

Electrokinetic flows about conducting drops

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We consider electrokinetic flows about a freely suspended liquid drop, deriving a macroscale description in the thin-double-layer limit where the ratio δ between Debye width and drop size is asymptotically small. In this description, the electrokinetic transport occurring within the diffuse part of the double layer (the ‘Debye layer’) is represented by effective boundary conditions governing the pertinent fields in the electro-neutral bulk, wherein the generally non-uniform distribution of ζ , the dimensionless zeta potential, is *a priori* unknown. We focus upon highly conducting drops. Since the tangential electric field vanishes at the drop surface, the viscous stress associated with Debye-scale shear, driven by Coulomb body forces, cannot be balanced locally by Maxwell stresses. The requirement of microscale stress continuity therefore brings about a unique velocity scaling, where the standard electrokinetic scale is amplified by a δ^{-1} factor. This reflects a transition from slip-driven electro-osmotic flows to shear-induced motion. The macroscale boundary conditions display distinct features reflecting this unique scaling. The effective shear-continuity condition introduces a Lippmann-type stress jump, appearing as a product of the local charge density and electric field. This term, representing the excess Debye-layer shear, follows here from a systematic coarse-graining procedure starting from the exact microscale description, rather than from thermodynamic considerations. The Neumann condition governing the bulk electric field is inhomogeneous, representing asymptotic matching with transverse ionic fluxes emanating from the Debye layer; these fluxes, in turn, are associated with non-uniform tangential ‘surface’ currents within this layer. Their appearance at leading order is a manifestation of dominant advection associated with the large velocity scale. For weak fields, the linearized macroscale equations admit an analytic solution, yielding a closed-form expression for the electrophoretic velocity. When scaled by Smoluchowski’s speed, it reads

$$\delta^{-1} \frac{\sinh(\bar{\zeta}/2)/\bar{\zeta}}{1 + \frac{3}{2}\mu + 2\alpha \sinh^2(\bar{\zeta}/2)},$$

wherein $\bar{\zeta}$, the ‘drop zeta potential’, is the uniform value of ζ in the absence of an applied field, μ the ratio of drop to electrolyte viscosities, and α the ionic drag coefficient. The difference from solid-particle electrophoresis is manifested in two key features: the δ^{-1} scaling, and the effect of ionic advection, as represented by the appearance of α . Remarkably, our result differs from the small- δ limit of the mobility expression predicted by the weak-field model of Ohshima, Healy & White (*J. Chem. Soc. Faraday Trans. 2*, vol. 80, 1984, pp. 1643–1667). This discrepancy is related to the dominance of advection on the bulk scale, even for weak fields, which feature

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cannot be captured by a linear theory. The order of the respective limits of thin double layers and weak applied fields is not interchangeable.

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1. Introduction

When a solid particle (radius a^* , zeta potential ζ^*) suspended in unbounded electrolyte (permittivity ϵ^* , viscosity μ^*) is exposed to an otherwise uniform electric field of magnitude E^* , it migrates in the field direction. In the thin-double-layer limit, Smoluchowski (1903) explained this phenomenon assuming that an electro-osmotic slip mechanism applies locally at each point of the particle boundary, thus obtaining his celebrated formula

$$v_s^* = \frac{\epsilon^* \zeta^*}{\mu^*} E^* \quad (1.1)$$

for the electrophoretic velocity. What would be the corresponding formula for a liquid drop?

1.1. Approximation methodology

As in other fundamental problems in electrokinetic transport (e.g. solid-particle electrophoresis, streaming potential), existing analyses of drop electrophoresis have employed two types of linearization procedure. The earlier studies assume small zeta potentials (Booth 1951); following the methodology of O'Brien & White (1978), subsequent studies made use of weak-field linearization, describing small deviations from spherically-symmetric equilibrium. This scheme was applied to metal drops by Ohshima, Healy & White (1984) and to electrolyte drops by Baygents & Saville (1991*a,b*).

The inherent simplification in a weak-field scheme notwithstanding, the linear analyses remain technically challenging. Making use of symmetry arguments, the ingenious methods of O'Brien & White (1978) allow the governing partial differential equations to be reduced into ordinary differential equations. The latter however can only be solved numerically; thus, the key output of a weak-field approximation is a set of numerically calculated mobility curves, rather than a closed-form approximation.

More importantly, the weak-field linearization implicitly entails the assumption that electric-potential variations on the particle scale are small compared with the thermal voltage. This point, not always appreciated, warrants some clarification. In their § 3, O'Brien & White (1978) write: 'The difficulties involved in solving this set of coupled nonlinear partial differential equations are formidable, but fortunately we are only concerned with the solution of these equations in the case when the applied field E is small compared with the fields that occur in the double layer'. As their analysis is performed for Debye thickness comparable with particle size, this statement is equivalent to the above assumption.

When the Debye layer is thin, as in the follow-up analysis of O'Brien & Hunter (1981), the two criteria are no longer equivalent; careful inspection reveals that the underlying linearization is in fact predicated upon the more strict assumption expressed in terms of particle size. Even for solid-particle electrophoresis, where the size of typical colloidal particles ranges in the micron scale, this assumption is rather

strained (see Schnitzer & Yariv 2012*d,a*). When considering drops and bubbles of typical millimetric dimensions, the weak-field approximation is of quite limited value (Baygents & Saville 1989).

An approximation which does suit realistic scenarios is that of thin double layers, where the Debye width $1/\kappa^*$ is assumed small compared with drop size a^* . This assumption, so useful in the analysis of solid colloids (Anderson 1989; Yariv 2010*a*; Schnitzer & Yariv 2012*c*), is even more suitable for analysing the typically larger (by orders of magnitudes) drop and bubbles. We here propose to analyse drop electrophoresis using the thin-double-layer limit $\delta \ll 1$, with $\delta = 1/\kappa^* a^*$. This singular limit is to be handled using boundary-layer asymptotic analysis. Such an analysis would provide a useful macroscale model wherein the Debye-layer physics is embodied in effective boundary conditions, whereby the inherent scale disparity is removed. As in other electrokinetic macroscale models following the same methodology (Yariv 2010*a,b*; Yariv, Schnitzer & Frankel 2011; Schnitzer & Yariv 2012*c*), it is not restricted by the assumption of small zeta potentials or weak fields.

1.2. Conducting drops

We focus here on ‘conducting’ drops, considering situations where drop conductivity is much higher than that of the suspending electrolyte. This is clearly the case for liquid-metal (e.g. mercury) drops. It may also constitute a good approximation for various systems involving highly concentrated electrolyte drops (Pascall & Squires 2011).

The pioneering analysis of liquid-metal drops was carried out by Frumkin (1946), as described in Levich (1962). More intuitive than rigorous, this analysis resembles the classical derivation of Smoluchowski (1903); moreover, it is *a priori* limited to weak applied fields. Applying thermodynamic arguments, Levich (1962) represents the mechanical aspect of the double layer in terms of an apparent surface tension, determined by the local value of the zeta potential through a Lippmann–Helmholtz constitutive equation.

The most significant finding of Levich (1962) concerns the velocity scaling. For solid-particle electrophoresis the characteristic velocity is provided by Smoluchowski’s scale, see (1.1); this would also be the proper scaling for an electrolyte drop. When the drop is highly conducting, however, the characteristic scale is that of (1.1) multiplied by δ^{-1} . This remarkable feature is absent from the analysis of Booth (1951), who obtained an electrophoretic velocity comparable with (1.1) for all conductivity ratios. As explained by Levine & O’Brien (1973) (see also Pascall & Squires 2011), this discrepancy can be traced back to the *ad hoc* superposition procedure in Booth (1951). The unique Frumkin–Levich velocity scaling has been experimentally confirmed (Levich 1962).

The first systematic analysis of conducting drops was carried out by Ohshima *et al.* (1984) using a weak-field linearization procedure in the spirit of O’Brien & White (1978). This analysis, resulting in a numerical scheme for the calculation of the electrophoretic mobility, is valid for arbitrary values of Debye thickness and zeta potential. For thin double layers, Ohshima *et al.* (1984) were able to reduce their mobility calculation into a closed-form expression, which reproduced the enhanced velocity scaling of Levich (1962) but did not entirely agree with his results.

Our goal is to derive a thin-double-layer macroscale model which is restricted to neither weak fields nor small zeta potentials. A further objective is to resolve the lack of agreement between the corresponding mobility results of both of the above classic analyses in their apparent overlapping domain of validity. Our starting

point on the microscale level is the standard nonlinear electrokinetic description, sharing the physical assumptions underlying the (linear) model of Ohshima *et al.* (1984). Thus, we assume a drop of infinite electric conductivity; the drop charge is accordingly distributed over its surface, with the internal electric field identically vanishing. Following Ohshima *et al.* (1984), the drop is further assumed to be ideally polarizable, whereby ionic sorption is absent. The total drop charge is accordingly set through the initial configuration, prior to the application of an applied field. It is therefore considered as a prescribed non-varying quantity.

1.3. Macroscale description

The desired macroscale model is obtained via a boundary-layer analysis. It results in an approximate description of the electro-neutral bulk outside the Debye layer, together with effective boundary conditions which represent the transport processes taking place in that layer. This method has been extensively exploited for systematically deriving approximate descriptions of electrokinetic flows about solid surfaces (Yariv 2010*a,b*; Yariv *et al.* 2011; Schnitzer, Frankel & Yariv 2012; Schnitzer & Yariv 2012*d,c*). In the present context of conducting drops, it exhibits three unique features.

The first is an effective tangential-stress condition, incorporating a stress-jump term representing the excess shear associated with the unique velocity profile within the narrow Debye layer. For weak fields, this jump degenerates to the Lippmann-type term presented in Levich (1962). The tangential-stress condition emphasizes the shear mechanism which here drives the leading-order electrokinetic flow, whose magnitude is asymptotically larger than that of ‘standard’ slip-driven flow generated about solid surfaces.

This amplified velocity scaling leads to the second feature: the inhomogeneous Neumann condition governing the bulk electric field. Conventional electrokinetic flows at moderate zeta potentials are typically governed by a homogeneous Neumann condition (Keh & Anderson 1985; Anderson 1989; Yariv 2010*a*), representing the absence of charge conduction into the Debye layer. In the present class of problems, strong advection gives rise to significant non-uniform ‘surface currents’, necessitating comparable Debye-layer charging from the Ohmic bulk.

The third feature is also a byproduct of the inherently-strong advection. Just as it induces the above-mentioned Debye-scale transverse charge current, it also generates comparable salt fluxes, which in turn necessitate salt supply from the bulk. This however is incompatible with the uniform salt distribution enforced in that domain – by the very same intense advection. This incompatibility results in a diffusive boundary layer of thickness $O(\delta^{1/2})$, thicker than the Debye layer. In this intermediate layer, salt relaxation through both advection and diffusion ensures salt-flux continuity on the macroscale. Intermediate diffusive layers under dominant advection occur in a variety of other electrokinetic problems (Baygents & Saville 1989; Yariv *et al.* 2011; Schnitzer & Yariv 2012*d*).

A subtle issue in the present model concerns the notion of the zeta potential. This concept emerges naturally in any systematic thin-double-layer analysis (Yariv 2010*a,b*; Schnitzer & Yariv 2012*c*) as the leading-order Debye-layer voltage, which is essentially linked to the surface-charge density. When considering dielectric solid surfaces, a plausible assumption is that the latter is a specified – say uniformly distributed – quantity, whereby the associated zeta-potential distribution is a derived one. When considering liquid drops, on the other hand, the surface charge is mobile; its density is generally non-uniform, and may not be considered as a prescribed

quantity. This is evident in the limit of a conducting drop, where the equipotential condition on the very drop boundary readily results in a non-uniform zeta-potential distribution once an electric field is applied.

The paper is organized as follows. In the next section we formulate the ‘exact’ microscale model for a conducting drop. In § 3 we discuss the unique velocity scaling associated with the thin-double-layer limit and derive the appropriate description of the electrokinetic transport in the bulk. The companion Debye-scale analysis is provided in § 4, where we derive the effective boundary conditions governing the bulk fields. In this section we also identify the emergence of a diffusive boundary layer of an intermediate asymptotic thickness. The resulting macroscale model is recapitulated in § 5. To facilitate comparison with existing weak-field approximations, we analyse in § 6 the linearized version of our model, obtaining the drop electrophoretic mobility. The mismatch with Ohshima *et al.* (1984) is discussed in § 6.1, while the relation to Levich (1962) is explained in § 6.2. Our findings are summarized in § 7. The problem governing the diffusive boundary layer is outlined in the [Appendix](#).

Readers who are primarily interested in the macroscale model rather than the detailed asymptotic derivation may want to skip from § 3.1 directly to the macroscale formulation of § 5.

2. Exact formulation

We consider an ideally-polarizable charged metal drop suspended in an unbounded liquid electrolyte of permittivity ϵ^* and viscosity μ^* . (Dimensional quantities are hereafter shown with an asterisk.) The electrolyte is symmetric, with valencies $\pm Z$ and equilibrium concentrations c^* ; for simplicity, we assume an identical ionic diffusivity D^* for both ionic species. This system is exposed to a uniform applied electric field E^* in a direction denoted by the unit vector \hat{i} . Our interest is in the calculation of the resulting steady-state electrokinetic transport, and, specifically, the electrophoretic velocity \mathcal{U}^* of the drop relative to the otherwise quiescent electrolyte – the experimentally observable quantity.

We assume that surface tension is sufficiently strong to retain a spherical drop shape (see § 4.6). The drop radius a^* is used to normalize length variables. It is convenient to employ spherical coordinates (r, θ, ϖ) attached to the moving drop, $r = 0$ corresponding to the drop centre and the polar axis $\theta = 0$ pointing in the applied-field direction. Following Saville (1977), we normalize ionic concentrations by c^* and electric potentials by the thermal scale $\varphi^* = k^*T^*/Ze^*$, wherein k^*T^* is the Boltzmann temperature and e^* the elementary charge. Stress variables are accordingly normalized by the Maxwell scale $M^* = \epsilon^*\varphi^{*2}/a^{*2}$. Balancing this term with characteristic viscous stress then provides the electrokinetic velocity scale

$$v^* = \frac{\epsilon^*\varphi^{*2}}{\mu^*a^*}, \quad (2.1)$$

used here to normalize all velocity fields.

In describing ionic transport within the electrolyte we employ the Nernst–Planck expressions for the molecular fluxes, comprising both diffusion and electro-migration. Normalized by D^*c^*/a^* , these fluxes therefore take the form

$$\mathbf{j}^\pm = -\nabla c^\pm \mp c^\pm \nabla \varphi, \quad (2.2)$$

wherein c^\pm are the ionic concentrations and φ the electric potential. The steady-state Poisson–Nernst–Planck description of the electrokinetic transport within the electrolyte

then consists of the following.

(a) The ionic conservation equations,

$$\nabla \cdot \mathbf{j}^\pm + \alpha \mathbf{u} \cdot \nabla c^\pm = 0, \quad (2.3)$$

in which \mathbf{u} is the electrolyte velocity field. The dimensionless drag coefficient

$$\alpha = \frac{\varepsilon^* \varphi^{*2}}{\mu^* D^*} \quad (2.4)$$

is independent of drop size a^* and salt concentration c^* ; for typical diffusivities in aqueous solutions ($D^* \sim 10^{-9} \text{ m}^2 \text{ s}^{-1}$) $\alpha \approx 0.5$ (Saville 1977). Superficially, this coefficient appears to play the role of a primitive Péclet number.

(b) Poisson's equation,

$$-2\delta^2 \nabla^2 \varphi = c^+ - c^-, \quad (2.5)$$

wherein $\delta = 1/\kappa^* a^*$ is the dimensionless Debye thickness, in which the Debye width $1/\kappa^*$ is defined by

$$\kappa^{*2} = \frac{2Z^2 e^{*2} c^*}{\varepsilon^* k^* T^*}. \quad (2.6)$$

An alternative formulation to (2.2)–(2.3) is obtained using the mean ('salt') concentration (normalized by c^*) and the volumetric charge density (normalized by $2Ze^*c^*$)

$$c = \frac{1}{2}(c^+ + c^-), \quad q = \frac{1}{2}(c^+ - c^-), \quad (2.7)$$

together with the salt flux $\mathbf{j} = (\mathbf{j}^+ + \mathbf{j}^-)/2$ and current density $\mathbf{i} = (\mathbf{j}^+ - \mathbf{j}^-)/2$. The constitutive relations (2.2) then read

$$\mathbf{j} = -\nabla c - q \nabla \varphi, \quad \mathbf{i} = -\nabla q - c \nabla \varphi, \quad (2.8)$$

while the ionic conservation equations (2.3) take the form

$$\nabla \cdot \mathbf{j} + \alpha \mathbf{u} \cdot \nabla c = 0, \quad \nabla \cdot \mathbf{i} + \alpha \mathbf{u} \cdot \nabla q = 0. \quad (2.9)$$

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

$$\delta^2 \nabla^2 \varphi = -q. \quad (2.10)$$

The Poisson–Nernst–Planck equations are supplemented by the continuity

$$\nabla \cdot \mathbf{u} = 0 \quad (2.11)$$

and Stokes

$$\nabla p = \nabla^2 \mathbf{u} + \nabla^2 \varphi \nabla \varphi \quad (2.12)$$

equations governing the motion of a fluid subject to Coulomb body forces. The inhomogeneous Stokes equation can be interpreted as a statement of zero stress divergence,

$$\nabla \cdot \mathbf{S} = 0, \quad (2.13)$$

wherein \mathbf{S} is the sum of Newtonian

$$-p\mathbf{I} + \nabla \mathbf{u} + (\nabla \mathbf{u})^\dagger \quad (2.14)$$

and Maxwell

$$\nabla\varphi\nabla\varphi - \frac{1}{2}\nabla\varphi\cdot\nabla\varphi\mathbf{I} \quad (2.15)$$

stresses, in which \mathbf{I} is the idemfactor and \dagger denotes transposition. In principle, the isotropic part of the Maxwell stress comprises an additional term, associated with the density dependence of the dielectric constant (Landau & Lifshitz 1960). As explained by Saville (1997), when considering an incompressible liquid this term can be absorbed in the pressure. This common practice is justified even in the presence of free surfaces, as the pertinent boundary conditions only involve the total stress. The symbol p appearing in both (2.12) and (2.14) thus represents a modified pressure.

Within the highly-conducting drop the electric potential is uniform and the electric field vanishes; the drop charge is distributed over its boundary so as to satisfy this condition. Since the drop is ideally polarizable, no ions adsorb to its surface from the electrolyte. The net charge of the drop is therefore considered a prescribed quantity. Normalized by $\epsilon^*\kappa^*\varphi^*a^{*2}$, we denote it $4\pi\bar{\sigma}$, $\bar{\sigma}$ thus representing the average surface charge density. As usual, the drop is treated as another Newtonian liquid. The flow equations governing the drop-phase velocity field $\bar{\mathbf{u}}$ and pressure field \bar{p} then read

$$\nabla\cdot\bar{\mathbf{u}}=0, \quad \nabla\bar{p}=\mu\nabla^2\bar{\mathbf{u}}, \quad (2.16)$$

in which μ is the ratio of the drop viscosity to that of the electrolyte.

At the interface $r=1$ the normal ionic fluxes vanish,

$$\hat{\mathbf{e}}_r\cdot\mathbf{j}^\pm=0, \quad (2.17)$$

and the electric potential equals \mathcal{V} , the (arbitrary) value of the uniform potential of the drop,

$$\varphi=\mathcal{V}. \quad (2.18)$$

The velocity fields $\mathbf{u}=\hat{\mathbf{e}}_ru+\hat{\mathbf{e}}_\theta v$ and $\bar{\mathbf{u}}=\hat{\mathbf{e}}_r\bar{u}+\hat{\mathbf{e}}_\theta\bar{v}$ further satisfy the tangential-velocity continuity and the impermeability conditions

$$v=\bar{v}, \quad u=\bar{u}=0 \quad (2.19)$$

together with the tangential-stress balance

$$\frac{\partial v}{\partial r}-v=\mu\left(\frac{\partial\bar{v}}{\partial r}-\bar{v}\right). \quad (2.20)$$

Note that no Maxwell stresses appear in the latter, in accordance with the vanishing tangential electric field at $r=1$. The surface charge density σ on the drop boundary, normalized by $\epsilon^*\kappa^*\varphi^*$, is provided by the local form of Gauss' law

$$\sigma=-\delta\frac{\partial\varphi}{\partial r}. \quad (2.21)$$

Unlike the comparable analysis of solid particles (Yariv 2010a; Schnitzer & Yariv 2012c), here this law does not provide a boundary condition governing φ , since the charge density is not *a priori* prescribed. Rather, it serves to determine σ once the electric field has been calculated.

At large distances away from the drop the concentrations approach unity and $-\nabla\varphi$ approaches the uniformly imposed field,

$$c^\pm\rightarrow 1, \quad \nabla\varphi\rightarrow-\beta\hat{\mathbf{i}}. \quad (2.22)$$

Here,

$$\beta = \frac{E^* a^*}{\varphi^*} \quad (2.23)$$

is the dimensionless magnitude of the applied field. The velocity field approaches a uniform stream of magnitude \mathcal{U} ,

$$\mathbf{u} \rightarrow -\mathcal{U} \hat{\mathbf{i}} \quad (2.24)$$

representing the drop electrophoretic velocity.

The preceding equations are supplemented by a pair of integral conditions. The first is the familiar force-free condition, requiring that the resultant force exerted on the drop by the combined Newtonian and Maxwell stresses (see (2.14)–(2.15)) vanishes:

$$\oint_{r=1} \mathbf{s} \cdot \hat{\mathbf{n}} \, dA = 0; \quad (2.25)$$

here dA is a differential areal element normalized by a^{*2} . In view of (2.13), the integral in (2.25) can be evaluated over any closed surface enclosing the drop. The second is essentially a ‘memory condition’ specifying the invariance of the total drop charge,

$$\oint_{r=1} \sigma \, dA = 4\pi\bar{\sigma}. \quad (2.26)$$

As already indicated, for an ideally polarizable drop $\bar{\sigma}$ is a prescribed quantity, which is unaffected by the application of an external field. Thus, conditions (2.25)–(2.26) serve to uniquely determine the electrophoretic velocity and the electric-field distribution (see (2.21)). Generally, the electrophoretic velocity \mathcal{U} is a (nonlinear) function of $\bar{\sigma}$, vanishing for $\bar{\sigma} = 0$.

The problem thus formulated is rather intractable. Furthermore, even numerical simulations are difficult owing to the scale disparity associated with the smallness of δ prevailing in practical scenarios. This very feature is however what allows us to make progress by means of asymptotic methods. This is addressed next.

3. Thin-double-layer limit

We now consider the limit $\delta \ll 1$. It is well known that this limit is singular, the non-uniformity being associated with the multiplication of the highest-order derivative in Poisson’s equation (2.10) by the small asymptotic parameter. The electrolyte domain, where (2.10) holds, is conceptually decomposed into two asymptotic subdomains: a thin boundary (‘Debye’) layer of thickness δ , formed about $r = 1$, and the remaining ‘bulk’ exterior to it. No such decomposition is required in the ion-free liquid drop.

Before proceeding to postulate separate asymptotic expansions in the Debye layer and bulk regions, it is necessary to carefully inspect the velocity scale appropriate to the limit $\delta \rightarrow 0$.

3.1. Velocity scaling

In the familiar case of a solid boundary, field scaling within the Debye layer is essentially the same as that implied by the above normalization of the governing equations. Thus, the ionic concentration, electric potential, and tangential velocity

are $O(1)$. The associated $O(\delta^{-1})$ velocity gradient is manifested in an electro-osmotic velocity jump in the macroscale description.

When considering electrokinetic flows about a free surface, tangential-shear-stress continuity must be satisfied locally. In the case of an electrolyte drop it is readily verified that the preceding scaling remains valid, the $O(\delta^{-1})$ large viscous stress being balanced by a comparable Maxwell stress, originating from the quadratic interaction of the $O(\delta^{-1})$ Debye-layer transverse electric field with the respective $O(1)$ tangential field.

With the same velocity scaling, however, tangential-stress continuity cannot be satisfied in the case of a conducting drop considered here. With the tangential field vanishing on the interface, the Maxwell traction is normal thereto and cannot balance the Debye-scale shear. Nor can this viscous shear be balanced by comparable drop-phase stresses: because of tangential-velocity continuity, fluid velocities within the drop are of the same asymptotic magnitude as those in the Debye layer; however, in the absence of a Debye layer in the drop phase, the Newtonian stress there is asymptotically smaller.

Following Levich (1962), this incompatibility is resolved by postulating a unique velocity scaling, different from the classical thin-double-layer limit. In the bulk, the fluid velocity is asymptotically large,

$$\mathbf{u} \sim O(\delta^{-1}). \quad (3.1)$$

In the Debye layer, the tangential velocity is of the same asymptotic order. It is however transversely *uniform*, variations across the layer only appearing at the next $O(1)$ asymptotic term. Thus, the leading-order tangential velocity constitutes an extrapolation of the bulk flow. This allows satisfaction of tangential-stress continuity. Indeed, the Debye-layer shear is again $O(\delta^{-1})$, but now resulting from transverse variation of the $O(1)$ velocity correction. The associated viscous stress may then be balanced by two separate contributions (see (4.16) below). The first is the curvature-induced stress associated with the transversely uniform $O(\delta^{-1})$ velocity. The second is contributed by the drop-phase viscous stresses: because of tangential-velocity continuity, the velocity field within the drop is also $O(\delta^{-1})$; in the absence of a Debye layer within the drop, the rate of strain there is of the same asymptotic magnitude. It is useful to note that, unlike the case of planar interfaces, the former contribution allows a tangential-stress balance at the drop surface even when its viscosity is very small.

Since the analysis of Levich (1962) is focused on the weak-field limit, his scaling model entails a transition from the Smoluchowski scale v_s^* (see (1.1)) to $\delta^{-1}v_s^*$. For $\beta \sim O(1)$, v_s^* coincides with the Maxwell scale v^* (see (2.1) and (2.23)). In the present scheme, which is not restricted to the weak-field limit $\beta \ll 1$, the primitive velocity scale is v^* , originally presented by Saville (1977). The thin-double-layer limit is therefore represented by a transition to dimensional velocities of order $\delta^{-1}v^*$, as indicated in (3.1).

3.2. Outer expansions

In the outer bulk region the position vector \mathbf{x} is replaced by the ‘coarse-grained’ vector $\tilde{\mathbf{x}}$, which does not resolve the fine details of the Debye layer. Thus, the effective boundary $\tilde{r} = 1$ represents the outer edge of the Debye layer, rather than the actual interface $r = 1$.

We accordingly employ the generic expansion

$$f(\mathbf{x}; \delta) = \tilde{f}_0(\tilde{r}, \theta) + \delta \tilde{f}_1(\tilde{r}, \theta) + \dots, \quad (3.2)$$

which holds for all bulk electrochemical fields. In view of (3.1), the dynamic fields possess the expansions,

$$\mathbf{u} = \delta^{-1}\tilde{\mathbf{u}}_{-1} + \tilde{\mathbf{u}}_0 + \dots, \quad p = \delta^{-1}\tilde{p}_{-1} + \tilde{p}_0 + \dots, \quad (3.3)$$

with comparable expansions for the drop-phase velocity $\bar{\mathbf{u}}$ and pressure \bar{p} ,

$$\bar{\mathbf{u}} = \delta^{-1}\bar{\tilde{\mathbf{u}}}_{-1} + \bar{\tilde{\mathbf{u}}}_0 + \dots, \quad \bar{p} = \delta^{-1}\bar{\tilde{p}}_{-1} + \bar{\tilde{p}}_0 + \dots. \quad (3.4)$$

It then follows that the drop electrophoretic velocity is also $O(\delta^{-1})$:

$$\mathcal{U} = \delta^{-1}\mathcal{U}_{-1} + \mathcal{U}_0 + \dots. \quad (3.5)$$

In view of the large velocity scaling, the salt balance equation (2.9) at $O(\delta^{-1})$ is advection dominated:

$$\tilde{\mathbf{u}}_{-1} \cdot \nabla \tilde{c}_0 = 0. \quad (3.6)$$

It follows that \tilde{c}_0 is constant along the streamlines of the leading-order flow. We assume, subject to *a posteriori* verification, that these lines are open, originating at infinity, where $\tilde{c}_0 = 1$. Thus the strong advection results in a homogeneous salt concentration,

$$\tilde{c}_0 \equiv 1. \quad (3.7)$$

In a similar manner it is readily established that $\tilde{q}_0 \equiv 0$. It follows that at $O(1)$ the current density is Ohmic and the salt flux vanishes,

$$\tilde{\mathbf{i}}_0 = -\nabla \tilde{\varphi}_0, \quad \tilde{\mathbf{j}}_0 = \mathbf{0}. \quad (3.8)$$

The leading-order charge balance (2.9) is then dominated by Ohmic conduction,

$$\nabla^2 \tilde{\varphi}_0 = 0. \quad (3.9)$$

Poisson's equation (2.10) reveals that the charge density q vanishes up to $O(\delta^2)$ inclusive.

Lastly, the large velocity scaling implies that the leading-order flow is governed by the homogeneous Stokes equations without any body forces

$$\nabla \cdot \tilde{\mathbf{u}}_{-1} = 0, \quad \nabla \tilde{p}_{-1} = \nabla^2 \tilde{\mathbf{u}}_{-1}; \quad (3.10)$$

similar equations govern the drop-phase flow,

$$\nabla \cdot \bar{\tilde{\mathbf{u}}}_{-1} = 0, \quad \nabla \bar{\tilde{p}}_{-1} = \mu \nabla^2 \bar{\tilde{\mathbf{u}}}_{-1}. \quad (3.11)$$

4. Debye-scale analysis

4.1. Debye-scale formulation

In analysing the Debye-scale fields, we employ the inner coordinate

$$Z = \frac{r-1}{\delta}. \quad (4.1)$$

As in the outer region, ionic concentrations and the electric potential are expected to remain $O(1)$,

$$c^\pm = C_0^\pm + \delta C_1^\pm + \dots, \quad \varphi = \Phi_0 + \delta \Phi_1 + \dots. \quad (4.2)$$

In view of (2.17) and the matching requirement, we also anticipate $O(1)$ transverse fluxes in the radial direction

$$\hat{\mathbf{e}}_r \cdot \mathbf{j}^\pm = J_0^\pm(Z, \theta) + \dots, \quad (4.3)$$

with similar expansions for the radial current and salt flux (see (2.8))

$$\hat{\mathbf{e}}_r \cdot \mathbf{i} = I_0(Z, \theta) + \dots, \quad \hat{\mathbf{e}}_r \cdot \mathbf{j} = J_0(Z, \theta) + \dots. \quad (4.4)$$

At $Z = 0$ the following conditions apply (cf. (2.17)–(2.18)):

$$J_0^\pm = 0, \quad \Phi_0 = \mathcal{V}. \quad (4.5)$$

The leading-order surface-charge density is provided by (cf. (2.21))

$$\sigma_0 = -\frac{\partial \Phi_0}{\partial Z}. \quad (4.6)$$

At large Z the Debye-layer fields must match their electroneutral-bulk counterparts, thus

$$\Phi_0 \rightarrow \tilde{\varphi}_0, \quad C_0^\pm \rightarrow 1 \quad \text{as } Z \rightarrow \infty. \quad (4.7)$$

Hereafter, outer (shown with a tilde) variables (or their radial derivatives) appearing in any Debye-scale equation are understood to be evaluated at the effective boundary $\tilde{r} = 1$, and are accordingly functions of θ alone.

Balancing the large Coulombic body force in the Stokes equations (2.12) requires a comparable $O(\delta^{-2})$ pressure,

$$p = \delta^{-2} P_{-2} + \dots. \quad (4.8)$$

Here, large- Z asymptotic matching implies that

$$P_{-2} \rightarrow 0 \quad \text{as } Z \rightarrow \infty. \quad (4.9)$$

Following the discussion in § 3.1 the tangential velocity is expanded as

$$v = \delta^{-1} V_{-1}(\theta) + V_0(Z, \theta) + \dots, \quad (4.10)$$

with V_{-1} independent of Z . Asymptotic matching with the bulk velocity readily yields

$$V_{-1} = \tilde{v}_{-1}. \quad (4.11)$$

Furthermore, the transverse uniformity of V_{-1} and the need for velocity-gradient matching implies that the shear associated with the correction V_0 must satisfy

$$\frac{\partial V_0}{\partial Z} \rightarrow \frac{\partial \tilde{v}_{-1}}{\partial \tilde{r}} \quad \text{as } Z \rightarrow \infty. \quad (4.12)$$

Since V_{-1} , as given by (4.11), is effectively an extrapolation of the bulk flow, the microscale velocity–continuity condition (2.19) is transformed into the macroscale continuity condition

$$\tilde{v}_{-1}(r = 1) = \tilde{v}_{-1}(\tilde{r} = 1). \quad (4.13)$$

The continuity equation (2.11) in conjunction with the impermeability condition (2.19) implies that the radial velocity is $O(1)$:

$$u = U_0(Z, \theta) + \delta U_1(Z, \theta) + \dots. \quad (4.14)$$

At leading order, (2.19) then yields

$$U_0 = 0 \quad \text{at } Z = 0. \quad (4.15)$$

With the preceding expansions, the tangential-stress balance equation (2.20) yields at leading order

$$\frac{\partial V_0}{\partial Z} - V_{-1} = \mu \left(\frac{\partial \bar{v}_{-1}}{\partial r} - \bar{v}_{-1} \right) \quad \text{at } Z = 0. \quad (4.16)$$

Note that by (4.11) and (4.13) both V_{-1} and \bar{v}_{-1} can be replaced with \tilde{v}_{-1} .

The Debye-scale analysis which follows consists of three steps: (i) the leading-order ionic conservation equations are solved to yield a quasi-equilibrium Gouy–Chapman structure (§ 4.2); (ii) the subdominant $O(1)$ electro-osmotic flow is analysed, resulting in an effective macroscale stress-jump condition (§ 4.3); (iii) the $O(1)$ transverse ionic fluxes, driven by the $O(\delta^{-1})$ tangential velocity, are calculated; the associated current density is matched to the corresponding bulk flux, resulting in an effective Neumann boundary condition governing the bulk potential (§ 4.4). The role of the comparable salt flux is discussed in § 4.5.

4.2. Gouy–Chapman structure

The absence of $O(\delta^{-1})$ transverse ionic fluxes (see (4.3)) in conjunction with (2.2) written in inner variables yields

$$-\frac{\partial C_0^\pm}{\partial Z} \mp C_0^\pm \frac{\partial \Phi_0}{\partial Z} = 0. \quad (4.17)$$

Integrating with respect to Z and applying (4.7) provides the Boltzmann distribution

$$C_0^\pm = e^{\mp \Psi}. \quad (4.18)$$

Here $\Psi = \Phi_0 - \tilde{\varphi}_0$ is the ‘excess’ Debye-layer potential. Substituting into the Poisson equation (2.5) yields the Poisson–Boltzmann equation

$$\frac{\partial^2 \Psi}{\partial Z^2} = \sinh \Psi. \quad (4.19)$$

Integrating once with respect to Z and applying (4.7) we obtain the first-order differential equation

$$\frac{\partial \Psi}{\partial Z} = -2 \sinh \frac{\Psi}{2}. \quad (4.20)$$

We adopt the following definition of the zeta potential:

$$\zeta = \Psi(Z = 0), \quad (4.21)$$

namely the leading-order local voltage across the diffuse Debye layer. With (4.5), this potential difference can be written

$$\zeta(\theta) = \mathcal{V} - \varphi_0(\theta). \quad (4.22)$$

With definition (4.21), the surface-charge density obtained from (4.6) and (4.20) is

$$\sigma_0 = 2 \sinh \frac{\zeta}{2}. \quad (4.23)$$

4.3. Flow

The leading-order radial momentum equation, at $O(\delta^{-3})$, represents a balance between pressure gradients and the electrical body force,

$$\frac{\partial P_{-2}}{\partial Z} = \frac{\partial^2 \Phi_0}{\partial Z^2} \frac{\partial \Phi_0}{\partial Z}. \tag{4.24}$$

Integration with respect to Z in conjunction with the matching conditions (4.7) and (4.9) yields

$$P_{-2} = \frac{1}{2} \left(\frac{\partial \Psi}{\partial Z} \right)^2. \tag{4.25}$$

Substitution into the $O(\delta^{-2})$ tangential-momentum equation yields

$$\frac{\partial^2 V_0}{\partial Z^2} = \frac{\partial \Psi}{\partial Z} \frac{\partial^2 \Psi}{\partial Z \partial \theta} - \frac{\partial^2 \Psi}{\partial Z^2} \left(\frac{\partial \Psi}{\partial \theta} + \frac{d\tilde{\varphi}_0}{d\theta} \right). \tag{4.26}$$

Integration with respect to Z (employing (4.20) and the matching condition (4.12)) then gives

$$\frac{\partial V_0}{\partial Z} - \frac{\partial \tilde{v}_{-1}}{\partial \tilde{r}} = - \frac{\partial \Psi}{\partial Z} \frac{d\tilde{\varphi}_0}{d\theta}. \tag{4.27}$$

No further integration is needed as our objective is the $O(\delta^{-1})$ shear stress associated with the electro-osmotic flow V_0 rather than V_0 itself. Indeed, substitution of (4.27), evaluated at $Z = 0$, into the tangential-stress-balance equation (4.16) yields the required condition

$$\frac{\partial \tilde{v}_{-1}}{\partial \tilde{r}} - \tilde{v}_{-1} + 2 \sinh \frac{\zeta}{2} \frac{d\tilde{\varphi}_0}{d\theta} = \mu \left(\frac{\partial \tilde{v}_{-1}}{\partial \tilde{r}} - \tilde{v}_{-1} \right) \quad \text{at } \tilde{r} = 1 \tag{4.28}$$

specifying the macroscale stress discontinuity.

For future reference, use of the leading-order continuity equation (see (2.11))

$$\frac{\partial U_0}{\partial Z} + \frac{1}{\sin \theta} \frac{d}{d\theta} (\tilde{v}_{-1} \sin \theta) = 0, \tag{4.29}$$

in conjunction with the impermeability condition (4.15), yields the radial velocity

$$U_0 = - \frac{Z}{\sin \theta} \frac{d}{d\theta} (\tilde{v}_{-1} \sin \theta). \tag{4.30}$$

4.4. Transverse current

To obtain an effective boundary condition governing the bulk potential $\tilde{\varphi}_0$ it is necessary to calculate the $O(1)$ current density normal to the interface. At $O(\delta^{-1})$, the Nernst–Planck equations (2.3) read

$$\frac{\partial J_0^\pm}{\partial Z} + \alpha \left(U_0 \frac{\partial C_0^\pm}{\partial Z} + \tilde{v}_{-1} \frac{\partial C_0^\pm}{\partial \theta} \right) = 0. \tag{4.31}$$

Integration from $Z = 0$ to ∞ in conjunction with (4.5) yields the fluxes

$$J_0^\pm(Z \rightarrow \infty) = -\alpha \int_0^\infty dZ \left(U_0 \frac{\partial}{\partial Z} + \tilde{v}_{-1} \frac{\partial}{\partial \theta} \right) (C_0^\pm - 1), \tag{4.32}$$

where we have replaced C_0^\pm , which appears only under differentiation, by $C_0^\pm - 1$. Integration by parts in conjunction with (4.30) furnishes the expression

$$J_0^\pm(Z \rightarrow \infty) = -\frac{\alpha}{\sin \theta} \frac{d}{d\theta} \left\{ \tilde{v}_{-1} \sin \theta \int_0^\infty (C_0^\pm - 1) dZ \right\}, \quad (4.33)$$

wherein convergence of the integrals is ensured by the large- Z exponentially rapid decay of $C_0^\pm - 1$.

The transverse-current density, $I_0 = (J_0^+ - J_0^-)/2$, is obtained using (4.18):

$$I_0(Z \rightarrow \infty) = \frac{\alpha}{\sin \theta} \frac{d}{d\theta} \left\{ \tilde{v}_{-1} \sin \theta \int_0^\infty \sinh \Psi dZ \right\}. \quad (4.34)$$

The integral $\int_0^\infty \sinh \Psi dZ = 2 \sinh(\zeta/2)$ is readily evaluated using (4.20). Matching with the $O(1)$ bulk current (3.8) finally furnishes the requisite effective macroscale boundary condition

$$\frac{\partial \tilde{\varphi}_0}{\partial \tilde{r}} = -\frac{2\alpha}{\sin \theta} \frac{d}{d\theta} \left\{ \tilde{v}_{-1} \sinh \frac{\zeta}{2} \sin \theta \right\} \quad \text{at } \tilde{r} = 1. \quad (4.35)$$

Inhomogeneous Neumann conditions in the thin-double-layer limit are usually encountered in weak-field analyses of the electrophoresis of highly charged solid particles (large zeta potentials), where the enabling ‘surface conduction’ mechanism is related to the extremely large counter-ion concentration near the surface (Derjaguin & Dukhin 1974; O’Brien & Hunter 1981; O’Brien 1983; Schnitzer & Yariv 2012c). The emergence of that mechanism is associated with the pertinent Dukhin number (of order $\delta e^{\zeta/2}$, see Dukhin 1993) attaining $O(1)$ values. In contrast, the present condition (4.35) has been derived for a moderate surface-charge density, where this Dukhin number is vanishingly small: see (4.23); in such circumstances the bulk electric field would normally be governed by a homogeneous Neumann condition (Keh & Anderson 1985; Anderson 1989; Yariv 2010a; Schnitzer & Yariv 2012c).

The present problem, where an inhomogeneous condition represents an effective surface-conduction mechanism at moderate zeta potentials, is reminiscent of both large-Péclet-number streaming-potential phenomena (Yariv *et al.* 2011) and solid-particle electrophoresis in the strong-field limit (Schnitzer & Yariv 2012d). These two different electrokinetic phenomena share the feature of a strong externally imposed field – hydrodynamic in the former, electric in the latter. In the present problem, where the imposed field is moderate, the surface conduction mechanism is instead driven by the singularly large shear-driven velocity inherent in electrokinetic flows about highly conducting drops.

4.5. Salt-flux incompatibility: diffusive boundary layer

The preceding effective boundary conditions are sufficient for prescribing a self-contained macroscale model. Specifically, no need arises for specifying a boundary condition governing the salt concentration, since its distribution has already been found to be uniform, see (3.7). Note, however, that addition of the transverse fluxes (4.33) predicts a non-zero salt flux $J_0 = (J_0^+ + J_0^-)/2$, which, using (4.18), reads

$$J_0(Z \rightarrow \infty) = -\frac{\alpha}{\sin \theta} \frac{d}{d\theta} \left\{ \tilde{v}_{-1} \sin \theta \int_0^\infty (\cosh \Psi - 1) dZ \right\}. \quad (4.36)$$

The integral $\int_0^\infty (\cosh \Psi - 1) dZ = 4\sinh^2(\zeta/4)$ is evaluated using (4.20), whereby the salt flux adopts the form

$$J_0(Z \rightarrow \infty) = -\frac{4\alpha}{\sin \theta} \frac{d}{d\theta} \left\{ \tilde{v}_{-1} \sinh^2 \frac{\zeta}{4} \sin \theta \right\}. \tag{4.37}$$

Obviously, this non-zero salt flux emanating from the Debye layer is incompatible with the homogeneous bulk (3.7).

In resolving this apparent paradox we note that, with $O(\delta^{-1})$ velocities, the limit $\delta \rightarrow 0$ represents a twofold singularity, resulting from the multiplication of the highest derivative by the small parameter in two separate equations. The first singularity occurs in Poisson’s equation (2.10); this is the familiar singularity giving rise to the $O(\delta)$ -wide Debye layer. The second, associated with the dominance of ionic advection, appears in (2.3), when the scaling (3.1) is incorporated. This newly-identified singularity gives rise to a diffusive boundary layer. Since the tangential velocity already approaches its large $O(\delta^{-1})$ value on the Debye scale, one finds by balancing transverse diffusion with (transverse and tangential) advection that the width of this intermediate layer is $\delta^{1/2}$ (Leal 2007).

The structure of the $O(\delta^{1/2})$ -wide diffusive layer is resolved using the stretched radial coordinate (cf. (4.1))

$$\dot{Z} = \frac{r - 1}{\delta^{1/2}}. \tag{4.38}$$

The scaling of the diffusive-layer fields is determined by matching requirements: on one hand, the need to approach the unity concentration and $O(1)$ electric field in the bulk; on the other, the need to match the $O(1)$ fluxes, of both salt and charge, emanating from the Debye layer. We therefore postulate the expansions

$$c = 1 + \delta^{1/2} \dot{C}_{1/2}(\dot{Z}, \theta) + \dots, \quad \varphi = \dot{\Phi}_0(\theta) + \delta^{1/2} \dot{\Phi}_{1/2}(\dot{Z}, \theta) + \dots. \tag{4.39}$$

It is readily verified via asymptotic matching that $\dot{\Phi}_0(\theta) = \tilde{\varphi}_0(\theta)$. (As in § 4.1, all bulk-scale fields are understood to be evaluated at $\tilde{r} = 1$.) Moreover, Poisson’s equation together with asymptotic matching also yields

$$\dot{\Phi}_{1/2} = \dot{Z} \frac{\partial \tilde{\varphi}_0}{\partial r}(\theta). \tag{4.40}$$

The requirements of velocity and pressure matching, in conjunction with the continuity equation (2.11), also suggest the expansions

$$v = \delta^{-1} \dot{V}_{-1}(\theta) + \dots, \quad u = \delta^{-1/2} \dot{U}_{-1/2}(\dot{Z}, \theta) + \dots, \quad p = \delta^{-1} \dot{P}_{-1}(\theta) + \dots \tag{4.41}$$

Here,

$$\dot{V}_{-1}(\theta) = \tilde{v}_{-1}(\theta) \tag{4.42}$$

and

$$\dot{U}_{-1/2} = -\frac{\dot{Z}}{\sin \theta} \frac{d}{d\theta} (\tilde{v}_{-1} \sin \theta). \tag{4.43}$$

The last result follows from the continuity equation and small- \dot{Z} asymptotic matching with the $O(1)$ Debye-layer transverse velocity (cf. (4.30)).

The preceding expansions are consistent with $q = o(\delta)$. The salt balance then yields at leading order

$$\frac{\partial^2 \dot{C}_{1/2}}{\partial \dot{Z}^2} = \alpha \left(\dot{U}_{-1/2} \frac{\partial \dot{C}_{1/2}}{\partial \dot{Z}} + \dot{V}_{-1} \frac{\partial \dot{C}_{1/2}}{\partial \theta} \right). \quad (4.44)$$

Furthermore, $\dot{C}_{1/2}$ must satisfy the boundary condition

$$\frac{\partial \dot{C}_{1/2}}{\partial \dot{Z}} = \frac{4\alpha}{\sin \theta} \frac{d}{d\theta} \left(\tilde{v}_{-1} \sinh^2 \frac{\zeta}{4} \sin \theta \right) \quad \text{at } \dot{Z} = 0, \quad (4.45)$$

representing the small- \dot{Z} asymptotic matching with the Debye-layer flux (4.37), together with the decay condition

$$\dot{C}_{1/2} \rightarrow 0 \quad \text{as } \dot{Z} \rightarrow \infty, \quad (4.46)$$

representing asymptotic matching with the bulk.

The parabolic problem (4.44)–(4.46) closely resembles that governing the similarly scaled boundary layer appearing in the problem of solid-particle electrophoresis under strong fields (Schnitzer & Yariv 2012*d*). It is solved in the [Appendix](#) following the same integral-transform procedure presented in that paper. Some adaptation is needed however to cope with slight added complications resulting from the explicit functional forms of both $\tilde{v}_{-1}(\theta)$ and $\zeta(\theta)$ being *a priori* unknown here.

The presence of the intermediate layer implies that the Debye-layer expansion for the salt (4.2) needs to be modified to incorporate an $O(\delta^{1/2})$ term. Inspection verifies that this term is independent of Z and therefore does not affect the Debye-layer analysis relevant to the derivation of the effective boundary conditions. The presence of the diffusive layer may further introduce similar intermediate orders in the Debye-layer expansions of other fields. This, in turn, may enhance the asymptotic error in the macroscale model from $O(\delta)$ to $O(\delta^{1/2})$.

4.6. Normal-stress balance

As our analysis considers a spherical drop shape, it implicitly assumes that surface-tension forces preclude any surface deformation. Concretely, consider a uniform (microscale) surface tension γ^* . A spherical shape is approximately retained provided that the capillary pressure, of order γ^*/a^* , is large compared with viscous and Maxwell stresses acting on the interface. Note that, within the suspending electrolyte, these stresses are associated with the Debye-scale fields.

While both the Debye-layer pressure and Maxwell stress are $O(\delta^{-2})$, their contributions to the normal-stress balance mutually cancel, see (4.25). The stresses that affect drop deformation are accordingly $O(\delta^{-1})$, and are contributed by both the electrolyte and drop phases. In dimensional terms, these correspond to magnitudes of order $\delta^{-1} \mu^* v^*/a^*$. Using (2.1), we conclude that deviation from a spherical drop shape is small if $Ca \ll 1$, where

$$Ca = \frac{\epsilon^* \varphi^{*2}}{\gamma^*} \kappa^* \quad (4.47)$$

is the pertinent capillary number. Consistent with our model which assumes no adsorption at the drop interface, (4.47) shows that for a given pair of drop and suspending liquids the capillary number is essentially determined by the bulk

electrolyte concentration (through κ^*). For a typical system consisting of a mercury drop in aqueous solution ($\epsilon^* \approx 7 \times 10^{-10} \text{ kg m s}^{-2} \text{ V}^{-2}$, $\gamma^* \approx 0.4 \text{ kg s}^{-2}$) $Ca \approx 10^{-12} \kappa^*$, where κ^* is measured in m^{-1} ; even for nano-metric Debye thickness, Ca is very small.

The $O(Ca)$ leading-order drop deformation may be determined from the normal-stress jump across the interface calculated using the solution for a spherical drop (Leal 2007). At $O(\delta^{-1})$, this jump is provided by the difference

$$\left(-P_{-1} + 2 \frac{\partial U_0}{\partial Z} + \frac{\partial \Psi}{\partial Z} \frac{\partial \Phi_1}{\partial Z}\right)_{Z=0} - \left(-\bar{p}_{-1} + 2\mu \frac{\partial \bar{u}_{-1}}{\partial r}\right)_{r=1}, \tag{4.48}$$

involving both Debye-scale and drop-phase fields. It is tacitly understood that the large $O(1/Ca)$ pressure terms associated with the equilibrium spherical shape are omitted from both P_{-1} and \bar{p}_{-1} .

To write the stress jump (4.48) in terms of macroscale fields, we first note from the Debye-scale continuity equation (4.29) and the bulk continuity equation that $\partial U_0/\partial Z$ is equal to $\partial \tilde{u}_{-1}/\partial r$. (As in §4.1, bulk-scale fields are understood to be evaluated at $\tilde{r} = 1$.) Next, we consider the $O(\delta^{-2})$ transverse momentum equation within the Debye layer,

$$\frac{\partial P_{-1}}{\partial Z} = \frac{\partial^2 U_0}{\partial Z^2} + \frac{\partial}{\partial Z} \left(\frac{\partial \Psi}{\partial Z} \frac{\partial \Phi_1}{\partial Z}\right) + 2 \left(\frac{\partial \Psi}{\partial Z}\right)^2. \tag{4.49}$$

In view of (4.29), the first term on the right-hand side vanishes. Integration with respect to Z from 0 to ∞ in conjunction with (4.20) and the large- Z exponential decay of $\partial \Psi/\partial Z$ yields

$$\tilde{p}_{-1} - P_{-1}|_{Z=0} = - \frac{\partial \Psi}{\partial Z} \frac{\partial \Phi_1}{\partial Z} \Big|_{Z=0} + 8 \int_0^\infty \sinh^2 \frac{\Psi(Z)}{2} dZ, \tag{4.50}$$

in which the matching condition

$$P_{-1} \rightarrow \tilde{p}_{-1} \text{ as } Z \rightarrow \infty \tag{4.51}$$

has been employed. The integral in (4.50) is evaluated using (4.20) as $2\sinh^2(\zeta/4)$. Substituting into (4.48) reveals that the terms involving Φ_1 mutually cancel, hence no need arises to calculate this field. In terms of the macroscale fields, the normal-stress jump is accordingly given by

$$\left(-\tilde{p}_{-1} + 2 \frac{\partial \tilde{u}_{-1}}{\partial r}\right)_{\tilde{r}=1} - \left(-\bar{p}_{-1} + 2\mu \frac{\partial \bar{u}_{-1}}{\partial r}\right)_{r=1} + 16\sinh^2 \frac{\zeta}{4}, \tag{4.52}$$

where the last term represents a macroscale ‘surface-tension’ contribution, corresponding to an ‘electro-capillary’ deviation of magnitude

$$-8\sinh^2 \frac{\zeta}{4} \tag{4.53}$$

of the effective surface-tension coefficient from its original uniform value.

For a well-posed macroscale problem, this jump is considered known at this stage. It is therefore possible in principle to calculate the leading-order deviation from the equilibrium spherical shape. Presenting the deformed interface shape as

$$r = 1 + Ca R(\theta) + \dots, \tag{4.54}$$

the mean curvature reads

$$2 - Ca \left(\frac{d^2 R}{d\theta^2} + \cot \theta \frac{dR}{d\theta} \right) + \dots \quad (4.55)$$

The shape perturbation R is accordingly governed by the differential equation,

$$\frac{d^2 R}{d\theta^2} + \cot \theta \frac{dR}{d\theta} = \left(\tilde{p}_{-1} - 2 \frac{\partial \tilde{u}_{-1}}{\partial r} \right)_{\tilde{r}=1} - 16 \sinh^2 \frac{\zeta}{4} - \left(\bar{p}_{-1} - 2\mu \frac{\partial \bar{u}_{-1}}{\partial r} \right)_{r=1}, \quad (4.56)$$

regularity on the polar axis, and the volume-conservation constraint

$$\int_0^\pi R(\theta) \sin \theta \, d\theta = 0. \quad (4.57)$$

5. Macroscale model

For easy reference, we recapitulate here the macroscale model for the electrophoretic motion of a conducting drop in the thin-double-layer limit. Within the framework of this description, the presence of the Debye layer is lumped into a set of boundary conditions, applying at the effective boundary $\tilde{r} = 1$.

For simplicity we hereafter omit the tilde decoration identifying the outer variables: since the suspending phase is represented only through these variables, no confusion should arise. We also omit all indices. Thus, the pertinent variables correspond to the respective first terms in the asymptotic expansions (3.2)–(3.3). With this notation, the effective normalization procedure of § 2 applies to all fields, except for the dynamic variables. Velocity is now understood to be scaled by the product of δ^{-1} and the original Maxwell scale v^* , namely

$$\frac{(2c^* \epsilon^*)^{1/2} (k^* T^*)^{3/2}}{\mathcal{Z} \mu^* e^*}. \quad (5.1)$$

Stress variables are accordingly understood to be normalized by $\delta^{-1} M^*$.

The bulk electrolyte ($r > 1$) is homogenized ($c \equiv 1$) by the dominance of advection. The absence of $O(1)$ charge diffusion and advection then implies that the electrical potential is harmonic,

$$\nabla^2 \varphi = 0. \quad (5.2)$$

The flows in both the suspending electrolyte and the suspended drop are governed by the homogeneous Stokes equations

$$\nabla \cdot \mathbf{u} = 0, \quad \nabla p = \nabla^2 \mathbf{u}, \quad \nabla \cdot \bar{\mathbf{u}} = 0, \quad \nabla \bar{p} = \mu \nabla^2 \bar{\mathbf{u}}. \quad (5.3)$$

The boundary conditions applying at the effective interface comprise the following.

(a) The inhomogeneous Neumann condition

$$\frac{\partial \varphi}{\partial r} + \frac{\alpha}{\sin \theta} \frac{\partial}{\partial \theta} (v \sigma \sin \theta) = 0 \quad \text{at } r = 1, \quad (5.4)$$

arising from the non-uniform advection of charge within the Debye layer. Here,

$$\sigma = 2 \sinh \frac{\zeta}{2} \quad (5.5)$$

is the surface-charge density at the drop surface, wherein the zeta potential ζ is given by

$$\zeta = \mathcal{V} - \varphi(r = 1). \tag{5.6}$$

In general, ζ (and hence σ) is a function of θ . We choose to formulate the macroscale model in terms of σ (rather than ζ) which results in a more compact description. Thus, with the macroscale charge density of the Debye layer being $-\sigma$, condition (5.4) represents a balance between Ohmic charging and surface divergence of advective currents.

(b) Continuity of tangential velocity,

$$v = \bar{v} \quad \text{at } r = 1, \tag{5.7}$$

representing the uniformity of the leading-order velocity across the Debye layer.

(c) Flow impermeability

$$u = 0, \quad \bar{u} = 0 \quad \text{at } r = 1, \tag{5.8}$$

wherein the former represents the absence of $O(\delta^{-1})$ radial velocity within the Debye layer (see (4.14)) and the latter is a genuine kinematic condition.

(d) Tangential-stress discontinuity,

$$\left(\frac{\partial v}{\partial r} - v \right) - \mu \left(\frac{\partial \bar{v}}{\partial r} - \bar{v} \right) + \sigma \frac{\partial \varphi}{\partial \theta} = 0, \tag{5.9}$$

where the last term on the left-hand side is an effective stress jump which originates from the excess shear within the Debye layer, driven, in turn, by the Coulomb body force acting on the Debye-layer charge. Note that this jump conveniently appears as the product of local Debye-layer charge, $-\sigma$, and tangential field, $-\partial\varphi/\partial\theta$.

At large distances away from the drop, the electric field tends to the uniform applied field while the velocity approaches a uniform stream,

$$\nabla\varphi \rightarrow -\beta\hat{i}, \quad \mathbf{u} \rightarrow -\mathcal{U}\hat{i}. \tag{5.10}$$

The first condition entails the main input parameter to the problem – the magnitude β of the applied field; the second entails the principal outcome of the electrokinetic process – the electrophoretic velocity \mathcal{U} .

The macroscale model is ‘closed’ by imposing two integral constraints. The first is the zero-force condition, originally provided in the microscale form (2.25); it is now understood to apply at any closed surface within the bulk electrolyte. Since the contribution of $O(1)$ Maxwell stress in the bulk is dominated by the $O(\delta^{-1})$ contribution of the Newtonian stress, we obtain the simplified macroscale version

$$\oint \{-p\mathbf{I} + \nabla\mathbf{u} + (\nabla\mathbf{u})^\dagger\} \cdot \hat{\mathbf{n}} \, dA = 0. \tag{5.11}$$

This constraint is readily satisfied by rejecting a Stokeslet term in the solution for the Stokes flow \mathbf{u} . The second constraint represents the invariance of the net charge of the drop:

$$\oint \sigma \, dA = 4\pi\bar{\sigma}. \tag{5.12}$$

A subtle issue concerns the value \mathcal{V} of the drop potential, which enters this constraint through (5.5)–(5.6). In general, the electric potential in the fluid is only defined to within an arbitrary additive constant (apparently suggesting that the value of \mathcal{V} is devoid of physical meaning); this arbitrariness is however implicitly exploited when choosing a specific member of the family of harmonic functions satisfying (5.4) and (5.10). Once this choice is made, the value of \mathcal{V} cannot be prescribed arbitrarily. Indeed, this value affects the (physically objective) distribution of σ and ζ , see (5.5)–(5.6) (cf. Yariv 2005, 2008). In fact, \mathcal{V} is uniquely determined from these equations together with (5.12): see § 6.

The preceding macroscale description is substantially simplified compared to the exact problem formulation. Furthermore, it enjoys the advantage of describing transport on the single length scale a^* , as opposed to the scale disparity at the microscale level of description. The removal of the small scale is clearly useful when attempting a numerical solution of the problem. The effective boundary conditions, representing the Debye-layer physics, constitute a lumped description of both tangential-stress discontinuity and double-layer polarization which clearly illuminate the physical mechanisms involved. Further simplification may be provided using Stokes stream functions (Happel & Brenner 1965) in both the suspending electrolyte and drop phase,

$$\mathbf{u} = \frac{1}{r \sin \theta} \hat{\mathbf{e}}_{\varpi} \times \nabla \psi, \quad \bar{\mathbf{u}} = \frac{1}{r \sin \theta} \hat{\mathbf{e}}_{\varpi} \times \nabla \bar{\psi}. \quad (5.13)$$

Notwithstanding the above, the macroscale model is still nonlinear (see (5.4)–(5.5) and (5.9)) and in general does not admit a closed-form solution. In what follows, we consider weak applied fields, where an analytic approximation is obtained.

6. Weak-field approximation

In the absence of an applied field ($\beta = 0$) the stationary solution is described by zero electric field, say $\varphi = 0$, where the zeta potential is uniform, being equal to $\bar{\mathcal{V}}$. The surface charge density is uniform, and is related to the net charge $4\pi\bar{\sigma}$ by (5.12), thus simply giving the uniform density

$$\sigma = \bar{\sigma}. \quad (6.1)$$

To address the weak-field limit $\beta \ll 1$, representing a small perturbation of this reference state, we employ the generic expansion

$$f = \beta f' + \dots \quad (6.2)$$

describing φ , the flow fields (\mathbf{u}, p) and $(\bar{\mathbf{u}}, \bar{p})$, and the electrophoretic velocity \mathcal{U} . The corresponding expansion for the surface-charge density is

$$\sigma = \bar{\sigma} + \beta \sigma' + \dots \quad (6.3)$$

The linearized potential φ' is governed by Laplace's equation, the Neumann condition

$$\frac{\partial \varphi'}{\partial r} = -\frac{\alpha \bar{\sigma}}{\sin \theta} \frac{\partial}{\partial \theta} (v' \sin \theta) \quad \text{at } r = 1, \quad (6.4)$$

and the far-field condition $\nabla \varphi' \rightarrow -\hat{\mathbf{i}}$. We observe that, even after linearization, the coupling with the bulk flow (\mathbf{u}', p') persists. This flow, in turn, is governed by the

Stokes equations, the effective stress-jump condition at $r = 1$

$$\left(\frac{\partial v'}{\partial r} - v'\right) - \mu \left(\frac{\partial \bar{v}'}{\partial r} - \bar{v}'\right) + \bar{\sigma} \frac{\partial \varphi'}{\partial \theta} = 0, \tag{6.5}$$

and the requirement that $u' = 0$ there. It must further satisfy the far-field condition $u' \rightarrow -\mathcal{U}'\hat{i}$ and the force-free constraint

$$\oint \{-p'I + \nabla u' + (\nabla u')^\dagger\} \cdot \hat{n} \, dA = 0. \tag{6.6}$$

Condition (6.5) couples the bulk flow to the Stokes flow (\bar{u}', \bar{p}') within the drop, satisfying $\bar{u}' = 0$ and $\bar{v}' = v'$ at $r = 1$.

The solution of the above linear problem is readily obtained. The electric potential is represented by a superposition of the uniformly applied field and a dipole disturbance,

$$\varphi' = -\left(r + \frac{1 - 3\alpha\bar{\sigma}\mathcal{U}'}{2r^2}\right) \cos \theta; \tag{6.7}$$

the bulk flow is irrotational, consisting of a uniform stream and a doublet,

$$\psi' = \frac{1}{2}\mathcal{U}'\left(r^2 - \frac{1}{r}\right) \sin^2 \theta, \tag{6.8}$$

where the absence of a Stokeslet term guarantees the satisfaction of the force-free constraint equation (6.6). The flow within the drop is then given by the Hill-type vortex (Batchelor 1967)

$$\bar{\psi}' = \frac{3}{4}\mathcal{U}'(r^4 - r^2)\sin^2 \theta. \tag{6.9}$$

The electrophoretic velocity, obtained from (6.5), is

$$\mathcal{U}' = \frac{\bar{\sigma}}{2 + 3\mu + \alpha\bar{\sigma}^2}. \tag{6.10}$$

The surface-charge perturbation is readily obtained from (5.5)–(5.6) and (6.7):

$$\sigma' = \frac{3(2 + 3\mu)(4 + \bar{\sigma}^2)^{1/2}}{4(2 + 3\mu + \alpha\bar{\sigma}^2)} \cos \theta. \tag{6.11}$$

In passing, we note that the irrotational flow equation (6.8) indeed conforms to the general postulate (§ 3.2) of open streamlines originating at infinity.

6.1. *Mismatch with Ohshima et al. (1984)*

The electrophoretic mobility (6.10) is expressed in terms of $\bar{\sigma}$ which is the most fundamental attribute of the drop in the present model. For the purpose of comparison with the literature, (6.10) is recast in the form

$$\mathcal{U}' = \frac{\sinh(\bar{\zeta}/2)}{1 + \frac{3}{2}\mu + 2\alpha\sinh^2(\bar{\zeta}/2)}. \tag{6.12}$$

In this formula, the symbol $\bar{\zeta}$ refers to the uniform value of the zeta potential at the reference state – the ‘drop zeta potential’. This value is linked to the drop charge $4\pi\bar{\sigma}$ via the relation $\bar{\sigma} = 2 \sinh(\bar{\zeta}/2)$: see (5.5) and (6.1).

We recall that (6.12) has been derived by applying a weak-field linearization to a macroscale description valid in the thin-double-layer limit. As discussed in § 1.2,

Ohshima *et al.* (1984) calculated the drop mobility for arbitrary Debye thickness, starting from the linearized formulation appropriate to weak fields. For thin double layers, the mobility was found to approach the limit

$$\frac{\sinh(\bar{\zeta}/2)}{1 + \frac{3}{2}\mu + 8\alpha \cosh(\bar{\zeta}/2)\sinh^2(\bar{\zeta}/4)} \quad (6.13)$$

(their equation (72) in the present notation), which differs from (6.12).

The difference between (6.12) and (6.13) appears in the last term of the denominator, associated with surface conduction (Ohshima *et al.* 1984). Resolving this discrepancy requires a careful inspection of the salt transport. Similarly to all other dependent variables in the weak-field scheme of Ohshima *et al.* (1984), salt concentration is represented as the sum of an equilibrium distribution, valid in the absence of an applied field, and a small $O(\beta)$ perturbation. (Ohshima *et al.* 1984 actually solve for the chemical potentials of the ionic species, and do not explicitly consider the salt concentration; this technical aspect is however irrelevant to the present discussion.) Beyond the Debye layer, this equilibrium distribution approaches unity exponentially rapidly. According to our solution, owing to the inherent strong advection, the bulk salt is constrained to a unity value (irrespective of field strength).

The non-zero bulk-salt perturbation implicit in the scheme of Ohshima *et al.* (1984) can be traced back to the order at which the two limits (thin double layer and weak field) are calculated. When taking first $\beta \rightarrow 0$ for δ fixed the term that represents the advection of that perturbation becomes $O(\beta^2)$ and is therefore *a priori* absent from the linearized scheme of Ohshima *et al.* (1984). Effectively, the salt perturbation in Ohshima *et al.* (1984) is therefore governed by a diffusive process in the bulk, driven by the salt flux (4.37) from double layer (which is $O(\beta)$ in the scheme of Ohshima *et al.* 1984). Indeed, when the homogenizing role of advection is overlooked, this flux would appear to penetrate the bulk, rather than being accommodated within a diffusive boundary layer. With a non-uniform salt perturbation in the bulk, the mobility in Ohshima *et al.* (1984) is apparently affected by diffuso-osmotic slip, which is absent in our leading-order scheme. This leads to the difference in the mobility expressions.

The limits $\delta \ll 1$ and $\beta \ll 1$ are not interchangeable. The correct limit process for a specific problem depends upon the relative smallness of δ and β . Since the advection term outside the Debye layer is of order $\beta\delta^{-1}$ (see (2.3) and (3.1), and recall that α is $O(1)$), the limit process of Ohshima *et al.* (1984) is technically valid for very weak fields, i.e. $\beta \ll \delta \ll 1$. Practical experiments do not conform to this limit, since drop motion is then virtually indiscernible; rather, in typical experiments involving thin double layers, the relevant values correspond to the limit $\delta \ll \beta$, addressed in the present paper.

On top of the above quantitative estimates, there are other reasons suggesting that the limit process considered in the present paper is preferable. The singular limit $\delta \ll 1$ represents a conceptual spatial decomposition of the fluid domain, suggesting that it should precede the weak-field limit – essentially a regular perturbation. The order by which these two limits are taken here is also consistent with typical experimental procedure, where one first sets the salt concentration (thereby fixing the Debye thickness) and only then applies a voltage source.

In the small- $\bar{\zeta}$ limit (6.12) and (6.13) coincide, yielding the mobility

$$\frac{\bar{\zeta}}{2 + 3\mu}. \quad (6.14)$$

In this limit the surface conduction mechanism is negligible, hence the double limit $\delta \ll 1$ and $\beta \ll 1$ is commutative.

Drop electrophoresis in the thin-double-layer limit was recently discussed by Pascall & Squires (2011) using an intuitive approach limited to both weak fields and small zeta potentials. Their mobility expression (7.18) consists of two terms. In the present notation their first term, $O(\delta^{-1}\beta)$, agrees with the above degenerate small- ζ limit (6.14) of both (6.12) and (6.13); their second term is higher order in δ , namely $O(\delta^0\beta)$. Incorporation of such terms in a weak-field approximation – which altogether neglects terms quadratic in β – is rather dubious. As already explained, the proper limit describing typical experiments is $\delta \ll \beta$, implying $\beta \ll \delta^{-1}\beta^2$; but these larger $O(\delta^{-1}\beta^2)$ terms are neglected at the outset when starting from a weak-field approximation.

6.2. Comparison with Levich (1962)

Remarkably, our weak-field approximation (6.10) agrees with that obtained from the Frumkin–Levich model. The analysis of Frumkin (1946) and Levich (1962), starting from a linearized weak-field model, is different from the present one. Thus, it does not consider the Debye-layer structure. Rather, this layer is effectively represented as an interface between the drop and the bulk electrolyte. The dynamic macroscale effects of the double layer are accordingly embodied in an apparent interfacial tension varying with the local bulk potential according to the Lippmann–Helmholtz relation. Furthermore, their analysis does not address the issue of salt transport. It is therefore desirable to rationalize the fortuitous agreement of the final result.

Formally, the derivation of the electrophoretic velocity in Levich (1962) hinges upon three key elements. The first is the use of Laplace’s equation in the statement of the problem governing the bulk electric potential. While this is not justified by Levich (1962), our asymptotic analysis reveals that applicability of Laplace’s equation only follows from the dominance of salt advection in the bulk. The second is an inhomogeneous Neumann condition, also governing the electric potential. This condition represents the surface divergence of the advective Debye-layer currents (see (6.4)). As explained by Levich (1962), this effective condition does not depend upon the Debye-layer structure because of the uniformity of the tangential velocity across this layer.

The third element in Levich (1962) is the representation of the shear-stress discontinuity in the macroscale dynamic boundary condition through a Lippmann term. This is equivalent to the term representing the stress jump in (5.9). Indeed, with $d\zeta = -d\varphi$ (see (5.6)) the present term is provided by the tangential derivative of $-8\sinh^2(\zeta/4)$, the latter quantity already known to play the role of an electro-capillary deviation of the effective interfacial tension from an equilibrium value, see (4.53). When linearized for weak applied fields, this quantity degenerates to that postulated by Levich (1962).

Some of the literature implies that the Frumkin–Levich analysis is limited to small zeta potentials. For example, (2.5) of Pascall & Squires (2011), linear in the zeta potential, is presented as the mobility derived by that analysis, while in fact it is a linearization of the original result given in both Frumkin (1946) and Levich (1962). This confusion may be related to the conclusion of Ohshima *et al.* (1984) that ‘the theory of Levich and Frumkin for the electrophoresis and sedimentation of mercury drops is valid only for very small ζ ...’. This conclusion is based upon comparison with their mobility prediction; in view of the above discussion in § 6.1, this statement is unwarranted.

Levich (1962) also obtained a macroscale expression for the normal-stress jump across the effective interface. To compare that expression with the present model, we note that in our weak-field terminology, the variable ζ appearing in (4.52) needs to be replaced here by $\bar{\zeta} + \beta\zeta'$. The term $16\sinh^2(\zeta/4)$ appearing in (4.52) therefore reads

$$16\sinh^2\frac{\bar{\zeta}}{4} + 4\beta\zeta' \sinh\frac{\bar{\zeta}}{2} + O(\beta^2). \quad (6.15)$$

The first term (6.15) is uniform and does not affect deviations from spherical shape. The second term represents the product of local curvature, 2, reference Debye-layer charge, $-2\sinh(\bar{\zeta}/2)$, and electric-potential perturbation, $\beta\varphi' = -\beta\zeta'$; it is equivalent to the expression obtained by Levich (1962) via thermodynamic reasoning. Calculation of the radial-stress jump (4.52) at $O(\beta)$ using the latter term and the velocity fields (6.8)–(6.9) yields a nil result. Thus, as already noted by Levich (1962), the jump in the normal stress does not lead to a deviation from a spherical shape. This should not be expected to hold outside the linear régime.

7. Discussion

We have constructed a macroscale description of electrokinetic flows about a perfectly conducting drop in the thin-double-layer limit $\delta \ll 1$, where the double-layer physics is embodied in effective boundary conditions. Our model, derived from ‘first principles’, is restricted to neither small zeta potentials nor weak applied fields. The distinction between free and solid surfaces is rooted in the microscale dynamic boundary conditions (e.g. pointwise continuity of shear stress). Moreover, since unlike a solid particle this surface is mobile, the electrolyte velocity does not vanish there.

In standard thin-double-layer descriptions of electrokinetic flows, Coulomb body forces drive intense velocity gradients across the narrow Debye layer, giving rise to asymptotically large Newtonian shear stress within the electrolyte phase. Normally, this stress is balanced by a comparable Maxwell stress, whereby the fluid velocity is characterized by the Maxwell scale v^* defined in (2.1). When the drop is highly conducting, however, the tangential electric field vanishes and the Maxwell traction on its surface is purely normal, resulting in an essentially new scaling. This is the limit considered here.

In the new asymptotic structure corresponding to this limit the fluid velocity is enhanced to the larger scale $\delta^{-1}v^*$ provided in (5.1). At this asymptotic order, the fluid velocity does not vary across the Debye layer. Nevertheless, owing to surface curvature, this velocity is associated with a tangential-stress contribution comparable to the stress resulting from transverse gradients of the velocity correction; this allows a dominant stress balance even in the absence of Maxwell stresses. The drop-phase shear stress may also enter this leading-order balance: while no double layer is formed on the drop side of the interface, velocity continuity there mandates large $O(\delta^{-1}v^*)$ velocities varying on the drop scale. The new structure implies a radical departure from conventional slip-driven electro-osmotic flows to a different régime, where electrokinetic flows are driven by interfacial shear.

Our starting point at the microscale level is the standard electrokinetic model. In the physicochemical modelling of the drop we follow Ohshima *et al.* (1984), describing the drop as an ideally polarizable (no chemical reactions) perfectly conducting (uniform electric potential) medium. Drop-phase charge is thus confined to the interface, its total amount being an invariant of the problem. This is the natural model for describing metal drops.

Exploiting the thinness of the double layer we employ matched asymptotic expansions to derive a coarse-grained description of the problem. The unique features of this macroscale model, which distinguish it from those describing flows about solid surfaces (Yariv 2010a; Schnitzer & Yariv 2012c), stem from the above-mentioned large velocity scaling. In the electro-neutral bulk the salt concentration is rendered uniform by the strong advection of salt from the homogeneous far field. The dominance of advection in the bulk is accompanied by strong tangential fluxes within the Debye layer. As these ‘surface’ currents are generally non-uniform, they give rise to transverse ionic fluxes. The transverse flux of charge is manifested by a novel inhomogeneous Neumann condition governing the electric potential, replacing the standard homogeneous Neumann condition in ‘conventional’ electrokinetic flows (Yariv 2010a). The transverse flux of salt, on the other hand, is incompatible with the homogeneous distribution in the bulk. This necessitates an intermediate diffusive boundary layer over which salt relaxation takes place.

In a sense, the present dominance of advection in the Debye-layer transport represents an effective ‘surface conduction’ mechanism at moderate zeta potentials. We have already encountered similar ‘zero-Dukhin-number’ phenomena in the context of other thin-double-layer problems, namely electro-viscous effects at large Péclet numbers (Yariv *et al.* 2011) and particle electrophoresis under strong fields (Schnitzer & Yariv 2012d). Here surface conduction at moderate zeta potentials is inherent in the problem, being imposed by neither by large ambient velocities (as in Yariv *et al.* 2011), nor by strong applied fields (as in Schnitzer & Yariv 2012d).

Surface conduction is traditionally associated with a non-vanishing Dukhin number defined as the ratio of surface-to-bulk conductivities (Dukhin 1993; Lyklema 1995). In the common class of problems concerning electrokinetic transport about dielectric solids, and in the absence of anomalous conduction behind the slip plane, this number scales as the product of δ and an exponential of ζ (cf. (4.35) *et seq.*). Obviously, this ‘conventional’ Dukhin number, which is vanishingly small in the present analysis limited to moderate zeta potentials, does not represent the unique advective mechanism of surface conduction in the present free-surface problem. In view of this one may attempt to define a ‘modified Dukhin number’ (see Khair & Squires 2009a,b) more representative of the physical mechanisms of ionic transport actually involved. From (5.4) $\alpha\sigma$ seems to represent the ratio of surface-to-bulk conductivities. The inherent non-uniformity of σ suggests that we should instead take $\alpha\bar{\sigma}$ (see (5.12)) as the definition of that modified Dukhin number; furthermore, within the framework of the present assumptions the latter is invariably $O(1)$. Note, however, that the anticipated large variations of σ under an applied field which is not weak render questionable the usefulness of the latter choice as well. Moreover, when $\bar{\sigma} = 0$ (i.e. for an uncharged drop), the surface-conduction magnitude is essentially field dependent through a nonlinear charging process (cf. Schnitzer & Yariv 2012b). Finally, as our analysis is limited to moderate zeta potentials, we do not know what the scaling of the conductivity ratio at larger potentials (due to either large drop charge or applied field) is. Thus, no useful definition of a modified Dukhin number seems feasible here.

Perhaps the key feature in the macroscale description is the appearance of a discontinuity in the effective tangential-stress condition (5.9). On the microscale, this discontinuity originates from the excess shear, driven by Coulomb body forces within the narrow Debye layer. On the macroscale level, this jump condition marks a fundamental transition from slip-driven to shear-driven electrokinetic flows. In fact, the present shear mechanism is remarkably similar to that in Marangoni-type flows (Leal 2007). It must be emphasized that, in contrast to the thermodynamic approach of

Levich (1962), the stress jump in the present derivation is a direct consequence of the transition from the exact microscale description (where the surface tension is uniform) to the macroscale one.

The resulting macroscale model, albeit nonlinear, is substantially simpler than the original microscale model. The removal of scale disparity inherent in the latter facilitates numerical solutions using standard techniques. Since nonlinearity appears only through the effective boundary conditions, a numerical solution would be straightforward using eigen-function expansions (see Yariv 2008; Yariv & Davis 2010). In principle, such a numerical solution would provide the drop velocity \mathcal{U} as a function of the applied field β and the drop charge $4\pi\bar{\sigma}$. The formulation of the problem in terms of the latter parameter represents its fundamental role in the present physical model. The zeta potential is generally non-uniform and cannot play a similar role.

An analytic solution is obtained for the linearized system governing weak-field electrophoresis, $\beta \ll 1$, wherein drop velocity scales as β . In this case, the electrophoretic velocity (6.10) may be expressed through an effective ‘drop zeta potential’ representing the uniform value of ζ at the equilibrium reference state corresponding to $\beta = 0$, see (6.12). Note that the mobility \mathcal{U}' attains a maximum at $\bar{\sigma} = \sqrt{(2 + 3\mu)/\alpha}$; this corresponds to an $O(1)$ value of the reference zeta potential. As in the classical analysis of O’Brien & Hunter (1981), the appearance of a mobility maximum is related to non-uniform Debye-layer currents. In their analysis, these currents are associated with finite Dukhin numbers, hence the mobility maximum appears at a zeta potential that depends upon the Debye thickness. Here, however, the ‘surface-conduction’ mechanism is an essentially advective one, related to the large velocities involved, and accordingly has already emerged at moderate zeta potentials.

The dimensional counterpart of (6.10) is obtained via multiplication of \mathcal{U}' by the product of the velocity scale $\delta^{-1}v^*$, provided in (5.1), with β . Since, βv^* is the Smoluchowski scale v_S^* , defined in (1.1), this product is simply the Frumkin–Levich scale $\delta^{-1}v_S^*$. In terms of the primitive quantities of the problem, this scale is (cf. (5.1))

$$\frac{E^* a^*}{\mu^*} (2\epsilon^* k^* T^* c^*)^{1/2}. \quad (7.1)$$

In the weak-field limit, the electrophoretic velocity is accordingly linear in drop size.

The mobility obtained by the present scheme differs from that calculated by Ohshima *et al.* (1984). Careful inspection reveals that the two limits involved in the mobility calculation, namely thin double layers and weak fields, do not commute. Unsurprisingly, the failure in interchanging the order of these limits is related to the large velocities involved in electrokinetic flows about conducting drops in the thin-double-layer limit. Thus, the present limit process $\delta \ll \beta \ll 1$ represents convection-dominated salt transport in the bulk as opposed to the diffusion-governed process represented by the limit $\beta \ll \delta \ll 1$ implicit in Ohshima *et al.* (1984). Considering typical values of δ and β in concrete systems, the former is more representative of realistic scenarios. For small zeta potentials, the two double limits result in an identical mobility, namely (6.14).

Formally, the mobility decays at sufficiently large drop charge (or, equivalently, zeta potential) in the reference state, see (6.10)–(6.12). We expect the true decay rate at large zeta potentials to be even larger because of the suppressing role of ‘classical’ surface conduction, associated with the intensification of counter-ion concentration near the surface. This mechanism, which becomes quite complex in the nonlinear régime (Schnitzer & Yariv 2012c), has not been taken into account in our model.

Another formal limit, also predicting vanishing mobility, is that of relatively large drop-phase viscosity, $\mu \gg 1$. In that limit one might expect to retrieve the mobility expression for a chemically-inert conducting solid particle (Yariv 2008). The latter quantity is however of smaller asymptotic order in δ and cannot be discerned in the present analysis: in fact, the same applies to all slip-driven electrokinetic effects.

The macroscale thin-double-layer description of electrolyte drops in the spirit of the present methodology constitutes a desirable extension. This is a challenging goal since the modelling of such drops is considerably more complicated. Until this extension is accomplished, the present model may under certain limits be applicable to electrolyte drops. Thus, the pioneering weak-field analysis of this problem (Baygents & Saville 1991a) suggests that when the ionic concentration within the drop is much higher than that within the surrounding liquid the drop approximates a perfect conductor. Such approximations are in fact widely used in the related fields of electrohydrodynamics (Tseluiko *et al.* 2008) and electrowetting (Mugele & Baret 2005).

Finally, it is important to note that the Frumkin–Levich mobility, which agrees with our weak-field prediction, was confirmed by ingenious experiments (Levich 1962). The present paper will hopefully stimulate further experiments, as well as complementary numerical solution of the present macroscale model, which would help illuminate the nonlinear drop behaviour under stronger applied fields.

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Appendix. Diffusive boundary layer: scaling and analysis

We assume without loss of generality that $\bar{\sigma} > 0$, whereby $\mathcal{U} > 0$ as well. (The case $\bar{\sigma} < 0$ is readily treated using symmetry arguments.) Since in the drop-fixed reference system the incident flow is in the negative- \hat{i} direction, we employ the plausible assumption that

$$\tilde{v}_{-1}(\theta) > 0 \quad \text{for } 0 < \theta < \pi. \quad (\text{A } 1)$$

This is certainly true for weak fields, wherein (see (6.8))

$$\tilde{v}_{-1} = \frac{3}{2}\beta\mathcal{U}'\sin\theta. \quad (\text{A } 2)$$

(It may well be that (A 1) is satisfied as a consequence of the open-streamline structure, assumed in § 3.2.)

We employ the coordinate transformation $(\dot{Z}, \theta) \rightarrow (\eta, \theta)$, wherein

$$\eta = \sqrt{\alpha}\dot{Z}\tilde{v}_{-1}(\theta)\sin\theta \quad (\text{A } 3)$$

is proportional to the local stream function. Defining the reduced concentration $g(\eta, \theta)$ by

$$\dot{C}_{1/2}(\dot{Z}, \theta) = 4\alpha g(\eta, \theta), \quad (\text{A } 4)$$

we find that it satisfies the diffusion-type equation

$$\frac{\partial g}{\partial \theta} = \tilde{v}_{-1}(\theta)\sin^2\theta \frac{\partial^2 g}{\partial \eta^2}, \quad (\text{A } 5)$$

the Neumann condition

$$\frac{\partial g}{\partial \eta} = \frac{1}{\tilde{v}_{-1}(\theta)\sin^2\theta} \frac{d}{d\theta} \left[\tilde{v}_{-1}(\theta) \sin \theta \sinh^2 \frac{\zeta(\theta)}{4} \right] \quad \text{at } \eta = 0, \tag{A 6}$$

and the requirement of decay at large η .

This linear problem is solved by means of a Fourier cosine transform, defined as

$$G(k, \theta) = \left(\frac{2}{\pi}\right)^{1/2} \int_0^\infty g(\eta, \theta) \cos k\eta \, d\eta. \tag{A 7}$$

Applying (A 7) to (A 5)–(A 6) provides the first-order differential equation

$$\frac{\partial G}{\partial \theta} + k^2 \tilde{v}_{-1}(\theta)\sin^2\theta G = -\left(\frac{2}{\pi}\right)^{1/2} \frac{d}{d\theta} \left[\tilde{v}_{-1}(\theta) \sin \theta \sinh^2 \frac{\zeta(\theta)}{4} \right] \tag{A 8}$$

whose solution is

$$G = A(k)e^{-k^2\xi(\theta)} - \left(\frac{2}{\pi}\right)^{1/2} \int_0^\theta \frac{d}{dt} \left[\tilde{v}_{-1}(t) \sin t \sinh^2 \frac{\zeta(t)}{4} \right] e^{k^2[\xi(t)-\xi(\theta)]} dt, \tag{A 9}$$

in which

$$\xi(\theta) = \int_{\pi/2}^\theta \tilde{v}_{-1}(t) \sin^2 t \, dt. \tag{A 10}$$

In view of (A 1), $\xi(\theta)$ is a monotonically increasing function for $0 < \theta < \pi$. Thus, the second term in (A 9) decays for large k . On the other hand, since $\xi(\theta) < 0$ for $0 < \theta < \pi/2$, the exponent in the first term of (A 9) diverges in that limit. We therefore find that $A = 0$. Employing the inverse transform and reverting to the original variables then yields the requisite salt profile

$$\begin{aligned} \dot{C}_{1/2} = & -\frac{4\alpha}{\pi^{1/2}} \int_0^\theta [\xi(\theta) - \xi(t)]^{-1/2} \\ & \times \frac{d}{dt} \left[\tilde{v}_{-1}(t) \sin t \sinh^2 \frac{\zeta(t)}{4} \right] \exp \left\{ -\frac{\alpha \dot{Z}^2 \tilde{v}_{-1}^2(\theta) \sin^2 \theta}{4[\xi(\theta) - \xi(t)]} \right\} dt. \end{aligned} \tag{A 11}$$

As a specific illustration, consider the weak-field limit $\beta \ll 1$, where (A 2) implies

$$\xi(\theta) = -\frac{3}{2}\beta \mathcal{U}'\lambda(\theta) \tag{A 12}$$

in which $\lambda(\theta) = \cos \theta - (1/3)\cos^3\theta$. Then,

$$\dot{C}_{1/2} = -\alpha \left(\frac{96\beta \mathcal{U}'}{\pi}\right)^{1/2} \sinh^2 \frac{\bar{\zeta}}{4} \int_0^\theta \frac{\sin t \cos t}{\sqrt{\lambda(t) - \lambda(\theta)}} \exp \left\{ -\frac{3\alpha\beta \dot{Z}^2 \sin^4 \theta}{8[\lambda(t) - \lambda(\theta)]} \right\} dt, \tag{A 13}$$

in which $\bar{\zeta}$ denotes the reference zeta potential at the unperturbed state $\beta = 0$.

Note that the fluxes responsible for the generation of the diffusive layer are antisymmetric in the weak-field limit, varying as $\cos \theta$: see (4.45) and (A 2). Because of the biasing role of advection, however, that antisymmetry is not preserved in the diffusive-layer structure. Indeed, while $\dot{C}_{1/2}$ approaches a finite values as $\theta \rightarrow 0$, it diverges as $\theta \rightarrow \pi$. This divergence may, in turn, suggest the formation of a salt wake (Leal 2007).

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