Induced-charge electro-osmosis beyond weak fields

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Standard thin-double-layer modeling of electro-osmotic flows about metal objects typically predicts an induced zeta-potential distribution whose characteristic magnitude varies linearly with the applied voltage. At moderately large zeta potential, comparable with several thermal voltages, surface conduction enters the dominant electrokinetic transport, throttling that linear scaling. We derive here a macroscale model for induced-charge electro-osmosis accounting for that mechanism. Unlike classical analyses of surface conduction about dielectric surfaces, the present nonlinear problem cannot be linearized about a uniform-zeta-potential reference state. With the transition to moderately large zeta potentials taking place nonuniformly, the Dukhin number, representing the magnitude of surface conduction, is reinterpreted as a local dimensionless group, varying along the boundary. Debye-scale analysis provides effective boundary conditions about two types of generic boundary points, corresponding to small and moderate Dukhin numbers. The boundary decomposition into the respective asymptotic domains is unknown in advance and must be determined throughout the solution of the macroscale problem, itself hinging upon the proper formulation of effective boundary conditions. This conceptual obstacle is surmounted via introduction of a uniform approximation to these conditions.

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I. INTRODUCTION

A. Induced-charge electro-osmosis

Classical electrokinetic analyses typically consider dielectric solids on which the surface charge at the solid boundary is immobile [1]. Starting in the mid 1990s a new type of electrokinetic mechanism, driven by metal electrodes under AC voltage, was observed by several research groups [2–7]. In this "AC electro-osmosis" mechanism [8] the voltage applied to the electrode results in both an induced Debye double layer about its surface and an electric field acting on it, giving rise to a clear nonlinear dependence of the flow-field magnitude. Such flows ubiquitously occur when the electrodes–fluid configuration is not one-dimensional, since the electric field then possesses a component which is tangential to the double layer at the metal-electrolyte interface; the associated Coulomb forces are then generally nonconservative and cannot be balanced by pressure gradients alone.

Squires and Bazant [9] have identified the linkage between AC electro-osmosis and electro-osmotic flows about metal particles, the latter having been investigated in the Russian literature for quite some time [10–12]. In both types of electrokinetic problems the electric field acts upon an induced charge adjacent to the metal boundary. A similar mechanism also occurs when colloidal particles are suspended at the vicinity of an electrode [13], again, disturbing the equilibrium one-dimensional structure. Coining the entire host of such phenomena "induced-charge electro-osmosis" (ICEO), Squires and Bazant suggested that such flows may be useful in microfluidic devices [9,14].

The prototypic problem in ICEO, as analyzed in the Russian literature, entails a metal sphere suspended in an unbounded electrolyte solution and exposed to an otherwise uniform electric field [11]. The metal is a perfect conductor but is assumed chemically inert. Since the ensuing electro-osmotic flow is highly symmetric, no net hydrodynamic force arises. Motivated by microfluidic applications, Squires and Bazant [9] analyzed the similar problem of two-dimensional flow about an infinitely long metal cylinder, modeling the flow engendered about a thin metal wire [15]. The general structure of the flow about more complex geometries was discussed by Yariv [16] and Squires and Bazant [17]. Due to asymmetries, such geometries may result in net pumping [18,19], mixing and stirring [20–24], and animation of particle translation and rotation [17,25–29]. The preceding analyses were carried out in the thin-double-layer limit [30], ubiquitously realized in colloidal and microfluidic systems. This underlying approximation allows for the convenient use of well-established macroscale descriptions [31].

As in the earlier modeling of AC electro-osmosis [8,32,33], the initial analysis of Squires and Bazant [9] was carried out using a linear double-layer model, valid when the zeta potential is small compared with the thermal voltage [see (3.1)]. Since the zeta potential is induced by the applied field, this implicitly implies $\beta \ll 1$, β representing the ratio of the electric-potential drop on the particle and the thermal voltage [see (3.26)]. The linear scaling of the zeta potential with β suggests in principle the possibility of attaining large zeta potentials; this is an attractive feature in engineering applications, as typical zeta potentials characterizing dielectric solids are difficult to manipulate and, in any event, are usually comparable with the thermal voltage. Indeed, with the induced zeta potentials scaling as β, the resulting ICEO flow scales as β^2, supposedly allowing for much larger velocities than those familiar with classical electrokinetic phenomena. In addition, the quadratic dependence upon field strength allows for net fluid motion even under AC fields [9].

Squires and Bazant [9] have pointed out that the ICEO mechanism applies to any polarizable solid object, which could be either metal or dielectric. While this is conceptually true, the effect of dielectric solid polarization is negligible in the very thin-double-layer limit considered in Ref. [9]. Indeed, it was shown by Yossifon *et al.* [25] that solid polarization becomes appreciable in that limit only if the ratio of solid-to-electrolyte dielectric constants is $O(1/\delta)$ large, $\delta(\ll 1)$ being the ratio of the Debye thickness to the linear dimension of the solid

object [27,29,34,35]. For most relevant solids, the permittivity is actually smaller than that of the fluid. Dielectric-solid polarization may play a role in certain important problems, such as the electro-osmotic flow near sharp corners [36,37], contamination of metal surface [9,38], and electrophoresis under strong fields [39,40]. Otherwise, within the prevailing thin-double-layer limit, ICEO is practically associated with metal surfaces.

With the zeta potential being an induced property, presumably independent of any surface chemistry, electrokinetic flows about metal surfaces may appear to hold the promise of advantageous quantitative predictions, compared to their counterparts about dielectric surfaces. Remarkably, however, existing theoretical models have persistently failed to agree with experimental measurements [15,28,41]. Thus, electro-osmotic velocities predicted by the standard ICEO model have always overestimated experimental observations, sometimes by orders of magnitudes [42]. Other trends observed in experiments, namely, high-frequency flow reversal and concentration-dependent flow magnitude, are also incompatible with standard ICEO modeling. Similar discrepancies are ubiquitous in AC electro-osmosis as well [42].

B. Modeling ICEO beyond weak fields

Realizing the inadequacy of the standard ICEO descriptions, Bazant and coworkers [43,44] have focused upon large zeta potentials, where the Poisson-Nernst-Planck equations break down due to nondilute effects. Their analysis of these extreme conditions entails the incorporation of steric effects and ion-ion correlations. The rational for going to such high zeta potentials is the scaling of the induced zeta potential with β. For practical systems, even at mild values of the applied voltages, this scaling implies extremely high values. For example, Bazant *et al.* [43] refer to several volts (about 100 thermal voltages) "applied" to the thin double layer. Such values are much higher than those characterizing dielectric materials in contact with electrolytes (a few thermal voltages at most); if indeed attained in ICEO, there is no question that the Poisson-Nernst-Planck description would break down.

It is important, however, to note that the zeta-potential scaling with β is predicted by the original *weak-field* ($\beta \ll 1$) ICEO models [45]; by no means is that linear scaling retained at strong fields $\beta \gg 1$. Since the zeta-potential scaling with β is unknown at this regime, it is actually unclear whether the zeta-potential values stipulated by Bazant and coworkers are indeed realized. Note that it is the applied field magnitude β, rather than the zeta-potential distribution, which can be directly controlled in an experiment. The linear scaling existing in weak fields, effectively rendering the zeta potential a "prescribed" quantity, is accordingly misleading.

In fact, the presumed linear scaling with β implies moderate zeta potentials, easily reaching several thermal voltages, at rather mild applied fields. Under such conditions, surface conduction is known to affect the leading-order electrokinetic transport [46]. The standard ICEO model, which has predicted this very scaling, then breaks down. With the zeta potential being an induced quantity here, moreover, surface conduction becomes an inherently *nonlinear* mechanism.

With an unknown nonlinear dependence of the zeta potential upon β, the logical approach in going beyond weak fields is to consider those field magnitudes wherein the induced zeta-potential distribution becomes moderately large. At this regime, surface conduction necessarily enters the picture, while the Poisson-Nernst-Planck equations may still be considered applicable [47]. Analysis of this problem would help unravel the dependence of the zeta potential upon β beyond the linear regime. More importantly, systematic ICEO models that properly account for surface conduction can shed some light on the disturbing discrepancy between theory and experiment.

Before attempting to incorporate surface conduction effects into the ICEO paradigm, it is useful to review the manner in which it is modeled in the context of dielectric surfaces, especially when going beyond the linear-response regime.

C. Modeling surface conduction beyond weak fields

The surface conduction mechanism in the thin-double-layer limit was explained by Dukhin and coworkers [48–52] in the context of a classical colloid-science problem: weak-field electrophoresis of dielectric solid particles possessing immobile surface charge. In view of the exponential Boltzmann distributions existing within thin double layers, counterion concentration near the surface becomes large even at moderately large values of the zeta potential. The associated tangential flux, which normally does not affect the leading-order transport [53], becomes significant: On a macroscale description, it appears as an effective surface current. The nonuniformity of this current then gives rise to a transverse counterion flux into the electroneutral bulk. The resulting polarized double-layer structure was reviewed by Derjaguin and Dukhin [51]. Denoting by ζ the ratio of the particle zeta potential and the thermal voltage, surface conduction appears when

$$e^{|\zeta|/2} \sim O(\delta^{-1}). \tag{1.1}$$

A systematic analysis of particle electrophoresis using Dukhin's ideas was carried out by O'Brien and Hunter [54] in the thin-double-layer limit $\delta \ll 1$ (see also Refs. [55–57]). At low and moderate zeta potentials, when surface conduction is negligible, O'Brien and Hunter obtain the familiar linear variation of the electrophoretic mobility with ζ, as predicted by Smoluchowski [58,59]. At somewhat higher ζ values, corresponding to (1.1), surface conduction enter the picture and the linear variation breaks down. These results are in excellent agreement with the numerical calculations of O'Brien and White [60], showing a nonmonotonic mobility dependence upon ζ.

In a later paper, O'Brien [61] derived a macroscale thin-double-layer description of surface conduction for a generic geometry, not limited to the spherical-particle configuration. This approach clarifies the limit process representing the appearance of surface conduction. Thus, O'Brien [61] has retained in his small-δ analysis terms which are formally $O(\delta)$ small, but which become $O(1)$ at moderately large ζ, as defined by the limit (1.1). This limit can be represented using a dimensionless group, usually denoted the "Dukhin

number" [62]; defining that number as

$$\mathrm{Du} = \delta e^{|\zeta|/2}, \tag{1.2}$$

surface conduction appears when Du becomes $O(1)$.

Following Dukhin's work, surface conduction has been modeled in various electrokinetic phenomena, such as electroviscous forces [63,64], dielectric enhancement [55,56,65,66], electrophoresis of nonuniformly charged colloids [67], effective properties of suspensions [68,69], particle interactions [70], and mobility approximations [71,72]. More recently, Khair and Squires have investigated the effects of surface conduction in a host of problems of current interest, including patterned surfaces [73], surface-charge discontinuities [74] (correcting and extending the initial model of Yariv [75]), and (following Ajdari [76]) combined hydrodynamic and electrokinetic slip [77].

All of the above-mentioned thin-double-layer analyses were carried out using the linearized equations appropriate to weak-field phenomena. When the applied field is not weak compared with the thermal scale the problem becomes significantly more complicated. Thus, salt polarization in the bulk, animated by surface conduction, becomes appreciable, leading to an inherently nonlinear bulk transport. This complication also introduces a conceptual difficulty: With a nonuniform bulk concentration, the zeta-potential distribution is nonuniform even when the surface-charge density on the dielectric surface is uniform. Definition (1.2), introduced in the context of weak-field transport (where ζ represents the leading-order Debye-layer voltage), thus becomes vague.

In an earlier paper [78] we have presented a generic asymptotic analysis of electrokinetic flows in the thin-double-layer limit, not restricted to weak fields. It results in a macroscale model consisting of approximate differential equations governing transport in the electroneutral bulk as well as effective boundary conditions constituting a lumped representation of the double-layer physics. The analysis in Ref. [78] is presented in two stages, first addressing moderate zeta potentials and only then considering the more difficult case of moderately large potentials [in the sense (1.1)], where surface conduction appears. The transition is quantified by identifying a dimensionless Bikerman number which represents the *global* appearance of surface conduction. At weak fields, this number practically coincides with the Dukhin number (1.2).

In analyzing electrokinetic transport at $O(1)$ Bikerman numbers, the intuitive procedure used in weak-field analyses, where asymptotically small terms which change magnitude at large ζ are retained in the governing equations, was abandoned in favor of a more systematic approach. Following Hinch *et al.* [65], the localization of surface conduction near the solid was identified with the appearance of a boundary ("Dukhin") layer within the Debye layer itself. Separate asymptotic expansions are accordingly introduced in the electroneutral bulk, the Debye layer, and the newly identified Dukhin layer, which turns out to be $O(\delta^2)$ wide. The derivation of effective boundary conditions requires asymptotic matching between these three separate regions.

Our goal here is to construct a comparable macroscale description of ICEO accounting for surface conduction.

II. SURFACE CONDUCTION IN ICEO

A. Conceptual difficulties

In view of (1.1), surface conduction becomes appreciable when ζ is comparable with $2\ln\delta$. Practically, even for very narrow double layers, this figure is not much greater than unity. For example, for a Debye thickness of 10 nanometers and a conducting-object size of 10 μm, where $\delta = 0.001$, the threshold zeta potential is about 14 thermal voltages. At larger values of δ (still reasonably within the thin-double-layer approximation) even more moderate values are predicted. For $\delta = 0.1$, for example, surface conduction appears at about 5 thermal voltages. This is barely distinguishable from "moderate" potentials $\zeta \sim O(1)$.

Now, with typical values of the applied voltages in common experiments, the stipulated linear scaling of the zeta potential in that voltage easily leads to the prediction of much larger zeta potentials [43]. There is no question then that surface conduction is inherent in virtually any ICEO application. (Incidentally, this is less so in the classical context of dielectric surfaces, where typical zeta-potential values, say, 70mV, are quite mild!) The discrepancy of standard ICEO models with experiments is therefore hardly surprising. We propose that a proper understanding of surface-conduction effects at moderately large zeta potentials is essential. As shown in our previous paper [78], there is a significant interval of the key parameters representing practical systems within which surface conduction appears well before nondilute effects are introduced.

The goal of the present paper is accordingly to derive a macroscale description of ICEO accounting for surface conduction. This problem introduces new conceptual difficulties, having to do with the physical modeling of the metal boundary. Unlike flows about a dielectric colloid, the zeta-potential distribution about a metal object is an intrinsic nonequilibrium property. Thus, the procedure of weak-field linearization about a reference equilibrium state, underlying all the above-mentioned classical analyses of surface conduction, is inapplicable.

As indicated in our previous analysis of surface conduction about a dielectric solid [78], a uniform charge density does not transform into a uniform zeta potential when going beyond weak fields. Nonetheless, some linkage does exist on a global level. Thus, a key feature in [78] is the identification of a Bikerman number which sensibly quantifies the relative role of surface conduction even beyond weak fields, where the zeta potential distribution is inherently nonlinear. In the preset problem, however, when attempting to analyze ICEO with surface conduction, with "large zeta potentials" typically implying a "strong" applied field, the comparable definition of a global dimensionless number is not as useful. Indeed, consider the prototypic problem of ICEO flow about a sphere or a cylinder of zero net charge. Because of the antisymmetric distribution of the zeta potential along the boundary, the zeta potential vanishes at the intersection of the solid boundary with the transverse symmetry plane (normal to the applied field). Thus, even at sufficiently strong fields where the typical zeta-potential magnitude is large for surface conduction to appear, there are always boundary regions where the zeta potential is small. Moreover, the implied decomposition of the

boundary to "moderate" and "moderately large" zeta-potential domains cannot be inferred *a priori*; rather, it is the outcome of the very macroscale description we are trying to construct. This description, in turn, depends upon proper modeling of surface conduction at those regions where it is appreciable.

With such conceptual difficulties, it is hardly surprising that the modeling of surface condition in ICEO has remained an open problem. Certain aspects of the problem have been addressed in the literature, but only in rather limited contexts. Thus, Chu and Bazant [46] have analyzed electrochemical relaxation about conducting bodies but have entirely ignored the induced flow; not only does this preclude ICEO, it also results in the omittance of ionic convection, thereby undermining the attempt to properly model the electrochemical processes when going beyond the weak-field regime. Gregersen *et al.* [79] have partially accounted for surface conduction in their analysis of ICEO flow driven by a biasing electrode, incorporating charge flux in the macroscale Neumann condition governing the electric potential. These authors however employed the *ad hoc* assumption that the salt concentration remains uniform. It is well known, however, that, even at weak-field phenomena [54], the role of salt polarization is comparable with that of the electric field in affecting global properties of the electrokinetic transport (e.g., electrophoretic mobility).

B. Solution scheme

For simplicity, we begin by considering the simple prototypic configuration of a circular metal cylinder, introduced by Squires and Bazant [9]. Focusing on that simple geometry allows us to illuminate the fundamental features associated with the appearance of surface conduction in ICEO. The generalization of the resulting macroscale model to more complicated geometries, carried out in Sec. VII, is straightforward. We also limit the discussion to steady ICEO; the generalization to unsteady flows, in particular those due to AC forcing, is discussed in Sec. VIII.

As in our earlier study [78] of dielectric surfaces, we begin by deriving the macroscale model for moderate fields, where surface conduction is absent. In considering the transition to stronger fields, we follow a different path than the one we employed in that study. Thus, we perform a local Debye-scale analysis about an arbitrary boundary point where the zeta potential is assumed to be logarithmically large, in the sense (1.1). The Dukhin number, as defined by (1.2), is employed, with the understanding that it varies along the boundary (in a manner which remains to be determined). Following the methodology of our previous paper [78], the localization of surface conduction near the boundary is exploited in the local analysis about a generic boundary point via the introduction of a Dukhin sublayer.

This novel procedure eventually furnishes effective boundary conditions for two types of boundary points: those on which the zeta potential is moderate, and those on which it is (logarithmically) large (either positive or negative). We then obtain a uniform approximation for these conditions, which applies over the entire boundary. This allows us to furnish a complete macroscale model for ICEO beyond weak fields.

While part of the analysis is reminiscent of our previous paper [78], the conceptual and technical differences are significant. In particular, with an inherently nonuniform surface-charge density on the solid boundary, the Dukhin-layer counterion distribution varies along the boundary, whereby a diffusive component contributes to the surface-conduction effect. This is in contrast with the case of a dielectric surface [78], where the uniform surface charge is essentially screened by an unpolarized Dukhin layer, and surface conduction is merely due to electromigration and convection. We have therefore written the present paper in a self-contained manner. In the next section we formulate the exactly posed problem using the standard electrokinetic model. The thin-double-layer limit is addressed in Sec. IV, wherein asymptotic matching between the electroneutral bulk and the Debye layer results in effective boundary conditions for moderate zeta potentials. A local analysis at moderately large zeta potentials is performed at Sec. V, providing a different set of effective conditions. A uniform approximation for the boundary conditions is derived in Sec. VI. In Sec. VII we recapitulate our macroscale model and generalize it for arbitrary geometries. We conclude in Sec. VIII.

III. PROBLEM FORMULATION

Our idealized configuration comprises of an infinitely long circular cylinder of radius a^* held fixed in an unbounded fluid domain. (Dimensional quantities are hereafter decorated by an asterisk.) The cylinder is made out of metal which is assumed to be chemically inert; it is free of any net charge. The surrounding fluid is a symmetric electrolyte solution (permittivity ϵ^*, viscosity μ^*). The two ionic species are characterized by the ionic valencies $\pm\mathcal{Z}$ and diffusivities $D^{*\pm}$. At equilibrium both species possess an identical ionic concentration c^*. Our interest is in the steady-state two-dimensional flow, which is animated by the application of a constant and uniform electric field E^* in a direction perpendicular to the cylinder axis.

We employ the dimensionless notation of our previous paper [78]. Thus, length variables are normalized by a^*, ionic concentrations by c^*, and electric potentials by the thermal voltage

$$\varphi^* = \frac{k^*T^*}{\mathcal{Z}e^*}, \tag{3.1}$$

in which k^*T^* is the Boltzmann temperature and e^* the elementary charge. Stress variables are normalized by the Maxwell scale $M^* = \epsilon^*\varphi^{*2}/a^{*2}$; a balance with viscous stresses yields the scale $u^* = \epsilon^*\varphi^{*2}/a^*\mu^*$ used to normalize velocity variables. We employ cylindrical coordinates (r,θ) with $r = 0$ at the cylinder axis and $\theta = 0$ in the applied-field direction.

The electrokinetic transport in the fluid is described in terms of the two ionic concentrations $c^{\pm}$, the electric potential φ, the pressure p, and the velocity field

$$\mathbf{u} = \hat{\mathbf{e}}_r u + \hat{\mathbf{e}}_\theta v. \tag{3.2}$$

The molecular ionic fluxes, respectively normalized by $D^{*\pm}c^*/a^*$, are provided by the constitutive expressions

$$\mathbf{j}^{\pm} = -\boldsymbol{\nabla} c^{\pm} \mp c^{\pm}\boldsymbol{\nabla}\varphi \tag{3.3}$$

representing the combined action of of diffusion and electromigration. As an alternative to the use of $c^{\pm}$ one can employ the average ("salt") concentration (normalized by c^*) and volumetric charge density (normalized by $2\mathcal{Z}e^*c^*$)

$$c = \tfrac{1}{2}(c^+ + c^-), \quad q = \tfrac{1}{2}(c^+ - c^-). \tag{3.4}$$

Defining the salt flux and current density

$$\mathbf{j} = \tfrac{1}{2}(\mathbf{j}^+ + \mathbf{j}^-), \quad \mathbf{i} = \tfrac{1}{2}(\mathbf{j}^+ - \mathbf{j}^-), \tag{3.5}$$

we find, using (3.3),

$$\mathbf{j} = -\boldsymbol{\nabla} c - q\boldsymbol{\nabla}\varphi, \quad \mathbf{i} = -\boldsymbol{\nabla} q - c\boldsymbol{\nabla}\varphi. \tag{3.6}$$

The governing differential equations are as follows:

(1) Ionic conservation,

$$\boldsymbol{\nabla}\cdot(\mathbf{j}^{\pm} + \alpha^{\pm}c^{\pm}\mathbf{u}) = 0, \tag{3.7}$$

wherein

$$\alpha^{\pm} = \frac{\epsilon^*\varphi^{*2}}{\mu^* D^{*\pm}} \tag{3.8}$$

are the ionic drag coefficients. These coefficients are independent of both system dimension a^* and electrolyte concentration c^*. Moreover, in view of the Stokes-Einstein relations, they are also independent of the liquid viscosity. Substitution of typical values (see Ref. [1]) for ionic diffusivities ($\approx 10^{-9}$ m^2 s^{-1}) in univalent aqueous solutions at room temperature (where $\varphi^* \approx 26$ mV, $\mu^* \approx 10^{-3}$ kg m^{-1} s^{-1}, and $\epsilon^* \approx 7\times 10^{-10}$ kg m s^{-2} V^{-2}) yields the characteristic value ≈ 0.5.

(2) Poisson,

$$q = -\delta^2\nabla^2\varphi. \tag{3.9}$$

Here

$$\delta = \frac{1}{\kappa^* a^*} \tag{3.10}$$

is the dimensionless Debye thickness, wherein the Debye width $1/\kappa^*$ is defined by

$$\kappa^{*2} = \frac{2\mathcal{Z}e^*c^*}{\epsilon^*\varphi^*}. \tag{3.11}$$

(3) Continuity,

$$\boldsymbol{\nabla}\cdot\mathbf{u} = 0, \tag{3.12}$$

or, explicitly, using (3.2),

$$\frac{1}{r}\frac{\partial}{\partial r}(ru) + \frac{1}{r}\frac{\partial v}{\partial\theta} = 0. \tag{3.13}$$

(4) Inhomogeneous Stokes equations, incorporating Coulomb body forces [using (3.9)],

$$\boldsymbol{\nabla} p = \nabla^2\mathbf{u} + \nabla^2\varphi\boldsymbol{\nabla}\varphi. \tag{3.14}$$

Explicitly, the radial and tangential balances respectively read

$$\frac{\partial p}{\partial r} = \nabla^2 u - \frac{2}{r^2}\frac{\partial v}{\partial\theta} + \nabla^2\varphi\frac{\partial\varphi}{\partial r}, \tag{3.15}$$

$$\frac{1}{r}\frac{\partial p}{\partial\theta} = \nabla^2 v + \frac{2}{r^2}\frac{\partial u}{\partial\theta} + \frac{1}{r}\nabla^2\varphi\frac{\partial\varphi}{\partial\theta}. \tag{3.16}$$

In view of the continuity equation (3.12), the ionic balances (3.7) may be written in the more familiar form

$$\boldsymbol{\nabla}\cdot\mathbf{j}^{\pm} + \alpha^{\pm}\mathbf{u}\cdot\boldsymbol{\nabla}c^{\pm} = 0, \tag{3.17}$$

or, alternatively, using (3.5),

$$\boldsymbol{\nabla}\cdot\mathbf{j} + \frac{\alpha^+ + \alpha^-}{2}\mathbf{u}\cdot\boldsymbol{\nabla}c + \frac{\alpha^+ - \alpha^-}{2}\mathbf{u}\cdot\boldsymbol{\nabla}q = 0, \tag{3.18a}$$

$$\boldsymbol{\nabla}\cdot\mathbf{i} + \frac{\alpha^+ - \alpha^-}{2}\mathbf{u}\cdot\boldsymbol{\nabla}c + \frac{\alpha^+ + \alpha^-}{2}\mathbf{u}\cdot\boldsymbol{\nabla}q = 0. \tag{3.18b}$$

The boundary conditions at the metal-electrolyte interface $r = 1$ comprise the following:

(1) Electric-potential continuity,

$$\varphi = 0 \quad \text{at} \quad r = 1, \tag{3.19}$$

where, with no loss of generality, the uniform value of the electric potential within the metal is set to zero.

(2) Flow impermeability,

$$u = 0 \quad \text{at} \quad r = 1. \tag{3.20}$$

(3) No-slip,

$$v = 0 \quad \text{at} \quad r = 1. \tag{3.21}$$

(4) No-flux,

$$\hat{\mathbf{e}}_r\cdot\mathbf{j}_{\pm} = 0 \quad \text{at} \quad r = 1, \tag{3.22}$$

representing the inability of the electrolyte ions to discharge on the chemically inert solid metal.

Since the electric field vanishes within the metal, the local form of Gauss's law reads

$$\sigma = -\delta\frac{\partial\varphi}{\partial r} \quad \text{at} \quad r = 1, \tag{3.23}$$

in which σ is the (generally nonuniform) surface-charge density (normalized by $\epsilon^*\kappa^*\varphi^*$) on the metal boundary. Equation (3.23) does not constitute an additional boundary condition; rather, it provides σ as a function of θ.

As the cylinder was uncharged to begin with, the no-flux conditions (3.22), which apply during the transient charging process, imply that at steady state the net charge (per unit length) must vanish as well. Equation (3.23) then yields the "memory" condition

$$\int_{r=1}\frac{\partial\varphi}{\partial r}\,d\theta = 0. \tag{3.24}$$

Last, consider the behavior at large distances from the cylinder, as $r\to\infty$. The electric field must approach the externally imposed uniform field,

$$\varphi \sim -\beta r\cos\theta. \tag{3.25}$$

Here

$$\beta = \frac{a^* E^*}{\varphi^*}, \tag{3.26}$$

is the dimensionless magnitude the applied field. In addition, the ionic concentrations $c^{\pm}$ approach the equilibrium unity values, implying that

$$c\to 1, \quad q\to 0, \tag{3.27}$$

and the velocity goes to zero.

IV. THIN-DOUBLE-LAYER LIMIT

We consider thin double layers, where

$$\delta \ll 1. \tag{4.1}$$

Our goal is a leading-order description in that asymptotic limit. Substitution of (4.1) into (3.9) yields leading-order electroneutrality, $q \equiv 0$. The salt and charge balances (3.18) thus, respectively, read

$$\nabla^2 c = \frac{\alpha^+ + \alpha^-}{2}\mathbf{u}\cdot\nabla c \tag{4.2}$$

and

$$\nabla\cdot(c\nabla\varphi) = \frac{\alpha^+ - \alpha^-}{2}\mathbf{u}\cdot\nabla c, \tag{4.3}$$

while the flow equations (3.12) and (3.14) remain unaltered. With electroneutrality, the salt flux and current density (3.6) become

$$\mathbf{j} = -\nabla c, \quad \mathbf{i} = -c\nabla\varphi, \tag{4.4}$$

whereby use of (3.5) yields

$$\mathbf{j}^+ = -\nabla c - c\nabla\varphi, \quad \mathbf{j}^- = -\nabla c + c\nabla\varphi. \tag{4.5}$$

The preceding description is incompatible with the boundary conditions at $r = 1$. Indeed, conditions (3.22) imply that φ satisfies an homogenous Neumann condition there, which, together with the Dirichlet condition (3.19) and the approach (3.25) to a uniform field, over-specifies the electrostatic problem. The source of this nonuniformity is rooted in Poisson's equation (3.9), where the highest derivative is multiplied by a small parameter. The limit (4.1) is a singular one.

The electroneutral description (4.2)–(4.5) therefore constitutes an *outer* "bulk" approximation in the limit (4.1), valid outside an *inner* boundary ("Debye") layer about $r = 1$. This conceptual decomposition is made explicit by the introduction of a "coarse-grained" radial coordinate $\bar{r}$ which cannot discern the fine details within the Debye layer. Thus, as opposed to the literal interface $r = 1$, the surface $\bar{r} = 1$ represents the "outer edge" of that layer, where asymptotic matching between the inner and outer regions takes place.

In what follows, we consider the Debye-layer structure. Once calculated, matching with the bulk fields provides effective boundary conditions at $\bar{r} = 1$. This is the standard approach in analyzing electrokinetic phenomena in the thin-double-layer limit [61].

A. Debye layer scaling

The $O(\delta)$-wide Debye layer is resolved by the stretched inner variable

$$Z = \frac{r-1}{\delta}. \tag{4.6}$$

Assuming $O(1)$ ionic concentrations and electric potential, we postulate the following asymptotic expansions:

$$c^\pm = C^\pm(Z,\theta) + \cdots, \quad \varphi = \Phi(Z,\theta) + \cdots. \tag{4.7}$$

A similar scaling of the tangential velocity component also suggests the expansion

$$v = V(Z,\theta) + \cdots. \tag{4.8}$$

The continuity equation (3.13) in conjunction with the impermeability condition (3.20) then implies an $O(\delta)$ radial velocity component,

$$u = \delta U(Z,\theta) + \cdots. \tag{4.9}$$

In addition, the large $O(\delta^{-3})$ Coulomb body forces in the radial-momentum balance (3.15) necessitate an $O(\delta^{-2})$ large pressure

$$p = \delta^{-2}P(Z,\theta) + \cdots. \tag{4.10}$$

Finally, asymptotic matching suggests $O(1)$ ionic fluxes in the radial direction

$$\hat{\mathbf{e}}_r\cdot\mathbf{j}^\pm = J_r^\pm(Z,\theta) + \cdots, \tag{4.11}$$

whereby the presumed absence of $O(\delta^{-1})$ fluxes implies [see (3.3) and (4.7)]

$$-\frac{\partial C^\pm}{\partial Z} \mp C^\pm\frac{\partial\Phi}{\partial Z} = 0. \tag{4.12}$$

At large Z the Debye-scale variables must match the corresponding bulk-domain fields. Thus,

$$\Phi \to \varphi, \quad V \to v \qquad \text{as} \qquad Z \to \infty. \tag{4.13}$$

Also, in view of leading-order bulk electroneutrality,

$$C^\pm \to c \quad \text{as} \quad Z \to \infty. \tag{4.14}$$

Hereafter, bulk-domain variables appearing in equations involving Debye-layer fields are understood to be evaluated at the effective boundary $\bar{r} = 1$ and are accordingly functions of θ alone. The matching requirement also implies that P, which represents an asymptotically large $O(\delta^{-2})$ field, must vanish at large Z, as it matches an $O(1)$ bulk field there:

$$P \to 0 \quad \text{as} \quad Z \to \infty. \tag{4.15}$$

For the same reason, we also require

$$\frac{\partial\Phi}{\partial Z}, \frac{\partial V}{\partial Z} \to 0 \quad \text{as} \quad Z \to \infty. \tag{4.16}$$

The boundary conditions (3.21)–(3.23) must be rewritten in terms of the Debye-layer variables. Thus, the conditions of equipotential surface (3.19), impermeability (3.20), no-slip (3.21) and no-flux (3.22) now read

$$\Phi = 0, \quad U = 0, \quad V = 0, \quad J_r^\pm = 0 \quad \text{at} \quad Z = 0. \tag{4.17}$$

In addition, the memory condition (3.24) becomes

$$\int_{Z=0}\frac{\partial\Phi}{\partial Z}\,d\theta = 0. \tag{4.18}$$

B. Analysis

Integration of (4.12) in conjunction with the matching conditions (4.13)–(4.14) provides the Boltzmann distributions

$$C^\pm = c\,e^{\mp\Psi} \tag{4.19}$$

wherein

$$\Psi = \Phi - \varphi \tag{4.20}$$

is the "excess" boundary-layer potential relative to the bulk potential at $\bar{r} = 1$. Substitution into Poisson's equation (3.9) yields at leading order

$$\frac{\partial^2 \Psi}{\partial Z^2} = c \sinh \Psi. \tag{4.21}$$

Integration in conjunction with (4.16) yields

$$\frac{\partial \Psi}{\partial Z} = -2\sqrt{c} \sinh \frac{\Psi}{2}. \tag{4.22}$$

Specifically, in view of (4.17) and (4.20),

$$\frac{\partial \Psi}{\partial Z} = 2\sqrt{c} \sinh \frac{\varphi}{2} \quad \text{at} \quad Z = 0. \tag{4.23}$$

The memory condition thus becomes (3.24)

$$\int_{\bar{r}=1} \sqrt{c} \sinh \frac{\varphi}{2}\, d\theta = 0. \tag{4.24}$$

With $\partial \Phi / \partial Z = \partial \Psi / \partial Z$ considered known, the pressure field P is obtained from the leading-order balance of (3.15),

$$\frac{\partial P}{\partial Z} = \frac{\partial^2 \Phi}{\partial Z^2} \frac{\partial \Phi}{\partial Z}. \tag{4.25}$$

Integration in conjunction with (4.13) and (4.15) readily yields

$$P = \frac{1}{2} \left(\frac{\partial \Psi}{\partial Z} \right)^2. \tag{4.26}$$

Substitution into the leading-order balance of (3.16) in conjunction with definition (4.20) then yields

$$\frac{\partial^2 V}{\partial Z^2} = \frac{\partial \Psi}{\partial Z} \frac{\partial^2 \Psi}{\partial Z\, \partial \theta} - \frac{\partial^2 \Psi}{\partial Z^2} \left(\frac{\partial \Psi}{\partial \theta} + \frac{\partial \varphi}{\partial \theta} \right). \tag{4.27}$$

Use of (4.22) allows one integration of this differential equation (see Ref. [80]),

$$\frac{\partial V}{\partial Z} = -\frac{\partial \Psi}{\partial Z} \frac{\partial \varphi}{\partial \theta} - \frac{4}{\sqrt{c}} \frac{\partial c}{\partial \theta} \sinh^2 \frac{\Psi}{4}, \tag{4.28}$$

where the constant of integration must vanish in view of (4.16). Integration of (4.28) from Z to ∞, making use of both (4.13) and (4.22), yields the profile

$$v - V = \Psi \frac{\partial \varphi}{\partial \theta} - \frac{4}{c} \frac{\partial c}{\partial \theta} \ln \cosh \frac{\Psi}{4}. \tag{4.29}$$

Use of conditions (4.17) thus furnishes the slip condition,

$$v = -\varphi \frac{\partial \varphi}{\partial \theta} + 2 \ln \left(1 - \tanh^2 \frac{\varphi}{4} \right) \frac{\partial \ln c}{\partial \theta}, \tag{4.30}$$

consisting of both electro-osmosis and diffuso-osmosis.

Finally, the ion-conservation equations (3.17) read at $O(\delta^{-1})$

$$\frac{\partial J_r^{\pm}}{\partial Z} = 0, \tag{4.31}$$

implying that $J_r^{\pm}$ are functions of θ alone. The no-flux condition [see (4.17)] then yields

$$J_r^{\pm} \equiv 0. \tag{4.32}$$

C. Effective boundary conditions

Asymptotic matching can now be used to obtain effective boundary conditions governing the bulk fields. The boundary condition governing the tangential velocity component was already obtained in (4.30). Since the Debye-layer radial velocity (4.9) is $O(\delta)$, asymptotic matching readily implies the effective impermeability condition

$$u = 0 \quad \text{at} \quad \bar{r} = 1. \tag{4.33}$$

(This explains why we did not bother calculating U.)

Consider now the radial ionic fluxes in the electroneutral bulk, given by (4.5). Asymptotic matching with the nil Debye-layer fluxes (4.32) yields

$$-\frac{\partial c}{\partial \bar{r}} - c \frac{\partial \varphi}{\partial \bar{r}} = 0, \quad -\frac{\partial c}{\partial \bar{r}} + c \frac{\partial \varphi}{\partial \bar{r}} = 0 \quad \text{at} \quad \bar{r} = 1, \tag{4.34}$$

or, equivalently,

$$\frac{\partial \varphi}{\partial \bar{r}} = 0, \quad \frac{\partial c}{\partial \bar{r}} = 0 \quad \text{at} \quad \bar{r} = 1. \tag{4.35}$$

The zeta potential ζ is defined in the usual manner as the Debye-layer voltage, which in the present context means that [see (4.17) and (4.20)]

$$\zeta = -\varphi, \tag{4.36}$$

where φ is evaluated at $\bar{r} = 1$. In view of this simple relation, there is no benefit here in using ζ as an explicit variable; indeed, all the effective boundary conditions are here expressed in terms of φ. This is in contrast to the usual practice in analyzing flows about dielectric surfaces [78], where the zeta potential is employed as a convenient alternative to the surface-charge density: a prescribed quantity in such problems.

The present local Debye-layer analysis implicitly entails the assumption that $\zeta (= -\varphi)$ is at most $O(1)$. If that restriction holds over the entire boundary, it is readily verified that the trivial solution to the salt-transport problem is $c \equiv 1$, whereby the familiar formulation of Squires and Bazant [9] is recovered. Note, however, that the zeta potential is an inherently nonuniform induced quantity in the present problem. Thus, the implicit assumption $|\varphi| \lesssim O(1)$ does not necessarily hold over the entire boundary: Unless the applied field is weak, there will be boundary regions where the zeta potential becomes large enough for the present analysis to locally break down. This is discussed next.

D. Breakdown

Because of surface conduction, the preceding Debye-layer analysis breaks down at boundary points where the zeta potential is logarithmically large; see (1.1). In the present context the zeta potential distribution is given by (4.36) and is hence inherently nonuniform, implying that the emergence of surface condition does not take place uniformly over the boundary. Moreover, since the dependence of ζ upon θ is unknown *a priori*, the associated decomposition of the boundary into "moderate" and "moderately large" zeta-potential domains must be determined as part of the solution scheme. Remarkably, regardless of how large β is, there are always regions of the boundary where the local zeta potential is not

large: it is expected, e.g., that the neighborhood of $\theta = \pi/2$ is such a region (see Sec. VII). Thus, unlike our previous analysis of the electrokinetic transport about a dielectric surface [78], there is no practical benefit in defining here a dimensionless Bikerman number which quantifies the *global* intensity of the surface conduction mechanism.

Our approach here is a *local* one. Thus, we consider a generic boundary point (namely, an angle θ) about which the local Dukhin number, as defined by (1.2), is $O(1)$. We then reanalyze the electrokinetic transport in the adjacent Debye layer with the goal of deriving effective boundary conditions which apply at the corresponding macroscale point, namely, the counterparts of (4.30) and (4.33)–(4.35).

Until stated otherwise, we assume that the local value of ζ is positive. Once the effective condition corresponding to that choice are obtained, the comparable description for negative ζ is readily derived. Thus, we define the local Dukhin number [cf. (1.2) and (4.36)]

$$\mathrm{Du} = \delta e^{\zeta/2} = \delta e^{-\varphi/2} \tag{4.37}$$

and consider hereafter those points where ζ is logarithmically large, wherein $\mathrm{Du} \sim O(1)$.

V. LOGARITHMICALLY LARGE ZETA POTENTIALS

When the local value of ζ is moderately large, the Debye-layer analysis of the previous section breaks down near the surface. We address this problem following the methodology of our previous paper [78], introducing within the Debye layer a new boundary layer adjacent to the surface: the Dukhin sublayer. With cationic density scaling as e^{ζ} near the surface [see (4.19)], Poisson's equation implies a region of width $\delta e^{-\zeta/2} (\ll \delta)$ wherein surface conduction is localized. Since surface conduction affects leading-order transport when $e^{\zeta/2}$ is comparable to $1/\delta$ [see (1.1)], we postulate that the thickness of the new sublayer is $O(\delta^2)$. The $O(\delta)$-wide Debye layer is redefined by excluding from it the Dukhin layer. With this asymptotic paradigm, the Debye-layer analysis of Sec. IV remains valid, except for those results obtained using boundary conditions at $Z = 0$: In the present scheme, the boundary conditions describing the metal-electrolyte interface apply at a surface which is no longer part of the Debye layer.

Our multiscale approach results in two major modifications to the effective boundary conditions. The first has to do with evaluation of tangential velocity V. While (4.29) remains valid, the slip condition (4.30) prescribing v needs in principle to be reconsidered, as it hinges upon the no-slip condition. Thus, the unknown bulk velocity v remains as an integration constant in (4.29). It is to be determined by asymptotic matching with the Dukhin sublayer.

The second modification is more important and has to do with the radial ionic fluxes. As equations (4.31) retain their validity, $J_r^{\pm}$ are still functions of θ alone. However, conditions (4.32), derived using the no-flux condition at $Z = 0$, are expected to break down. In the present paradigm, the values of $J_r^{\pm}$ at a given θ must be determined by asymptotic matching with the Dukhin layer. This is where the main effect of surface conduction is manifested.

A. Dukhin-layer formulation

We define the Dukhin-layer transverse coordinate [cf. (4.6)]

$$\tilde{Z} = \frac{r-1}{\delta^2} = \frac{Z}{\delta}, \tag{5.1}$$

and analyze the near-boundary region $\tilde{Z} \sim O(1)$. In view of the Boltzmann distributions (4.19) and the scaling (1.1), it is anticipated that the anionic concentration in the sublayer is $O(\delta^{-2})$

$$c^- = \delta^{-2}\tilde{C}^-(\tilde{Z},\theta) + \cdots, \tag{5.2}$$

while the cation concentration is $O(\delta^2)$. Since the electric potential is only logarithmically large in δ, it is considered as $O(1)$ in expansion in powers of δ (see Ref. [81]):

$$\varphi = \tilde{\Phi}(\tilde{Z},\theta) + \cdots. \tag{5.3}$$

The radial momentum balance (3.15) suggests an $O(\delta^{-4})$ large pressure in the sublayer,

$$p = \delta^{-4}\tilde{P}(\tilde{Z},\theta) + \cdots. \tag{5.4}$$

We still postulate $O(1)$ tangential velocities

$$v = \tilde{V}(\tilde{Z},\theta) + \cdots, \tag{5.5}$$

whereby the continuity equation (3.13) and the impermeability condition (3.21) in conjunction with the scaling (5.1) imply an $O(\delta^2)$ normal velocity,

$$u = \delta^2\tilde{U}(\tilde{Z},\theta) + \cdots. \tag{5.6}$$

Last, consider the anionic fluxes. The requirement of matching with the Debye-layer radial flux suggests a comparable $O(1)$ magnitude in the Dukhin sublayer:

$$\hat{\mathbf{e}}_r \cdot \mathbf{j}^- = \tilde{J}_r^-(\tilde{Z},\theta) + \cdots. \tag{5.7}$$

On the other hand, as the large anionic concentration (5.2) suggests $O(\delta^{-2})$ fluxes in the tangential directions, we postulate

$$\hat{\mathbf{e}}_\theta \cdot \mathbf{j}^- = \delta^{-2}\tilde{J}_\theta^-(\tilde{Z},\theta) + \cdots, \tag{5.8}$$

wherein [see (3.3)]

$$\tilde{J}_\theta^- = -\frac{\partial \tilde{C}^-}{\partial\theta} + \tilde{C}^-\frac{\partial\tilde{\Phi}}{\partial\theta}. \tag{5.9}$$

The boundary conditions on the metal surface apply now to the sublayer fields. Conditions (4.17) are accordingly replaced by

$$\tilde{\Phi} = 0, \quad \tilde{U} = 0, \quad \tilde{V} = 0, \quad \tilde{J}_r^- = 0 \quad \text{at} \quad \tilde{Z} = 0. \tag{5.10}$$

In addition, at large $\tilde{Z}$ the Dukhin-layer fields must match the small-Z expansions of the corresponding Debye-layer fields. The memory condition (3.24) is not addressed at this point, as it entails the entire boundary: The local analysis presented herein applies (at most) to part of it.

B. Dukhin-layer analysis

Since the radial anionic flux in the radial direction are presumed $O(1)$ [see (5.7)], the term

$$-\frac{\partial\tilde{C}^-}{\partial\tilde{Z}} + \tilde{C}^-\frac{\partial\tilde{\Phi}}{\partial\tilde{Z}}, \tag{5.11}$$

representing an $O(\delta^{-4})$ flux, must vanish; this results in the Boltzmann distribution

$$\tilde{C}^- = c\,\mathrm{Du}^2 e^{\tilde{\Phi}} \tag{5.12}$$

wherein matching with the Debye-layer fields has been accounted for using both (4.19) and definition (4.37). [As in the preceding Debye-layer analyses, bulk-scale variables appearing in boundary-layer equations are understood to be evaluated at the macroscale boundary $\bar{r} = 1$.] Substitution of (5.12) into (5.9) yields the tangential anionic flux,

$$\tilde{J}_\theta^- = -e^{\tilde{\Phi}} \frac{d}{d\theta}(c\,\mathrm{Du}^2), \tag{5.13}$$

consisting of both diffusion and electromigration contributions.

Consider now Poisson's equation (3.9) at leading $O(\delta^{-4})$. In this asymptotic order the electric potential is affected only by the counterions,

$$2\frac{\partial^2 \tilde{\Phi}}{\partial \tilde{Z}^2} = \tilde{C}^-_{-2}. \tag{5.14}$$

Substitution of (5.12) followed by integration yields

$$\left(\frac{\partial \tilde{\Phi}}{\partial \tilde{Z}}\right)^2 = c\,\mathrm{Du}^2 e^{\tilde{\Phi}} + B(\theta). \tag{5.15}$$

Since $\partial\tilde{\Phi}/\partial\tilde{Z}$ and $e^{\tilde{\Phi}}$ are respectively proportional to the $O(\delta^{-2})$ transverse electric field and anionic concentration within the Dukhin layer, they must decay at large $\tilde{Z}$ due to the different scaling of these variables in the Debye layer. Thus, the integration constant B must vanish. Since the radial electric field is positive, we then obtain

$$\frac{\partial \tilde{\Phi}}{\partial \tilde{Z}} = -c^{1/2}\,\mathrm{Du}\, e^{\tilde{\Phi}/2}. \tag{5.16}$$

Integration in conjunction with (5.10) yields the excess potential

$$\tilde{\Phi} = 2\ln\frac{2}{2 + c^{1/2}\,\mathrm{Du}\,\tilde{Z}}, \tag{5.17}$$

from which (5.12) yields the counterion concentration

$$\tilde{C}^- = \frac{4c\,\mathrm{Du}^2}{(2 + c^{1/2}\,\mathrm{Du}\,\tilde{Z})^2}. \tag{5.18}$$

Note that $\tilde{\Phi}$ behaves as $\ln\tilde{Z}$ at large $\tilde{Z}$, while $\tilde{C}^-$ decays there as $\tilde{Z}^{-2}$.

Consider now the leading $O(\delta^{-5})$ balance of the radial Stokes equation (3.15),

$$\frac{\partial \tilde{P}_{-4}}{\partial \tilde{Z}} = \frac{\partial^2 \tilde{\Phi}}{\partial \tilde{Z}^2}\frac{\partial \tilde{\Phi}}{\partial \tilde{Z}}. \tag{5.19}$$

Integration followed by asymptotic matching yields

$$\tilde{P}_{-4} = \frac{1}{2}\left(\frac{\partial \tilde{\Phi}}{\partial \tilde{Z}}\right)^2. \tag{5.20}$$

Substitution of both (5.16) and (5.20) into the leading $O(\delta^{-4})$ balance of the tangential Stokes equation (3.16) yields

$$\frac{\partial^2 \tilde{V}}{\partial \tilde{Z}^2} = -e^{\tilde{\Phi}/2}\frac{\partial \tilde{\Phi}}{\partial \tilde{Z}}\frac{d}{d\theta}(c^{1/2}\,\mathrm{Du}). \tag{5.21}$$

A single integration gives

$$\frac{\partial \tilde{V}}{\partial \tilde{Z}} = -2e^{\tilde{\Phi}/2}\frac{d}{d\theta}(c^{1/2}\,\mathrm{Du}), \tag{5.22}$$

where the integration constant must vanish by the requirement of asymptotic matching. A subsequent integration using (5.16) yields

$$\tilde{V} = 2\tilde{\Phi}\frac{d}{d\theta}\ln(c^{1/2}\,\mathrm{Du}) \tag{5.23}$$

where the integration constant again vanishes, now because of the no-slip and equipotential boundary conditions; see (5.10). Note that $\tilde{V}$ possesses the same dependence upon $\tilde{Z}$ as does $\tilde{\Phi}$; specifically, at large $\tilde{Z}$ it behaves as $\ln\tilde{Z}$. From the leading $O(1)$ balance of the continuity equation (3.13)

$$\frac{\partial \tilde{U}}{\partial \tilde{Z}} + \frac{\partial \tilde{V}}{\partial \theta} = 0, \tag{5.24}$$

it then follows that $\tilde{U}$ diverges as $\tilde{Z}\ln\tilde{Z}$ at large $\tilde{Z}$.

Last, consider the leading $O(\delta^{-2})$ anionic balance [see (3.17)]:

$$\frac{\partial \tilde{J}_r^-}{\partial \tilde{Z}} + \frac{\partial \tilde{J}_\theta^-}{\partial \theta} + \alpha^-\left(\tilde{U}\frac{\partial \tilde{C}^-}{\partial \tilde{Z}} + \tilde{V}\frac{\partial \tilde{C}^-}{\partial \theta}\right) = 0. \tag{5.25}$$

Integration over $\tilde{Z}$ in conjunction with (5.10) yields

$$-\tilde{J}_r^-(\tilde{Z}\to\infty) = \frac{d}{d\theta}\int_0^\infty \tilde{J}_\theta^-\,d\tilde{Z} + \alpha^-\int_0^\infty\left(\tilde{U}\frac{\partial \tilde{C}^-}{\partial \tilde{Z}} + \tilde{V}\frac{\partial \tilde{C}^-}{\partial \theta}\right)d\tilde{Z}, \tag{5.26}$$

where we have interchanged the order of radial integration and tangential differentiation in the first term on the right-hand side. Substitution of (5.17) into (5.13) followed by integration yields for this term

$$-4\frac{d^2}{d\theta^2}(c^{1/2}\,\mathrm{Du}). \tag{5.27}$$

Making use of the leading-order continuity equation (5.24) and integration by parts yields for the second term on the right-hand side of (5.26)

$$\alpha^-\int_0^\infty \frac{\partial}{\partial\theta}(\tilde{C}^-\tilde{V})\,d\tilde{Z} = \alpha^-\frac{d}{d\theta}\int_0^\infty \tilde{C}^-\tilde{V}\,d\tilde{Z},$$

where use has been made of both the impermeability condition [see (5.10)] and the large-$\tilde{Z}$ decay of $\tilde{C}^-\tilde{V}$. Substitution of (5.17)–(5.18) and (5.23) followed by integration over $\tilde{Z}$ eventually yields for this term

$$-8\alpha^-\frac{d^2}{d\theta^2}(c^{1/2}\,\mathrm{Du}). \tag{5.28}$$

Substitution of (5.27)–(5.28) into (5.26) furnishes the counterion flux at the outer edge of the Dukhin layer

$$\tilde{J}_r^-(\tilde{Z}\to\infty) = 4(1+2\alpha^-)\frac{d^2}{d\theta^2}(c^{1/2}\,\mathrm{Du}). \tag{5.29}$$

Because of the asymptotically small cationic concentration, it is evident that the comparable $O(1)$ cationic flux vanishes.

C. Effective boundary conditions

With the Dukhin-layer fields known, we can now obtain the effective boundary conditions which locally represent a Debye layer of (positive) large zeta potential. Because the Debye-layer scaling (4.7)–(4.11) remains intact, the impermeability condition (4.33) is unaffected. The slip condition (4.30) is, however, modified. Thus, asymptotic matching between (5.23) and (4.29) yields

$$v = (4\ln 2 + \varphi)\frac{\partial}{\partial\theta}\ln c - \varphi\frac{\partial\varphi}{\partial\theta} \quad \text{at} \quad \bar{r} = 1. \tag{5.30}$$

Inspection reveals that (5.30) is simply the large-φ (i.e., large-ζ) limit of (4.30).

More importantly, consider the $O(1)$ ionic fluxes in the radial direction. For positive ζ the anionic flux at the outer edge of the Dukhin layer is provided by (5.29), while the comparable cationic flux vanishes. These fluxes should match their Debye-layer counterparts, which are transversely uniform; see (4.31). This implies that the Dukhin-layer fluxes can be matched directly with those in the bulk. Using (4.5) we therefore obtain at $\bar{r} = 1$

$$-\frac{\partial c}{\partial\bar{r}} - c\frac{\partial\varphi}{\partial\bar{r}} = 0, \tag{5.31a}$$

$$-\frac{\partial c}{\partial\bar{r}} + c\frac{\partial\varphi}{\partial\bar{r}} = 2(1+2\alpha^-)\frac{d^2}{d\theta^2}(c^{1/2}\mathrm{Du}), \tag{5.31b}$$

replacing (4.34). The inhomogeneous condition (5.31b) represents the emergence of surface conduction, unaccounted by the moderate-zeta-potential model.

D. Negative zeta potentials

The appropriate conditions for large but negative zeta potentials, where the roles of cations and anions are interchanged, are readily obtained. In the Dukhin layer, the cationic concentration is now $O(\delta^{-2})$ large, while the anionic concentration is small. Equation (5.16) becomes

$$\frac{\partial\tilde{\Phi}}{\partial\tilde{Z}} = c^{1/2}\,\mathrm{Du}\,e^{-\tilde{\Phi}/2}, \tag{5.32}$$

wherein the local Dukhin number is redefined as [see (1.2) and (4.37)]

$$\mathrm{Du} = \delta e^{\varphi/2}. \tag{5.33}$$

The transverse cationic flux is $O(1)$ [cf. (5.7)]

$$\hat{\mathbf{e}}_r\cdot\mathbf{j}^+ = \tilde{J}_r^+(\tilde{Z},\theta) + \cdots \tag{5.34}$$

wherein [cf. (5.29)]

$$\tilde{J}_r^+(\tilde{Z}\to\infty) = 4(1+2\alpha^+)\frac{d^2}{d\theta^2}(c^{1/2}\mathrm{Du}). \tag{5.35}$$

The anionic flux vanishes at that order.

With the modifications in the Dukhin-layer fields, the slip condition (5.30) is replaced by

$$v = (4\ln 2 - \varphi)\frac{\partial}{\partial\theta}\ln c - \varphi\frac{\partial\varphi}{\partial\theta}, \tag{5.36}$$

and (5.31) are replaced by

$$-\frac{\partial c}{\partial\bar{r}} - c\frac{\partial\varphi}{\partial\bar{r}} = 2(1+2\alpha^+)\frac{d^2}{d\theta^2}(c^{1/2}\mathrm{Du}), \tag{5.37a}$$

$$-\frac{\partial c}{\partial\bar{r}} + c\frac{\partial\varphi}{\partial\bar{r}} = 0. \tag{5.37b}$$

VI. UNIFORM APPROXIMATION FOR EFFECTIVE BOUNDARY CONDITIONS

At this stage we have at our possession effective boundary conditions for boundary regions where the zeta potential is moderate, as well as comparable conditions for the complementary regions where the (positive or negative) ζ value is logarithmically large. Of course, the decomposition of the boundary into these different regions is unknown *a priori*: It is determined by the solution to the electrokinetic problem, which in turn depends upon proper use of the effective boundary conditions.

This paradigmatic circular obstacle is circumvented via use of *uniform* asymptotic approximations (see Ref. [82]) for the effective conditions, valid at all ζ values (and hence for all boundary points) [83].

Since (5.30) and (5.36) are simply the appropriate extrapolations of (4.30) for the respective cases of positive and negative large zeta potentials, it is evident that (4.30) constitutes a uniform approximation for the slip.

To obtain comparable uniform condition governing c and φ, we simply employ (5.29), derived for large and positive zeta potential, for the anionic flux, regardless of the zeta-potential value. Similarly, we uniformly employ (5.35)—derived for large and negative zeta potential—for the cationic flux. Using (4.37) and (5.33) thus yields

$$-\frac{\partial c}{\partial\bar{r}} - c\frac{\partial\varphi}{\partial\bar{r}} = 2\delta(1+2\alpha^+)\frac{d^2}{d\theta^2}(c^{1/2}e^{\varphi/2}), \tag{6.1a}$$

$$-\frac{\partial c}{\partial\bar{r}} + c\frac{\partial\varphi}{\partial\bar{r}} = 2\delta(1+2\alpha^-)\frac{d^2}{d\theta^2}(c^{1/2}e^{-\varphi/2}). \tag{6.1b}$$

For ζ large and positive the cationic flux is exponentially small, and we recover (5.31). For ζ large and negative, the anionic flux is exponentially small and we recover (5.37). If ζ is moderate, both fluxes are $O(\delta)$, and we recover the homogenous conditions (4.34).

In addition to conditions (6.1) we also employ the memory condition (4.24), originally derived for moderate zeta potentials. Indeed, use of (5.16) and (4.37) reveals that (4.23) provides a leading-order approximation for the radial electric field at the surface even at large and positive zeta potential. Similarly, use of (5.32) and (5.33) reveals that (4.23) provides a leading-order approximation for the radial electric field at the surface even at large and negative zeta potential.

VII. RECAPITULATION

A. ICEO flow about a cylinder

For easy reference, we recapitulate here the entire macroscale model describing the thin-double-layer limit $\delta \ll 1$. We focus upon the case of equal ionic diffusivities, where $\alpha^\pm$ are identical, equal, say to α [see (3.8)]. For brevity we also

omit the bar decoration from the coarse-grained radial coordinate; since only the macroscale model is addressed hereafter, no confusion should arise. Our macroscale model governs the salt concentration c, electric potential φ, velocity field $\mathbf{u} = \hat{\mathbf{e}}_r u + \hat{\mathbf{e}}_\theta v$ and pressure field p within the electroneutral bulk. It comprises the following:

(1) Differential equations:

$$\nabla^2 c = \alpha \mathbf{u} \cdot \nabla c, \tag{7.1}$$

$$\nabla \cdot (c \nabla \varphi) = 0, \tag{7.2}$$

$$\nabla \cdot \mathbf{u} = 0, \tag{7.3}$$

$$\nabla p = \nabla^2 \mathbf{u} + \nabla^2 \varphi \nabla \varphi. \tag{7.4}$$

(2) Boundary conditions on the effective boundary $r = 1$, consisting of the impermeability

$$u = 0 \tag{7.5}$$

and slip

$$v = -\varphi \frac{\partial \varphi}{\partial \theta} + 2 \ln \left(1 - \tanh^2 \frac{\varphi}{4}\right) \frac{\partial \ln c}{\partial \theta} \tag{7.6}$$

conditions, together with the inhomogeneous Neumann-type conditions [cf. (4.35)]

$$\frac{\partial c}{\partial r} = -4\delta(1 + 2\alpha) \frac{\partial^2}{\partial \theta^2} \left(c^{1/2} \cosh \frac{\varphi}{2}\right), \tag{7.7}$$

$$c \frac{\partial \varphi}{\partial r} = -4\delta(1 + 2\alpha) \frac{\partial^2}{\partial \theta^2} \left(c^{1/2} \sinh \frac{\varphi}{2}\right), \tag{7.8}$$

obtained via respective addition and subtraction of (6.1).

(3) Far-field conditions at $r \to \infty$, consisting of the required approach to a uniform electric field

$$\nabla \varphi \to -\beta \hat{\boldsymbol{\imath}}, \tag{7.9}$$

velocity decay

$$\mathbf{u} \to \mathbf{0}, \tag{7.10}$$

and the approach to the equilibrium salt concentration,

$$c \to 1. \tag{7.11}$$

(4) Memory condition,

$$\int_{r=1} c^{1/2} \sinh \frac{\varphi}{2} \, d\theta = 0. \tag{7.12}$$

The problem prescribed by (7.1)–(7.12) is coupled and highly nonlinear. No closed-form solution seems to be available. Nonetheless, certain symmetry properties may be deduced. It is readily verified that c, p, and u are even functions of $x = r \cos\theta$ while φ and v are odd functions of x. The charge-invariance condition (7.12) is then automatically satisfied. With φ vanishing along the transverse symmetry plane $x = 0$ (where $\theta = \pm\pi/2$), it becomes evident that even for large β there are always boundary regions where the zeta potential $-\varphi$ is moderate.

B. Arbitrary geometry

It is straightforward to generalize the macroscale model to an arbitrary geometry, where the boundary of the metal object (still assumed fixed) is described in terms of the unit normal vector $\hat{\mathbf{n}}$ pointing into the fluid. Conditions (7.5)–(7.8) are replaced by the following conditions, written in an invariant notation:

$$\mathbf{u} = -\varphi \nabla_s \varphi + 2 \ln \left(1 - \tanh^2 \frac{\varphi}{4}\right) \nabla_s \ln c, \tag{7.13}$$

$$\frac{\partial c}{\partial n} = -4\delta(1 + 2\alpha) \nabla_s^2 \left(c^{1/2} \cosh \frac{\varphi}{2}\right), \tag{7.14}$$

$$c \frac{\partial \varphi}{\partial n} = -4\delta(1 + 2\alpha) \nabla_s^2 \left(c^{1/2} \sinh \frac{\varphi}{2}\right). \tag{7.15}$$

Here $\nabla_s = (\mathsf{I} - \hat{\mathbf{n}}\hat{\mathbf{n}}) \cdot \nabla$ is the surface gradient operator (in which I is the idemfactor), ∇_s^2 is the surface Laplacian, and $\partial/\partial n = \hat{\mathbf{n}} \cdot \nabla$. The memory condition (7.12) is replaced by

$$\int_s c^{1/2} \sinh \frac{\varphi}{2} \, dA = 0, \tag{7.16}$$

in which dA is a differential area element, normalized by a^{*2}.

The appearance of $\delta(\ll 1)$ in the boundary conditions (7.14) and (7.15) is an artifact of the use of uniform asymptotic approximations; see Sec. VI. While δ is asymptotically small, it multiples terms that become $O(1/\delta)$ for moderately large β values, of order $2 \ln \delta$.

Fundamentally the electric potential is determined only up to an additive constant. It may therefore seem surprising that conditions (7.13)–(7.15) are not invariant to the transformation $\varphi \to \varphi +$ constant. Note, however, that the arbitrariness in φ has already been exploited in the microscale analysis, where the potential of the metal was conveniently set to zero [see (3.19)]. The consequent uniqueness of φ is conveyed to the macroscale description through memory condition (7.16). In the case of a fore-aft symmetric shape, like a cylinder, this necessitates that φ is an odd function of x.

VIII. CONCLUDING REMARKS

Starting from the standard microscale electrokinetic description, we have derived a macroscale model governing ICEO flows about metal objects, valid beyond moderately applied fields. At this regime, where the zeta potential distribution is characterized by values exceeding the thermal voltage, surface conduction affects the leading-order transport processes.

Incorporating surface conduction in ICEO modeling is not straightforward. The traditional linearization approach of colloidal science entails a weak field that acts upon the Debye cloud associated with an essentially uniform zeta potential distribution, of moderately large magnitude. In ICEO, this weak-field approach is evidently irrelevant: As the zeta potential distribution is induced by the applied field, large zeta potentials go together with *strong* fields.

In analyzing the present highly nonlinear problem we have followed the approach of our recent paper [78] where a macroscale model was developed for electro-osmotic flow about a highly charged dielectric solid without the weak field limitation. Even that approach can only be partially applied. Thus, the derivation [78] is facilitated by the identification of a dimensionless Bikerman number which represents the global role of surface conduction (and which degenerates to a Dukhin number in the weak-field limit, where the zeta potential becomes uniform). In ICEO, where the surface-charge distribution is polarized, the comparable definition of

a dimensionless number does not appear to be as useful in the subsequent analysis.

We have therefore adopted a complementary paradigm, where the Dukhin number Du was interpreted as a local dimensionless group which varies along the liquid-metal interface. The Debye layer adjacent to any generic point on that interface has been treated according to two possible scenarios, corresponding to small Du (moderate zeta potential) or moderate Du (logarithmically large zeta potential). The former leads to the familiar boundary conditions of thin-double-layer electrokinetics [53]. The latter, involving surface conduction, results in different boundary conditions. Following [78], the derivation of these conditions is facilitated by a separate analysis of the Dukhin sublayer, formed adjacent to the interface, where surface conduction is localized.

With the zeta potential being an inherently induced quantity, the asymptotic decomposition of the boundary into the moderate- and large-ζ regions, where the effective boundary conditions differ, is *a priori* unknown and must be determined as part of the solution of the macroscale problem. Proper formulation of this problem, on the other hand, relies upon the appropriate use of these very conditions. This obstacle is overcome via the construction of a uniform approximation for the effective conditions, valid along the entire boundary.

The resulting model readily clarifies the transition to moderately large fields where surface conduction is appreciable. Indeed, consider the case of small β, where φ is $O(\beta)$. The surface conduction mechanism, represented by the right-hand-sides of (7.14) and (7.15), is $O(\delta)$ small. Thus, $c-1$ satisfies a homogenous linear problem whose solution is trivial, giving $c \equiv 1$. With a uniform salt concentration, we recover the problem solved by Squires and Bazant [9]. The electric potential becomes harmonic, with the solution $\varphi = -\beta\,(r + 1/r)\cos\theta$, where the integration constant must vanish by the fore-aft antisymmetry of φ [or, equivalently, by (7.12)]. Note that the maximum absolute value of the zeta potential $-\varphi$ over the cylinder boundary is 2β. This implies that it is actually not necessary that β be small for the preceding solution to apply. Indeed, it readily follows from (7.14) and (7.15) that the surface conduction mechanism is negligible if

$$\delta e^{\beta} \ll 1. \tag{8.1}$$

Since this is the only approximation made in solving (7.1)–(7.12), the solution given by the standard ICEO model is valid provided $\beta \ll \ln\delta$. Criterion (8.1) suggests that the present counterpart to the Bikerman number of Ref. [78] is δe^{β}.

For $\beta \sim O(\ln\delta)$, practically meaning $O(1)$ β values, surface conduction enters the picture. The macroscale model derived herein allows for the first time to analyze the resulting ICEO flows. Note that the β values characterizing most practical systems may actually be quite large. Nonetheless, since the macroscale manifestation of surface conduction typically represents a negative feedback mechanism, we anticipate that the resulting salt polarization would be such as to maintain the zeta-potential distribution comparable to the thermal voltage, even for $\beta \gg 1$. If that is indeed the case, dilute systems (in the sense of Fig. 5 in Ref. [78]) are adequately described by the standard Poisson-Nernst-Planck equations even at very large β values; the present macroscale model is then rather robust. This speculation of slowly growing (or even bounded) zeta-potential magnitude can only be confirmed by a numerical solution of our model. We are currently pursuing this route. Thus, preliminary numerical simulations of our macroscale equations at moderate field values, up to about $\beta \approx 6$, indicate that the linear zeta-potential scaling with β breaks down; the dependence of the typical flow magnitude upon β exhibits an inflection point, representing a transition from the convex β^2 dependence to a concave one.

In view of the complexity of the surface-conduction mechanism, we have confined the present analysis to DC fields, where the electrokinetic transport is steady. A desirable extension of our analysis should then address the more general scenario of time-dependent fields. Practically speaking, most experimental realizations of ICEO are carried out under AC fields [15]. Moreover, time-dependent fields are inherent in "AC electro-osmosis," where the metal object on which the electro-osmotic slip occurs is also the electric-field driver [8]. Such an extension may be quite challenging. Indeed, even in one-dimensional analyses of electrochemical cells, where neither flow nor surface conduction are present, the nonlinear double-layer capacitance leads to multi-time-scale dynamics under AC forcing [84] accompanied by a diffusive boundary layer where salt relaxation takes place. A rigorous attempt to analyze time-dependent ICEO may therefore require the simultaneous analysis of at least four different asymptotic domains.

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