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Strong-field electrophoresis

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We analyse particle electrophoresis in the thin-double-layer limit for asymptotically large applied electric fields. Specifically, we consider fields scaling as δ^{-1}, δ ($\ll 1$) being the dimensionless Debye thickness. The dominant advection associated with the intense flow mandates a uniform salt concentration in the electro-neutral bulk. The $O(\delta^{-1})$ large tangential fields in the diffuse part of the double layer give rise to a novel 'surface conduction' mechanism at moderate zeta potentials, where the Dukhin number is vanishingly small. The ensuing $O(1)$ electric current emerging from the double layer modifies the bulk electric field; the comparable $O(1)$ transverse salt flux, on the other hand, is incompatible with the nil diffusive fluxes at the homogeneous bulk. This contradiction is resolved by identifying the emergence of a diffusive boundary layer of $O(\delta^{1/2})$ thickness, resembling thermal boundary layers at large-Reynolds-number flows. The modified electric field within the bulk gives rise to an irrotational flow, resembling those in moderate-field electrophoresis. At leading order, the particle electrophoretic velocity is provided by Smoluchowski's formula, describing linear variation with applied field.

Key words: colloids, low-Reynolds-number flows

1. Introduction

In his pioneering analysis of electrophoresis, Smoluchowski considered what may be the simplest model problem: a uniformly charged spherical particle (zeta potential ζ^*) suspended in an unbounded liquid electrolyte (permittivity ϵ^*, viscosity μ^*) and exposed to a uniform electric field E^*. (Dimensional quantities being hereafter denoted by an asterisk.) For Debye length $1/\kappa^*$ (see (2.6)) thin compared with particle size a^*, Smoluchowski obtained the celebrated formula

$$\mathscr{U}^* = \frac{\epsilon^*\zeta^*}{\mu^*}E^* \tag{1.1}$$

for the electrophoretic velocity. It was later realized (Morrison 1970) that (1.1) is rather universal, being independent of particle size, shape and orientation relative to the applied field.

In the prevailing literature it is common to interpret (1.1), which is linear in the applied field, as (the first term in) a 'weak-field' approximation. For moderate zeta potentials (i.e. comparable to the thermal scale), there is actually no need for such an approximation when analysing thin ($\delta = 1/\kappa^* a^* \ll 1$) double-layer configurations.

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Indeed, formal use of matched asymptotic expansions to analyse this singular limit (Prieve *et al.* 1984; Rubinstein & Zaltzman 2001) leads to a conceptual decomposition of the fluid domain into an $O(1/\kappa^*)$-wide boundary ('Debye') layer, where the ionic distributions are in quasi-equilibrium, and an electro-neutral 'bulk'. This decomposition is not limited to weak fields (Yariv 2010); it effectively replaces the Debye-layer physics with macroscale boundary conditions, consisting of homogeneous Neumann conditions governing the electric potential and salt concentration, and the Dukhin–Derjaguin osmotic slip formula. In the absence of imposed salt gradients the salt distribution turns out to be uniform in the bulk, which therefore acts as an Ohmic conductor. Within that framework, (1.1) is readily obtained.

The misconception in the interpretation of (1.1) may have to do with the seminal analysis of Dukhin (1965), who considered thin double-layer electrophoresis for relatively large zeta potentials, analysing the role of 'surface conduction'. Dukhin's analysis (see Dukhin & Derjaguin 1974), simplified later on by O'Brien & Hunter (1981), is indeed limited to weak fields where the field-magnitude parameter (Saville 1977)

$$\beta = \frac{a^* E^*}{\varphi^*}, \tag{1.2}$$

representing the ratio of the typical voltage drop across the particle to the thermal voltage φ^* ($\approx$25 mV in a univalent solution, see (2.1)), is asymptotical small. This restriction is necessary because the incorporation of surface-conduction effects is naturally accompanied by concentration polarization, which, in turn, gives rise to inherent nonlinearities. Formally speaking, Dukhin's analysis, developed for $O(1)$ Dukhin numbers and $\beta \ll 1$, breaks down at $\beta \sim O(1)$. On the other hand, if one does not consider asymptotically large zeta potentials, no need arises for a weak-field linearization (Yariv 2010). Not only is the weak-field approximation unnecessary, it is also rather crude. Even for moderate field values, say 100 V cm^{-1}, the voltage drop across a micrometre-size particle is several multiples of the thermal voltage, whereby β is of order unity.

Of course, β increases linearly with both particle size and electric field. Since the use of 10–50 μm particles and 10 kV cm^{-1} fields is not uncommon (Prieve, Sides & Wirth 2010), it actually appears that the proper limit to consider for a significant number of practical applications is that of *strong* applied fields, $\beta \gg 1$. In that limit, residing outside the scope of Yariv (2010), it is not *a priori* clear whether Smoluchowski's formula remains valid. For strongly applied fields it is anticipated that the slip-driven velocity field is large as well. In the electro-neutral bulk, the associated strong advection will only tend to maintain the already-uniform salt concentration distribution; that would not cause any modifications in that region. However, the intense tangential conduction (and, presumably, advection) within the Debye layer is expected to modify the classical quasi-equilibrium structure.

In recent electrophoresis measurements (Kumar *et al.* 2006) it was found, nonetheless, that the linear variation with applied field is retained even at moderately large β values. In their careful experiments an electric field of up to 1000 V cm^{-1} in magnitude was applied over polystyrene spheres of 4 μm diameter, corresponding to $\beta \approx 8$. Admittedly, these field values are rather mild; nevertheless, the observations of linear field–velocity correlations provide yet another motive to investigate the strong-field regime.

Our goal is to construct a theoretical model for strong-field electrophoresis at moderate zeta potentials. To this end, we need to quantify what is 'strong'. We

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have already noted that Smoluchowski's formula applies for $\beta \sim O(1)$ and moderate zeta potentials (of the order of φ^*). Moreover, since the transverse field within the Debye layer is of (dimensionless) order δ^{-1}, it is anticipated that for $1 \ll \beta \ll \delta^{-1}$ the thin-double-layer structure would remain unaltered. It therefore appears that the interesting situation to consider entails the linkage $\beta \sim O(\delta^{-1})$, where the tangential field within the diffuse part of the double layer is comparable to the transverse field.

In what follows, we accordingly analyse electrophoretic motion for thin double layers ($\delta \ll 1$) and strong $O(\delta^{-1})$ applied field.

2. Problem formulation

Consider a spherical dielectric particle (radius a^*) suspended in a symmetric electrolyte solution (permittivity ϵ^*, valencies $\pm\mathscr{Z}$, equilibrium ionic concentration c^*) of an unbounded extent. An immobile layer of adsorbed ions, bounded to the particle surface, is represented by a uniform surface-charge distribution (density σ^*). This system is exposed to a uniformly applied electric field E^* pointing in a direction specified by the unit vector $\hat{\boldsymbol{\imath}}$. Owing to the ensuing electrokinetic transport, the particle acquires an electrophoretic velocity $\mathscr{U}^*$ (defined as positive in the applied-field direction) relative to the otherwise quiescent fluid. Our goal is to calculate this velocity.

In formulating a steady-state problem, we employ a reference frame attached to the particle centre. We use the dimensionless notation of Saville (1977), normalizing length variables by a^*, the ionic concentrations $c^{\pm}$ by c^*, and the electric potential φ by the thermal voltage

$$\varphi^* = \frac{k^*T^*}{\mathscr{Z}e^*}, \tag{2.1}$$

wherein k^*T^* is the Boltzmann temperature and e^* the elementary charge. Electric fields are accordingly normalized by φ^*/a^*. This field scale readily provides the Maxwell stress scale $\epsilon^*(\varphi^*/a^*)^2$. Balancing with viscous stresses suggests normalizing the velocity field $\boldsymbol{u}$ by $\epsilon^*\varphi^{*2}/\mu^*a^*$, μ^* being the viscosity of the electrolyte solution. In this notation, the governing equations are as follows.

(*a*) The Nernst–Planck equations,

$$\boldsymbol{\nabla}\cdot\boldsymbol{j}^{\pm} + \alpha\boldsymbol{u}\cdot\boldsymbol{\nabla}c^{\pm} = 0. \tag{2.2}$$

Here

$$\boldsymbol{j}^{\pm} = \mp c^{\pm}\boldsymbol{\nabla}\varphi - \boldsymbol{\nabla}c^{\pm} \tag{2.3}$$

are the molecular ionic fluxes, normalized by D^*c^*/a^*, D^* being the ionic diffusivity (assumed identical for both species). The dimensionless group

$$\alpha = \frac{\epsilon^*\varphi^{*2}}{\mu^*D^*} \tag{2.4}$$

is independent of both particle dimension a^* and electrolyte concentration c^*; for typical diffusivities ($D^* \approx 10^{-9}$ m^2 s^{-1}) in aqueous solutions ($\mu^* \approx 10^{-3}$ kg m^{-1} s^{-1}), $\alpha \approx 0.5$ (Saville 1977). Saville (1977) considered that group as a Péclet number. This interpretation, valid for moderate β, ceases to hold for strongly applied fields, to be considered here.

(*b*) Poisson's equation

$$-2\delta^2\nabla^2\varphi = c^+ - c^-. \tag{2.5}$$

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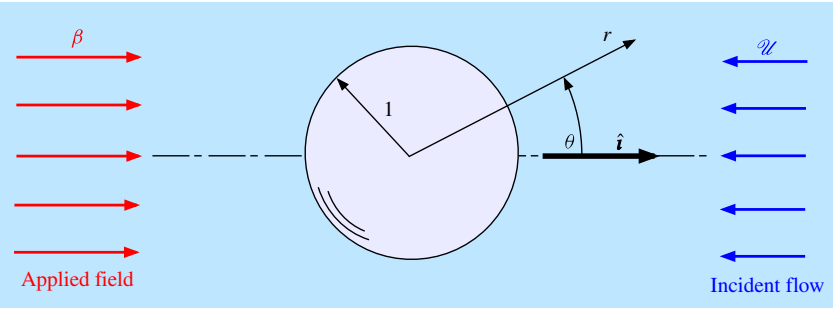


FIGURE 1. (Colour online available at journals.cambridge.org/flm) Schematic depicting the particle and (r, θ) spherical coordinates in a particle-fixed reference system.

Here, $\delta = 1/\kappa^* a^*$ is the dimensionless Debye thickness, with

$$\kappa^{*2} = \frac{2\mathscr{Z}^2 e^{*2} c^*}{\epsilon^* k^* T^*}. \tag{2.6}$$

(*c*) The continuity

$$\boldsymbol{\nabla} \cdot \boldsymbol{u} = 0 \tag{2.7}$$

and Stokes equations

$$\boldsymbol{\nabla} p = \nabla^2 \boldsymbol{u} + \nabla^2 \varphi \boldsymbol{\nabla} \varphi, \tag{2.8}$$

governing the motion of a fluid subject to Coulomb body forces.

Equations (2.2)–(2.8) represent the standard electrokinetic model. The assumption of equal ionic diffusivity may be relaxed, but with the cost of obscuring the analysis. Fortunately, it will become evident from the following derivation that the main result of this paper, namely formula (7.2), remains valid even for different diffusivities.

It is convenient to employ spherical polar coordinates r and θ, $\theta = 0$ in the applied-field direction $\hat{\boldsymbol{t}}$ (see figure 1), whereby the velocity and flux vectors adopt the forms

$$\boldsymbol{u} = \hat{\boldsymbol{e}}_r u + \hat{\boldsymbol{e}}_\theta v, \quad \boldsymbol{j}^{\pm} = \hat{\boldsymbol{e}}_r j_r^{\pm} + \hat{\boldsymbol{e}}_\theta j_\theta^{\pm}. \tag{2.9a,b}$$

The boundary conditions at the particle surface $r = 1$ consist of:

(*a*) no flux of ions into the (presumed inert) particle boundary

$$j_r^{\pm} = 0 \quad \text{at } r = 1; \tag{2.10}$$

(*b*) velocity impermeability and no slip

$$u = v = 0 \quad \text{at } r = 1; \tag{2.11}$$

(*c*) Gauss law,

$$\frac{\partial \varphi}{\partial r} = -\delta^{-1}\sigma \quad \text{at } r = 1, \tag{2.12}$$

relating the electric field to the dimensionless charge density $\sigma = \sigma^*/\epsilon^* \varphi^* \kappa^*$. Following Saville (1977), the electric displacement within the solid is neglected.

At large distances away from the particle the ionic concentrations approach their equilibrium value, the electric field approaches a uniform field of magnitude β

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(see (1.2)), and the flow approaches a uniform profile of magnitude $-\mathscr{U}$ in the applied-field direction:

$$c^{\pm} \to 1, \quad \nabla\varphi \to -\beta\hat{\boldsymbol{\imath}}, \quad \boldsymbol{u} \to -\mathscr{U}\hat{\boldsymbol{\imath}} \quad \text{as } r \to \infty. \tag{2.13a,b,c}$$

The requisite closure condition for calculating $\mathscr{U}$ is provided by the constraint of a force-free particle, requiring the vanishing of the resultant force exerted on the particle by the sum of Newtonian and Maxwell stresses, evaluated at $r = 1$:

$$\int_{r=1} \{-p\boldsymbol{I} + \nabla\boldsymbol{u} + (\nabla\boldsymbol{u})^{\dagger} + \nabla\varphi\nabla\varphi - \tfrac{1}{2}\nabla\varphi\cdot\nabla\varphi\boldsymbol{I}\}\cdot\hat{\boldsymbol{n}}\,\mathrm{d}A = \boldsymbol{0}. \tag{2.14}$$

Here $\boldsymbol{I}$ is the idemfactor, $\dagger$ denotes tensor transposition, and $\mathrm{d}A$ is a differential area element (normalized by a^2). Since the inhomogeneous Stokes equations (2.8) represent the vanishing of the divergence of this sum, the above integral can be alternatively evaluated over any close surface enclosing the sphere.

An alternative formulation is obtained using the mean ('salt') concentration (normalized by c^*) and the volumetric charge density (normalized by $2\mathscr{Z}e^*c^*$)

$$c = \tfrac{1}{2}(c^+ + c^-), \quad q = \tfrac{1}{2}(c^+ - c^-), \tag{2.15a,b}$$

together with the salt flux and current density

$$\boldsymbol{j} = \tfrac{1}{2}\left(\boldsymbol{j}^+ + \boldsymbol{j}^-\right), \quad \boldsymbol{i} = \tfrac{1}{2}\left(\boldsymbol{j}^+ - \boldsymbol{j}^-\right), \tag{2.16a,b}$$

which, using (2.3), adopt the respective forms

$$\boldsymbol{j} = -q\nabla\varphi - \nabla c, \quad \boldsymbol{i} = -c\nabla\varphi - \nabla q. \tag{2.17a,b}$$

In polar components, the vector fields $\boldsymbol{j}$ and $\boldsymbol{i}$ possess forms similar to (2.9),

$$\boldsymbol{j} = \hat{\boldsymbol{e}}_r j_r + \hat{\boldsymbol{e}}_\theta j_\theta, \quad \boldsymbol{i} = \hat{\boldsymbol{e}}_r i_r + \hat{\boldsymbol{e}}_\theta i_\theta. \tag{2.18a,b}$$

In terms of these reduced variables, Poisson's equation (2.5) becomes

$$\delta^2\nabla^2\varphi = -q; \tag{2.19}$$

while addition and subtraction of (2.2) yield the salt and charge balances, respectively,

$$\nabla\cdot\boldsymbol{j} + \alpha\boldsymbol{u}\cdot\nabla c = 0, \quad \nabla\cdot\boldsymbol{i} + \alpha\boldsymbol{u}\cdot\nabla q = 0. \tag{2.20a,b}$$

The no-flux conditions (2.10) become

$$j_r = i_r = 0 \quad \text{at } r = 1, \tag{2.21}$$

and the far-field conditions (2.13*a*) imply that

$$c \to 1, \quad q \to 0 \tag{2.22a,b}$$

as $r \to \infty$.

3. Thin-double-layer limit

We consider the thin-double-layer limit

$$\delta \ll 1. \tag{3.1}$$

In that framework, we focus upon the strong-field limit $\beta = O(1/\delta)$. This is expressed in the form

$$\beta = \delta^{-1}\bar{\beta} \tag{3.2}$$

wherein $\bar{\beta} = O(1)$.

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In postulating asymptotic scalings we assume, subject to *a posteriori* verification, that the velocity field $\boldsymbol{u}$ is $O(1/\delta)$ (and, hence, so is the pressure p, see (2.8)). On the other hand, it is expected that the ionic concentrations (and, hence, c and q) remain $O(1)$:

$$\left.\begin{aligned} &c = c_0 + \delta c_1 + \cdots, \quad q = q_0 + \delta q_1 + \cdots, \\ &\varphi = \delta^{-1}\varphi_{-1} + \varphi_0 + \cdots, \\ &\boldsymbol{u} = \delta^{-1}\boldsymbol{u}_{-1} + \boldsymbol{u}_0 + \cdots, \quad p = \delta^{-1}p_{-1} + p_0 + \cdots. \end{aligned}\right\} \tag{3.3}$$

In view of the fluid-velocity scaling, we postulate the particle speed

$$\mathscr{U} = \delta^{-1}\mathscr{U}_{-1} + \cdots. \tag{3.4}$$

Note that α no longer plays the role of a Péclet number. Rather, with $\alpha = O(1)$, the effective Péclet number is $O(\delta^{-1})$.

The $O(1)$ balance of Poisson's equation (2.19) yields leading-order electro-neutrality

$$q_0 \equiv 0. \tag{3.5}$$

At $O(\delta^{-1})$, the salt balance (2.20*a*) is dominated by advection,

$$\boldsymbol{u}_{-1}\cdot\boldsymbol{\nabla} c_0 = 0. \tag{3.6}$$

This equation is alternatively written $\mathrm{D}_{-1}c_0/\mathrm{D}t = 0$, where $\mathrm{D}_{-1}/\mathrm{D}t$ is the material derivate associated with the leading-order flow. Since this flow is steady, c_0 is constant on its streamlines. We assume, subject to *a posteriori* verification, that these lines are open, originating at infinity, where $c_0 = 1$ (see (2.22*a*)). Thus,

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

Use of (3.5) and (3.7) reveals that the charge balance (2.20*b*) at $O(\delta^{-1})$ is then dominated by *conduction*, whereby

$$\nabla^2\varphi_{-1} = 0. \tag{3.8}$$

Proceeding to higher-order balances, it is readily found that the charge density vanishes at each asymptotic order, as do all salt perturbations,

$$q_n = 0, \quad c_n = 0 \quad \text{for } n = 1, 2, 3, \ldots, \tag{3.9}$$

while the electric potential is harmonic at each order:

$$\nabla^2\varphi_n = 0 \quad \text{for } n = 0, 1, 2, \ldots. \tag{3.10}$$

The Coulomb body force therefore vanishes at all orders of the Stokes equations (2.8). Specifically, at leading order we have

$$\boldsymbol{\nabla}\cdot\boldsymbol{u}_{-1} = 0, \quad \boldsymbol{\nabla} p_{-1} = \nabla^2\boldsymbol{u}_{-1}. \tag{3.11a,b}$$

In view of (2.17), the salt flux vanishes identically, while the current density adopts an Ohmic form:

$$\boldsymbol{j} = \boldsymbol{0}, \quad \boldsymbol{i} = -\boldsymbol{\nabla}\varphi = -\delta^{-1}\boldsymbol{\nabla}\varphi_{-1} + \boldsymbol{\nabla}\varphi_0 + \cdots. \tag{3.12a,b}$$

The far-field conditions in the thin-double-layer limit are obtained from (2.13). Conditions (2.13*a*) are consistent with (3.7), while (2.13*b*,*c*) yield

$$\boldsymbol{\nabla}\varphi_{-1} \to -\bar{\beta}\hat{\boldsymbol{\imath}}, \quad \boldsymbol{\nabla}\varphi_0 \to \boldsymbol{0} \quad \text{as } r \to \infty \tag{3.13a,b}$$

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and

$$\boldsymbol{u}_{-1} \to -\mathscr{U}_{-1}\hat{\boldsymbol{\imath}} \quad \text{as } r \to \infty. \tag{3.13a,b}$$

On the other hand, the literal conditions on the particle surface are incompatible with the above approximations. This is a manifestation of the singular nature of the thin-double-layer limit (3.1), where the small parameter multiplies the highest derivative in (2.5). The preceding results therefore constitute an *outer* approximation, valid outside an $O(\delta)$-wide *inner* boundary ('Debye') layer surrounding the particle surface. Hereafter, we refer to r as an outer coordinate, $r \to 1$ representing the matching region with the Debye layer rather than the literal particle surface, where the boundary conditions apply. (Note that these boundary conditions have not been used in deriving (3.5)–(3.12).)

We now turn to analyse the inner Debye layer.

4. Debye layer

4.1. *Scaling*

In the Debye layer we employ the stretched radial coordinate

$$Z = \frac{r-1}{\delta}. \tag{4.1}$$

As in the outer region, we anticipate $O(1)$ ionic concentrations,

$$c^{\pm} = C_0^{\pm}(Z,\theta) + \cdots, \tag{4.2}$$

whereby

$$c = C_0(Z,\theta) + \cdots, \quad q = Q_0(Z,\theta) + \cdots. \tag{4.3a,b}$$

The electric potential, on the other hand, is anticipated to be $O(\delta^{-1})$ due to the requirement of electric-field matching with the outer electric field. This suggests the expansion

$$\varphi = \delta^{-1}\Phi_{-1}(\theta) + \Phi_0(Z,\theta) + \cdots \tag{4.4}$$

where the leading-order term is independent of Z.

The ionic fluxes in the r- and θ-directions then possess the expansions

$$j_r^{\pm} = \delta^{-1}J_{-1}^{\pm\perp} + J_0^{\pm\perp} + \cdots, \quad j_\theta^{\pm} = \delta^{-1}J_{-1}^{\pm\parallel} + J_0^{\pm\parallel} + \cdots, \tag{4.5a,b}$$

where the $O(\delta^{-1})$ radial and tangential fluxes are

$$J_{-1}^{\pm\perp} = -\frac{\partial C_0^{\pm}}{\partial Z} \mp C_0^{\pm}\frac{\partial \Phi_0}{\partial Z}, \quad J_{-1}^{\pm\parallel} = \mp C_0^{\pm}\frac{\mathrm{d}\Phi_{-1}}{\mathrm{d}\theta}. \tag{4.6a,b}$$

Comparable expansions hold for the respective components of the salt flux $\boldsymbol{j}$

$$j_r = \delta^{-1}J_{-1}^{\perp} + J_0^{\perp} + \cdots, \quad j_\theta = \delta^{-1}J_{-1}^{\parallel} + J_0^{\parallel} + \cdots, \tag{4.7a,b}$$

and the current density $\boldsymbol{i}$

$$i_r = \delta^{-1}I_{-1}^{\perp} + I_0^{\perp} + \cdots, \quad i_\theta = \delta^{-1}I_{-1}^{\parallel} + I_0^{\parallel} + \cdots. \tag{4.8a,b}$$

Balancing the large Coulomb forces in the Stokes equations (2.8) requires an $O(\delta^{-2})$-large pressure:

$$p = \delta^{-2}P_{-2}(Z,\theta) + \cdots. \tag{4.9}$$

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Owing to asymptotic matching, we anticipate $O(\delta^{-1})$ tangential-velocity scaling,

$$v = \delta^{-1} V_{-1}(Z,\theta) + V_0(Z,\theta) + \cdots. \tag{4.10}$$

Continuity equation (2.7) then suggests $O(1)$ radial velocities,

$$u = U_0(Z,\theta) + \cdots. \tag{4.11}$$

4.2. *Governing equations*

Retaining two leading asymptotic terms, the Nernst–Planck equations (2.2) read

$$\delta^{-2}\frac{\partial J_{-1}^{\pm\perp}}{\partial Z} + \delta^{-1}\left\{\frac{\partial J_0^{\pm\perp}}{\partial Z} + 2J_{-1}^{\pm\perp} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(J_{-1}^{\pm\parallel}\sin\theta)\right\} + \cdots$$
$$+\alpha\left\{\delta^{-1}\left(V_{-1}\frac{\partial C_0^{\pm}}{\partial\theta} + U_0\frac{\partial C_0^{\pm}}{\partial Z}\right) + \cdots\right\} = 0. \tag{4.12}$$

At $O(1)$, Poisson's equation (2.5) yields

$$-2\frac{\partial^2\Phi_0}{\partial Z^2} = C_0^+ - C_0^-. \tag{4.13}$$

The radial and tangential components of the Stokes equations (2.8) yield at $O(\delta^{-3})$

$$\frac{\partial P_{-2}}{\partial Z} = \frac{\partial^2\Phi_0}{\partial Z^2}\frac{\partial\Phi_0}{\partial Z}, \quad 0 = \frac{\partial^2 V_{-1}}{\partial Z^2} + \frac{\partial^2\Phi_0}{\partial Z^2}\frac{\mathrm{d}\Phi_{-1}}{\mathrm{d}\theta}, \tag{4.14a,b}$$

while the continuity equation (2.7) at $O(\delta^{-1})$ possesses the form

$$\frac{\partial U_0}{\partial Z} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(V_{-1}\sin\theta) = 0. \tag{4.15}$$

The preceding differential equations are supplemented by boundary conditions at the particle surface $Z = 0$. The no-flux conditions (2.10) yield

$$J_{-1}^{\pm\perp} = 0, \quad J_0^{\pm\perp} = 0, \quad \ldots \quad \text{at } Z = 0; \tag{4.16}$$

the impermeability and no-slip conditions (2.11) read, at leading order

$$U_0 = 0, \quad V_{-1} = 0 \quad \text{at } Z = 0; \tag{4.17a,b}$$

while the leading-order balance of Gauss's condition (2.12) gives

$$\frac{\partial\Phi_0}{\partial Z} = -\sigma \quad \text{at } Z = 0. \tag{4.18}$$

At large Z the pertinent variables must match the corresponding outer fields,

$$C_0^{\pm} \to 1, \quad \Phi_0 \to \varphi_0, \quad P_{-2} \to 0, \quad V_{-1} \to v_{-1} \quad \text{as } Z \to \infty. \tag{4.19a,b,c,d}$$

Hereafter, bulk-scale variables appearing in Debye-layer equations are understood to be evaluated on the effective boundary $r \to 1$, and are accordingly functions of θ alone. Matching also implies that

$$\Phi_{-1}(\theta) = \varphi_{-1}. \tag{4.20}$$

4.3. *Analysis*

At leading $O(\delta^{-2})$ the Nernst–Planck balances (4.12) yield $\partial J_{-1}^{\pm\perp}/\partial Z = 0$, which, in conjunction with the no-flux condition (4.16), imply

$$J_{-1}^{\pm\perp} \equiv 0. \tag{4.21}$$

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Substitution of (4.6*a*) in conjunction with (4.19) yields the Boltzmann distribution

$$C_0^{\pm} = \mathrm{e}^{\mp\Psi} \tag{4.22}$$

in which $\Psi = \Phi_0(Z,\theta) - \varphi_0$ is the 'excess potential' in the layer. The salt and charge distributions are then given by

$$C_0 = \cosh\Psi, \quad Q_0 = -\sinh\Psi. \tag{4.23a,b}$$

Substitution into Poisson's equation (4.13) yields the nonlinear Poisson–Boltzmann equation

$$\frac{\partial^2\Psi}{\partial Z^2} = \sinh\Psi; \tag{4.24}$$

in view of (4.19*b*), Ψ must attenuate at large Z. Integration of (4.24) in conjunction with this decay condition readily yields

$$\frac{\partial\Psi}{\partial Z} = -2\sinh\frac{\Psi}{2}. \tag{4.25}$$

In principle, this first-order equation is to be solved subject to Gauss's condition (4.18), $\partial\Psi/\partial Z = -\sigma$. Following usual practice, we replace this Neumann-type condition with the equivalent Dirichlet condition

$$\Psi(Z=0) = \zeta \tag{4.26}$$

wherein the Debye layer voltage ζ (the 'zeta potential') is provided by the relation $\sigma = 2\sinh(\zeta/2)$ (see (4.25)). Thus, we conveniently consider ζ (rather than the surface-charge density) as a prescribed quantity. The solution of (4.25) subject to (4.26) provides the well-known Gouy–Chapman distribution. In our asymptotic scheme we implicitly assume $\sigma = O(1)$, hence so is ζ; this is indeed the case with typical values of colloidal particles. The Dukhin number is therefore $O(\delta)$ small.

Using the radial momentum balance (4.14*a*) in conjunction with (4.19*c*) yields the osmotic pressure $P_{-2} = (1/2)\,(\mathrm{d}\Psi/\mathrm{d}Z)^2$. (Since we assume that σ is uniform then so must be ζ, whereby Ψ, and then also P_{-2}, is a function of Z alone.) Two successive integrations of the tangential momentum balance (4.14*b*) in conjunction with the no-slip condition (4.17*b*) and the definition (4.26) yield

$$V_{-1} = (\zeta - \Psi)\frac{\mathrm{d}\Phi_{-1}}{\mathrm{d}\theta}; \tag{4.27}$$

the continuity equation (4.15) in conjunction with (4.17*a*) then yields

$$U_0 = -\frac{1}{\sin\theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Phi_{-1}}{\mathrm{d}\theta}\right)\int_0^Z(\zeta - \Psi')\,\mathrm{d}Z' \tag{4.28}$$

wherein Ψ' denotes $\Psi(Z')$.

For future reference, we note from (4.25)–(4.26) that Ψ is an odd function of ζ. It follows that, under the transformation $\zeta \to -\zeta$,

$$C_0 \to C_0, \quad Q_0 \to -Q_0, \quad V_{-1} \to -V_{-1}. \tag{4.29a,b,c}$$

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4.4. *Effective boundary conditions*

In view of the outer velocity scaling, and since (4.28) approaches a finite limit as $Z \to \infty$, velocity matching provides the effective electro-osmotic slip condition

$$u_{-1} = 0, \quad v_{-1} = \zeta \frac{\mathrm{d}\Phi_{-1}}{\mathrm{d}\theta} \quad \text{at } r = 1. \tag{4.30a,b}$$

The effective boundary condition governing φ_{-1} is obtained by asymptotic matching with the Ohmic current (3.12*b*). The nil electric current at $O(\delta^{-1})$ (see (4.21)) therefore provides the homogeneous Neumann condition

$$\frac{\partial \varphi_{-1}}{\partial r} = 0 \quad \text{at } r = 1. \tag{4.31}$$

The absence of inner salt flux at that order is consistent with (3.12*a*).

For moderate values of applied fields and zeta potentials, the counterpart of (4.31), governing the $O(1)$ leading bulk potential, is obtained from matching with the inner $O(1)$ transverse current, which turns out to vanish identically (see Yariv 2010). In these problems, the additional vanishing of the $O(1)$ transverse salt flux results in a similar homogeneous condition governing the salt distribution in the bulk, eventually leading to the establishment of a uniform distribution. In the present context, with a δ^{-1} electric-field scaling, condition (4.31) follows automatically from matching with the nil current at $O(\delta^{-1})$, while salt uniformity in the outer region follows from the strong advection (itself driven by the intense electric field).

The solution of (3.8) subject to the far-field condition (3.13*a*) and the effective Neumann condition (4.31) is

$$\varphi_{-1} = -\bar{\beta}\left(r + \frac{1}{2r^2}\right)\cos\theta. \tag{4.32}$$

For future use, we note that (4.6*b*) and (4.28) now read

$$J_{-1}^{\pm\parallel} = \mp\frac{3}{2}\bar{\beta}C_0^{\pm}\sin\theta, \quad U_0 = -3\bar{\beta}\cos\theta\int_0^Z \left(\zeta - \Psi'\right)\mathrm{d}Z', \tag{4.33a,b}$$

while (4.20) becomes

$$\Phi_{-1}(\theta) = -\tfrac{3}{2}\bar{\beta}\cos\theta. \tag{4.34}$$

In 'conventional' ($\beta \sim O(1)$) electrophoretic analyses, knowledge of the leading-order potential is sufficient for calculating the leading-order electrophoretic velocity (Yariv 2010). In the present problem, where the leading-order potential is $O(\delta^{-1})$, such a calculation also requires the $O(1)$ correction φ_0 (see § 7). The derivation of the effective boundary condition governing this field entails the evaluation of the $O(1)$ radial fluxes emanating from the double layer. This is carried out in the next section.

5. Surface conduction at zero Dukhin number

In conventional electrophoretic problems the $O(1)$ ionic fluxes normal to the surface vanish within the Debye layer when the zeta potential is moderate (vanishingly small Dukhin number): see Yariv (2010). In the present context, the combination of intense advection and electro-migration yields non-zero $O(1)$ transverse ionic fluxes within the Debye layer.

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Indeed, recalling that $J_{-1}^{\pm\perp} \equiv 0$ and that $C_0^{\pm}$ are independent of θ, the $O(\delta^{-1})$ balances of the Nernst–Planck equations (4.12) read

$$\frac{\partial J_0^{\pm\perp}}{\partial Z} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(J_{-1}^{\pm\parallel}\sin\theta) + \alpha U_0 \frac{\partial C_0^{\pm}}{\partial Z} = 0. \tag{5.1}$$

Integration in conjunction with (4.16) and (4.33*a*,*b*) yields

$$J_0^{\pm\perp} = 3\bar{\beta}\cos\theta \int_0^Z \mathrm{d}Z' \left\{ \mp C_0^{\pm}(Z') + \alpha \frac{\partial C_0^{\pm}}{\partial Z'} \int_0^{Z'} \mathrm{d}t\,(\zeta - \Psi(t)) \right\}. \tag{5.2}$$

In what follows, we separately calculate the associated salt flux and current density.

5.1. *Transverse salt flux*

Addition of (5.2) provides the $O(1)$ salt flux in the radial direction, see (4.7*a*). Substitution of (4.22) yields

$$J_0^{\perp} = -3\bar{\beta}\cos\theta \int_0^Z \mathrm{d}Z' \left\{ \sinh\Psi' - \alpha\sinh\Psi' \frac{\mathrm{d}\Psi'}{\mathrm{d}Z'} \int_0^{Z'} \mathrm{d}t\,(\zeta - \Psi(t)) \right\}, \tag{5.3}$$

in which $\Psi' = \Psi(Z')$. For asymptotic matching with the bulk we need the behaviour of $J_0^{\perp}$ as $Z \to \infty$,

$$J_0^{\perp} \sim -3\bar{\beta}\,\mathscr{J}(\zeta)\cos\theta \quad \text{as } Z \to \infty, \tag{5.4}$$

in which

$$\mathscr{J}(\zeta) = \int_0^{\infty} \mathrm{d}Z \left\{ \sinh\Psi - \alpha\sinh\Psi \frac{\mathrm{d}\Psi}{\mathrm{d}Z} \int_0^Z \mathrm{d}Z'(\zeta - \Psi') \right\}. \tag{5.5}$$

Using (4.25) to switch to integrations over Ψ and Ψ' yields

$$\mathscr{J}(\zeta) = \int_0^{\zeta} \mathrm{d}\Psi\,\cosh\frac{\Psi}{2} + \alpha\int_0^{\zeta}\mathrm{d}\Psi\sinh\Psi\int_{\Psi}^{\zeta}\mathrm{d}\Psi'\frac{\zeta-\Psi'}{2\sinh\dfrac{\Psi'}{2}}. \tag{5.6}$$

The first integral in (5.6) is $2\sinh(\zeta/2)$. Interchanging the order of integration transforms the second integral to the single integral $\int_0^{\zeta}\mathrm{d}\Psi\,(\zeta-\Psi)\sinh(\Psi/2)$, whose evaluation yields $4\sinh(\zeta/2) - 2\zeta$. We therefore obtain

$$\mathscr{J}(\zeta) = 2\sinh\frac{\zeta}{2} + \alpha\left(4\sinh\frac{\zeta}{2} - 2\zeta\right). \tag{5.7}$$

5.2. *Transverse current density*

Subtraction of (5.2) provides the $O(1)$ current density in the radial direction, see (4.8*a*). Here, substitution of (4.22) yields

$$I_0^{\perp} = 3\bar{\beta}\cos\theta \int_0^Z \mathrm{d}Z' \left\{ \cosh\Psi' - \alpha\cosh\Psi' \frac{\mathrm{d}\Psi'}{\mathrm{d}Z'} \int_0^{Z'} \mathrm{d}t\,(\zeta - \Psi(t)) \right\}. \tag{5.8}$$

Care must be taken when deriving the large-Z behaviour of $I_0^{\perp}$ since, unlike (5.3), the integrand does not decay here at large Z. Decomposing $\cosh\Psi'$ as $1 + (\cosh\Psi' - 1)$ allows us to write

$$I_0^{\perp} \sim 3\bar{\beta}\cos\theta\,\{Z + \mathscr{I} + o(1)\} \quad \text{as } Z \to \infty \tag{5.9}$$

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wherein

$$\mathscr{I}(\zeta) = \int_0^\infty \mathrm{d}Z \left\{ \cosh\Psi - 1 - \alpha \cosh\Psi \frac{\mathrm{d}\Psi}{\mathrm{d}Z} \int_0^Z \mathrm{d}\Psi'(\zeta - \Psi') \right\}. \tag{5.10}$$

Using (4.25) to switch to integrations over Ψ and Ψ' yields

$$\mathscr{I}(\zeta) = \int_0^\zeta \mathrm{d}\Psi \ \sinh\frac{\Psi}{2} + \alpha \int_0^\zeta \mathrm{d}\Psi \cosh\Psi \int_\Psi^\zeta \mathrm{d}\Psi' \frac{\zeta - \Psi'}{2\sinh\dfrac{\Psi'}{2}}. \tag{5.11}$$

The first integral in (5.11) is $4\sinh^2(\zeta/4)$. Interchanging the order of integration transforms the second integral in (5.11) to the single integral $\int_0^\zeta \mathrm{d}\Psi\ (\zeta - \Psi)\cosh(\Psi/2)$, whose evaluation yields $8\sinh^2(\zeta/4)$. We therefore obtain

$$\mathscr{I}(\zeta) = 4(1 + 2\alpha)\sinh^2\frac{\zeta}{4}. \tag{5.12}$$

5.3. *Asymptotic matching*

The effective boundary condition governing the bulk-potential correction φ_0 is obtained from asymptotic matching between (5.9) and the radial current in the bulk. The latter is obtained from a Taylor expansion of (3.12*b*) about the macroscale boundary $r = 1$,

$$-\delta^{-1}\left\{\frac{\partial\varphi_{-1}}{\partial r} + (r-1)\frac{\partial^2\varphi_{-1}}{\partial r^2} + \cdots\right\} - \left\{\frac{\partial\varphi_0}{\partial r} + \cdots\right\} - \cdots, \tag{5.13}$$

where the derivatives are evaluated at $r = 1$. Use of the 2–1 van Dyke matching rule (Van Dyke 1964) in conjunction with (4.31) and (4.32) yields the effective inhomogeneous Neumann condition

$$\frac{\partial\varphi_0}{\partial r} = -3\bar{\beta}\mathscr{I}(\zeta)\cos\theta \quad \text{at } r = 1. \tag{5.14}$$

The potential φ_0, governed by this condition together with Laplace's equation (see (3.10)) and the decay condition (3.13*b*), is provided by the dipole

$$\varphi_0 = 3\bar{\beta}\mathscr{I}(\zeta)\frac{\cos\theta}{2r^2}. \tag{5.15}$$

Naïvely, we could have stopped here and proceed to the calculation of the bulk flow. However, just as the current density must match between the Debye layer and the bulk, so does the salt flux. When attempting to perform similar asymptotic matching between the respective salt fluxes, we encounter an impasse: the $O(1)$ salt flux (5.4) is clearly incompatible with the nil flux (3.12*a*) in the electro-neutral bulk.

6. Diffusive boundary layer

Resolution of the above paradox hinges upon the observation that the limit $\delta \to 0$ is associated here with a *twofold* singularity, both related to the multiplication of the small parameter by the highest derivative. The first occurs in Poisson's equation (2.5), resulting in the familiar $O(\delta)$-wide Debye layer. The second is due to the effective $O(\delta^{-1})$ Péclet-number scaling, resulting in the establishment of a *diffusive* boundary layer. Since this layer originates at distances where the tangential velocity has already achieved $O(\delta^{-1})$ values, the present situation resembles large-Reynolds-number flows. This analogy implies that the layer thickness scales inversely with the

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square root of the Péclet number, namely as $\delta^{1/2}$. This suggests the definition of the stretched radial variable (cf. (4.1))

$$\tilde{Z} = \frac{r-1}{\delta^{1/2}}. \tag{6.1}$$

The need to match an $O(1)$ salt flux from the Debye layer together with a unity concentration (see (3.7) and (3.9)) and $O(\delta^{-1})$ electric field in the outer region motivates the expansions

$$c = 1 + \delta^{1/2}\tilde{C}_{1/2}(\tilde{Z},\theta) + \cdots, \quad \varphi = \delta^{-1}\tilde{\Phi}_{-1}(\theta) + \tilde{\Phi}_0(\tilde{Z},\theta) + \cdots. \tag{6.2a,b}$$

The requirements of velocity and pressure matching, in conjunction with the continuity equation, also suggest

$$\left.\begin{aligned} v &= \delta^{-1}\tilde{V}_{-1}(\theta) + \cdots, \quad u = \delta^{-1/2}\tilde{U}_{-1/2}(\tilde{Z},\theta) + \cdots, \\ p &= \delta^{-1}\tilde{P}_{-1}(\theta) + \cdots. \end{aligned}\right\} \tag{6.3a,b,c}$$

The preceding expansions are consistent with $q = o(\delta)$. Matching with the outer region implies that $\tilde{V}_{-1}(\theta) = v_{-1}$, namely

$$\tilde{V}_{-1}(\theta) = \tfrac{3}{2}\bar{\beta}\zeta\sin\theta; \tag{6.4}$$

the continuity equation and the requirement of matching with the Debye-scale velocity (4.28) then provides the radial velocity

$$\tilde{U}_{-1/2} = -3\tilde{Z}\bar{\beta}\zeta\cos\theta. \tag{6.5}$$

The salt balance (2.20) yields at leading $O(\delta^{-1/2})$

$$\frac{\partial^2\tilde{C}_{1/2}}{\partial\tilde{Z}^2} = \alpha\left(\tilde{U}_{-1/2}\frac{\partial\tilde{C}_{1/2}}{\partial\tilde{Z}} + \tilde{V}_{-1}\frac{\partial\tilde{C}_{1/2}}{\partial\theta}\right). \tag{6.6}$$

In addition, $\tilde{C}_{1/2}$ also satisfies an inhomogeneous Neumann condition at $\tilde{Z} = 0$, representing salt-flux matching with the Debye-layer flux (5.4)

$$\frac{\partial\tilde{C}_{1/2}}{\partial\tilde{Z}} = 3\bar{\beta}\,\mathscr{J}(\zeta)\cos\theta, \tag{6.7}$$

as well as asymptotic matching with the electro-neutral bulk

$$\tilde{C}_{1/2} \to 0 \quad \text{as } \tilde{Z} \to \infty. \tag{6.8}$$

For $\zeta > 0$, the solution of the parabolic boundary-value problem (6.6)–(6.8) is (see Appendix)

$$\tilde{C}_{1/2} = -\left(\frac{6\bar{\beta}}{\pi\alpha\zeta}\right)^{1/2}\mathscr{J}(\zeta)\int_0^\theta \frac{\sin t\cos t}{\{\lambda(t)-\lambda(\theta)\}^{1/2}}\exp\left\{-\frac{3\alpha\bar{\beta}\zeta}{8}\frac{\tilde{Z}^2\sin^4\theta}{\lambda(t)-\lambda(\theta)}\right\}\mathrm{d}t \tag{6.9}$$

wherein λ is defined in (A 9). The solution for $\zeta < 0$ is readily obtained by noting that the problem (6.6)–(6.8) is invariant under the transformation

$$\zeta \to -\zeta, \quad \theta \to \pi - \theta. \tag{6.10}$$

The preceding boundary-value problem resembles large-Péclet-number forced convection at large Reynolds numbers and small Prandtl numbers (Leal 2007): because

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of the irrotational flow in both situations, the differential equation is the same. In these classical problems, however, the transported quantity (say temperature) is typically governed by an inhomogeneous Dirichlet condition, as opposed to the present Neumann condition (6.7).

In the present problem, the diffusive boundary layer resides in the overlap region of the Debye layer and electro-neutral bulk. This intermediate layer, which resolves the salt-flux matching paradox, does not affect the calculation of $\mathscr{U}_{-1}$. The detailed structure (6.9) is however required if one were to calculate the next term in the asymptotic expansion (3.4).

7. Electrophoretic velocity

The bulk flow is governed by the homogeneous Stokes equations (3.11), the far-field condition (3.13*a*,*b*) and the effective electro-osmotic slip condition (4.30). It is made uniquely determinate by the force-free condition (2.14), where the integration surface is taken now to be positioned within the bulk domain. This condition begins at $O(\delta^{-2})$, but is affected by the flow only at $O(\delta^{-1})$. To determine the flow, we must satisfy it at these two successive asymptotic orders. This is the reason why φ_0 had to be calculated.

At $O(\delta^{-2})$, condition (2.14) is affected by the quadratic interaction of the leading-order electric field, driven from φ_{-1}, with itself. By extending the integration surface to infinity, it is readily verified (Rivette & Baygents 1996; Yariv 2006) that the fast r^{-3} decay rate to a uniform ambient value (see (4.32)) does not result in any force.

At $O(\delta^{-1})$, the Maxwell stresses in (2.14) represent quadratic interaction of the leading-order potential φ_{-1} with the leading-order correction φ_0. Since the latter is a dipole (see (5.15)), it is easily verified using an identical argument that its interaction with either term in φ_{-1} does not result in a non-zero force.

It then follows from the $O(\delta^{-1})$ balance of (2.14) that the leading-order hydrodynamic force must vanish. This places us at the classical setup considered by Morrison (1970) in the context of moderate-field electrophoresis. We accordingly postulate the potential flow

$$\boldsymbol{u}_{-1} = \zeta \boldsymbol{\nabla} \varphi_{-1} \tag{7.1}$$

representing a combination of a uniform streaming and a doublet. Being an irrotational flow associated with an harmonic potential, it evidently satisfies the homogeneous Stokes equations (3.11), with $p_{-1} \equiv 0$. The slip condition (4.30) is likewise automatically satisfied. Owing the absence of a Stokeslet term in (7.1), the Newtonian stresses associated with (7.1) do not contribute a force, as required. Finally, since the streamlines of any potential flow in a simply connected region are always open, the underlying *a priori* assumption allowing the derivation of (3.7) is confirmed.

Use of the far-field condition (3.13*a*,*b*) finally furnishes the leading-order particle velocity

$$\mathscr{U}_{-1} = \bar{\beta}\zeta, \tag{7.2}$$

namely (1.1) in dimensionless notation.

8. Discussion

Having established the validity of Smoluchowski's formula for $O(\delta^{-1})$-large β values, it is expedient to illuminate the physical aspects of the problem. It is hardly surprising that the intense electric field associated with the large-β limit

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is accompanied by a comparably strong flow field. The inherent advection then necessitates that the salt concentration is constant along a streamline, effectively enforcing a uniform bulk concentration.

The $O(\delta^{-1})$ electric and flow fields are continued into comparable fields of the same order in the longitudinal (θ) direction within the Debye layer. These result in $O(\delta^{-1})$ advective and electro-migratory fluxes of both salt and charge in that direction. The longitudinal non-uniformity in these fluxes, in conjunction with the $O(\delta)$ cross-sectional Debye thickness, gives rise to $O(1)$ transverse fluxes in the radial directions.

The dependence of these transverse fluxes upon ζ and θ (see (5.7)) can be explained by illuminating the transport mechanism. Consider first the case of negative zeta potential, where the diffuse charge is positive. At $O(\delta^{-1})$, the longitudinal salt flux within the Debye layer is provided by the electro-migratory expression $J^{\parallel}_{-1} = -Q_0\,\mathrm{d}\Phi_{-1}/\mathrm{d}\theta$ (see (4.6*b*) and (4.7*b*)). With $Q_0 > 0$, this molecular flux is in the electric-field direction. In view of (4.27), the same holds for the $O(\delta^{-1})$ advective salt flux C_0V_{-1}. The electric-field variation with θ (see (4.34)) therefore implies a nonzero surface divergence of the total longitudinal salt flux, whereby salt conservation necessitates outward transverse fluxes for $0 < \theta < \pi/2$ and inward fluxes for $\pi/2 < \theta < \pi$, in agreement with (5.7). For $\zeta > 0$, with $Q_0 < 0$, the electro-migratory flux flips direction, see (4.29*b*); in view of (4.29*a*,*c*), so does the advective flux C_0V_{-1}. This explains why the transverse salt flux (5.7) is an odd monotonic function of ζ.

Consider now the $O(\delta^{-1})$ longitudinal electric current. For negative ζ, similar arguments show that both its electro-migratory component $I^{\parallel}_{-1} = -C_0\,\mathrm{d}\Phi_{-1}/\mathrm{d}\theta$ (see (4.6*b*) and (4.8*b*)) and advective component Q_0V_{-1} are in the same direction as the respective components in the salt fluxes; the resulting transverse current therefore retains the same polarity. Here, however, the transformation $\zeta \to -\zeta$ has no effect on neither fluxes (see (4.29)), implying that the transverse current is invariant to the sign of ζ. This is in agreement with (5.12).

The salt flux emerging from the Debye layer cannot penetrate the advection-dominated electro-neutral bulk, where the salt concentration is uniform. This results in the establishment of an $O(\delta^{1/2})$-wide diffusive boundary layer to which this flux is directed. The electric current, on the other hand, flows directly into the bulk, where it results in a non-uniform distribution of the $O(1)$ electric potential. In figure 2 we schematically portray the above-mentioned mechanisms.

To illuminate the effect of the Debye-layer flux polarity upon the diffusive-layer salt perturbation $\tilde{C}_{1/2}$, consider its distribution at $\tilde{Z} = 0$. From (6.9) we find, after scaling by $(6\bar{\beta}/\pi\alpha\zeta)^{1/2}\,\mathscr{J}(\zeta)$,

$$-\int_0^{\theta} \frac{\sin t \cos t}{\{\lambda(t) - \lambda(\theta)\}^{1/2}}\,\mathrm{d}t. \tag{8.1}$$

For $\theta \to 0$, it is readily verified that the integral approaches a finite value, $\pi/2$, while for $\theta \to \pi$ it diverges, representing the familiar breakdown of diffusive boundary layers near the 'rear stagnation point' (Leal 2007). In figure 3 we plot the 'interfacial concentration' (8.1) as a function of θ. The negative values at the particle 'front' and positive values at its 'rear', respectively associated with inward and outward diffusive fluxes, are consistent with the Debye-layer flux-generation mechanism (for $\zeta > 0$) explained above. The distribution of (8.1) does not possess the simple left–right polarity of the Debye-layer transport because of the offsetting role of advection, transporting salt-depleted fluid from the front to the back.

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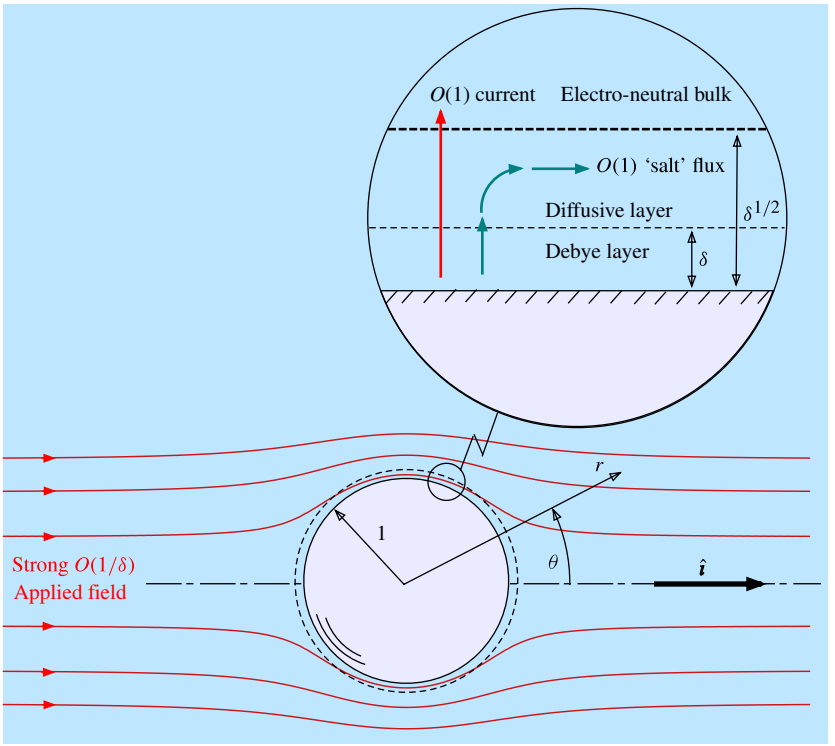


FIGURE 2. (Colour online) Fluxes emerging from the Debye layer for $\zeta < 0$. In the particle-fixed reference system, the bulk streamlines coincide with the (schematically indicated) field lines. For $0 < \theta < \pi/2$ the surface divergence of the longitudinal salt and charge fluxes within the layer is negative, necessitating $O(1)$ comparable transverse fluxes in the outward direction. The electric current flows into the electro-neutral bulk, while the salt flux is redirected into the diffusive layer.

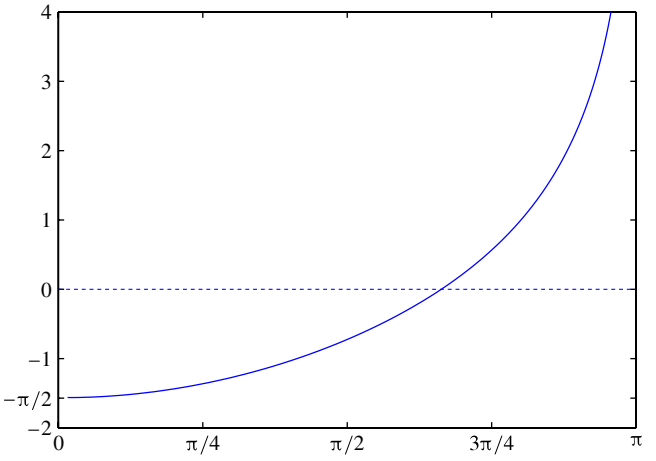


FIGURE 3. (Colour online) Variation with θ of $\tilde{C}_{1/2}(\tilde{Z}=0)$, scaled by $(6\bar{\beta}/\pi\alpha\zeta)^{1/2}\mathscr{J}(\zeta)$.

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A comparable diffusive boundary layer also appears in streaming-potential problems at moderate Hartmann numbers (Yariv, Schnitzer & Frankel 2011). In that case, where the Péclet number is inherently large, the transverse fluxes are exclusively associated with ionic advection along the Debye layer. As in the present problem, the salt flux emerging from the Debye layer cannot penetrate the advection-dominated electro-neutral bulk, resulting again in a diffusive boundary layer. The $O(\delta^{-2})$-scaling of the Péclet number in these problems, in conjunction with the associated linear velocity variation within the Debye layer, results in an $O(\delta^{2/3})$ scaling for thickness of that layer; this is in contrast with the $O(\delta^{1/2})$ thickness in the present problem, associated with an $O(\delta^{-1})$ Péclet-number scaling and a Debye-layer velocity profile which approaches its ambient limit exponentially fast. As in the present scenario, the diffusive-layer structure in the streaming-potential problems does not affect the leading-order bulk transport. Of course, an important difference between the two classes of problems has to do with the transverse electric current, which in streaming-potential problems affects (actually animates) the leading-order bulk electric field.

The emergence of transverse $O(1)$ ionic fluxes within the Debye layer in the present problem happens already at moderate zeta potentials. The underlying machinery is accordingly quite different from the classical 'surface conduction' mechanism associated with moderately large zeta potentials (Dukhin & Shilov 1969). In the latter, the Boltzmann distributions in the quasi-equilibrium Debye layer result in asymptotically large concentration of counter ions near the solid surface. The non-uniform $O(\delta^{-2})$ counter-ionic fluxes passing through an $O(\delta^2)$-wide portion of the Debye thickness (Hinch *et al.* 1984) give rise to $O(1)$ transverse fluxes. This mechanism already occurs at $\beta = O(1)$ (and was actually only analysed for $\beta \ll 1$). For such moderate fields, the transverse fluxes modify the leading-order transport within the electro-neutral bulk. This is in sharp contrast with the present problem, where surface conduction is animated by the intense magnitude of the electric field (and concomitant fluid flow) in the bulk, and does not involve any asymptotic asymmetry between the co- and counter-ions. It is exactly this intense magnitude that prevents the leading-order bulk electric field and salt concentration from being affected by the transverse ionic fluxes emanating from the double layer.

The present analysis therefore establishes a new mode of surface conduction, associated with moderate zeta potentials. In contrast to classical surface conduction at high zeta potentials, where Smoluchowski's formula breaks down already at $\beta \ll 1$, the present mechanism leaves it unaffected even for $\beta \sim O(\delta^{-1})$, practically at the upper limit of field values in current applications.

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Appendix. Calculation of the diffusive-layer concentration profile

For $\zeta > 0$, we define the reduced concentration perturbation

$$R(\psi, \theta) = \frac{1}{\mathscr{J}(\zeta)} \left(\frac{\alpha \zeta}{3\bar{\beta}} \right)^{1/2} \tilde{C}_{1/2}(\tilde{Z}, \theta) \tag{A 1}$$

wherein the stream function

$$\psi = \frac{(3\alpha\bar{\beta}\zeta)^{1/2}}{2} \tilde{Z} \sin^2\theta \tag{A 2}$$

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is used as a new coordinate. The change of variables $(\tilde{Z}, \theta) \to (\psi, \theta)$ transforms (6.6)–(6.8) into the universal problem

$$\frac{\partial R}{\partial \theta} = \frac{\sin^3\theta}{2}\frac{\partial^2 R}{\partial \psi^2} \quad \text{for } 0 < \psi < \infty, \tag{A 3}$$

$$\frac{\partial R}{\partial \psi} = 2\frac{\cos\theta}{\sin^2\theta} \quad \text{at } \psi = 0, \tag{A 4}$$

$$R \to 0 \quad \text{as } \psi \to \infty. \tag{A 5}$$

We employ the cosine Fourier transform

$$\hat{R}(k, \theta) = \left(\frac{2}{\pi}\right)^{1/2} \int_0^\infty R(\psi, \theta) \cos k\psi \, \mathrm{d}\psi, \tag{A 6}$$

whereby (A 3)–(A 5) yield

$$\frac{\partial \hat{R}}{\partial \theta} + \frac{k^2}{2}\hat{R}\sin^3\theta = -\left(\frac{2}{\pi}\right)^{1/2} \sin\theta\cos\theta. \tag{A 7}$$

The solution of (A 7) is

$$\hat{R} = A(k)\mathrm{e}^{(1/2)k^2\lambda(\theta)} - \left(\frac{2}{\pi}\right)^{1/2} \int_0^\theta \mathrm{e}^{-(1/2)k^2(\lambda(t)-\lambda(\theta))} \sin t \cos t \, \mathrm{d}t \tag{A 8}$$

with $A(k)$ an arbitrary function and

$$\lambda(\theta) = \cos\theta - \tfrac{1}{3}\cos^3\theta. \tag{A 9}$$

Consider the behaviour of (A 8) for large k. Since $\lambda(t) - \lambda(\theta) > 0$ for $0 < t < \theta$, the integrand of the second term in (A 8) decay exponentially fast as $k \to \infty$; using Laplace's method (Bender & Orszag 1978) it is readily verified that this term decays as $1/k$. Since $\lambda(\theta) > 0$ for $0 < \theta < \pi/2$, $A(k)$ must vanish to ensure the existence of the inverse transform for all $0 < \theta < \pi$. Performing the inverse transform yields

$$R = -\left(\frac{2}{\pi}\right)^{1/2} \int_0^\theta \frac{\sin t \cos t}{\{\lambda(t) - \lambda(\theta)\}^{1/2}} \exp\left\{-\frac{\psi^2}{2\,(\lambda(t) - \lambda(\theta))}\right\} \mathrm{d}t. \tag{A 10}$$

Reverting to the diffusive-layer variables finally furnishes (6.9).

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