Nonlinear electrophoresis of colloidal particles

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Abstract

Advances over the past decade in nonlinear electrophoresis of charged, dielectric colloidal particles in aqueous electrolytes are reviewed. Here, the word nonlinear refers to the fact that the ratio of the electrophoretic speed of the particle to the magnitude of the applied electric field — the electrophoretic mobility — is not independent of field strength. This is in stark contrast to the vast majority of work on (linear) colloidal electrophoresis over the last century, where the mobility is assumed to be a material property dependent only on the particle-electrolyte combination. The present discussion is focused on: (i) experimental measurements of the field-dependent mobility; (ii) an asymptotic scheme to calculate the mobility in the common thin-Debye-layer limit; and (iii) computations of nonlinear electrophoresis from numerical solution of the electrokinetic equations. The article concludes with suggestions for future work in this evolving area of colloid science.

Keywords: Electrophoresis, Colloid, Electrokinetics, Microhydrodynamics, Electrolyte

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1. Introduction

Electrophoresis refers to the movement of a charged particle in a liquid electrolyte under an imposed electric field. Historical developments in electrophoresis, and more generally electrokinetic phenomena, are reviewed by Wall [1]. An early experimental observation of electrophoresis is often attributed to the German scientist Reuss in 1808, who noticed the migration of clay particles in water under an applied voltage. Biscombe [2] suggests, in fact, that electrophoresis was discovered by the French scientist Gautherot in 1801, who observed the drift of a water drop between electrified metal plates. Today, electrophoresis finds applications in microfluidics, colloidal directed assembly, DNA sequencing, iontophoretic drug delivery, analytical chemistry, and display devices, to name but a few areas. Electrophoresis is a scientifically rich subject, comprising (low Reynolds number) fluid mechanics, electrostatics, physical chemistry, and ion transport. A central goal is to determine the *electrophoretic mobility* of a particle, which is the quantity relating the particle motion to the applied field. In this article, we focus on the specific case of a rigid, spherical, dielectric particle of uniform surface charge density residing in an unbounded, strong (i.e., fully ionized) electrolyte. The electrophoretic motion of the particle is animated by a spatially uniform and steady electric field. Here, under the *assumption* that the particle undergoes steady, rectilinear motion, there is a scalar relation between the particle velocity $\boldsymbol{U}^*_{EP}$ and applied field $\boldsymbol{E}^*$, $\boldsymbol{U}^*_{EP} = M^*_{EP}\boldsymbol{E}^*$, where M^*_{EP} is the electrophoretic mobility.

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Above and henceforth, dimensional quantities will be adorned with an asterisk superscript; dimensionless quantities will carry no superscript. In principle, this velocity-field relation is nonlinear, since the mobility itself can be a function of the electric field strength, $E^* = |\boldsymbol{E}^*|$. Most theoretical analyses have focused on the limit of a 'weak' applied field, $\beta = a^* E^*/\phi_T^* \ll 1$, where a^* is the particle radius and ϕ_T^* is the thermal voltage scale. In a binary electrolyte with anion and cation valences $-\mathcal{Z}$ and $+\mathcal{Z}$, respectively, $\phi_T^* = k_B^* T^*/\mathcal{Z} e^*$, where k_B^* is Boltzmann's constant; T^* is the absolute temperature, and e^* is the charge on a proton: for reference, $\phi_T^* \approx 25\text{mV}$ at $T^* = 298\text{K}$ and $\mathcal{Z} = 1$. For a particle with $a^* = 1\mu\text{m}$ a field $E^* \approx 0.25\text{kV/cm}$ is required to yield $\beta = 1$.

The mobility can be calculated in the weak-field limit through linearization to first order in β of the electrokinetic equations governing electrophoresis [3]. In this regime, M_{EP}^* is independent of field strength. In 1903 Smoluchowski [4] calculated that $M_{EP}^* = \varepsilon^* \zeta^*/\eta^*$, where ε^* and η^* are the dielectric permittivity and viscosity of the electrolyte, respectively, and ζ^* is 'zeta potential' of the particle. In the weak-field limit the zeta potential is equivalent to the electric potential at the 'plane of shear.' Here, we will not deal with the presence of a Stern layer; hence, the particle surface and plane of shear are the same. Smoluchowski's formula is valid in the so-called 'thin-Debye-layer limit,' where the Debye length $1/\kappa^*$, which characterizes the width of the diffuse charge cloud screening the surface charge of the particle, is small compared to particle size: $\delta = 1/(\kappa^* a^*) \ll 1$. At the opposite extreme of a thick Debye cloud, $\delta \gg 1$, Debye and Hückel in 1924 [5] found $M_{EP}^* = 2\varepsilon^* \zeta^*/(3\eta^*)$. These two results were bridged by Henry in 1931 [6], who calculated M_{EP}^* for arbitrary δ, under the assumption that ζ^*/ϕ_T^* is small.

Formally, Henry's result is valid to first order in ζ^*/ϕ_T^*, and the mobility was later computed as a perturbation expansion through fourth order in this ratio by Booth [7]. Booth's analysis revealed that at fixed δ the mobility does increase linearly with ζ^* indefinitely. For example, in figure 3 of that paper the mobility is plotted versus ζ^*/ϕ_T^* at $\delta = 0.16$: after an initial linear increase up to $\zeta^*/\phi_T^* \approx 1$ (in accordance with Smoluchowski's formula) the mobility increases sub-linearly and eventually attains a maximum at $\zeta^*/\phi_T^* \approx 3.2$, after which it decreases until $\zeta^*/\phi_T^* = 4$, the largest value of ζ^*/ϕ_T^* considered. A numerical computation of the mobility was undertaken by Wiersema *et al.* in 1966 [8] for a binary electrolyte, and their results also show a sub-linear increase of M_{EP}^* with ζ^*/ϕ_T^* beyond small ζ^*/ϕ_T^*; however, a mobility maximum was not evident. In their landmark 1978 paper, O'Brien and White [9] employed symmetry arguments and utilized the linearity of the weak-field electrokinetic equations to numerically compute the mobility for an (in principle) arbitrary electrolyte up to larger values of ζ^*/ϕ_T^* than [8]. Their results shows a mobility maximum for a particle in a KCl solution for $\delta \lesssim 1/3$. S. S. Dukhin had, in fact, some years earlier performed a boundary layer analysis of the weak-field equations for a symmetric binary electrolyte in the thin-Debye-layer limit, which furnished an analytical formula for M_{EP}^* that exhibited a mobility maximum [10]. Dukhin's analysis was streamlined by O'Brien and Hunter in 1981 [11] and generalized to a multicomponent electrolyte by O'Brien in 1983 [12]. An interesting finding in the latter paper is that $M_{EP} \sim \ln 4(\phi_T^* \varepsilon^*/\eta^*)$ as $\zeta^*/\phi_T^* \to \infty$, which is independent of zeta potential and particle size. The departure from Smoluchowski's formula is due to tangential ionic currents, or 'surface conduction,' in the Debye layer, which occur due to the appreciable counter-ion buildup therein at sufficiently large zeta potentials. Specifically, surface conduction becomes important at 'logarithmically large' zeta potentials, $\zeta^*/\phi_T^* = O(\ln(1/\delta))$ [12, 13]. The non-uniformity of surface conduction over the curved particle necessitates compensating (normal) ionic fluxes across the Debye layer, which affect the electric potential and ionic concentration distributions in the 'bulk' electroneutral electrolyte outside it. Hence, M_{EP}^* departs from Smoluchowski's formula.

Contributions to our understanding of weak-field, or *linear*, electrophoresis were made essentially throughout the last century. Here, by contrast, we focus on *nonlinear* electrophoresis, which has seen major advances — theoretical, computational, and experimental — over the last decade; this is the period that the present review is centered on. Crucially, in nonlinear electrophoresis the mobility is no longer independent of the field strength, which, as we shall see, presents new experimental opportunities and theoretical challenges. The rest of this article is organized as follows. We start by reviewing experimental evidence for nonlinear electrophoresis. Next, we present the electrokinetic equations governing nonlinear electrophoresis, which, being nonlinear, require asymptotic or numerical treatment. In the former vein, we review recent asymptotic approximations in the thin-Debye-layer limit, and connect said approximations to the aforementioned experimental studies. This is followed by a discussion of numerical computations of nonlinear electrophoresis. We close by charting directions for future work.

2. Experiments on nonlinear electrophoresis

Here, we discuss recent studies on nonlinear electrophoresis of dielectric colloids in aqueous electrolytes. In 2020, Cardenas-Benitez *et al.* [14] measured the electrophoretic velocity of negatively charged carboxylated polystyrene spheres at varying field strength in a PDMS microchannel. The largest particles had radii $a^* = 2.55\mu\text{m}$ and were exposed to a maximum field strength of $E^* = 0.8\text{kV/cm}$. The surface charge density, σ^* say, on the colloids is reported as being between -1.41 and $-5.93\mu\text{C/cm}^2$; we will take $\sigma^* = -5\mu\text{C/cm}^2$ as a representative value. The particles were immersed at low concentration (to avoid multi-particle interactions) in deionized water, to which different amounts of KCl were added depending on the colloid size: a $53.3\mu\text{M}$ KCl solution (for which $1/\kappa^* = 41.6\text{nm}$) was used for the $5.1\mu\text{m}$ diameter colloids. The electrolyte concentration was chosen to minimize Joule heating while remaining in the thin-Debye-layer limit. Particle motion under an applied field was recorded using particle tracking velocimetry. This measurement yields the 'total' particle velocity, $\boldsymbol{U}_T^*$, which is a sum of oppositely directed contributions from the electrophoretic velocity $\boldsymbol{U}_{EP}^*$ and the electro-osmotic flow at the negatively charged walls. The latter is assumed to advect the particle at a velocity given by the the Helmholtz-Smoluchowski formula $\boldsymbol{U}_{EO}^* = -\varepsilon\zeta_w^*\boldsymbol{E}^*/\eta$, where ζ_w^* is the wall zeta potential. At small fields an initial positive linear increase in $\boldsymbol{U}_T^*$ with field strength is seen. Here, a positive velocity indicates the particles are traveling in the direction of the applied field; thus, $\boldsymbol{U}_{EO}^*$ must be greater than $\boldsymbol{U}_{EP}^*$, since the particles and wall are negatively charged. The regime of nonlinear electrophoresis is reached upon further increase of the field strength, where $\boldsymbol{U}_T^*$ proceeds to increase sub-linearly with E^*; reaches a maximum; crosses zero; and finally becomes negative. This last behavior indicates the dominance of $\boldsymbol{U}_{EP}^*$ over $\boldsymbol{U}_{EO}^*$ at large field strengths. Note, the latter can reasonably be assumed to always be linear in the field strength, since the channels walls are flat and, therefore, non-uniform surface conduction should be negligible in their adjacent Debye layers. Further work from this group has reported similar findings for the nonlinear electrophoretic velocity of other types of particles and biological cells [15]. Additionally, they have proposed that nonlinear electrophoresis plays an important role in 'direct current insulator-based electrokinetics (DC-iEK),' which is a microfluidic protocol to manipulate micro-particles and cells via non-uniform electric fields.

Tottori *et al.* [16] in 2019 reported on the nonlinear electrophoresis of polystyrene particles ($a^* = 0.31\mu$m, $\sigma^* = -51.2$mC/m^2) and poly(methylmethacrylate) (PMMA) particles ($a^* = 0.26\mu$m, $\sigma^* = -13.1$mC/m^2) in a PDMS microchannel under a dc voltage. The microchannel is connected to two open reservoirs whose heights are adjusted to eliminate pressure-driven flow. A 1mM KCl solution was used, for which $1/\kappa^* = 9.6$nm. The largest field strength tested was $E^* = 2.5$kV/cm. The measured particle velocity is again a sum of electrophoretic and electro-osmotic contributions. At field strengths below approximately 1kV/cm the particle velocity is linear in the field strength, and at larger field strengths the nonlinear electrophoretic velocity is found by subtracting this linear component from the total particle velocity. A nonlinear dependence of the electrophoretic velocity on field strength is clearly evident; further, the experiments compare reasonably well to a numerical solution of the electrokinetic equations via COMSOL and a weakly-nonlinear asymptotic theory from Schnitzer & Yariv [17], of which more will be said later. Finally, the nonlinear electrophoretic response was used to enable field-driven particle trapping in a micro-channel.

In 2016 Youssefi and Diez [18] reported 'ultrafast' electrophoretic motion of carboxyl functionalized polystyrene spheres ($a^* = 0.1\mu$m) suspended in deionized water through a PDMS microchannel. We assume $1/\kappa^* = 0.96\mu$m [19] since the Debye length was not reported in [18]. The surface charge of the particles was also not stated, although they assumed a zeta potential of magnitude $|\zeta^*| = 100$mV when comparing various theoretical predictions to their experiments. The electrophoretic particle velocity is found from the difference between the total particle velocity and electro-osmotic velocity: the former is measured via PIV and the latter via the rate of filling of one of the two reservoirs that the channel is connected to. A maximum field strength of $E^* = 250$kV/m was used, for which the electrophoretic velocity is reported as 2.3m/s. Remarkably, this implies that the particle translates at approximately twenty three times its radius per microsecond. Such large speeds call into question whether inertial effects are relevant; the Reynolds number based on the electrophoretic velocity is around 0.23, which is certainly not negligibly small. The electrophoretic velocity $\boldsymbol{U}^*_{EP}$ at the largest field strengths appears to increases faster than linearly with E^* but slower than $E^{*3/2}$, which implies a sublinear increase of the mobility with field strength.

Mishchuk and Barinova [20] in 2011 reported measurements on the electrophoresis of latex particles in horizontal and vertical working cells, using pulsed and steady electric fields. A largest field of around 0.8kV/cm was applied to drive the motion of 6μm radii particles with zeta potential of magnitude 28mV. The electrolyte used is not reported; however, a nonlinear dependence of the EP velocity on field strength is clearly seen.

In 2009, Barany [21] reviewed studies of electrophoresis in strong fields, which included presentation of experimental data for the electrophoretic velocity of 'bare' (i.e., uncoated) dielectric particles; polymer coated particles; and 'unipolar' conducting particles. The latter refers to a particle through which a counter-ion current can flow, such as an ion-exchange granule, and electron-conducting or semi-conducting particles. We restrict our attention to uncoated dielectric particles. Here, Barany reports earlier experiments of Shilov *et al.* [22] on emulsifier-free latex particles of $a^* = 15\mu$m in 5mM KCl (for which $1/\kappa^* = 4.29$nm). This work used an apparatus where a voltage is applied orthogonal to the direction of gravity, such that a sedimenting particle experiences a lateral drift under an electric field, from which its electrophoretic velocity is inferred. A maximum field strength of $E^* = 0.25$kV/m was used. A nonlinear variation in the electrophoretic velocity with field strength is evident, which is compared to a theoretical model developed in [22]. The particle surface charge was not reported; however, a value of 0.8×10^{-8}m^2/Vs is given for the magnitude of the electrophoretic mobility in the weak-field regime. This is converted to a zeta potential of magnitude 11.2mV through Smoluchowski's formula, which in turn yields a surface charge of magnitude $|\sigma^*| = 1.86$mC/m^2, via the Gouy-Chapman relation, $\sigma^* = 2\varepsilon^* \kappa^* \phi_T^* \sinh(\zeta^*/2\phi_T^*)$.

In 2006, Kumar *et al.* [23] measured the electrophoresis of carboxylated latex particles of $a^* = 2.1\mu$m in deionized water under steady and alternating fields through a silica capillary that is connected to open reservoirs. A maximum field strength of 1kV/cm was used. They estimate $1/\kappa^* = 0.16\mu$m from the known solution conductivity and calculate $\zeta^* = -20$mV from Smoluchowski's formula. The latter corresponds to a surface charge density of $\sigma^* = -91.2\mu$C/m^2 from the Gouy-Chapman relation. The total particle velocity is observed via microscope and the electro-osmotic flow velocity is inferred by measurement of the fluid collection rate into one of the reservoirs. Thus, the electrophoretic velocity is the difference between the total velocity and electro-osmotic velocity: this is essentially the same approach adopted by [18, 14], but differs from [16] who did not attempt to measure the electro-osmotic flow. A linear increase in the electrophoretic velocity with field strength is reported up to the maximum field strength used; there is no evidence for nonlinear electrophoresis. Thus, the results in [23] seemingly stand apart from the other studies discussed above, which exhibit nonlinear electrophoresis at sufficiently large field strengths. To put these experimental efforts into a proper context requires formulation of a mathematical model to predict nonlinear electrophoresis, which is presented next.

3. Electrokinetic equations for nonlinear electrophoresis

Having discussed the relevant experimental observations, we present governing equations for nonlinear electrophoresis, based on the standard electrokinetic model of dilute electrolyte solutions [3]. We focus on the simplest geometrical case of a rigid, neutrally buoyant, spherical particle of radius a^* immersed in an unbounded electrolyte (Fig. 1). The particle is a dielectric with uniform surface charge density σ^*. The electrolyte is binary and fully ionized: the cations have valence $+\mathcal{Z}$ and diffusion coefficient D_+^*, and anions have valence $-\mathcal{Z}$ and diffusion coefficient D_+^*. Thus, the Debye length $1/\kappa^* = \sqrt{\epsilon^* k^* T^* / 2n^* \mathcal{Z}^2 e^{*2}}$, where $2n^*$ is the ion concentration far from the particle. A steady, uniform electric field $\boldsymbol{E}^*$ is applied at large distances from the particle. We shall assume that the particle translates at a steady velocity $\boldsymbol{U}^*$, from which

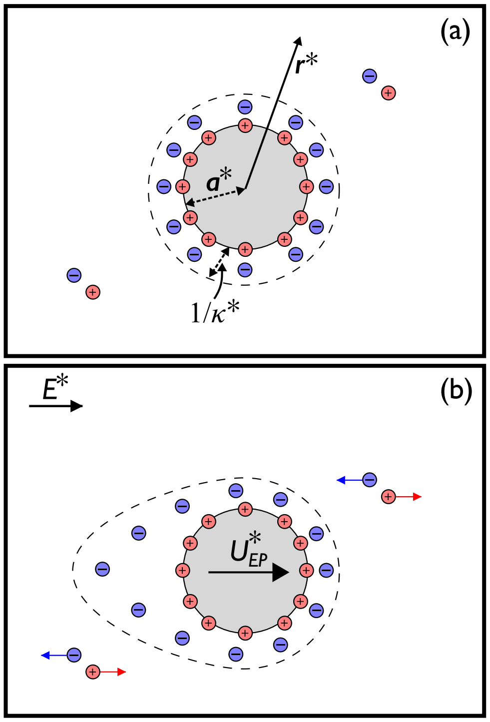

Figure 1: Definition sketch for electrophoresis of a dielectric, charged sphere of radius a^*. The particle is shown with a uniform, positive surface charge distribution, and $\boldsymbol{r}^*$ denotes the position vector from the centroid of the particle. In (a) the particle rests in the absence of an applied field; hence, the Debye layer of counterions around it, of characteristic width $1/\kappa^*$, is spherically symmetric. Here, the ionic concentrations are only a function of $r^* = |\boldsymbol{r}^*|$. The electrolyte outside the Debye layer is electroneutral. In (b) the particle is set into motion by an electric field $\boldsymbol{E^*}$; consequently, the counter-ion cloud deforms from its equilibrium configuration and looses spherical symmetry. As the field strength increases, the cloud will compress(extend) at the front(back) of the particle. This can be understood from the electric force on the ions due to applied field, which results in electro-migration of cations(anions) to the right(left), as depicted by the arrows. The goal is to calculate the velocity $\boldsymbol{U^*}$ at which the particle moves, from which the electrophoretic mobility $M^*_{EP} = |\boldsymbol{U}^*|/|\boldsymbol{E}^*|$. The field dependence of the mobility can be rationalized in a pictorial sense as due to the increased deformation of the Debye layer with increasing field strength.

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The variables of interest are the electric potential in the electrolyte, ϕ^*; the fluid velocity, $\boldsymbol{u}^*$, and pressure, p^*; and the cation, n^*_+, and anion, n^*_-, number concentrations. In principle, Gauss' law at the particle surface introduces a coupling to the potential in the solid particle. However, this can typically be neglected for a dielectric particle in an aqueous electrolyte, due to the small solid-to-liquid permittivity ratio. The ionic flux density is given by the Nernst-Planck equation

$$\boldsymbol{j}^*_\pm = \mp \frac{D^*_\pm \mathcal{Z} e^*}{k^* T^*} n^*_\pm \nabla^* \phi^* - D^*_\pm \nabla^* n^*_\pm + \boldsymbol{u}^* n^*_\pm, \tag{1}$$

which includes electro-migration (the first term); diffusion (the second term); and advection. In (1) the plus sign is taken for cations and the minus sign for anions. At steady state $\boldsymbol{\nabla}^* \cdot \boldsymbol{j}^*_\pm = 0$. The problem is made dimensionless by normalizing distance with a^*; electric potential with ϕ^*_T; velocity by $\varepsilon^* \phi^{*2}_T / \eta^* a^*$ and pressure by $\varepsilon^* \phi^{*2}_T / a^{*2}$; and ion concentrations by n^*. Thus, the electric potential satisfies the (dimensionless)

Poisson equation,

$$\delta^2\nabla^2\phi = -\frac{1}{2}(n_+ - n_-). \tag{2}$$

The absence of an asterisk superscript on a variable indicates that it is the dimensionless counterpart of the appropriate dimensional variable: for example, the dimensionless potential $\phi = \phi^*/\phi_T^*$. The fluid flow is governed by the Stokes equations

$$\nabla^2\boldsymbol{u} - \boldsymbol{\nabla}p + (\nabla^2\phi)\nabla\phi = 0 \;\text{ and }\; \boldsymbol{\nabla}\cdot\boldsymbol{u} = 0. \tag{3}$$

The first equation in (3) is a momentum balance on an inertialess fluid element accounting for hydrodynamic stresses and an electric (Coulomb) body force, and the second is the continuity equation for an incompressible fluid. Using the continuity equation with $\boldsymbol{\nabla}^*\cdot\boldsymbol{j}_\pm^* = 0$ yields

$$\boldsymbol{\nabla}\cdot(n_\pm\boldsymbol{\nabla}\phi) - \nabla^2 n_\pm + m_\pm\boldsymbol{u}\cdot\boldsymbol{\nabla}n_\pm = 0. \tag{4}$$

Here, $m_\pm = \epsilon^*\phi_T^{*2}/\mu^* D_\pm^*$ are ionic drag coefficients with a value of around 0.5 for univalent aqueous electrolytes at room temperature [3].

We adopt an (inertial) frame of reference translating with the particle. Let (r, θ, φ) be spherical polar coordinates anchored at the particle centroid, where r is the distance from the centroid; θ is the polar angle from the direction of the applied field (denoted by unit vector $\hat{\boldsymbol{z}}$); and φ is the azimuthal angle about $\hat{\boldsymbol{z}}$. Hence, far from the particle

$$\boldsymbol{u} \to -\beta M_{EP}\hat{\boldsymbol{z}}, \;\; p \to 0, \;\; n_\pm \to 1, \;\text{ and }\; \nabla\phi \to -\beta\hat{\boldsymbol{z}} \;\text{ as }\; r \to \infty, \tag{5}$$

where $M_{EP} = M_{EP}^*/(\varepsilon^*\phi_T^*/\eta^*)$. Since the fluid is incompressible, the pressure is only defined up to an additive constant and hence we state that it attenuates at large distances. At the surface of the sphere, $r = 1$, we impose

$$\boldsymbol{u} = 0, \;\; -\delta\hat{\boldsymbol{n}}\cdot\boldsymbol{\nabla}\phi = \sigma \;\text{ and }\; \hat{\boldsymbol{n}}\cdot(\mp n_\pm\nabla\phi - \nabla n_\pm) = 0 \;\text{ at }\; r = 1, \tag{6}$$

where $\hat{\boldsymbol{n}}$ is the outward unit vector to the particle surface. The first condition in (6) stipulates no slip and no fluid penetration at the particle surface. The second condition is Gauss's law, in which $\sigma = \sigma^*/\varepsilon^*\kappa^*\phi_T^*$ is the dimensionless surface charge density. We have asserted that the surface charge density retains its equilibrium distribution, despite the particle being in motion. A common alternative is to specify the potential at the particle surface. O'Brien and White [9] state that the weak-field mobility is independent of the electrostatic condition at the particle surface: that is, any perturbation to the equilibrium charge density (or surface potential, if that is specified) due to the applied field does not affect the value of the mobility. However, there is no reason to believe that this holds beyond the weak-field regime, as they also note. The third condition imposes zero ionic flux across the inert particle surface.

The problem is closed by enforcing zero net force on the particle,

$$\int_S (\boldsymbol{N} + \boldsymbol{M})\cdot\hat{\boldsymbol{n}}\,\mathrm{d}S = 0, \tag{7}$$

Article	β	δ	$\|\sigma\|$	$Bi = \delta\|\sigma\|$
Carndenas-Benitez *et al.* [14]	15.7	0.02	113	2.26
Kumar *et al.* [23]	7.94	0.08	0.78	0.06
Tottori *et al.* [16]	2.98	0.03	26.7	0.80
Shilov *et al.* [22]	14.4	0.00029	0.43	0.00012
Youssefi & Diez [18]	96	9.6	unknown	unknown

Table 1: Estimated dimensionless field strength β, dimensionless Debye length δ, dimensionless surface charge density σ, and Bikerman number Bi for the experimental studies discussed in section 2. The value of β is for the maximum field strength in each experiment. The values for [16] pertain to their experiments using polystyrene particles. The surface charge density and zeta potential of the particles in [18] were not reported; hence, we cannot reliably estimate σ or Bi here. A field-dependent mobility is observed in all experiments excepting [23].

where S is the particle surface; $\boldsymbol{N} = -p\boldsymbol{I} + \boldsymbol{\nabla u} + (\boldsymbol{\nabla u})^\dagger$ is the Newtonian hydrodynamic stress (with $\boldsymbol{I}$ the identity tensor and † denoting transposition); and $\boldsymbol{M} = \boldsymbol{\nabla}\phi\boldsymbol{\nabla}\phi - \frac{1}{2}(\boldsymbol{\nabla}\phi \cdot \boldsymbol{\nabla}\phi)\boldsymbol{I}$ is the Maxwell stress. The axial symmetry of the problem about $\hat{\boldsymbol{z}}$, whereby no field variables depend on φ, means that Maxwell stresses do not generate an electrical torque on the sphere; the particle does not rotate. Since $\boldsymbol{\nabla} \cdot \boldsymbol{N} = \boldsymbol{\nabla} \cdot \boldsymbol{M} = 0$ the integral (7) may, in fact, be taken over any closed surface enclosing the particle. Choosing that surface to lie far from the particle, it may be shown that Maxwell stresses do not contribute to the integral in the weak-field limit. Hence, there is zero hydrodynamic force on the particle to first order in $O(\beta)$, which implies that the velocity field decays faster than $1/r$ at large distances from the particle. Consequently, hydrodynamic interactions between a pair of particles undergoing linear electrophoresis are weak compared to a sedimenting pair. Application of (7) can be cumbersome as the velocity gradient must be computed. As an alternative, the Lorentz reciprocal theorem yields a direct quadrature for the mobility [24]

$$M_{EP} = \frac{1}{6\pi\beta} \int \hat{\boldsymbol{z}} \cdot \left[\left(-1 + \frac{3}{4r} + \frac{1}{4r^3} \right) \boldsymbol{I} + \left(\frac{3}{4r} - \frac{3}{4r^3} \right) \frac{\boldsymbol{rr}}{r^2} \right] \cdot \left(\nabla^2 \phi\right) \left(\boldsymbol{\nabla}\phi\right) \, \mathrm{d}\boldsymbol{r}, \tag{8}$$

where $\boldsymbol{r}$ is the position vector from the particle centroid, and the integral is over the fluid volume. In summary, the nonlinear electrophoresis problem is governed by the field equations (2)-(4), boundary conditions (5)-(6), and constraint (7). There are three dimensionless groups: σ, δ and β.

It is instructive to characterize the experimental studies discussed in section 2 in terms of these dimensionless groups (table 1). All the studies except for [18] fall within the thin-Debye-layer limit, where δ is considerably smaller than unity. The nonlinear electrophoresis problem is amenable to asymptotic analysis in this limit, as discussed in the next section. Note, the thick-Debye-layer limit $\delta \gg 1$ can also be tackled by asymptotic methods [25]. Here, the colloid can be approximated as a point charge to leading order in $1/\delta$, yielding an analytic formula for the field-dependent mobility. This prediction compares reasonably well to experiments on the electrophoresis of polystyrene particles in a surfactant-doped aliphatic hydrocarbon [26].

4. Thin-Debye-layer limit

4.1. The Schnitzer and Yariv macro-scale model

A systematic analysis of the thin-Debye-layer limit for nonlinear electrokinetic transport has been conducted by Schnitzer and Yariv (hereafter SY) [13]. Previous analyses of linear electrophoresis first assumed a weak applied field ($\beta \ll 1$) and then took the limit $\delta \to 0$ [10, 11, 12]. In contrast, SY [13] let $\delta \to 0$ without the imposition of a weak field. Conceptually, when $\delta \ll 1$ the electrolyte can be partitioned into two regions: an 'outer,' or 'bulk,' region with $r = O(1)$ as $\delta \to 0$; and an 'inner' region, the Debye layer, with $(r-1)/\delta = O(1)$ as $\delta \to 0$. The singular nature of the limit $\delta \to 0$ is evidenced by the small parameter δ multiplying the highest order derivative in the Poisson equation (2). Setting $\delta = 0$ in this equation gives leading order bulk electroneutrality: $n_+ = n_- = c$, where c is the mean 'salt' concentration. Hence, the ionic species balances (4) reduce to

$$\nabla^2 c = \frac{1}{2}(m_+ + m_-)\boldsymbol{u}\cdot\boldsymbol{\nabla} c, \tag{9}$$

$$\boldsymbol{\nabla}\cdot(c\boldsymbol{\nabla}\phi) = \frac{1}{2}(m_+ - m_-)\boldsymbol{u}\cdot\boldsymbol{\nabla} c. \tag{10}$$

The salt concentration satisfies an advection-diffusion equation, and the potential is non-harmonic in the event of salt gradients, or 'concentration polarization.' The Stokes equations remain of the form (3); thus, (3), (9) and (10) describe the leading order bulk dynamics. The leading order bulk charge density is $O(\delta^2)$ from (2), and it is this charge density that generates the Coulomb body forces on the bulk fluid. The bulk equations can meet the far-field boundary conditions (5) but cannot satisfy the boundary conditions at the particle surface (6). As mentioned above, there exists a boundary layer, or inner region, of width $O(\delta)$ adjacent to the particle — the Debye layer — in which electroneutrality is violated at leading order, enabling the surface boundary conditions to be met. Separate asymptotic expansions must be performed in the Debye layer, which are then matched to the bulk equations to yield effective boundary conditions on the bulk variables applied at $r = 1$. Here, $r = 1$ does not correspond to the actual particle surface; rather, it represents the outer edge of the Debye layer; in the thin-Debye-layer limit the two are indistinguishable when viewed on the particle scale. Hence, SY arrive at a 'macro-scale' model, wherein the Debye-scale transport is coarse-grained into the effective boundary conditions. Since the weak-field limit has not been invoked, their approach captures the effects of nonlinear (i.e. field dependent) surface conduction for highly charged particles under strong fields, which is the essential mechanism for a field-dependent mobility.

SY [13] identify 'moderate' and 'high' surface charge regimes based on the value of σ. The moderate regime corresponds to $\sigma = O(1)$. Here, the effective boundary conditions at $r = 1$ are simply the homogenous Neumann conditions $\partial\phi/\partial r = 0$ and $\partial c/\partial r = 0$, which signify the absence of surface conduction over a moderately charged particle. The fluid velocity is subject to the slip condition

$$\boldsymbol{u} = \zeta\boldsymbol{\nabla}_s\phi + 2\ln\left(1 - \tanh^2\left(\frac{\zeta}{4}\right)\right)\boldsymbol{\nabla}_s \ln c, \tag{11}$$

where the surface gradient operator $\boldsymbol{\nabla}_s = (\boldsymbol{I} - \hat{\boldsymbol{n}}\hat{\boldsymbol{n}})\cdot\boldsymbol{\nabla}$. The first term at the right side of (11) represents electro-osmotic slip, and the second term is a diffusio-osmotic slip owing to gradients in the bulk salt. This form of the slip velocity appears in a 1961 paper by Derjaguin *et al.* [27]. Finally, the surface charge is related to the zeta potential via $\sigma = 2\sqrt{c}\sinh(\zeta/2)$. Here, the zeta potential is defined as the difference between the uniform potential at the actual particle surface and the potential at the outer edge of the Debye layer. The latter is given by the value of the bulk potential ϕ at $r = 1$. Clearly, variations in the bulk salt concentration c at $r = 1$ will lead to a non-uniform zeta potential. However, it is evident from (5) and the effective Neumann conditions that the bulk salt is uniform, $c = 1$. Consequently, the bulk potential is harmonic, and the bulk flow solves the homogeneous Stokes equations subject to only the electro-osmotic slip portion of (11), wherein the uniform zeta potential is $\zeta = 2\sinh^{-1}(\sigma/2)$. Thus, $\sigma = O(1)$ for a moderately charged particle implies that $\zeta = O(1)$. Note, the Debye-Huckel limit corresponds to σ and ζ much less than unity. The disturbance to the imposed electric field due to the particle decays as a dipole, $1/r^3$, and therefore Maxwell stresses do not contribute to the force balance (7). Morrison [28] originally showed that the velocity field has the potential flow solution $\boldsymbol{u} = \zeta\boldsymbol{\nabla}\phi$ with zero accompanying pressure field, which satisfies the reduced condition of zero hydrodynamic force on any surface enclosing the particle. From (5) and the irrotational flow solution it is seen that the particle translates at velocity $\beta\zeta\hat{\boldsymbol{z}}$ in the laboratory frame; hence, the mobility is a constant: $M_{EP} = \zeta$. This is, of course, nothing but Smoluchowski's formula. However, as pointed out in [13], this result is *not* restricted to the weak-field limit for $\sigma = O(1)$. Indeed, in a earlier paper [29] these authors showed that Smoluchowski's formula holds even under a strong field $\beta = O(1/\delta)$ for a moderately charged particle, despite the strong field animating surface conduction that renders the bulk concentration non-uniform within a $O(\delta^{1/2})$ thin diffusive boundary later atop the Debye layer. In another paper SY suggest that Smoluchowski's formula could be invalidated at such large fields by polarization of the dielectric particle [30].

The high surface charge regime is $\sigma = O(1/\delta)$. Here, SY [13] show that there exists a nested boundary layer structure consisting of the $O(1)$ wide electroneutral bulk; the $O(\delta)$ wide Debye layer; and a 'Dukhin (sub-) layer,' *i.e.* an inner-inner layer, of width $O(\delta^2)$. The presence of the latter at a highly charged surface was identified by Hinch *et al.* [31] in their study of the low-frequency dielectric response of particles with thin Debye layers. Surface conduction occurs primarily in the Dukhin layer due to the large accumulation of counterions near the highly charged surface. The inevitable non-uniformity of the resulting tangential ionic fluxes over the curved particle surface necessitates that ions must be exchanged between the Dukhin layer, Debye layer, and bulk. Hence, the effective boundary conditions of the moderate surface charge regime are no longer valid. Instead, SY [13] derive the following conditions at $r = 1$ for a positively charged particle ($\sigma > 0$)

$$\frac{\partial c}{\partial r} + c\frac{\partial \phi}{\partial r} = 0, \tag{12}$$

$$\frac{\partial c}{\partial r} - Bi(1 + 2m_-)\nabla_s^2(\phi - \ln c) = 0, \tag{13}$$

where $Bi = \delta\sigma$ is a 'Bikerman number' that, by definition, is $O(1)$ for a highly charged surface and $O(\delta)$ for a moderately charged surface. The grouping $Du = Bi(1 + 2m_-)$ can be viewed as a Dukhin number. The slip boundary boundary condition on the fluid velocity now reads

$$\boldsymbol{u} = 4\ln 2\boldsymbol{\nabla}_s \ln c + \zeta\boldsymbol{\nabla}_s(\phi - \ln c), \tag{14}$$

where $\zeta = 2\ln\sigma - \ln c$. For a negatively charged particle the above conditions are modified by replacing m_- with m_+; ϕ with $-\phi$; and ζ with $-\zeta$. Further, in this case, $\zeta = -2\ln(-\sigma) + \ln c$ and $Bi = -\delta\sigma$. The effective boundary conditions (12) and (13) cannot allow a uniform salt distribution. An important consequence is that the zeta potential is non-uniform even though the particle surface bears a uniform charge distribution. Hence, the notion of a 'particle zeta potential' needs to be treated with caution.

The macro-scale model at high surface charge density must generally be solved numerically. However perturbation methods can be applied in certain limits. For instance, consider a weak applied field $\beta \ll 1$. Here, the mobility has the asymptotic expansion

$$M_{EP} = M_{EP,0} + M_{EP,2}\beta^2 + O(\beta^4), \tag{15}$$

where the absence of odd powers of β is dictated by the fore-aft symmetry of a uniformly-charged spherical particle (or any fore-aft symmetric particle, for that matter). SY [13] find the leading order mobility

$$M_{EP,0} = \frac{\zeta_0 + Du\ln 16}{1 + Du}, \tag{16}$$

where $\zeta_0 = 2\ln\sigma$ is the equilibrium zeta potential. Equation (16) agrees with previous calculations based on a weak-field linearization of the electrokinetic equations [11, 12]. In a subsequent paper, SY computed the mobility through $O(\beta^2)$ [17]. Here, they show that the weak-field limit is, in fact, singular, due to the competition between salt advection versus diffusion. To illustrate this, in [17] the advection-diffusion equation (9) is re-written as

$$\nabla^2\bar{c} = \frac{1}{2}(m_+ + m_-)\beta\bar{\boldsymbol{u}}\cdot\boldsymbol{\nabla}\bar{c}, \tag{17}$$

in terms of a rescaled velocity $\boldsymbol{u} = \beta\bar{\boldsymbol{u}}$ and salt concentration $c = 1 + \beta\bar{c}$. The $O(1)$ contribution to $\bar{c}$, say $\bar{c}_1$, is a diffusive dipole decaying as $1/r^2$. Hence, advection balances diffusion in (17) at (large) distances $r = O(1/\beta)$, even though β is assumed small. This situation is analogous to the classic problem of forced convection of heat or mass from a particle in a uniform stream at small Péclet number [32]. The resolution is to employ matched inner-outer asymptotic expansions on the macro-scale model, with the inner and outer regions corresponding to $r = 1$ and $r = O(1/\beta)$, respectively. Since $\beta\bar{c}_1 \sim \beta^3$ at $r = O(1/\beta)$, the first contribution to the non-uniform salt distribution in the outer region is at $O(\beta^3)$. This contribution is needed to determine the $O(\beta^3)$ salt and potential variations in the inner region, say c_3 and ϕ_3, respectively, which in turn are needed for calculation of the $O(\beta^2)$ contribution to the mobility $M_{EP,2}$. That calculation requires one to determine the force balance (7) at $O(\beta^3)$; there are four components to the balance at this order: (i) the Stokes drag; (ii) the hydrodynamic force due to the (electro- and diffusio-osmotic) slip velocity; (iii) the hydrodynamic force due to the Coulomb body force distribution; and (iv) an electrostatic (Maxwell) force. The existence of a non-zero electric force acting on the particle and its (polarized) Debye layer beyond the weak-field regime was previously identified by O'Brien and White [9] and Shilov *et al.* [22]. An important consequence of this net electric force is that there will be a non-zero hydrodynamic force on any surface enclosing the particle. Hence, the velocity field due to a particle undergoing nonlinear electrophoresis will decay as $1/r$ at large distances. This should be contrasted to the weak-field regime, where the velocity decay is faster than $1/r$ due to the zero electric force on the particle at first order in β. Thus, the notion that hydrodynamic interactions between particles undergoing electrophoresis are weaker than sedimenting particles [33] is valid only in the weak-field regime.

An analytical formula for $M_{EP,2}$ is provided in equation (5.9) of [17]; we do not state it here due to its length. However, we note that $M_{EP,2}$ is a function of Du, m_+, m_-, and ζ_0. The numerical value of $M_{EP,2}$ is particularly sensitive to m_+ and m_- and may even change sign depending on the values thereof, which illustrates the highly ion-specific nature of nonlinear electrophoresis. SY [17] demonstrate good agreement between their asymptotic calculation of $M_{EP,2}$ and a finite-volume solution of the macro-scale model up to $\beta = 0.8$. The form of $M_{EP,2}$ derived by [17] differs from an expression for $M_{EP,2}$ derived by [22]; the latter work neglects ion advection and asserts a uniform zeta potential, which are questionable approximations. It should be acknowledged, nonetheless, that Shilov *et al.* [22] did identify that the first nonlinear contribution to the mobility occurs at $O(\beta^2)$, following earlier works by Siminova and Dukhin [34, 35]. Indeed, A. S. Dukhin and S. S. Dukhin [36] proposed that a field-squared contribution could lead to net electrophoretic drift of a particle in an alternating applied field, which they termed ‘aperiodic electrophoresis.’

A second case where asymptotic analysis is possible is when $Du \ll 1$ with β fixed. Here, SY [37] expand the bulk variables to first order in Du as

$$\phi = \phi_0 + Du\phi_1 + \cdots , \; c = 1 + Duc_1 + \cdots , \; \boldsymbol{u} = \boldsymbol{u}_0 + Du\boldsymbol{u}_1 + \cdots , \; p = p_0 + Dup_1 + \cdots , \tag{18}$$

where the zeroth order terms correspond to Morrison’s solution[28], for which the irrotational flow $\boldsymbol{u}_0 = \zeta_0 \boldsymbol{\nabla}\phi_0$ is accompanied by a null pressure field $p_0 = 0$. Consequently, the mobility has the expansion

$$M_{EP} = M_{EP,0} + DuM_{EP,1} + \cdots , \tag{19}$$

where $M_{EP,0} = \zeta_0$, and $M_{EP,1}$ is the field-dependent $O(Du)$ correction. The essential step in determining $M_{EP,1}$ is to solve an advection-diffusion equation for the perturbed salt field c_1, wherein the relative importance of advection versus diffusion is parametrized by a Péclet number $Pe = (m_+ + m_-)\zeta_0\beta/2$. The perturbed potential ϕ_1 can be immediately determined from knowledge of c_1, and it is only these two quantities that are required to evaluate $M_{EP,1}$ from an appropriate approximation of the force balance (7). The advection-diffusion equation is amenable to analytic treatment for small and large Pe. The former case is realized (assuming ζ_0 fixed) at weak fields, $\beta \ll 1$, or for small ions $(m_+ + m_-) \ll 1$. In the weak-field limit, SY [37] show that for a positively-charged particle $M_{EP,1} \sim -[4 \ln \cosh(\zeta_0/4) + \zeta_0]\beta$, which corresponds to a retardation in the particle motion, since $M_{EP,1}$ is evidently negative. The retarding influence of surface conduction at weak fields is in agreement with previous calculations [12]. A more surprising result occurs for small ions: here, SY [37] show that $M_{EP,1} \sim -[4 \ln \cosh(\zeta_0/4) + \zeta_0]\beta + 2\beta^3/21$. Hence, $M_{EP,1}$ transitions from negative to positive values as β increases, which corresponds to a transition from retardation to enhancement of particle motion. At large Pe (realized by $\beta \gg 1$) a diffusive boundary layer of width $O(\beta^{-1/2})$

develops at $r = 1$ in which the salt is strongly polarized, $c_1 \sim O(\beta^{1/2})$. This salt scaling has been previously recognized [38, 39]. SY [37] solve for c_1 to yield an asymptotic formula that shows $M_{EP,1} \sim \beta^{3/2}$ at large Pe. This scaling has been derived in previous studies [20, 39, 40]; however, the coefficients therein of the $O(\beta^{3/2})$ term differ from [37]. SY also solve the advection-diffusion equation for c_1 by a numerical scheme to bridge the above-mentioned limiting cases.

It is time to revist the experimental conditions summarized in table 1. The lack of a field-dependent mobility in the [23] can be now be understood as these experiments are in the moderate surface charge regime, $Bi = 0.06$. However, so too are the experiments of [22], which do exhibit a field-dependent mobility: indeed Bi is much smaller than unity here. The reason for this is unclear, although, recall, these experiments measured the lateral field-induced drift of sedimenting particles, unlike the microfluidic approach of the other studies in table 1. Finally, the conditions in [14] and, arguably, [16] correspond to $O(1)$ values of β and Bi (and thus Du), which are beyond the range of validity of the asymptotic approximations to the SY model discussed above. Numerical computations of the SY model are required at such values of β and Bi.

4.2. Applications of the SY model

Sherwood and Ghosal [41] used concepts from the SY macro-scale model to study nonlinear electrophoresis of a tightly fitting sphere in a tube of circular cross section. The sphere travels along the axis of the tube at a speed proportional to $E^*(\zeta_s^* - \zeta_c^*)$ to first order in field strength, where ζ_s^* and ζ_c^* are the zeta potentials of the sphere and tube wall. Interestingly, the first nonlinear correction to this speed is found to be proportional to $E^{*3}(\zeta_s^* + \zeta_c^*)^2(\sigma_s^* + \sigma_c^*)$, where σ_s^* and σ_c^* are the surface charge densities of the sphere and wall. Therefore, this correction should be measurable, in principe, for particles and tubes with zeta potentials close to one another, since the linear speed will be small.

Calero *et al.* [42] used the small-Du approximation to the SY model [37] to calculate the flow around a charged, dielectric circular cylinder immersed in a symmetric binary electrolyte under an alternating electric field. Under the assumption that Pe is small, they predicted that surface conduction is responsible for a rectified, or stationary, quadrupolar flow around the cylinder whose magnitude is proportional to the square of the field strength. The flow is directed such that fluid is drawn toward the cylinder along the direction of the applied field and pushed outward along the direction perpendicular to the field. This field-squared scaling can loosely be understood as follows: 'one power' of the field induces a non-uniform (dipolar) zeta potential via surface-conduction, the action of the applied field (the 'second power') on this induced potential drives a quadrupolar flow. Such flows were also predicted by Gamayunov *et al.* [43], who suggested that they would lead to net relative motion between a pair of particles in an alternating field. Indeed, experiments by Mittal [44] observed a steady force between two polystyrene latex particles in a KCl solution under an alternating field, where one particle is held fixed in an optical trap and the other is brought successively closer to it. Calero *et al.* [42] compare their theoretical predictions against experimental observation of the flow around a square array of cylindrical pillars, where the diameter of an individual pillar is 20μm. Reasonably good agreement between their theory and experiments is observed: in particular, both suggest that the flow velocity decays in magnitude with the inverse square root of the field frequency. These authors term the observed rectified flow as ‘concentration-polarization electro-osmosis’ (CPEO), perhaps to a draw a distinction with the well known quadrupolar induced-charge electro-osmotic (ICEO) flow around an ideally polarizable, uncharged cylinder [45, 46]. For instance, the characteristic ICEO flow velocity for their experimental conditions is about an order of magnitude smaller than what is observed. Another paper by this group [47] observed the CPEO flow around a charged dielectric latex sphere of 3μm diameter. Here, the particle size is such that the Dukhin number is not small; hence, calculations based on the weak-field approximation to the SY model [17] are performed, which, again, compare favorably to the experiments. In [42] and [47] unsteadiness is accounted for by adding the time derivative of salt, $\partial c/\partial t$, to the right side of the bulk equations (9) and (10). However, the steady effective boundary conditions (12) and (13) are employed; that is, the dynamics of Debye-layer charging are unaccounted for. This is an assumption worth revisiting.

5. Numerical computations

Asymptotic techniques can be utilized to analyze nonlinear electrophoresis for $\delta \ll 1$ and $\delta \gg 1$. Computations are required to bridge the gap between these limiting cases. Here we discuss a few papers that analyze nonlinear electrophoresis from numerical solution of the electrokinetic equations. Fixman and Jagannathan [48] used multipole expansions of these equations to compute the nonlinear electrophoresis of a charged dielectric sphere of fixed surface potential (ζ_0) in a uniform field. Their framework can, in principle, account for a gravitational force on the sphere and hydrodynamic slippage at the particle surface, although results are only presented for a neutrally buoyant particle. One set of computations was conducted for $\zeta_0 = 6$ and $\delta = 0.02$ up to a maximum field strength of $\beta = 2$. This value of δ falls within the thin-Debye-layer limit, and the surface potential corresponds to an equilibrium surface charge density of $\sigma_0 \approx 2\sinh(\zeta_0/2) = 20$. Hence, these conditions correspond to the moderate surface charge regime described above; therefore, it is reassuring that [48] do not observe a dependence of electrophoretic mobility on field strength. A second set of computations is conducted for $\zeta_0 = 3$ with $\delta = 1/3$ up to $\beta = 1.8$; again, a field-independent mobility is obtained. However, these authors show that the net charge and dipole moment of the sphere do vary with field strength. Additionally, they present a lucid discussion of how the structure of the ion concentration distributions change with increasing field strength. In particular, at the largest fields considered variation in the bulk salt concentration can extend for many Debye lengths from the particle surface, in a fore-aft asymmetric manner that is reminiscent of the boundary-layer/wake structure encountered in forced convection of heat and mass past a particle [32].

Bhattacharyya and Gopmandal [49] used a finite volume scheme to solve the electrokinetic equations for a a dielectric sphere with fixed surface potential, under the actions of collinear uniform flow and electric fields. Their computations use the Navier-Stokes equations, as opposed to creeping flow equations. Figures 8 and 9 of their paper plots the anion concentration and charge density around a positively charged particle for $\delta = 0.03125$, $\zeta_0 = 1$, and $\beta = 1$. The magnitude of the imposed flow is characterized by a number α, where $\alpha = 1$ corresponds to no flow (solely electrophoretic motion, that is), and increasing α increases the flow strength. Only a slight for-aft asymmetry in the ionic distribution is seen at $\alpha = 1$, which is to be expected as $\beta = 1$ is a rather modest value. However, a prominent fore-after asymmetry is seen when α is increased to 500 and then 1000. Here, the strong imposed flow sweeps ions past the particle; a thin boundary layer of rapid ion concentration variation forms at the upstream face of the particle, and a wake persists downstream. A similar ion distribution was shown by Keller *et al.* [50] in their finite element computation of a charged particle held fixed in a uniform flow of an electrolyte.

The above studies assume that a steady imposed field (and/or flow) elicits steady electrophoretic motion. A recent paper by Frants *et al.* [51] has challenged this assumption. These authors used a finite-difference scheme coupled with semi-implicit Runge-Kutta time stepping to compute the electrophoresis of a dielectric sphere of fixed surface charge. Their computations indicate that a long-time steady state is attained for $\delta = O(1)$; a markedly different situation occurs at small δ. Specifically, streamlines around the particle are presented in their figure 3 for $\beta = 320$, $\delta = 0.0086$, and $\sigma = 5$, which indicate the presence of steady toroidal vortices at the rear of the sphere. Similar vortices have been observed around ion-selective particles [52, 53]. Under these conditions $\beta\delta = 2.752$ and $\sigma\delta = 0.043$, corresponding to a very strong field applied around a moderately charged particle. Upon further increase of β the flow becomes unsteady: at first the vortices are shed periodically from the sphere and then at even larger β the shedding is chaotic. Frants *et al.* [51] draw an analogy of this situation with the Karman vortex street, which refers to inertially-driven vortex shedding in flow past a bluff body. The computations in [51] are, in contrast, at zero-Reynolds-number, which begs the question: what is the origin of the vortex shedding? Clearly, shedding must arise from some nonlinear feature of the flow problem: Frants *et al.* [51] suggest it is due to the Coulomb body force on the fluid, which is nonlinear in the electrostatic potential. Additionally, the ion conservation equations involve a nonlinear coupling through the material derivative of the ion concentration. These seem like plausible ingredients for a transition from steady to chaotic flow, which, naturally, would be accompanied by a transition from steady to unsteady particle motion, where the instantaneous particle velocity possesses components misaligned with the electric field. (However, it is expected that the time-averaged particle motion is along the field direction.) Hence, as suggested in section 1, it is not guaranteed that a particle undergoes steady, rectilinear translation under a steady applied field. Indeed, the work of Frants *et al.* [51] hints at a rich, dynamical response for sufficiently large field strengths. Of course, it is questionable if such field strengths are feasible in experiment without complicating factors, such as Joule heating: for example, $E^* = 81.3\text{kV/cm}$ for $a^* = 1\mu\text{m}$ at $\beta = 325$.

The discussion in this section is synthesized into a regime map, with axes σ and β, for nonlinear electrophoresis in the thin-Debye-layer limit (Fig. 2). Smoluchowski's formula for M_{EP} is valid for $\sigma = O(1)$ and $\beta = O(1)$, corresponding to a moderately charged particle in a moderate strength field. SY's weak-field expansion [17] is applicable to a highly charged particle ($\sigma = O(1/\delta)$) in a weak field ($\beta < O(1)$). In the transition zone from a moderately to highly charged particle, such that $\delta\sigma < 1$ but not much smaller than unity, the small Dukhin number expansion of SY [37] can be used to compute M_{EP} up to moderate fields. Numerical computations are required to determine M_{EP} for a highly charged particle $\sigma = O(1/\delta)$ in a moderate field $\beta = O(1)$. These computations could involve solving the SY macro-scale model or full electrokinetic

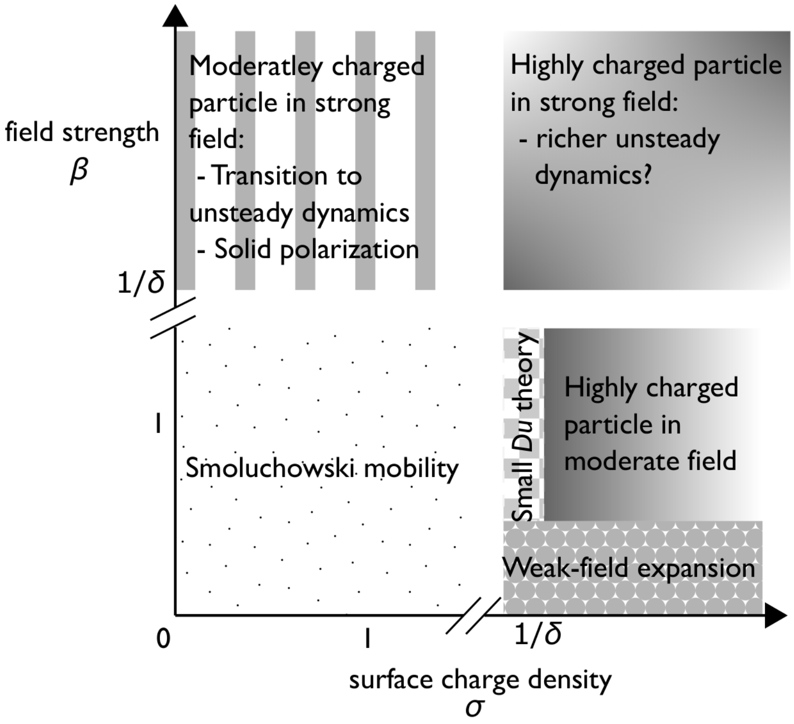

Figure 2: A regime map for nonlinear electrophoresis in the thin Debye layer limit, $\delta \ll 1$.

equations under these conditions. For $\sigma = O(1)$ and $\beta = O(1/\delta)$ a moderately charged particle is exposed to a strong field. Here, Smoluchowski's mobility may be invalidated by solid polarization. Additionally, the computations of Frants *et al.* [51] suggest a progression from steady to unsteady to chaotic dynamics as β increases in this range. The final area of this map, which remains to be explored, is for a highly charged particle $\sigma = O(1/\delta)$ in a strong field $\beta = O(1/\delta)$. Here, numerical computations must be used: it is expected that this regime also exhibits a transition to unsteady motion.

6. Aspects not covered here

This short review is focused on electrophoresis of a dielectric particle with a fixed surface charge density. While the electrostatic condition at the particle surface makes no impact on the linear electrophoretic mobility, this does not hold in the nonlinear regime. In this regard, consider the field-dependent mobility of a charged, ideally polarizable (e.g. metallic) particle [54, 55, 56]. Here, an imposed field induces a non-uniform surface charge distribution, in addition to the uniform equilibrium distribution. Consequently, the uniform potential of the conducting particle must adjust from its equilibrium value to maintain the same total charge on the particle. There is, in general, a nonlinear relation between the surface potential and particle charge, i.e. a voltage-dependent differential capacitance, which yields a field-dependent electro-osmotic slip velocity and, thereby, a field-dependent mobility. Thus, surface conduction is not required for a field-dependent mobility, although it can be an additional factor for conductors with a sufficiently large equilibrium charge [57]. This should be contrasted to a dielectric particle with fixed charge, for which the charge distribution is unaffected by an applied field. In this case, a non-uniform, field-dependent zeta potential is induced by surface conduction, which then yields a field-dependent mobility. There has also been work performed on the electrophoresis of ion selective particles. Here, concentration polarization occurs even in the absence of surface conduction due to charge selective transport through the particle. At sufficiently large imposed fields, an over-limiting current (i.e., exceeding the Nernst limit) is sustained by a non-equilibrium space-charge later atop the Debye layer on the ‘cathodic’(‘anodic’) side of a cation(anion) selective particle. A ‘second-kind’ electro-osmotic flow is set up in this space-charge layer [58], leading to second-kind, or ‘super-fast,’ electrophoresis, where the mobility is field dependent [52, 53, 59]. Finally, our discussion has been restricted to particle motion in strong electrolytes. There exists a body of work on the field-dependent mobility of dielectric particles in surfactant-doped non-polar fluids [60, 26]. The low conductivity of these fluids relative to aqueous ionic solutions means that much larger field strengths can be applied without Joule heating or electrochemical reactions at the driving electrodes [61]. The charge carriers in these weak electrolytes are inverse micelles of the surfactant. Positively and negatively charged micelles can be separated in the vicinity of a charged particle by an imposed electric field: the field strength determines the extent of separation and thus changes the local ionic atmosphere around the particle, which yields a field-dependent mobility [62]. These systems can also exhibit ‘field-induced charging’ [63], where the surface charge varies with the applied field strength, which is an additional factor leading to a field-dependent mobility.

7. Conclusion and future directions

Major advances in nonlinear electrophoresis have been made over the last decade, including asymptotic schemes for thick and thin Debye layers; numerical computations using the full electrokinetic equations; and experimental measurements of field-dependent mobilities. However, we would be remiss not to acknowledge the contributions to this subject over several decades from the Ukrainian school of S. S. Dukhin and colleagues. We close this review by suggesting directions for future research. It would be of interest to pursue numerical computations of the SY macro-scale model for $O(1)$ values of the field strength β and Dukhin number Du, which are experimentally relevant (cf. table 1). The results thereof should be compared against numerical solutions of the full electrokinetic equations where possible. In this regard, we reiterate the utility of the SY scheme [13], which encapsulates the Debye-scale transport into effective boundary conditions on a macro-scale model that is, consequently, free from the scale disparity between the Debye length and particle size that renders the full electrokinetic equations difficult to solve. Further, one could use the SY model to compute the field-dependent, anisotropic mobility of non-spherical particles, with spheroids being a natural case to examine first. Here, note that SY used their macro-scale model to compute the mobility of rod-like particles in the weak field limit [64]. Extension of the SY model to alternating fields, or more general unsteady fields, would also be useful in light of the recent work on CPEO, and also to predict net interaction between particles in time periodic fields. This extension would require consideration of the time dependence of the bulk salt and flow (as done in [42]), and dynamical charging of the Debye layer.

As mentioned before, the nonlinear electrophoretic mobility is dependent of the electrostatic condition at the particle surface. Thus, the field-dependent mobility may provide a route to infer the nonequilibrium physicochemical state of a particle-electrolyte interface. This provides motivation to analyze the nonlinear electrophoresis of: (i) a solid particle whose surface charge is regulated by the local pH; or (ii) a drop with ionic charges that advect, diffuse, or electro-migrate along the drop interface, and are in adsorption-desorption equilibrium with the bulk electrolyte [65]. It would also be interesting to consider nonlinear electrophoresis in weak electrolytes, accounting for incomplete dissociation of ionic species [66].

The field-dependence of the mobility at $\beta = O(1)$ for a dielectric particle of fixed charge is caused by surface conduction of counterions. Surface conduction arises due to the large accumulation of counterions near a particle of sufficiently high charge, $\sigma = O(1/\delta)$. This accumulation is allowed by the inherent assumption within the PNP model that ions are non-interacting, point-sized charges. An implication of this assumption is that the PNP model can predict impossibly large ion concentrations near a highly charged surface, which has prompted analysis of linear electrophoresis with modified PNP equations that account for non-dilute effects, such as steric repulsion between finite-sized ions [67] or electrostatic correlations [68]. A natural question to ask, therefore, is whether nonlinear surface conduction is of physical relevance or merely a consequence of the unphysical predictions of the PNP model. The answer, provided by SY [13], is that surface conduction plays a dominant role relative to non-dilute effects over the range $O(1) \lesssim Bi \lesssim Bi_{cr}$. Here, the critical Bikerman number is $Bi_{cr} = (\varepsilon^* k^* T^*/(2\mathcal{Z}^2 e^* 2 l^{*3}))^{1/2}(N_A M^* a^*)^{-1}$, where $l^* = \mathcal{Z}e^* 2/(4\pi\varepsilon^* k^* T^*)$ is the Bjerrum length, N_A is Avogadro's number, and M^* is the molar electrolyte concentration. Using this definition of Bi_{cr}, surface conduction should dominate over non-dilute effects in a monovalent electrolyte provided that $M^* a^* \lesssim 6.8 \times 10^{-4}$, where M^* is in molars and a^* is in microns. For an electrolyte at millimolar concentration this requires $a^* \lesssim 0.68\mu$m. It would, nonetheless, be of interest to analyze the field-dependent mobility including non-dilute effects, to ascertain the interplay of such effects and surface conduction. Figliuzzi *et al.* [69] took a step in this direction by computing the nonlinear electrophoresis of fixed charge and ideally polarizable spheres in an electrolyte with steric repulsion between ions. These authors also incorporated the effect of 'dielectric decrement,' which refers to the linear reduction of the permittivity with ion concentration [70].

There are opportunities for experimental studies that parallel the suggestions made above, including: (i) probing larger field strengths, with one (ambitious) goal here being to test the predicted transition to unsteady motion [51]; (ii) expanding the library of particle-electrolyte surface chemistries on which nonlinear mobility measurements are made; (iii) measurement of the field-dependent mobility of non-spherical particles; (iii) observation of the field-dependent net interaction between pairs (or even multiple) particles driven by CPEO; (iv) quantifying the dynamic nonlinear mobility under alternating fields; and (v) measurements of nonlinear electrophoresis on drops or bubbles.

In conclusion, it is without question that linear electrophoresis played a central role in the development of colloid science over the twentieth century. It is hoped that this review has persuaded the reader that nonlinear electrophoresis has the potential to do the same over this century.

8. Declaration of competing interests

The author declares that he has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

9. Acknowledgements

I acknowledge support from the National Science Foundation through Grant No. CBET-200212. I thank Ory Schnitzer for helpful comments on this manuscript.

10. References and recommended reading

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* of special interest
** of outstanding interest

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