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Ion steric effects on electrophoresis of a colloidal particle

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We calculate the electrophoretic mobility M_e of a spherical colloidal particle, using modified Poisson–Nernst–Planck (PNP) equations that account for steric repulsion between finite sized ions, through Bikerman's mean-field model (Bikerman, *Phil. Mag.*, vol. 33, 1942, p. 384). Ion steric effects are controlled by the bulk volume fraction of ions ν, and for $\nu = 0$ the standard PNP equations are recovered. An asymptotic analysis in the thin-double-layer limit reveals at small zeta potentials ($\zeta < k_BT/e \approx 25$ mV) M_e to increase linearly with ζ for all ν, as expected from the Helmholtz–Smoluchowski (HS) formula. For larger ζ, however, it is well known that surface conduction of ions within the double layer reduces M_e below the HS result. Crucially, however, in the PNP equations surface conduction becomes significant *precisely* because of the aphysically large and unbounded counter-ion densities predicted at large ζ. In contrast, ion steric effects impose a limit on the counter-ion density, thereby mitigating surface conduction. Hence, M_e does not fall as far below HS for finite sized ions ($\nu \neq 0$). Indeed, at sufficiently large ν, ion steric effects are so dramatic that a maximum in M_e is not observed for physically reasonable values of $\zeta (\leqslant 10k_BT/e)$, in stark contrast to the PNP-based calculations of O'Brien & White (*J. Chem. Soc. Faraday Trans.* II, vol. 74, 1978, p. 1607) and O'Brien (*J. Colloid Interface Sci.*, vol. 92, 1983, p. 204). Finally, by calculating a Dukhin–Bikerman number characterizing the relative importance of surface conduction, we collapse M_e versus ζ data for different ν onto a single master curve.

Key words: colloidal systems, low-Reynolds-number flows, micro-/nano-fluid dynamics

1. Introduction

In 1809, exactly two centuries ago, Ferdinand Friedrich Reuss published his pioneering experiments on the movement of electrically charged clay particles immersed in viscous electrolytes, under an imposed electric field (Reuss 1809). Today, this phenomenon is known as electrophoresis, and it plays a crucial role in microfluidics (Squires & Quake 2005), colloidal science (Russel, Saville & Schowalter 1989) and separation of biomolecules such as DNA (Viovy 2000). The relationship between the imposed field and the particle velocity is of fundamental importance. A uniformly charged spherical colloid in a uniform field E translates with velocity $\boldsymbol{U} = M_e \boldsymbol{E}$, where M_e is called the electrophoretic mobility. Over the last century, the calculation of M_e has been a central focus in colloid science (Lyklema 1995). In this

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regard, the size of the ionic screening cloud surrounding the particle, characterized by the Debye length κ^{-1}, relative to the particle radius R is of particular relevance. Together, the screening cloud and charged particle comprise the electrical double layer, and in the 'thick' double-layer limit, $\kappa R \rightarrow 0$, Huckel (1924) found $M_e = (2/3)\varepsilon\zeta/\eta$. Here, ε and η are the dielectric permittivity and viscosity of the fluid, respectively, and ζ is the electrical 'zeta' potential at the particle surface. In the opposite, and more frequently encountered, 'thin' double-layer limit, $\kappa R \rightarrow \infty$, M_e follows the Helmholtz–Smoluchowski (HS) formula, $M_e = \varepsilon\zeta/\eta$ (Smoluchowski 1903).

In a tour de force analysis, O'Brien & White (1978) computed M_e over a wide range of κR and ζ. In particular, for thin double layers and $\zeta < k_B T/e$ their results agree with the HS formula. Here, $k_B T/e \approx 25$ mV is the thermal voltage, where k_B is Boltzmann's constant, T is temperature and e is the fundamental charge. For larger ζ, however, O'Brien and White (1978) found M_e to drop below HS, to attain a maximum value, and to finally decrease with increasing ζ. These results were confirmed by O'Brien (1983) who, building on the work of Dukhin & Deryaguin (1974), conducted an asymptotic thin-double-layer analysis. O'Brien (1983) also showed that M_e reaches a finite value as $\zeta \rightarrow \infty$, for example, for a binary z–z electrolyte $\mu \rightarrow \ln 4(k_B T/ze)\varepsilon\eta$. The discrepancy between the HS result and O'Brien & White (1978) and O'Brien (1983) occurs due to surface transport, or conduction, of ions within the thin screening cloud, which is neglected in the HS analysis but becomes significant at sufficiently large ζ, due to the large ion concentration within the screening cloud (Dukhin & Deryaguin 1974). A description of the mechanisms by which surface conduction reduces M_e below the HS result can be found in Lyklema (1995) and Khair & Squires (2009).

The vast majority of theoretical work on colloidal electrokinetics, including O'Brien & White (1978) and O'Brien (1983), utilizes the Poisson–Nernst–Planck (PNP) equations, wherein ions are assumed to be point-sized and non-interacting. At equilibrium, the PNP equations reduce to the celebrated Poisson–Boltzmann (PB) equation, whose solution gives the Gouy–Chapman (GC) model of the double layer. The shortcomings of GC are well known: it predicts impossibly large (counter)-ion concentrations near highly charged surfaces, giving a double-layer capacitance that grows exponentially with zeta potential. Recognizing this fault, Bikerman (1942) derived a modified PB equation (2.6) – which we shall call the Poisson–Bikerman (PBik) equation – accounting for steric effects associated with the finite size of ions and solvent molecules. (Note, by 'steric effects' we refer to repulsion between finite sized ions, as opposed to interactions between colloidal particles arising from polymer adsorbates, to which the term is more commonly applied.) Subsequently, Freise (1952) calculated the double-layer capacitance from the PBik equation, which decreases at large zeta potentials, as $\zeta^{-1/2}$. Furthermore, the PBik equation does not predict aphysically large ion densities adjacent to highly charged surfaces; instead, at a certain 'critical' zeta potential a maximum density is reached. Following Bazant *et al.* (2009), we refer to the PBik double-layer structure as the Bikerman–Freise (BF) model. Variants of the PBik equation have since been rediscovered independently by several groups; we direct the reader to Bazant *et al.* (2009) for a complete history. The PBik equation has been solved around a uniformly charged flat plate (Kilic, Bazant & Ajdari 2007*a*), a circular cylinder (Wiegel, Strating & Garcia 1993; Bohinc *et al.* 2002) and a sphere (Strating & Wiegel 1993; Lopez-Garcia, Aranda-Rascon & Horno 2007). Kilic, Bazant & Ajdari (2007*b*) extended the theory of Borukhov, Andelman & Orland (1997) to derive modified PNP (MPNP) equations, that reduce to the PBik equation at equilibrium, which they applied to study the dynamical charging of an electrochemical cell. Storey *et al.* (2008) demonstrated that the MPNP equations can predict flow reversal in ac-electro-osmosis at high frequencies, as has been been observed experimentally.

Recall that the maximum in the mobility calculated by O'Brien & White (1978) and O'Brien (1983) occurs for $\zeta \sim O(k_BT/e)$, and reflects the rising influence of surface conduction of ions within the double layer. This relative importance, however, results from the aphysically large and unbounded ion densities predicted by the PNP equations. It is thus natural to ask whether the mobility maximum calculated by O'Brien & White (1978) and O'Brien (1983) is a direct result of these aphysical predictions. Given that ion steric effects prohibit this unbounded growth in ion density, can ion sterics mitigate surface conduction so much as to prevent the mobility maximum? This issue forms our central focus: indeed, we show that ion steric effects can change the qualitative behaviour of the mobility, such that a maximum may not be observed for physically reasonable ζ. Lopez-Garcia, Aranda-Rascon & Horno (2008) have considered ion steric effects on electrophoresis by solving the MPNP equations numerically for a range of κR and ζ. We, on the other hand, provide a simpler and physically based analysis of ion steric effects in the thin-double-layer limit $\kappa R \gg 1$ – precisely the regime in which they have the greatest impact.

Before continuing, we emphasize that Bikerman's model is but one of several approaches to account for finite ion size steric effects in electrical double layers. The earliest, and perhaps most popular, is the Stern layer: a molecularly thin region at the particle surface acting as a linear capacitor in 'series' with the diffuse double layer (Lyklema 1995, see also § 5). The Stern layer capacitance can be adjusted to prevent the diffuse zeta potential from becoming large enough for the PB equation to yield aphysical ion concentrations. Nevertheless, the Stern layer does not directly deal with ion sterics in the diffuse part of the double layer. Detailed models for ion-ion interactions (both steric and electrostatic) have been developed using non-equilibrium statistical mechanics, density functional theory and liquid state theory (see Kilic *et al.* 2007*a* for a discussion and references); however, they are technically quite involved and not amenable to simple or intuitive analysis. Here, we employ Bikerman's model, which is a mean-field approach (like PB) that accounts for ion steric effects in perhaps the most conceptually and mathematically straightforward manner. Furthermore, as Bikerman's model has garnered renewed interest in recent years (e.g. Paunov *et al.* 1996; Borukhov *et al.* 1997; Kilic *et al.* 2007*a*; Kornyshev 2007; Storey *et al.* 2008), our motivation here is to explore its consequences for the most well known of electrokinetic phenomena: electrophoresis.

In § 2 we provide an introduction to ion steric effects. In § 3 we present a thin-double-layer analysis to calculate M_e. Results are discussed in § 4. Finally, in § 5 we offer concluding remarks.

2. Ion steric effects: the basic picture

Consider a uniformly charged flat plate in contact with a binary z—z electrolyte (figure 1). At equilibrium, the electrochemical potential $\mu_\pm$ of an ion is spatially constant, $\nabla\mu_\pm \equiv 0$ (Russel *et al.* 1989). (Here, $\pm$ denotes the sign of the charge.) In the classic dilute-solution theory of electrolytes, wherein ions are treated as non-interacting point charges, $\mu_\pm$ are given by (Lyklema 1995)

$$\mu_\pm = \pm ze\phi - k_BT \ln n_\pm, \tag{2.1}$$

where ϕ is the electric potential, and $n_\pm$ are the ion number densities. The first and second terms in (2.1) are the electrostatic and osmotic contributions, respectively, to the electrochemical potential. At equilibrium ($\nabla\mu_\pm \equiv 0$), the ion densities follow the

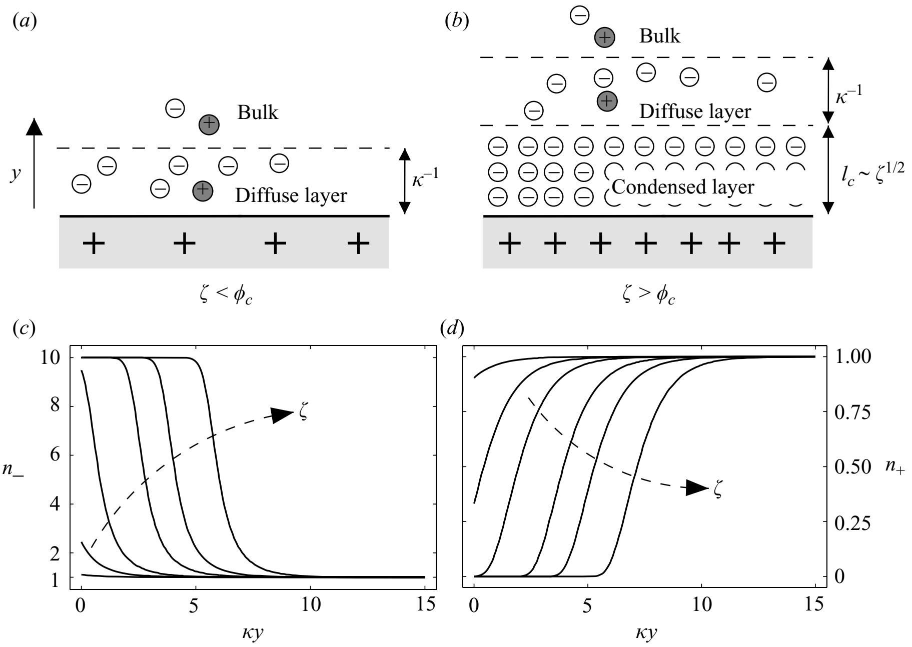

FIGURE 1. Physical picture of Bikerman's model of ion steric effects. (*a*) $\zeta < \phi_c = (k_B T/ze)\ln(2/\nu)$; hence, the surface charge is screened solely by a diffuse layer of counter-ions. (*b*) Conversely, for $\zeta > \phi_c$ a condensed counter-ion layer of density $n_- = 2/\nu$ and width $l_c \sim \zeta^{1/2}$ forms adjacent to the plate. (*c*) and (*d*) The counter-ion n_- and co-ion n_+ density profiles, respectively, above a positively-charged plate, from numerical solution of the PBik equation (2.6). Here, $\nu = 0.2$, and arrows indicate increasing ζ: solid lines are for $ze\zeta/k_B T = 0.1, 1, 5, 25, 50$ and 100. At sufficiently large ζ, a condensed layer grows into the bulk electrolyte.

Boltzmann distribution

$$n_\pm = n_\infty \mathrm{e}^{\mp ze\phi/k_B T}, \tag{2.2}$$

where n_∞ is the ion concentration far from the plate. Note, (2.2) predicts an unbounded, and aphysical, growth in counter-ion concentration with increasing electric potential ϕ.

To complete the description of the double layer, Poisson's equation, $\varepsilon\nabla^2\phi = -\rho$, relates the electric potential to the charge density in the fluid, $\rho = ze(n_+ - n_-)$. Substituting (2.2) into Poisson's equation yields the PB equation (Russel *et al.* 1989)

$$\varepsilon\nabla^2\phi = 2zen_\infty \sinh(ze\phi/k_B T), \tag{2.3}$$

which is solved by specifying the 'zeta' potential or surface charge density on the plate. Importantly, from (2.3) there emerges a length scale – the Debye screening length, $\kappa^{-1} = \sqrt{\varepsilon k_B T/2n_\infty(ze)^2}$ – characterizing the distance over which the charge density in the fluid decays. For monovalent ions at millimolar concentration and room temperature, the Debye length is approximately 10 nm.

One does not have to solve (2.3) to reveal its shortcomings. Following Kilic *et al.* (2007*a*), we ascribe to each ion a size a, such that the maximum allowable number density of ions equals $1/a^3$. From (2.2), the 'critical' potential ϕ_c at which this density is reached is $\phi_c = (k_B T/ze)\ln(2/\nu)$, where $\nu = 2a^3 n_\infty$ is the bulk volume fraction of ions. The logarithmic dependence of ϕ_c on ν implies that the maximum density can be attained at potentials of the order of the thermal voltage $k_B T/ze$, even for relatively dilute solutions, that is, the PB equation can predict aphysical densities for $\phi \gtrsim k_B T/ze$.

Bikerman (1942) proposed a simple model to account for the finite size of ions and solvent molecules. As shown by Kilic *et al.* (2007*b*), Bikerman's model is equivalent to modifying the electrochemical potentials to read

$$\mu_\pm = \pm ze\phi - k_B T \ln n_\pm - k_B T \ln(1 - n_+ a^3 - n_- a^3), \tag{2.4}$$

where the last term encapsulates steric effects due to finite sized ions. Borukhov, Andelman & Orland (2000) derived (2.4) from statistical mechanical arguments, by assuming that ions and solvent molecules occupy sites on a square lattice of unit cell size a. Remarkably, the equilibrium conditions $\nabla \mu_\pm = 0$ can be solved analytically to give an explicit relation between the electric potential and ion densities:

$$n_\pm = \frac{n_\infty \mathrm{e}^{\mp ze\phi/k_B T}}{1 + 2\nu \sinh^2(ze\phi/2k_B T)}. \tag{2.5}$$

Hence, at large potentials the counter-ion density saturates at $2n_\infty/\nu = 1/a^3$. Combining (2.5) with Poisson's equation yields the PBik equation:

$$\varepsilon \nabla^2 \phi = 2zen_\infty \frac{\sinh(ze\phi/k_B T)}{1 + 2\nu \sinh^2(ze\phi/2k_B T)}. \tag{2.6}$$

In figures 1(*c*) and 1(*d*) we plot the counter- and co-ion densities, respectively, above a charged plate for several zeta potentials ζ and bulk volume fraction $\nu = 0.2$, from the numerical solution of (2.6). In this case, $\phi_c \approx 2.3 k_B T/ze$ and for $ze\zeta/k_B T = 25$, 50 and 100, a condensed counter-ion layer with density $n_- = 2/\nu = 10$ (and $n_+ = 0$) is evident. Moreover, the size of the condensed layer l_c grows with ζ, which can be understood as follows. First, the surface charge density on the plate q balances the charge in the condensed layer, $q \sim zel_c/a^3$. Second, from Gauss' law $q = \varepsilon(\partial\phi/\partial y) \sim \varepsilon\zeta/l_c$. Hence, $l_c \sim \kappa^{-1}\sqrt{\nu ze\zeta/k_B T}$ – the condensed layer grows like $\zeta^{1/2}$, in agreement with Kilic *et al.* (2007*a*).

3. The electrophoretic mobility

We now consider a uniformly charged spherical particle of radius R freely suspended in a binary symmetric electrolyte. An imposed electric field $\boldsymbol{E}$ gives rise to electrophoresis of the particle, which translates at a velocity $\boldsymbol{U} = M_e \boldsymbol{E}$. The electrolyte is described to first order in $\boldsymbol{E}$ by coupled linear partial differential equations governing the perturbations to the equilibrium electrochemical potentials $\delta\mu_\pm$ and the fluid velocity $\boldsymbol{u}$. As derived by O'Brien & White (1978), the perturbed electrochemical potentials satisfy

$$\nabla^2 \delta\mu_\pm + \nabla \ln n_\pm^0 \boldsymbol{\cdot} \nabla \delta\mu_\pm = \tfrac{1}{2} m \boldsymbol{u} \boldsymbol{\cdot} \nabla \ln n_\pm^0. \tag{3.1}$$

In the above, and henceforth, we employ dimensionless variables: distances are scaled by R, electrochemical potentials by $k_B T$; ion number densities by n_∞; and velocity by $\varepsilon(k_B T/ze)^2/\eta a$. In (3.1), $n_\pm^0$ are the equilibrium ion densities given by the PBik equation, and $m = 2\varepsilon(k_B T/ze)^2/\eta D$, where the ion diffusivity D is assumed to be equal for all ions.

The velocity field is incompressible, $\nabla \boldsymbol{\cdot} \boldsymbol{u} = 0$, and satisfies the inhomogeneous Stokes equations

$$\nabla^2(\nabla \times \boldsymbol{u}) = \tfrac{1}{2}(\kappa R)^2 (\nabla n_+^0 \times \nabla \delta\mu_+ + \nabla n_-^0 \times \nabla \delta\mu_-), \tag{3.2}$$

where the body force on the fluid arises from gradients in electrochemical potentials. O'Brien & White (1978) and O'Brien (1983) have presented equations almost identical to (3.1) and (3.2) for general electrolytes. Although their focus was on the PNP equations, we note that (3.1) and (3.2) are in fact valid for any mean-field model of electrolyte dynamics.

In a reference frame translating with the particle, we require $\nabla\delta\mu_\pm \to \mp\hat{\boldsymbol{E}}$ and $\boldsymbol{u}\to -M_e\hat{\boldsymbol{E}}$ at large distances ($r\to\infty$), where the mobility is scaled by $\varepsilon k_BT/ze\eta$, $\hat{\boldsymbol{E}}=\boldsymbol{E}/|\boldsymbol{E}|$, and r is the scaled distance from the particle centre. On the surface of the particle ($r=1$) there is zero normal flux of ions $\boldsymbol{n}\cdot\nabla\delta\mu_\pm=0$, and the fluid velocity obeys the no-slip condition $\boldsymbol{u}=0$, where $\boldsymbol{n}$ is the unit normal into the fluid.

We now invoke the thin-double-layer limit $\kappa R\gg 1$, for which the majority of the electrolyte is uncharged, except for a thin and locally planar counterion-rich layer adjacent to the particle surface. Our analysis of the non-equilibrium double-layer structure follows very closely that of O'Brien (1983); for brevity, we do not present details here. However, a central outcome is that the perturbed electrochemical potentials are constant across the thin diffuse layer, $(\partial/\partial y)\delta\mu_\pm=0$, where $y=\kappa a(r-1)$ is a local coordinate perpendicular to the particle surface. As noted by Dukhin & Deryaguin (1974) and O'Brien (1983), this implies that the double layer attains a quasi-equilibrium structure. Rescaling (3.2) with y reveals that the dominant fluid flow in the double layer is parallel to the surface, with a velocity field given by

$$\boldsymbol{u}_\parallel = -\frac{1}{2}\nabla_s\delta\mu_+\int_0^y\int_t^\infty (n_+^0-1)\,\mathrm{d}s\,\mathrm{d}t - \frac{1}{2}\nabla_s\delta\mu_-\int_0^y\int_t^\infty (n_-^0-1)\,\mathrm{d}s\,\mathrm{d}t, \tag{3.3}$$

where $\nabla_s=(\boldsymbol{I}-\boldsymbol{nn})\cdot\nabla$ is the surface gradient operator. From (3.3), the 'slip' velocity $\boldsymbol{u}_\parallel^s$ at the outer edge of the double layer ($y\to\infty$) is

$$\boldsymbol{u}_\parallel^s = -\frac{1}{2}\nabla_s\delta\mu_+\int_0^\infty y(n_+^0-1)\,\mathrm{d}y - \frac{1}{2}\nabla_s\delta\mu_-\int_0^\infty y(n_-^0-1)\,\mathrm{d}y, \tag{3.4}$$

and the mobility of the sphere is calculated from $\boldsymbol{u}_\parallel^s$ via the formula (Anderson 1989)

$$M_e\hat{\boldsymbol{E}} = -\frac{1}{4\pi}\oint_{r=1}\boldsymbol{u}_\parallel^s\,\mathrm{d}S. \tag{3.5}$$

To explicitly compute M_e one requires the surface derivatives of the electrochemical potentials, $\nabla_s\delta\mu_\pm$, at the double-layer-bulk interface, $r=1$. To this end, in the bulk electrolyte the equilibrium ion densities are equal to the uniform bulk concentration, $n_\pm^0=1$, and hence (3.1) reduces to $\nabla^2\delta\mu_\pm=0$. Thus, by symmetry and linearity, $\delta\mu_\pm$ are given by

$$\delta\mu_\pm = \left(\mp r + \frac{C_\pm}{r^2}\right)\hat{\boldsymbol{E}}\cdot\hat{\boldsymbol{r}}, \tag{3.6}$$

from which $\nabla_s\delta\mu_\pm$ can readily be calculated. Using (3.6) and (3.4) with (3.5) gives

$$M_e = \frac{1}{3}(C_+-1)\int_0^\infty y(n_+^0-1)\,\mathrm{d}y + \frac{1}{3}(C_-+1)\int_0^\infty y(n_-^0-1)\,\mathrm{d}y. \tag{3.7}$$

Finally, one must determine the dipole coefficients $C_\pm$. To accomplish this, we utilize the known quasi-equilibrium double-layer structure to construct effective boundary conditions on the bulk electrochemical potentials (3.6), which are to be applied at the double-layer-bulk interface, $r=1$. Again, our approach is almost identical to O'Brien

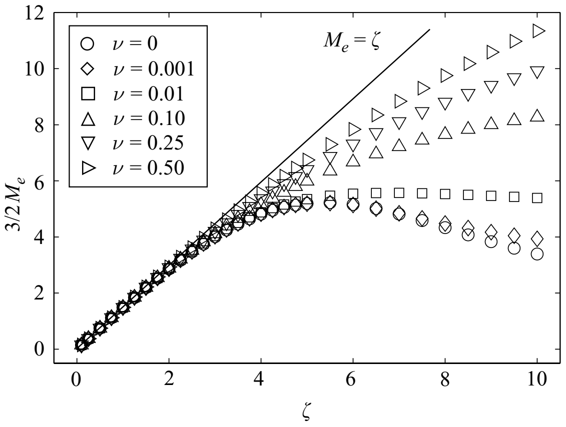

FIGURE 2. Mobility M_e as a function of zeta potential ζ for various volume fractions ν and $\kappa R = 50$. At sufficiently low $\zeta (< 1)$ all the data follow the HS result $M_e = \zeta$ (solid line). At larger ζ surface conduction causes the mobility to fall below the HS result.

(1983), hence we do not present details here. The effective boundary conditions are

$$\frac{\partial \delta\mu_+}{\partial r} = f_+ \nabla_s^2 \delta\mu_+ + g_+ \nabla_s^2 \delta\mu_-, \quad \text{and} \quad \frac{\partial \delta\mu_-}{\partial r} = g_- \nabla_s^2 \delta\mu_+ + f_- \nabla_s^2 \delta\mu_-, \quad \text{at} \quad r = 1. \tag{3.8}$$

These conditions express ion conservation, balancing the flux of ions across the double-layer-bulk interface (left-hand side of (3.8)) with the variation in the (integrated) tangential ionic flux along the particle surface. The surface flux coefficients are

$$\left.\begin{aligned} f_\pm &= -\frac{1}{\kappa R}\int_0^\infty (n_\pm^0 - 1)\,\mathrm{d}y - \frac{m}{4\kappa a}\int_0^\infty (n_\pm^0 - 1) I_\pm \,\mathrm{d}y, \\ g_\pm &= -\frac{m}{4\kappa R}\int_0^\infty (n_\pm^0 - 1) I_\mp \,\mathrm{d}y, \end{aligned}\right\} \tag{3.9}$$

where

$$I_\pm(y) = y\int_y^\infty (n_\pm^0 - 1)\,\mathrm{d}s + \int_0^y s(n_\pm^0 - 1)\,\mathrm{d}s. \tag{3.10}$$

Finally, substituting (3.6) in (3.8) yields

$$C_\pm = \frac{(f_\mp - 1)\left(\pm\frac{1}{2} \mp g_+ \pm f_\pm\right) - g_\pm\left(\mp\frac{1}{2} \pm g_+ \mp f_\mp\right)}{(f_+ - 1)(f_- - 1) - g_- g_+}. \tag{3.11}$$

Using (3.11) with (3.7) completes the calculation for the mobility.

4. Results

In figure 2 we plot the mobility M_e against zeta potential ζ for $\kappa R = 50$ and six different bulk volume fractions, ranging from an infinitely dilute solution ($\nu = 0$) to a highly concentrated one ($\nu = 0.5$). The range $0 < \zeta \leqslant 10$ is chosen to match the figures in O'Brien & White (1978), and our results for $\nu = 0$ are in quantitative agreement with theirs.

Evidently, ion steric effects make little difference for $\zeta < 1$: M_e follows the HS formula $M_e = \zeta$ for all ν. For $\zeta < 1$ there is only a small excess of ions within

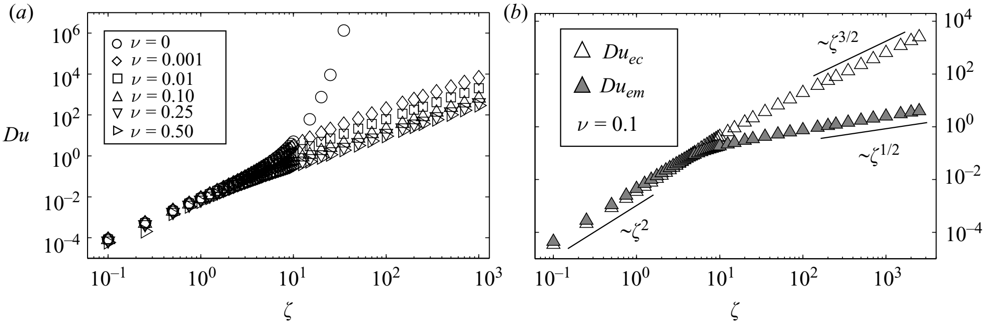

FIGURE 3. The Dukhin–Bikerman number Du. (a) Du versus ζ for various volume fractions ν. For $\nu = 0$, Du grows exponentially with ζ at large ζ, whereas for $\nu \neq 0$ the growth is algebraic $\sim \zeta^{3/2}$. (b) The electromigrative Du_{em} and electroconvective Du_{ec} contributions to Du for $\nu = 0.1$.

the double layer, and hence neither surface conduction nor ion steric effects are important. Thus, (3.8) reduce to $\partial\mu_\pm/\partial r = 0$, giving from (3.6) $C_\pm = \mp 1/2$ – the electrochemical potentials $\delta\mu_\pm$ adopt the profile of an insulator, since there is almost no ion transport across the double-layer-bulk interface. Furthermore, $n_\pm^0$ follow the linearized Debye–Hückel profiles, $n_\pm^0 = 1 \mp \zeta \mathrm{e}^{-y}$; therefore, from (3.7) we find $M_e = \zeta$.

At larger zeta, however, surface conduction becomes increasingly important and M_e falls below the HS formula. The greatest departure from HS is in the absence of ion sterics, $\nu = 0$, and M_e increases with ν for a given ζ. This is readily understood: surface conduction diminishes with increasing ν, due to the reduced maximum ion density $2/\nu$ in the condensed layer. Thus, surface conduction primarily determines M_e, rather than ζ itself. And since ion steric effects reduce surface conduction, one should plot M_e versus an appropriate measure of surface conduction: namely, the Dukhin–Bikerman number $Du = \sigma_s/\sigma_b R$, which signifies the relative importance of surface (double layer) σ_s to bulk σ_b conductivities. To calculate Du, note that the electrical current $\boldsymbol{j}$ in response to $\hat{\boldsymbol{E}}$ is $\boldsymbol{j} = (n_+^0 + n_-^0)\hat{\boldsymbol{E}} + \frac{m}{2}(n_+^0 - n_-^0)\boldsymbol{u}$, where the first and second terms correspond to the electromigrative and electroconvective current arising from the imposed field and ensuing electro-osmotic flow $\boldsymbol{u}$, respectively. In the bulk electrolyte $n_\pm^0 = 1$; hence, $\boldsymbol{j}_b = 2\hat{\boldsymbol{E}}$, giving $\sigma_b = 2$. The surface current $\boldsymbol{j}_s = \sigma_s\hat{\boldsymbol{E}}$ is simply the 'excess' current $\boldsymbol{j} - \boldsymbol{j}_b$ integrated over the double layer. Thus, substituting the velocity field $\boldsymbol{u}_\parallel$ (3.3) into the definition of $\boldsymbol{j}$ yields σ_s, from which Du readily follows as

$$Du = \frac{1}{2\kappa R}\int_0^\infty (n_+^0 + n_-^0 - 2)\,\mathrm{d}y + \frac{m}{8\kappa R}\int_0^\infty (n_+^0 - n_-^0)(I_+ - I_-)\,\mathrm{d}y. \tag{4.1}$$

The first and second terms in (4.1) represent the electromigrative (Du_{em}) and electroconvective (Du_{ec}) contributions to Du, respectively. For $\nu = 0$ we have (Lyklema 1995)

$$Du_{\nu=0} = \frac{4(1+m)}{\kappa R}\sinh^2\left(\frac{ze\zeta}{2k_B T}\right). \tag{4.2}$$

Thus, Du_{em} and Du_{ec} differ only by a factor of m. Moreover, they scale as ζ^2 at small ζ, while growing exponentially with ζ at large ζ, reflecting the unbounded counter-ion density in the double layer. For finite ion size $\nu \neq 0$, Du must be evaluated numerically (figure 3a). At small ζ, $Du \sim \zeta^2$ – the counter-ion density is small and hence ion steric effects are unimportant. However, Du grows algebraically rather than exponentially

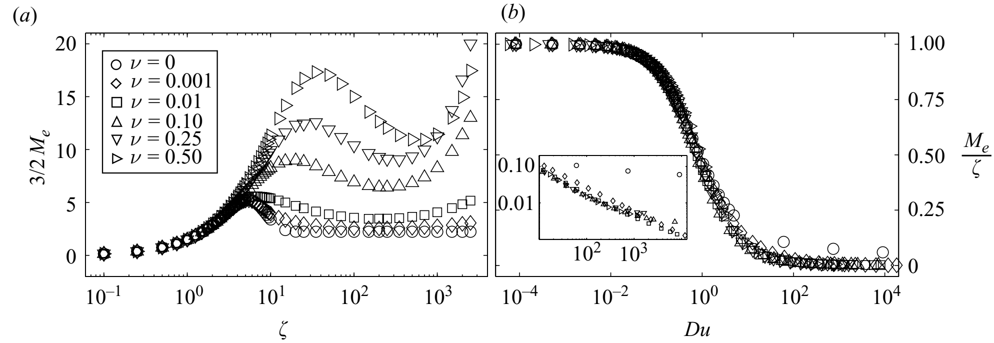

FIGURE 4. (*a*) Mobility M_e versus zeta potential ζ for various volume fractions ν, over the extended range $\zeta < 2500$. (*b*) The same M_e data scaled by ζ and plotted versus the Dukhin–Bikerman number Du (inset shows log–log plot at large Du).

at large ζ, showing the dramatic reduction in surface conduction due to ion sterics. Separate plots of Du_{em} and Du_{ec} appear in figure 3(*b*) for $\nu = 0.1$. Again, at small ζ both Du_{em} and Du_{ec} scale as ζ^2; however, at large ζ, $Du_{ec} \sim \zeta^{1/2}$ while $Du_{ec} \sim \zeta^{3/2}$. Note, Du_{em} is simply proportional to the excess ion concentration in the double layer, which scales as the condensed-layer width $l_c \sim \sqrt{\nu\zeta}$ for $\zeta \gg 1$ (Kilic *et al.* 2007*a*). The electroconvective flux, however, varies like $\zeta^{3/2}$: the fluid flow $\boldsymbol{u}_{\parallel}$ (3.3) is $O(\zeta)$ in the condensed layer and advects the $O(\zeta^{1/2})$ excess ion concentration, giving $Du_{ec} \sim \zeta^{3/2}$. Formally, from (4.1), and using $I_+ - I_- \sim l_c^2/\nu$ at large ζ (cf. (3.10)), we have

$$\left.\begin{aligned} Du_{em} &\sim \frac{1}{2\kappa R}\int_0^{l_c} \frac{2}{\nu} - 2\,\mathrm{d}y = \frac{1-\nu}{\kappa R \nu^{1/2}}\zeta^{1/2}, \\ Du_{ec} &\sim \frac{m}{8\kappa R}\int_0^{l_c} \frac{2}{\nu}(I_+ - I_-)\,\mathrm{d}y = \frac{m}{4\kappa R \nu^{1/2}}\zeta^{3/2}. \end{aligned}\right\} \tag{4.3}$$

Note, no maximum in the mobility appears in figure 2 for $\nu = 0.1$ and larger; does a maximum exist for $\zeta > 10$? To answer this interesting, if perhaps academic, question we plot M_e up to $\zeta = 2500$ (figure 4*a*) – a mobility maximum is indeed observed. More surprising, however, is the mobility minimum at even larger ζ (for $\nu \neq 0$), after which the mobility increases with ζ. In contrast, for $\nu = 0$, M_e decreases upon attaining its maximum, until a value of ln 4 is reached as $\zeta \to \infty$ (O'Brien 1983). The increase in M_e at very large ζ is readily explained: the bulk counter-ion electrochemical potential $\delta\mu_-$ (3.6) is that of a conductor ($C_- = 1$), to ensure maximal transport of counter-ions into or out of the double layer. Conversely, co-ions are excluded from the double layer; $\delta\mu_+$ adopts the profile of an insulator, $C_+ = 1/2$. Thus, from (3.7)

$$M_e \to -\frac{1}{2}\int_0^{\infty} y(n_+^0 - 1)\,\mathrm{d}y \quad \text{as} \quad \zeta \to \infty, \tag{4.4}$$

that is, M_e is proportional to the integrated co-ion deficit across the double layer. For $\nu = 0$, (4.4) yields $M_e \to \ln 4$. For non-zero ν, (4.4) is approximated by noting that the dominant contribution comes from the condensed layer ($l_c \sim \sqrt{\nu\zeta}$) in which $n_+ = 0$. Thus, from (4.4) $M_e \to \nu\zeta/4$, giving a mobility that grows linearly with ζ and ν. The data in figure 4(*a*) at large $\zeta (>1000)$ do not quite conform to this linear scaling, owing to a weak ζ-dependence of C_+ that is not accounted for in the above argument.

Since M_e is expected to depend primarily on surface conduction, we plot M_e scaled by ζ versus Du in figure 4(*b*). Data at different ν collapse onto a single master curve, at least up to $Du \approx 100$ (see inset), after which the no-sterics ($\nu = 0$) data set is slightly above the rest. This is simply due to the difference in the scaling of Du for $\nu = 0$ at large ζ (exponential with ζ) versus $\nu \neq 0$ (algebraic). In a recent paper (Khair & Squires 2009), we considered the influence of hydrodynamic slip at the surface of a particle on its electrophoretic mobility (in the absence of ion sterics $\nu = 0$). Again, by plotting M_e scaled by its HS-like limiting form versus Du (which was modified to account for slip), data for different slip lengths were collapsed onto a master curve. That both the effects of hydrodynamic slip and ion sterics can be scaled out in this manner is striking and highlights that it is surface conduction – encapsulated in the Dukhin number Du – rather than the surface (zeta) potential ζ that primarily determines M_e beyond the HS approximation.

5. Concluding remarks

For over a century, the PNP equations have served as the de facto theoretical model of electrokinetic phenomena. However, the non-interacting, point-sized ions assumed by PNP can lead to impossibly large ion concentrations near even moderately charged surfaces. Here, we have computed the electrophoretic mobility M_e of a colloidal particle, using modified PNP equations that account finite-sized ion steric effects through Bikerman's model. Ion steric effects lead to a saturation of the counter-ion density near a highly charged surface, which diminishes surface conduction and thus has significant consequences for the mobility. Indeed, the behaviour of M_e can be altered to the extent that the maximum in M_e predicted by O'Brien & White (1978) and O'Brien (1983) may not occur at physically reasonable zeta potentials. Further, ion sterics bring M_e closer to the HS result, precisely because the reduction in surface conduction delays the onset of the large-Du regime, and HS is valid for any mean-field model of the double layer at small Du.

It is worth asking whether the effect of ion sterics upon electrophoresis could be observed experimentally? This requires both $\zeta > k_BT/e$ and a sufficiently large bulk volume fraction (cf. figure 2). First, $\zeta \sim 2 - 4k_BT/e$ are often encountered in colloidal systems (Russel *et al.* 1989). Second, in a simple electrolyte to achieve, for example, $\nu = 0.1$ requires a bulk concentration $n_\infty \approx 0.67$ M, assuming an ion size of $a = 0.5$ nm (including a hydration shell). At this concentration, however, the Debye length $\kappa^{-1} \approx 0.4$ nm, which is smaller than the Bjerrum length and thus can be expected to invalidate the mean-field approximation of electrostatic interactions. Therefore, while ion steric effects may affect electrophoresis under such conditions, it is unlikely that their consequences could be examined in the absence of additional effects; more highly charged particles would be required. Larger volume fractions (approaching unity, perhaps) may be possible in ionic liquids, which are effectively solvent-free (Kornyshev 2007); electrophoresis may well be affected significantly in such systems. In aqueous electrolytes, ion sterics may be more readily encountered in induced-charge electrokinetics (Squires & Bazant 2004) or AC electrokinetics (Ramos *et al.* 1999; Storey *et al.* 2008), wherein electric fields are applied around polarizable particles and electrodes. In these systems, the strength of the applied field sets the zeta potential, and $\zeta \gg k_BT/e$ are routinely encountered, necessitating a much lower bulk concentration for ion sterics to potentially matter (Kilic *et al.* 2007*a*).

The impossibly large counter-ion densities predicted by the PB equation at large zeta potentials ζ are usually circumvented by introducing a Stern layer between the particle surface and the plane of shear (i.e. the location at which ζ is defined and beyond which fluid flows). Physically, the Stern layer accounts for steric repulsion between a diffuse counter-ion and the surface; the thickness of the Stern layer corresponds to the distance of closest approach of the two. Hence, the Stern layer is devoid of ions and acts as a linear capacitor in series with the diffuse layer. The zeta potential is related to the potential at the particle surface ϕ_s via $\zeta = \phi_s/(1 + C_{Diff}/C_{Stern})$, where C_{Diff} and C_{Stern} are the capacitances of the diffuse and Stern layers, respectively. When $C_{Stern} \ll C_{Diff}$, the surface potential is mostly dropped over the Stern layer, and $\zeta \ll \phi_s$. In this case, ζ may not be sufficiently large for the PB equation to yield aphysically large counter-ion densities. Conversely, if $C_{Stern} \gg C_{Diff}$ then $\zeta \approx \phi_s$ – only a small portion of ϕ_s is dropped across the Stern layer. Importantly, our calculations for ion steric effects on the electrophoretic mobility are robust, since inclusion of a Stern layer would simply set a difference between ϕ_s and ζ; if ζ surpasses the critical potential ϕ_c a condensed layer of counter-ions will still form at the plane of shear. A further refinement of the Stern picture accounts for counter-ion adsorption at the particle surface (Lyklema 1995). While fluid cannot flow in the Stern layer, the adsorbed counter-ions are mobile, allowing for conduction within the Stern layer. Kijlstra, van Leeuwen & Lyklema (1992) performed a thin double-layer analysis of the PNP equations accounting for Stern layer conduction, which showed the mobility M_e for a given ζ to decrease as the ratio of Stern layer-to-diffuse layer conductivities increases; indeed, for a sufficiently large ratio a maximum in M_e is not observed. Qualitatively similar conclusions were reached by Mangelsdorf & White (1990), who studied a more detailed model of counter-ion adsorption and Stern layer conductance. Conduction within the Stern layer increases the Dukhin number Du for a given ζ, thereby lowering M_e. Conversely, as we have shown, ion steric effects lower Du for a given ζ, leading to an increase in M_e. Thus, Bikerman's model is fundamentally distinct from the Stern layer: the former accounts for steric repulsion between ions; and the latter for interactions between ions and the charged particle.

Our analysis was conducted in the thin-double-layer limit $\kappa R \gg 1$. The bulk governing equations and effective boundary conditions derived in § 3 can (and should) be used to study ion steric effects on other classic electrokinetic phenomena, such as the electroviscous effect, streaming currents/potentials, and the effective electrical conductivity of dilute suspensions. However, the notion of a 'thin' double layer is itself subtle, since at large enough ζ the condensed-layer thickness l_c grows like $\zeta^{1/2}$, effectively increasing the width of the double layer. Indeed this is responsible for the decay of the differential capacitance at large voltages (Freise 1952). Properly, the thin-double-layer assumption is voltage dependent, requiring that $l_c + \kappa \ll R$. Hence, there is merit in solving numerically the full linearized MPNP equations, thereby allowing a systematic study of the validity of thin-double-layer assumption in computing M_e.

Recall, Bikerman's model assumes that ions and solvent molecules have equal size and occupy sites on a square lattice. The resulting 'excess' chemical potential of ion i due to ion steric effects is $\mu_i^{ex,Bik}/k_B T = -\ln(1-\nu)$ (cf. (2.4)). However, Bikerman's model underestimates ion steric effects, since it neglects the volume excluded to other ions as a result of the volume occupied by a single ion; for example, a spherical ion excludes eight times its own volume (Biesheuvel & van Soestbergen 2007; Bazant *et al.* 2009). Accounting for excluded-volume effects requires adjusting $\mu_i^{ex,Bik}$ to read $\mu_i^{ex}/k_B T = -\ln(1-8\nu)$ (Biesheuvel & van Soestbergen 2007). In fact, this expression is the low-volume-fraction limit of the Carnahan–Starling (CS) equation-of-state for monodisperse hard spheres $\mu_i^{ex,CS}/k_B T = \nu(8 - 9\nu + 3\nu^2)/(1-\nu)^3$ (Carnahan & Starling 1969). A modified PB equation based on the CS equation of state (the CS MPB equation) was solved by Bazant *et al.* (2009) for the double-layer structure over a flat electrode. While we focused on Bikerman's model, our analysis in § 3 applies to other equations of state, and simply requires the appropriate equilibrium ion density profiles $n^0_{\pm}$.

Our thin-double-layer analysis can be extended to multi-component systems containing ions of different size and valency. Indeed, ion steric effects can lead to a qualitatively different double-layer structure in such systems. For example, the GC model predicts the counter-ion with the highest valency to be overwhelmingly present in the double layer at large ζ. By contrast, Shapovalov & Brezesinski (2006) measured the double-layer structure adjacent to a negatively charged Langmuir monolayer in an aqueous solution containing ions of different size and charge. They noted significant departures from the GC model, including 'counter-ion segregation', wherein smaller ions with lower valence were present in greater number in the double layer than larger ions with higher valence. Their experiments were theoretically modelled by Biesheuvel & van Soestbergen (2007), via a modified PB equation based on the 'Boublik–Mansoori–Carnahan–Starling–Leland' equation of state for mixtures of unequal hard spheres. The implications of counter-ion segregation and electrolyte asymmetry on electrophoresis are worth investigation, and have garnered attention in induced-charge electrophoresis of charged polarizable particles (Bazant *et al.* 2009).

We have assumed that the viscosity η and permittivity ε of the electrolyte remain uniform. These assumptions are questionable, especially for a highly charged particle, where one expects that η increases and ε decreases within the double layer, due to the large concentration of ions present. For the same reason, the ion diffusivity D is also anticipated to decrease in the double layer. Bazant *et al.* (2009) proposed a simple model for 'charge-induced thickening', where η increases with charge density ρ, and diverges in the condensed-layer limit $\rho = ze/a^3$. Physically, this has the effect of moving the plane-of-shear from the particle surface to the edge of the condensed layer, reducing the electro-osmotic flow within the double layer and thus the electrophoretic mobility. Hence, the condensed layer begins to resemble a Stern-type layer, over which a potential can drop but through which fluid cannot flow.

Of the various techniques that have been developed to account for ion steric effects in electrical double layers, Bikerman's model is perhaps the most simple and straightforward. Our treatment using Bikerman's model was thus able to derive the dramatic effects – both quantitative and qualitative – that ion sterics can have on the electrophoretic mobility of a colloidal particle, without sacrificing physical intuition and clarity. As discussed above, there are several physical effects not included in Bikerman's model whose implications for electrophoresis may be as dramatic and hence warrant further investigation. Despite its shortcomings, however, Bikerman's model seems a useful starting point to treat ion steric effects in this and other electrokinetic phenomena.

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