \rangle = \text{const}$, then $\langle \mathbf{E}_f^0 \rangle = 0$; i.e., there are no macroscopic static fields.

The equations governing the disturbances [Eqs. (30)–(38)] are now averaged in the following manner: (1) The volume average is applied; (2) Slattery's theorem is used; (3) the corresponding solid and fluid equations are added; (4) boundary conditions (39)–(43) are applied; (5) the relative fluid-solid flow vector $\mathbf{v}$ is introduced,

$$\mathbf{v} = \dot{\mathbf{u}}_f - \dot{\bar{\mathbf{u}}}_s, \tag{58}$$

where $\dot{\bar{\mathbf{u}}}_s$ is the phase-averaged velocity of the solid phase; and (6) the electroneutrality condition prior to disturbances is applied,

$$\sum_{\ell=1}^{L} e z_\ell \langle N_\ell^0 \rangle V_A + Q_s^0 S_w = 0. \tag{59}$$

Such a procedure directly results in the following macroscopic form of Maxwell's equations:

$$\nabla \cdot \overline{\mathbf{B}} = 0, \tag{60}$$

$$\nabla \cdot \overline{\mathbf{D}} = \phi \sum_{\ell=1}^{L} e z_\ell \bar{n}_\ell, \tag{61}$$

$$\nabla \times \overline{\mathbf{E}} = i\omega \overline{\mathbf{B}}, \tag{62}$$

$$\nabla \times \overline{\mathbf{H}} = -i\omega \overline{\mathbf{D}} + \overline{\mathbf{J}}, \tag{63}$$

where $\overline{\mathbf{B}}$, $\overline{\mathbf{D}}$, $\overline{\mathbf{E}}$, $\overline{\mathbf{H}}$, and $\overline{\mathbf{J}}$ are "total" averages [Eq. (55)] while $\bar{n}_\ell$ is a phase average in the fluid. The macroscopic-current density $\overline{\mathbf{J}}$ has four distinct contributions:

$$\overline{\mathbf{J}} = \phi (\mathbf{J}_d + \mathbf{J}_c + \mathbf{J}_s + \mathbf{J}_n). \tag{64}$$

$\mathbf{J}_d$ is part of the average "diffusion" current density in the fluid (the total diffusion current will have a contribution from $\mathbf{J}_n$ as well),

$$\mathbf{J}_d = -\sum_{\ell=1}^{L} e z_\ell b_\ell kT \nabla \bar{n}_\ell; \tag{65}$$

$\mathbf{J}_c$ is the average "conduction" current density,

$$\mathbf{J}_c = \frac{1}{V_f} \int_{V_f} \left(\sum_{\ell=1}^{L} (e z_\ell)^2 b_\ell N_\ell^0 \right) \mathbf{e}_f \, dV; \tag{66}$$

$\mathbf{J}_s$ is the average "streaming" current density,

$$\mathbf{J}_s = \frac{1}{V_f} \int_{V_f} \left(\sum_{\ell=1}^{L} e z_\ell N_\ell^0 \right) \mathbf{v} \, dV; \tag{67}$$

and $\mathbf{J}_n$ is the average current density due to locally induced diffusion currents normal to the pore walls,

$$\mathbf{J}_n = -\frac{1}{V_f} \sum_{\ell=1}^{L} e z_\ell b_\ell kT \left[\int_{S_w} \mathbf{n} n_\ell dS - \int_{V_f} \frac{\nabla N_\ell^0}{N_\ell^0} n_\ell \, dV \right]. \tag{68}$$

In this last expression, the equilibrium condition $\mathbf{E}_f^0 = (kT/e z_\ell) \nabla N_\ell^0 / N_\ell^0$ has been employed in the volume integral. In general, a complete description would retain all four of these contributions to the current density. In practice, it will be argued in Sec. IV that $\mathbf{J}_n$ is neglibile for the problem at hand of modeling acoustic-electromagnetic wave propagation in porous media. The electromagnetic description will be complete once these current densities have been expressed in terms of the macroscopic fields generating them.

It will now be argued that the macroscopic-diffusion current induced by wave fields, $\mathbf{J}_d$, is negligible in homogeneous-porous media. Taking the divergence of Ampère's law gives the macroscopic statement of charge conservation:

$$\sum_{\ell=1}^{L} e z_\ell \left[i\omega \bar{n}_\ell + b_\ell kT \nabla^2 \bar{n}_\ell \right] = \nabla \cdot (\mathbf{J}_c + \mathbf{J}_s + \mathbf{J}_n). \tag{69}$$

Comparing the first term on the left-hand side (the net rate of ion accumulation) to the second term (the diffusion flux) gives the dimensionless ratio

$$\frac{|b_\ell kT \nabla^2 \bar{n}_\ell|}{|i\omega \bar{n}_\ell|} \simeq \frac{16 b_\ell kT f}{2\pi c^2}, \tag{70}$$

where c is wave speed and f is frequency in hertz and where it has been assumed that $\bar{n}_\ell$ varies over distances of a quarter wavelength of the macroscopic field inducing $\bar{n}_\ell$ (either acoustic or electromagnetic). Using values of $T = 298$ K, $b_\ell = 3 \times 10^{11}$ N s/m (a typical inorganic ion such as sodium), and $c = 10^3$ m/s (acoustic waves) gives the condition that if frequencies are much less than 10^{14} Hz, macroscopic-diffusion currents can be neglected in homogeneous media. This condition will always be met.

Alternatively, if the porous material is assumed to possess macroscopic heterogeneities that vary (significantly) over distances h, then the above dimensionless ratio is

$$\frac{|b_\ell kT\nabla^2\bar{n}_\ell|}{|i\omega\bar{n}_\ell|} \simeq \frac{b_\ell kT}{2\pi f h^2}. \tag{71}$$

If $h = 1$ mm (perhaps the smallest macroscopic length that can be considered in a volume-averaged theory—this, of course, depends on the grain sizes), then diffusion will be negligible if frequencies are much greater than 10^{-3} Hz. This will almost always be the case as well.

It should be noted that the actual macroscopic diffusivity (obtained by allowing for $\mathbf{J}_n$ as well) is always less than $b_\ell kT$ so that the above conditions are overestimating the actual diffusion currents. Because we are only interested in macroscopic deviations $\bar{n}_\ell$ that are induced by wave fields (not those, for example, that are due to injected contaminants), it is safe to assume that diffusion currents associated with these deviations are negligible. This assumption will be made throughout what follows.

It is convenient to rewrite the current-density integrals under the assumption of a thin, uniform, double layer. With the definition of bulk-fluid conductivity,

$$\sigma_f = \sum_{\ell=1}^{L}(ez_\ell)^2 b_\ell \mathcal{N}_\ell, \tag{72}$$

the conduction-current density becomes

$$\mathbf{J}_c = \frac{\sigma_f}{V_f}\int_{V_f}\mathbf{e}_f\,dV + \frac{1}{V_f}\int_{S_w}dS\int_0^D\left(\sum_{\ell=1}^{L}(ez_\ell)^2 b_\ell(N_\ell^0-\mathcal{N}_\ell)\right)\mathbf{e}_f\,d\chi. \tag{73}$$

The coordinate χ represents distance measured normal from the wall surface S_w (into the fluid) and D represents the distance over which the charge excess $N_\ell^0 - \mathcal{N}_\ell$ associated with the diffuse double layer is significant (say, a few Debye lengths). In practice, it will be argued that $\mathbf{e}_f$ can be taken as constant across the double layer.

If Coulomb's law for the static field [Eq. (20)] is substituted into the streaming-current integral [Eq. (67)], then

$$\mathbf{J}_s = \frac{\epsilon_0\kappa_f}{V_f}\int_{V_f}(\nabla\cdot\mathbf{E}_f^0)\,\mathbf{v}\,dV \tag{74}$$

$$= \frac{\epsilon_0\kappa_f}{V_f}\int_{V_f}[\nabla\cdot(\mathbf{E}_f^0\mathbf{v}) - \mathbf{E}_f^0\cdot\nabla\mathbf{v}]\,dV \tag{75}$$

$$= \frac{\epsilon_0\kappa_f}{V_f}\left[\int_{S_e}\mathbf{n}_e\cdot\mathbf{E}_f^0\mathbf{v}\,dS + \int_{S_w}\mathbf{n}\cdot\mathbf{E}_f^0\mathbf{v}\,dS - \int_{S_w}dS\int_0^D\mathbf{E}_f^0\cdot\nabla\mathbf{v}\,d\chi\right]. \tag{76}$$

In the last equation, S_e is the surface of intersection between the fluid and the averaging-volume surface and $\mathbf{n}_e$ is the outward normal to S_e. We can expect that, on average, the weight $\mathbf{n}_e\cdot\mathbf{E}_f^0$ is as often positive as negative on S_e so that the integral over S_e vanishes (this integral will also vanish if there is no macroscopic variations in the material properties). The second integral also vanishes because $\mathbf{v} = 0$ on S_w. Thus, only the last term is retained:

$$\mathbf{J}_s = \frac{\epsilon_0\kappa_f}{V_f}\int_{S_w}dS\int_0^D\nabla\Phi^0\cdot\nabla\mathbf{v}\,d\chi. \tag{77}$$

Note that, in general, it should not be assumed that $\nabla\mathbf{v}$ has constant components across the thin double layer.

Finally, although $\mathbf{J}_n$ will be neglected later, it is consistent here to also rewrite it under the thin-double-layer assumption. The volume integral within $\mathbf{J}_n$ can be written as

$$\int_{V_f}\frac{\nabla N_\ell^0}{N_\ell^0}n_\ell\,dV = -\int_{S_w}\mathbf{n}\,dS\int_0^D\frac{n_\ell}{N_\ell^0}\frac{\partial N_\ell^0}{\partial\chi}\,d\chi \tag{78}$$

$$= -\int_{S_w}\mathbf{n}\,dS\int_0^D\left[\frac{\partial}{\partial\chi}\left(N_\ell^0\frac{n_\ell}{N_\ell^0}\right) - N_\ell^0\frac{\partial}{\partial\chi}\left(\frac{n_\ell}{N_\ell^0}\right)\right]d\chi \tag{79}$$

$$= \int_{S_w}\mathbf{n}n_\ell\,dS + \int_{S_w}\mathbf{n}\,dS\int_0^D N_\ell^0\frac{\partial}{\partial\chi}\left(\frac{n_\ell}{N_\ell^0}\right)d\chi, \tag{80}$$

so that the final expression for $\mathbf{J}_n$ is

$$\mathbf{J}_n = \frac{1}{V_f}\int_{S_w}\mathbf{n}\,dS\int_0^D\sum_{\ell=1}^{L}ez_\ell b_\ell kTN_\ell^0\frac{\partial}{\partial\chi}\left(\frac{n_\ell}{N_\ell^0}\right)d\chi. \tag{81}$$

Perhaps, now, $\mathbf{J}_n$ is more clearly seen to be the average value of the diffusion currents induced normal to the grain surfaces because of local deviations n_ℓ.

In Sec. IV, the actual induced fields $\mathbf{e}_f$ and $\mathbf{v}$ will be expressed in terms of the macroscopic forces generating them (namely, the macroscopic-electric field and pressure gradient). Then, in Sec. V, the above integrals will be carried out and the final macroscopic ion-flux-force law will be obtained for $\overline{\mathbf{J}}$.

It remains, here, to average the electromagnetic constitutive laws. Averaging $\mathbf{d}_\xi = \epsilon_0 \kappa_\xi \mathbf{e}_\xi$ gives

$$\overline{\mathbf{D}} = \epsilon_0 \left[\phi \kappa_f \overline{\mathbf{e}}_f + (1-\phi)\kappa_s \overline{\mathbf{e}}_s\right]. \tag{82}$$

From the definition $\overline{\mathbf{E}} = \phi \overline{\mathbf{e}}_f + (1-\phi)\overline{\mathbf{e}}_s$, we then have

$$\overline{\mathbf{D}} = \epsilon_0 \left[\phi(\kappa_f - \kappa_s)\overline{\mathbf{e}}_f + \kappa_s \overline{\mathbf{E}}\right]. \tag{83}$$

Once $\overline{\mathbf{e}}_f$ has been expressed in terms $\overline{\mathbf{E}}$, this law will be complete.

Because the magnetic susceptibilities are assumed negligible in both the fluid and solid phases (iron, nickle, and cobalt are not assumed to be major constituents), we simply have

$$\overline{\mathbf{B}} = \mu_0 \overline{\mathbf{H}}. \tag{84}$$

B. Averaging the mechanical equations

The force balances on the fluid [Eq. (44)] and the solid [Eq. (45)] are averaged and then added to give a macroscopic-force balance on the bulk material (i.e., fluid and solid taken together),

$$-i\omega\left(\rho_B \dot{\overline{\mathbf{u}}}_s + \rho_f \dot{\overline{\mathbf{w}}}\right) = \nabla \cdot \boldsymbol{\tau}_B + \phi(\mathbf{f}_a + \mathbf{f}_d + \mathbf{f}_n), \tag{85}$$

where the three electrical body forces are defined as

$$\mathbf{f}_a = \frac{Q^0}{V_f}\int_{S_w} \mathbf{e}_s \, dS, \tag{86}$$

$$\mathbf{f}_d = \frac{1}{V_f}\int_{V_f} \left(\sum_{\ell=1}^{L} e z_\ell N_\ell^0\right) \mathbf{e}_f \, dV, \tag{87}$$

$$\mathbf{f}_n = \frac{1}{V_f}\int_{V_f} \left(\sum_{\ell=1}^{L} e z_\ell n_\ell\right) \mathbf{E}_f^0 \, dV. \tag{88}$$

Here, $\mathbf{f}_a$ comes from the boundary conditions and represents the average force acting on the excess charge of the adsorbed layer, $\mathbf{f}_d$ represents the average force acting on the diffuse layer, while $\mathbf{f}_n$ is the average force acting normal to S_w due to any induced-charge excesses in the double layer. In the above force balance, we have introduced the definitons

$$\dot{\overline{\mathbf{w}}} = \phi \overline{\mathbf{v}} = \phi(\dot{\overline{\mathbf{u}}}_f - \dot{\overline{\mathbf{u}}}_s), \tag{89}$$

$$\boldsymbol{\tau}_B = \phi \overline{\boldsymbol{\tau}}_f + (1-\phi)\overline{\boldsymbol{\tau}}_s, \tag{90}$$

$$\rho_B = \phi\rho_f + (1-\phi)\rho_s, \tag{91}$$

where $\dot{\overline{\mathbf{w}}}$ is called the "filtration velocity" (volume flux of fluid per unit time and per unit area of porous material) and where a subscript B stands for "bulk."

In this work, $\mathbf{f}_n$ will be assumed negligible. The conditions of validity for this assumption are essentially the same as ignoring the $\mathbf{J}_n$ contribution to the current density and will be discussed in the next section. Using the charge-balance condition

$$Q^0 = -\int_0^D \sum_{\ell=1}^{L} e z_\ell N_\ell^0(\chi)\, d\chi, \tag{92}$$

where χ is the same coordinate used previously to measure distance normal to S_w and where D is several Debye lengths, the body forces $\mathbf{f}_a + \mathbf{f}_d$ within the thin uniform double-layer approximation become

$$\mathbf{f}_a + \mathbf{f}_d = \frac{1}{V_f}\int_{S_w} dS \int_0^D \sum_{\ell=1}^{L} e z_\ell N_\ell^0 \left[\mathbf{e}_f - \mathbf{e}_s(0)\right] d\chi. \tag{93}$$

It will be seen that for thin double layers and when $\kappa_s \ll \kappa_f$ (e.g., quartz and water), $\mathbf{e}_f(\chi) \simeq \mathbf{e}_s(0)$ throughout the double layer so that

$$\mathbf{f}_a + \mathbf{f}_d = 0. \tag{94}$$

This states that the force acting on the adsorbed-layer charge is balanced by that acting on the diffuse-layer counter charge.

Next, the average-force balance on the fluid in relative motion is obtained. The relative-flow velocity $\mathbf{v} = \dot{\mathbf{u}}_f - \dot{\mathbf{u}}_s$ is substituted into the fluid-force balance [Eq. (44)] along with the fluid-stress tensor and the assumption that the local relative flow is incompressible ($\nabla \cdot \mathbf{v} = 0$) with the result

$$\begin{aligned} -i\omega\rho_f \mathbf{v} = {} & -\nabla p + i\omega\rho_f \dot{\mathbf{u}}_s - \eta \nabla \times \nabla \times \mathbf{v} \\ & + \sum_{\ell=1}^{L} e z_\ell \left(N_\ell^0 \mathbf{e}_f + n_\ell \mathbf{E}_f^0\right). \end{aligned} \tag{95}$$

The incompressibility assumption for oscillatory flow is justified as long as $f^2 r^2 / c_f^2 \ll 1$ where f is frequency in hertz, r is a characteristic grain size, and c_f is the speed of sound in the fluid. This condition is roughly equivalent to the no-grain-scattering condition underlying the entire analysis. Upon averaging over the fluid, we have

$$-i\omega\rho_f \overline{\mathbf{v}} = -\nabla \overline{p} + i\omega\rho_f \dot{\overline{\mathbf{u}}}_s + \mathbf{f}_d + \mathbf{d} - \eta \nabla \times \overline{\nabla \times \mathbf{v}}, \tag{96}$$

where $\mathbf{d}$, the drag force, is defined as

$$\mathbf{d} = \mathbf{d}^{\text{form}} + \mathbf{d}^{\text{fric}}, \tag{97}$$

where

$$\mathbf{d}^{\text{form}} = \frac{1}{V_f}\int_{S_w} -\mathbf{n} p \, dS, \tag{98}$$

$$\mathbf{d}^{\text{fric}} = \frac{\eta}{V_f}\int_{S_w} -\mathbf{n} \times \nabla \times \mathbf{v} \, dS. \tag{99}$$

Another application of the averaging theorem gives

$$\overline{\nabla \times \mathbf{v}} = \nabla \times \overline{\mathbf{v}} + \frac{1}{V_f} \int_{S_w} \mathbf{n} \times \mathbf{v}\, dS. \tag{100}$$

Since $\mathbf{v} = 0$ on S_w, we have that

$$\eta \nabla \times \overline{\nabla \times \mathbf{v}} = \eta \nabla \times \nabla \times \overline{\mathbf{v}}. \tag{101}$$

The importance of this macroscopic-shear term is determined by comparing it to the inertial term

$$\frac{|\eta \nabla \times \nabla \times \overline{\mathbf{v}}|}{|i\omega \rho_f \overline{\mathbf{v}}|} \simeq \frac{\eta}{\rho_f c^2} f, \tag{102}$$

where c is the speed of the mechanical wave producing the shear disturbance. For water and, say, $c = 10^3$ m/s, we have that as long as frequencies are much less than 10^{12} Hz, the macroscopic shearing in the fluid is negligible.

In the next section, expressions will be obtained that linearly relate the local-fluid velocity $\mathbf{v}$ and fluid pressue p to the macroscopic forces that are generating them ($-\nabla \overline{p} + i\omega\rho_f \dot{\overline{\mathbf{u}}}_s$ and $\overline{\mathbf{E}}$). It will be seen that it is more direct to simply volume average the expression for $\mathbf{v}$ to obtain the macroscopic flux-force law than to carryout the integrals contained within $\mathbf{f}_d$ and $\mathbf{d}$ of the above averaged-force balance; however, the two approaches are equivalent.

It remains to average the stress-strain relations so that $\boldsymbol{\tau}_B$ and $\overline{p}$ are linearly related to the induced deformation. Because the stress-strain relations utilized here are independent of any explicit electromagnetic coupling (e.g., no piezoelectric deformation is allowed for), the volume-averaged results of Pride, Gangi, and Morgan[7] are directly applicable. Their results are identical to those of Biot and Willis[10] (who, however, did not employ volume averaging) and are

$$\boldsymbol{\tau}_B = (K_G \nabla \cdot \overline{\mathbf{u}}_s + C \nabla \cdot \overline{\mathbf{w}})\mathbf{I} + G_{\text{fr}} \left(\nabla \overline{\mathbf{u}}_s + \nabla \overline{\mathbf{u}}_s^T - \frac{2}{3} \nabla \cdot \overline{\mathbf{u}}_s \mathbf{I} \right), \tag{103}$$

$$-\overline{p} = C \nabla \cdot \overline{\mathbf{u}}_s + M \nabla \cdot \overline{\mathbf{w}}, \tag{104}$$

where

$$K_G = \frac{K_{\text{fr}} + \phi K_f + (1+\phi) K_s \Delta}{1+\Delta}, \tag{105}$$

$$C = \frac{K_f + K_s \Delta}{1+\Delta}, \tag{106}$$

$$M = \frac{1}{\phi} \frac{K_f}{1+\Delta}, \tag{107}$$

and the parameter Δ is

$$\Delta = \frac{K_f}{\phi K_s^2} \left[(1-\phi) K_s - K_{\text{fr}} \right]. \tag{108}$$

The moduli K_{fr} and G_{fr} are the bulk and shear moduli of the "framework of grains" when the fluid is absent—in practice, K_{fr} and G_{fr} can be defined when the saturating fluid is a gas (e.g., air). The boundary-value problem that defines K_{fr} and G_{fr} will not be discussed in this paper because it is not clearly related to the boundary-value problems for $\mathbf{e}_f$, $\mathbf{v}$, and p. The frame moduli may either be considered experimentally determined (just like K_f, K_s, and G) or may be obtained from one of the many approximate theoretical models available for specific (and very simple) pore-grain geometries (see Refs. 11 and 12 for a review). In conclusion, although the electromagnetic fields do not directly appear in the above stress-strain relations, their influence is present if they induce relative fluid-solid motion $\overline{\mathbf{w}}$.

IV. BOUNDARY-VALUE PROBLEMS

A. Averaging disk

To complete the averaging procedure, the local fields $\mathbf{e}_f$, $\mathbf{v}$, and p involved in the various integrals above must be related to the macroscopic fields. In order to accomplish this, the idea of an averaging disk is introduced. Consider an imaginary volume within the porous material defined by two large plane-parallel faces of area A separated by a distance H. One might imagine a circular disk with radius much greater than thickness. The volume of this disk is AH. We imagine that a macroscopic-potential difference exists between the two flat faces. The potential difference may be one of fluid pressure and/or electric potential. This potential difference is defined so that when it is divided by H, one obtains the appropriate macroscopic field (pressure gradient or electric field) in the direction normal to the disk face. The normal to the disk face will be defined as the z direction in what follows. These potential differences represent the boundary values for the local fields in the pores and grains.

The macroscopic-electromagnetic disturbances have wavelengths dramatically larger than H (which may be as small as 10^{-3} m depending on the grain sizes). Thus, it can be assumed that for the purpose of determining transport in the averaging disk, $\nabla \times \mathbf{e}_f = \nabla \times \mathbf{e}_s = 0$ at the pore and grain scale, or, $\mathbf{e}_f = -\nabla \varphi_f$ and $\mathbf{e}_s = -\nabla \varphi_s$. Thus, on the averaging disk, we have that

$$\hat{\mathbf{z}} \cdot \overline{\mathbf{E}} = -\frac{\Delta \phi}{H}, \tag{109}$$

where

$$\Delta \phi = \varphi_f(H) - \varphi_f(0) = \varphi_s(H) - \varphi_s(0) \tag{110}$$

is the potential difference between the two flat faces.

B. Pore-scale electric fields and ion-number-density deviations

In this subsection, the boundary-value problems controlling the electric potentials and deviations n_ℓ will be considered. The conditions required for the neglect of the n_ℓ (at the pore scale) will be defined.

Let us begin by rewriting the current density in the fluid [Eq. (38)] using the static-equilibrium condition $e z_\ell N_\ell^0 \mathbf{E}_f^0 = kT \nabla N_\ell^0$. The result is

$$\mathbf{j}_f = \sum_{\ell}^{L} e z_\ell N_\ell^0 \left[\mathbf{v} - b_\ell kT \nabla \left(\frac{n_\ell}{N_\ell^0} + \frac{e z_\ell}{kT} \varphi_f \right) \right] \tag{111}$$

and will be used in the conservation of charge,

$$\nabla \cdot \mathbf{j}_f = i\omega \sum_{\ell}^{L} e z_\ell n_\ell . \tag{112}$$

Because this conservation law must hold for an electrolyte of arbitrary specifications, we then have

$$\nabla \cdot \left\{ N_\ell^0 \left[\mathbf{v} - b_\ell kT \nabla \left(\frac{n_\ell}{N_\ell^0} + \frac{e z_\ell}{kT} \varphi_f \right) \right] \right\} = i\omega n_\ell \tag{113}$$

for each of the L ionic species. Upon distributing the divergence and noting that $\nabla \cdot \mathbf{v} = 0$, a general statement of ion conservation is obtained (the ion balance):

$$\nabla^2 \left(\frac{n_\ell}{N_\ell^0} + \frac{e z_\ell}{kT} \varphi_f \right) + \frac{i\omega}{b_\ell kT} \frac{n_\ell}{N_\ell^0} = \frac{\nabla N_\ell^0}{N_\ell^0} \cdot \left[\frac{\mathbf{v}}{b_\ell kT} - \nabla \left(\frac{n_\ell}{N_\ell^0} + \frac{e z_\ell}{kT} \varphi_f \right) \right] . \tag{114}$$

The boundary condition of no ion accumulation on S_w ($\mathbf{n} \cdot \mathbf{j}_f = 0$ on S_w) is equivalent to the conditions

$$\mathbf{n} \cdot \nabla \left(\frac{n_\ell}{N_\ell^0} + \frac{e z_\ell}{kT} \varphi_f \right) = 0, \tag{115}$$

$$\mathbf{n} \cdot \mathbf{v} = 0, \tag{116}$$

on S_w.

The right-hand side of the ion balance can be understood as a source term for ion accumulation. The gradient ∇N_ℓ^0 is everywhere normal to the grain surfaces and is nonzero only in the double layer. There can only be such a source term if either the flow field $\mathbf{v}$ or the force $\mathbf{f}_\ell = -\nabla(n_\ell/N_\ell^0 + e z_\ell \varphi_f/kT)$ driving the ion flux has a component normal to the grain surface within the double layer. From the boundary conditions just given, we expect that when the thickness of the double layer d is much smaller than the radii of curvature r of the grain surfaces (which are responsible for the spatial deviations in $\mathbf{v}$ and $\mathbf{f}_\ell$), there effectively will be no normal component to either $\mathbf{v}$ or $\mathbf{f}_\ell$ within the double layer. It has previously been discussed that the condition $d \ll r$ is well satisfied for sedimentary media.

Under such thin-double-layer conditions and in the low-frequency limit where $\omega \ll b_\ell kT/r^2$ [using values of $b_\ell = 3 \times 10^{11}$ N s/m (typical inorganic ion), $T = 298$ K, and $r = 10^{-4}$ m (e.g., sand grains) gives $f \ll 2 \times 10^{-2}$ Hz; using $r = 10^{-6}$ m (e.g., clay particles) gives $f \ll 200$ Hz], we have the boundary-value problem on the averaging disk,

$$\psi_\ell = \frac{n_\ell}{N_\ell^0} + \frac{e z_\ell}{kT} \varphi_f , \tag{117}$$

$$\nabla^2 \psi_\ell = 0, \tag{118}$$

$$\mathbf{n} \cdot \nabla \psi_\ell = 0 \quad \text{on } S_w , \tag{119}$$

and

$$\psi_\ell = \begin{cases} \frac{e z_\ell}{kT} \Delta\phi & \text{on } z = H, \\ 0 & \text{on } z = 0. \end{cases} \tag{120}$$

This last condition is a statement that there exists a macroscopic-electric-potential difference of $\Delta\phi$ between the two flat faces of the averaging disk but that no macroscopic gradients in n_ℓ exist. A solution for ψ_ℓ may be expressed in terms of a related, purely geometric, field Γ possessing units of length and defined to satisfy

$$\nabla^2 \Gamma = 0, \tag{121}$$

$$\mathbf{n} \cdot \nabla \Gamma = 0 \quad \text{on } S_w , \tag{122}$$

$$\Gamma = \begin{cases} H & \text{on } z = H, \\ 0 & \text{on } z = 0. \end{cases} \tag{123}$$

Thus, for thin double layers, we have

$$\frac{n_\ell(\mathbf{r})}{N_\ell^0} = \frac{e z_\ell}{kT} \left[\Gamma(\mathbf{r}) \frac{\Delta\phi}{H} - \varphi_f(\mathbf{r}) \right] . \tag{124}$$

The field $\Gamma(\mathbf{r})$ will be important in all that follows.

We next consider the boundary-value problem for φ_f defined by Coulomb's law

$$\nabla^2 \varphi_f = - \sum_{\ell=1}^{L} \frac{e z_\ell}{\epsilon_0 \kappa_f} n_\ell \tag{125}$$

$$= - \sum_{\ell=1}^{L} \frac{(e z_\ell)^2}{\epsilon_0 \kappa_f kT} N_\ell^0 \left(\Gamma \frac{\Delta\phi}{H} - \varphi_f \right) , \tag{126}$$

where on S_w

$$\mathbf{n} \cdot \nabla \varphi_f = \frac{\kappa_s}{\kappa_f} \mathbf{n} \cdot \nabla \varphi_s \tag{127}$$

and on the flat faces

$$\varphi_f = \begin{cases} \Delta\phi & z = H, \\ 0 & z = 0. \end{cases} \tag{128}$$

The presence of φ_s in the boundary condition requires specification of the boundary-value problem for φ_s,

$$\nabla^2 \varphi_s = 0, \tag{129}$$

$$\varphi_s = \varphi_f \quad \text{on } S_w , \tag{130}$$

$$\varphi_s = \begin{cases} \Delta\phi, & z = H, \\ 0, & z = 0. \end{cases} \tag{131}$$

A particular solution for φ_f (i.e., satisfying the differential equation but not, necessarily, the boundary conditions) is

$$\varphi_f^p = \Gamma \frac{\Delta\phi}{H}. \tag{132}$$

To the extent that $\kappa_s/\kappa_f \ll 1$, so that $\mathbf{n} \cdot \nabla\varphi_f \simeq 0$ on S_w, this particular solution will, in fact, be the actual solution. In this case, we then have $n_\ell \simeq 0$ and the integrals $\mathbf{J}_n$ and $\mathbf{f}_n$ from the volume averaging vanish. For the quartz-electrolyte interface, the contrast is $\kappa_s/\kappa_f \simeq 1/20$, and this approximation is appropriate.

In physical terms, if the dielectric contrast is large, then large polarization-charge densities are induced on those portions of S_w that have $\mathbf{n}\cdot\hat{\mathbf{z}} \neq 0$. These polarization charges produce local fields that keep $\mathbf{n} \cdot \nabla\varphi_s \simeq 0$ everywhere along S_w and, thus, $n_\ell \simeq 0$ throughout the fluid. If the dielectric contrast is small, then electric-field lines can pass through S_w, thus producing an electric field in the fluid that has components normal to S_w near S_w. These normal components will drive an electromigration that must be balanced by an equal and opposite diffusion flux so that ions do not accumulate on S_w [Eq. (115)]; i.e., deviations n_ℓ are necessarily induced near S_w when the dielectric contrast is small.

For the case of a small dielectric contrast, we can express the actual thin-double-layer electric potential as

$$\varphi_f = \Gamma\frac{\Delta\phi}{H} + \delta\varphi, \tag{133}$$

where the field $\delta\varphi$ is defined by the problem

$$\nabla^2\delta\varphi = 0, \tag{134}$$

$$\mathbf{n}\cdot\nabla\delta\varphi = \frac{\kappa_s}{\kappa_f}\mathbf{n}\cdot\nabla\varphi_s \quad \text{on } S_w, \tag{135}$$

$$\delta\varphi = \begin{cases} 0 & z = H, \\ 0 & z = 0; \end{cases} \tag{136}$$

i.e., the source for the $\delta\varphi$ field is the electric field passing normal through S_w. Finally, the ion-number deviations are related to $\delta\varphi$ as

$$\frac{n_\ell}{N_\ell^0} = -\frac{ez_\ell}{kT}\delta\varphi. \tag{137}$$

As frequencies increase, there is progressively less time available for these ion-number deviations to take place and we expect that n_ℓ will decrease. Indeed, when $\omega \gg b_\ell kT/r^2$ we must have $n_\ell \to 0$ from the ion balance [Eq. (114)].

In order to neglect n_ℓ in our modeling of the fields in the pore space, we therefore must satisfy two conditions: (1) The electric-double layer must be much thinner than the effective grain sizes so that the right-hand side of the ion balance [Eq. (114)] is negligible, and (2) there must be a large contrast in the dielectric constant between the grains and the electrolyte so that $\delta\varphi$ as defined by Eqs. (134)–(136) is negligible. Both of these conditions are assumed to be met by the materials being considered.

By neglecting n_ℓ, we will be ignoring all grain-scale diffusion currents. Experimentally, it is found that at low frequencies (as defined above) in sedimentary materials containing significant quantities of clay, the electric current has a small phase shift relative to the applied electric field.[13,14] This phase shift is on the order of a few milliradian. The details of how these small phase shifts arise remains unknown in sedimentary materials; however, the effect is almost certainly due to accumulations n_ℓ induced by the electric field. It can safely be assumed that ignoring this milliradian-phase-shift effect (also sometimes called the "low-frequency dielectric enhancement") will not produce significant error in the coupled electromagnetic-acoustic wave-propagation problem of interest in this work.

In conclusion, if the n_ℓ are ignored, then we have that for all frequencies the electric-field in the fluid is given by

$$\mathbf{e}_f(\mathbf{r}) = -\nabla\varphi_f(\mathbf{r}) = -\nabla\Gamma(\mathbf{r})\,\frac{\Delta\phi}{H}. \tag{138}$$

This field can be assumed to be both constant and tangential to S_w throughout the thin double layer.

C. Pore-scale flow fields

The fluid-flow boundary-value problem is expressed on the averaging disk as [cf. Eq. (95) and note that $\nabla\times\nabla\times\mathbf{v} = -\nabla^2\mathbf{v}$]

$$\eta\nabla^2\mathbf{v} + i\omega\rho_f\mathbf{v} = \nabla p + \epsilon_0\kappa_f(\nabla\cdot\mathbf{E}_f^0)\nabla\Gamma\,\frac{\Delta\phi}{H}, \tag{139}$$

$$\nabla\cdot\mathbf{v} = 0, \tag{140}$$

$$\mathbf{v} = 0 \qquad \text{on } S_w, \tag{141}$$

$$p = \begin{cases} \Delta P \equiv \hat{\mathbf{z}}\cdot(\nabla\bar{p}_f - i\omega\rho_f\dot{\bar{\mathbf{u}}}_s)H, & z = H, \\ 0, \quad z = 0. \end{cases} \tag{142}$$

The deviations n_ℓ have been neglected.

The solution for $\mathbf{v}$ and p can be separated into mechanically and electrically induced portions

$$\mathbf{v} = \mathbf{v}_m + \mathbf{v}_e, \tag{143}$$

$$p = p_m + p_e; \tag{144}$$

i.e., the m stands for fields induced by $\Delta P/H$, while the e stands for fields induced by $\Delta\phi/H$. Introducing the viscous skin depth (units of length)

$$\delta = \sqrt{\frac{\eta}{\omega\rho_f}}, \tag{145}$$

the boundary-value problem is then separated as

$$\nabla^2\mathbf{v}_m + \frac{i}{\delta^2}\mathbf{v}_m = \frac{\nabla p_m}{\eta}, \tag{146}$$

$$p_m = \begin{cases} \Delta P, & z = H, \\ 0, & z = 0, \end{cases} \tag{147}$$

and

$$\nabla^2 \mathbf{v}_e + \frac{i}{\delta^2}\mathbf{v}_e = \frac{\nabla p_e}{\eta} - \frac{\epsilon_0 \kappa_f}{\eta}(\nabla^2 \Phi^0)\nabla\Gamma\,\frac{\Delta\phi}{H}, \tag{148}$$

$$p_e = \begin{cases} 0, & z = H, \\ 0, & z = 0. \end{cases} \tag{149}$$

We also have that $\mathbf{v}_m = \mathbf{v}_e = 0$ on S_w and $\nabla \cdot \mathbf{v}_m = \nabla \cdot \mathbf{v}_e = 0$ everywhere.

The electrically induced flow problem is treated first. Because the electrical body force inducing flow only acts in the thin double layer and is purely tangential to S_w, we have that $\mathbf{n} \cdot \nabla p_e = 0$ on S_w so that

$$p_e = 0 \tag{150}$$

everywhere and for all frequencies. In the limit of very low frequencies ($\delta \to \infty$), the flow velocity $\mathbf{v}_{e0}$ is

$$\mathbf{v}_{e0} = -\frac{\epsilon_0 \kappa_f}{\eta}(\Phi^0 - \zeta)\nabla\Gamma\,\frac{\Delta\phi}{H}. \tag{151}$$

The only vorticity in this flow field is present in the thin double layer. Thus, for general frequency dependence, the flow is governed by the boundary-layer-type equation

$$\frac{\partial^2 \mathbf{v}_e}{\partial \chi^2} + \frac{i}{\delta^2}\mathbf{v}_e = -\frac{\epsilon_0 \kappa_f}{\eta}\frac{\partial^2 \Phi^0}{\partial \chi^2}\nabla\Gamma\,\frac{\Delta\phi}{H}, \tag{152}$$

where χ is the local coordinate measuring distance normal from the grain surfaces (into the fluid). For water-based electrolytes at room temperature, the Debye length in meters goes as $d = 3 \times 10^{-10}/\sqrt{C}$ where C is salt concentration in moles per liter, while the viscous skin depth goes as $\delta = 4 \times 10^{-4}/\sqrt{f}$ where f is frequency in hertz. Thus, these lengths are related as

$$\frac{d}{\delta} = 10^{-6}\sqrt{\frac{f}{C}}. \tag{153}$$

Taking $f = 10^6$ Hz (the largest possible frequency) it is seen that as long as

$$C \gg 10^{-6} \ \text{mol/liter}, \tag{154}$$

we will always be in the regime where

$$\frac{d}{\delta} \ll 1. \tag{155}$$

This condition on concentration will always be met in rocks. Even if a sample is saturated with distilled water, after the water has come to equilibrium with the grains, the condition should again be fulfilled. Thus, the particular solution

$$\mathbf{v}_e^p = -\frac{\epsilon_0 \kappa_f}{\eta}\Phi^0 \nabla\Gamma\,\frac{\Delta\phi}{H} \tag{156}$$

will hold regardless of frequency; i.e., $|\partial^2 \mathbf{v}_e^p/\partial\chi^2| \gg |i\mathbf{v}_e^p/\delta^2|$ throughout the double layer. To this must be added the homogeneous solution $A\exp(i^{3/2}\chi/\delta)$, which then gives the general frequency-dependent field

$$\mathbf{v}_e = -\frac{\epsilon_0 \kappa_f}{\eta}\left(\Phi^0 - \zeta e^{i^{3/2}\chi/\delta}\right)\nabla\Gamma\,\frac{\Delta\phi}{H}. \tag{157}$$

Note that if the Debye approximation $\Phi^0 \simeq \zeta\exp(-\chi/d)$ is used in Eq. (152), the solution, regardless of the value of d/δ, is

$$\mathbf{v}_e^{\text{Debye}} = -\frac{\epsilon_0 \kappa_f}{\eta}\frac{\left(\Phi^0 - \zeta e^{i^{3/2}\chi/\delta}\right)}{1 + id^2/\delta^2}\nabla\Gamma\,\frac{\Delta\phi}{H}. \tag{158}$$

The two results are consistent to order d/δ. Because of Eq. (155), we only bother to retain terms to order d/δ throughout what follows.

The mechanically induced flow problem is less tractable because the vorticity is not always confined to a thin boundary layer near S_w. As is explained at the start of the next section, we only have need of the low-frequency and high-frequency solutions defined by whether the inertial term is significant or not. The transition frequency f_t (in hertz) is estimated as

$$f_t = \frac{\eta}{2\pi\rho_f}\frac{|\nabla^2 \mathbf{v}_m|}{|\mathbf{v}_m|} \simeq \frac{\eta}{2\pi\rho_f r^2}, \tag{159}$$

where r can be taken as a typical pore radius. For water and $r = 10^{-5}$ m, this gives $f_t \sim 2000$ Hz.

When $f \ll f_t$ (low frequencies), the vorticity extends throughout the fluid and the inertial term is everywhere negligible. The fluid flow and pressure fields can be represented as

$$\mathbf{v}_{m0}(\mathbf{r}) = \frac{\mathbf{g}(\mathbf{r})}{\eta}\,\frac{\Delta P}{H} \tag{160}$$

and

$$p_{m0}(\mathbf{r}) = h(\mathbf{r})\,\frac{\Delta P}{H}, \tag{161}$$

where $\mathbf{g}(\mathbf{r})$ has the units of length squared and $h(\mathbf{r})$ has the units of length and both are independent of fluid properties. These pore-geometery functions are solutions to the fundamental Stokes problem [obtained from Eqs. (146) and (147) and $\nabla \cdot \mathbf{v}_m = 0$]

$$\nabla^2 \mathbf{g} = \nabla h, \tag{162}$$

$$\nabla^2 h = 0, \tag{163}$$

$$\mathbf{g} = 0 \quad \text{on } S_w, \tag{164}$$

$$h = \begin{cases} H, & z = H, \\ 0, & z = 0. \end{cases} \tag{165}$$

In general, $\mathbf{n}\cdot\nabla h \; (= \mathbf{n}\cdot\nabla^2 \mathbf{g} = -\mathbf{n}\cdot\nabla\times\nabla\times\mathbf{g}) \neq 0$ on S_w, so that $h \neq \Gamma$. The only way for $\mathbf{n} \cdot \nabla h$ to be everywhere zero on S_w is if all the pores are constant-width channels, e.g., $h = z$. Nonetheless, it proves convenient to express the h function as

$$h = \Gamma + \delta h, \tag{166}$$

where δh therefore satisfies

$$\nabla^2 \delta h = 0, \tag{167}$$

$$\mathbf{n} \cdot \nabla \delta h = -\mathbf{n} \cdot \nabla \times \nabla \times \mathbf{g} \quad \text{on } S_w, \tag{168}$$

$$\delta h = \begin{cases} 0, & z = H, \\ 0, & z = 0. \end{cases} \tag{169}$$

The source for the δh field is the rotation of vorticity on the pore walls. As will be seen, the existence of the Stokes-flow geometery field $\mathbf{g}$ is all that is needed to establish relations between the various macroscopic-transport coefficients. Explicit expressions for $\mathbf{g}$ (or h) will not be required.

Continuing now to the case $f \gg f_t$ (high frequencies), the vorticity is confined to a thin boundary layer of thickness δ. The flow in this boundary layer is like flow past a planar wall and, accordingly, has the property that $\mathbf{n} \cdot \nabla p_{m\infty} = 0$ on S_w. Thus, the high-frequency pressure field $p_{m\infty}$ is simply

$$p_{m\infty}(\mathbf{r}) = \Gamma(\mathbf{r}) \frac{\Delta P}{H}. \tag{170}$$

This leads to the boundary-layer equation

$$\frac{\partial^2 \mathbf{v}_{m\infty}}{\partial \chi^2} + \frac{i}{\delta^2} \mathbf{v}_{m\infty} = \frac{\nabla \Gamma}{\eta} \frac{\Delta P}{H}, \tag{171}$$

which has the solution

$$\mathbf{v}_{m\infty} = -\frac{i\delta^2}{\eta} \left(1 - e^{i^{3/2}\chi/\delta}\right) \nabla \Gamma \frac{\Delta P}{H}. \tag{172}$$

All the pore-scale fields required to obtain the macroscopic-transport coefficients have now been defined.

V. TRANSPORT COEFFICIENTS

Using the pore-scale fields just developed on the averaging disk, we must next evaluate the integrals defined by $\mathbf{J}_c$ (conduction current), $\mathbf{J}_s$ (streaming current), and $\overline{\mathbf{v}}$ (relative fluid flow) in order to obtain the macroscopic-transport coefficients. We will obtain flux-force relations in the form

$$\overline{\mathbf{J}} \equiv \phi\,(\mathbf{J}_c + \mathbf{J}_s) \tag{173}$$

$$= \sigma(\omega)\overline{\mathbf{E}} + L_m(\omega)\left(-\nabla \overline{p} + i\omega\rho_f \dot{\overline{\mathbf{u}}}_s\right) \tag{174}$$

and

$$\dot{\overline{\mathbf{w}}} \equiv \phi \overline{\mathbf{v}} \tag{175}$$

$$= \frac{k(\omega)}{\eta}\left(-\nabla \overline{p} + i\omega\rho_f \dot{\overline{\mathbf{u}}}_s\right) + L_e(\omega)\overline{\mathbf{E}}. \tag{176}$$

It is demonstrated in Appendix B that

$$L_m(\omega) = L_e(\omega) \tag{177}$$

for all frequencies. The only requirement used to arrive at this statement of Onsager reciprocity is that double layers are thin relative to grain sizes.

The frequency dependence in the coefficients is obtained following the general procedure outlined by Johnson, Koplik, and Dashen[15] as is now described. We have obtained the pore-scale fields in the limits of high and low frequencies. These fields will first be integrated to give the high- and low-frequency definition of the transport coefficients. The two limits are then connected by a simple postulated function. Although there is nonuniqueness in defining such a frequency function, it nonetheless must satisfy certain properties on the complex ω plane in addition to the frequency limits on the real ω axis. For example, causality requires the coefficients to be free of zeros and singularities in the upper-half ω plane.[16] More specifically, in Appendix A of their paper, Johnson, Koplik, and Dashen[15] have shown that the poles and zeros of $k(\omega)$ all lie on the negative imaginary ω axis. Following their argument exactly but using a modified pressure p' given by [cf. Eq. (139)]

$$p' = p + \epsilon_0 \kappa_f \left(\nabla \cdot \mathbf{E}_f^0\right) \Gamma \frac{\Delta\phi}{H}, \tag{178}$$

one ends up with the result that both $k(\omega)$ and $L(\omega)$ have all their poles and zeros on the negative imaginary ω axis (for a thin double layer where $\nabla\Gamma$ is perpendicular to the double-layer variation). Thus the frequency functions used to define $k(\omega)$ and $L(\omega)$ should also have this property. Improper location of any singularities in the complex ω plane can lead to spurious contributions from the residue theorem when we (inevitably) return to the time domain via the inverse Fourier transform.

A. Conduction current $\mathbf{J}_c$ and $\overline{\mathbf{e}}_f$

The neglect of the deviations n_ℓ means that both $\mathbf{J}_c$ and $\overline{\mathbf{e}}_f$ are independent of frequency and that they do not depend on the macroscopic-pressure variations. Both are only proportional to $\overline{\mathbf{E}}$. If $\mathbf{e}_f = -\nabla\Gamma\,\Delta\phi/H$ is averaged over the pore volume of the averaging disk, we have

$$\overline{\mathbf{e}}_f = -\frac{1}{V_f}\int_{V_f} \nabla\varphi_f \, dV \tag{179}$$

$$= -\frac{1}{V_f}\left[\phi H A \hat{\mathbf{z}} + \int_{S_w} \mathbf{n}\Gamma \, dS\right] \frac{\Delta\phi}{H} \tag{180}$$

$$= -\left[\hat{\mathbf{z}} + \frac{1}{V_f}\int_{S_w} \mathbf{n}\Gamma \, dS\right] \frac{\Delta\phi}{H}. \tag{181}$$

The macroscopic-electric field is $\overline{\mathbf{E}} = -\hat{\mathbf{z}}\Delta\phi/H$ so that (for isotropic media) we have

$$\overline{\mathbf{e}}_f = \frac{1}{\alpha_\infty}\overline{\mathbf{E}}, \tag{182}$$

where

$$\frac{1}{\alpha_\infty} \equiv 1 + \frac{\hat{\mathbf{z}}}{V_f}\cdot\int_{S_w}\mathbf{n}\Gamma\,dS. \tag{183}$$

The unitless parameter α_∞ is the first of three fundamental porous-material "geometery" terms and is often called the "tortuosity." It must be identical to the α_∞ defined by Johnson, Koplik, and Dashen[15] which is

$$\frac{1}{\alpha_\infty} = \frac{1}{V_f}\int_{V_f}\nabla\Gamma\cdot\nabla\Gamma\,dV, \tag{184}$$

thus establishing an identity for the Γ field.

The average conduction current in the fluid $\mathbf{J}_c$ [Eq. (73)] is now

$$\mathbf{J}_c = \frac{\sigma_f}{\alpha_\infty}\overline{\mathbf{E}} - \frac{1}{V_f}\int_{S_w}\nabla\Gamma\,dS\int_0^D\sum_{\ell=1}^{L}(ez_\ell)^2 b_\ell\left[\mathcal{N}_\ell^0(\chi) - \mathcal{N}_\ell\right]d\chi\,\frac{\Delta\phi}{H}. \tag{185}$$

If we define

$$\frac{2}{\Lambda} = \frac{\alpha_\infty}{V_f}\int_{S_w}\hat{\mathbf{z}}\cdot\nabla\Gamma\,dS \tag{186}$$

and

$$C_{\mathrm{em}} = \int_0^D\sum_{\ell=1}^{L}(ez_\ell)^2 b_\ell\mathcal{N}_\ell\left[\exp\left(-\frac{ez_\ell\Phi^0}{kT}\right) - 1\right]d\chi, \tag{187}$$

then (for isotropic media) we have

$$\mathbf{J}_c = \left(\frac{\sigma_f}{\alpha_\infty} + \frac{2C_{\mathrm{em}}}{\alpha_\infty\Lambda}\right)\overline{\mathbf{E}}. \tag{188}$$

The parameter Λ is the second fundamental porous-material geometery term. It possesses the units of length and is seen to be a weighted volume-to-surface ratio where the dimensionless weight function $\hat{\mathbf{z}}\cdot\nabla\Gamma$ emphasizes the constricted portions of the pore space (i.e., the "pore throats" where the local field $\nabla\Gamma$ is large in order that $\nabla\cdot\nabla\Gamma = 0$). It will be seen that this "Λ parameter" must be identical to that defined by Johnson, Koplik, and Dashen which is

$$\frac{2}{\Lambda} = \frac{\alpha_\infty}{V_f}\int_{S_w}\nabla\Gamma\cdot\nabla\Gamma\,dS, \tag{189}$$

thus establishing another identity for the Γ field. Note that the integrands in Eqs. (186) and (189) cannot be equated because Γ is dependent on S_w.

The parameter C_{em} is the excess conductance associated with the electromigration of double layer ions. For a general multicomponent electrolyte with no restrictions placed on ζ, an exact expression for C_{em} requires a numerical solution of the Poisson-Boltzmann equation followed by a numerical integration. However, it is possible to obtain an extremely accurate estimate by using the Debye approximation $\Phi^0 = \zeta\exp(-\chi/d)$ in the following manner. Define the dimensionless surface potential

$$Z_\ell = \frac{ez_\ell}{kT}\zeta \tag{190}$$

and insert the Debye approximation into C_{em} obtaining

$$C_{\mathrm{em}} \simeq \sum_{\ell=1}^{L}(ez_\ell)^2 b_\ell\mathcal{N}_\ell\int_0^D\left[\exp\left(-Z_\ell e^{-\chi/d}\right) - 1\right]d\chi \tag{191}$$

$$= \sum_{\ell=1}^{L}(ez_\ell)^2 b_\ell\mathcal{N}_\ell\int_0^D\left[-Z_\ell e^{-\chi/d} + \frac{Z_\ell^2}{2!}e^{-2\chi/d} - \frac{Z_\ell^3}{3!}e^{-3\chi/d} + \cdots\right]d\chi \tag{192}$$

$$= \sum_{\ell=1}^{L}(ez_\ell)^2 b_\ell\mathcal{N}_\ell d\left[-Z_\ell + \frac{Z_\ell^2}{2\times 2!} - \frac{Z_\ell^3}{3\times 3!} + \cdots\right] \tag{193}$$

$$\simeq 2d\sum_{\ell=1}^{L}(ez_\ell)^2 b_\ell\mathcal{N}_\ell\left[\exp\left(-\frac{ez_\ell\zeta}{2kT}\right) - 1\right]. \tag{194}$$

For the special case of a binary symmetric electrolyte ($L = 2$; $z_1 = -z_2$; $\mathcal{N}_1 = \mathcal{N}_2$) this gives

$$C_{\mathrm{em}} = 2d(ez_1)^2\mathcal{N}_1\left\{(b_1 + b_2)\left[\cosh\left(\frac{ez_1\zeta}{2kT}\right) - 1\right] + (b_1 - b_2)\sinh\left(\frac{ez_1\zeta}{2kT}\right)\right\}. \tag{195}$$

It turns out that this is the exact result using the exact analytic expression for Φ^0 given in Appendix A for this special case. Remarkably, the approximation made in the first expression for C_{em} [Eq. (191)] is exactly compensated by the approximate summation used to obtain the final expression. This gives good confidence in the above estimate of C_{em} [Eq. (194)] for a general electrolyte. Under conditions where $|ez_\ell\zeta/kT| \ll 1$, we also have the Debye estimate

$$C_{\mathrm{em}}^{\mathrm{Debye}} = -\frac{\zeta d}{kT}\sum_{\ell=1}^{L}(ez_\ell)^3 b_\ell\mathcal{N}_\ell\left(1 - \frac{ez_\ell\zeta}{4kT}\right). \tag{196}$$

Two terms of the expansion are retained here because if all the b_ℓ are equal, the first term sums to zero.

B. Streaming current $\mathbf{J}_s$

We next consider the average streaming current in the fluid $\mathbf{J}_s$ [Eq. (77)],

$$\mathbf{J}_s = \frac{\epsilon_0 \kappa_f}{V_f} \int_{S_w} dS \int_0^D \nabla \Phi^0 \cdot \nabla \mathbf{v} \, d\chi, \tag{197}$$

where $\nabla\Phi^0 \cdot \nabla\mathbf{v} = (\partial\Phi^0/\partial\chi)(\partial\mathbf{v}/\partial\chi)$. Because of the separation into an electrically induced field $\mathbf{v}_e$ and a mechanically induced field $\mathbf{v}_m$, we also have $\mathbf{J}_s = \mathbf{J}_{se} + \mathbf{J}_{sm}$.

Focusing on the electrical portion first with $\mathbf{v}_e$ given by Eq. (157) gives

$$\mathbf{J}_{se} = \frac{2C_{\text{os}}}{\alpha_\infty \Lambda} \overline{\mathbf{E}}, \tag{198}$$

where

$$C_{\text{os}} = \frac{(\epsilon_0 \kappa_f)^2}{\eta} \int_0^D \frac{\partial \Phi^0}{\partial \chi} \frac{\partial}{\partial \chi} \left(\Phi^0 - \zeta e^{i^{3/2}\chi/\delta} \right) d\chi. \tag{199}$$

C_{os} represents the conductance due to electrically induced streaming (convection) of the excess double-layer ions. This may be called the "electro-osmotic" conductance. Because $\delta \gg d$, the variation of the exponential across the double layer is negligible and we have

$$C_{\text{os}} = \frac{(\epsilon_0 \kappa_f)^2}{\eta} \left[\zeta^2 \frac{i^{3/2}}{\delta} + \int_0^D \left(\frac{\partial \Phi^0}{\partial \chi} \right)^2 d\chi \right]. \tag{200}$$

We can obtain a nice approximation for the integral here using exactly the same procedure as for C_{em}. Starting with the Poisson-Boltzmann equation

$$\frac{\partial^2 \Phi^0}{\partial \chi^2} = - \sum_{\ell=1}^{L} \frac{e z_\ell}{\epsilon_0 \kappa_f} \mathcal{N}_\ell \exp\left(-\frac{e z_\ell}{kT} \Phi^0 \right), \tag{201}$$

both sides are multiplied by $\partial\Phi^0/\partial\chi$ and the equation integrated to give

$$\left(\frac{\partial \Phi^0}{\partial \chi} \right)^2 = \frac{2kT}{\epsilon_0 \kappa_f} \sum_{\ell=1}^{L} \mathcal{N}_\ell \left[\exp\left(-\frac{e z_\ell}{kT} \Phi^0 \right) - 1 \right]. \tag{202}$$

Integrating this over the double layer using the sequence of steps defined by Eqs. (191)–(194) then gives the estimate

$$C_{\text{os}} = \frac{(\epsilon_0 \kappa_f)^2}{\eta} \left\{ \frac{4kTd}{\epsilon_0 \kappa_f} \sum_{\ell=1}^{L} \mathcal{N}_\ell \left[\exp\left(-\frac{e z_\ell \zeta}{2kT} \right) - 1 \right] + \frac{i^{3/2}}{\delta} \zeta^2 \right\}. \tag{203}$$

There is a weak frequency dependence through the presence of the skin depth $\delta = \sqrt{\eta/\rho_f \omega}$ in the last term. It provides insight to expand the exponent to second order in $e z_\ell \zeta/2kT$ (note that the first-order term vanishes from bulk-charge neutrality) and obtain

$$C_{\text{os}} = \frac{(\epsilon_0 \kappa_f)^2 \zeta^2}{2d\eta} \left(1 + 2i^{3/2} \frac{d}{\delta} \right), \tag{204}$$

where the definition of the Debye length has been used. This is valid whenever $|e z_\ell \zeta/2kT| \ll 1$. Alternatively, if the Debye-approximation flow field [Eq. (158)] is used in $\mathbf{J}_s$ along with $\Phi^0 = \zeta \exp(-\chi/d)$, then we obtain the Debye approximation estimate $C_{\text{os}}^{\text{Debye}}$ that is valid (if $|e z_\ell \zeta/2kT| \ll 1$) regardless of the d/δ magnitude:

$$C_{\text{os}}^{\text{Debye}} = \frac{(\epsilon_0 \kappa_f)^2 \zeta^2}{2d\eta} \left(1 - i^{3/2} \frac{d}{\delta} \right)^{-2}. \tag{205}$$

Thus, when terms only to first order in d/δ are kept, Eqs. (204) and (205) are seen to be consistent.

It is important to note, however, that the frequency dependence defined by $C_{\text{os}}^{\text{Debye}}$ has no singularities in the complex ω plane; nor can it lead to there being zeros of $\sigma(\omega)$ as long as analysis is carried out on a Riemann surface (there is a branch point at the origin due to $\delta^{-1} = \sqrt{\omega \rho_f/\eta}$ that must be respected). Contrarily, the frequency dependence of Eq. (204) can lead to $\sigma(\omega)$ having zeros in the upper-half ω plane ($\omega_I > 0$); i.e., C_{os} can be a real negative number when $\omega_I > 0$. Causality requires that $\sigma(\omega)$ be free from zeros or singularities when $\omega_I > 0$. Thus, because we are only developing a theory to first order in d/δ, we can rewrite Eq. (203) as

$$C_{\text{os}} = \frac{(\epsilon_0 \kappa_f)^2 \zeta^2}{2d\eta} P \left(1 - \frac{2i^{3/2}}{P} \frac{d}{\delta} \right)^{-1}, \tag{206}$$

where the dimensionless parameter P is greater than or equal to 1 and is defined as

$$P = \frac{8kTd^2}{\epsilon_0 \kappa_f \zeta^2} \sum_{\ell=1}^{L} \mathcal{N}_\ell \left[\exp\left(-\frac{e z_\ell \zeta}{2kT} \right) - 1 \right]. \tag{207}$$

P goes to one when $|e z_\ell \zeta/2kT| \ll 1$. This estimate leads to no problems when $\omega_I > 0$.

Finally, we compare the electroosmotic conductance C_{os} (at frequencies where d/δ can be completely neglected) to the double-layer electromigration conductance C_{em} for the special case of a binary-symmetric electrolyte with $b_1 = b_2 = b$ (e.g., KCl). At room temperature we have

$$\frac{C_{\text{os}}}{C_{\text{em}}} = \frac{2\epsilon_0 \kappa_f kT}{(ez)^2 \eta b} \simeq \frac{1}{2}. \tag{208}$$

Thus, we have the important conclusion that C_{os} contributes nearly as much as C_{em} to the total conduction and should, therefore, not be neglected.

The mechanically induced streaming current is now determined. If the identity $\nabla\Phi^0 \cdot \nabla\mathbf{v}_m = \nabla \cdot (\Phi^0 \nabla \mathbf{v}_m) - \Phi^0 \nabla^2 \mathbf{v}_m$ is introduced into Eq. (197), then, because $\nabla^2 \mathbf{v}_m$ (unlike $\nabla^2 \mathbf{v}_e$) varies negligibly across the thin double layer compared to Φ^0, we have

$$\mathbf{J}_{sm} = \frac{\epsilon_0\kappa_f\zeta}{V_f}\int_{S_w}\left(\mathbf{n}\cdot\nabla\mathbf{v}_m - \tilde{d}\,\nabla^2\mathbf{v}_m\right)dS, \tag{209}$$

where the length $\tilde{d}$ is defined as

$$\tilde{d} = \int_0^D \frac{\Phi^0(\chi)}{\zeta}\,d\chi. \tag{210}$$

For the Debye approximation, we have $\tilde{d} = d$ while, in general, $\tilde{d} \leq d$.

As previously discussed, the mechanically induced flow separates into low-frequency and high-frequency regimes. Starting at low frequencies, we insert Eq. (160) into Eq. (209) and obtain

$$\phi\mathbf{J}_{sm0} = L_{m0}\left(-\nabla\bar{p} + i\omega\rho_f\dot{\bar{\mathbf{u}}}_s\right), \tag{211}$$

where the subscripts $sm0$ stand for "streaming, mechanical, and low frequencies" and where the low-frequency coupling coefficient L_{m0} is

$$L_{m0} = -\phi\frac{\epsilon_0\kappa_f\zeta}{\eta}\frac{\hat{\mathbf{z}}}{V_f}\cdot\int_{S_w}\left(\mathbf{n}\cdot\nabla\mathbf{g} - \tilde{d}\,\nabla h\right)dS, \tag{212}$$

where $\nabla^2\mathbf{g} = \nabla h$ [Eq. (162)] was used. If $\nabla^2\mathbf{g} = \nabla h$ is integrated over the pore volume and $h = \Gamma + \delta h$ introduced, one obtains

$$\frac{\hat{\mathbf{z}}}{V_f}\cdot\int_{S_w}\mathbf{n}\cdot\nabla\mathbf{g}\,dS = \frac{1}{\alpha_\infty} + \frac{\hat{\mathbf{z}}}{V_f}\cdot\int_{S_w}\mathbf{n}\,\delta h\,dS. \tag{213}$$

Using this and the definition of Λ [Eq. (186)] in L_{m0} then gives

$$L_{m0} = -\frac{\phi}{\alpha_\infty}\frac{\epsilon_0\kappa_f\zeta}{\eta}\left[1 - 2\frac{\tilde{d}}{\Lambda} + \alpha_\infty\frac{\hat{\mathbf{z}}}{V_f}\cdot\int_{S_w}\left(\mathbf{n}\delta h - \tilde{d}\,\nabla\delta h\right)dS\right]. \tag{214}$$

We leave this low-frequency definition for now and will consider it again after L_{e0} has been defined.

At high frequencies, the coupling coeffcient $L_{m\infty}$ is obtained by inserting Eq. (172) into Eq. (209) which gives

$$\phi\mathbf{J}_{sm\infty} = L_{m\infty}\left(-\nabla\bar{p} + i\omega\rho_f\dot{\bar{\mathbf{u}}}_s\right), \tag{215}$$

where

$$L_{m\infty} = -2\frac{\phi}{\alpha_\infty}\frac{\epsilon_0\kappa_f\zeta}{\eta}\frac{i^{1/2}\delta}{\Lambda}\left(1 + i^{3/2}\frac{\tilde{d}}{\delta}\right) \tag{216}$$

$$= -2\frac{\phi}{\alpha_\infty}\frac{\epsilon_0\kappa_f\zeta}{\eta}\frac{i^{1/2}\delta}{\Lambda}\left(1 - i^{3/2}\frac{\tilde{d}}{\delta}\right)^{-1}. \tag{217}$$

Equation (217) leads to no problems when $\omega_I > 0$ (again, the branch point at the origin must be allowed for) and is the estimate to be employed. Note that if the Debye approximation is used, then, regardless of the d/δ ratio, we have

$$L_{m\infty}^{\text{Debye}} = -2\frac{\phi}{\alpha_\infty}\frac{\epsilon_0\kappa_f\zeta}{\eta}\frac{i^{1/2}\delta}{\Lambda}\left(1 - i^{3/2}\frac{d}{\delta}\right)^{-1}, \tag{218}$$

thus confirming the form of Eq. (217). Note that the general estimate [Eq. (217)] involves $\tilde{d}$ while the Debye estimate involves d.

C. Relative flow $\bar{\mathbf{v}}$

The average value of the relative fluid flow $\bar{\mathbf{v}}$ can be separated into electrically- and mechanically-induced portions $\bar{\mathbf{v}} = \bar{\mathbf{v}}_e + \bar{\mathbf{v}}_m$, as well as analyzed in the limits of low and high frequencies. Furthermore, it can be evaluated either by directly averaging the pore-scale field or by utilizing the averaged-force balance [Eq. (96)] and evaluating the drag integral $\mathbf{d}$ and the electrical body force $\mathbf{f}_d$. It is more efficient to simply volume average the pore-scale field.

Consider first the mechanically induced flow. In the limit of low frequencies, a direct averaging of Eq. (160) gives

$$\phi\bar{\mathbf{v}}_{m0} = \frac{k_0}{\eta}\left(-\nabla\bar{p} + i\omega\rho_f\dot{\bar{\mathbf{u}}}_s\right), \tag{219}$$

where ϕ is porosity and

$$k_0 = -\frac{\phi}{V_f}\int_{V_f}\hat{\mathbf{z}}\cdot\mathbf{g}\,dV. \tag{220}$$

The negative sign arises because $\mathbf{g}$, by definition of its boundary-value problem on the averaging disk, is directed on average in the $-\hat{\mathbf{z}}$ direction. The parameter k_0 is the dc permeability and is our third and final pore-geometery parameter.

In the limit of high frequencies, Eq. (172) is directly averaged to give

$$\phi\bar{\mathbf{v}}_{m\infty} = \frac{k_\infty}{\eta}\left(-\nabla\bar{p} + i\omega\rho_f\dot{\bar{\mathbf{u}}}_s\right), \tag{221}$$

where

$$k_\infty = i\delta^2\phi\frac{\hat{\mathbf{z}}}{V_f}\cdot\left[\int_{V_f}\nabla\Gamma\,dV - \int_{S_w}\nabla\Gamma\,dS \times \int_0^{D_v} e^{i^{3/2}\chi/\delta}d\chi\right] \tag{222}$$

$$= i\delta^2\frac{\phi}{\alpha_\infty}\left(1 - 2i^{1/2}\frac{\delta}{\Lambda}\right) \tag{223}$$

$$= i\delta^2\frac{\phi}{\alpha_\infty}\left(1 + 2i^{1/2}\frac{\delta}{\Lambda}\right)^{-1}. \tag{224}$$

In the high-frequency limit ($\delta \to 0$), Eqs. (224) and (223) are equivalent; however, Eq. (224) leads to no problems when $\omega_I > 0$ (as long as the branch point at the origin is respected). The distance D_v in Eq. (222) can be taken as a few viscous-skin depths.

Next, Eq. (151) for the low-frequency electrically induced flow is integrated to give

$$\phi\bar{\mathbf{v}}_{e0} = L_{e0}\bar{\mathbf{E}}, \tag{225}$$

where the low-frequency coupling coefficient L_{e0} is

$$L_{e0} = \phi \frac{\epsilon_0 \kappa_f}{\eta} \frac{\hat{\mathbf{z}}}{V_f} \cdot \int_{V_f} (\Phi^0 - \zeta) \nabla \Gamma \, dV \tag{226}$$

$$= -\frac{\phi}{\alpha_\infty} \frac{\epsilon_0 \kappa_f \zeta}{\eta} \left(1 - 2\frac{\tilde{d}}{\Lambda}\right) . \tag{227}$$

Comparing this expression to Eq. (214) for L_{m0} and using Onsager reciprocity ($L_e = L_m$) as independently derived in Appendix B, then gives the identities

$$\frac{\hat{\mathbf{z}}}{V_f} \cdot \int_{S_w} \mathbf{n} \delta h \, dS = 0, \tag{228}$$

$$\frac{\hat{\mathbf{z}}}{V_f} \cdot \int_{S_w} \nabla \delta h \, dS = 0. \tag{229}$$

When these are introduced into Eqs. (213) and (186), we have the apparently new results involving the Stokes flow:

$$\frac{\hat{\mathbf{z}}}{V_f} \cdot \int_{S_w} \mathbf{n} \cdot \nabla \mathbf{g} \, dS = \frac{1}{\alpha_\infty}, \tag{230}$$

$$\frac{\hat{\mathbf{z}}}{V_f} \cdot \int_{S_w} \nabla^2 \mathbf{g} \, dS = \frac{2}{\alpha_\infty \Lambda}. \tag{231}$$

Heretofore, α_∞ and Λ were defined solely in terms of the potential field Γ (e.g., as in Ref. 15).

In the high-frequency limit, Eq. (157) is volume integrated to give

$$\phi \overline{\mathbf{v}}_{e\infty} = L_{e\infty} \overline{\mathbf{E}}, \tag{232}$$

where the high-frequency coupling coefficient is

$$L_{e\infty} = -\phi \frac{\epsilon_0 \kappa_f \zeta}{\eta} \frac{\hat{\mathbf{z}}}{V_f} \cdot \int_{S_w} \nabla \Gamma \, dS \left[\int_0^{D_v} e^{i^{3/2} \chi / \delta} \, d\chi - \int_0^D \frac{\Phi}{\zeta} \, d\chi \right] \tag{233}$$

$$= -2 \frac{\phi}{\alpha_\infty} \frac{\epsilon_0 \kappa_f \zeta}{\eta} \frac{i^{1/2} \delta}{\Lambda} \left(1 + i^{3/2} \frac{\tilde{d}}{\delta}\right) \tag{234}$$

$$= -2 \frac{\phi}{\alpha_\infty} \frac{\epsilon_0 \kappa_f \zeta}{\eta} \frac{i^{1/2} \delta}{\Lambda} \left(1 - i^{3/2} \frac{\tilde{d}}{\delta}\right)^{-1} . \tag{235}$$

It is seen that $L_{e\infty} = L_{m\infty}$, thus providing a check on the validity of this expression.

D. Final coefficients

We have obtained above the low-frequency and high-frequency limits of the coupling coefficient $L (= L_e = L_m)$ and the permeability k. It is easy to verify that (note $\delta = \sqrt{\eta / \rho_f \omega}$)

$$\frac{k(\omega)}{k_0} = \left[\left(1 - i \frac{\omega}{\omega_t} \frac{4}{m}\right)^{\frac{1}{2}} - i \frac{\omega}{\omega_t} \right]^{-1} \tag{236}$$

and

$$\frac{L(\omega)}{L_0} = \left[1 - i \frac{\omega}{\omega_t} \frac{m}{4} \left(1 - 2\frac{\tilde{d}}{\Lambda}\right)^2 \left(1 - i^{3/2} \tilde{d} \sqrt{\frac{\omega \rho_f}{\eta}}\right)^2 \right]^{-\frac{1}{2}} \tag{237}$$

are two possible functions that simply and smoothly connect these frequency limits. These functions have the correct behavior on the complex ω plane. The transition frequency ω_t separating low-frequency viscous flow and high-frequency inertial flow is defined as

$$\omega_t \equiv \frac{\phi}{\alpha_\infty k_0} \frac{\eta}{\rho_f}. \tag{238}$$

The dimensionless number m is defined as

$$m \equiv \frac{\phi}{\alpha_\infty k_0} \Lambda^2 \tag{239}$$

and consists only of the pore-space geometery terms. The low-frequency coupling coefficient L_0 is defined

$$L_0 = -\frac{\phi}{\alpha_\infty} \frac{\epsilon_0 \kappa_f \zeta}{\eta} \left(1 - 2\frac{\tilde{d}}{\Lambda}\right) . \tag{240}$$

All the remaining parameters have been defined in the previous sections.

Despite the negative sign in its definition, L_0 will lead to positive streaming-current densities for positive values of $-\nabla \bar{p}$. This is because the ζ potential is negative when the diffuse layer contains excess positive charge and positive when the diffuse layer contains excess negative charge. Note also that the correction term $1 - 2\tilde{d}/\Lambda$ is only valid under the thin-double-layer assumption and at most represents a correction of a few percent. We do not have that $L_0 \to 0$ as $\tilde{d} \to \Lambda/2$. For the special case of a single cylindrical tube of radius R, it easy to show (using the Debye approximation) that the coupling coefficient is given by

$$L_0^{\text{tube}} = -\frac{\epsilon_0 \kappa_f \zeta}{\eta} \frac{I_2(R/d)}{I_0(R/d)}, \tag{241}$$

where I_2 and I_0 are modified Bessel functions. In the limit as $R/d \to \infty$ (thin double layers), we have that $I_2(R/d)/I_0(R/d) \to 1 - 2d/R$. It will be seen that for a cylindrical tube, $\Lambda = R$. Thus the form of Eq. (240) is confirmed for this special case. However, when $R/d = 2$ (double layers half the radius of the tube), we have that $I_2(2)/I_0(2) = 0.3$, while the correction factor of Eq. (240) would predict zero. Again, the thin-double-layer assumption must be satisfied for the analysis of this paper to be valid.

The above expression for $k(\omega)$ is identical to the one defined by Johnson, Koplik, and Dashen[15] using energy arguments thus giving that the Λ defined by Eq. (186) is identical to the Λ defined by Eq. (189).

The conductivity $\sigma(\omega)$ of the material is defined by Eqs. (173) and (174), which then gives [from Eqs. (188) and (198)]

$$\sigma(\omega) = \frac{\phi\sigma_f}{\alpha_\infty}\left[1+\frac{2\left[C_{\rm em}+C_{\rm os}(\omega)\right]}{\sigma_f\Lambda}\right]. \tag{242}$$

The weak dependence on frequency comes only from the electro-osmotic conductance and is due to the electrically driven viscous-flow to inertial-flow transition. The definitions of σ_f, $C_{\rm em}$, and $C_{\rm os}(\omega)$ are given by Eqs. (72), (194), and (206), respectively. Again, it is emphasized that $C_{\rm os}$ is of the same order of magnitude as $C_{\rm em}$ and should not be neglected [Eq. (208)].

A central question is whether the pore-geometery number m is a universal constant for all porous media. Rearranging the definition of m gives an equation for the dc permeability:

$$k_0 = \frac{1}{m}\frac{\phi}{\alpha_\infty}\Lambda^2. \tag{243}$$

There is both laboratory[17,18] and numerical[15,19,20] evidence suggesting that when k_0, ϕ, α_∞, and Λ are independently measured, m lies in the range

$$4 \le m \le 8 \tag{244}$$

for a variety of porous media ranging from grain packings to networks of variable-radii tubes. However, it is difficult to independently measure Λ and α_∞ in rocks that contain significant amounts of clay so that the value of m in, for example, shaley sandstones is uncertain.

In this work, we have developed expressions for k_0, α_∞, and Λ. These can be expressed as

$$\frac{k_0}{\phi} = -\frac{\hat{\mathbf{z}}}{V_f}\cdot\int_{V_f}\mathbf{g}\,dV, \tag{245}$$

$$\frac{1}{\alpha_\infty} = \frac{\hat{\mathbf{z}}}{V_f}\cdot\int_{S_w}\mathbf{n}\cdot\nabla\mathbf{g}\,dS\;\left(=1+\frac{\hat{\mathbf{z}}}{V_f}\cdot\int_{S_w}\mathbf{n}\Gamma\,dS\right), \tag{246}$$

$$\frac{2}{\alpha_\infty\Lambda} = \frac{\hat{\mathbf{z}}}{V_f}\cdot\int_{S_w}\nabla^2\mathbf{g}\,dS\;\left(=\frac{\hat{\mathbf{z}}}{V_f}\cdot\int_{S_w}\nabla\Gamma\,dS\right). \tag{247}$$

Note that α_∞ and Λ can also be defined by Eqs. (184) and (189) as derived in Ref. 15. Although all three pore-geometery terms are expressed as integrals of the Stokes flow $\mathbf{g}$ [defined by Eqs. (162)–(165)], it has proven difficult to use these relations to make general correlations between m and material types. It is trivial to demonstrate that for a cylindrical tube of radius R with axis directed in the $\hat{\mathbf{z}}_1$ direction (perhaps different than $\hat{\mathbf{z}}$), the Stokes-flow vector is (in cylindrical coordinates) $\mathbf{g} = \hat{\mathbf{z}}_1(r^2 - R^2)/4$, and Eqs. (245)–(247) satisfy Eq. (243) with $m = 8$. In this particular case, we have $\Lambda = R$ as pointed out in Ref. 15.

VI. SUMMARY

We now summarize the final form of the macroscopic governing equations. All overbars denoting averaging are dropped. For the problem of modeling the propagation of coupled electromagnetic and mechanical disturbances in an isotropic-porous material, the following equations represent a complete set:

$$\nabla\times\mathbf{E} = i\omega\mathbf{B}, \tag{248}$$

$$\nabla\times\mathbf{H} = -i\omega\mathbf{D}+\mathbf{J}, \tag{249}$$

$$\nabla\cdot\boldsymbol{\tau}_B = -\omega^2\left(\rho_B\mathbf{u}_s+\rho_f\mathbf{w}\right), \tag{250}$$

$$\mathbf{J} = \sigma(\omega)\mathbf{E}+L(\omega)\left(-\nabla p+\omega^2\rho_f\mathbf{u}_s\right), \tag{251}$$

$$-i\omega\mathbf{w} = L(\omega)\mathbf{E}+\frac{k(\omega)}{\eta}\left(-\nabla p+\omega^2\rho_f\mathbf{u}_s\right), \tag{252}$$

$$\mathbf{D} = \epsilon_0\left[\frac{\phi}{\alpha_\infty}(\kappa_f-\kappa_s)+\kappa_s\right]\mathbf{E}, \tag{253}$$

$$\mathbf{B} = \mu_0\mathbf{H}, \tag{254}$$

$$\boldsymbol{\tau}_B = (K_G\nabla\cdot\mathbf{u}_s+C\nabla\cdot\mathbf{w})\,\mathbf{I} + G_{\rm fr}\left(\nabla\mathbf{u}_s+\nabla\mathbf{u}_s^T-\frac{2}{3}\nabla\cdot\mathbf{u}_s\mathbf{I}\right), \tag{255}$$

$$-p = C\nabla\cdot\mathbf{u}_s+M\nabla\cdot\mathbf{w}. \tag{256}$$

All coupling is present in the transport equations [Eqs. (251) and (252)] and comes from the coefficient $L(\omega)$. If, for some reason, we want to calculate the macroscopic-charge density $\rho\equiv\phi\sum_\ell ez_\ell\bar{n}_\ell$ induced in the porous material by the above disturbances, we utilize the macroscopic statement of Coulomb's law $\rho = \nabla\cdot\mathbf{D}$, once $\mathbf{D}$ has been determined; however, it is unclear why such a calculation would be of interest. The definitions of $\sigma(\omega)$, $k(\omega)$, and $L(\omega)$ have been given in the previous section [Eqs. (242), (236), and (237), respectively]. There are two distinct frequency relaxations present in the above equations. One is in the transport equations and is due to the transition from viscous flow to inertial flow while the other is in Ampère's law [Eq. (249)] and is due to the transition from ion transport $\mathbf{J}$ to dielectric-displacement current $-i\omega\mathbf{D}$.

Two interesting observations can be made concerning the relaxation in the transport equations. First, $k(\omega)$ relaxes at the frequency ω_t [Eq. (238)] while $L(\omega)$ relaxes at the frequency $4\omega_t/m$. Observation of the two relaxation frequencies would provide an independent means for determining m. Second, $k(\omega)$ falls off as ω when $\omega>\omega_t$ while $L(\omega)$ falls off as $\omega^{1/2}$ when $\omega>4\omega_t/m$. If it is possible to stress the material with equal amplitude over a wide range of frequencies, then $|-\nabla p+\omega^2\rho_f\mathbf{u}_s|$ increases directly as ω so that $|\dot{\mathbf{w}}|$ remains constant above ω_t while $|\mathbf{J}|$ continues to increase (as $\omega^{1/2}$) above $4\omega_t/m$; this states that there continues to be enhancement in the wave-induced streaming current even above the relaxation frequency.

Finally, if flow is being induced by applied pressure gradients and electric fields that are steady in time, we may set

$$\mathbf{E} = -\nabla\Phi \tag{257}$$

and obtain the following complete set of static equations:

$$\nabla\cdot\mathbf{J} = 0, \tag{258}$$

$$\nabla\cdot\dot{\mathbf{w}} = 0, \tag{259}$$

$$\mathbf{J} = \frac{\phi}{\alpha_\infty}\sigma_f \left[1 + \frac{2(C_{\rm em} + C_{\rm os})}{\sigma_f \Lambda}\right](-\nabla\Phi) - \frac{\phi}{\alpha_\infty}\frac{\epsilon_0\kappa_f\zeta}{\eta}\left[1 - 2\frac{\tilde{d}}{\Lambda}\right](-\nabla p) \tag{260}$$

$$\dot{\mathbf{w}} = -\frac{\phi}{\alpha_\infty}\frac{\epsilon_0\kappa_f\zeta}{\eta}\left[1 - 2\frac{\tilde{d}}{\Lambda}\right](-\nabla\Phi) + \frac{k_0}{\eta}(-\nabla p), \tag{261}$$

where the dc transport coefficients have been explicitly written out [σ_f, $C_{\rm em}$, $C_{\rm os}$, and $\tilde{d}$ are defined by Eqs. (72), (194), (206), and (210), respectively, with the skin-depth term in Eq. (206) neglected]. When gravity effects are important, the pressure gradient in Eqs. (260) and (261) must be generalized to $\nabla p + \rho_f \mathbf{g}$, where $\mathbf{g}$ is the acceleration of gravity. If it is known that the applied frequencies are greater than zero but less than the above mentioned transition frequencies (i.e., quasistatic disturbances), then Eq. (259) should be replaced by Eqs. (250), (255), and (256). For hydrology problems in which flow occurs due to externally applied quasistatic pressure gradients or electric fields, if the material is highly consolidated so that $K_{\rm fr} \gg K_f$, it is further possible to ignore the $\nabla\cdot\mathbf{u}_s$ term in Eq. (256) and replace Eq. (259) simply by $i\omega p = M\nabla\cdot\dot{\mathbf{w}}$. Note, however, that this simplification cannot be made (even if $K_{\rm fr} \gg K_f$) if flow is being induced by mechanical (seismic) waves or by deformation of the bulk-porous material in general.

In conclusion, it is emphasized that the above results have been obtained by volume averaging and not simply postulated. Boundary conditions and wave properties for the governing equations are discussed in Ref. 9.

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APPENDIX A: DOUBLE-LAYER DESCRIPTION

As discussed in the text, we need to have a solution for the Poisson-Boltzmann [Eq. (27)] next to a plane wall. Writing the equation as

$$\frac{\partial^2\Phi^0}{\partial\chi^2} - \sum_{\ell=1}^{L}\frac{(ez_\ell)^2\mathcal{N}_\ell}{\epsilon_0\kappa_f kT}\left[1 - \frac{1}{2!}\frac{ez_\ell}{kT}\Phi^0 + \cdots\right]\Phi^0 = 0, \tag{A1}$$

it is seen that if $|ez_\ell\zeta/kT| \ll 2$, where $\zeta = \Phi^0(0)$ (i.e., the potential at the shear plane), then the equation linearizes, and the solution is the Debye approximation

$$\Phi^0 = \zeta e^{-\chi/d}, \tag{A2}$$

where the Debye length d is given by Eq. (29). Using this estimate, the ion-number densities are estimated as

$$N_\ell^0 = \mathcal{N}_\ell \exp\left(-Z_\ell e^{-\chi/d}\right), \tag{A3}$$

where

$$Z_\ell = \frac{ez_\ell\zeta}{kT}. \tag{A4}$$

This estimate of N_ℓ^0 is quite accurate even when $|Z_\ell| > 2$, i.e., even when the linearization of Eq. (A1) is not valid. However, the linearized estimate [obtained by expanding Eq. (A3)]

$$N_\ell^0 \simeq \mathcal{N}_\ell\left(1 - Z_\ell e^{-\chi/d}\right) \tag{A5}$$

should only be used when $|Z_\ell| \ll 1$.

One way that Eq. (A2) can lead to considerable error when $|Z_\ell| > 2$ is if it is used to relate ζ to the surface-charge density Q^0. A blind application of the boundary condition $\epsilon_0\kappa_f\mathbf{n}\cdot\mathbf{E}_f^0 = Q^0$ would give $\zeta = Q^0 d/(\epsilon_0\kappa_f)$, which is a very poor approximation when $|Z_\ell| > 2$. It is far better to obtain the relation between ζ and Q^0 using Eq. (A3) and the assumption that there is bulk-charge neutrality,

$$Q^0 \simeq -\int_0^\infty \sum_{\ell=1}^{L} ez_\ell\mathcal{N}_\ell \exp\left(-Z_\ell e^{-\chi/d}\right) \tag{A6}$$

$$\simeq -2d\sum_{\ell=1}^{L} ez_\ell\mathcal{N}_\ell \exp\left(-\frac{ez_\ell\zeta}{2kT}\right), \tag{A7}$$

where the integral is evaluated using the steps defined in Eqs. (191)–(194). This is a generally valid result even when $|Z_\ell| > 2$.

Indeed, for the special case of a binary symmetric electrolyte ($L = 2$, $z_1 = -z_2$, and $\mathcal{N}_1 = \mathcal{N}_2$) we have the exact solution of the Poisson-Boltzmann equation

$$\frac{ez_1\Phi^0}{2kT} = \ln\left[\frac{1 + \exp(-\chi/d)\tanh[ez_1\zeta/(4kT)]}{1 - \exp(-\chi/d)\tanh[ez_1\zeta/(4kT)]}\right], \tag{A8}$$

which gives

$$\zeta = \frac{2kT}{ez_1}\sinh^{-1}\left(\frac{Q^0}{2ez_1\mathcal{N}_1 d}\right). \tag{A9}$$

But this exact result is identical to our result [Eq. (A7)] for this special case. This gives good confidence in both Eq. (A7) and Eq. (A3) for more general electrolytes even when $|Z_\ell| > 2$.

APPENDIX B: ONSAGER RECIPROCITY

In this appendix, Onsager reciprocity is derived for frequency-dependent electrokinetic phenomena in porous media satisfying the thin-double-layer assumption.

The general boundary-value problem on the averaging disk for mechanically induced flow $\mathbf{v}_m$ is given by Eqs. (146) and (147). Note that the problem can also be stated as

$$\eta\nabla^2\mathbf{v}_m + i\omega\rho_f\mathbf{v}_m = \nabla\left(\delta p_m + \Gamma\frac{\Delta P}{H}\right), \tag{B1}$$

where $\delta p_m = 0$ on the disk faces. The problem for the electrically induced flow $\mathbf{v}_e$ is

$$\eta\nabla^2\mathbf{v}_e + i\omega\rho_f\mathbf{v}_e = \nabla p_e + \rho^0\nabla\Gamma\,\frac{\Delta\phi}{H}, \qquad \text{(B2)}$$

where $p_e = 0$ on the disk faces and ρ^0 is the excess-charge density in the diffuse double layer ($\rho^0 = \sum_{\ell=1}^{L} e z_\ell N_\ell^0$). We also have that $\nabla\cdot\mathbf{v}_m = \nabla\cdot\mathbf{v}_e = 0$ everywhere and $\mathbf{v}_m = \mathbf{v}_e = 0$ on S_w.

If $\mathbf{v}_e$ is dotted into Eq. (B1) and $\mathbf{v}_m$ is dotted into Eq. (B2) and the result subtracted and integrated over the pore volume V_f, one obtains

$$\int_{V_f}\nabla\cdot\left[\eta\left(\nabla\mathbf{v}_m\cdot\mathbf{v}_e - \nabla\mathbf{v}_e\cdot\mathbf{v}_m\right) + \delta p_m\mathbf{v}_e - p_e\mathbf{v}_m\right]dV$$
$$= \int_{V_f}\left\{\nabla\cdot\left[\Gamma\left(\mathbf{v}_e\frac{\Delta P}{H} - \rho^0\mathbf{v}_m\frac{\Delta\phi}{H}\right)\right] + \Gamma\nabla\rho^0\cdot\mathbf{v}_m\right\}dV.$$

We have used the identities $\nabla\cdot(\nabla\mathbf{v}_m\cdot\mathbf{v}_e) = (\nabla^2\mathbf{v}_m)\cdot\mathbf{v}_e + \nabla\mathbf{v}_e{:}(\nabla\mathbf{v}_m)^T$ and $\nabla\mathbf{v}_e{:}(\nabla\mathbf{v}_m)^T = (\nabla\mathbf{v}_e)^T{:}\nabla\mathbf{v}_m$ plus the fact that $\nabla\cdot\mathbf{v}_m = \nabla\cdot\mathbf{v}_e = 0$. Because Eq. (B2) is only valid in the thin-double-layer approximation, we are justified in setting $\nabla\rho^0\cdot\mathbf{v}_m = 0$ (the two vectors are orthogonal when double layers are thin). The divergence theorem plus the boundary conditions then gives

$$\eta\int_{z=H}\hat{\mathbf{z}}\cdot\left(\nabla\mathbf{v}_m\cdot\mathbf{v}_e - \nabla\mathbf{v}_e\cdot\mathbf{v}_m\right)dS - \eta\int_{z=0}\hat{\mathbf{z}}\cdot\left(\nabla\mathbf{v}_m\cdot\mathbf{v}_e - \nabla\mathbf{v}_e\cdot\mathbf{v}_m\right)dS$$
$$= H\int_{z=H}\hat{\mathbf{z}}\cdot\left(\mathbf{v}_e\frac{\Delta P}{H} - \rho^0\mathbf{v}_m\frac{\Delta\phi}{H}\right)dS.$$

If the material has no significant macroscopic variation over distances H so that the distribution of grains (and, therefore, flow) near $z = 0$ is similar to that near $z = H$, then the two integrals on the left-hand side will cancel (one may additionally establish that each of the integrals on the left-hand side individually goes to zero). Thus, we have

$$H\int_{z=H}\hat{\mathbf{z}}\cdot\left(\mathbf{v}_e\frac{\Delta P}{H} - \rho^0\mathbf{v}_m\frac{\Delta\phi}{H}\right)dS = 0. \qquad \text{(B3)}$$

The definitions of the cross-coupling coefficients L_e and L_m are now introduced:

$$\hat{\mathbf{z}}\cdot\bar{\mathbf{v}}_e = L_e\frac{\Delta\phi}{H} = \frac{\hat{\mathbf{z}}}{V_f}\cdot\int_{V_f}\mathbf{v}_e\,dV$$

and

$$\hat{\mathbf{z}}\cdot\bar{\mathbf{j}}_m = L_m\frac{\Delta P}{H} = \frac{\hat{\mathbf{z}}}{V_f}\cdot\int_{V_f}\rho^0\mathbf{v}_m\,dV.$$

We can thus form

$$V_f\frac{\Delta\phi}{H}\frac{\Delta P}{H}(L_e - L_m) = \hat{\mathbf{z}}\cdot\int_{V_f}\left(\mathbf{v}_e\frac{\Delta P}{H} - \rho^0\mathbf{v}_m\frac{\Delta\phi}{H}\right)dV$$
$$= \int_{V_f}\nabla\cdot\left[z\left(\mathbf{v}_e\frac{\Delta P}{H} - \rho^0\mathbf{v}_m\frac{\Delta\phi}{H}\right)\right]dV$$
$$= H\int_{z=H}\hat{\mathbf{z}}\cdot\left(\mathbf{v}_e\frac{\Delta P}{H} - \rho^0\mathbf{v}_m\frac{\Delta\phi}{H}\right)dS,$$

where the thin-double-layer assumption $\nabla\rho^0\cdot\mathbf{v}_m = 0$ was used again. Thus, from Eq. (B3), the desired result $L_e = L_m$ is arrived at.

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