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GEOMETRY-DRIVEN CHARGE ACCUMULATION IN ELECTROKINETIC FLOWS BETWEEN THIN, CLOSELY SPACED LAMINATES

B. S. TILLEY†, B. VERNESCU†, AND J. D. PLUMMER‡

Abstract. Fluid flows through anisotropic media are found in a wide variety of geophysical and biological systems. The macroscale behavior of these systems depends on the microstructure, which in turn may depend on local and global physical processes. Classically, geometric restrictions are needed to model these systems on the largest length scale, and we are interested in developing effective models which relax these restrictions. To explore the development of these multiscale models, we consider an array of closely spaced, purely dielectric rigid laminates with nonuniform thickness. The laminate thickness and spacing varies on a length scale much longer than the characteristic thickness of the laminates. In the spacing between the laminates, an electrically conducting fluid is driven by an applied electric field through electroosmosis and electrophoresis along with an applied pressure gradient. Debye layers occur at the laminate-fluid interface, which are assumed to be much smaller than the laminate thickness. From a modification of the classical homogenization approach that relies on a physical microscale constraint in place of a geometric constraint, we derive an effective set of equations that describe the fluid pressure, the anion and cation concentrations in the fluid, and the electric potential. Anisotropic dispersion effects in the electric field are included, and electroneutrality in the fluid is not imposed. We find that gradients in the laminate spacing can lead to charge accumulation when electroosmosis and the electrophoresis induced from the anisotropic dispersion effects balance.

Key words. homogenization theory, lubrication theory, electrokinetic flow, and charge accumulation

AMS subject classifications. 35B27, 76D08, 76S05

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1. Introduction. Flows in deformable porous media are found in a wide variety of contexts, such as flow through clay-based soils [19] and its impact on erosion and soil evolution [31], transport in biological materials (e.g., [29], [7], [13], [3], [11]), food science [38], and protocols for remediation of contaminated former industrial sites [10], [14], [8], [16], [17], [6], [5], [1]. In all of these contexts, the effective transport by the medium is hindered by the small pore scales, charge and surface energy effects that are pertinent on small scales, and capillary effects when multiple fluid phases coexist. These are significant mathematical challenges when the porous matrix is rigid. Having a mathematical formulation which fundamentally addresses the processes and is amenable to inclusion of additional physical effects would impact the development of these scientific fields.

Layered media are found in stratification of different soil layers in geology [41], layering of mineral deposit separated by fluid in clays [43], and anisotropic geometries found in biological materials [32], [13]. Characteristic of these systems is that the thickness of the media is significantly smaller than the length scale over which their properties or geometries vary, and their effective tortuosity is small. For example, in...
saturated soils the layers may be separated by a fluid layer on the order of $500\,\mu\text{m}$ in thickness, but the geometries can vary over several centimeters.

In soil remediation applications, the chemical or microbial treatment strategy depends on the chemical remediation process, but also on the local constituent properties of the soil and surrounding fluid. These strategies are based experimentally on the local properties of the site. The competing physical effects include fluid flow through the porous matrix, elastic deformation of the matrix, charge transport, and heat and mass transfer. A quantitative understanding of how these different mechanisms interact with each other can significantly improve the design of current treatment strategies. Our current study describes a mathematical approach for investigating these systems in a context where elastic deformations are negligible, the fine scale and macroscale are separated, and the fluid-layer thickness varies over the macroscale.

Electrokinetic phenomena, such as electroosmosis and electromigration, are found in a wide variety of applications [24], [25], [39], [20], [18], [4], [9]. The fundamental issue surrounding the process is the coupling between electric double layers, an applied electric field, and the momentum of the solution fluid. In modeling the double layers whose thickness scales on the Debye characteristic length, a slip velocity can be considered along the solid-fluid interface when the characteristic flow scales are much larger than the Debye layer [2]. One interesting resulting feature is the fact that the interface properties introduce a size effect: The effective properties are no longer scale invariant. Moreover, the effective properties can have totally different behavior at the same volume fraction but at different sizes of inclusions or fibers, as was observed in Lipton and Vernescu in [26], [27], [28]. The analytical results and numerical simulations should shed more light onto the influence of interstitial fluid counterion concentration on the compressive, tensile, and shear properties in clays [32]. At the same time, it should provide an estimate of the influence of hydration of clay particles versus ion concentration in the swelling effects in clays [30].

Homogenization techniques have been utilized in understanding the electroosmotic and chemoosmotic effects of swelling pressure. In a pair of papers, Moyne and Murad derived a set of averaged equations which depend on both the microscale and the mesoscale (see [33], [34]). Their model begins with the assumption of a periodic structure over which the microscale quantities can be averaged to arrive at bulk averages of each independent variable, and they show how their model can be consistent with a formulation based on Onsager relations. In a computational investigation of this model [34], they consider only the case of stratified fluid-clay material in parallel layers, whose geometry remains planar and parallel on the macroscale.

Our interest here is to develop a new mathematical approach to layered systems whose geometry depends on the macroscale and whose tortuosity is small. Our approach removes two geometric restrictions. First, we average over a canonical laminate-galley pair whose overall spacing may be an unknown to be solved in the problem and which may vary spatially on the mesoscale. In order to close the homogenization portion of the analysis, we require a physical conservation principle to hold over the typical laminate-galley pair. Second, we consider the anisotropy of the material ab initio in the analysis, which simplifies the model significantly and allows for the inclusion of nonlinear effects in the flow direction which are comparable to the effective behavior on the macroscale. This approach allows us to solve the fundamental physical equations on the fine scale for predictable geometries and is a complementary approach to developing effective medium models based on the statistical properties of the underlying porous media (see, e.g., [12] and [15]).

Lubrication theory has been used for over a century to find effective models of
physical systems where the aspect ratio is large. Reynolds [36] originally developed a differential equation for the pressure field between a slider bearing moving parallel to a substrate. In this case, the nonuniform spacing between the bearing and the substrate is much smaller than the width of the bearing. This observation allows a decoupling of the scales across the fluid film from those in the direction of the bearing motion. From this decoupling, Reynolds was able to optimize the attack angle of the bearing in order to maximize the load the fluid film could carry, hence reducing the effective coefficient of friction between the bearing and the substrate. The fundamentals to this approach, called lubrication theory, have been used to great effect in air bearings, which are critical for the operation of computer hard-disk drives [45], along with general applications and extensions [35], [40].

By reducing the number of spatial dimensions to investigate in the full problem, the complexity of the mathematical modeling is significantly reduced. This reduction allows us flexibility to include additional physical effects that would otherwise be prohibitive. Examples can be found in a wide variety of problems, including electrokinetic mixing in thin channels [39], electric field effects on thin fluid sheets [42, 37], and microwave heating of laminate panels [21].

We apply lubrication theory to consider the transport of charge through an array of nearly parallel laminates whose spacing, called the galley, is nonuniform. These geometries have been of interest in determining geometry modes to induce mixing for lab-on-a-chip applications (see [22]). This model system provides a simple framework to isolate the competition between electroosmotic effects and electrophoresis effects. These effects necessarily compete in the removal of either the cations or the anions, and it is of interest to understand under what operating conditions this competition inhibits the remediation process. Our approach determines that there is a potential for charge accumulation within the matrix, and this depends on the dielectric ratio between the laminate and the fluid, the charge mobility in the pore, and the maximum variation of the pore spacing. We find that the local geometry can induce competition between electroosmotic and electrophoresis effects on charge distribution. Further, pore spacing variations spanwise to the flow can give rise to fringe electric fields that then lead to localized regions of increased conductivity.

The remainder of the paper consists of the derivation of the effective model equations for ion concentrations, electric potential, and fluid pressure over the longest length scales in section 2. We investigate the solutions of this system of equations over one spatial dimension, where variation of the matrix depends only on the flow direction in section 3, along with examples of the charge behavior when variations of the matrix over both spatial variables are pertinent. We conclude our paper in section 4.

2. Model derivation. Consider the problem shown in Figure 2.1. Two rigid laminates, whose midlines are spaced a distance of order \( H \) apart, surround a galley spacing filled with a Newtonian liquid. We consider the transport of ion species through this medium, which depends on the evolution of the fluid flow and the electric potential. We assume that the laminates are charge-free, for simplicity, and the resulting equation for the electric potential \( E^* = -\nabla \Phi^* \) is given by Gauss’s law

\[
\nabla \cdot \{ \varepsilon_s \nabla \Phi^* \} = 0,
\]

where \( \varepsilon_s \) is the dielectric constant of the laminate.

In the liquid, the velocity \( \mathbf{v}^* = (v_x^*, v_y^*) \) is governed by the following Navier–Stokes equations with additional stresses due to the presence of the charged particles in the
Fig. 2.1. Schematic of problem formulation. Ion species are in the fluid between thin, closely spaced laminates. An applied electric field is imposed in the direction along the laminate axes. The characteristic length scale in $x$ is on the order of centimeters, while that of $z$ is in microns. Debye electric double layers exist along each of the laminate-fluid boundaries.

galley region:

\[
\nabla \cdot \mathbf{v}^* = 0,
\]

\[
\rho_i \frac{D\mathbf{v}^*}{Dt^*} = -\nabla p^* + \rho_i \mathbf{g} + \mu_i \nabla^2 \mathbf{v}^* - \rho_E^* \nabla \Phi^*,
\]

\[
\epsilon_i \nabla^2 \Phi^* = -\rho_E^*,
\]

\[
\frac{DC_{1}^{*}}{Dt^*} = -\nabla \cdot \mathbf{J}_{1}^{*},
\]

\[
\frac{DC_{2}^{*}}{Dt^*} = -\nabla \cdot \mathbf{J}_{2}^{*},
\]

where $\rho_i$ is the fluid density, $\mu_i$ is the dynamic viscosity of the liquid, $\mathbf{g} = (0, -g)$ is the gravitational vector, $\rho_E^* = z_1 F C_1^* + z_2 F C_2^*$ is the charge density, $\epsilon_i$ is the dielectric constant of the liquid, $C_1^*$ is the cation concentration, $C_2^*$ is the anion concentration with respective valences $z_1$, $z_2$, and $F$ is Faraday’s constant. The fluxes $\mathbf{J}_{1,2}^{*}$ of the ionic concentrations are given by

\[
\mathbf{J}_{1,2}^{*} = -D_{1,2} \nabla C_{1,2}^{*} + z_{1,2} k_{1,2} e C_{1,2}^{*} \nabla \Phi^*,
\]

where $z_{i}$ are their respective valences, $D_{i} = k_{B} T k_{i}$ is the diffusion coefficient for each concentration, $N_a$ is Avogadro’s number, $k_{B}$ is Boltzmann’s constant, $T$ is the uniform temperature, $k_{1,2}$ is the ion mobility for each ion concentration, and $e$ is the elementary electron charge. For simplicity, we shall assume that $D_1 = D_2 = D$ and $k_1 = k_2 = k$ in the following analysis.
We prescribe no current across the laminate-fluid interfaces \( y^* = -h_1^*(x^*, t^*) \), \( y^* = h_2^*(x^*, t^*) \), continuity of the tangential component of the electric field, no fluid penetration from the galley into the laminates, and that the tangential fluid velocity is driven by electrokinetics

\[
\dot{J}_j^* \cdot \mathbf{n}_j = 0,
\]
\[
[E^* \cdot t_j]|_s = 0,
\]
\[
[v^* \cdot \mathbf{n}_j]|_s = 0,
\]
where \( \mathbf{n}_j \) denotes the normal vector pointing into the laminate at \( y^* = (-1)^j h_j^*(x^*, t^*) \), \( t_j \) is the analogous tangential vector along each surface, whose \( x^* \)-component is positive, and \([f]|_s^*\) is the difference of the quantity \( f \) from the liquid \( l \) to the solid \( s \). On the macroscale, pressure and electric potential differences can be applied, and these differences are the driving forces for flow and ion transport through the medium. We shall return to this point after our derivation of the effective equations.

The goal of this local analysis is to determine the net jump in the voltage potential over \( y^* = -h_3^* \) to \( y^* = h_4^* \), and to see the net effect over the larger scale \( L \), which is comparable to the pore length in Figure 2.1. The asymptotic approach used here is homogenization combined with lubrication theory, where we assume that all of the dependent variables depend on one “long” horizontal variable \( x_1 = x^* / L \), and on one “short” vertical variable \( x_2 = y^* / L \) and \( y = y^* / H \), respectively.

We introduce the following nondimensionalization:

\[
x_1 = \frac{x^*}{L}, \quad y = \frac{y^*}{H}, \quad x_2 = \frac{y^*}{L}, \quad h_1 = \frac{h_1^*}{H}, \quad h_2 = \frac{h_2^*}{H}, \quad v_x = \frac{v_x^*}{V},
\]

where

\[
V = \frac{\rho_l L}{\mu}, \quad v_y = \frac{\delta \frac{v_y^*}{V}}, \quad p = \frac{p^*}{P}, \quad P = \frac{\mu^2}{\rho_l H^2}, \quad t = \frac{t^*}{\tau}, \quad \tau = \frac{\rho_l L^2}{\mu},
\]

\[
\Phi = \frac{\Phi^*}{\Phi_0}, \quad \rho_e = \frac{\rho_e^*}{\Delta C_o}, \quad c_1 = \frac{C_1^*}{C_o}, \quad c_2 = \frac{C_2^*}{C_o},
\]

where \( \delta = H / L \ll 1 \).

Gauss’s law in the laminate becomes

\[
\frac{\partial^2 \Phi}{\partial y^2} + 2\delta \frac{\partial \Phi}{\partial y \partial x_2} + \delta^2 \left\{ \frac{\partial^2 \Phi}{\partial x_1^2} + \frac{\partial^2 \Phi}{\partial x_2^2} \right\} = 0.
\]

The problem in the liquid becomes

\[
\frac{\partial v_x}{\partial x_1} + \frac{\partial v_y}{\partial y} + \delta \frac{\partial v_y}{\partial x_2} = 0,
\]

\[
\delta^2 \frac{\partial^2 v_x}{\partial t^2} = -\frac{\partial \rho}{\partial x_1} + \frac{\partial^2 v_x}{\partial y^2} + 2\delta \frac{\partial v_y}{\partial y \partial x_2} + \delta^2 \left\{ \frac{\partial^2 v_x}{\partial x_1^2} + \frac{\partial^2 v_y}{\partial x_2^2} \right\} - E \rho_e \frac{\partial \Phi}{\partial x_1},
\]

\[
\delta^2 \frac{\partial^2 v_y}{\partial t^2} = -\frac{\partial \rho}{\partial y} - \delta \frac{\partial \rho}{\partial x_2} - \delta G a + \delta^2 \left\{ \frac{\partial^2 v_y}{\partial y^2} + 2\delta \frac{\partial v_x}{\partial y \partial x_2} + \delta^2 \left[ \frac{\partial^2 v_y}{\partial x_1^2} + \frac{\partial^2 v_y}{\partial x_2^2} \right] \right\} - E \rho_e \left[ \frac{\partial \Phi}{\partial y} + \epsilon \frac{\partial \Phi}{\partial x_2} \right],
\]
If we assume that the solution in the galley is close to electroneutrality, then let
\[
\frac{\partial^2 \Phi}{\partial y^2} + 2\delta \frac{\partial^2 \Phi}{\partial y \partial x_2} + \delta^2 \left\{ \frac{\partial^2 \Phi}{\partial x_1^2} + \frac{\partial^2 \Phi}{\partial x_2^2} \right\} = -\frac{\Delta C_o H^2}{\epsilon_l \Phi_0} \rho_c,
\]
\[
\delta^2 S_c \frac{D c_i}{D t} = -\nabla \cdot J_i,
\]
where \(\nabla = \delta \partial_{x_1} i + [\partial_y + \delta \partial_{x_2}] j\), and the current density \(J_i\) is defined by
\[
J_i = -\left( \frac{\delta \partial c_i}{\partial y} + \delta z_i c_i M \frac{\partial \Phi}{\partial x_1} + \delta \left[ \frac{\partial c_i}{\partial x_2} + z_i c_i M \frac{\partial \Phi}{\partial x_2} \right] \right),
\]
\(Ga = \rho_l^2 g H^2 L / \mu_l^2\) is the Galileo number, or, a measure of hydrostatic forces to fluid viscous forces, \(E = \Delta C_o \Phi_o \rho_l H^2 / \mu_l^2\) measures the applied electric field strength, \(S_c = \mu_l / (\rho_l D)\) is the Schmidt number, and \(M = \Phi_o e / (k_B T)\) is the ion mobility.

We begin the analysis by applying the divergence theorem to (2.15) in the fluid, with \(J_i \cdot n_j = 0,^1\) along each interface to find that
\[
\int_{-h_1}^{h_2} \delta^2 S_c \frac{D c_i}{D t} dy = -\delta \frac{\partial}{\partial x_1} \int_{-h_1}^{h_2} J_i \cdot i dy,
\]
which, after we balance the leading-order terms in powers of \(\delta\), gives
\[
S_c \left\{ \frac{\partial c_i}{\partial t} + \bar{v}_x \frac{\partial c_i}{\partial x_1} \right\} = \frac{1}{h} \frac{\partial}{\partial x_1} \left\{ h \left[ \frac{\partial c_i}{\partial x_1} + z_i M c_i \frac{\partial \Phi}{\partial x_1} \right] \right\},
\]
where \(\bar{v}_x\) is the depth averaged \(x\)-component of the fluid velocity, and \(h = h_1 + h_2\) is the net galley spacing, or the local volume fraction of the fluid.

Next, we apply the divergence theorem on Gauss's law (2.14) in the fluid region, noting that there is a vertical component of the electric field in each laminate. Using the nondimensional version of (2.8) and noting that to leading order in \(\delta\), \(\rho_e\) is independent of \(y\), we find that
\[
\epsilon \left[ A^{(2)} - A^{(1)} \right] = -\left\{ \delta^2 \frac{\partial}{\partial x_1} \left\{ h \frac{\partial \Phi}{\partial x_1} \right\} + h \frac{\Delta C_o H^2}{\epsilon_l \Phi_0} \rho_c \right\},
\]
where \(A^{(2)} = \partial \Phi / \partial y\) in the upper laminate while \(A^{(1)} = \partial \Phi / \partial y\) in the lower laminate. If we assume that the solution in the galley is close to electroneutrality, then let \((\Delta C_o H^2 / (\epsilon_l \Phi_0)) = O(\delta^2)\), which chooses our difference concentration scale
\[
\Delta C_o = \frac{\epsilon_l \Phi_0}{L^2}.
\]
This limits the validity of the analysis to the electric field strength in the \(y\)-direction also to \(O(\delta^2)\). This implies that to leading order in \(\delta\), \(\partial \Phi / \partial y = 0\), or, from the \(y\)-component of the momentum equation (2.14), that \(\partial p / \partial y = 0\) to leading order in \(\delta\). Electroneutrality has not been imposed based on this choice, and in general will not hold for the solutions of the final model.

This choice of \(\Delta C_o\), then fixes our electric field strength parameter \(E = (\epsilon_l \Phi_0^2 \rho_l / \mu_l^2) \delta^2\). In electrokinetic mixing applications (e.g., [39]), this coefficient is unit order, which corresponds to large electric field strengths (10⁴ V/cm). However, in bioremediation

\(^1i\) denotes which ion, and \(j\) denotes the interface.
applications, the field strengths are considerably smaller (1 V/m). We formally continue with our modeling assuming that $E = O(1)$, although recognizing that its value may still be small depending on the application. All of our results in section 3 assume that $E = O(\delta^2)$.

We apply homogenization theory on the electric field to close (2.17). The equations to be considered on $-h_3 < y < h_2$ are

$$
\epsilon \left\{ \frac{\partial^2 \Phi}{\partial y^2} + 2\delta \frac{\partial^2 \Phi}{\partial y \partial x_2} + \delta^2 \nabla^2 \Phi \right\} = 0, \quad -h_3 < y < -h_1, 
$$

$$
\frac{\partial^2 \Phi}{\partial y^2} + 2\delta \frac{\partial^2 \Phi}{\partial y \partial x_2} + \delta^2 \nabla^2 \Phi = -\delta^2 \rho_e, \quad -h_1 < y < h_2, 
$$

where $\nabla^2 \Phi$ is the Laplacian operator over the macro length scales $x_1, x_2$. Equations (2.18), (2.19) are subject to the boundary conditions along $y = -h_1$:

$$
\left[ \frac{\partial \Phi}{\partial x_1} + \frac{\partial \Phi}{\partial y} - \delta \frac{\partial \Phi}{\partial x_2} \frac{\partial h_1}{\partial x_1} \right]_s^l = 0, 
$$

$$
\left[ \epsilon \left\{ \frac{\partial \Phi}{\partial y} + \epsilon \frac{\partial \Phi}{\partial x_2} + \delta^2 \frac{\partial \Phi}{\partial x_1} \frac{\partial h_1}{\partial x_1} \right\} \right]_s^l = 0. 
$$

In place of imposing periodicity in $x_2$, we use the additional constraint that the normal component of the electric field is continuous over each laminate-galley pair

$$
\nabla \Phi \cdot n \big|_{y = h_2} = \epsilon \nabla \Phi \cdot n \big|_{y = -h_3}. 
$$

We expand the electric potential $\Phi$ in a power series in $\delta$,

$$
\Phi = \Phi^{(0)} + \delta \Phi^{(1)} + \cdots, 
$$

and solve the subsequent problems in powers of $\delta$. At leading order we find that

$$
\frac{\partial^2 \Phi^{(0)}}{\partial y^2} = 0
$$

in the liquid and solid. In the cases that we are considering for the ionic concentrations $c_1$ and the fluid motion, we assume that $\partial \Phi^{(0)}/\partial y = 0$ in each phase. This gives that the leading-order electric potential is the same in both layers, and is of the form

$$
\Phi^{(0)} = \Phi^{(0)}(x_1, x_2, t).
$$

At next order, we find that

$$
\frac{\partial^2 \Phi^{(1)}}{\partial y^2} = 0,
$$

with boundary conditions along $y = -h_1$,

$$
\left[ \frac{\partial \Phi^{(1)}}{\partial x_1} + \left( \frac{\partial \Phi^{(1)}}{\partial y} + \frac{\partial \Phi^{(0)}}{\partial x_2} \right) \frac{\partial h_1}{\partial x_1} \right]_s^l = 0, 
$$

$$
\left[ \epsilon \left\{ \frac{\partial \Phi^{(1)}}{\partial y} + \frac{\partial \Phi^{(0)}}{\partial x_2} \right\} \right]_s^l = 0.
$$
The homogenization requirement (2.22) on the electric field gives that
\[
\frac{\partial \Phi^{(1)}}{\partial y} = -\frac{\partial \Phi^{(0)}}{\partial x_2},
\]
and the continuity of the potential condition (2.20) gives that
\[
\Phi^{(1)} = -y \frac{\partial \Phi^{(0)}}{\partial x_2} + \beta(x_1, x_2, t).
\]
Note that since the electric problem is linear in \(\Phi\), \(\beta\) above can be included in the leading-order term \(\Phi^{(0)}\), and we set \(\beta = 0\) below.

At \(O(\delta^2)\), the equations for \(\Phi^{(2)}\) are
\[
\epsilon \left\{ \frac{\partial^2 \Phi^{(2)}}{\partial y^2} + 2 \frac{\partial^2 \Phi^{(1)}}{\partial y \partial x_2} + \nabla^2 \Phi^{(0)} \right\} = 0,
\]
\[
\frac{\partial^2 \Phi^{(2)}}{\partial y^2} + 2 \frac{\partial^2 \Phi^{(1)}}{\partial y \partial x_2} + \nabla^2 \Phi^{(0)} = -\rho_e,
\]
subject to the boundary conditions at \(y = -h_1\),
\[
\left. \left[ \frac{\partial \Phi^{(2)}}{\partial x_1} - \frac{\partial \Phi^{(2)}}{\partial y} - \frac{\partial \Phi^{(1)}}{\partial x_2} \frac{\partial h_1}{\partial x_1} \right] \right|_t = 0,
\]
\[
\left. \left[ \epsilon \left\{ \frac{\partial \Phi^{(2)}}{\partial y} + \frac{\partial \Phi^{(1)}}{\partial x_2} + \frac{\partial \Phi^{(0)}}{\partial x_1} \right\} \right] \right|_t = 0,
\]
along with the homogenization condition
\[
\left. \frac{\partial \Phi^{(2)}}{\partial y} + \frac{\partial \Phi^{(1)}}{\partial x_2} - \frac{\partial \Phi^{(0)}}{\partial x_1} \frac{\partial h_2}{\partial x_1} \right|_{y=h_2} = \epsilon \left\{ \frac{\partial \Phi^{(2)}}{\partial y} + \frac{\partial \Phi^{(1)}}{\partial x_2} + \frac{\partial \Phi^{(0)}}{\partial x_1} \frac{\partial h_3}{\partial x_1} \right\} \bigg|_{y=-h_3}.
\]
Since we are interested in a compatibility condition for \(\Phi^{(0)}\), we can integrate (2.25) and (2.26) over their respective domains in \(y\) to find that
\[
\epsilon \left. \frac{\partial \Phi^{(2)}}{\partial y} \right|_{-h_3}^{-h_1} + \left. \frac{\partial \Phi^{(2)}}{\partial y} \right|_{-h_1}^{h_2} + 2 \epsilon \left. \frac{\partial \Phi^{(1)}}{\partial x_2} \right|_{-h_3}^{-h_1} + 2 \left. \frac{\partial \Phi^{(1)}}{\partial x_2} \right|_{-h_1}^{h_2} + \{\epsilon [h_3 - h_1] + (h_2 + h_1)\} \nabla^2 \Phi^{(0)} + (h_2 + h_1) \rho_e = 0.
\]
We find the following effective equation for the voltage potential \(\Phi^{(0)}\) (we drop the superscript notation):
\[
\frac{\partial}{\partial x_1} \left\{ \epsilon \frac{\partial \Phi}{\partial x_1} \right\} + 4 \epsilon \frac{\partial^2 \Phi}{\partial x_2^2} = -h \rho_e,
\]
where \(\epsilon = \epsilon [h_3 - h_1] + h\) is the local effective dielectric value of the homogenized material. Note that this local operator is not isotropic.

With this result, we look at the \(x\)-momentum equation (2.12), to leading order in \(\delta\),
\[
\frac{\partial^2 v_x}{\partial y^2} = \frac{\partial p}{\partial x_1} + E \rho_e \frac{\partial \Phi}{\partial x_1}.
\]
This has to be evaluated with the electrokinetic boundary condition $v_x = -Z \frac{\partial \Phi}{\partial x_1}$ along $y = -h_1$, $y = h_2$, where $Z = (\epsilon_1 \rho_1 \zeta \Phi_o) / (\mu^2)$ is the ratio of the electroosmotic velocity to the viscous velocity scale. Since the right-hand side of (2.32) is independent of $y$, utilizing the no-slip boundary conditions along the galley walls yields

$$ v_x = \frac{1}{2} \left\{ \frac{\partial p}{\partial x_1} + E \rho_e \frac{\partial \Phi}{\partial x_1} \right\} (y + h_1)(y - h_2) - Z \frac{\partial \Phi}{\partial x_1}. \tag{2.33} $$

Requiring incompressibility in the galley and imposing zero normal velocity along the galley walls, we find the following Reynolds equation for $p$:

$$ \frac{1}{12} \frac{\partial}{\partial x_1} \left\{ h^3 \left\{ \frac{\partial p}{\partial x_1} + E \rho_e \frac{\partial \Phi}{\partial x_1} \right\} \right\} = -hZ \frac{\partial^2 \Phi}{\partial x_1^2}. \tag{2.34} $$

In summary, we need to solve the following equations for the ionic concentrations $c_1, c_2$, the electric potential $\Phi$, and the pressure $p$:

$$ Sc \left\{ \frac{\partial c_1}{\partial t} + \bar{v}_x \frac{\partial c_1}{\partial x_1} \right\} = \frac{1}{h} \frac{\partial}{\partial x_1} \left\{ h \left[ \frac{\partial c_1}{\partial x_1} + z_1 M c_1 \frac{\partial \Phi}{\partial x_1} \right] \right\}, \tag{2.35} $$

$$ Sc \left\{ \frac{\partial c_2}{\partial t} + \bar{v}_x \frac{\partial c_2}{\partial x_1} \right\} = \frac{1}{h} \frac{\partial}{\partial x_1} \left\{ h \left[ \frac{\partial c_2}{\partial x_1} + z_2 M c_2 \frac{\partial \Phi}{\partial x_1} \right] \right\}, \tag{2.36} $$

$$ \frac{\partial}{\partial x_1} \left\{ h \frac{\partial \Phi}{\partial x_1} \right\} + 4 \epsilon_2 \frac{\partial^2 \Phi}{\partial x_1^2} = -h \rho_e, \tag{2.37} $$

$$ \frac{1}{12} \frac{\partial}{\partial x_1} \left\{ h^3 \left\{ \frac{\partial p}{\partial x_1} + E \rho_e \frac{\partial \Phi}{\partial x_1} \right\} \right\} = -hZ \frac{\partial^2 \Phi}{\partial x_1^2}. \tag{2.38} $$

where

$$ \bar{v}_x = h^2 \left[ \frac{\partial p}{\partial x_1} + E \rho_e \frac{\partial \Phi}{\partial x_1} \right] + Z \frac{\partial \Phi}{\partial x_1}. $$

To gain an understanding of the results of this model, we consider the problem on a strip $-1 < x_1 < 1$ and $-1 < x_2 < 1$. Equations (2.35)–(2.38) are solved subject to Neumann boundary conditions on the ion concentrations $c_1, c_2$ and prescribed pressure and electric potentials along $x_1 = \pm 1$:

$$ \frac{\partial c_i}{\partial x_1} = 0, \quad i = 1, 2, \tag{2.39} $$

$$ p = 0, \tag{2.40} $$

$$ \Phi = \mp 1. \tag{2.41} $$

Note that the boundary conditions in the $x_2$-direction are needed only on the electric potential problem, and for simplicity we take Neumann boundary conditions at $x_2 = \pm 1$:

$$ \frac{\partial \Phi}{\partial x_2} = 0. \tag{2.42} $$
3. Results. We are concerned with understanding the limitations of using electric fields in charge transport in soils, and we consider this context in our application of the model. For the soil applications of interest, electric body forces acting on the fluid are small \( E = 0 \), electrodiffusion effects are significant \( M \approx 10 \), but on the viscous time-scale, advective effects induced by electroosmosis are comparable \( ScZ \approx 5 \). We focus on these two effects in the results below.

The competition between electroosmosis and electrophoresis is pertinent in galleys that are spatially uniform. Since the laminates are pure dielectrics, charge can only move through the fluid. The phenomena governing charge transport are diffusion, electrodiffusion, and electroosmosis. If there is no fluid flow (i.e., electroosmotic flows are zero), then the presence of an applied electric field results in positive charges being attracted to the anode, and the negative charges attracted to the cathode. In this way the ion species are removed. When electroosmosis effects are included, the advective and electrodiffusive effects would act in concert to aid transport of one charge species, and in competition for the other species. Further, the effect of spatial variation in the local porosity varies the local electric field due to the spatial variation of the dielectric constant in (2.37).

3.1. One-dimensional model. To understand how spatially varying porosity \( h \) can affect the charge transport in this system, let us consider solutions that are independent of \( x_2 \). To clarify the phenomenon, we present our results in terms of conductivity and charge density:

\[
\sigma = c_1 + c_2, \quad \rho_e = c_1 - c_2,
\]

so \( \sigma \to 0 \) implies that all charge is removed from the galley.

We apply pseudospectral methods in space using Chebyshev polynomials and march in time using a Crank–Nicolson discretization linearized about the solution at the previous time step. This scheme is spectrally accurate in space and second-order accurate in time. Richardson extrapolation is then used at each time step to ensure that local relative time-step errors in the solution are kept within a specific tolerance, typically on the order of \( 10^{-7} \). Results from this scheme have been checked with the small amplitude results in the following subsection, along with the code used for the two-dimensional simulation on problems with one-dimensional behavior. The parameter values are chosen to mimic the ex situ experimental conditions found in electrokinetic remediation processes; however, we assume that the ions found in our system are monovalent \(|z_i| = 1\). Note that a direct comparison of these effective values from our model and experimental measurements is not experimentally feasible. Most experiments measure average values of ion concentrations and flow rates over the entire experimental domains. The results shown below are qualitatively in agreement with the trends in these experiments, but without knowledge of the fine scale geometry, a direct comparison is not possible.

The geometry was chosen to be of the form

\[
h = \bar{h} + \Delta h \cos \left( k_x \pi \left( \frac{x_1 + 1}{2} \right) \right),
\]

where \( k_x \) is an integer. We chose \( \bar{h} = 0.25 \) as an initial value, vary \( \Delta h \), and set \( k_x = 2 \) in the cases considered below. We assume that the laminate layers were of unit thickness.
Fig. 3.1. Long-term spatial profiles (solid curves) of the conductivity (upper left), charge density (upper right), deviation electric potential (lower left), and pressure (lower right) for $\Delta h = 0.02$, $M = 10$, $Z = 0.005$, $Sc = 1000$, $E = 0$ and (a) $k_x = 2$, (b) $k_x = 5$. Note that the conductivity and charge-density plots are relative to the spatial mean, which is time dependent. Profiles with dashed-dotted lines denote the initial profiles of the respective quantity.

We assumed that the initial voltage potential and pressure were the same as the uniform thickness profiles $\Phi = -x_1$ and $p = 0$. For the ion concentrations, we prescribe the initial conditions

$$c_i = c_o + \Delta c \sin \left(\frac{\pi x_1}{2}\right), \quad i = 1, 2, \quad t = 0,$$

implying that the system is initially electrically neutral.

Figures 3.1 and 3.2 outline the evolution of the conductivity $\sigma$, the charge density $\rho$, the electric potential $\Phi$, and the pressure $p$. Note in Figure 3.1 that after the initial profile denoted by the solid curve, the profiles relative to their spatial means remain fixed over time. The conductivity shows the competition between electroosmosis, which would like to move charge to the right and electrophoresis, which would like to move negative charge to the left. Similarly, from the charge-density plot in Figure 3.1, we note that anions prefer to be near the cathode $x = -1$ due to electrophoresis, and the anode $x = 1$ due to advection from electroosmosis.
Although the spatial profiles of the conductivity and charge density do not change with respect to their mean, the mean does evolve over time. Figure 3.2 shows the evolution of the spatial average of the conductivity (Figure 3.2(a)) and the charge density (Figure 3.2(b)). Note that the change in time appears linear in time for the conductivity, and is nearly zero for the evolution of the charge density. This evolution is algebraic in time and does not correspond to the exponential transients that are observed in standard diffusion processes. Algebraic evolution in time is significantly slower than exponential evolution, and a better understanding as to the physical mechanisms for this result is warranted.

3.1.1. Small amplitude galley variations. Note that the computational results yield solutions whose mean conductivity varies linearly in time, while the mean charge density remains constant. Further, the spatial variation of the potential, the conductivity, and the charge density appear to be stationary with respect to their mean values. To gain insight for the mechanisms which lead to these solutions, we consider solutions for small pore variations $\Delta h/\bar{h} \ll 1$. If we linearize our solutions

Fig. 3.2. (a) Average conductivity in sample as a function of time $t$ for different pore amplitude variations $\Delta h$; (b) average charge density in sample as a function of time $t$ for different pore amplitude variations $\Delta h$; (c) average conductivity in sample as a function of time for different pore amplitudes and $k_x = 5$; and (d) average charge density in sample as a function of time for different pore amplitudes. Other parameters are the same as in Figure 3.1.
about constant conductivity, electroneutrality, and electric field strength, then

\[ \sigma = \sigma_o + \frac{\Delta h}{h} \sigma_1, \quad \rho_e = \frac{\Delta h}{h} \rho_{e,1}, \quad \Phi = -x_1 + \frac{\Delta h}{h} \Phi_1, \quad \tilde{\epsilon} = \tilde{\epsilon}_o + \frac{\Delta h}{h} \tilde{\epsilon}_1. \]

Note that the correction to the pressure field depends solely on the correction to the electric potential. Since our concern is understanding the evolution of the corrections to the conductivity, charge density, and the base velocity field \( \tilde{v}_x = Z \, Sc \) in this limit, the pressure does not play a role in the evolution.

Substituting these assumptions into the full system and neglecting terms that scale quadratically with \( \Delta h/h \), we find that

\[
(3.3) \quad Sc \frac{\partial \sigma_1}{\partial t} + Z \, Sc \frac{\partial \sigma_1}{\partial x_1} = \frac{\partial^2 \sigma_1}{\partial x_1^2} - M \frac{\partial \rho_{e,1}}{\partial x_1}, \\
(3.4) \quad Sc \frac{\partial \rho_{e,1}}{\partial t} + Z \, Sc \frac{\partial \rho_{e,1}}{\partial x_1} = \frac{\partial^2 \rho_{e,1}}{\partial x_1^2} - M \frac{\partial \sigma_1}{\partial x_1} + M \left[ \sigma_o \left( \frac{\partial^2 \Phi_1}{\partial x_1^2} - \frac{\partial h_1}{\partial x_1} \right) \right], \\
(3.5) \quad \tilde{\epsilon} \frac{\partial^2 \Phi_1}{\partial x_1^2} - \frac{\partial \Theta_1}{\partial x_1} = -h \rho_{e,1},
\]

subject to the boundary conditions \( \partial \sigma_1/\partial x_1 = 0 \), \( \partial \rho_{e,1}/\partial x_1 = 0 \), and \( \Phi_1 = 0 \) on \( x_1 = \pm 1 \). The system (3.3)–(3.5) consists of two inhomogeneous terms. In (3.4), the inhomogeneity arises in gradients in electrophoresis due to changes in the pore shape, while in (3.5), fringe electric fields are induced due to spatial variations in the dielectric constant. These are the two physical effects that can lead to either charge removal or charge accumulation in this regime.

Note that we can use (3.5) to substitute for \( \Phi_1 \) in (3.4), which then leads to the following coupled system for \( \sigma_1, \rho_{e,1} \):

\[
(3.6) \quad Sc \frac{\partial \sigma_1}{\partial t} + Z \, Sc \frac{\partial \sigma_1}{\partial x_1} = \frac{\partial^2 \sigma_1}{\partial x_1^2} - M \frac{\partial \rho_{e,1}}{\partial x_1}, \\
(3.7) \quad Sc \frac{\partial \rho_{e,1}}{\partial t} + Z \, Sc \frac{\partial \rho_{e,1}}{\partial x_1} = \frac{\partial^2 \rho_{e,1}}{\partial x_1^2} - M \frac{\partial \sigma_1}{\partial x_1} - M \sigma_o \left\{ \frac{\tilde{h}}{\tilde{\epsilon}_o} \rho_{e,1} + \frac{\partial h_1}{\partial x_1} - \frac{1}{\tilde{\epsilon}_o} \frac{\partial \Theta_1}{\partial x_1} \right\}.
\]

It is interesting to note here that if \( \sigma_1, \rho_1 \) are periodic on \( x_1 \), then their spatial averages do not vary in time. This, however, is not the behavior that we have seen in Figures 3.1 and 3.2, on which Neumann boundary conditions are applied. Thus we subject to the Neumann conditions \( \frac{\partial \sigma_1}{\partial x_1} = \frac{\partial \rho_{e,1}}{\partial x_1} = 0 \) along \( x_1 = \pm 1 \).

From the computational results, we are looking for long-time solutions of the form

\[ \sigma_1 = \bar{\sigma}(t) + \tilde{\sigma}(x), \quad \rho_{e,1} = \bar{\rho}(t) + \tilde{\rho}(x), \]

where \( \tilde{\sigma}, \tilde{\rho} \) have zero mean in space. The goal of the following is to understand how the pore variation conditions in (3.7) affect the rate of growth of the corrections in the mean conductivity and charge density \( \bar{\sigma}, \bar{\rho} \). In order for the assumption (3.8) to hold, we need that \( \bar{\rho} \) is constant and \( \bar{\sigma}(t) = At \). With these prescriptions, (3.6), (3.7) is a well-posed boundary-value problem for \( \bar{\sigma}, \bar{\rho} \). The zero-mean conditions of these functions then give compatibility conditions to find \( \bar{\rho}, A \).

The benefit of this small-amplitude approach is to perform parameter studies on the potential for charge accumulation in this problem. For example, we can efficiently determine the algebraic growth or decay of the mean of the conductivity as a function of advection (measured using the mean electroosmotic flow speed \( Z \, Sc \)) and
electrophoresis, measured by the parameter $M$. In Figure 3.3, we show the contour plots of the slope of the mean conductivity growth or decay in time in the $M, Z Sc$ parameter space. Notice that in Figure 3.3(a), the mean conductivity decays for any of the parameter values, although the net charge is removed at different rates. However, in Figure 3.3(b), we note that there are values below a critical value of $M$ for each $Z Sc$, where the conductivity growth increases on average over time. This conductivity growth suggests that cations cannot be removed on average, since electroosmosis and electrophoresis balance. The presence of the excess charge modifies the electric potential, and allows for the attraction, locally in the space of anions, to maintain a fixed average charge density.

### 3.1.2. Larger amplitude pore variations.

When $\Delta h/\bar{h}$ is sufficiently large, the analysis from section 3.1.1 ceases to be valid, and we need to rely on computational approaches. The parameter space to be examined, even in this simplified model, is much too large to consider in full detail. However, we explain here how the small-amplitude results are modified when the amplitude increases, and determine how the dynamics vary as the dielectric constant ratio $\epsilon$ is increased.

Note in Figure 3.2 that charge removal or accumulation in each of these cases does change as the amplitude $\Delta h$ increases. In Figures 3.2(a),(c), the growth rate of the average conductivity increases or decreases with pore variation amplitude. Further, the short-term transient of the charge density, as shown in Figures 3.2(c),(d), changes its sense from negative for $k_x = 2$ to positive for $k_x = 5$. The profiles of the disturbance electric potential shown in the lower right-hand figure in Figure 3.1 suggests that the charge accumulation is driven by a disturbance electric field that is polarized against the base-state field. This then biases the disturbance conductivity for the case of $k_x = 5$ in the opposite sense as that found in $k_x = 2$. This change in the relative growth rate can be seen in Figure 3.4, where we show the relative growth rate over the $(M, k_x)$ parameter space for $Z Sc = 5$.

However, this behavior is not uniform for all parameter values. In Figure 3.5, we show the evolution of the average conductivity for $\epsilon = 0.01$ with $k_x = 4$. Note that in the case $k_x = 4$, we are near the neutral charge removal curve from the small-amplitude analysis, and the charge removal of the conductivity depends on the
Fig. 3.4. Relative growth rate of the mean conductivity for $ZSc = 5$ in the $M, k$ parameter space. Notice that the spatial wavenumbers in a band between $4 < k_x < 9$ lead to mean conductivity growth over time.

Fig. 3.5. Average conductivity evolution near the neutral charge removal curve as $\Delta h$ increases for the parameter values in Figure 3.2 with $k_x = 4$. Notice that the increase in pore amplitude variation leads to net removal of charge in the sample.

amplitude $\Delta h$. For small $\Delta h$, the total amount of charge grows in the sample, while for larger $\Delta h$, this amount of charge decreases over time.

Limits on using electric fields to remove charge can be found when the laminate dielectric constant is sufficiently large. Figures 3.6(a),(b) show the change in the mean conductivity and charge density for the cases $k_x = 2$ and $M = 10$ with $\epsilon = 10$. In these cases, either the cation or anion concentrations are eliminated in the sample with a final distribution of the charge remaining. Profiles of these charge distributions are shown in Figures 3.7(a),(b) for the case $k_x = 2$ and $\Delta h = 0.02$.

3.2. Two-dimensional model. The results from section 3.1 provide a framework for understanding the behavior of the medium over two spatial dimensions. We note that the only change that incorporates $x_2$ is in the electric potential equation (2.37). To better understand how variations in the electric potential in the $x_2$-direction affect the charge distribution through the medium, we consider two different cases. Note that the small-amplitude analysis does not apply for pore variations in $x_2$. Due to this limitation, we have to use computational methods to investigate the behavior of (2.35)–(2.38) subject to boundary conditions (2.39)–(2.42).
As a first approximation, we considered pore structures that varied only in the \( x_2 \)-direction. We found in this case that the average conductivity decays to a uniform value. The initial ion concentrations are the same as those that were used in the one-dimensional study, with the only difference being the initial scaling \( (\bar{c}_i = 2) \). Figure 3.8 shows the time evolution of the average conductivity and its minimum value, and their evolution to the same value requires that the conductivity is uniform in the sample. Further, the charge density evolves to zero over the timeframe, suggesting that the sample is electrically neutral after the process.

In order to understand how the pore variation in both \( x_1 \) and \( x_2 \) affects the conductivity transients in the sample, we consider pore structures of the form

\[
h = \bar{h} + \Delta h \left\{ \cos \left( \frac{k_1 \pi (x_1 + 1)}{2} \right) \cos (k_2 \pi x_2) \right\},
\]

while \( c_i \) are chosen to be the same as those listed in (3.2).
GEOMETRY-DRIVEN CHARGE ACCUMULATION

Fig. 3.8. (a) Transient of conductivity over time for a sample whose pore spacing varies only in the $x_2$-direction. (b) Transient of the charge density. Note that the sample is electrically neutral at the end of the process and has a uniform electrical conductivity.

Fig. 3.9. $L_2$ norm of the (a) conductivity and (b) charge density for the case $\Delta h = 0.04$, with $\bar{h} = 0.25$, with $k_1 = k_2 = 2$, $\epsilon = 0.01$. The final distributions at $t = 5000$ of the (c) conductivity and (d) charge density are also shown. Note that the charge is removed in layers between regions with significantly large charge concentrations.

An example of the difference between the one- and two-dimensional pore variations is shown in Figure 3.9. Figures 3.9(a),(b) show that the average conductivity and
charge density vary significantly over time, while the minimum values of the charge density decays in this sample. An initial transient induced by electromigration is seen in the minimum values (dashed curve). However, the average conductivity (solid curve) gradually increases in the sample over time, while the average charge density is slowly reduced. Figures 3.9(c),(d) show the spatial distribution of the conductivity and charge density at time $t = 5000$, and accumulation of net charge is shown to occur in layers in $x_2$. Further, the magnitude of the amount of charge accumulation depends on the spatial variation of the pore spacing (see Figure 3.10). Larger amplitude variations in the geometry appear to lead to larger anion charge accumulations within the sample.

The mechanisms for the charge accumulation, however, are not readily apparent, but one explanation appears consistent over several simulations. While electroosmosis transports charge along the axes of the galley layers (in the $x_1$-direction), the $x_2$-component of the electric field can lead to charge transport that varies in $x_2$. To understand this, we note that the geometry varies the effective dielectric constant $\bar{\epsilon}$ in the $x_1$-direction. From Gauss’s law (2.37), the fringe electric field is driven by this geometric variation and the base electric field. The fringe field varies on $x_2$, and in locations where electroosmosis and electromigration from the base electric field compete, this fringe field can act to trap charge near these locations. Figure 3.11(a) shows a plot of the $x_2$-component of the electric field, and we notice that there are several locations where the field vanishes, but field lines converge at isolated points (e.g., near the values $(x_1, x_2) = (-0.45, \pm 0.45)$). Figure 3.11(b) shows the distribution of the electroosmotic velocity, and the minimum value of this velocity occurs near $(x_1, x_2) = (-0.45, \pm 0.45)$.

A second example looks at a pore distribution of the form

$$h = \bar{h} + \Delta h \left\{ \cos \left( \frac{k_1 \pi (x_1 + 1)}{2} \right) \cos \left( k_2 \pi x_2 \right) \right\}^2.$$  

This pore distribution allows for variations in both $x_1, x_2$, but the variations are in-phase. A case for $\Delta h = 0.04$ is shown in Figure 3.12, where we show the simulation after $t = 5000$ time units. Although it is not clear if net charge accumulation over the
Fig. 3.11. (a) $x_2$-component of the fringe electric field for the case described in Figure 3.9. 
(b) Electroosmotic velocity $\bar{v}_x$ as a function of $x_1, x_2$ at $t = 5000$ for the case described in Figure 3.9. Note that the maximum value of conductivity coincides with the points where the electroosmotic velocity is minimum and the $x_2$-component of the electric field is converging near $(x_1, x_2) \approx (-0.45, \pm 0.45)$.

![Image](a)

![Image](b)

Fig. 3.12. (a) Comparison of average and minimum conductivities for the pore distribution shown in (3.9). (b) Conductivity distribution at $t = 5000$. (c) $x_2$-component of the electric field. 
(d) Electroosmotic velocity at $t = 5000$. Note that the maximum values of conductivity coincide to where the focusing of the electric field occurs simultaneously with the minimum of electroosmotic velocity.

![Image](a)

![Image](b)

![Image](c)

![Image](d)
whole sample is possible, charge accumulates locally where the electric field in the \(x_2\)-direction focuses cations in the opposite sense of the transport due to electroosmotic flow.

**4. Conclusions.** We have derived a system of effective medium equations for the electrokinetic transport of charge through an array of rigid nonuniform laminates. The equations were derived based on the small aspect ratio between the typical laminate spacing and the variation over which this laminate spacing varies. This approach, a combination between lubrication theory and homogenization theory, allows for the inclusion of local nonlinear effects in the flow direction that are comparable to the dispersion effects found through homogenization. These equations suggest a build-up of charge due to small changes in local geometry driven by electroosmosis, electrophoresis, and the fringe electric field. The resulting equations are significantly simpler to solve computationally than the full physical system of equations over the same macroscale.

For media whose pore spacing varies only in the streamwise direction, a small-amplitude analysis of the evolution suggests that only specific ranges of wavenumbers are susceptible to charge accumulation. This range of wavenumbers depends on the strength of the applied electric field, the zeta-potential between the laminates and the fluid, and the mobility of charge within the fluid. However, this analysis breaks down when the medium’s pore spacing varies over two spatial dimensions. We have found instances when charge accumulation occurs in this case, when no charge accumulation takes place for pores that vary only over the streamwise coordinate. This suggests that the removal of charge from a specimen depends on the initial conductivity in the sample and the gradient of pore variation transverse to the flow direction. For sufficiently large gradients in this direction and sufficiently large initial charge, charge accumulation can occur. This phenomenon has been seen in practice (see, e.g., [23]) when absorption/desorption of the species in the matrix is small. To make extensions in these applications, the appropriate chemistry would need to be incorporated into this modeling framework.

We note that extending this particular model to three spatial dimensions on the macroscale can be performed directly, if the laminates are isotropic in the \((x_1, x_3)\) planes

\[
\begin{align*}
Sc \left\{ \frac{\partial c_i}{\partial t} + \bar{v}_{13} \cdot \nabla_{13} c_i \right\} &= \frac{1}{h} \nabla_{13} \cdot \left\{ h \nabla_{13} c_i + z_i M c_i \nabla_{13} \Phi \right\}, \\
\nabla_{13} \cdot \left\{ \epsilon \nabla_{13} \Phi \right\} + 4 \epsilon \frac{\partial^2 \Phi}{\partial x_{22}^2} &= -h \rho_e, \\
\frac{1}{12} \nabla_{13} \left\{ h^3 \left[ \nabla_{13} p + E \rho_e \nabla_{13} \Phi \right] \right\} &= -h Z \nabla_{13}^2 \Phi,
\end{align*}
\]

where \(\nabla_{13} = i \partial_{x_1} + k \partial_{x_3} \). Note that this formulation is not appropriate for pore spacing which varies on the fine scale, as is found in [44].

Finally, we note that this mathematical approach is amenable to many physical problems whose geometries possess these small aspect ratios. In particular, a future work will focus on utilizing this method in solving for the matrix shapes given constraints on the flow and stress in the effective medium.
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