PHYSICAL REVIEW E **94**, 023115 (2016)

Nonlinear electrophoresis in the presence of dielectric decrement

B. Figliuzzi,[1,*] W. H. R. Chan,[2] C. R. Buie,[3] and J. L. Moran[4]
[1]*Mines ParisTech, PSL Research University, Center for Mathematical Morphology, 35 rue Saint-Honoré 77305 Fontainebleau Cedex, France*
[2]*Mechanical Engineering Department, Stanford University, 450 Serra Mall CA94305 Stanford, USA*
[3]*Department of Mechanical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue MA02139 Cambridge, USA*
[4]*Department of Nuclear Science and Engineering, Massachusetts Institute of Technology,*
77 Massachusetts Avenue MA02139 Cambridge, USA

(Received 24 February 2016; revised manuscript received 10 June 2016; published 30 August 2016)

The nonlinear phenomena that occur in the electric double layer (EDL) that forms at charged surfaces strongly influence electrokinetic effects, including electro-osmosis and electrophoresis. In particular, saturation effects due to either dielectric decrement or ion crowding effects are of paramount importance. Dielectric decrement significantly influences the ionic concentration in the EDL at high ζ potential, leading to the formation of a condensed layer near the particle's surface. In this article, we present a model incorporating both steric effects due to the finite size of ions and dielectric decrement to describe the physics in the electric double layer. The model remains valid in both weakly and strongly nonlinear regimes, as long as the electric double layer remains in quasiequilibrium. We apply this model to the study of two archetypal problems in electrokinetics, namely the electrophoresis of particles with fixed surface charges and the electrophoresis of ideally polarizable particles.

DOI: 10.1103/PhysRevE.94.023115

I. INTRODUCTION

When a charged surface is placed in an electrolyte, ions of opposite charges migrate and screen the surface, eventually forming an electric double layer (EDL). The structure of the electric double layer strongly influences electrokinetic phenomena, including electro-osmosis and electrophoresis. In 1903, Smoluchowski [1] predicted that the electrophoretic velocity U is proportional to the applied field E according to relation

$$U = \frac{\epsilon_m \zeta}{\eta} E, \tag{1}$$

where ϵ_m is the permittivity of the electrolyte, η its dynamic viscosity, and ζ the ζ potential at the surface of the particle. Later, it was shown that Smoluchowski's formula holds for a particle of arbitrary shape [2,3] and for assemblages of spherical particles with identical ζ potentials [4].

Smoluchowski's formula remains valid as long as the ζ potential is of the same order of magnitude as the thermal voltage [5]. At large applied voltages, ionic fluxes arise between the electric double layer and the bulk solution. These ionic exchanges result in a polarization of the concentration field around the particle, that in turn drives a diffusio-osmotic flow at the surface [6–9]. This particular regime is referred to as electrophoresis of the first kind [10–13]. Electrokinetics phenomena of the first kind have received considerable attention in the past few years [7,8]. The classical approach to incorporate surface conduction in the description of electrophoresis is the one proposed by O'Brien and coworkers [7,14–16]. They adopt a perturbative method by considering that the applied electric field perturbs the equilibrium of the electric double layer to derive the model's equations. More elaborate models have been developed, notably by Yariv and Schnitzer, that carefully study surface conduction phenomena in the weakly and strongly nonlinear regimes for quasiequilibrium electric double layers [5,17–19]. Other recent contributions that focus more specifically on diffusio-osmotic phenomena are the ones of Khair [20] and Rica and Bazant [21].

In addition to surface conduction phenomena, nonlinear effects arise in the EDL at high ζ potential. In this situation, the Gouy-Chapman model [22–24] classically used to describe the EDL does not correctly predict the ionic concentration profile. A first explanation is that this model relies on the assumption of pointwise ions. As reviewed by Bazant *et al.*, several models have been developed to account for steric effects due to the finite size of ions [25–31]. In particular, back in 1942, Bikerman [25,26] proposed a model based on a cubic lattice of spacing a that predicts counter-ion saturation as the concentration approaches closed-packing density. In 2008, Khair and Squires applied Bikerman's model to study the electrophoresis of particles with fixed surface charges [32]. They demonstrated that steric effects reduce surface conduction, which results in an increase of the mobility when compared to the classical models of O'Brien [14–16].

Bikerman's model provides a convenient analytical description but has been shown to significantly underestimate steric effects in hard-sphere liquids. Hence, more accurate approaches based on the Carnahan-Starling equation of state for a bulk monodisperse hard-sphere liquid have been proposed [33], notably to investigate polyelectrolyte adsorption on charged interfaces [34,35] and sedimentation [36]. An extensive discussion on the structure of the EDL can be found in the article of Giera *et al.* [37], which compares molecular dynamics simulations with local-density approximations. In their study, Giera *et al.* demonstrate that the Carnahan-Starling model yields an excellent agreement with molecular dynamics simulations. On the contrary, they show that Bikerman's model poorly captures excluded volume interactions. However, as discussed in the review article of Bazant *el al.* [38], by considering an effective ion size in Bikerman's lattice-based model, we recover a differential capacitance that is very similar to the one obtained with the Carnahan-Starling equation.

---

[*] bruno.figliuzzi@mines-paristech.fr

2470-0045/2016/94(2)/023115(14)

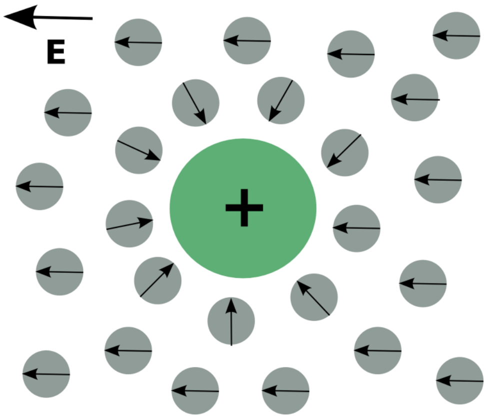


FIG. 1. Schematic view of dielectric decrement effects: In the immediate vicinity of the soluted ions, the water molecules are oriented toward the electrostatic field created by the solvated ion. This phenomenon causes the concentration to saturate in the EDL.

A second major nonlinear effect in the electric double layer is the dielectrophoretic force, which is caused by the effective polarizability of hydrated ions. Ions usually have smaller dielectric constant than water. Therefore, when included in water, ions create dielectric holes in the solution, leading to an overall decrease of the permittivity. In addition, in the immediate vicinity of the soluted ions, the orientation of the water molecules is largely dictated by the electrostatic field created by the ion, as shown in Fig. 1. These polarization phenomena result in a significant dielectric decrement. Ben-Yaakov *et al.* [39,40] and Hatlo *et al.* [41] have investigated in detail the effect of dielectric decrement on the structure of the EDL. Starting from thermodynamical considerations, they demonstrated that dielectric decrement causes the counter-ion concentration to saturate in the EDL at high ζ potential, a phenomenon referred to as dielectrophoretic saturation. This behavior is very similar to the one that is observed in the EDL in the presence of ion crowding effects. Recently, Nakayama and Andelman [42] incorporated both dielectric decrement and steric effects in a model aimed at predicting the differential capacitance of the EDL. The influence of dielectric decrement on electrophoresis of particles with fixed surface charges has been studied by Zhao and Zhai [43], who showed that dielectric decrement significantly reduces surface conduction, therefore yielding higher electrophoretic velocities.

Finally, nonlinearities in electrokinetics also stem from polarization phenomena. When an electric field is applied to an ideally polarizable particle in an electrolyte, its surface charges recombine. This yields a nonlinear electro-osmotic flow that arises due to the action of the electric field on its own induced diffuse charge. This phenomenon, termed induced-charge electro-osmosis, has first been described by Murtsovkin [44] and has subsequently been studied by Bazant and Squires [45,46]. In 2008, Yariv derived an expression for the electrophoretic mobility of ideally polarizable particles [47]. In his study, the electric double layer is described by the Gouy-Chapman model. The model predicts that at high applied voltages, the electrophoretic velocity goes to zero. This is an immediate consequence of the Gouy-Chapman model, which assumes pointwise ions. In 2008, by relying on the steric model developed in Refs. [29,30], Bazant *et al.* showed that the electrophoretic mobility scales as the square root of the applied electric field [38] for asymptotically high fields.

In this article, we present a model incorporating both steric effects due to the finite size of ions and dielectric decrement to describe the electrophoresis of particles with thin electric double layers. The model remains valid in both weakly and strongly nonlinear regimes, as long as the electric double layer remains in quasiequilibrium. We apply the model to study two archetypal problems in electrokinetics, namely the electrophoresis of particules with fixed surface charges and the electrophoresis of ideally polarizable particles. Following numerous studies in electrokinetics [48–52], we rely on numerical simulations to incorporate nonlinear effects including crowding effects due to the finite size of ions, dielectric decrement in the electric double layer, surface conduction, and concentration polarization and advection in the bulk solution and in the electric double layer. To our knowledge, the present study is the first to build on the steric-dielectric decrement model of Nakayama and Andelman [42] to quantitatively describe electrophoresis in the nonlinear regime.

The manuscript is organized as follows. In Sec. II, we derive the equations for the ionic concentration and the excess electric potential in the electric double layer in the presence of both crowding and dielectric decrement effects. Electro-osmotic and diffusio-osmotic flows in the electric double layer are discussed in Sec. III. In Sec. IV, we discuss the model's equations in the bulk solution. We account for several nonlinear effects, including concentration polarization, advective transport, and the effect of the body force that acts on the fluid in the vicinity of the particle due to conductivity gradients. In Secs. V and VI, we apply our model to two classic problems in electrokinetics, namely the electrophoresis of particles with fixed surface charges and of ideally polarizable particles. Conclusions are drawn in the last section.

II. ELECTRIC DOUBLE LAYER MODEL

Electric potential in the electric double layer

To describe the EDL, we rely on the assumption that the electric field is determined by the local mean charge density. The total free energy in the electric double layer is the sum of an electrostatic energy $\mathcal{U}$ and an entropic contribution $-T\mathcal{S}$. The electrostatic energy depends on the excess electric potential ϕ, defined as the electric potential difference $\psi - \psi_b$ between the electric double layer and the bulk solution and on the local ionic concentrations c_+ and c_-:

$$\mathcal{U} = \int_V \left[-\frac{\epsilon_m}{2}|\nabla\phi|^2 + ze(c_+ - c_-)\phi \right] d\mathbf{r}. \tag{2}$$

In this expression, z denotes ion valence and e elementary charge.

In the dielectric decrement model [41,43], it is assumed that the permittivity ϵ_m of the solvent varies linearly with the concentration:

$$\epsilon_m = [\epsilon_w - \alpha(c_+ + c_-)]\epsilon_0, \tag{3}$$

where ϵ_w is the relative permittivity of water and ϵ_0 is the permittivity of free space. The coefficient α depends on the ions of the solution. Typical values of α are 17 M^{-1} for H^+ ions, 11 M^{-1} for Li^+, 8 M^{-1} for Na^+, or 13 M^{-1} for OH^- [43]. In our model, to simplify the analysis, we consider that the dielectric decrement parameters of both co-ions and counter-ions are equal.

To account for steric effects due to the finite size of ions, we rely on Bikerman's lattice-based model. This model significantly underestimates volume exclusion effects when the lattice spacing is set equal to the ionic diameter. However, as shown by Bazant *et al.* [38], by considering an effective ion size a accounting for solvation effects, it estimates the differential capacitance of the EDL with good accuracy. With Bikerman's lattice-based model, in the presence of crowding effects, the entropic contribution yields [30]

$$-T\mathcal{S} = \int_V \frac{kT}{a^3}[a^3c_+\ln(a^3c_+) + a^3c_-\ln(a^3c_-) + [1 - a^3(c_+ + c_-)]\ln[1 - a^3(c_+ + c_-)]]d\mathbf{r}, \quad (4)$$

where k denotes the Boltzmann constant and T ambient temperature. The dimensionless packing parameter ν accounts for steric effects due to the packing of ions. It can be related to the effective ionic diameter a and to the bulk solution concentration $c_{b,\infty}$ through the estimate [29] $\nu = 2a^3c_{b,\infty}$. A characteristic value for the effective ion size is $a = 7$ Å [38]. Hence, the parameter ν ranges from 1.0×10^{-4} for dilute solutions to 0.1 for highly concentrated solutions.

From now on, we employ dimensionless variables to facilitate the physical analysis. We define the Debye length

$$\lambda_D = \sqrt{\frac{\epsilon_0\epsilon_m kT}{2z^2e^2c_{b,\infty}}} \quad (5)$$

as the characteristic length, the thermal voltage

$$\varphi_T = \frac{kT}{ze} \quad (6)$$

as the potential scale, and $c_{b,\infty}$ as the concentration scale. We finally introduce the dimensionless quantity

$$\hat{\alpha} = \frac{\alpha c_{b,\infty}}{\epsilon_w}. \quad (7)$$

For the remainder of the paper, we will omit the hat on $\hat{\alpha}$ to keep simple notations. $\hat{\alpha}$ ranges from 1.0×10^{-3} for dilute solutions to 0.05 for highly concentrated solutions.

Setting the variational derivatives of the free energy $\delta\mathcal{F}/\delta c_\pm$ to zero, we obtain an expression for the local ionic concentrations that takes into account both steric and dielectric decrement effects:

$$c_\pm = c_b\frac{\exp(\mp\phi - \alpha|\nabla\phi|^2)}{1 + \nu[\cosh(\phi)\exp(-\alpha|\nabla\phi|^2) - 1]}. \quad (8)$$

In this expression, c_b denotes the dimensionless bulk concentration in the immediate vicinity of the EDL.

Similarly, setting the variational derivative $\delta\mathcal{F}/\delta\phi$ to zero, we obtain the modified Poisson-Boltzmann equation in a similar form as those obtained by Hatlo *et al.* [41] and Zhao *et al.* [43]:

$$\nabla[(1 - 2\alpha(c_+ + c_-))\nabla\phi] = c_- - c_+. \quad (9)$$

The right-hand side of this equation represents the negative of the local charge density ρ_E. Note that for $\nu = 0$ and $\alpha = 0$, we recover the classical Poisson-Boltzmann equation [53].

It is not possible to solve Eq. (9) analytically. As a consequence, we rely on a pseudo-spectral method to calculate the excess potential in the electric double layer [54]. The model that we consider is strongly nonlinear. Therefore, we linearize Eq. (9) with respect to the electric potential and we use Newton's method to solve the complete nonlinear equation. We use a Chebyshev grid with 300 grid points for discretizing the linearized equations. Simulation results are shown in Fig. 2. We observe that both dielectric decrement and ion crowding effects result in ionic saturation in the electric double layer near the particle surface. In mathematical terms, near the surface of the particle, the saturation condition reads

$$\frac{dc_\pm}{dy} = 0, \quad (10)$$

y being the direction parallel to the surface of the particle. When dielectrophoretic saturation is reached before close packing of ions, we can neglect the denominator in expression (8) of the concentration. Hence, we find, in the saturated region,

$$\frac{d\phi}{dy}\left(1 - 2\alpha\frac{d^2\phi}{dy^2}\right) = 0. \quad (11)$$

Since local charge is constant in the presence of ionic saturation, the Poisson equation becomes

$$\frac{d^2\phi}{dy^2} = -\rho_c, \quad (12)$$

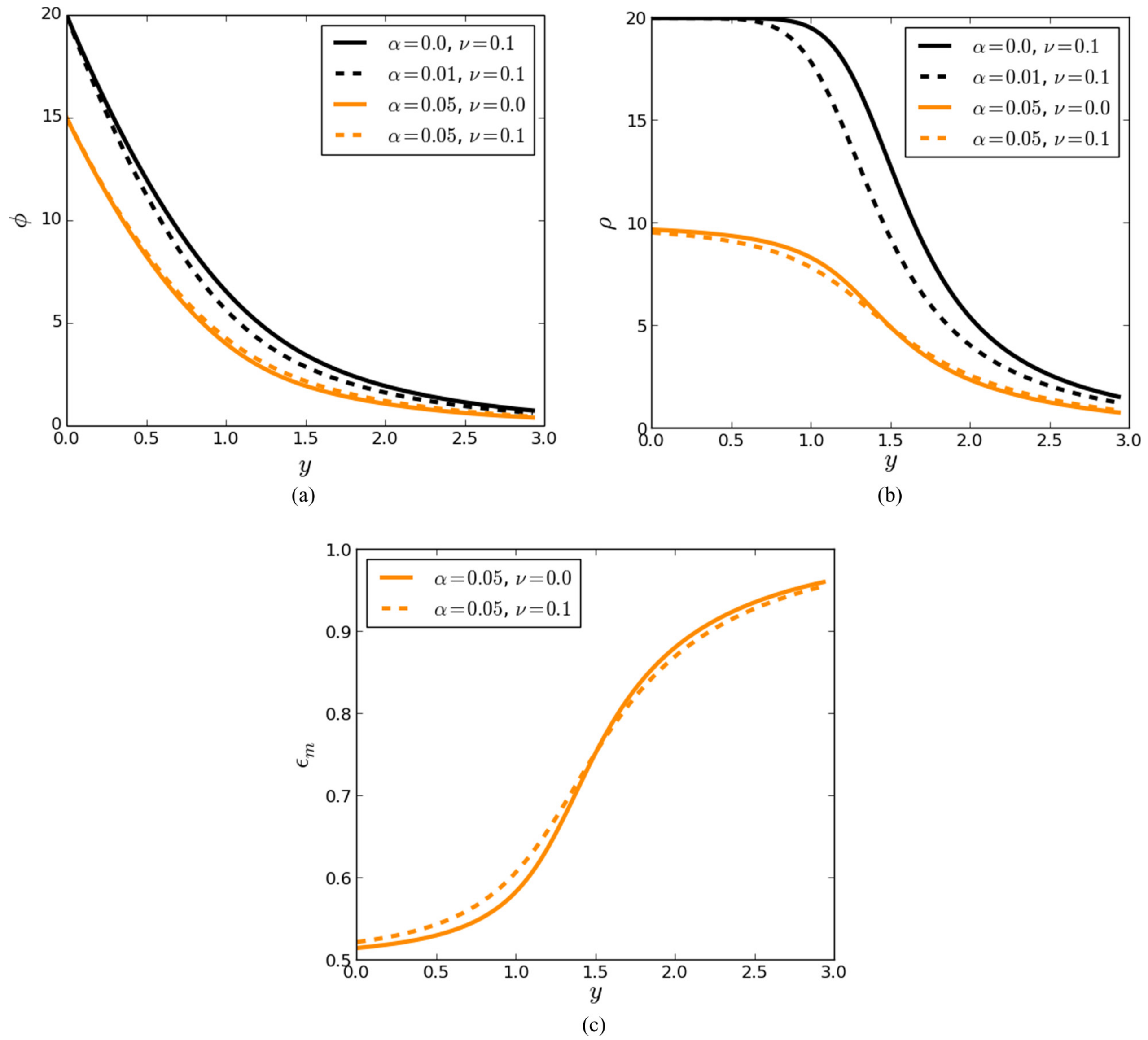
where ρ_c is the local charge in the saturated part of the EDL, given by

$$\rho_c = \frac{1}{2\alpha}. \quad (13)$$

In a similar manner, when saturation results from steric effects, the term $\exp(-\alpha|\nabla\phi|^2) \simeq 1$ remains of order $O(1)$, so when $\phi \gg 1$, we find

$$\rho \simeq \frac{2}{\nu}. \quad (14)$$

In Fig. 2, we note that saturation is caused either by dielectric decrement or steric effects due to the finite size of ions. In situations where $1/2\alpha \ll 2/\nu$, we observe that steric effects due to the finite size of ions are almost negligible. Similarly, when $1/2\alpha \gg 2/\nu$, dielectric decrement effects can be neglected. As a first approximation, to simplify the physical analysis, it is then legitimate to consider a steric only or a dielectric decrement only model depending on the value of the quantity $4\alpha/\nu$. In the Appendix, we present a simplified model where we decompose the electric double layer into two distinct regions, namely a condensed and a diffuse layer. This



(a)

(b)

(c)

FIG. 2. Excess electric potential (a), excess charge (b), and dimensionless permittivity (c) in the EDL for distinct values of the dimensionless packing parameter ν and of the dimensionless dielectric decrement parameter α. Note that our model predicts the correct saturation values for the concentration, that are, respectively, $2/\nu = 20$ and $1/2\alpha = 10$.

simpler model captures relatively well crowding effects and dielectrophoretic saturation and provides us with a simple but accurate analytical description of the electric double layer.

III. ELECTRO- AND DIFFUSIO-OSMOTIC MOBILITIES

In this section, we establish the equations for the fluid motion in the EDL. The fluid motion results from two distinct physical phenomena, namely electro- and diffusio-osmosis [6,8]. Electro-osmotic flow in the electric double layer arises under the action of the external electric field which perturbs the equilibrium of the double layer in the direction tangent to the surface of the particle. Diffusio-osmotic flow is caused by concentration gradients in the bulk solution that similarly perturb the double layer equilibrium in the direction parallel to the surface.

The equations for fluid motion in the EDL are obtained by solving the Stokes equation subject to the effect of external electric field. When projected on $\mathbf{e_y}$, since the electric double layer remains at equilibrium, the Stokes equation becomes

$$-\frac{\partial P}{\partial y} - \rho_E \frac{\partial \phi}{\partial y} = 0, \qquad (15)$$

where P is the local pressure, ρ_E the local electric charge density, and η the dynamic viscosity, assumed to be constant. This relation expresses that the pressure gradient equilibrates the action of the electric field within the EDL. In general, the local charge depends on the excess electric potential ϕ and on its gradient $\nabla\phi$. We can integrate Eq. (15) and perform the change of variables $y \to \phi(y)$ to obtain the pressure profile in the EDL:

$$P(y) = P_\infty + \int_y^{+\infty} \rho_E(\phi(y),\nabla\phi(y))\frac{\partial \phi}{\partial y}(y)dy. \qquad (16)$$

The EDL is not at equilibrium along direction $\mathbf{e_x}$. Therefore, when projected on $\mathbf{e_x}$, the Stokes equation reads

$$-\frac{\partial P}{\partial x} - \rho_E \frac{\partial \psi}{\partial x} + \eta \frac{\partial^2 u}{\partial y^2} = 0, \tag{17}$$

where u is the velocity in direction x. Using expression (16) found for osmotic pressure, we find

$$\frac{\partial}{\partial y}\left(\epsilon_m \frac{\partial \phi}{\partial y}\right)\frac{\partial \psi_b}{\partial x} + \eta \frac{\partial^2 u}{\partial y^2} - \left(\int_y^{+\infty} \frac{\partial}{\partial c_b}\left[\rho_E(\phi(y),\nabla\phi(y))\frac{\partial \phi}{\partial y}(y)\right]\mathrm{d}y\right)\frac{\partial c_b}{\partial x} = 0. \tag{18}$$

Far from the surface, the velocity gradient vanishes between the electric double layer and the bulk solution

$$\frac{\partial u}{\partial y}|_{y\to\infty} \to 0, \tag{19}$$

and there is no-slip at the surface of the particle

$$u|_{y=0} = 0, \tag{20}$$

which fixes the boundary conditions of the problem. Hence, we can integrate (18), first between y and $+\infty$ and then between 0 and y, to obtain the electro-osmotic mobility μ_{eo} and the diffusio-osmotic mobility μ_{do} in the EDL. We find

$$u(y) = \mu_{\mathrm{eo}}(y)\frac{\partial \psi_b}{\partial x} + \mu_{\mathrm{do}}(y)\frac{\partial c_b}{\partial x}, \tag{21}$$

where

$$\mu_{\mathrm{eo}}(y) = \frac{1}{\eta}\int_0^y \epsilon_m(y)\frac{\partial \phi}{\partial y}(y)dy \tag{22}$$

and

$$\mu_{\mathrm{do}}(y) = \frac{1}{\eta}\left[\int_0^y \int_{y_1}^{\infty} \int_{y_2}^{\infty} \frac{\partial}{\partial c_b}\left(\rho_E(\phi,\nabla\phi)\frac{\partial \phi}{\partial y}\right)dy_3dy_2dy_1\right]. \tag{23}$$

When the electric double layer is described by the classical Gouy-Chapman model, the local permittivity remains constant, and the electro-osmotic mobility is classically given by Smoluchowski's formula (1). This expression also holds for the Kilic model that accounts for ion crowding effects in the EDL but neglects dielectric decrement [29,30]. In the presence of dielectric decrement effects, the electrophoretic mobility must be calculated through a numerical integration of Eq. (22). One of the benefits of the composite-layers model described in the Appendix is that one can obtain an analytical formula approximating the electro-osmotic mobility that accounts for dielectric decrement effects:

$$\mu_{\mathrm{eo}} = \begin{cases} \dfrac{\epsilon_m}{2\eta}\left(\zeta + \ln\dfrac{1}{2\alpha}\right) & \text{if } \zeta > \ln(1/2\alpha) \\ \dfrac{\epsilon_m \zeta}{\eta} & \text{if } \zeta \leqslant \ln(1/2\alpha) \end{cases}. \tag{24}$$

In Fig. 3, we show a comparison between the electro-osmotic mobility calculated numerically with the model's equations and the electro-osmotic mobility calculated with (24) using the composite model. We note the good agreement between both models.

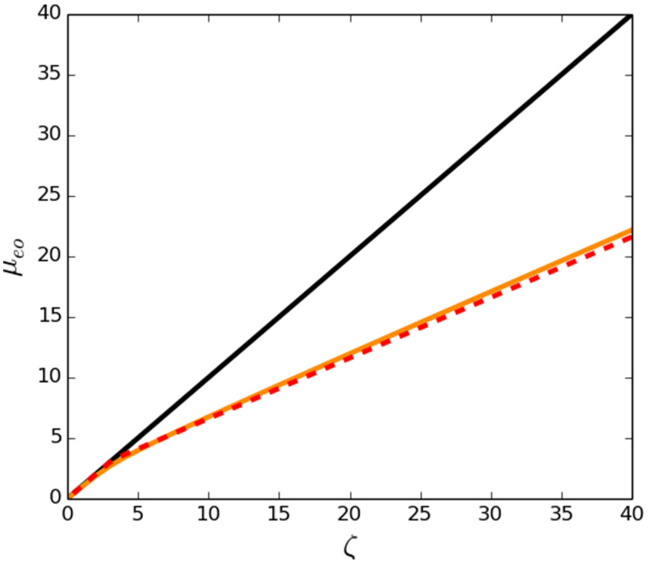


FIG. 3. Dimensionless electro-osmotic mobility as a function of the ζ potential for the steric model (in black) and the dielectric decrement model (in yellow). The electro-osmotic mobility calculated with the composite layer model using formula (24) is plotted with a dashed line. In this simulation, the dimensionless dielectric decrement parameter is $\alpha = 0.02$.

Similarly, explicit expressions for the diffusio-osmotic mobility have been found by Prieve *et al.* [8] and Rica and Bazant [21] when the electric potential in the EDL is described by the Gouy-Chapman model, and by Figliuzzi *et al.* [52] for the steric only model.

IV. ELECTROKINETICS IN THE BULK SOLUTION

In this section, we study the electrophoresis of charged particles in an electrolyte. We restrict our study to large particles with thin electric double layers. For such particles, the physical domain is classically divided into two regions, namely the bulk solution and the electric double layer. Both regions are described by asymptotic solutions which are matched using appropriate boundary conditions.

A. Electrokinetics in the bulk solution

Following classical approaches, we assume that the bulk solution is electroneutral. To simplify the physical analysis, we also assume that the diffusivities of the cations and anions are the same. The ion fluxes in the bulk solution are given by Nernst-Planck relations [55]

$$\begin{aligned} \nabla^2 c_b - \mathrm{m}_b \mathrm{div}(c_b \mathbf{u}) &= 0, \\ \mathrm{div}(c_b \nabla \Psi_b) &= 0, \end{aligned} \tag{25}$$

where m_b is a dimensionless ionic drag coefficient defined by

$$m_b = \frac{VR}{D} = \frac{\epsilon_m \varphi_T^2}{\eta D}. \tag{26}$$

These equations describe the concentration and the electric potential fields in the bulk solution.

B. Surface conduction phenomena

The inner and the outer asymptotic solutions are matched by appropriate boundary conditions expressing the conservation of ions across the diffuse interface between the electric double layer and the bulk solution [56]. We define the excess ion fluxes in the electric double layer as the difference between ion fluxes in the diffuse layer and ion fluxes in the bulk solution:

$$\mathbf{J}_{\mathbf{exc}}^{\pm} = -\frac{D}{kT}(c_{\pm} - c_b)\nabla\mu_b + c_{\pm}\mathbf{u} - c_b\mathbf{u}_{\mathbf{s}}. \tag{27}$$

In this expression, μ_b denotes the electrochemical potential in the bulk solution, $\mathbf{u}$ the fluid velocity in the EDL, and $\mathbf{u}_{\mathbf{s}}$ the slip velocity. We calculate the excess surface fluxes by integrating (27) between $y = 0$ and $+\infty$ in the electric double layer. In outer spherical coordinates, we obtain

$$\begin{aligned}\mathbf{J}_{\mathbf{S}}^{\pm} = \int_0^{+\infty} \mathbf{J}_{\mathbf{exc}}^{\pm}(y)dy = -\frac{D}{kT}c_b\Gamma_{\pm}\nabla_S\mu_b \\ + c_b\Gamma_{\pm}\mathbf{u}_{\mathbf{s}} + \int_0^{+\infty} c_{\pm}(\mathbf{u} - \mathbf{u}_{\mathbf{s}})dy,\end{aligned} \tag{28}$$

where $\Gamma_{\pm}$ is a surface adsorption coefficient [29], defined by

$$\Gamma_{\pm} = \frac{1}{c_b}\int_0^{+\infty} (c_{\pm}(y) - c_b)dy, \tag{29}$$

and ∇_S denotes the surface gradient operator in the outer spherical coordinates system. The equation for ionic transport normal to the boundary is

$$j_n^{\pm} = -\frac{D}{kT}c_b\frac{\partial\mu_b}{\partial r}. \tag{30}$$

Finally, the conservation of ionic species at the interface of the EDL reads

$$j_n^{\pm} + \mathrm{div}_S\mathbf{J}_{\mathbf{S}}^{\pm} = 0. \tag{31}$$

In dimensionless form, the equations describing ionic conservation across the diffuse interface are thus

$$\begin{aligned}\frac{\partial c_b}{\partial n} &= -\frac{\epsilon}{2}\mathrm{div}_S\bigg[w\nabla_S \ln c_b + q\nabla_S\Psi_b \\ &\quad - \mathrm{m}\bigg(w\mathbf{u}_{\mathbf{s}} + \int_0^{+\infty}(c_+ + c_-)(\mathbf{u} - \mathbf{u}_{\mathbf{s}})dy\bigg)\bigg], \\ c_b\frac{\partial\Psi_b}{\partial n} &= -\frac{\epsilon}{2}\mathrm{div}_S\bigg[q\nabla_S \ln c_b + w\nabla_S\Psi_b \\ &\quad - \mathrm{m}\bigg(q\mathbf{u}_{\mathbf{s}} + \int_0^{+\infty}(c_+ - c_-)(\mathbf{u} - \mathbf{u}_{\mathbf{s}})dy\bigg)\bigg],\end{aligned} \tag{32}$$

where ϵ denotes the ratio between the Debye length and the radius of the particle and m is a dimensionless ionic drag coefficient defined for the EDL:

$$m = \frac{\epsilon_m\varphi_T^2}{\eta D}. \tag{33}$$

These boundary conditions state that fluxes of ions are transported across the electric double layer-bulk interface to balance the tangential surface flux gradients in the electric double layer. In this relation, q denotes the excess charge stored in the electric double layer and w the excess ion concentration. These quantity are defined by

$$q = \int_0^{+\infty}(c_+ - c_-)dy \tag{34}$$

and

$$w = \int_0^{+\infty}(c_+ + c_- - 2c_b)dy. \tag{35}$$

Analytical expressions have been derived for q and w for the Gouy-Chapman model and for the steric-only model [29,30]. However, when dielectric decrement effects are added, we cannot proceed analytically for the calculation of both q and w and we have to rely on numerical integrations to estimate these quantities from relations (34) and (35).

C. Velocity field in the bulk solution

Expression (25) shows that advective transport introduces a coupling between the ionic concentration and the velocity. Hence, to calculate the electrophoretic mobility of the particle, the velocity field must be completely determined. In the bulk solution, the velocity is solution of the Stokes equation

$$\eta\nabla^2\mathbf{u} - \nabla P + \epsilon_m\nabla^2\Psi_b\nabla\Psi_b = \mathbf{0}. \tag{36}$$

In this equation, $\mathbf{u}$ denotes the fluid velocity, P the pressure field, ϵ_m the solvent permittivity, and Ψ_b the electric potential in the bulk electrolyte. The term $\epsilon_m\nabla^2\Psi_b\nabla\Psi_b$ refers to the effects of a body force caused by the field-induced variations of the bulk concentration. These fluctuations result in corresponding variations of the solution conductivity. The conductivity gradient in turn results in a body force acting on the bulk fluid. The velocity field is finally solution of the continuity equation

$$\nabla\cdot\mathbf{u} = 0. \tag{37}$$

We determine the velocity field by relying on the Stokes stream function Ψ, which is defined in spherical coordinates by

$$u_r = \frac{1}{r^2\sin\theta}\frac{\partial\Psi}{\partial\theta}, \quad u_\theta = -\frac{1}{r\sin\theta}\frac{\partial\Psi}{\partial r}. \tag{38}$$

We can formulate the momentum conservation in terms of the Stokes stream function to yield

$$\eta\nabla^2\bigg(\frac{1}{r\sin\theta}\mathcal{L}\bigg)\Psi - \nabla\times\epsilon_m\nabla^2\Psi_b\nabla\Psi_b = \mathbf{0}, \tag{39}$$

where operator $\mathcal{L}$ is defined by

$$\mathcal{L} = \frac{\partial^2.}{\partial r^2} + \frac{1}{r^2}\frac{\partial^2.}{\partial\theta^2} - \frac{\cot\theta}{r^2}\frac{\partial.}{\partial\theta}. \tag{40}$$

We complete the problem description by specifying boundary conditions in the reference frame anchored at the center of the particle. At infinity, the flow is a steady uniform stream at velocity $-U$, where U is the electrophoretic velocity of the particle, which remains unknown. At the surface of the particle, the velocity field must match the slip velocity given by relation (21):

$$\frac{1}{r^2\sin\theta}\frac{\partial\Psi}{\partial\theta}\bigg|_{r=R} = 0, \quad -\frac{1}{r\sin\theta}\frac{\partial\Psi}{\partial r}\bigg|_{r=R} = u_s. \tag{41}$$

To complete the calculation of the velocity field, we are finally left with the determination of U. The global charge of the system constituted by the particle and its surrounding EDL vanishes. Hence, mechanical equilibrium is expressed by

$$\int_S \sigma_{\mathbf{E}}\cdot\mathbf{n}dS + \int_S \sigma_{\mathbf{H}}\cdot\mathbf{n}dS = 0, \tag{42}$$

where S denotes the external surface of the EDL, $\sigma_{\mathbf{E}}$ the Maxwell stress tensor, and $\sigma_{\mathbf{H}}$ the hydrodynamic stress tensor. The Maxwell stress tensor is given by

$$\sigma_{\mathbf{E}} = \tfrac{1}{2}\epsilon_m[\nabla\psi_b\nabla\psi_b - (\nabla\psi_b\cdot\nabla\psi_b)\mathrm{I}] \tag{43}$$

and accounts for the effects of the body force $\mathbf{f}$. By making use of the reciprocal theorem and introducing the companion velocity field

$$\tilde{\mathbf{u}} = \frac{1}{2}\cos\theta\left(\frac{3R}{r} - \frac{R^3}{r^3}\right)\mathbf{e_r} - \frac{1}{4}\sin\theta\left(\frac{3R}{r} + \frac{R^3}{r^3}\right)\mathbf{e}_\theta. \tag{44}$$

we can show that

$$U = \frac{1}{6\pi\eta R}\left(\mathbf{e_z}\cdot\int_S \sigma_{\mathbf{E}}\cdot\mathbf{n}dS - \frac{3\eta}{2R}\mathbf{e_z}\cdot\int_S \mathbf{u_s}dS - \mathbf{e_z}\cdot\int_V \tilde{\mathbf{u}}\cdot\mathbf{f}dV\right). \tag{45}$$

We refer the reader interested in a complete derivation of this result to Ref. [52].

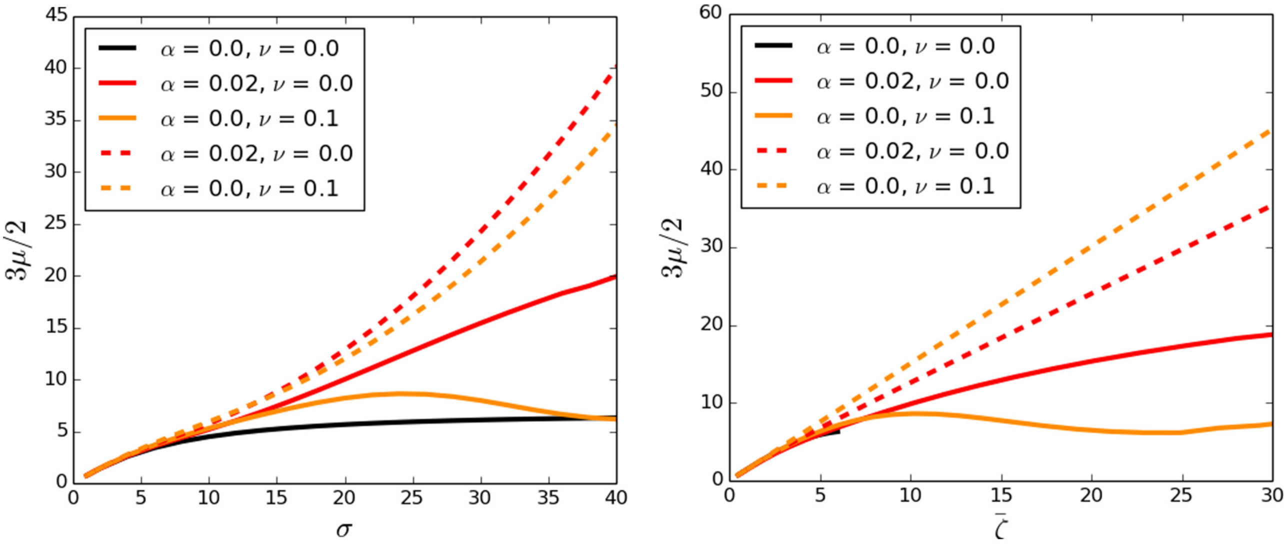
V. ELECTROPHORESIS OF PARTICLES WITH FIXED SURFACE CHARGE

In this section, we apply the dielectric decrement model to electrophoresis of spherical particles with fixed surface charges. This problem is classically studied by relying on the weak-field approximation. In this approach, the applied electric field is considered to perturb the equilibrium of the electric double layer. Hence, the model equations are linearized at first order in the applied electric field. This approach was originally introduced by O'Brien *et al.* [14]. It was applied by Khair and Squires [32] to study electrophoresis of fixed surface charge particles in the presence of steric effects due to the finite size of ions and by Zhao and Zhang [43] to investigate the influence of dielectric decrement effects.

In our model, we consider that the electric potential and the ionic concentration fields are described by the modified Poisson-Boltzmann equation (9) in the EDL. The slip at the surface of the particle is expressed by Eq. (21) as a combination of electro- and diffusio-osmotic flows. The concentration and the ionic concentrations in the bulk solution are given by Eqs. (25). To match the asymptotic solutions in the EDL and in the bulk solution, we rely on Eqs. (32) that describe the conservation of ions across the diffuse interface between the EDL and the bulk solution. The velocity field in the bulk solution is finally described by relation (39) along with the boundary conditions (41) and Eq. (42). The parameters of the model are the dimensionless applied electric field E, the dimensionless charge Q of the particle, and the ratio ϵ between the Debye length and the particle radius.

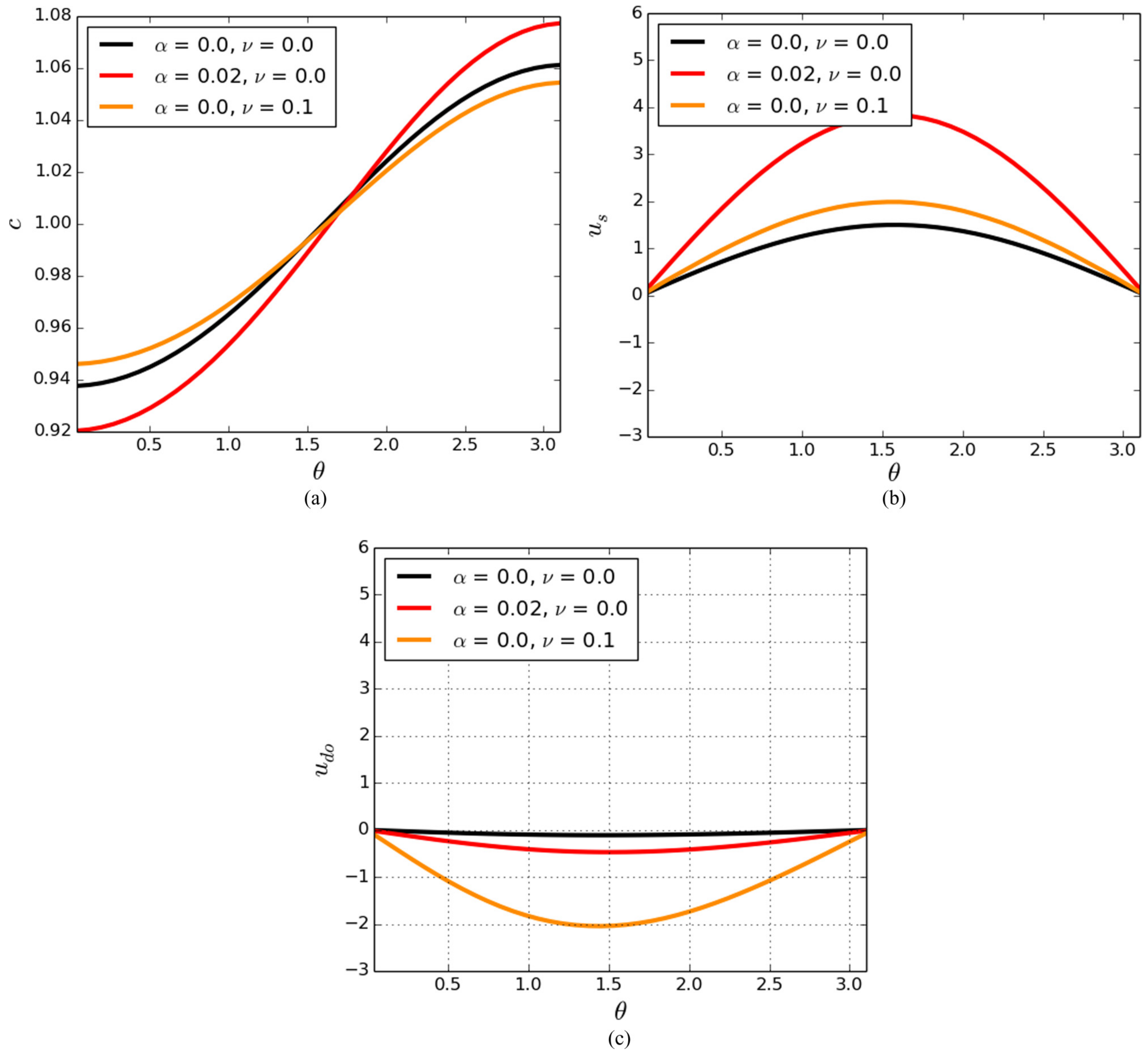
The only quantity that remains to be determined is the ζ potential. For particles with fixed surface charges, the ζ potential can be directly deduced from relation (34). Since the surface charge is known *a priori*, the ζ potential only depends on the bulk concentration. Due to concentration polarization phenomena that occur in the presence of surface conduction, the ζ potential varies around the particle.

The set of equations describing the model are highly nonlinear. Hence, to solve the model, we linearize the equations and use Newton's method to solve. The linearized equation are solved using a pseudospectral method based on the tensor product grid of a Chebyshev basis and of a sine cardinal basis. The main advantage of pseudospectral scheme over



(a) (b)

FIG. 4. Electrophoretic mobility as a function of surface charge (a) and mean ζ potential (b) at the surface of the particle for distinct values of the packing parameter ν and dielectric decrement parameter α. The ionic drag coefficients are $m = m_b = 0.1$. The ratio ϵ between the Debye length and the radius of the particle is 0.02 for the continuous curves. The dashed lines correspond to calculations conducted in the absence of surface conduction phenomena ($\epsilon = 0$).



(a) (b) (c)

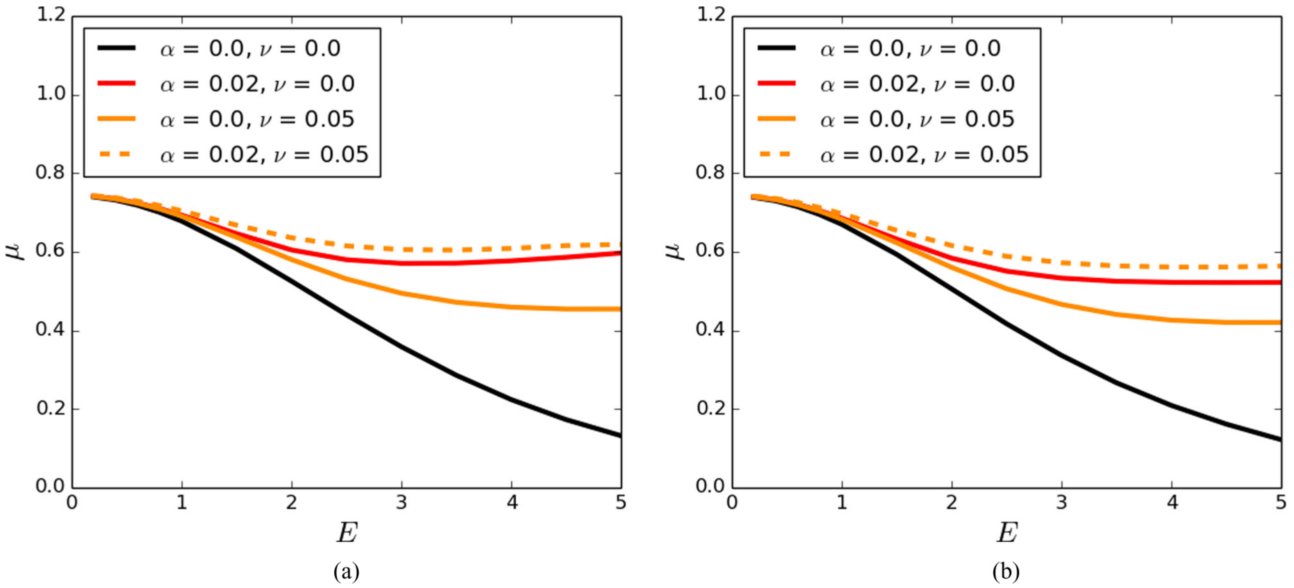
FIG. 5. Concentration field (a), slip velocity (b), and diffusio-osmotic velocity (c) along the surface of the particle for distinct values of the packing parameter ν and of the dielectric decrement parameter α. The ionic drag coefficients are $m = 0.1 = m_b = 0.1$. The ratio ϵ between the Debye length and the radius of the particle is 0.02. The dimensionless surface charge of the particle is $\sigma = -q = 40$. Panel (c) shows the diffusio-osmotic contribution to the total slip velocity, which is shown in panel (b).

other methods is that since the geometry remains relatively simple, a high accuracy can be reached even with a limited number of discretization nodes [54].

In Fig. 4, we plot the electrophoretic mobility as a function of surface charge and the mean ζ potential at the surface of the particle for distinct values of the packing parameter ν and the dielectric decrement parameter α. The ionic drag coefficients are $m = 0.1$ and $m_b = 0.1$. The ratio ϵ between the Debye length and the radius of the particle is 0.02 for the continuous curve and 0 for the dashed curves. Surface conduction significantly reduces the electrophoretic mobility of the particle. An explanation for this observation is that the diffusio-osmotic flow due to concentration polarization opposes the electro-osmotic flow, hence significantly slowing down the particle as shown in Fig. 5. Our calculations reproduce the same pattern as the one observed by Khair and Squires [32]. At low ζ potential, the mobility increases linearly with the ζ potential. Then, surface conduction effects become non-negligible, which leads to a nonlinear relation between mobility and ζ potential (see Fig. 4).

VI. INDUCED-CHARGE ELECTROPHORESIS OF PARTICLES

In this section, we apply our model to study the electrophoresis of ideally polarizable particles. These particles are constituted of an ideal conductor, so the surface charges of the particle rearrange when an electric field is applied. As a result, the ζ-potential varies on the surface of the particle and an induced electric field appears in the bulk solution. The problem



(a) (b)

FIG. 6. Electrophoretic mobility as a function of applied electric field for distinct values of the packing parameter ν and the dielectric decrement parameter α, with and without surface conduction. The ionic drag coefficients are $m = 0.1$ and $m_b = 0.1$. Surface conduction only slightly reduces the mobility, and ionic saturation in the electric double layer prevents the decrease of the mobility with the applied field.

is similar to the one of particles with fixed surface charges, except for the polarization of the ζ potential. To evaluate the electric potential of the particle, we note that the total charge Q of the particle remains constant during the formation of the electric double layer [19]. Hence, we have

$$Q = -\int_S q\,dA = -2\pi R^2 \int_0^\pi q(\theta)\sin\theta d\theta, \tag{46}$$

where q is the local surface charge. If we scale the global charge Q of the particle by the quantity

$$Q^* = 4\pi R^2 zec_{b,\infty}\lambda_D, \tag{47}$$

then we obtain the dimensionless equation

$$Q = -\frac{1}{2}\int_0^\pi q(\theta)\sin\theta d\theta. \tag{48}$$

Before considering the general case, it is of interest to investigate induced-charge electrophoresis in the absence of surface conduction. At low applied electric field, the excess charge q and the excess ionic concentration w remain of order $O(1)$. As a consequence, the right-hand sides of Equations (32) describing surface conduction phenomenon remain of order $O(\epsilon)$. In this situation, it appears legitimate to consider the model's equations in the limit $\epsilon \to 0$, i.e., to neglect surface conduction phenomena. At higher applied fields, surface conduction becomes significant in the electric double layer. However, studying induce-charge electrophoresis in the absence of surface conduction remains interesting from a theoretical perspective.

According to Eq. (25), in the absence of surface conduction, the concentration is uniform in the bulk solution. Hence, the electric potential yields [47]

$$\Psi_b(r,\theta) = -E\left(r + \frac{R^3}{2r^2}\right)\cos\theta. \tag{49}$$

The ζ potential is defined as the difference of potential between the surface of the particle and the bulk solution, so

$$\zeta(\theta) = \Psi_P + \tfrac{3}{2}E\cos\theta. \tag{50}$$

In this expression, Ψ_P is the (constant) potential of the charged particle and remains to be determined. Using relation (50), we can perform a change of variable in (48) to yield

$$Q = \frac{1}{3E}\int_{\frac{3E}{2}-\Psi_P}^{\frac{3E}{2}+\Psi_P} q(\zeta)d\zeta. \tag{51}$$

At high values of applied electric field E, the ζ potential ζ increases significantly near the poles of the particle. This implies that steric effects and dielectric decrement strongly impact the electrophoretic mobility. At high applied electric fields, it was shown [52] that

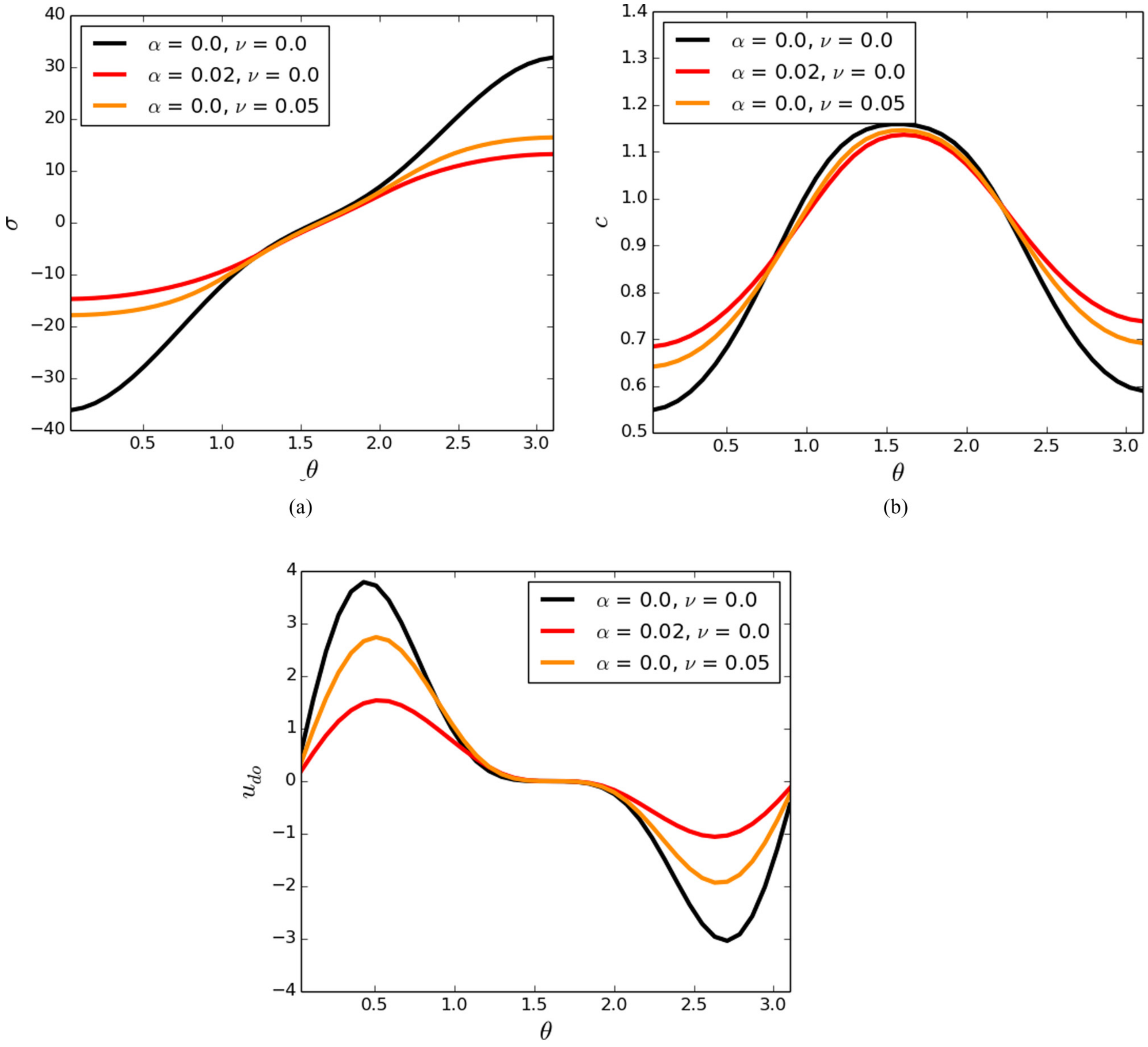
$$\mu \simeq \tfrac{3}{8}Q\sqrt{3E\nu}. \tag{52}$$

The situation is more complicated for the dielectric decrement model, since there is no analytical formula relating the surface charge to the ζ potential. In addition, the electrophoretic mobility cannot be expressed analytically from the ζ potential. However, by relying on the composite layers model, we can get an estimate of the electric potential of the particle. At high applied electric field $E \gg \ln(1/2\alpha)$ and in the limit $E \gg \Psi_P$, we have the asymptotic estimate

$$\Psi_P \simeq Q\sqrt{\tfrac{3}{2}E\alpha}. \tag{53}$$

At high applied electric fields, the particle is highly polarized and the region of the surface where the ζ potential is less than the critical potential $\ln(1/2\alpha)$ can be neglected in the calculation. Hence, using Eq. (24), we can show that

$$\mu \simeq \frac{Q}{2}\sqrt{\frac{3}{2}E\alpha}. \tag{54}$$



(a) (b)

(c)

FIG. 7. Surface charge (a), concentration (b), and diffusio-osmotic velocity (c) at the surface of the particle for distinct values of the packing parameter ν and of the dielectric decrement parameter α. The ionic drag coefficients are $m = 0.1$ and $m_b = 0.1$. The ratio ϵ between the Debye length and the radius of the particle is 0.01. The applied electric field is $E = 4.5$. Note that for a 1-μm particle, the characteristic electric field is $E^* = 250$ V/cm.

In Fig. 6, we plot the mobility of an ideally polarizable particle as a function of the applied electric field, with and without surface conduction and for distinct values of the packing parameter ν and the dielectric decrement α. The ionic drag coefficients are $m = 0.1$ and $m_b = 0.1$, and the dimensionless charge of the particle is $Q = 1$. Both steric and dielectric decrement effects prevent the decrease of the mobility predicted by the Gouy-Chapman model [47]. We can see in Fig. 7 that dielectric decrement and steric effects significantly impact the charge recombination at the surface of the particle. For the Gouy-Chapman model, the outside charge repartition is almost symmetrical around the particle, so the slip velocities on both sides of the particle compensate each other. For the other simulations, due to ionic saturation in the EDL caused by both dielectric decrement and steric effects, the charge repartition is not symmetrical, yielding net motion of the particle.

It is also interesting to take a closer look at the curve corresponding to parameters $\nu = 0.05$ and $\alpha = 0.02$. In this situation, the ratio $4\alpha/\nu$ yields 1.6, indicating that dielectric decrements effects are dominant over steric effects. The ratio remains, however, close to one. Still, we see that steric effects can almost be neglected for the electrophoretic mobility calculation.

Finally, we see that surface conduction reduces the electrophoretic mobility of the particle. The mechanism here is very similar to the one observed for electrophoresis of particles with fixed surface charge. As is evident in Fig. 7, a concentration gradient arises in the immediate vicinity of the particle due to surface conduction. The concentration gradient in turn drives diffusio-osmotic flow at the surface of the particle, which significantly reduces the slip velocity.

VII. CONCLUSION

In this article, we studied the electrophoresis of particles with thin electric double layers in the presence of both dielectric decrement and steric effects. We conducted numerical simulations to calculate the electrophoretic mobility of the particle. These calculations demonstrated that dielectric decrement and steric effects due to the finite size of ions play a very similar role regarding the motion of the particle and both predict ionic saturation in the electric double layer.

Our simulations show that a proper description of the electric double layer is a prerequisite to any attempt to calculate the electrophoretic mobility at high applied voltages. The modeling of the electric double layer for large ζ potential and high applied electric fields remains a very active field of study. In the present study, we considered dielectric decrement and crowding effects altogether. However, we assumed that the dynamic viscosity remains constant across the electric double layer. This assumption most certainly breaks down at high ionic concentrations, as pointed out by Bazant *et al.* in Ref. [38]. Another possible extension of this study could be to incorporate the Carnahan-Starling equation to describe crowding effects in the EDL. Finally, our description of the electric double layer also relies on a mean-field description. Recently, Bazant, Storey, and co-workers have developed models for the electric double layer when the mean-field approximation breaks down [57,58]. Incorporating these additional effects constitutes a natural extension of this study.

ACKNOWLEDGMENTS

The authors acknowledge the reviewers for providing relevant references for this study. The work presented in this paper was partially supported by Institut Carnot Mines (B.F.), the National Science Scholarship from A*STAR (W.H.R.C), and the Department of Mechanical Engineering of the Massachusetts Institute of Technology (C.R.B. and J.L.M).

APPENDIX: CONDENSED LAYER MODEL

The model developed in this article predicts a saturation of the ionic concentration in the electric double layer at high ζ potential. The saturation is either caused by ion polarizability or by crowding effects due to the finite size of ions. As a first approximation, to simplify the physical analysis, it is legitimate to consider a steric only or a dielectric decrement only model depending on the value of the quantity $4\alpha/\nu$. In this document, in the spirit of Kilic *et al.* [29,30], we present a simplified model where we decompose the electric double layer into two distinct regions, namely a condensed and a diffuse layer, as sketched in Fig. 8. In the following, without loss of generality, we will assume that the wall is positively charged.

a. Diffuse layer. In the diffuse layer, we assume that the standard Poisson-Boltzmann equation holds, so the electric potential is the solution of the Poisson-Boltzmann equation,

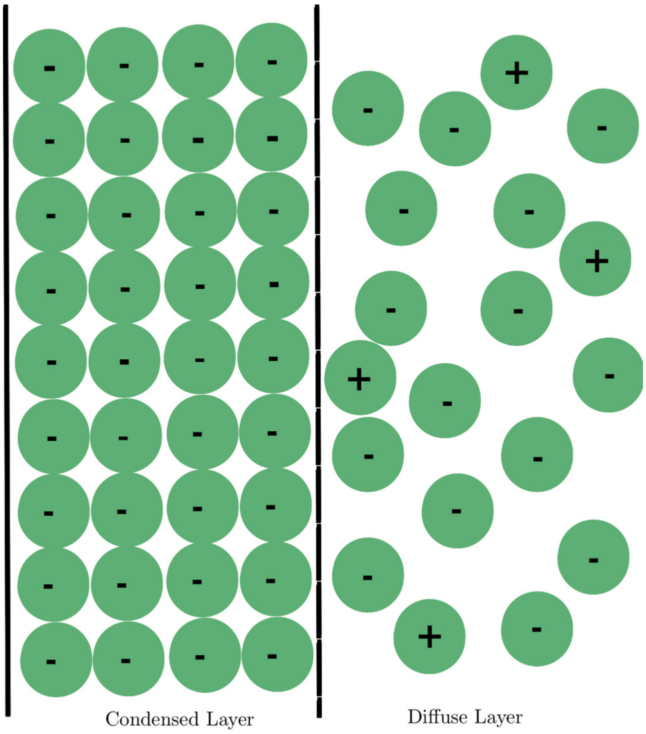


FIG. 8. Schematic view of the composite layer model. The EDL is subdivided in two sublayers: a condensed layer where the counterion concentration saturates and a diffuse layer.

$$\frac{d^2\phi}{dy^2} = \frac{2zec_b}{\epsilon_0\epsilon_w}\sinh\left(\frac{ze\phi}{kT}\right). \tag{A1}$$

We can integrate this relation to find

$$\frac{d\phi}{dy} = -2\sqrt{\frac{2kTc_b}{\epsilon_0\epsilon_w}}\sinh\left(\frac{ze\phi}{2kT}\right). \tag{A2}$$

b. Condensed layer. Within the condensed layer, we assume that the co-ion concentration vanishes and that the counter-ion concentration saturates. Hence, we have

$$\rho_c = -zec_b\exp\left(\frac{ze|\phi_c|}{kT}\right), \tag{A3}$$

so the crossover value for the excess electric potential is

$$\phi_c = \frac{kT}{ze}\ln\left(\frac{\rho_c}{zec_b}\right). \tag{A4}$$

The Poisson equation becomes

$$\frac{d^2\phi}{dy^2} = -\frac{\rho_c}{\epsilon_{cl}}, \tag{A5}$$

where ϵ_{cl} is the permittivity in the condensed layer. The excess electric potential profile is therefore quadratic, yielding

$$\phi(y) = -\frac{1}{2}\frac{\rho_c}{\epsilon_{cl}}y^2 + \frac{q}{\epsilon_{cl}}y + \zeta. \tag{A6}$$

In relation (A6), we note that the integration constant can be expressed as

$$q = \epsilon_{cl} \frac{d\phi}{dy}\bigg|_{y=0}. \tag{A7}$$

In parallel, we note that this quantity exactly corresponds to the integral

$$\epsilon(y)\frac{d\phi}{dy}(y)\bigg|_{y=0} = \int_0^{+\infty} \rho(y)dy. \tag{A8}$$

Hence, the integration constant q simply corresponds to the global charge embedded in the EDL.

c. Matching. To completely determine the potential profile across the EDL, we are left with the determination of q and y_c. The continuity of the excess electric potential and of its first derivative at $y = y_c$ yields the following relations:

$$\begin{aligned} -\frac{1}{2}\frac{\rho_c}{\epsilon_{cl}} y_c^2 + \frac{q}{\epsilon_{cl}} y_c + \zeta &= \phi_c, \\ q = \rho_c y_c - 4zec_b\lambda_D &\left(\frac{\epsilon_{cl}}{\epsilon_0\epsilon_w}\right) \sinh\left(\frac{ze\phi_c}{2kT}\right), \end{aligned} \tag{A9}$$

so we obtain the dimensionless relation

$$(\zeta - \phi_c) - 2\sinh\left(\frac{\phi_c}{2}\right) y_c + \frac{1}{4}\rho_c \frac{\epsilon_0\epsilon_w}{\epsilon_{cl}} y_c^2 = 0. \tag{A10}$$

d. Steric VS dielectrophoretic saturation. When ionic saturation results from steric effects due to the finite size of ions, we have

$$\rho_c = -\frac{2}{\nu} \tag{A11}$$

and

$$\epsilon_{cl} = \epsilon_0\epsilon_w. \tag{A12}$$

The crossover occurs for $\phi_c = \ln(2/\nu)$. Therefore, when $\zeta > \ln(2/\nu)$, the thickness y_c of the condensed layer is given by

$$y_c = -\sqrt{2\nu}\left[\left(1 - \frac{\nu}{2}\right) + \sqrt{\left(1 - \frac{\nu}{2}\right)^2 + \zeta - \ln\left(\frac{2}{\nu}\right)}\right], \tag{A13}$$

and the charge is found to be

$$q = -2\sqrt{\frac{2}{\nu}}\sqrt{\left(1 - \frac{\nu}{2}\right)^2 + \zeta - \ln\left(\frac{2}{\nu}\right)}. \tag{A14}$$

When $\zeta < \ln(2/\nu)$, the charge embedded in the EDL is simply given by the classical Gouy-Chapman model:

$$q = -4\sinh\left(\frac{\zeta}{2}\right). \tag{A15}$$

Similarly, when ionic saturation results from dielectric decrement, we have, when $\zeta > \ln(1/2\alpha)$,

$$\rho_c = -\frac{1}{2\alpha} \tag{A16}$$

and

$$\frac{\epsilon_0\epsilon_w}{\epsilon_{cl}} = 2. \tag{A17}$$

The crossover occurs for

$$\phi_c = \text{sign}(\zeta)\ln\frac{1}{2\alpha}, \tag{A18}$$

so

$$y_c = \sqrt{2\alpha}\left[(1 - 2\alpha) + \sqrt{(1 - 2\alpha)^2 + 2\zeta - 2\ln\left(\frac{1}{2\alpha}\right)}\right]. \tag{A19}$$

Finally, the total charge embedded in the EDL is

$$q = -\sqrt{\frac{1}{2\alpha}}\sqrt{(1 - 2\alpha)^2 + 2\zeta - 2\ln\left(\frac{1}{2\alpha}\right)}. \tag{A20}$$

Again, when $\zeta < \ln(1/2\alpha)$, the charge embedded in the EDL is simply given by the classical Gouy-Chapman model:

$$q = -4\sinh\left(\frac{\zeta}{2}\right). \tag{A21}$$

e. Excess salt in the EDL. Another quantity of interest is the excess ionic concentration, defined to be

$$w = \int_0^{+\infty} (c_+ + c_- - 2c_b)dy. \tag{A22}$$

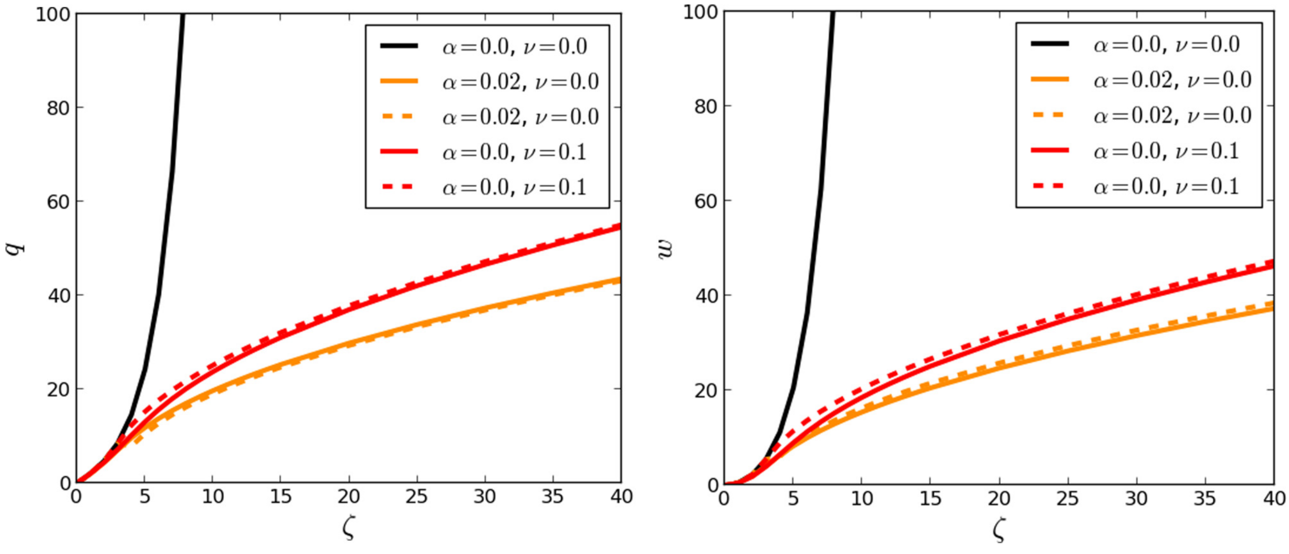
This quantity is related to the dimensionless Dukhin number and plays a key role in describing surface conduction phenomena in the EDL. For steric dominated saturation, we find, using the composite layer model,

$$w = 2c_b\lambda_D\left(\sqrt{\frac{2}{\nu}} + \sqrt{\frac{\nu}{2}} - 2\right) + c_b y_c\left(\frac{2}{\nu} - 2\right). \tag{A23}$$

Similarly, when saturation in the EDL is caused by dielectric decrement, we find

$$w = 2c_b\lambda_D\left(\sqrt{\frac{1}{2\alpha}} + \sqrt{2\alpha} - 2\right) + c_b y_c\left(\frac{1}{2\alpha} - 2\right). \tag{A24}$$

The excess charge and the excess ionic concentration are plotted for distinct values of the packing parameter ν and of the dielectric decrement parameter α in Fig. 9 as a function of the ζ potential. We note the good agreement between the numerical calculations and the results of the composite layers model.



(a) (b)

FIG. 9. Excess charge (a) and excess ionic concentration (b) in the EDL as a function of the ζ potential for distinct values of the packing parameter ν and of the dimensionless dielectric decrement parameter α. The dashed lines correspond to calculations conducted with the composite layer model, while the continuous lines correspond to the full numerical solution.

---

[1] M. Von Smoluchowski, Contribution à la théorie de l'endosmose électrique et de quelques phénomènes corrélatifs, Bull. Acad. Sci. Cracov. **8**, 182 (1903).

[2] J. L. Anderson, Colloid transport by interfacial forces, Annu. Rev. Fluid Mech. **21**, 61 (1989).

[3] F. A. Morrison, Jr, Electrophoresis of a particle of arbitrary shape, J. Colloid Interface Sci. **34**, 210 (1970).

[4] A. Sellier, Sur l'électrophorèse d'un ensemble de particules portant la même densité uniforme de charges, Compt. Rend. Acad. Sci. IIB **327**, 443 (1999).

[5] O. Schnitzer and E. Yariv, Macroscale description of electrokinetic flows at large zeta potentials: Nonlinear surface conduction, Phys. Rev. E **86**, 021503 (2012).

[6] B. V. Derjaguin, S. S. Dukhin, and V. N. Shilov, Kinetic aspects of electrochemistry of disperse systems. Part I. Introduction, Adv. Colloid Interface Sci. **13**, 141 (1980).

[7] J. Th. G. Overbeek, Theory of electrophoresis—The relaxation effect, Kolloid-Beihefte **54**, 287 (1943).

[8] D. C. Prieve, J. L. Anderson, J. P. Ebel, and M. E. Lowell, Motion of a particle generated by chemical gradients. Part 2. Electrolytes, J. Fluid Mech. **148**, 247 (1984).

[9] A. S. Khair and T. M. Squires, Fundamental aspects of concentration polarization arising from nonuniform electrokinetic transport, Phys. Fluids **20**, 087102 (2008).

[10] S. S. Dukhin, Electrophoresis at large peclet numbers, Adv. Colloid Interface Sci. **36**, 219 (1991).

[11] S. S. Dukhin and V. N. Shilov, Kinetic aspects of electrochemistry of disperse systems. Part II. Induced dipole moment and the non-equilibrium double layer of a colloid particle, Adv. Colloid Interface Sci. **13**, 153 (1980).

[12] A. S. Dukhin and S. S. Dukhin, Aperiodic capillary electrophoresis method using an alternating current electric field for separation of macromolecules, Electrophoresis **26**, 2149 (2005).

[13] S. S. Dukhin and B. V. Derjaguin, Electrokinetic phenomena, in *Surface and Colloid Science*, edited by E. Matijevic (Wiley, New York, 1974), Vol. 7, pp. 1–351.

[14] R. W. O'Brien and L. R. White, Electrophoretic mobility of a spherical colloidal particle, J. Chem. Soc. Faraday Trans. 2 **74**, 1607 (1978).

[15] R. W. O'Brien and R. J. Hunter, The electrophoretic mobility of large colloidal particles, Can. J. Chem. **59**, 1878 (1981).

[16] R. W. O'Brien and D. N. Ward, The electrophoresis of a spheroid with a thin double layer, J. Colloid Interface Sci. **121**, 402 (1988).

[17] O. Schnitzer, R. Zeyde, I. Yavneh, and E. Yariv, Weakly nonlinear electrophoresis of a highly charged colloidal particle, Phys. Fluids **25**, 052004 (2013).

[18] O. Schnitzer and E. Yariv, Strong-field electrophoresis, J. Fluid Mech. **701**, 333 (2012).

[19] E. Yariv, An asymptotic derivation of the thin-debye-layer limit for electrokinetic phenomena, Chem. Eng. Commun. **197**, 3 (2009).

[20] A. S. Khair, Transient phoretic migration of a permselective colloidal particle, J. Colloid Interface Sci. **381**, 183 (2012).

[21] R. A. Rica and M. Z. Bazant, Electrodiffusiophoresis: Particle motion in electrolytes under direct current, Phys. Fluids **22**, 112109 (2010).

[22] M. Gouy, Sur la constitution de la charge électrique à la surface d'un électrolyte, J. Phys. Théor. Appliq. **9**, 457 (1910).

[23] D. L. Chapman, A contribution to the theory of electrocapillarity, Philos. Mag. **25**, 475 (1913).

[24] O. Stern, The theory of the electrolytic double-layer, Zeit. Elektrochem **50**, 1014 (1924).

[25] J. J. Bikerman, Electrokinetic equations and surface conductance. A survey of the diffuse double layer theory of colloidal solutions, Trans. Farad. Soc. **35**, 154 (1940).

[26] J. J. Bikerman, Structure and capacity of electrical double layer, Philos. Mag. **33**, 384 (1942).

[27] I. Borukhov, D. Andelman, and H. Orland, Steric Effects in Electrolytes: A Modified Poisson-Boltzmann Equation, Phys. Rev. Lett. **79**, 435 (1997).

[28] P. M. Biesheuvel and M. Van Soestbergen, Counterion volume effects in mixed electrical double layers, J. Colloid Interface Sci. **316**, 490 (2007).

[29] M. S. Kilic, M. Z. Bazant, and A. Ajdari, Steric effects in the dynamics of electrolytes at large applied voltages. I. Double-layer charging, Phys. Rev. E **75**, 021502 (2007).

[30] M. S. Kilic, M. Z. Bazant, and A. Ajdari, Steric effects in the dynamics of electrolytes at large applied voltages. II. Modified Poisson-Nernst-Planck equations, Phys. Rev. E **75**, 021503 (2007).

[31] M. S. Kilic, Induced-charge Electrokinetics at Large Voltages, Ph.D. thesis, Massachusetts Institute of Technology, 2008.

[32] A. S. Khair and T. M. Squires, Ion steric effects on electrophoresis of a colloidal particle, J. Fluid Mech. **640**, 343 (2009).

[33] J. J. López-García, J. Horno, and C. Grosse, Influence of steric interactions on the dielectric and electrokinetic properties in colloidal suspensions, J. Colloid Interface Sci. **458**, 273 (2015).

[34] P. M. Biesheuvel, Volume exclusion effects in the ground-state dominance approximation for polyelectrolyte adsorption on charged interfaces, Eur. Phys. J. E **16**, 353 (2005).

[35] E. Spruijt, P. M. Biesheuvel, and W. M. de Vos, Adsorption of charged and neutral polymer chains on silica surfaces: The role of electrostatics, volume exclusion, and hydrogen bonding, Phys. Rev. E **91**, 012601 (2015).

[36] E. Spruijt and P. M. Biesheuvel, Sedimentation dynamics and equilibrium profiles in multicomponent mixtures of colloidal particles, J. Phys.: Condens. Matter **26**, 075101 (2014).

[37] B. Giera, N. Henson, E. Kober, M. Shell, and T. Squires, Electric double-layer structure in primitive model electrolytes: Comparing molecular dynamics with local-density approximations, Langmuir **31**, 3553 (2015).

[38] M. Z. Bazant, M. S. Kilic, B. D. Storey, and A. Ajdari, Towards and understanding of induced-charge electrokinetics at large applied voltages in concentrated solutions, Adv. Colloid Interface Sci. **152**, 48 (2009).

[39] D. Ben-Yaakov, D. Andelman, D. Harries, and R. Podgornik, Beyond standard Poisson–Boltzmann theory: ion-specific interactions in aqueous solutions, J. Phys.: Condens. Matter **21**, 424106 (2009).

[40] D. Ben-Yaakov, D. Andelman, and R. Podgornik, Dielectric decrement as a source of ion-specific effects, J. Chem. Phys. **134**, 074705 (2011).

[41] M. M. Hatlo, R. H. H. G. Van Roij, and L. Lue, The electric double layer at high surface potentials: The influence of excess ion polarizability, Europhys. Lett. **97**, 28010 (2012).

[42] Y. Nakayama and D. Andelman, Differential capacitance of the electric double layer: The interplay between ion finite size and dielectric decrement, J. Chem. Phys. **142**, 044706 (2015).

[43] H. Zhao and S. Zhai, The influence of dielectric decrement on electrokinetics, J. Fluid Mech. **724**, 69 (2013).

[44] V. A. Murtsovkin, Nonlinear flows near polarized disperse particles, Coll. J. Russ. Acad. Sci. **58**, 341 (1996).

[45] T. M. Squires and M. Z. Bazant, Induced-charge electro-osmosis, J. Fluid Mech. **509**, 217 (2004).

[46] M. Z. Bazant and T. M. Squires, Induced-Charge Electrokinetic Phenomena: Theory and Microfluidic Applications, Phys. Rev. Lett. **92**, 066101 (2004).

[47] E. Yariv, Nonlinear electrophoresis of ideally polarizable particles, Europhys. Lett. **82**, 54004 (2008).

[48] S. Bhattacharyya and S. De, Numerical study of the influence of solid polarization on electrophoresis at finite debye thickness, Phys. Rev. E **92**, 032309 (2015).

[49] S. Bhattacharyya and S. De, Gel electrophoresis and size selectivity of charged colloidal particles in a charged hydrogel medium, Chem. Eng. Sci. **141**, 304 (2016).

[50] S. Bhattacharyya and S. De, Influence of rigid core permittivity and double layer polarization on the electrophoresis of a soft particle: A numerical study, Phys. Fluids (1994-present) **28**, 012001 (2016).

[51] N. N. Dingari and C. R. Buie, Theoretical investigation of bacteria polarizability under direct current electric fields, Langmuir **30**, 4375 (2014).

[52] B. Figliuzzi, W. H. R. Chan, J. L. Moran, and C. R. Buie, Nonlinear electrophoresis of ideally polarizable particles, Phys. Fluids (1994-present) **26**, 102002 (2014).

[53] Brian J. Kirby, *Micro-and Nanoscale Fluid Mechanics: Transport in Microfluidic Devices* (Cambridge University Press, Cambridge, 2010).

[54] J. P. Boyd, *Chebyshev and Fourier Spectral Methods* (Courier Dover, London, 2013).

[55] K. T. Chu and M. Z. Bazant, Nonlinear electrochemical relaxation around conductors, Phys. Rev. E **74**, 011501 (2006).

[56] Kevin T. Chu and Martin Z. Bazant, Surface conservation laws at microscopically diffuse interfaces, J. Colloid Interface Sci. **315**, 319 (2007).

[57] M. Z. Bazant, B. D. Storey, and A. A. Kornyshev, Double Layer in Ionic Liquids: Overscreening Versus Crowding, Phys. Rev. Lett. **106**, 046102 (2011).

[58] B. D. Storey and M. Z. Bazant, Effects of electrostatic correlations on electrokinetic phenomena, Phys. Rev. E **86**, 056303 (2012).