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Streaming-potential phenomena in the thin-Debye-layer limit. Part 1. General theory

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Electrokinetic streaming-potential phenomena are driven by imposed relative motion between liquid electrolytes and charged solids. Owing to non-uniform convective ‘surface’ current within the Debye layer Ohmic currents from the electro-neutral bulk are required to ensure charge conservation thereby inducing a bulk electric field. This, in turn, results in electro-viscous drag enhancement. The appropriate modelling of these phenomena in the limit of thin Debye layers $\delta \to 0$ (δ denoting the dimensionless Debye thickness) has been a matter of ongoing controversy apparently settled by Cox's seminal analysis (*J. Fluid Mech.*, vol. 338, 1997, p. 1). This analysis predicts electro-viscous forces that scale as δ^4 resulting from the perturbation of the original Stokes flow with the Maxwell-stress contribution only appearing at higher orders. Using scaling analysis we clarify the distinction between the normalizations pertinent to field- and motion-driven electrokinetic phenomena, respectively. In the latter class we demonstrate that the product of the Hartmann & Péclet numbers is $O(\delta^{-2})$ contrary to Cox (1997) where both parameters are assumed $O(1)$. We focus on the case where motion-induced fields are comparable to the thermal scale and accordingly present a singular-perturbation analysis for the limit where the Hartmann number is $O(1)$ and the Péclet number is $O(\delta^{-2})$. Electric-current matching between the Debye layer and the electro-neutral bulk provides an inhomogeneous Neumann condition governing the electric field in the latter. This field, in turn, results in a velocity perturbation generated by a Smoluchowski-type slip condition. Owing to the dominant convection, the present analysis yields an asymptotic structure considerably simpler than that of Cox (1997): the electro-viscous effect now already appears at $O(\delta^2)$ and is contributed by both Maxwell and viscous stresses. The present paradigm is illustrated for the prototypic problem of a sphere sedimenting in an unbounded fluid domain with the resulting drag correction differing from that calculated by Cox (1997). Independently of current matching, salt-flux matching between the Debye layer and the bulk domain needs also to be satisfied. This subtle point has apparently gone unnoticed in the literature, perhaps because it is trivially satisfied in field-driven problems. In the present limit this requirement seems incompatible with the uniform salt distribution in the convection-dominated bulk domain. This paradox is resolved by identifying the dual singularity associated with the limit $\delta \to 0$ in motion-driven problems resulting in a diffusive layer of $O(\delta^{2/3})$ thickness beyond the familiar $O(\delta)$-wide Debye layer.

Key words: colloids, low-Reynolds-number flows, micro-/nano-fluid dynamics

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1. Introduction

When brought in contact with an aqueous (polar) medium most solids spontaneously acquire surface electric charge. Electrostatic attraction then creates an excess of counter-ions within the solution next to the solid thereby forming the Debye double layer which screens the charged solid from the electro-neutral bulk solution. An external agency upsetting the mechanical equilibrium of the Debye layer gives rise to electrokinetic phenomena. These are second order in the thermodynamic sense (i.e. forces of a certain kind generating fluxes or flows of another type) with conjugate forces and fluxes obeying Onsager-type relations (Doi & Makino 2008). Thus, an externally applied electric field exerts a Coulomb body force on the charged fluid inducing a tangential motion relative to the solid. Alternatively, streaming-potential phenomena originate from a mechanical external agency (e.g. pressure drop, relative motion of bounding surfaces, gravitational or centrifugal settling) imposing a relative motion of the diffuse portion of the Debye layer and adjacent charged solid thus generating an electric field.

Streaming-potential phenomena are relevant to suspension rheology (Booth 1950; Russel 1978; Sherwood 1980; Hinch & Sherwood 1983), geophysical two-phase flows through fine porous media (as in oil recovery and water seepage through porous rock formations: Boléve *et al.* 2007; Sherwood 2007, 2008, 2009; Lac & Sherwood 2009) and in the accurate measurement of zeta potentials (Lyklema 1995). Furthermore, streaming-potential phenomena constitute the key to the resolution of a variety of puzzles associated with the motion of colloidal particles as in the anomalous repulsion of polystyrene microspheres from an adjacent wall in the presence of an imposed shear flow. Owing to the symmetry properties of the linear Stokes equations (Leal 2007) hydrodynamic repulsion is inadmissible in the absence of inertial effects. These, in turn, have been ruled out in the experiments of Prieve and co-workers (Alexander & Prieve 1987; Bike, Lazarro & Prieve 1995).

Similarly to electrokinetic problems in general, streaming-potential problems are rather formidable owing to nonlinear coupling of their electrochemical and dynamic aspects (see § 2). Analyses of these problems have therefore relied upon various approximations. Thus, Booth (1954) analysed the electric field caused by the sedimentation of a spherical particle assuming a small zeta potential, while Ohshima *et al.* (1984) obtained the excess drag on a sedimenting sphere via linearization about a spherically symmetric ionic cloud (which is valid for small settling speeds).

A different approach is based upon the smallness of $1/\kappa^*$, the Debye scale, where

$$\kappa^{*2} = \frac{2\mathscr{Z}^2 e^{*2} c^*}{\epsilon^* k^* T^*}, \tag{1.1}$$

with ϵ^* the dielectric permittivity of the solution, k^*T^* the Boltzmann temperature, c^* the bulk ionic concentration, $\pm\mathscr{Z}$ the (presumed equal) ionic valences, and e^* the elementary charge (dimensional quantities being herein decorated by an asterisk). For aqueous solutions at room temperature and millimolar concentration (1.1) typically yields $1/\kappa^* \approx 10$ nm. With a^* denoting a characteristic dimension of the problem geometry the thin-Debye-layer limit is predicated upon the assumption

$$\delta = \frac{1}{\kappa^* a^*} \ll 1. \tag{1.2}$$

This singular limit has been applied extensively in field-driven electrokinetic phenomena (Anderson 1989). The usefulness of this approximation derives from its providing a macro-scale bulk description wherein the Debye layer is represented

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through effective boundary conditions (Prieve *et al.* 1984; Yariv 2010). As such, the resulting scheme is not limited to highly symmetric configurations.

The study of streaming-potential phenomena within the framework of the thin-Debye-layer limit $\delta \ll 1$ dates back to the pioneering work of Smoluchowski (1921). Interest in these problems has renewed with the investigations of Prieve and co-workers. The forced motion of a particle parallel to a neighbouring wall was studied by Bike & Prieve (1990) by means of a lubrication approximation. The lift force predicted was, however, orders of magnitude smaller than the Debye-layer repulsion. Seeking to relax the lubrication approximation (which was hypothesized to fail owing to particle repulsion from the wall) Bike & Prieve (1992) presented a general analysis of streaming-potential phenomena which was subsequently applied (Bike & Prieve 1995) to the calculation of the lift force on a particle in a configuration appropriate to modelling the experiments of Alexander & Prieve (1987). The paradigm underlying these calculations assumes that the original Stokes flow remains essentially unchanged, the correction to the hydrodynamic force being therefore exclusively associated with the Maxwell stress. This, in turn, is obtained through calculation of the electric field generated by 'surface' charge convection within the Debye layer resulting from the prescribed flow. A similar methodology was employed by other investigators (van de Ven, Warszynski & Dukhin 1993*a*,*b*).

The persistent discrepancy between the force predictions and the (much larger) experimental measurements of particle–wall interactions motivated Cox (1997) to re-examine the generic streaming-potential problem within the framework of a consistent asymptotic scheme in the limit $\delta \to 0$. In appropriately normalized notation, where the Stokes drag associated with the background flow is $O(1)$, the resultant of the Maxwell-stress distribution is an $O(\delta^6)$ force. Cox's analysis, however, revealed that the perturbation to the flow neglected in the preceding analyses is responsible for a larger $O(\delta^4)$ correction thus disproving the basic tenet of the above paradigm. (In retrospect the attempt to exclusively attribute drag correction to Maxwell stresses is evidently questionable. Thus, e.g. in the prototypic problem of particle sedimentation in an unbounded fluid the analysis of Bike & Prieve (1992) fails to predict any drag correction.) Subsequent analyses of particle–wall interaction (Tabatabaei, van de Ven & Rey 2006; Tabatabaei & van de Ven 2010) have employed the general theory of Cox (1997).

1.1. *Field-driven versus motion-driven phenomena*

The high asymptotic orders inherent in Cox's scheme which result in intractable equations practically excluding the possibility of making theoretical predictions which could be compared to experimental observations. Even the calculation of the excess drag on a spherical particle necessitates the use of the further simplifying assumption of small Péclet numbers (Cox 1997). Obviously, such assumptions are inevitable in more complex calculations (Tabatabaei *et al.* 2006; Tabatabaei & van de Ven 2010). This technical complexity seems somewhat surprising, particularly in view of the relative simplicity of the physically motivated scheme of Bike & Prieve (1992).

We therefore turn to re-examine the distinct scalings appropriate to field-driven and motion-driven phenomena, respectively. This will also help resolve an apparent paradox associated with the thin-Debye-layer limit of streaming-potential phenomena: it is well known that standard models of field-driven electrokinetics for thin Debye layers prescribe a homogeneous Neumann condition for the bulk-scale electric potential (Anderson 1989; Yariv 2010); with such a condition, however, no electric field can be generated by the imposed motion (Doi & Makino 2008).

A natural scale for the electric potential in electrokinetic processes is the thermal voltage

$$\varphi^* = \frac{k^* T^*}{\mathscr{Z} e^*}, \tag{1.3}$$

which is ≈25 mV in a uni-valent solution. Field-driven phenomena are characterized by yet another scale, say E^*, of the external electric field. Thus, the important parameter (Saville 1977)

$$\beta = \frac{a^* E^*}{\varphi^*}, \tag{1.4}$$

representing the ratio between the applied- and thermal-field scales, is externally controlled.

In motion-driven phenomena, on the other hand, the driver of the electrokinetic processes is the imposed relative velocity, of order v^*, between the charged boundary and the ionic solution. Thus, the scale E^* characterizing the electric field in the bulk is determined by a Debye-layer charging mechanism: the imposed flow generates a convective 'surface' current through the Debye layer. This current is generally non-uniform and therefore necessitates the generation of bulk currents to 'feed' the Debye layer. In the Ohmic bulk domain such currents imply electric fields. The characteristic value E^* quantifying these fields clearly depends upon the magnitude of v^*. In the thin-Debye-layer limit $\delta \to 0$ a scaling relation is readily obtainable. From the velocity gradients being $O(v^*/a^*)$ in conjunction with the no-slip condition we conclude that the fluid velocity within the Debye layer is $O(\delta v^*)$. The convective 'surface' current through the layer scales as the product of this velocity with the Debye width $1/\kappa^*$ and the characteristic charge density $e^* c^*$. The non-zero divergence of the surface current is hence of order $\delta^2 v^* e^* c^*$. To ensure charge conservation, this divergence needs to be balanced by bulk Ohmic currents which scale as the product of E^* and the $O(e^{*2} c^* D^*/k^* T^*)$ ionic conductivity, D^* being a typical ionic diffusivity. Use of the definition (1.3) then reveals that the scale E^* is provided by $\delta^2 v^* \varphi^*/D^*$. Substitution into (1.4) furnishes the scaling relation

$$\beta = \delta^2 Pe, \tag{1.5}$$

in which

$$Pe = \frac{a^* v^*}{D^*} \tag{1.6}$$

is the Péclet number characterizing ionic transport.

As opposed to the above, in field-driven flows the Smoluchowski slip condition readily implies

$$Pe = O(\beta). \tag{1.7}$$

The difference between the scaling relations (1.5) and (1.7) resolves the above apparent contradiction between the classic thin-Debye-layer models and the induction of electric fields by the motion of charged surfaces. Indeed, the homogeneous Neumann condition in these models, obtained for both β and Pe of order unity, is clearly inapplicable to streaming-potential phenomena where (1.5) holds.

1.2. *An oversight in Cox (1997)*

The relation (1.5) implies that β and Pe cannot both be $O(1)$ at the same time. This has apparently been overlooked by Cox (1997) who postulates $Pe = O(1)$ and (implicitly) $\beta = O(1)$ (see § 2.3). The relegation of the electro-viscous effect to $O(\delta^4)$ thus seems an artifact reflecting this oversight. The aim of the present contribution is therefore to reconsider the generic streaming-potential problem in a consistent asymptotic limit. Relation (1.5) is obviously compatible with a variety of limit processes (see § 12). Since the Péclet numbers in experiments concerned with electro-viscous effects on colloidal particles often exceed unity (Warszynski & van de Ven 2000) there is evident interest in the limit of strong convection $Pe = O(\delta^{-2})$ (whose desirability is already implied in Saville 1977). With $\beta = O(1)$, this specific limit possesses the further 'technical' advantage of a single field scale. The dominance of convection imposes a new asymptotic ordering. Thus, the leading-order force corrections turn out to be of order δ^2; moreover, these corrections are contributed by *both* the flow correction and the Maxwell stresses associated with the induced field.

The rest of our contribution is organized as follows. In the next section we formulate the generic electrokinetic problem. For clarity we initially focus upon steady situations where all solid boundaries are assumed stationary. The thin-Debye-layer limit is considered in § 3 where the need for matched inner–outer asymptotic expansions is demonstrated. The scaling and geometry of the inner Debye-layer domain are discussed in § 4. In doing this we follow Cox (1997) and employ a local inner reference system about a general point on the solid surface which facilitates the study of a generic geometry. In § 5 the Debye-layer fields are analysed which is followed by asymptotic matching in § 6 yielding effective bulk-scale boundary conditions. Leading-order flow corrections are subsequently calculated in § 7. In § 8 the present scheme is recapitulated and is then illustrated in § 9 for a sphere sedimenting in an unbounded fluid. The drag correction thus obtained differs in both form and scale from that calculated by Cox (1997) in the same problem. In § 10 and § 11 we respectively extend our scheme to allow for the analysis of weakly unsteady problems and non-uniform surface-charge distributions. Concluding remarks are made in § 12. Finally, while the need for the generation of bulk Ohmic currents originating from non-uniform 'surface' charge convection within the Debye layer has been recognized before (Bike & Prieve 1992), the concomitant non-uniform 'surface' salt convection has gone unnoticed. This, in turn, requires comparable influx of salt which seems incompatible with the uniform outer salt distribution mandated by the dominant convection. This apparent paradox regarding salt-flux matching is resolved in the Appendix.

2. Problem formulation

We consider a generic streaming-potential problem, where one or more solid surfaces are in contact with a symmetric binary electrolyte solution (valencies $\pm\mathscr{Z}$, permittivity ϵ^*). With increasing distance from the solid surfaces both ionic concentrations approach a uniform value c^*. The electrokinetic transport is driven by an imposed relative solid–liquid motion, characterized by velocity variations of order v^* over distances of order a^*. For simplicity, we assume identical diffusivity D^* of both ionic species. While this assumption can be relaxed, it is retained for brevity. Furthermore, we initially consider stationary solid boundaries possessing uniform surface-charge densities (allowing for different densities on separate boundaries). These assumptions are reassessed later on (see §§ 10 and 11).

The governing equations and boundary conditions are rendered dimensionless through scaling the position vector $\boldsymbol{x}$ by a^*, the ionic concentrations $c^{\pm}$ by c^*, and the electric potential φ by φ^*(see (1.3)). The fluid velocity $\boldsymbol{v}$ is normalized by v^* and the pressure p by $\mu^* v^*/a^*$ (μ^* denoting the solution viscosity). Lastly, the ionic fluxes are normalized by $D^* c^*/a^*$, the volume charge density by $2\mathscr{Z} e^* c^*$ and the current density by $\mathscr{Z} e^* D^* c^*/a^*$.

2.1. *Differential equations*

The ionic concentrations are governed by the Nernst–Planck equations, describing transport by the combined action of electro-migration, diffusion, and convection:

$$\nabla \cdot \boldsymbol{j}^{\pm} + Pe\, \boldsymbol{v} \cdot \nabla c^{\pm} = 0. \tag{2.1}$$

Here

$$\boldsymbol{j}^{\pm} = \mp c^{\pm} \nabla \varphi - \nabla c^{\pm} \tag{2.2}$$

are the ionic fluxes. The electric potential φ satisfies Poisson's equation

$$\delta^2 \nabla^2 \varphi = -q, \tag{2.3}$$

in which

$$q = \tfrac{1}{2}(c^+ - c^-) \tag{2.4}$$

is the volumetric charge density and $\delta = (\kappa^* a^*)^{-1}$ is the dimensionless Debye thickness. Finally, the motion of fluid subject to Coulomb body force is governed by the continuity equation

$$\nabla \cdot \boldsymbol{v} = 0 \tag{2.5}$$

together with the inhomogeneous Stokes equations

$$\nabla^2 \boldsymbol{v} - \nabla p = \lambda q \nabla \varphi, \tag{2.6}$$

where

$$\lambda = \frac{2k^* T^* a^* c^*}{\mu^* v^*} \tag{2.7}$$

is the Hartmann number representing the relative magnitude of the Coulomb body forces and viscous stresses (cf. Cox 1997).

A useful alternative to the balance equations (2.1) is obtained via replacing $c^{\pm}$ with the charge density q and the mean ('salt') concentration

$$c = \tfrac{1}{2}(c^+ + c^-). \tag{2.8}$$

Addition of the two equations (2.1) yields the 'salt balance' equation,

$$\nabla \cdot \boldsymbol{j} + Pe\, \boldsymbol{v} \cdot \nabla c = 0 \tag{2.9}$$

in which

$$\boldsymbol{j} = -q \nabla \varphi - \nabla c \tag{2.10}$$

is the mean ('salt') flux; subtraction of the two equations (2.1) yields the charge balance equation,

$$\nabla \cdot \boldsymbol{i} + Pe\, \boldsymbol{v} \cdot \nabla q = 0, \tag{2.11}$$

wherein

$$\boldsymbol{i} = -c \nabla \varphi - \nabla q \tag{2.12}$$

is the current density. Note that

$$\boldsymbol{j} = \tfrac{1}{2}(\boldsymbol{j}^{+} + \boldsymbol{j}^{-}), \quad \boldsymbol{i} = \tfrac{1}{2}(\boldsymbol{j}^{+} - \boldsymbol{j}^{-}). \tag{2.13}$$

2.2. *Boundary conditions*

The above equations are supplemented by appropriate boundary conditions imposed on the pertinent fields. On a generic solid surface S the fluid velocity satisfies both impermeability and no-slip conditions

$$\boldsymbol{v} = \boldsymbol{0} \quad \text{on } S. \tag{2.14}$$

We only consider inert surfaces (i.e. in the absence of Faradaic reactions) whence the normal components of the fluxes $\boldsymbol{j}^{\pm}$ need to vanish,

$$\hat{\boldsymbol{n}} \boldsymbol{\cdot} \boldsymbol{j}^{\pm} = 0 \quad \text{on } S, \tag{2.15}$$

with $\hat{\boldsymbol{n}}$ being a unit vector normal to S (pointing into the fluid). By (2.13) these conditions can be expressed alternatively as

$$\hat{\boldsymbol{n}} \boldsymbol{\cdot} \boldsymbol{j} = 0, \quad \hat{\boldsymbol{n}} \boldsymbol{\cdot} \boldsymbol{i} = 0 \quad \text{on } S. \tag{2.16}$$

The electric field normal to S is related through Gauss's law to the (presumably prescribed) surface charge density on S and the electric field within the solid wall.

At large distances away from the wall the ionic concentrations approach their equilibrium value,

$$c^{\pm} \to 1 \quad \text{as } |\boldsymbol{x}| \to \infty, \tag{2.17}$$

and the electric field vanishes,

$$\nabla \varphi \to \boldsymbol{0} \quad \text{as } |\boldsymbol{x}| \to \infty; \tag{2.18}$$

the flow field satisfies appropriate conditions representing the approach to a prescribed far-field flow.

2.3. *Péclet-number scaling*

In field-driven phenomena, a natural velocity scale results from a balance between the Coulomb body forces and viscous stresses in (2.6) and is therefore given by $\epsilon^{*}\varphi^{*2}/\mu^{*}a^{*}$. With that choice, the corresponding intrinsic Péclet number is provided by the dimensionless group (Saville 1977)

$$\alpha = \frac{\epsilon^{*}\varphi^{*2}}{\mu^{*}D^{*}}, \tag{2.19}$$

which is independent of both the particle dimension a^{*} and the electrolyte concentration c^{*}. Thus, for typical ionic diffusivities ($D^{*} \approx 10^{-9}$ m^{2} s^{-1}) in aqueous solutions ($\epsilon^{*} \approx 6 \times 10^{-10}$ kg m s^{-2} V^{-2}, $\mu^{*} \approx 10^{-3}$ kg m^{-1} s^{-1}),

$$\alpha \approx 0.5. \tag{2.20}$$

By the Stokes–Einstein relation, (2.19) is independent of μ^{*} whence α is of order unity also for highly viscous polar solutions.

In contrast with this, in the present context the velocity scale v^{*} is *externally* imposed (e.g. by a prescribed shear flow, or by the sedimentation of a particle relative to a suspending electrolyte). From (1.2), (2.7) and (2.19) we obtain the corresponding Péclet number

$$Pe = \frac{\alpha}{\lambda}\delta^{-2}. \tag{2.21}$$

Thus, when assuming $\lambda = O(1)$, we find that the Péclet number is $O(\delta^{-2})$. This scaling implies a major modification of the electrokinetic transport process.

The analysis of Cox (1997) is based upon the limit $\delta \to 0$ with both λ and Pe of order unity (Cox 1997 actually allows for unequal diffusivities of the ionic species, leading to two Péclet numbers). The relation (2.21) indicates that this choice is inconsistent. Of course, the magnitude of Pe is set externally and one could also envision situations where Pe is of order unity (e.g. in sedimentation problems) but then it follows that $\lambda = O(\delta^{-2})$, in contrast to the explicit assumption and scaling in Cox (1997).

The magnitude of λ clearly determines the scaling of the electric field induced by the imposed flow. Indeed, substitution of (2.21) into (1.5) yields

$$\beta = \frac{\alpha}{\lambda}. \tag{2.22}$$

Thus, when assuming $\lambda = O(1)$, then $\beta = O(1)$ as well, i.e. the thermal and induced electric-field scales are comparable. In this paper we focus upon this natural limit, where $Pe = O(\delta^{-2})$ (which has already been implied by Saville 1977).

Of the three parameters related to the magnitude of the imposed motion – β, λ and Pe – only one is independent. In terms of the parameter λ, the Nernst–Planck equations (2.1) therefore read

$$\nabla \cdot \boldsymbol{j}^{\pm} + \frac{\alpha}{\lambda}\delta^{-2}\boldsymbol{v} \cdot \nabla c^{\pm} = 0, \tag{2.23}$$

while the salt and charge balances, (2.9) and (2.11), become

$$\nabla \cdot \boldsymbol{j} + \frac{\alpha}{\lambda}\delta^{-2}\boldsymbol{v} \cdot \nabla c = 0 \tag{2.24}$$

and

$$\nabla \cdot \boldsymbol{i} + \frac{\alpha}{\lambda}\delta^{-2}\boldsymbol{v} \cdot \nabla q = 0, \tag{2.25}$$

respectively.

3. Thin-Debye-layer limit

We focus upon the thin-Debye-layer limit, $\delta \ll 1$. The above governing equations (2.3) and (2.23)–(2.25) suggest the generic expansion

$$f(\boldsymbol{x}; \delta) \sim f_0(\boldsymbol{x}) + \delta^2 f_1(\boldsymbol{x}) + \cdots. \tag{3.1}$$

Three features then readily follow.

(i) Poisson's equation (2.3) yields leading-order electro-neutrality:

$$q_0 \equiv 0, \tag{3.2}$$

implying that the two ionic densities are equal,

$$c_0^+(\boldsymbol{x}) = c_0^-(\boldsymbol{x}) = c_0(\boldsymbol{x}). \tag{3.3}$$

(ii) In the absence of Coulomb forcing, the equations (2.5)–(2.6) governing fluid motion reduce in leading order to the homogeneous Stokes equations

$$\nabla \cdot \boldsymbol{v}_0 = 0, \quad \nabla p_0 = \nabla^2 \boldsymbol{v}_0. \tag{3.4}$$

(iii) The $O(\delta^{-2})$ leading-order salt balance (2.24) yields a convection-dominated ionic concentration:

$$\boldsymbol{v}_0 \cdot \boldsymbol{\nabla} c_0 = 0. \tag{3.5}$$

Within the framework of the present steady problem, (3.5) can be written alternatively in the Lagrangian form

$$\frac{\mathrm{D}c_0}{\mathrm{D}t} = 0 \tag{3.6}$$

in which $\mathrm{D}/\mathrm{D}t$ is the leading-order material derivative.

We here focus upon flow fields characterized by open streamlines originating at infinity (which applies to most streaming-potential problems) where $c = 1$ (see (2.17)). Whence,

$$c_0 \equiv 1 \tag{3.7}$$

and by (2.10) and (2.12)

$$\boldsymbol{j}_0 = \boldsymbol{0}, \quad \boldsymbol{i}_0 = -\boldsymbol{\nabla}\varphi_0. \tag{3.8}$$

The dominance of convection in conjunction with (3.2) implies that the $O(\delta^{-2})$ leading-order balance of the charge-transport equation (2.25) is automatically satisfied and thus, in contrast with typical field-driven electrokinetic problems, does not provide an equation for φ_0 (see Yariv 2010). We therefore need to analyse the next, $O(1)$, order of (2.25), namely

$$\boldsymbol{\nabla} \cdot \boldsymbol{i}_0 + \frac{\alpha}{\lambda}\,(\boldsymbol{v}_0 \cdot \boldsymbol{\nabla} q_1 + \boldsymbol{v}_1 \cdot \boldsymbol{\nabla} q_0) = 0. \tag{3.9}$$

The $O(\delta^2)$ Poisson's equation (2.3) reads

$$q_1 = -\nabla^2\varphi_0 \tag{3.10}$$

which, when substituted together with (3.2) and (3.8) into (3.9), yields in Lagrangian form

$$q_1 + \frac{\alpha}{\lambda}\frac{\mathrm{D}q_1}{\mathrm{D}t} = 0. \tag{3.11}$$

Thus, following a fluid particle, q_1 decreases exponentially with time,

$$q_1 = A\mathrm{e}^{-\lambda t/\alpha}, \tag{3.12}$$

with the constant A being a particle property. Since, as mentioned above, we assume that all particle trajectories originate from infinity, where q_1 vanishes (see (2.17)), $A = 0$ for all fluid particles whence electro-neutrality also holds at $O(\delta^2)$,

$$q_1 \equiv 0. \tag{3.13}$$

By (3.10), then

$$\nabla^2\varphi_0 = 0. \tag{3.14}$$

This is supplemented by the attenuation condition

$$\boldsymbol{\nabla}\varphi_0 \to 0 \quad \text{as } |\boldsymbol{x}| \to \infty, \tag{3.15}$$

together with appropriate boundary conditions on S.

The no-flux condition (2.16), in conjunction with (3.8), requires that $\partial\varphi_0/\partial n = 0$ on S. This however is incompatible with the boundary condition associated with Gauss's law which in general prescribes non-zero values of $\partial\varphi_0/\partial n$. Similarly to field-driven phenomena, the limit $\delta \to 0$ is singular, being non-uniform near S. This singularity is associated with the small parameter multiplying the highest-order derivative in (2.3). A Debye boundary layer of thickness $O(\delta)$ thus develops.

We therefore refer to the above results as an *outer* solution, for which the boundary conditions on S do not formally apply. (Note that none of these conditions have been used in the preceding thin-Debye-layer analysis.) The outer solution will only be uniquely determined via matching with the yet-to-be-found Debye-layer solution. This matching will then provide bulk-scale boundary conditions for the outer fields. We denote by s the surface over which these conditions apply; on the bulk-scale s coincides with the solid surface. To obtain the boundary-layer structure, we need to analyse the problem within an $O(\delta)$-thick layer adjacent to the actual boundary S.

Incidentally, the above zeroth-order outer results constitute an exact solution of the governing differential equations. However, asymptotic matching may introduce non-zero corrections. Thus, we cannot *a priori* assume that (3.1) terminates after one term.

4. Debye-scale formulation

4.1. *Geometry and parametrization*

Following Cox (1997) each arbitrary point $\boldsymbol{x}$ on S is associated with two curvilinear surface coordinates, say (ξ, η). With no loss of generality, these coordinates are chosen to be locally orthogonal

$$\frac{\partial \boldsymbol{x}}{\partial \xi} \boldsymbol{\cdot} \frac{\partial \boldsymbol{x}}{\partial \eta} = 0 \tag{4.1}$$

and to constitute a natural parametrization on S

$$\frac{\partial \boldsymbol{x}}{\partial \xi} \boldsymbol{\cdot} \frac{\partial \boldsymbol{x}}{\partial \xi} = \frac{\partial \boldsymbol{x}}{\partial \eta} \boldsymbol{\cdot} \frac{\partial \boldsymbol{x}}{\partial \eta} = 1. \tag{4.2}$$

Consider an arbitrary point $\mathscr{P}$ on S. A local Cartesian system (x, y, z) is constructed by choosing the x and y coordinates axes tangent to the ξ and η coordinate lines, respectively, with the origin at $\mathscr{P}$. The z-axis points into the fluid in a direction normal to S. Locally, then, S is described by the approximate quadratic surface

$$z = a_{11}x^2 + 2a_{12}xy + a_{22}y^2 + \text{terms cubic and higher-order in } x \text{ and } y. \tag{4.3}$$

The position-dependent coefficients a_{ij} depend upon the (arbitrary) choice of the (ξ, η) coordinate curves on S. Note however that the sum $a_{11} + a_{22}$, which constitutes the dimensionless mean curvature of S at $\mathscr{P}$, is invariant to that choice.

Near $\mathscr{P}$ the Debye layer is described by the rescaled inner coordinates

$$X = x/\delta^{1/2}, \quad Y = y/\delta^{1/2}, \quad Z = z/\delta. \tag{4.4}$$

Since the boundary conditions apply on the curved surface S, the plane $Z = 0$ is only a leading-order local approximation to S. Thus, in deriving a systematic asymptotic approximation, direct use of the inner Cartesian coordinates is inconvenient. This subtle point was resolved by Cox (1997) via an elegant procedure: the pertinent variables are sought only on the Z-axis. Given the arbitrariness of $\mathscr{P}$ (which is implicit in its dependence upon ξ and η), this approach provides a description over the entire inner space. Thus, the generic description $F(X, Y, Z)$ is replaced by

$$F(\xi, \eta, Z). \tag{4.5}$$

The boundary conditions on the wall thus apply at $Z = 0$.

From (4.3) the following expressions for generic derivatives at $X = Y = 0$ are obtained (cf. Cox 1997):

$$\left.\frac{\partial F}{\partial X}\right|_{X=Y=0} = \delta^{1/2}\frac{\partial F}{\partial \xi}\{1+O(\delta)\}, \quad \left.\frac{\partial F}{\partial Y}\right|_{X=Y=0} = \delta^{1/2}\frac{\partial F}{\partial \eta}\{1+O(\delta)\}, \tag{4.6a}$$

$$\left.\frac{\partial^2 F}{\partial X^2}\right|_{X=Y=0} = -2a_{11}\frac{\partial F}{\partial Z}\{1+O(\delta)\}, \quad \left.\frac{\partial^2 F}{\partial Y^2}\right|_{X=Y=0} = -2a_{22}\frac{\partial F}{\partial Z}\{1+O(\delta)\}, \tag{4.6b}$$

where the derivatives on the right-hand side refer to the representation (4.5). Thus,

$$\left.\left(\frac{\partial^2}{\partial X^2}+\frac{\partial^2}{\partial Y^2}\right)F\right|_{X=Y=0} = (\nabla\cdot\hat{\boldsymbol{n}})\frac{\partial F}{\partial Z}\{1+O(\delta)\}, \tag{4.7}$$

with $\nabla\cdot\hat{\boldsymbol{n}} = -2(a_{11}+a_{22})$.

4.2. *Inner scaling*

Denoting inner fields by capital letters, we have in the inner domain

$$c^{\pm} = C^{\pm}, \quad c = C, \quad q = Q \tag{4.8}$$

as well as

$$\varphi = \Phi. \tag{4.9}$$

The coordinate re-scaling suggests the following definition of re-scaled flux in the z-direction:

$$\hat{\boldsymbol{n}}\cdot\boldsymbol{j}^{\pm} = \delta^{-1}J^{\pm\perp}, \tag{4.10}$$

where (cf. (2.2))

$$J^{\pm\perp} = -\frac{\partial C^{\pm}}{\partial Z} \mp C^{\pm}\frac{\partial \Phi}{\partial Z}. \tag{4.11}$$

Following (2.13), we also define

$$J^{\perp} = \tfrac{1}{2}(J^{+\perp}+J^{-\perp}), \quad I^{\perp} = \tfrac{1}{2}(J^{+\perp}-J^{-\perp}), \tag{4.12}$$

whereby

$$J^{\perp} = -\frac{\partial C}{\partial Z} - Q\frac{\partial \Phi}{\partial Z}, \quad I^{\perp} = -\frac{\partial Q}{\partial Z} - C\frac{\partial \Phi}{\partial Z}. \tag{4.13}$$

We also define the inner flow variables,

$$\boldsymbol{v} = \boldsymbol{V}, \quad p = P. \tag{4.14}$$

The continuity equation and the no-slip condition suggest the Cartesian representation

$$\boldsymbol{V} = \hat{\boldsymbol{e}}_x\delta U + \hat{\boldsymbol{e}}_y\delta V + \hat{\boldsymbol{e}}_z\delta^2 W \tag{4.15}$$

within the inner domain (cf. (6.2)).

4.3. *Governing equations and boundary conditions*

Rewriting the balance equations in terms of the inner variables we obtain within the Debye layer the Nernst–Planck equations (2.23)

$$\frac{\partial J^{\pm\perp}}{\partial Z} - \delta\left[\frac{\partial}{\partial X}\left(\frac{\partial C^{\pm}}{\partial X} \pm C^{\pm}\frac{\partial \Phi}{\partial X}\right) + \frac{\partial}{\partial Y}\left(\frac{\partial C^{\pm}}{\partial Y} \pm C^{\pm}\frac{\partial \Phi}{\partial Y}\right)\right] + \frac{\alpha}{\lambda}\left(\delta^{1/2}U\frac{\partial C^{\pm}}{\partial X} + \delta^{1/2}V\frac{\partial C^{\pm}}{\partial Y} + \delta W\frac{\partial C^{\pm}}{\partial Z}\right) = 0; \tag{4.16}$$

the Poisson equation (2.3)

$$\left[\frac{\partial^2}{\partial Z^2} + \delta\left(\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2}\right)\right]\Phi = -Q; \tag{4.17}$$

and the continuity equation (2.5)

$$\frac{\partial W}{\partial Z} + \delta^{-1/2}\left(\frac{\partial U}{\partial X} + \frac{\partial V}{\partial Y}\right) = 0. \tag{4.18}$$

The momentum equation (2.6) yields

$$\delta\left[\frac{\partial^2}{\partial Z^2} + \delta\left(\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2}\right)\right]W - \frac{\partial P}{\partial Z} = \lambda Q\frac{\partial \Phi}{\partial Z} \tag{4.19}$$

in the normal direction and

$$\left[\frac{\partial^2}{\partial Z^2} + \delta\left(\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2}\right)\right]U - \delta^{1/2}\frac{\partial P}{\partial X} = \delta^{1/2}\lambda Q\frac{\partial \Phi}{\partial X}, \tag{4.20a}$$

$$\left[\frac{\partial^2}{\partial Z^2} + \delta\left(\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2}\right)\right]V - \delta^{1/2}\frac{\partial P}{\partial Y} = \delta^{1/2}\lambda Q\frac{\partial \Phi}{\partial Y} \tag{4.20b}$$

in the tangential directions.

The boundary conditions on S consist of the vanishing of the normal flux

$$J^{\pm\perp} = 0 \quad \text{at } Z = 0, \tag{4.21}$$

and the no-slip and impermeability condition

$$U = V = W = 0 \quad \text{at } Z = 0. \tag{4.22}$$

At large distances the inner fields need to satisfy appropriate asymptotic matching with the corresponding outer fields.

4.4. *Asymptotic expansions*

To apply the boundary conditions (4.21)–(4.22) it is useful to shift to the representation (4.5) whereby these conditions apply at $Z = 0$. The differential equations (4.16)–(4.20) are therefore transformed using (4.6)–(4.7). Subsequently, all fields are expanded using the generic asymptotic series

$$F(Z, \xi, \eta; \delta) \sim F_0(Z, \xi, \eta) + \delta F_1(Z, \xi, \eta) + \cdots. \tag{4.23}$$

Substituting the corresponding expansions of $C^{\pm}$ and Φ in (4.11) we obtain for $J^{\pm\perp}$

$$J_0^{\pm\perp} = -\frac{\partial C_0^{\pm}}{\partial Z} \mp C_0^{\pm}\frac{\partial \Phi_0}{\partial Z}, \quad J_1^{\pm\perp} = -\frac{\partial C_1^{\pm}}{\partial Z} \mp C_0^{\pm}\frac{\partial \Phi_1}{\partial Z} \mp C_1^{\pm}\frac{\partial \Phi_0}{\partial Z}, \cdots \tag{4.24}$$

The boundary conditions on S apply to the expanded fields. The homogeneous conditions (4.22) apply at all orders. Conditions for large Z represent asymptotic matching with the outer solution. Specifically, leading-order matching specifies the behaviour of the outer field as $z \to 0$ (i.e. on s). Thus,

$$C_0^{\pm} \to 1, \quad \Phi_0 \to \varphi_0^{(s)} \quad P_0 \to p_0^{(s)} \quad \text{as } Z \to \infty, \tag{4.25}$$

where the superscript '(s)' indicates the inner limits of the outer fields, i.e. their evaluation on s (where $z \to 0$). Furthermore, because of re-scaling, derivatives with respect to Z of $O(1)$ inner fields must vanish at that limit. Specifically

$$J_0^{\pm\perp}, \frac{\partial \Phi_0}{\partial Z} \to 0 \quad \text{as } Z \to \infty. \tag{4.26}$$

5. Debye-scale analysis

5.1. *Leading-order electrokinetics: Gouy–Chapman distribution*

Employing expansion (4.23) in (4.16) and (4.17) readily yields the leading-order ionic-balance equation

$$\frac{\partial J_0^{\pm\perp}}{\partial Z} = 0 \tag{5.1}$$

and electrostatics equation

$$\frac{\partial^2 \Phi_0}{\partial Z^2} = -Q_0, \tag{5.2}$$

both decoupled from the flow field. Equation (5.1) in conjunction with (4.21) implies that $J_0^{\pm\perp} \equiv 0$. Use of the matching condition (4.25) then provides the equilibrium Boltzmann distribution

$$C_0^{\pm} = \mathrm{e}^{\mp\Psi} \tag{5.3}$$

in which

$$\Psi = \Phi_0(Z; \xi, \eta) - \varphi_0^{(s)}(\xi, \eta) \tag{5.4}$$

is the 'excess potential' in the layer. Back substitution into (5.2) reveals that Ψ is governed by the Poisson–Boltzmann equation

$$\frac{\partial^2 \Psi}{\partial Z^2} = \sinh \Psi; \tag{5.5}$$

in view of (4.25), it also satisfies the condition

$$\Psi \to 0 \quad \text{for } Z \to \infty. \tag{5.6}$$

Furthermore, it satisfies a Neumann-type boundary condition on $Z = 0$ relating $\partial\Psi/\partial Z$ to the prescribed surface charge on S. Following the usual practice in electrokinetics, we replace this Gauss-law condition with

$$\Psi(Z = 0) = \zeta \tag{5.7}$$

in which we treat the dimensionless zeta potential ζ (rather than the surface-charge density) as a prescribed quantity. We assume that the magnitude of the dimensional zeta potential is comparable to that of φ^*, the thermal voltage (i.e. $\zeta = O(1)$). The Dukhin number is therefore vanishingly small for $\delta \to 0$ implying that surface conduction is negligible.

The solution of (5.5) subject to boundary conditions (5.6)–(5.7) is well known (Prieve *et al.* 1984; Rubinstein & Zaltzman 2001). Thus, multiplication by $\partial\Psi/\partial Z$ and integration in conjunction with (5.6) yield

$$\frac{\partial\Psi}{\partial Z} = -2\sinh\frac{\Psi}{2}; \tag{5.8}$$

a subsequent integration in conjunction with (5.7) then furnishes the familiar Gouy–Chapman distribution

$$\tanh\frac{\Psi}{4} = \mathrm{e}^{-Z}\tanh\frac{\zeta}{4}, \tag{5.9}$$

i.e.

$$\Psi = 2\ln\frac{1+\mathrm{e}^{-Z}\tanh\dfrac{\zeta}{4}}{1-\mathrm{e}^{-Z}\tanh\dfrac{\zeta}{4}}. \tag{5.10}$$

Note that under the assumed uniform charge distribution on S, ζ is uniform for each separate solid boundary. Then, Ψ is a function of Z alone, independent of the surface coordinates ξ and η. By (5.3), the same applies to the ionic concentrations $C_0^{\pm}$.

5.2. *Leading-order flow*

The appearance of the equilibrium Boltzmann distribution at leading order is familiar from field-driven electrokinetic phenomena. In these phenomena, the tangential field acting on this equilibrium distribution is responsible for a steep velocity profile which approaches the Helmholtz–Smoluchowski slip value at large Z. The different scaling in the streaming-potential problems, however, gives rise to a different behaviour. Thus, the leading-order balances in (4.20) yield

$$\frac{\partial^2 U_0}{\partial Z^2} = 0, \quad \frac{\partial^2 V_0}{\partial Z^2} = 0, \tag{5.11}$$

in which the electric field does not appear.

The solution of (5.11) satisfying the no-slip condition at $Z=0$ is

$$U_0(Z,\xi,\eta) = A_0(\xi,\eta)Z, \quad V_0(Z,\xi,\eta) = B_0(\xi,\eta)Z. \tag{5.12}$$

Employing (4.6*a*) in (4.18) the leading-order continuity equation is

$$\frac{\partial U_0}{\partial\xi} + \frac{\partial V_0}{\partial\eta} + \frac{\partial W_0}{\partial Z} = 0 \tag{5.13}$$

which, together with the impermeability condition at $Z=0$, yields the normal-velocity component:

$$W_0 = -\frac{Z^2}{2}D_0(\xi,\eta), \tag{5.14}$$

wherein

$$D_0(\xi,\eta) = \frac{\partial A_0}{\partial\xi} + \frac{\partial B_0}{\partial\eta}. \tag{5.15}$$

5.3. *Convection-driven flux perturbations*

For future asymptotic matching, it is also necessary to calculate the leading-order corrections to the ionic fluxes. To evaluate the flux correction $J_1^{\pm\perp}$ we consider the $O(\delta)$ balance of the inner ionic conservation equations (4.16). Making use of (4.24) together with (4.6)–(4.7) we obtain

$$\frac{\partial J_1^{\pm\perp}}{\partial Z} + (\nabla \cdot \hat{\boldsymbol{n}}) J_0^{\pm\perp} + \frac{\alpha}{\lambda}\left(U_0 \frac{\partial C_0^{\pm}}{\partial \xi} + V_0 \frac{\partial C_0^{\pm}}{\partial \eta} + W_0 \frac{\partial C_0^{\pm}}{\partial Z} \right) = 0. \tag{5.16}$$

It is worthwhile to note the emergence of a convective surface flux. The boundary conditions (4.21) in conjunction with the vanishing of $J_0^{\pm\perp}$ and the fact that (for a uniform surface-charge distribution) $C_0^{\pm}$ is independent of ξ and η yields the flux

$$J_1^{\pm\perp} = -\frac{\alpha}{\lambda} \int_0^Z W_0 \frac{\partial C_0^{\pm}}{\partial Z'} \, \mathrm{d}Z'. \tag{5.17}$$

This convective 'surface' flux represents the streaming-potential scaling unique to large Péclet numbers. This is in marked contrast with field-driven phenomena where convection effects are relegated to higher orders and $J_1^{\pm\perp}$ vanishes (Yariv 2010).

Substitution of (5.14) and integration by parts yields

$$J_1^{\pm\perp} = -\frac{\alpha}{\lambda} D_0(\xi, \eta) \left\{ \int_0^Z Z' C_0^{\pm} \, \mathrm{d}Z' - \frac{Z^2}{2} C_0^{\pm} \right\}. \tag{5.18}$$

For future asymptotic matching it is required to evaluate $J_1^{\pm\perp}$ at $Z \to \infty$. This needs to be done with care since, while $J_1^{\pm\perp}$ must of course approach a finite limit, each term on the right-hand side of (5.18) is separately diverging. From the above solution of the Poisson–Boltzmann equation we know that $C_0^{\pm} - 1$ decays exponentially rapidly at large Z (see (5.3) and (5.10)). Thus, introducing the decomposition

$$C_0^{\pm} = 1 + (C_0^{\pm} - 1) \tag{5.19}$$

readily yields

$$J_1^{\pm\perp}(Z \to \infty) = -\frac{\alpha}{\lambda} D_0(\xi, \eta) \int_0^\infty Z (C_0^{\pm} - 1) \, \mathrm{d}Z. \tag{5.20}$$

6. Bulk-scale boundary conditions

Asymptotic matching between the inner and outer fields provides bulk-scale boundary conditions for the latter.

6.1. *Velocity matching*

Consider first the velocity field. Because of the scaling (4.15) all leading-order velocity components vanish as $z \to 0$ and we obtain the effective boundary condition

$$\boldsymbol{v}_0 = \boldsymbol{0} \quad \text{on } s, \tag{6.1}$$

which represents the 1–1 matching principle of Van Dyke (1964). Together with the homogeneous Stokes equations (3.4) and the prescribed far-field behaviour, it specifies a well-posed problem governing the leading-order outer hydrodynamics.

In the wall-fixed Cartesian coordinate system, the outer velocity field adopts the form $\boldsymbol{v} = \hat{\boldsymbol{e}}_x u + \hat{\boldsymbol{e}}_y v + \hat{\boldsymbol{e}}_z w$. The vanishing of u_0 and v_0 on s implies that their respective

x- and y-derivatives vanish at $x = y = 0$ (since at that point their gradients must point in the z-direction). Thus, the continuity equation yields

$$\frac{\partial w_0}{\partial z} = 0 \quad \text{on } s. \tag{6.2}$$

In view of (3.1), a 2–1 van Dyke matching readily yields

$$A_0 = \left(\frac{\partial u_0}{\partial z}\right)^{(s)}, \quad B_0 = \left(\frac{\partial v_0}{\partial z}\right)^{(s)}. \tag{6.3}$$

Substitution of (6.3) into (5.12) yields the leading-order inner flow

$$U_0 = \left(\frac{\partial u_0}{\partial z}\right)^{(s)} Z, \quad V_0 = \left(\frac{\partial v_0}{\partial z}\right)^{(s)} Z, \tag{6.4}$$

which, owing to the outer asymptotic structure (3.1), is simply equivalent to a Taylor-series expansion of the corresponding outer flow.

Consider next the expression (5.15) of $D_0(\xi, \eta)$ appearing in both (5.14) and (5.20). Substitution of (6.3), noting that differentiations with respect to ξ and η commute with evaluation at s, and making use of the leading-order outer continuity equation

$$\frac{\partial u_0}{\partial \xi} + \frac{\partial v_0}{\partial \eta} + \frac{\partial w_0}{\partial z} = 0, \tag{6.5}$$

reveals that $D_0 = -(\partial^2 w_0/\partial z^2)^{(s)}$. Moreover, the transformation (4.7) in conjunction with (6.2) readily yields

$$\frac{\partial^2 w_0}{\partial x^2} + \frac{\partial^2 w_0}{\partial y^2} = 0 \quad \text{on } s. \tag{6.6}$$

When making use of this in the leading-order outer momentum equation in the z-direction we obtain

$$D_0(\xi, \eta) = -\left(\frac{\partial p_0}{\partial z}\right)^{(s)}. \tag{6.7}$$

6.2. *Current matching*

The formulation of a well-posed problem for the outer field φ_0 requires the specification of a boundary condition on s. To this end we carry out asymptotic matching of the electric-current density. Owing to the scaling (4.10) in conjunction with the vanishing of $J_0^{\pm\perp}$ the requisite condition must be obtained via matching of the leading-outer outer current to the leading-order *correction* of the inner current:

$$\lim_{z\to 0} \hat{\boldsymbol{n}} \cdot \boldsymbol{i}_0 = \lim_{Z\to\infty} I_1^{\perp}. \tag{6.8}$$

In field-driven phenomena, where $I_1^{\perp}$ vanishes as well, this requirement leads to the familiar no-flux condition (Yariv 2010). Here, the large-Péclet-number scaling results in a net-flux condition, which reflects the streaming-potential mechanism (cf. the above calculation of $J_1^{\pm\perp}$).

To derive $\lim_{Z\to\infty} I_1^{\perp}$ we substitute (6.7) into (5.20) to obtain

$$J_1^{\pm\perp}(Z \to \infty) = \frac{\alpha}{\lambda}\left(\frac{\partial p_0}{\partial z}\right)^{(s)} \int_0^{\infty} Z(C_0^{\pm} - 1)\, \mathrm{d}Z. \tag{6.9}$$

Subtraction of the two equations (6.9) in conjunction with (5.2) yields

$$I_1^{\perp}(Z \to \infty) = -\frac{\alpha}{\lambda}\left(\frac{\partial p_0}{\partial z}\right)^{(s)} \int_0^{\infty} Z \frac{\partial^2 \Psi}{\partial Z^2}\, \mathrm{d}Z. \tag{6.10}$$

Integration by parts in conjunction with the definitions of Ψ and the zeta potential results in

$$I_1^{\perp}(Z \to \infty) = -\frac{\alpha\zeta}{\lambda}\left(\frac{\partial p_0}{\partial z}\right)^{(s)}, \tag{6.11}$$

which when substituted together with (3.8) into (6.8) yield the requisite boundary condition

$$\frac{\partial \varphi_0}{\partial n} = \frac{\alpha\zeta}{\lambda}\frac{\partial p_0}{\partial n} \quad \text{on } s. \tag{6.12}$$

The potential φ_0 is thus governed by Laplace's equation (3.14) together with the far-field decay condition (3.15) and the Neumann-type boundary condition (6.12). The result (6.12) has already been obtained via charge conservation by Bike & Prieve (1992). They have, however, overlooked the need to satisfy salt-flux matching which, in turn, introduces an apparent paradox in the asymptotic scheme. This is addressed next.

6.3. *Salt-flux matching*

Similarly to (6.8), matching of salt flux requires

$$\lim_{z\to 0} \hat{\boldsymbol{n}} \boldsymbol{\cdot} \boldsymbol{j}_0 = \lim_{Z\to\infty} J_1^{\perp}. \tag{6.13}$$

The inner flux obtained by addition of (6.9) in conjunction with (5.3) is

$$J_1^{\perp}(Z \to \infty) = \frac{\alpha}{\lambda}\left(\frac{\partial p_0}{\partial z}\right)^{(s)} \mathscr{H}(\zeta); \tag{6.14}$$

here,

$$\mathscr{H}(\zeta) = \int_0^{\infty} Z(\cosh \Psi - 1)\, \mathrm{d}Z \tag{6.15}$$

is nil only for $\zeta = 0$, being positive otherwise. Thus (6.13) is incompatible with the above vanishing of $\boldsymbol{j}_0$. Such a contradiction does not appear in field-driven phenomena, where $\hat{\boldsymbol{n}} \boldsymbol{\cdot} \boldsymbol{j}_0$ indeed vanishes on s (Yariv 2010) and salt matching is trivially satisfied.

To resolve the puzzle we observe that in the present large-*Pe* analysis the limit $\delta \to 0$ introduces a two-fold singularity. The multiplication of the highest-order derivative in Poisson's equation (2.3) by δ^2 gives rise to the above-analysed familiar $O(\delta)$-wide Debye layer. A similar multiplication of the highest derivatives by an $O(\delta^2)$ parameter now takes place in the Nernst–Planck equations (2.1) as well. This, in turn, results in a *diffusive* boundary layer whose width depends upon the nature of the velocity field near S. Since this field satisfies the no-slip condition and, unlike field-driven phenomena, is associated with $O(1)$ gradients near S, generic scaling arguments (Leal 2007) show that this width scales as $Pe^{-1/3}$, or, equivalently, as $\delta^{2/3}$, asymptotically thick compared with the Debye layer. The Debye-layer solution thus need not match the bulk solution (as expressed in (6.13)); rather, the diffusive layer smoothly joins the two.

In view of the rapid relaxation of the leading-order electric potential and ionic concentrations on the Debye scale, the analysis preceding (6.13) remains valid. Thus, within the present order of asymptotic approximation, resolution of the intermediate diffusion layer is not explicitly required for the calculation of the leading electro-viscous effect, but rather to verify consistency of the scheme. To avoid digression in the derivation of the effective outer description, the analysis of the diffusion-layer structure is relegated to the Appendix.

7. Flow corrections

We now turn to the leading-order flow correction in the Debye layer. A prerequisite for its calculation is the determination of the leading-order pressure P_0, obtained from the leading-order balance of the inner Navier–Stokes equation in the Z-direction (4.19)

$$\frac{\partial P_0}{\partial Z} = \lambda \frac{\partial^2 \Phi_0}{\partial Z^2}\frac{\partial \Phi_0}{\partial Z} \tag{7.1}$$

and the matching condition (4.25). These yield

$$P_0 = \frac{\lambda}{2}\left(\frac{\partial \Psi}{\partial Z}\right)^2 + p_0^{(s)}(\xi, \eta). \tag{7.2}$$

Consider the leading-order flow correction in the Debye layer. In the x-direction, the $O(\delta)$ balance in (4.20*a*) is

$$\frac{\partial^2 U_1}{\partial Z^2} + (\boldsymbol{\nabla} \cdot \hat{\boldsymbol{n}})\frac{\partial U_0}{\partial Z} - \frac{\partial P_0}{\partial \xi} = \lambda Q_0 \frac{\partial \Phi_0}{\partial \xi}. \tag{7.3}$$

Substitution of (5.2), (5.4), (6.4), and (7.2), in conjunction with Ψ being independent of ξ, yields

$$\frac{\partial^2 U_1}{\partial Z^2} = -\lambda \frac{\partial^2 \Psi}{\partial Z^2}\frac{\partial \varphi_0^{(s)}}{\partial \xi} + \frac{\partial p_0^{(s)}}{\partial \xi} - (\boldsymbol{\nabla} \cdot \hat{\boldsymbol{n}})\left(\frac{\partial u_0}{\partial z}\right)^{(s)}. \tag{7.4}$$

Integrating twice in conjunction with the no-slip condition and (5.7) we obtain

$$U_1 = \lambda(\zeta - \Psi)\frac{\partial \varphi_0^{(s)}}{\partial \xi} + \frac{Z^2}{2}\left[\frac{\partial p_0^{(s)}}{\partial \xi} - (\boldsymbol{\nabla} \cdot \hat{\boldsymbol{n}})\left(\frac{\partial u_0}{\partial z}\right)^{(s)}\right] + A_1(\xi, \eta) Z. \tag{7.5}$$

Performing a 3–2 van Dyke matching then yields $A_1 = 0$, as well as the requirement

$$\frac{\partial p_0^{(s)}}{\partial \xi} - (\boldsymbol{\nabla} \cdot \hat{\boldsymbol{n}})\left(\frac{\partial u_0}{\partial z}\right)^{(s)} = \left(\frac{\partial^2 u_0}{\partial z^2}\right)^{(s)}. \tag{7.6}$$

The latter, in view of the leading-order outer momentum balance (3.4) in the x-direction, is equivalent to

$$\left(\frac{\partial^2 u_0}{\partial x^2} + \frac{\partial^2 u_0}{\partial y^2}\right)^{(s)} = (\boldsymbol{\nabla} \cdot \hat{\boldsymbol{n}})\left(\frac{\partial u_0}{\partial z}\right)^{(s)}; \tag{7.7}$$

this, in fact, is simply (4.7) written in terms of the outer local coordinates (x, y, z), see (4.4). A similar calculation starting from the y-component of the momentum equation

(4.20*b*) yields

$$V_1 = \lambda(\zeta - \Psi)\frac{\partial \varphi_0^{(s)}}{\partial \eta} + \frac{Z^2}{2}\left[\frac{\partial p_0^{(s)}}{\partial \eta} - (\nabla \cdot \hat{\boldsymbol{n}})\left(\frac{\partial v_0}{\partial z}\right)^{(s)}\right]. \tag{7.8}$$

We can now solve for the leading-order $O(\delta^2)$ correction $(\boldsymbol{v}_1, p_1)$ to the outer flow, see (3.1). In view of (3.2) and (3.13), this flow field (just like $(\boldsymbol{v}_0, p_0)$) satisfies the homogeneous Stokes equations

$$\nabla \cdot \boldsymbol{v}_1 = 0, \quad \nabla p_1 = \nabla^2 \boldsymbol{v}_1. \tag{7.9}$$

A 3–3 van Dyke matching between the tangential velocity components yields

$$u_1^{(s)} = \lambda\zeta\frac{\partial \varphi_0^{(s)}}{\partial \xi}, \quad v_1^{(s)} = \lambda\zeta\frac{\partial \varphi_0^{(s)}}{\partial \eta}. \tag{7.10}$$

The corresponding matching of the normal velocity component, in conjunction with (5.14), yields

$$w_1^{(s)} = 0. \tag{7.11}$$

Furthermore, the latter matching reproduces (6.2) and provides the requirement

$$\left(\frac{\partial p_0}{\partial z}\right)^{(s)} = \left(\frac{\partial^2 w_0}{\partial z^2}\right)^{(s)}, \tag{7.12}$$

which, upon use of the leading-order outer momentum balance (3.4) in the z-direction, becomes (6.6).

Combining (7.10) and (7.11) we find that $\boldsymbol{v}_1$ is driven by the Smoluchowski-type slip condition

$$\boldsymbol{v}_1 = \lambda\zeta\nabla_s\varphi_0 \quad \text{on } s, \tag{7.13}$$

wherein

$$\nabla_s = (\boldsymbol{I} - \hat{\boldsymbol{n}}\hat{\boldsymbol{n}}) \cdot \nabla, \tag{7.14}$$

(with $\boldsymbol{I}$ being the unit dyadic) is the surface-gradient operator.

Unlike conventional field-driven electrokinetic phenomena (Yariv 2010), here one may not replace the surface gradient ∇_s by ∇, since φ_0 satisfies on s an inhomogeneous Neumann condition, see (6.12).

8. Recapitulation of solution procedure

Consider a generic drag problem wherein a stationary particle is placed under an imposed velocity field. The resultant force (normalized by $\mu^* a^* v^*$) on the particle is

$$\boldsymbol{F} = \oint_S \mathrm{d}A\, \hat{\boldsymbol{n}} \cdot (\boldsymbol{S}_N + \boldsymbol{S}_M). \tag{8.1}$$

In (8.1) $\boldsymbol{S}_N$ is the Cauchy stress, which for a Newtonian fluid is

$$\boldsymbol{S}_N = -p\boldsymbol{I} + (\nabla \boldsymbol{v}) + (\nabla \boldsymbol{v})^\dagger \tag{8.2}$$

(with † denoting dyadic transposition), and $\boldsymbol{S}_M$ is the Maxwell stress,

$$\boldsymbol{S}_M = \lambda\delta^2(\nabla\varphi\nabla\varphi - \tfrac{1}{2}\nabla\varphi \cdot \nabla\varphi\, \boldsymbol{I}) \tag{8.3}$$

(both fields normalized by $\mu^* v^*/a^*$). Similarly, the torque (normalized by $\mu^* a^{*2} v^*$) experienced by the particle about the point $\boldsymbol{x}_O$ is

$$\boldsymbol{T} = \oint_S \mathrm{d}A\, (\boldsymbol{x} - \boldsymbol{x}_O) \times [\hat{\boldsymbol{n}} \cdot (\boldsymbol{\mathsf{S}}_N + \boldsymbol{\mathsf{S}}_M)]. \tag{8.4}$$

Since the momentum balance (2.6) represents a statement of divergence-free stress,

$$\nabla \cdot (\boldsymbol{\mathsf{S}}_N + \boldsymbol{\mathsf{S}}_M) = \boldsymbol{0}, \tag{8.5}$$

use of Gauss's theorem allows evaluation of the integrals in (8.1)–(8.4) on any surface enclosing S which lies entirely within the fluid (and does not enclose another solid). It is convenient to employ the outer edge s of the Debye layer where the outer expansions (3.1) apply. This leads to the expansion

$$\boldsymbol{F} \sim \boldsymbol{F}_0 + \delta^2 \boldsymbol{F}_1 + \cdots \tag{8.6}$$

with a similar one for $\boldsymbol{T}$. Here,

$$\boldsymbol{F}_0 = \oint_s \mathrm{d}A\, \hat{\boldsymbol{n}} \cdot \boldsymbol{\mathsf{S}}_{N,0} \tag{8.7}$$

is the zeroth-order force with

$$\boldsymbol{\mathsf{S}}_{N,0} = -p_0 \boldsymbol{\mathsf{I}} + (\nabla \boldsymbol{v}_0) + (\nabla \boldsymbol{v}_0)^{\dagger}. \tag{8.8}$$

Clearly, this force represents the hydrodynamic load in the absence of any electrokinetic effects. The latter are represented by the correction

$$\boldsymbol{F}_1 = \oint_s \mathrm{d}A\, \hat{\boldsymbol{n}} \cdot \left(\boldsymbol{\mathsf{S}}_{N,1} + \boldsymbol{\mathsf{S}}_{M,0}\right) \tag{8.9}$$

with

$$\boldsymbol{\mathsf{S}}_{N,1} = -p_1 \boldsymbol{\mathsf{I}} + (\nabla \boldsymbol{v}_1) + (\nabla \boldsymbol{v}_1)^{\dagger}, \tag{8.10}$$

and

$$\boldsymbol{\mathsf{S}}_{M,0} = \lambda(\nabla\varphi_0 \nabla\varphi_0 - \tfrac{1}{2}\nabla\varphi_0 \cdot \nabla\varphi_0\, \boldsymbol{\mathsf{I}}). \tag{8.11}$$

Thus, calculation of the electro-viscous drag correction entails the evaluation of two asymptotic orders of the flow variables as well as the leading-order calculation of the electric field.

The following scheme then summarizes the evaluation of the drag correction.

(1) First, the leading-order outer flow $(\boldsymbol{v}_0, p_0)$ needs to be calculated. It is governed by the continuity and homogenous Stokes equations (3.4), the effective boundary condition (6.1), and appropriate conditions at infinity (e.g. prescribed velocity). This flow represents the Stokes flow associated with imposed motion in the absence of any electrokinetic effects.

(2) The leading-order electric potential is then calculated. It is governed by Laplace's equation (3.14), the attenuation condition (3.15) and the inhomogeneous Neumann condition (6.12).

For an important class of problems there is actually no need to solve the Neumann problem (Bike & Prieve 1992). In view of the Stokes equations governing the leading-order flow, p_0 is harmonic, and, in the absence of imposed pressure gradients, it attenuates at infinity. These properties are shared by φ_0 as

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well, see (3.14)–(3.15). If all solid surfaces possess the same zeta potential then (6.12) implies that

$$\varphi_0 = \frac{\alpha\zeta}{\lambda} p_0. \tag{8.12}$$

(3) The flow correction is evaluated. It is governed by the homogeneous Stokes equations (7.9), the decay requirement at infinity and the Smoluchoswki-type slip condition (7.13). Following Brenner (1964) the hydrodynamic part of the force (8.9) may be evaluated directly from (7.13) by use of the reciprocal theorem for Stokes flows (Happel & Brenner 1965) without actually calculating the details of the secondary flow $\boldsymbol{v}_1$.

The above scheme is illustrated in the next section for the prototypic problem of the drag on a translating particle.

9. Modified drag on a translating particle

As a typical example consider a uniformly charged axisymmetric particle which translates along its axis of symmetry in an otherwise quiescent unbounded fluid domain. The particle dimensional velocity is v^* and the direction of motion is identified by the unit vector $\hat{\boldsymbol{\imath}}$ pointing along the symmetry axis. In a reference frame attached to the particle, the matching condition (6.1) reads

$$\boldsymbol{v}_0 = \boldsymbol{0} \quad \text{on } s \tag{9.1}$$

while the far-field velocity is

$$\boldsymbol{v}_0 \to -\hat{\boldsymbol{\imath}} \quad \text{as } |\boldsymbol{x}| \to \infty. \tag{9.2}$$

Because of symmetry the resultant force (8.1) on the particle is aligned with the symmetry axis,

$$\boldsymbol{F} = -\hat{\boldsymbol{\imath}}\mathscr{D}, \tag{9.3}$$

while the torque (8.4) vanishes. The drag $\mathscr{D}$ possesses the asymptotic expansion (cf. (8.6))

$$\mathscr{D} \sim \mathscr{D}_0 + \delta^2 \mathscr{D}_1 + \cdots, \tag{9.4}$$

wherein the leading-order $O(1)$ term is simply the drag associated with $\boldsymbol{v}_0$, the Stokes flow set up by the imposed motion of the particle.

The drag correction $\mathscr{D}_1$ is provided by a quadrature of both Newtonian stresses associated with the Stokes flow $(\boldsymbol{v}_1, p_1)$ and Maxwell stresses associated with the leading-order potential φ_0 (see (8.9)). It is easily shown, however, that the latter contribution vanishes (see Bike & Prieve 1992). Indeed, since φ_0 is harmonic, it decays with increasing distance r from the particle at least as rapidly as $1/r$ implying that Maxwell stresses decay as $1/r^4$. Use of (3.14) allows one to evaluate the integral of $\mathsf{S}_{M,0}$ on a sphere of large radius, rather than on s. As the area of such a sphere scales as r^2, we readily conclude that the Maxwell contribution vanishes. Thus, the leading-order force correction is simply the excess drag associated with $(\boldsymbol{v}_1, p_1)$.

This excess drag,

$$\mathscr{D}_1 = -\oint_s \mathrm{d}A\, \hat{\boldsymbol{n}} \boldsymbol{\cdot} \mathsf{S}_{N,1} \boldsymbol{\cdot} \hat{\boldsymbol{\imath}}, \tag{9.5}$$

is calculated following Brenner (1964) as a quadrature of the velocity on s

$$\mathscr{D}_1 = -\oint_s \mathrm{d}A\, \hat{\boldsymbol{n}} \boldsymbol{\cdot} \boldsymbol{S}_T \boldsymbol{\cdot} \boldsymbol{v}_1, \tag{9.6}$$

wherein $\boldsymbol{S}_T$ is the hydrodynamic stress field associated with translation of the particle with velocity $\hat{\boldsymbol{\imath}}$. Substitution of (7.13) and (8.12) yields

$$\mathscr{D}_1 = -\alpha\zeta^2 \oint_s \mathrm{d}A\, \hat{\boldsymbol{n}} \boldsymbol{\cdot} \boldsymbol{S}_T \boldsymbol{\cdot} \nabla_s p_0. \tag{9.7}$$

The force can be evaluated explicitly only for a specific geometry. Consider a spherical particle of (dimensional) radius a. In the dimensionless formulation, it is described using spherical polar coordinates (r, θ, ϖ) where r is measured from the particle centre and the latitude angle θ from the symmetry axis such that $\theta = 0$ corresponds to the $\hat{\boldsymbol{\imath}}$-direction; ϖ is the azimuthal angle. The local orthogonal coordinates ξ, η, and z are then identified with θ, $\varpi \sin\theta$, and $r - 1$, respectively. Use of axial symmetry then yields

$$\mathscr{D}_1 = -2\pi\alpha\zeta^2 \int_0^{\pi} \mathrm{d}\theta\, \sin\theta\, \hat{\boldsymbol{n}} \boldsymbol{\cdot} \boldsymbol{S}_T \boldsymbol{\cdot} \nabla_s p_0. \tag{9.8}$$

For the Stokes flow resulting from particle translation with a unit velocity $\hat{\boldsymbol{\imath}}$ the dimensionless traction and pressure at the particle surface are $\hat{\boldsymbol{n}} \boldsymbol{\cdot} \boldsymbol{S}_T = -(3/2)\hat{\boldsymbol{\imath}}$ and $p_0 = (3/2)\cos\theta$ (Happel & Brenner 1965); we then readily find

$$\mathscr{D}_1 = 6\pi\alpha\zeta^2. \tag{9.9}$$

Notwithstanding its simple form, validity of this result is not restricted to small ζ (see (5.7) *et seq.*). Since $\mathscr{D}_0 = 6\pi$ for a spherical particle, the ratio of the drag to that applying in the absence of electrokinetic effects is

$$1 + \alpha\zeta^2\delta^2 + \cdots, \tag{9.10}$$

in agreement with Smoluchowski (1921). As must be the case, electrokinetic effects indeed augment the drag.

It is instructive to compare the drag correction (9.9) with that calculated by Cox (1997), who assumed a small Péclet number. In the present notation equation (14.10) in Cox (1997) provides the following $O(\delta^4)$ correction to the Stokes drag:

$$48\pi\delta^4\lambda\, Pe \left(\ln^2 \frac{1 + \mathrm{e}^{\zeta/2}}{2} + \ln^2 \frac{1 + \mathrm{e}^{-\zeta/2}}{2} \right). \tag{9.11}$$

Formally substituting (2.21) we find that the presumed $O(\delta^4)$ drag correction becomes $O(\delta^2)$, however with the complicated functional dependence upon ζ still markedly different from (9.9).

The drag correction obtained by Cox (1997) coincides with the thin-Debye-layer limit of the corresponding result of Ohshima *et al.* (1984) obtained for an arbitrary Debye thickness while assuming a weak gravity effect which only slightly distorts the Debye cloud. The linearization of Ohshima *et al.* (1984) about a spherically symmetric Debye layer is indeed tantamount to the assumption of a small Péclet number. At zero Péclet number the ionic distribution is not affected by convection, and remains spherical. Moreover, the conservative body forces associated with the symmetric charge distribution in that layer are balanced by pressure gradients, so the flow is unaffected by the presence of the Debye layer. This is exactly the reference state which is perturbed in the analysis of Ohshima *et al.* (1984).

10. Non-stationary walls

The analysis thus far assumes that all solid walls in contact with the electrolyte are stationary. While this assumption is applicable to a wide variety of problems (including flows through channels and orifices, flows in porous media, the sedimentation of axisymmetric particles through unbounded quiescent fluid, etc.) it is inapplicable to a variety of other problems (for instance, the lift on a particle under shear).

To begin with, extension of our analysis to non-stationary walls requires the modification of the no-slip condition (2.14) which now becomes

$$\boldsymbol{v} = \boldsymbol{v}_S \quad \text{on } S, \tag{10.1}$$

where $\boldsymbol{v}_S$ is the surface velocity distribution corresponding to a rigid-body motion of the solid. Furthermore, it may not be possible to select a frame of reference in which the problem geometry appears steady. Normalizing the time t by a^*/v^* the hydrodynamic problem is quasi-steady (provided that $a^*v^*/\nu^* \ll 1$), the unsteadiness being implicit in the time-dependent geometric configuration. This may affect the electrochemical aspects of the problem: the Nernst–Planck equations (2.23) now read

$$\nabla \boldsymbol{\cdot} \boldsymbol{j}^{\pm} + \frac{\alpha}{\lambda}\delta^{-2}\left(\frac{\partial c^{\pm}}{\partial t} + \boldsymbol{v} \boldsymbol{\cdot} \nabla c^{\pm}\right) = 0, \tag{10.2}$$

whereby the salt and charge balances, (2.24) and (2.25), become

$$\nabla \boldsymbol{\cdot} \boldsymbol{j} + \frac{\alpha}{\lambda}\delta^{-2}\left(\frac{\partial c}{\partial t} + \boldsymbol{v} \boldsymbol{\cdot} \nabla c\right) = 0, \tag{10.3}$$

and

$$\nabla \boldsymbol{\cdot} \boldsymbol{i} + \frac{\alpha}{\lambda}\delta^{-2}\left(\frac{\partial q}{\partial t} + \boldsymbol{v} \boldsymbol{\cdot} \nabla q\right) = 0, \tag{10.4}$$

respectively.

In the outer analysis, the leading-order salt balance (3.5) now reads

$$\frac{\partial c_0}{\partial t} + \boldsymbol{v}_0 \boldsymbol{\cdot} \nabla c_0 = 0. \tag{10.5}$$

It then follows that (3.6)–(3.8) remain valid. The $O(1)$ charge balance (3.9) now reads

$$\nabla \boldsymbol{\cdot} \boldsymbol{i}_0 + \frac{\alpha}{\lambda}\left(\frac{\partial q_1}{\partial t} + \boldsymbol{v}_0 \boldsymbol{\cdot} \nabla q_1 + \boldsymbol{v}_1 \boldsymbol{\cdot} \nabla q_0\right) = 0. \tag{10.6}$$

Consequently, (3.11)–(3.14) remain valid.

Consider now the inner analysis about an arbitrary point $\mathscr{P}$ on S. We still use the Cartesian coordinate system (x, y, z), defined with the x- and y-axes lying within the tangent plane at $\mathscr{P}$. Since this system rotates with the solid-wall angular velocity $\boldsymbol{\Omega}$ it is convenient to replace (4.14) with the representation

$$\boldsymbol{v} = \boldsymbol{v}_S + \boldsymbol{\Omega} \times \boldsymbol{r} + \boldsymbol{V}, \quad p = P, \tag{10.7}$$

where $\boldsymbol{r}=\hat{\boldsymbol{e}}_x x+\hat{\boldsymbol{e}}_y y+\hat{\boldsymbol{e}}_z z$ is a position vector relative to point $\mathscr{P}$, and $\boldsymbol{V}$ now represents the relative fluid-velocity vector as observed in a reference frame attached to the rotating wall. Since (4.22) is again satisfied, it is natural to employ the scaling (4.15).

We define $\partial/\partial T$ as the time derivative in the rotating reference system (i.e. with x, y, and z fixed),

$$\frac{\partial}{\partial T}=\frac{\partial}{\partial t}+(\boldsymbol{v}_S+\boldsymbol{\Omega}\times\boldsymbol{r})\boldsymbol{\cdot}\nabla. \tag{10.8}$$

Substitution of (10.7)–(10.8) into the Nernst–Planck equations yields in the inner domain (cf. (4.16))

$$\frac{\partial J^{\pm\perp}}{\partial Z}-\delta\left[\frac{\partial}{\partial X}\left(\frac{\partial C^{\pm}}{\partial X}\pm C^{\pm}\frac{\partial\Phi}{\partial X}\right)+\frac{\partial}{\partial Y}\left(\frac{\partial C^{\pm}}{\partial Y}\pm C^{\pm}\frac{\partial\Phi}{\partial Y}\right)\right]$$
$$+\frac{\alpha}{\lambda}\left(\frac{\partial C^{\pm}}{\partial T}+\delta^{1/2}U\frac{\partial C^{\pm}}{\partial X}+\delta^{1/2}V\frac{\partial C^{\pm}}{\partial Y}+\delta W\frac{\partial C^{\pm}}{\partial Z}\right)=0. \tag{10.9}$$

Apart from the modification of (5.1) to incorporate the time derivative of $C_0^{\pm}$, the leading-order inner electrochemical problem consists of the same equations and boundary conditions (4.21), (4.26), (5.2) and (5.7) as before, hence it is decoupled from the hydrodynamic problem. As such, unsteadiness can only be introduced through the initial conditions imposed upon $C_0^{\pm}$. The problem thus admits the same time-independent Boltzmann (5.3) and excess-potential (5.10) distributions as before. Unlike this, the equation governing $C_1^{\pm}$ involves the leading-order inner velocity field. Since this field represents an extrapolation of the respective outer field, it is in general time dependent.

To proceed, we focus upon the class of problems that can appear steady in the absence of electrokinetic effects (which includes the prototypic problem of a sphere in a shear flow near a wall). In these problems, unsteadiness results from the slow motion of the boundaries that is driven by the $o(1)$ electrokinetic forces ($O(\delta^2)$ in view of (8.6)). The term $\partial C_1^{\pm}/\partial T$ is then also absent from the $O(\delta)$ balance of (10.9) whereby the flux expression (5.20) still holds.

In performing the velocity matching, the 1–1 level now yields $\boldsymbol{v}_0=\boldsymbol{v}_S$ on s, cf. (10.1). The 2–1 level replaces (6.3) with

$$A_0=\left(\frac{\partial u_0}{\partial z}\right)^{(s)}-\Omega_y,\quad B_0=\left(\frac{\partial v_0}{\partial z}\right)^{(s)}+\Omega_x. \tag{10.10}$$

We therefore obtain, instead of (6.7)

$$D_0(\xi,\eta)=-\left(\frac{\partial p_0}{\partial z}\right)^{(s)}-\frac{\partial\Omega_y}{\partial\xi}+\frac{\partial\Omega_x}{\partial\eta}. \tag{10.11}$$

The last two terms in (10.11) constitute the z-component of $-\nabla\times\boldsymbol{\Omega}$, which vanishes since $\boldsymbol{\Omega}$ is a constant vector. We conclude that (6.7) is retained. From this point it is straightforward to verify that both the Neumann condition (6.12) and the slip condition (7.13) are retained as well. Thus, the scheme of § 8 remains valid for the extended class of unsteady problems considered here.

11. Non-uniform surface-charge distribution

The analysis in §§ 5.3, 6.2 and 7 makes use of the assumption of uniform surface-charge distribution on the solid boundary, whereby ζ (hence also Ψ and $C_0^{\pm}$) is independent of the surface coordinates ξ and η. We here extend the analysis to the general case of non-uniform distributions.

Consider first the derivation (§§ 5.3 and 6.2) of the macro-scale boundary condition governing φ_0. The flux expression (5.17) is replaced by

$$J_1^{\pm\perp} = -\frac{\alpha}{\lambda}\int_0^Z \left(U_0 \frac{\partial C_0^{\pm}}{\partial \xi} + V_0 \frac{\partial C_0^{\pm}}{\partial \eta} + W_0 \frac{\partial C_0^{\pm}}{\partial Z'} \right) \mathrm{d}Z'. \tag{11.1}$$

Use of the inner continuity equation (5.13) and boundary condition (4.22) yields

$$\begin{aligned} J_1^{\pm\perp} &= -\frac{\alpha}{\lambda}\int_0^Z \left[\frac{\partial(U_0 C_0^{\pm})}{\partial \xi} + \frac{\partial(V_0 C_0^{\pm})}{\partial \eta} + \frac{\partial(W_0 C_0^{\pm})}{\partial Z'} \right] \mathrm{d}Z' \\ &= -\frac{\alpha}{\lambda}\left[\frac{\partial}{\partial \xi}\int_0^Z U_0 C_0^{\pm}\, \mathrm{d}Z' + \frac{\partial}{\partial \eta}\int_0^Z V_0 C_0^{\pm}\, \mathrm{d}Z' + W_0 C_0^{\pm} \right], \end{aligned} \tag{11.2}$$

or, upon substitution of (5.12) and (5.14),

$$\begin{aligned} J_1^{\pm\perp} = -\frac{\alpha}{\lambda}&\left[\frac{\partial}{\partial \xi}\left\{ A_0(\xi,\eta)\int_0^Z Z' C_0^{\pm}\, \mathrm{d}Z' \right\} + \frac{\partial}{\partial \eta}\left\{ B_0(\xi,\eta)\int_0^Z Z' C_0^{\pm}\, \mathrm{d}Z' \right\} \right. \\ &\left. - \frac{Z^2}{2}\left(\frac{\partial A_0}{\partial \xi} + \frac{\partial B_0}{\partial \eta} \right) C_0^{\pm} \right]. \end{aligned} \tag{11.3}$$

Introducing the decomposition (5.19) and taking the limit $Z \to \infty$ we find that (5.20) is replaced by

$$\begin{aligned} J_1^{\pm\perp}(Z\to\infty) = -\frac{\alpha}{\lambda}&\left[\frac{\partial}{\partial \xi}\left\{ A_0(\xi,\eta)\int_0^\infty Z(C_0^{\pm} - 1)\, \mathrm{d}Z \right\} \right. \\ &\left. + \frac{\partial}{\partial \eta}\left\{ B_0(\xi,\eta)\int_0^\infty Z(C_0^{\pm} - 1)\, \mathrm{d}Z \right\} \right]. \end{aligned} \tag{11.4}$$

Subtracting the above two fluxes yields, using the Poisson equation (5.2),

$$\begin{aligned} I_1^{\perp}(Z\to\infty) = \frac{\alpha}{\lambda}&\left[\frac{\partial}{\partial \xi}\left\{ A_0(\xi,\eta)\int_0^\infty Z \frac{\partial^2 \Psi}{\partial Z^2}\, \mathrm{d}Z \right\} \right. \\ &\left. + \frac{\partial}{\partial \eta}\left\{ B_0(\xi,\eta)\int_0^\infty Z \frac{\partial^2 \Psi}{\partial Z^2}\, \mathrm{d}Z \right\} \right]. \end{aligned} \tag{11.5}$$

Integration by parts in conjunction with (5.6)–(5.7) then provides the current

$$I_1^{\perp}(Z\to\infty) = \frac{\alpha}{\lambda}\left[\frac{\partial}{\partial \xi}(\zeta A_0) + \frac{\partial}{\partial \eta}(\zeta B_0) \right]. \tag{11.6}$$

The requisite generalization of (6.11) is obtained by substituting (6.3) into the above equation and making use of (5.15) and (6.7):

$$I_1^{\perp}(Z\to\infty) = \frac{\alpha}{\lambda}\left[-\zeta \left(\frac{\partial p_0}{\partial z} \right)^{(s)} + \frac{\partial \zeta}{\partial \xi}\left(\frac{\partial u_0}{\partial z} \right)^{(s)} + \frac{\partial \zeta}{\partial \eta}\left(\frac{\partial v_0}{\partial z} \right)^{(s)} \right]. \tag{11.7}$$

Asymptotic matching (6.8) provides the macro-scale condition

$$\frac{\partial \varphi_0}{\partial n} = \frac{\alpha}{\lambda}\left(\zeta \frac{\partial p_0}{\partial n} - \frac{\partial \boldsymbol{v}_0}{\partial n} \cdot \boldsymbol{\nabla}_s \zeta \right) \quad \text{on } s, \tag{11.8}$$

which reduces to (6.12) for uniform ζ.

Consider next the derivation (§ 7) of the boundary condition governing $\boldsymbol{v}_1$. For non-uniform surface charge, substitution of (5.2), (5.4), (6.4) and (7.2) into (7.3) yields

$$\frac{\partial^2 U_1}{\partial Z^2} = \lambda \left[\frac{\partial^2 \Psi}{\partial Z \, \partial \xi} \frac{\partial \Psi}{\partial Z} - \frac{\partial^2 \Psi}{\partial Z^2} \frac{\partial \Psi}{\partial \xi} - \frac{\partial^2 \Psi}{\partial Z^2} \frac{\partial \varphi_0^{(s)}}{\partial \xi} \right] + \frac{\partial p_0^{(s)}}{\partial \xi} - (\boldsymbol{\nabla} \cdot \hat{\boldsymbol{n}}) \left(\frac{\partial u_0}{\partial z} \right)^{(s)}. \tag{11.9}$$

Use of (5.8) reveals that the first two terms on the right-hand side mutually cancel, whereby (7.4) is recovered. The macro-scale slip condition (7.13) remains valid.

12. Concluding remarks

The present contribution is motivated by the questionably small $O(\delta^4)$ electro-viscous effect predicted in Cox's seminal analysis of the thin-Debye-layer limit $\delta \to 0$. Our analysis demonstrates a fundamental difference between the scaling appropriate to field- and motion-driven phenomena, respectively. In the latter when $\delta \to 0$ the product of the Hartmann (λ) and Péclet (Pe) numbers is $O(\delta^{-2})$ which is in contrast with Cox's assumption of both λ and Pe being $O(1)$. (When illustrating his scheme he goes even further by assuming an asymptotically small Pe.)

From the variety of options, we focus upon $\lambda = O(1)$, i.e. assuming that the motion-induced electric field is comparable to the thermal scale (see (2.22)). In view of the above-mentioned scaling this requires that we address the limit process $\delta \to 0$ and $Pe = O(\delta^{-2})$ (which has already been mentioned in the review paper by Saville 1977). This limit representing dominance of convection effects is reflected in major changes in the structure of the present asymptotic scheme relative to that of Cox (1997). Thus, owing to significant non-uniform convective 'surface' currents, charge conservation necessitates Ohmic currents between the electro-neutral bulk and the Debye layer. These are represented by an inhomogeneous Neumann condition imposed upon the bulk electric potential.

The *ansatz* of strong convection considerably simplifies the actual calculation. The electro-viscous effect now already appearing at $O(\delta^2)$ (as opposed to $O(\delta^4)$ in Cox 1997) consists of contributions of both the Maxwell stress associated with the leading-order bulk electric field and the Newtonian stress associated with the leading-order perturbation to the original Stokes flow. This perturbation is driven, in turn, by a Smoluchowski-type slip condition. In view of the above, it is not surprising that the drag correction calculated for a sedimenting sphere differs from that obtained by Cox (1997) in both magnitude and functional form.

Our analysis is initially presented for steady configurations where all solid surfaces are stationary. It is subsequently established that the resulting scheme applies to weakly unsteady scenarios as well. These include problems which (in an appropriately chosen frame of reference) appear steady in the absence of electrokinetic effects. In these problems, the importance of the $O(\delta^2)$ electro-viscous effect is not necessarily in the correction to an existing force but rather in the introduction of qualitatively new phenomena (e.g. electrokinetic lift) which would not exist in the absence of electrokinetic transport.

Another interesting feature associated with the strong convection in the present problem is the need (apparently overlooked in the literature) to account for the salt flux between the Debye layer and the bulk. This flux seems incompatible with the uniform bulk salt distribution within the convection-dominated Ohmic bulk. This paradox is resolved through recognizing the dual singularity associated with the $\delta \to 0$ limit. Thus, diffusion balances electrostatic interactions within the $O(\delta)$-wide Debye layer, while it becomes comparable to convection in an $O(\delta^{2/3})$-wide intermediate layer existing in the overlap domain joining the Debye layer and the bulk.

The scaling relation (2.21) allows for a variety of limit processes other than the one studied here. Thus, for instance, one could conceive of $Pe = O(1)$ and λ large. The Péclet number is in principle externally controllable by the magnitude of the imposed relative motion. These other limits may thus be physically realizable and therefore warrant investigation.

Finally, with the availability of the present generic scheme, it is desirable to re-examine the classic problem of particle lift in Stokes shear flows. This work is currently in progress.

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Appendix. Diffusive boundary layer

To analyse the diffusive layer we define the local coordinates (cf. (4.4))

$$\tilde{X} = x/\delta^{1/3}, \quad \tilde{Y} = y/\delta^{1/3}, \quad \tilde{Z} = z/\delta^{2/3}. \tag{A 1}$$

Matching with the bulk ionic densities (3.7) implies that $c^{\pm} \to 1$ as $\tilde{Z} \to \infty$; ionic-flux matching then necessitates $O(\delta^{2/3})$ density perturbations. This suggests the definition of the diffusive-scale concentrations

$$c^{\pm} = 1 + \delta^{2/3}\tilde{C}^{\pm}. \tag{A 2}$$

Accordingly, we also define

$$c = 1 + \delta^{2/3}\tilde{C}; \tag{A 3}$$

the charge density q then being $O(\delta^{2/3})$ at most.

Velocity matching with the Debye-scale flow suggest an $O(\delta^{2/3})$ tangential velocity. The continuity equation then implies an $O(\delta^{4/3})$ normal velocity. Thus, we define (cf. (4.15))

$$\boldsymbol{v} = \hat{\boldsymbol{e}}_x\delta^{2/3}\tilde{U} + \hat{\boldsymbol{e}}_y\delta^{2/3}\tilde{V} + \hat{\boldsymbol{e}}_z\delta^{4/3}\tilde{W}. \tag{A 4}$$

Also, matching with the bulk indicates that both the pressure and electric potential are $O(1)$, whence we also define:

$$\varphi = \tilde{\Phi}, \quad p = \tilde{P}. \tag{A 5}$$

Each of the above diffusive-scale fields is expanded in the generic form (cf. (4.23))

$$\tilde{F} \sim \tilde{F}_0 + \delta^{2/3}\tilde{F}_1 + \cdots. \tag{A 6}$$

The leading-order velocity field is obtained in a similar way as in the Debye layer. Thus, tangential momentum balances and matching with the bulk yield

$$\tilde{U}_0 = \left(\frac{\partial u_0}{\partial z}\right)^{(s)}\tilde{Z}, \quad \tilde{V}_0 = \left(\frac{\partial v_0}{\partial z}\right)^{(s)}\tilde{Z}. \tag{A 7}$$

Following (6.4)–(6.7) we find

$$\tilde{W}_0 = \frac{\tilde{Z}^2}{2}\left(\frac{\partial p_0}{\partial z}\right)^{(s)}. \tag{A 8}$$

The charge balance (2.25) yields at $O(\delta^{-4/3})$

$$\frac{\partial^2 \tilde{\Phi}_0}{\partial \tilde{Z}^2} = 0; \tag{A 9}$$

also, electric-current matching with the Debye scale yields

$$\frac{\partial \tilde{\Phi}_0}{\partial \tilde{Z}} \to 0 \quad \text{as } \tilde{Z} \to 0. \tag{A 10}$$

It then follows that $\tilde{\Phi}_0$ is independent of $\tilde{Z}$. Thus, the $O(\delta^{-2/3})$ salt balance (2.24) yields the convective–diffusive equation:

$$\frac{\partial^2 \tilde{C}_0}{\partial \tilde{Z}^2} = \frac{\alpha}{\lambda}\left(\tilde{U}_0 \frac{\partial \tilde{C}_0}{\partial \xi} + \tilde{V}_0 \frac{\partial \tilde{C}_0}{\partial \eta} + \tilde{W}_0 \frac{\partial \tilde{C}_0}{\partial \tilde{Z}}\right). \tag{A 11}$$

Upon substitution of (A 7)–(A 8), this equation becomes

$$\frac{\partial^2 \tilde{C}_0}{\partial \tilde{Z}^2} = \frac{\alpha}{\lambda}\left[\tilde{Z}\left(\frac{\partial u_0}{\partial z}\right)^{(s)} \frac{\partial \tilde{C}_0}{\partial \xi} + \tilde{Z}\left(\frac{\partial v_0}{\partial z}\right)^{(s)} \frac{\partial \tilde{C}_0}{\partial \eta} + \frac{\tilde{Z}^2}{2}\left(\frac{\partial p_0}{\partial z}\right)^{(s)} \frac{\partial \tilde{C}_0}{\partial \tilde{Z}}\right]. \tag{A 12}$$

The field $\tilde{C}_0$ also satisfies at small $\tilde{Z}$ a boundary condition which follows from salt-flux matching with the Debye-scale solution (see (6.14)), namely

$$\frac{\partial \tilde{C}_0}{\partial \tilde{Z}} \to -\frac{\alpha}{\lambda}\left(\frac{\partial p_0}{\partial z}\right)^{(s)} \mathscr{H}(\zeta) \quad \text{as } \tilde{Z} \to 0, \tag{A 13}$$

while matching with the bulk implies that $\tilde{C}_0$ decays at large $\tilde{Z}$

$$\tilde{C}_0 \to 0 \quad \text{as } \tilde{Z} \to \infty. \tag{A 14}$$

Equations (A 12)–(A 14) specify a parabolic boundary-value problem governing $\tilde{C}_0$.

Note that (A 9) in conjunction with Poisson's equation (2.3) implies the vanishing of charge density at $O(\delta^{2/3})$. The density perturbations $\tilde{C}^{\pm}$ thus vary on the diffusive scale, and are equal at leading order.

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