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Nonlinear electrophoresis at arbitrary field strengths: small-Dukhin-number analysis

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Smoluchowski's formula for thin-double-layer electrophoresis does not apply for highly charged particles, where surface conduction modifies the electrokinetic transport in the electro-neutral bulk. To date, systematic studies of this nonzero Dukhin-number effect have been limited to weak fields. Employing our recent macroscale model [O. Schnitzer and E. Yariv, "Macroscale description of electrokinetic flows at large zeta potentials: Nonlinear surface conduction," *Phys. Rev. E* **86**, 021503 (2012)], valid for arbitrary Dukhin numbers, we analyze herein particle electrophoresis at small (but finite) Dukhin numbers; valid for arbitrary fields, this asymptotic limit essentially captures the practical range of parameters quantifying typical colloidal systems. Perturbing about the irrotational zero-Dukhin-number flow, we derive a linear scheme for calculating the small-Dukhin-number correction to Smoluchowski's velocity. This scheme essentially amounts to the solution of a linear diffusion–advection problem governing the salt distribution in the electro-neutral bulk. Using eigenfunction expansions, we obtain a semi-analytic solution for this problem. It is supplemented by asymptotic approximations in the respective limits of weak fields, small ions, and strong fields; in the latter singular limit, salt polarization is confined to a diffusive boundary layer. With the salt-transport problem solved, the velocity correction is readily obtained by evaluating three quadratures, corresponding to the contributions of (i) electro- and diffuso-osmotic slip due to polarization of both the Debye layer and the bulk; (ii) a net Maxwell force on the electrical double layer; and (iii) Coulomb body forces acting on the space charge in the "electro-neutral" bulk. The velocity correction calculated based upon the semi-analytic solution exhibits a transition from the familiar retardation at weak fields to velocity enhancement at moderate fields; this transition is analytically captured by the small-ion approximation. At stronger fields, the velocity correction approaches a closed-form asymptotic approximation which follows from an analytic solution of the diffusive boundary-layer problem. In this régime, the correction varies as the 3/2-power of the applied field. Our small-Dukhin-number scheme, valid at arbitrary field strengths, naturally lends itself to a tractable analysis of nonlinear surface-conduction effects in numerous electrokinetic problems. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4902331>]

I. INTRODUCTION

A. Background

Smoluchowski's celebrated electrophoresis formula predicts a particle velocity linear in both the applied-field magnitude and zeta potential.^{1,2} The derivation of this formula hinges on the prevalent assumption that the Debye thickness is small compared with particle size; under these conditions, the formula holds universally for particles of arbitrary shape and size.³ Smoluchowski's formula is useful in estimating zeta potentials from mobility measurements.^{4,5} These predictions are

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of great utility as the zeta potential is related to the surface charge of the particle⁶ whose value is important in many aspects of colloid science, such as in predicting the stability of solutions.

Notwithstanding its fundamental role, it is well known that Smoluchowski's formula is invalid for highly charged particles.⁷ As originally explained by Dukhin and coworkers,^{8,9} the high surface charge results in an exponential amplification of the counterion concentration near the surface, enabling significant ionic currents through the diffuse portion of the double layer. This "surface conduction" mechanism affects the dominant electrokinetic transport through counterion exchange between the diffuse-charge ("Debye") layer and the surrounding electro-neutral bulk. The electrophoretic velocity of the particle is accordingly modified. Employing a weak-field linearization, O'Brien and coworkers calculated the resulting electrophoretic velocity, which turns out smaller than the Smoluchowski value.^{10,11}

Formally speaking, appreciable surface conduction requires zeta potentials which are logarithmically large with respect to the small double-layer thickness, i.e., non-negligible Dukhin numbers [cf. (29) and (34)]. Practically, this implies rather moderate zeta-potential values even at very thin double layers, suggesting in turn that surface conduction, absent in Smoluchowski's picture, actually plays a role in many practical systems. It is unsurprising then that the papers of O'Brien and his coworkers have attracted significant attention. Indeed, following these papers, surface conduction effects were analyzed in the context of numerous electrokinetic phenomena, including electro-viscous forces,^{12,13} dielectric enhancement,^{14,15} and diffusio-phoresis.¹⁶ More recent analyses, by Khair and Squires, are motivated by microfluidic applications; these address patterned surfaces,¹⁷ surface-charge discontinuities¹⁸ (see Ref. 19), and the arrest of flow amplification triggered by the combination of hydrodynamic and electrokinetic slip.²⁰ An important consequence of surface conduction is the breakdown of Morrison's prediction of a shape-independent electrophoretic mobility. Unsurprisingly then, the work of O'Brien and coworkers was also followed by the analyses of both specific^{21,22} and generic²³ non-spherical geometries.

B. Nonlinear macroscale model

It is important to note that all of the above-mentioned papers are restricted to weak fields. In particular, both the models of O'Brien and coworkers and their numerous extensions yield electrophoretic velocities which are linear in the field. This is a serious limitation on the applicability of these models to practical systems, where the potential drop associated with the applied field is not necessarily small when compared with the thermal voltage [about 25 mV for a univalent electrolyte—see (2)]. In that respect, it is worth recalling that Smoluchowski's formula, despite being linear in the applied field, is *not* restricted to weak fields.²⁴

In principle, one can investigate surface-conduction effects beyond weak fields by numerically solving the standard "microscale" electrokinetic model (see Refs. 24 and 25). Because of the scale disparity existing in the thin-double-layer limit, however, this is a formidable task. The alternative is the extension of O'Brien's generic thin-double-layer analysis¹¹ beyond the weak-field régime via the construction of a generic "macroscale" model of electrokinetic flows about highly charged surfaces, where the electrokinetic processes occurring within the narrow diffuse-charge layer appear as effective boundary conditions. This procedure effectively removes the scale disparity.

Such a macroscale model, valid for arbitrary field strengths, was recently provided by Schnitzer and Yariv²⁴ (it is denoted hereafter the SY model). As this model preserves the inherent nonlinearity of the microscale description, it cannot be solved in closed form even for the simplest problem of spherical-particle electrophoresis. Nonetheless, the effective removal of the scale disparity allows for the use of various approximation methods, or, alternatively, the use of standard numerical schemes.

The SY model was used by Schnitzer *et al.*²⁶ who revisited the weak-field limit of particle electrophoresis. Going beyond the linear approximation of O'Brien and Hunter,¹⁰ this weakly nonlinear analysis yields a correction term, proportional to the applied-field cubed (improving and correcting earlier *ad hoc* expressions.²⁷) This is the first step in understanding nonlinear electrophoretic response.

C. Small Dukhin numbers

As we have already mentioned, the weak-field approximation is simply inadequate in many practical applications. It may therefore appear that the next logical step, following the weakly nonlinear analysis of Ref. 26, would be a numerical solution of the SY model. Initial attempts in that direction are actually presented in Ref. 26, where the weakly nonlinear analysis was corroborated by a finite-difference solution.

There is however another route. When considering typical zeta potentials of highly charged colloids, one readily notices that the corresponding Dukhin numbers are still relatively small.²⁸ This suggests an asymptotic analysis of the SY model in the limit of small (but nonzero) Dukhin number, allowing for *arbitrary* field strengths. This limit, which covers a significant practical range of the governing parameters, is analytically tractable. The scheme proposed herein thus entails a linearization of the SY model about the zero-Dukhin-number solution (which coincides with Smoluchowski's intuitive thin-double-layer picture). This procedure should be contrasted with the familiar weak-field analyses,^{10,11} where the linearization is carried about the equilibrium configuration in the absence of an applied field. Thus, while the electrophoretic velocity predicted by these analyses is linear in the applied field [and generally nonlinear in the Dukhin number, see (68)], the present scheme provides a velocity correction to Smoluchowski's velocity which is linear in the Dukhin number but is, in general, nonlinear in the field.

Earlier attempts to exploit the smallness of the Dukhin number have appeared in several papers by the Ukrainian school.^{29–31} Unlike the present analysis, these were not based upon a macroscale model. Moreover, while the present study allows for an arbitrary field magnitude, these papers appear to focus upon the respective limits of weak and strong fields. We do not fully understand the key assumptions underlying these papers, nor the resulting analyses. While certain elements in these analyses appear similar to those in the present contribution, the resulting approximations do not coincide.

The rest of the paper is structured as follows. In Sec. II, we describe the physical problem and the governing microscale model. Using the SY paradigm, we formulate in Sec. III the corresponding macroscale problem. In Sec. IV, we address the limit of small Dukhin numbers, providing a linear scheme for correcting Smoluchowski's formula. In Sec. V, we present a semi-analytic solution of this linear problem. In Sec. VI, we derive approximate solutions in the limits of weak fields, small ions, and strong fields. We discuss the results in Sec. VII. Appendix A outlines the details of the semi-analytic solution. Appendix B presents the singular boundary-layer analysis of the strong-field limit.

II. PROBLEM FORMULATION

The problem we consider is depicted in Fig. 1. A dielectric spherical particle (radius a^*) is suspended in a symmetric (ionic valencies $\pm z$) binary electrolyte (viscosity μ^* , permittivity ϵ^*). The diffusivities of the cations and anions are $D^{*\pm}$. The particle is uniformly charged, say with a surface charge density σ^* (which, with no loss of generality, is taken to be positive). Due to this immobile charge layer, a Debye layer of a characteristic thickness $1/\kappa^*$ is formed, with κ^* defined by

$$\kappa^{*2} = \frac{2ze^*c^*}{\epsilon^*\varphi^*} \quad (1)$$

in which c^* is the equilibrium ion concentration and

$$\varphi^* = \frac{k^*T^*}{ze^*} \quad (2)$$

is the thermal voltage (k^*T^* being the Boltzmann temperature and e^* the elementary charge). Far away from the particle, both species are at equilibrium, possessing the uniform concentration c^* . A steady and uniform electric field of magnitude E^* is externally applied, resulting in the electrophoretic motion of the particle. Our goal is to calculate the ensuing particle velocity U^* relative to the otherwise quiescent liquid.

The starting point of the analysis is the "exact" microscale electrophoresis problem, based upon the standard electrokinetic model. We employ the dimensionless formulation of Ref. 24, where length variables are normalized by a^* , the electric potential φ by the thermal voltage φ^* ,

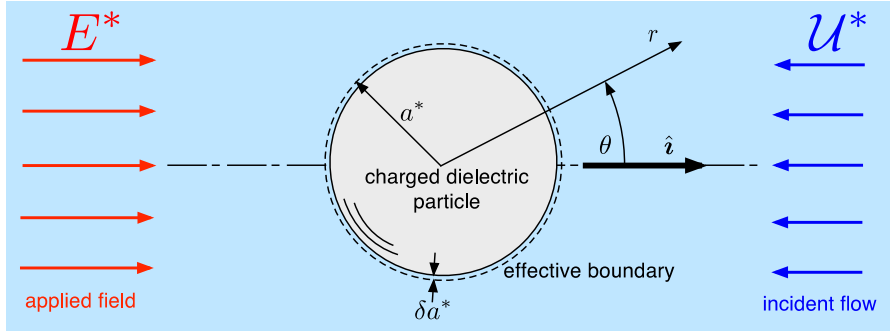


FIG. 1. Schematics of the problem: a dielectric spherical particle possessing a uniform surface charge density is suspended in an electrolyte solution and exposed to a uniform electric field of magnitude E^* , resulting in its motion with an electrophoretic velocity U^* . The macroscale boundary conditions of the SY model apply at an effective boundary lying at the outer edge of the electrical double layer.

the fluid velocity \mathbf{u} by $u^* = \epsilon^* \varphi^{*2} / \mu^* a^*$, and stress variables by the Maxwell scale $\epsilon^* \varphi^{*2} / a^{*2}$. The non-dimensionalization procedure results in the following dimensionless groups:

1. The dimensionless Debye thickness

$$\delta = \frac{1}{\kappa^* a^*}. \tag{3}$$

2. The dimensionless surface charge density

$$\sigma = \frac{\sigma^*}{\epsilon^* \kappa^* \varphi^*}. \tag{4}$$

3. The dimensionless applied-field magnitude

$$E = \frac{E^* a^*}{\varphi^*}. \tag{5}$$

4. The ratio γ of the respective dielectric constants in the solid and liquid phases.
5. The ionic drag coefficients

$$\alpha^\pm = \frac{\epsilon^* \varphi^{*2}}{\mu^* D^{\pm*}}. \tag{6}$$

Because of the Stokes–Einstein relation, $D^{\pm*}$ can be expressed as $k^* T^* / \xi^\pm \mu^* l^{\pm*}$, where $l^{\pm*}$ are the effective radii of the ions and ξ^\pm are $O(1)$ shape-dependent numerical coefficients (e.g., 6π for spherical ions). We accordingly find the more fundamental expressions

$$\alpha^\pm = \frac{\xi^\pm l^{\pm*} \epsilon^* \varphi^{*2}}{k^* T^*}, \tag{7}$$

which are linear in the ion size (and independent of μ^*). For typical aqueous solutions,

$$\alpha^\pm \lesssim 0.5. \tag{8}$$

In terms of the above parameters, formulation of the microscale problem is straightforward. The mean (“salt”) ionic concentration c (scaled by c^*) and charge density q (scaled by $2ze^* c^*$) are governed by the Nernst–Planck equations

$$\nabla \cdot (\nabla c + q \nabla \varphi) = \frac{\alpha^+ + \alpha^-}{2} \mathbf{u} \cdot \nabla c + \frac{\alpha^+ - \alpha^-}{2} \mathbf{u} \cdot \nabla q, \tag{9}$$

$$\nabla \cdot (\nabla q + c \nabla \varphi) = \frac{\alpha^+ - \alpha^-}{2} \mathbf{u} \cdot \nabla c + \frac{\alpha^+ + \alpha^-}{2} \mathbf{u} \cdot \nabla q; \tag{10}$$

the electric potential is governed by Poisson’s equation

$$\delta^2 \nabla^2 \varphi = -q; \tag{11}$$

and the flow is governed by the continuity

$$\nabla \cdot \mathbf{u} = 0; \quad (12)$$

and inhomogeneous Stokes

$$\nabla p = \nabla^2 \mathbf{u} + \nabla^2 \varphi \nabla \varphi \quad (13)$$

equations, where p denotes the pressure field.

The preceding equations are supplemented by appropriate boundary conditions. Given the symmetry of the problem, these are naturally provided using particle-fixed spherical coordinates (r, θ, ϖ) , $r = 0$ coinciding with the particle center and $\theta = 0$ in the applied field direction (provided by the unit vector $\hat{\mathbf{i}}$). (All scalar fields and velocity components are independent of ϖ .) At the particle boundary $r = 1$, we impose the no-flux conditions

$$\frac{\partial c}{\partial r} + q \frac{\partial \varphi}{\partial r} = 0, \quad \frac{\partial c}{\partial r} + c \frac{\partial \varphi}{\partial r} = 0; \quad (14)$$

impermeability and no-slip

$$\mathbf{u} = \mathbf{0}; \quad (15)$$

and Gauss's boundary condition

$$\frac{\partial \varphi}{\partial r} = -\delta^{-1} \sigma + \gamma \frac{\partial \varphi_s}{\partial r}, \quad (16)$$

wherein φ_s is the electric potential in the solid particle.³² At large distances from the particle, the ionic concentrations approach their reference value, whereby

$$c \rightarrow 1, \quad q \rightarrow 0; \quad (17)$$

the electric field approaches the uniformly imposed field

$$\varphi \sim -Er \cos \theta; \quad (18)$$

and the velocity field approaches a uniform velocity

$$\mathbf{u} \rightarrow -U \hat{\mathbf{i}}, \quad (19)$$

where $U = U^*/u^*$.

In addition to the above conditions, the pertinent fields must also satisfy the requirement that the total force acting on the particle vanishes. This force is contributed by both Newtonian

$$\mathbf{N} = -p \mathbf{I} + (\nabla \mathbf{u}) + (\nabla \mathbf{u})^\dagger \quad (20)$$

and Maxwell

$$\mathbf{M} = \nabla \varphi \nabla \varphi - \frac{1}{2} \nabla \varphi \cdot \nabla \varphi \mathbf{I} \quad (21)$$

stresses. Because of axial symmetry, it is sufficient to impose the scalar condition

$$\hat{\mathbf{i}} \cdot \oint_{r=1} \hat{\mathbf{n}} \cdot (\mathbf{N} + \mathbf{M}) dA = 0. \quad (22)$$

(The additional requirement of a zero torque is trivially satisfied.) Since the Stokes equation (13) equivalently states that the total stress $\mathbf{N} + \mathbf{M}$ is divergence free, the integral appearing in condition (22) may be evaluated over any closed surface enclosing the particle boundary $r = 1$.

The particle velocity U , appearing in condition (19), is a function of the dimensionless groups (3)–(6).

III. THIN-DOUBLE-LAYER LIMIT: MACROSCALE FORMULATION

In what follows, we consider the thin-double-layer limit

$$\delta \ll 1, \quad (23)$$

where the fluid domain outside the thin Debye layer is approximately electro-neutral. In this limit, we replace the microscale model (9)–(22) by the macroscale SY model, describing the transport in this electro-neutral “bulk.” Hereafter, we accordingly interpret all variables as representing the leading-order terms in their respective asymptotic expansions (in δ) within the bulk. In the thin-double-layer limit (23), it readily follows from (11) that this region becomes electro-neutral at leading order, $q \equiv 0$. The salt- and charge-balance equations (9) and (10) thus become

$$\nabla^2 c = \alpha \mathbf{u} \cdot \nabla c, \quad \nabla \cdot (c \nabla \varphi) = \acute{\alpha} \mathbf{u} \cdot \nabla c, \tag{24}$$

where we define, for convenience,

$$\alpha = \frac{\alpha^+ + \alpha^-}{2}, \quad \acute{\alpha} = \frac{\alpha^+ - \alpha^-}{2}. \tag{25}$$

The flow equations (12) and (13) are unaltered

$$\nabla \cdot \mathbf{u} = 0, \quad \nabla p = \nabla^2 \mathbf{u} + \nabla^2 \varphi \nabla \varphi. \tag{26}$$

(While the bulk is approximately electro-neutral, the asymptotically small volumetric charge density still results in a Coulomb body force in the leading-order momentum balance.²⁴) The far-field conditions are summarized as

$$\varphi \sim -Er \cos \theta, \quad \mathbf{u} \rightarrow -U\hat{\mathbf{i}}, \quad c \rightarrow 1 \quad \text{as} \quad |\mathbf{x}| \rightarrow \infty, \tag{27}$$

wherein \mathbf{x} is a position vector measured from the particle center. While the force-free condition (22) retains its form,

$$\hat{\mathbf{i}} \cdot \oint_{r=1} \hat{\mathbf{n}} \cdot (\mathbf{N} + \mathbf{M}) \, dA = 0, \tag{28}$$

the stresses appearing in (28) are now evaluated at the outer edge of the Debye layer (where $r = 1$ is hereafter reinterpreted), rather than the genuine particle boundary—see Figure 1. In the macroscale description, these two surfaces geometrically coincide. While for weak fields, the “outer” Maxwell-stress contribution to the stress integral trivially vanishes, this is not necessarily the case in general.

The essence of the SY model lies in the effective boundary conditions representing the electrokinetic transport within the Debye cloud. These conditions, replacing the exact conditions (14)–(16), also apply at the outer edge of the thin double layer. The derivation of the SY model allows for the possibility of a highly charged surface, where σ is comparable to δ^{-1} . This is explicit in the appearance of the dimensionless group [see (30)]

$$Du = (1 + 2\alpha^-)\delta\sigma, \tag{29}$$

namely, the Dukhin number. Thus, a zero Dukhin number represents the case where surface conduction is negligible.³³

The effective boundary conditions at the effective boundary $r = 1$ consist of the flux-matching conditions

$$\frac{\partial c}{\partial r} + c \frac{\partial \varphi}{\partial r} = 0, \quad \frac{\partial c}{\partial r} = Du \nabla_s^2 (\varphi - \ln c), \tag{30}$$

where

$$\nabla_s^2 = \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) \tag{31}$$

is the surface-Laplacian operator, together with the slip condition

$$\mathbf{u} = \zeta \nabla_s \varphi - 4 \ln(\cosh(\zeta/4)) \nabla_s \ln c, \tag{32}$$

where

$$\nabla_s = \hat{\mathbf{e}}_\theta \frac{\partial}{\partial \theta} \tag{33}$$

is the surface-gradient operator. The zeta potential ζ appearing in (32) is the leading-order Debye layer voltage; it is given by

$$\sigma = 2\sqrt{c} \sinh \frac{\zeta}{2}, \quad (34)$$

in which the dimensionless charge density σ is defined in (4) and c is evaluated at $r = 1$. Note that the zeta-potential distribution is itself part of the problem.

The two key parameters affecting electrophoresis are clearly the charge density σ and the applied-field magnitude E —no electrophoresis occurs if either of these vanishes. The effect of surface conduction is embodied in the Dukhin number Du , while ionic convection is represented by α and $\acute{\alpha}$. The dimensionless particle velocity u is a function of these five parameters.

IV. SMALL DUKHIN NUMBERS

In what follows, we address the small-Dukhin-number limit³⁴

$$Du \ll 1. \quad (35)$$

A. Zero Dukhin numbers: Smoluchowski's formula

Consider first the solution of the SY model for $Du = 0$, denoted in what follows by a “0” subscript. Conditions (30) become homogeneous

$$\frac{\partial \varphi_0}{\partial r} = 0, \quad \frac{\partial c_0}{\partial r} = 0 \quad \text{at } r = 1, \quad (36)$$

whereby surface conduction is absent. The salt concentration is accordingly uniform, $c_0 \equiv 1$. In the absence of salt polarization, the zeta potential ζ_0 is uniform as well; its value relates to the surface-charge density through (34), giving

$$\sigma = 2 \sinh \frac{\zeta_0}{2}. \quad (37)$$

With a uniform salt, the electrical potential φ_0 satisfies Laplace's equation, see (24). The solution satisfying the homogenous Neumann condition (36) and the large- r approach to a uniform field is

$$\varphi_0 = -E \left(r + \frac{1}{2r^2} \right) \cos \theta. \quad (38)$$

The flow field is governed by the homogenous Stokes equations

$$\nabla \cdot \mathbf{u}_0 = 0, \quad \nabla p_0 = \nabla^2 \mathbf{u}_0, \quad (39)$$

and the standard Helmholtz–Smoluchowski slip condition

$$\mathbf{u}_0 = \zeta_0 \nabla \varphi_0 \quad \text{at } r = 1. \quad (40)$$

Finally, as the Maxwell stresses associated with (38) do not contribute³⁵ to the force-free constraint (28), this constraint simply implies the vanishing of the hydrodynamic force, or, equivalently, the absence of a Stokeslet term in \mathbf{u}_0 .

As is well-known,³ the flow field satisfying the above problem is an irrotational one, namely,

$$\mathbf{u}_0 \equiv \zeta_0 \nabla \varphi_0, \quad p_0 \equiv 0. \quad (41)$$

This field corresponds to the Smoluchowski velocity

$$u_0 = \zeta_0 E. \quad (42)$$

While this zero-Dukhin-number approximation is linear in E , we emphasize that no weak-field linearization is invoked in its derivation.

B. Non-zero Dukhin numbers

For small but finite Du , we linearize about the preceding zero-Dukhin-number solution. Thus, the pertinent fields are expanded as

$$\varphi = \varphi_0 + Du \varphi_1 + \dots, \quad c = 1 + Du c_1 + \dots \quad \mathbf{u} = \zeta_0 \nabla \varphi_0 + Du \mathbf{u}_1 + \dots \quad (43)$$

and

$$p = Du p_1 + \dots \quad (44)$$

With salt polarization, the zeta potential is no longer uniformly distributed. Indeed, from (34), we find the expansion

$$\zeta = \zeta_0 - Du c_1 \tanh \frac{\zeta_0}{2} + \dots, \quad (45)$$

where c_1 is evaluated at $r = 1$. A comparable expansion of the stress tensors and the force-free constraint implies the following expansion of the electrophoretic velocity:

$$\mathbf{u} = \zeta_0 E + Du \mathbf{u}_1 + \dots \quad (46)$$

Our goal is the calculation of the correction \mathbf{u}_1 to Smoluchowski's velocity.

C. Polarization due to surface conduction at $O(Du)$

The salt perturbation is governed by the diffusion–advection equation [see (24)]

$$\nabla^2 c_1 = \alpha \zeta_0 \nabla \varphi_0 \cdot \nabla c_1, \quad (47)$$

together with the boundary condition

$$\frac{\partial c_1}{\partial r} = 3E \cos \theta \quad \text{at } r = 1, \quad (48)$$

obtained by substitution of (38) into (30). In addition, c_1 decays at large distances from the particle [see (27)]

$$c_1 \rightarrow 0 \quad \text{as } |\mathbf{x}| \rightarrow \infty. \quad (49)$$

Noting that φ_0/E is parameter-free, it is advantageous to rewrite (47) as

$$\nabla^2 c_1 = \text{Pe} \nabla(\varphi_0/E) \cdot \nabla c_1, \quad (50)$$

where

$$\text{Pe} = \alpha \zeta_0 E \quad (51)$$

is the effective Péclet number representing the ratio of advection to diffusion at $O(Du)$.³⁰ Equations (48)–(50) imply a solution of the form $c_1 = E f(\mathbf{x}; \text{Pe})$. Since Pe itself depends on E , the polarization is, in general, nonlinear in the applied field.

The electric potential perturbation φ_1 is governed by the equation [see (24)]

$$\nabla^2 \varphi_1 + (1 - \alpha \zeta_0) \nabla \varphi_0 \cdot \nabla c_1 = 0, \quad (52)$$

together with the boundary condition

$$\frac{\partial \varphi_1}{\partial r} = -3E \cos \theta \quad \text{at } r = 1, \quad (53)$$

and the attenuation condition

$$\varphi_1 \rightarrow 0 \quad \text{as } |\mathbf{x}| \rightarrow \infty. \quad (54)$$

Considering c_1 as known, the solution to this problem can actually be bypassed by noting from (50) and (52) that the linear combination

$$c_1 + \frac{\alpha \zeta_0}{1 - \alpha \zeta_0} \varphi_1$$

satisfies Laplace’s equation and can be readily solved for using (48), (49), (53), and (54). This yields

$$\varphi_1 = -\frac{3E(1 - \alpha\zeta_0 - \hat{\alpha}\zeta_0) \cos \theta}{2\alpha\zeta_0} \frac{1}{r^2} - \frac{1 - \hat{\alpha}\zeta_0}{\alpha\zeta_0} c_1. \tag{55}$$

Expression (55) should be handled with care in the limit $\alpha \rightarrow 0$. Since convection is absent from (50) in this limit, c_1 is readily found as the dipole

$$\lim_{\alpha \rightarrow 0} c_1 = -\frac{3E \cos \theta}{2r^2}. \tag{56}$$

The potential φ_1 is then obtained by solving (52) using (56) together with the boundary condition (53) and the far-field decay. This yields³⁶

$$\lim_{\alpha \rightarrow 0} \varphi_1 = E^2 \frac{4r^3 - 1}{8r^4} + \frac{3}{2r^2} EP^{(1)}(\cos \theta) + E^2 \frac{2r - 1 - 2r^3}{4r^4} P^{(2)}(\cos \theta), \tag{57}$$

wherein $P^{(n)}$ is the Legendre polynomial of degree n .

D. Leading order correction to Smoluchowski’s velocity

The $O(\text{Du})$ flow field is governed by the *inhomogenous* Stokes equations

$$\nabla \cdot \mathbf{u}_1 = 0, \quad \nabla p_1 = \nabla^2 \mathbf{u}_1 + \nabla^2 \varphi_1 \nabla \varphi_0, \tag{58}$$

together with the slip boundary condition

$$\mathbf{u}_1 = \zeta_0 \nabla_s \varphi_1 - c_1 \tanh \frac{\zeta_0}{2} \nabla_s \varphi_0 - 4 \ln(\cosh(\zeta_0/4)) \nabla_s c_1, \tag{59}$$

in which the three terms, respectively, represent electro-osmosis due to the action of the perturbed field on the equilibrium charge, electro-osmosis due to the action of the primary field on the perturbed Debye-layer charge, and diffuso-osmosis due to salt polarization. In addition, it satisfies the far-field condition

$$\mathbf{u}_1 \rightarrow -u_1 \hat{\mathbf{i}} \quad \text{as} \quad |\mathbf{x}| \rightarrow \infty. \tag{60}$$

The velocity correction u_1 must be chosen such that the zero-force condition (28) is satisfied at $O(\text{Du})$. At this order, (28) involves both a Newtonian-stress contribution

$$\mathbf{N}_1 = -p_1 \mathbf{l} + \nabla \mathbf{u}_1 + (\nabla \mathbf{u}_1)^\dagger, \tag{61}$$

and a Maxwell-stress contribution

$$\mathbf{M}_1 = \nabla \varphi_0 \nabla \varphi_1 + \nabla \varphi_1 \nabla \varphi_0 - \nabla \varphi_0 \cdot \nabla \varphi_1 \mathbf{l}. \tag{62}$$

Once φ_1 and c_1 are known, the preceding flow problem is self contained. While it may be solved in a rather straightforward manner, such a solution is actually not required as we are only interested in the electrophoretic speed. Thus, employing a method due to Brenner³⁷ (see also Ref. 38) which utilizes the Lorentz reciprocal theorem, we obtain

$$u_1 = \frac{1}{6\pi} \left[\oint_{r=1} dA \hat{\mathbf{n}} \cdot \tilde{\mathbf{N}} \cdot \mathbf{u}_1 + \hat{\mathbf{i}} \cdot \oint_{r=1} dA \hat{\mathbf{n}} \cdot \mathbf{M}_1 + \int_{r>1} dV \tilde{\mathbf{u}} \cdot \nabla \varphi_0 \nabla^2 \varphi_1 \right], \tag{63}$$

where $\tilde{\mathbf{u}}$ is an auxiliary flow field corresponding to pure translation of the particle with unit velocity in the $\hat{\mathbf{i}}$ direction and $\tilde{\mathbf{N}}$ is the corresponding stress tensor. Employing the well-known expressions for these fields³⁹ and using (38), we find that

$$\hat{\mathbf{n}} \cdot \tilde{\mathbf{N}} = \frac{3}{2} \sin \theta \hat{\mathbf{e}}_\theta, \quad \tilde{\mathbf{u}} \cdot \nabla \varphi_0 = E [a(r) + b(r)P^{(2)}(\cos \theta)], \tag{64}$$

in which

$$a(r) = -\frac{1 - r^2 + 4r^5}{4r^6}, \quad b(r) = -\frac{1 - 5r^2 - 2r^3 + 2r^5}{4r^6}. \tag{65}$$

According to the present scheme, evaluation of the velocity correction u_1 amounts to the solution of the diffusion–advection problem (48)–(50) governing the salt perturbation c_1 . With c_1 known, the potential perturbation φ_1 is found through (55). The velocity correction is u_1 then evaluated through (63).

V. SEMI-ANALYTIC SOLUTION

Since the diffusion–advection equation (50) does not possess a closed-form analytic solution, it is solved via a standard expansion in Legendre polynomials. The details of this semi-analytic calculation are provided in Appendix A.

Note that the velocity correction u_1 is a function of E and ζ_0 [the latter being directly related to σ through (37)], as well as the parameters α and $\acute{\alpha}$. In Fig. 2, we present u_1 as a function of E for the typical values $\zeta_0 = 5$ and $\alpha^\pm = 0.25$ (corresponding to $\alpha = 0.25$ and $\acute{\alpha} = 0$). The numerical simulations show a transition from negative values of u_1 at weak fields to positive values at stronger fields. (Because of the logarithmic scale, we employ two separate graphs, showing $-u_1$ at weaker fields and u_1 at stronger fields.) We also notice that the linear dependence upon E at weak fields transforms to a different power law at strong fields.

In what follows, we consider several limiting cases which allow for the derivation of closed-form approximations for the velocity correction. These approximations highlight the above-mentioned trends observed in the semi-analytic solution.

VI. APPROXIMATE EXPRESSIONS FOR THE VELOCITY CORRECTION

As already explained, calculation of u_1 is essentially reduced to solving the diffusion–advection problem (48)–(50) governing c_1 . The solution of that problem depends on the value of the effective

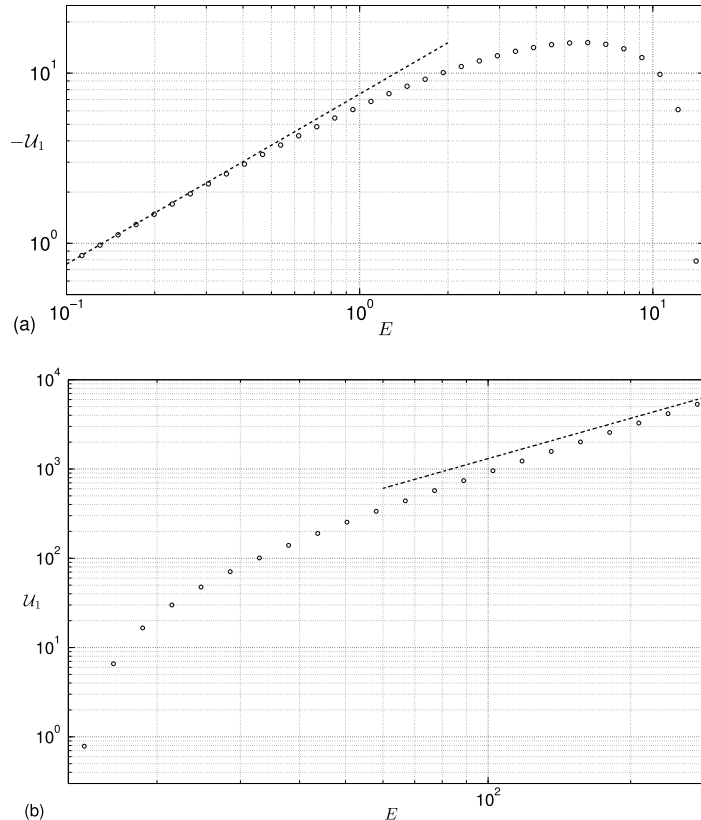


FIG. 2. The velocity correction u_1 as a function of E for $\zeta_0 = 5$ and $\alpha^\pm = 0.25$: (a) $-u_1$ (weaker fields); (b) u_1 (stronger fields). The dashed lines represent the weak-field linearization (67) and strong-field approximation (71).

Péclet number (51). This suggests carrying out asymptotic analyses for small and large Pe. Note that the three parameters forming Pe (namely, α , ζ_0 , and E) also appear independently in the calculation of the potential φ_1 [see (52) and (53)] and then also in the evaluation of u_1 using (63) [see (59)]. Thus, one must be more specific in defining the approximation involved when considering either small or large Péclet numbers.

Hereafter, we keep the zeta potential ζ_0 fixed carrying out the various approximations. Small Péclet numbers are then accordingly realized for either weak fields, $E \ll 1$, or, alternatively, moderate fields with weak ionic convection, $\alpha^\pm \ll 1$ [the latter limit corresponding to small ions, see (7)]. In view of (8), the approximation of large Péclet numbers is unique: it is only realized in the limit of strong fields, $E \gg 1$. We therefore have three separate limits to consider.

A. Weak fields

We first consider the weak-field limit, $E \ll 1$. In this régime, small Péclet numbers are realized [see (51)] whereby convection is absent from the salt balance (50). The salt perturbation is accordingly given by (56). The potential is then immediately obtained from (55)

$$\varphi_1 \sim \frac{3E \cos \theta}{2r^2}. \quad (66)$$

The velocity correction is found by evaluating (63) to leading order, namely, $O(E)$. Only the first term in the right-hand side, corresponding to the slip mechanism, contributes at this order; the second and third terms in the right-hand side of (63) are $O(E^2)$. Moreover, when calculating the slip term using (59), we find that only the first and third terms in that formula contribute at $O(E)$. Thus, substituting (56) and (66) into the slip boundary condition (59), the velocity correction u_1 is evaluated from (63) to be

$$u_1 \sim -[4 \ln \cosh(\zeta_0/4) + \zeta_0] E. \quad (67)$$

As $u_1 < 0$, the first effect of surface conduction is to retard the particle motion. The agreement of the weak-field approximation (67) with the numerical results is clearly seen in Fig. 2.

Of course, the weak-field mobility can be found directly from the macroscale model (24)–(28) *without* the restriction to small Dukhin numbers. Indeed, such a straightforward linearization was carried out in Ref. 24, yielding⁴⁰

$$u \sim \frac{\zeta_0 + \text{Du} [\zeta_0 - 4 \ln \cosh(\zeta_0/4)]}{1 + 2\text{Du}} E \quad (68)$$

(which is equivalent to the expression provided by O'Brien¹¹). At small Du, it is readily verified that the preceding approximation yields (67).

The weak-field approximations (67) and (68) are compared in Fig. 3 which portrays the variation of the electrophoretic mobility u/E as a function of ζ_0 for $\delta = 0.005$ and $\alpha^\pm = 0.25$. [With δ and α^\pm prescribed, the Dukhin number becomes a function of ζ_0 through (29) and (37).] Also shown is Smoluchowski's approximation, linear in ζ_0 , and the numerically calculated mobility based upon the weak-field scheme of O'Brien and White,⁷ valid for arbitrary Debye thickness. Note that Smoluchowski's formula breaks down before approximation (67) does. This is consistent with their formal range of validity, as the former is valid for zero Dukhin numbers while the latter is valid for small Dukhin numbers.

B. Small ions

Small Péclet numbers can also be realized under moderate fields [$E = O(1)$] when α is small, see (51). As is evident from (7), the limit $\alpha \ll 1$ corresponds to small ions. As already seen, in this limit the salt and potential perturbations are respectively given by (56) and (57). Evaluation of the integrals in (63) readily yields

$$u_1 \sim -[4 \ln \cosh(\zeta_0/4) + \zeta_0] E + \frac{2}{21} E^3. \quad (69)$$

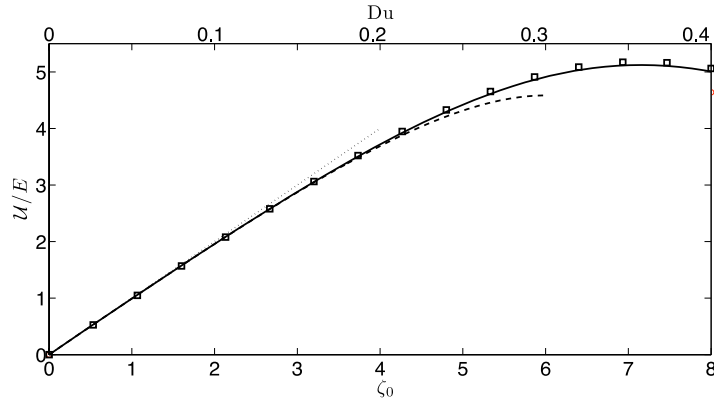


FIG. 3. Comparison of the various weak-field approximations of the electrophoretic mobility as a function of ζ_0 , with $\delta = 0.005$ and $\alpha^\pm = 0.25$: the numerical solution of O'Brien and White⁷ (squares); the finite-Du approximation (68) (solid curve); the small-Du approximation, given by (42) and (67) (dashed curve); and Smoluchowski's solution (dotted line). With δ and α^\pm prescribed, the Dukhin number becomes a function of ζ_0 through (29) and (37) and may accordingly be considered as alternative independent variable: see top abscissa.

In Fig. 4, we compare this approximation with the semi-analytic calculation of u_1 , now performed for $\zeta_0 = 3$ and $\alpha^\pm = 0.01$.

Both Figs. 2 and 4 show a transition from negative to positive values of u_1 . This transition is evident in (69). The first term in this approximation, which corresponds to the slip integral in

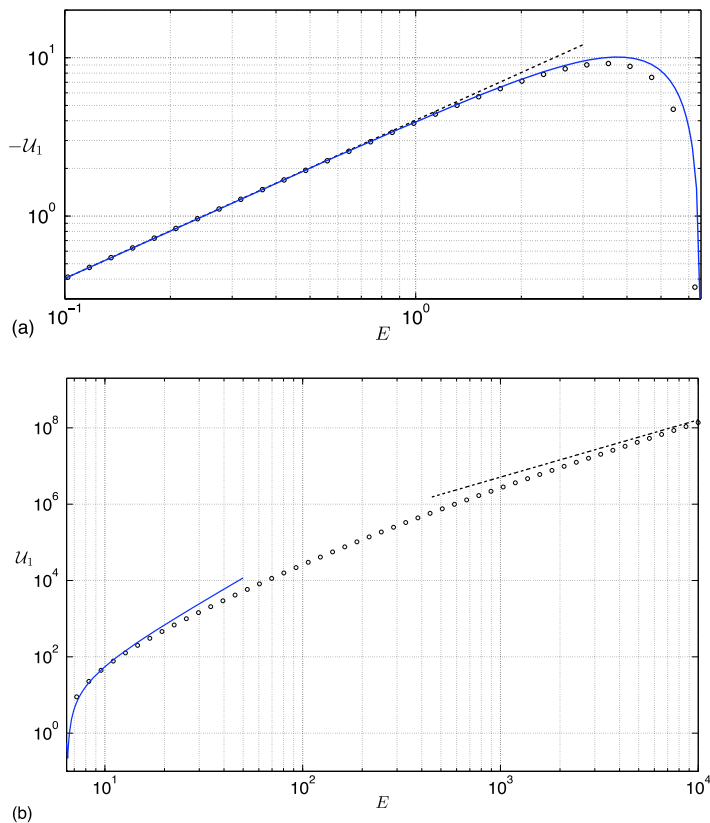


FIG. 4. The velocity correction u_1 as a function of E for $\zeta_0 = 3$ and $\alpha^\pm = 0.01$: (a) $-u_1$ (weaker fields); (b) u_1 (stronger fields). The solid line is the small-ion approximation (69). Also shown (dashed) are the weak-field linearization (67) and strong-field approximation (71).

(63), is linear in E , and coincides with the weak-field approximation. As already mentioned, this term is negative, representing particle retardation due to surface conduction. The second term, cubic in E , is positive, representing velocity enhancement. It is jointly contributed to by the two remaining integrals in (63): the positive contribution of the body-force integral, associated with the action of the applied field on space-charge distribution induced in the “electro-neutral” bulk, wins over the negative contribution of the Maxwell-stress integral. As the present approximation is not limited to small values of E , the combination of the linear and cubic terms in (69) represents—at $E = O(1)$ —the above mentioned transition.

In view of (50) and (51), the small-ion approximation (69) is expected to break down when E becomes comparable to $1/\alpha$. More accurately, we expect a nonuniformity in the approximation when E is of order $1/\zeta_0\alpha$. This seems in agreement with the observed deviation in Fig. 4 of the small-ion approximation (69) from the exact numerical solution.

Incidentally, approximation (69) explains some surprising results found in earlier numerical solutions of the SY model beyond weak fields: see Fig. 5 in Ref. 26. In that figure, the (numerically evaluated) deviation of the electrophoretic velocity from the linear weak-field approximation is shown as a function of the applied field (E , in the present notation). At sufficiently weak fields, the deviation is proportional to E^3 , in agreement with the weakly nonlinear analysis of Ref. 26. This proportionality eventually breaks down as the field is increased, as would be expected when entering the fully nonlinear régime. It was found, however, that for the specific case $\alpha = 0$, the proportionality persists even up to $E \approx 1$, implying a two-term polynomial variation of the electrophoretic velocity with E . This was quite surprising, as the SY model does not seem to admit a closed-form solution for $\alpha = 0$, and, in any event, would not be compatible with such a simple polynomial variation. Given the present (69), we now understand that the value $Du = 0.5$ used in Fig. 5 of Ref. 26 was apparently small enough to render the small-Dukhin-number approximation of the present paper effectively valid. [In fact, applying the double limit $Du \rightarrow 0$ and $\alpha \rightarrow 0$ to the cubic term in the weak-field approximation of Ref. 26 yields $2DuE^3/21$, in agreement with (69).]

C. Strong fields—diffusive boundary layer

When $E \gg 1$, the effective Péclet number (51) is large. In that limit, the diffusion–advection equation (50) becomes

$$\nabla(\varphi_0/E) \cdot \nabla c_1 \approx 0, \quad (70)$$

implying that c_1 is constant on the field lines of $\nabla\varphi_0$. From (38), we see that these field lines are open, originating at infinity. Given the decay condition (49), we conclude that c_1 vanishes at leading order. From (50), it then actually follows that c_1 vanishes at all higher asymptotic orders which are powers of E , implying that it is exponentially small. Such a situation, however, is incompatible with condition (48).

This incompatibility is resolved by recalling that the large-Péclet-number limit is a singular one, with a small parameter multiplying the highest derivative in the diffusion–advection equation (50). This indicates the formation of a boundary layer. The emergence of such a layer here follows from condition (48), which necessitates a concentration gradient normal to the effective boundary. As E increases, this gradient is more and more confined to the proximity of the effective boundary $r = 1$. Because of the intense gradients in that region, approximation (70) does not hold there. A *diffusive* boundary layer accordingly develops about $r = 1$, where the strong tangential advection is balanced by transverse diffusion.

The width of the new layer, namely, the length scale characterising the concentration polarization, is set by the balance between the two terms in (50). In view of the finite slip of the velocity field at $r = 1$, this width must be $O(E^{-1/2})$.³⁸ Condition (48) then reveals that c_1 is $O(E^{1/2})$ within the layer.

The boundary-layer analysis and the resulting calculation of u_1 are relegated to Appendix B, where we find

$$u_1 \sim \frac{2}{7} \sqrt{\frac{6}{\pi}} (9 - 4\sqrt{3}) \left(1 - \alpha\zeta_0 + \alpha\zeta_0 \tanh \frac{\zeta_0}{2} \right) \left(\frac{E}{\alpha\zeta_0} \right)^{3/2}. \quad (71)$$

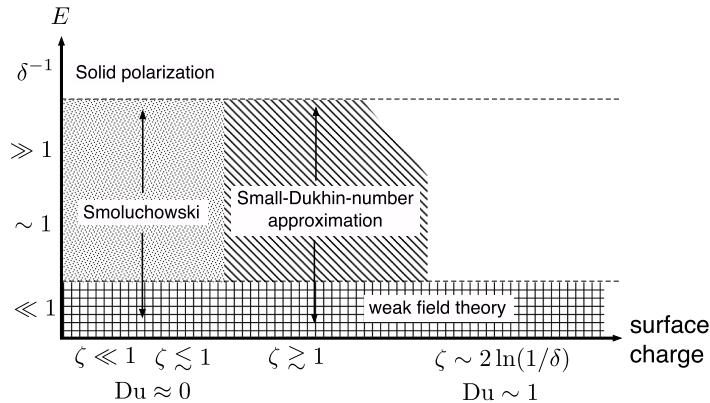


FIG. 5. Range of validity of solutions to the problem of dielectric particle electrophoresis in the thin-double-layer limit. The zeta potential is normalized by the thermal voltage; for the definitions of E and the Dukhin number Du see (5) and (29), respectively. Smoluchowski's formula is valid for exceedingly small Dukhin numbers at essentially arbitrary field strengths; it breaks down only under very intense fields, comparable to δ^{-1} , see Refs. 41 and 42. The weak-field theories of Dukhin⁸ and O'Brien and Hunter¹⁰ are valid for arbitrary Dukhin numbers but are limited to weak fields. The results derived in the present paper focus upon small but finite Dukhin numbers, thus removing the weak-field limitation.

The numerical pre-factor is ≈ 0.818 . The agreement of this asymptotic approximation with the numerically evaluated value of u_1 is illustrated in Figs. 2 and 4.

Of course, the present strong-field approximation breaks down when the first two terms in the underlying small-Dukhin-number expansion (46), respectively, of orders E and $Du E^{3/2}$, become comparable. Breakdown thus occurs when E becomes of order $1/Du^2$. Another restriction, $E \ll \delta^{-1}$, has to do with the solid-polarization effects.⁴¹ Since $1/Du^2 \sim \delta^{-2} e^{-\zeta}$, which is the stringent restriction depends upon the value of δe^{ζ} .

As already noted in the Introduction, the small-Dukhin-number limit was addressed in several previous publications, using what appears like an *ad hoc* approximation procedure. In the strong-field limit, these investigations also result in velocity expressions which are proportional to the 3/2 power of the electric field. The coefficients in these expressions do not coincide with that of the present (71).

VII. CONCLUDING REMARKS

We have employed our recently derived macroscale model²⁴ for electrokinetic flows about charged dielectric surfaces to analyze the electrophoresis of a spherical dielectric particle at small (but finite) Dukhin numbers, allowing for an arbitrary magnitude of the applied field. Our solutions are valid in significant portions of the Du - E parameter space which are covered by neither Smoluchowski's theory nor the weak-field models of O'Brien and his coworkers: see Fig. 5. In fact, with these additional portions, the theory of particle electrophoresis in the thin-double-layer limit now encompasses the entire parameter range typical of most realistic scenarios involving micron-sized particles in aqueous solutions, where the Dukhin numbers are rather small, while the applied fields are not necessarily weak.

According to our scheme, the small-Dukhin-number correction to Smoluchowski's velocity is expressed as a quadrature involving the perturbations to both the electric potential and salt concentration. The evaluation of the particle velocity then essentially amounts to the solution of a linear problem governing the salt polarization in the bulk. As the effective Péclet number is not necessarily small, the salt polarization is not harmonic; the same holds for the electric-potential perturbation. Consequently, the flow problem is affected by Coulomb body forces in the bulk—a rather non-standard feature in thin-double-layer analyses. Another novel aspect is the appearance of a net electric force on the material system bounded by the effective boundary $r = 1$ —namely, the particle together with the screening diffuse layer surrounding it. Use of Gauss law in conjunction

with (53) implies that this system is electro-neutral as a whole; nonetheless, the action of the electric field on this polarized system does yield a net electric force. The velocity correction u_1 is accordingly affected by three mechanisms: effective (electro- and diffusio-osmotic) slip, Coulomb body forces, and a net electrical force. This is explicit in (63).

Since no analytic solution exists for the diffusion–advection problem governing the salt polarization, it has been solved using an eigenfunction expansion in Legendre polynomials. The resulting dependence of the velocity correction u_1 upon the applied-field magnitude E is portrayed in Figs. 2 and 4. These figures show a transition from negative values of u_1 at weak fields to positive values at large fields.

These semi-analytic results are supplemented by useful asymptotic approximations for small ions and strong fields, respectively, realizing the opposite limits of small and large Péclet numbers. (Another small-Péclet-number limit, that of weak fields, is consistent with the classical weak-field expressions of O’Brien and Hunter.¹⁰) The small-ion approximation yields the velocity correction as a simple polynomial consisting of two terms, respectively, proportional to E and E^3 . The first represents the familiar velocity retardation due to surface conduction; the second represents a velocity enhancement effect dominated by the action of the applied field on the space-charge distribution induced in the bulk. The strong-field limit corresponds to the formation of a diffusive boundary layer of $O(E^{-1/2})$ thickness, where the induced salt polarization and the space charge are confined; an analytic solution of the boundary-layer profile results in a closed-form approximation for u_1 , proportional to $E^{3/2}$.

In the present contribution, we have employed the macroscale model of Ref. 24 as an infrastructure for the analysis of spherical-particle electrophoresis at small (but finite) Dukhin numbers and arbitrary field strengths. The scheme developed herein conveniently lends itself to the comparable analysis of non-spherical particles. With the zero-Dukhin-number base state being characterized by a uniform salt concentration and a Helmholtz–Smoluchowski type slip, Morrison’s analysis³ dictates the irrotational flow (41), where the particle translates with Smoluchowski’s velocity and does not rotate. Thus, evaluation of the $O(Du)$ velocity correction essentially follows the same prescription as in the present analysis. The difficulties associated with non-sphericity are merely technical, involving the solution of both the diffusion–advection problem (48)–(50), required for the calculation of c_1 , and the resistance-type Stokes problem, required for the evaluation of the auxiliary field $\tilde{\mathbf{u}}$ and $\tilde{\mathbf{N}}$ appearing in (63). More complicated electrophoresis problems may involve boundary effects and more than one particle. (Because of finite Maxwell forces,⁴³ the zero-Dukhin-number solution in these problems is not that given by Morrison.³)

Finally, recall that the macroscale model of Ref. 24 is not limited to electrophoresis problems. Thus, the small-Dukhin-number paradigm conceived in the present contribution provides a tractable scheme for systematically analyzing surface conduction beyond weak fields in a variety of electrokinetic phenomena. We propose that this scheme can be employed to study such fundamental problems as salt polarization in microchannel junctions, the generation of phoretic motion by imposed salt gradients, and nonlinear dielectric response of suspensions.

ACKNOWLEDGMENTS

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APPENDIX A: DETAILS OF THE NUMERICAL CALCULATION

1. Diffusion–advection equation

The field c_1 is expanded in terms of Legendre polynomials

$$c_1 = 3E \sum_{m=0}^{\infty} C^{(m)}(r; \text{Pe}) P^{(m)}(\cos \theta). \quad (\text{A1})$$

Substituting (A1) into the diffusion–advection equation (50), multiplying by $P^{(n)}(\cos \theta)$ and integrating using the orthogonality properties of the Legendre polynomials yields a set of coupled linear ordinary differential equations

$$\frac{d^2 C^{(n)}}{dr^2} + \frac{2}{r} \frac{dC^{(n)}}{dr} - \frac{n(n+1)}{r^2} C^{(n)}(r) = \text{Pe} \left\{ \left(\frac{1}{r^3} - 1 \right) \left[\frac{n}{2n-1} \frac{dC^{(n-1)}}{dr} + \frac{n+1}{2n+3} \frac{dC^{(n+1)}}{dr} \right] + \left(\frac{1}{r} + \frac{1}{2r^4} \right) \left[\frac{n(n-1)}{2n-1} C^{(n-1)}(r) - \frac{(n+1)(n+2)}{2n+3} C^{(n+1)}(r) \right] \right\}, \quad n = 0, 1, 2, \dots \tag{A2}$$

From (48), we find the corresponding boundary conditions

$$\frac{dC^{(n)}}{dr} = \delta_{n,1} \quad \text{at} \quad r = 1, \tag{A3}$$

while (49) implies attenuation of $C^{(n)}$ as $r \rightarrow \infty$ for all n .

Practically, the infinite series (A1) is truncated after a finite number of terms. This number increases with the value of the Péclet number. When the Péclet number becomes large, moreover, most of the variation in c_1 occur in proximity to $r = 1$, necessitating the use of a nonuniform discretization of r . The resulting truncated system of coupled ordinary differential equations is solved using Matlab’s `bvp4c` routine.

2. Numerical evaluation of the velocity correction

With the salt solved for, the potential φ_1 is given by (55). Thus, calculation of u_1 is reduced to evaluating the three integrals appearing in (63). It is straightforward to express these integrals in terms of the first three salt modes. Indeed, substitution of (59), and (64) and (65) followed by integration with respect to θ yields

$$\oint_{r=1} dA \hat{\mathbf{n}} \cdot \tilde{\mathbf{N}} \cdot \mathbf{u}_1 = 6\pi E \frac{1 - \alpha \zeta_0 - \alpha \zeta_0}{\alpha} + 12\pi E \left[4 \ln \cosh(\zeta_0/4) + \frac{1 - \alpha \zeta_0}{\alpha} \right] C^{(1)}(1) - 18\pi E^2 \tanh \frac{\zeta_0}{2} \left[C^{(0)}(1) - \frac{1}{5} C^{(2)}(1) \right]. \tag{A4}$$

Similarly, using (21), (38), and (55), the Maxwell-stress integral becomes

$$\hat{\mathbf{i}} \cdot \oint_{r=1} dA \hat{\mathbf{n}} \cdot \mathbf{M}_1 = -\frac{36\pi(1 - \alpha \zeta_0)E^2}{5\alpha \zeta_0} C^{(2)}(1). \tag{A5}$$

Finally, the body-force integral is evaluated by substituting (55) and (64) and integrating by parts with respect to r . This yields

$$\int_{r>1} dV \tilde{\mathbf{u}} \cdot \nabla \varphi_0 \nabla^2 \varphi_1 = \frac{12\pi(1 - \alpha \zeta_0)E^2}{\alpha \zeta_0} \left\{ \frac{9}{10} C^{(2)}(1) - \frac{3}{2} C^{(0)}(1) - \int_1^\infty [f(r)C^{(0)}(r) + g(r)C^{(2)}(r)] dr \right\}, \tag{A6}$$

where

$$f(r) = \frac{d}{dr} \left(r^2 \frac{da}{dr} \right), \quad g(r) = \frac{1}{5} \left[\frac{d}{dr} \left(r^2 \frac{db}{dr} \right) - 6b \right] \tag{A7}$$

in which the functions a and b are defined in (65).

APPENDIX B: STRONG-FIELD ANALYSIS

In analyzing the diffusive layer, we employ the stretched radial variable

$$Z = E^{1/2}(r - 1). \tag{B1}$$

Following the scaling arguments described in Sec. VI, we expand the excess salt as:

$$c_1 = E^{1/2}C(Z, \theta) + \tilde{C}(Z, \theta) + \dots \tag{B2}$$

The differential equation governing C is obtained by substituting (38) and (B2) into the diffusion–advection equation (50), yielding

$$\frac{\partial^2 C}{\partial Z^2} + 3\alpha\zeta_0 \left(Z \frac{\partial C}{\partial Z} \cos \theta - \frac{1}{2} \frac{\partial C}{\partial \theta} \sin \theta \right) = 0. \tag{B3}$$

This is supplemented by the boundary condition [see (48)]

$$\frac{\partial C}{\partial Z} = 3 \cos \theta \quad \text{at } Z = 0, \tag{B4}$$

and the requirement of exponential attenuation as $Z \rightarrow \infty$. We note for future reference that \tilde{C} satisfies a homogeneous condition

$$\frac{\partial \tilde{C}}{\partial Z} = 0 \quad \text{at } Z = 0; \tag{B5}$$

in view of the exponentially small salt perturbation outside the diffusive layer, this field (like C) decays at large Z . The boundary-layer problem governing C is similar to the one encountered in the investigation of strong-field electrophoresis of moderately charged particles.⁴² Thus, the solution of (B3)–(B5) is

$$C = -\sqrt{\frac{6}{\pi\alpha\zeta_0}} \int_0^\theta \frac{\sin t \cos t}{\sqrt{\lambda(t) - \lambda(\theta)}} \exp\left(-\frac{3\alpha\zeta_0}{8} \frac{Z^2 \sin^4 \theta}{\lambda(t) - \lambda(\theta)}\right) dt, \tag{B6}$$

where $\lambda(\theta) = \cos \theta - \frac{1}{3} \cos^3 \theta$.

With the salt profile solved for, the electric potential is readily obtained from (55). In the absence of salt polarization outside the thin diffusive layer, φ_1 is harmonic there up to exponentially small terms; it is simply given by the first term in (55). In the diffusive layer, φ_1 is obtained by substituting (B2) into (55)

$$\varphi_1 \sim -\frac{3}{2} E \frac{1 - \alpha\zeta_0 - \alpha\zeta_0 \cos \theta}{\alpha\zeta_0} \frac{1}{r^2} - \frac{1 - \alpha\zeta_0}{\alpha\zeta_0} [E^{1/2}C(Z, \theta) + \tilde{C}(Z, \theta) \dots]. \tag{B7}$$

(We do not bother to expand the harmonic dipole term in the inner variable Z .)

The velocity correction u_1 is calculated using the quadrature (63). In the present strong-field limit, the three integrals appearing in (63) must be calculated asymptotically. We show that all three integrals turn out to be $O(E^{3/2})$.

Consider the first integral in (63), representing the slip contribution. The integrand consists of fields evaluated at $r = 1$, corresponding to evaluation at $Z = 0$ of the respective diffusive-layer fields. Of the three terms in the slip expression (59), the second term is $O(E^{3/2})$, dominating the first and third terms in (59) which are readily seen to be $O(E)$ and $O(E^{1/2})$, respectively. Thus, to leading order, we find

$$\oint_{r=1} dA \hat{\mathbf{n}} \cdot \tilde{\mathbf{N}} \cdot \mathbf{u}_1 \sim -\frac{9\pi}{2} E^{3/2} \tanh \frac{\zeta_0}{2} \int_0^\pi d\theta \sin^3 \theta C|_{Z=0}. \tag{B8}$$

Consider next the second surface integral appearing in (63), namely, the ‘‘Maxwell force.’’ Substitution of (38) and (62) in conjunction with (36) yields

$$\hat{\mathbf{i}} \cdot \oint_{r=1} dA \hat{\mathbf{n}} \cdot \mathbf{M}_1 = -3\pi E \int_0^{2\pi} d\theta \sin^2 \theta \left(\frac{\partial \varphi_1}{\partial r} \sin \theta + \frac{\partial \varphi_1}{\partial \theta} \cos \theta \right) \Big|_{r=1}. \tag{B9}$$

To asymptotically evaluate this integral, we substitute (B7). We first note that the dipole term in (B7), which may appear to result in an E^2 force, is proportional to $\cos \theta$ and accordingly does not to contribute to (B9) (at any asymptotic order). Substituting the remaining series appearing in (B7)

gives

$$\frac{3\pi E(1 - \alpha\zeta_0)}{\alpha\zeta_0} \int_0^{2\pi} d\theta \sin^2\theta \left[\sin\theta \left(E \frac{\partial C}{\partial Z} + E^{1/2} \frac{\partial \tilde{C}}{\partial Z} \right) \Big|_{Z=0} + E^{1/2} \cos\theta \frac{\partial C}{\partial \theta} \Big|_{Z=0} + o(E^{1/2}) \right]. \quad (\text{B10})$$

The leading-order term in the integrand appears to result in an $O(E^2)$ contribution to the particle velocity. Condition (B4) implies however that this contribution vanishes. Thus, using (B5), we find

$$\hat{\mathbf{i}} \cdot \oint_{r=1} dA \hat{\mathbf{n}} \cdot \mathbf{M}_1 \sim \frac{3\pi(1 - \alpha\zeta_0)}{\alpha\zeta_0} E^{3/2} \int_0^\pi d\theta \sin^2\theta \cos\theta \frac{\partial C}{\partial \theta} \Big|_{Z=0}. \quad (\text{B11})$$

Last, consider the volumetric integral in (63) associated with the Coulomb body forces acting on the liquid. Since φ_1 satisfies Laplace’s equation outside the diffusive layer up to exponentially small errors, we only need to consider the contribution of the diffusive layer domain, whose volume is $O(E^{-1/2})$. In this domain, (65) give

$$a \sim -1 + \frac{3}{2} E^{-1/2} Z + \dots, \quad b \sim 1 - \frac{9}{2} E^{-1/2} Z + \dots, \quad (\text{B12})$$

from which (64) yields

$$\tilde{\mathbf{u}} \cdot \nabla \varphi_0 \sim E \left[P^{(2)}(\cos\theta) - 1 \right] + E^{1/2} \frac{3Z}{2} \left[1 - 3P^{(2)}(\cos\theta) \right] + \dots \quad (\text{B13})$$

From (B7), in which the first term is harmonic, we also find

$$\nabla^2 \varphi_1 \sim -\frac{1 - \alpha\zeta_0}{\alpha\zeta_0} \left[E^{3/2} \frac{\partial^2 C}{\partial Z^2} + E \left(2 \frac{\partial C}{\partial Z} + \frac{\partial^2 \tilde{C}}{\partial Z^2} \right) + \dots \right]. \quad (\text{B14})$$

The integrand is accordingly $O(E^{5/2})$. It may appear as though integration over the $O(E^{-1/2})$ -thick layer would result in a $O(E^2)$ contribution, dominating that of the other two integrals in (63). However, taking into account both (B4) and the exponential decay of C as $Z \rightarrow \infty$, we find that this leading-order contribution vanishes. The volumetric integral is accordingly $O(E^{3/2})$ as well:

$$\int_{r>1} dV \tilde{\mathbf{u}} \cdot \nabla \varphi_0 \nabla^2 \varphi_1 \sim -\frac{2\pi(1 - \alpha\zeta_0)}{\alpha\zeta_0} E^{3/2} \int_{-1}^1 d\mu \int_0^\infty dZ \left[\frac{3}{2} (1 - 3P^{(2)}(\mu)) Z \frac{\partial^2 C}{\partial Z^2} + (P^{(2)}(\mu) - 1) \left(\frac{\partial^2 \tilde{C}}{\partial Z^2} + 2Z \frac{\partial^2 C}{\partial Z^2} + 2 \frac{\partial C}{\partial Z} \right) \right]. \quad (\text{B15})$$

Integration by parts using the boundary conditions satisfied by C and \tilde{C} recasts (B15) as the single integral

$$-\frac{3\pi(1 - \alpha\zeta_0)}{\alpha\zeta_0} E^{3/2} \int_{-1}^1 [1 - 3P^{(2)}(\mu)] C|_{Z=0} d\mu. \quad (\text{B16})$$

We have thus expressed all three contributions to (63) solely in terms of the salt distribution at the effective boundary $Z = 0$. Evaluating (B6) there yields

$$C|_{Z=0} = -\sqrt{\frac{6}{\pi\alpha\zeta_0}} \mathcal{I}(\cos\theta), \quad (\text{B17})$$

where

$$\mathcal{I}(\mu) = \int_\mu^1 \frac{s ds}{\sqrt{s - \mu - \frac{1}{3}(s^3 - \mu^3)}}. \quad (\text{B18})$$

Substitution of (B8), (B11), and (B16) into (63), in conjunction with (B17), yields the velocity correction

$$u_1 \sim \frac{3E^{3/2}}{(6\pi\alpha\zeta_0)^{1/2}} \left\{ \int_{-1}^1 \frac{1 - \alpha\zeta_0}{\alpha\zeta_0} \left[\mu(1 - \mu^2)\mathcal{I}'(\mu) + (1 - 3P^{(2)}(\mu))\mathcal{I}(\mu) \right] d\mu + \frac{3}{2} \tanh \frac{\zeta_0}{2} \int_{-1}^1 (1 - \mu^2)\mathcal{I}(\mu) d\mu \right\}. \quad (\text{B19})$$

Note that the vanishing of an $O(E^2)$ contribution also follows from symmetry arguments.

Using integration by parts, we note that

$$\int_{-1}^1 \left[\mu(1 - \mu^2)\mathcal{I}'(\mu) + (1 - 3P^{(2)}(\mu))\mathcal{I}(\mu) \right] d\mu = \frac{3}{2} \int_{-1}^1 (1 - \mu^2)\mathcal{I}(\mu) d\mu. \quad (\text{B20})$$

Thus, expression (B19) is proportional to a single integral, which is readily obtained via substitution of (B18)

$$\int_{-1}^1 (1 - \mu^2)\mathcal{I}(\mu) d\mu = \frac{8}{21}(9 - 4\sqrt{3}). \quad (\text{B21})$$

The result (B19) is readily simplified to yield (71).

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- ³³ The case of a moderately charged particle ($\text{Du} = 0$) and that of highly charged particle [$\text{Du} = O(1)$] were actually considered separately in Ref. 24, leading to two macroscale models; combining them leads to a uniformly valid model, which may be used for arbitrary values of Du : see section VIII in Ref. 24. In the present paper, we employ the uniformly valid model.
- ³⁴ Strictly speaking, a small-Dukhin-number approximation corresponds to the domain $\delta \ll \text{Du} \ll 1$. The reason for the lower bound has to do with the derivation of the macroscale SY model. When $\text{Du} = O(\delta)$, errors of the same order as the correction might originate from higher-order terms in the thin-double-layer approximation $\delta \ll 1$.²⁴
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