

# The unusual fluid dynamics of particle electrophoresis

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## Abstract

The classical problem of the electrophoretic motion of a spherical particle has been treated theoretically by Overbeek in his 1941 PhD thesis and almost 40 years later by O'Brien & White. Although both approaches used identical assumptions, the details are quite different. Overbeek solved for the pressure, velocity fields as well as the electrostatic potential whereas O'Brien & White obtained the electrophoretic mobility without the need to consider the pressure and velocity explicitly. In this paper, we establish the equivalence of these two approaches which allow us to show that the tangential component of the fluid velocity has a maximum near the surface of the particle and outside the double layer, the velocity decays as  $1/r^3$ , where  $r$  is the distance from the sphere, instead of  $1/r$  in normal Stokes flow. Associated with this behavior is that of an irrotational outer flow field. This is consistent with the fact that a sphere moving with a constant electrophoretic velocity experiences zero net force. A study of the forces on the particle also provides a physical explanation of the independence of the electrophoretic mobility on the electrostatic boundary conditions or dielectric permittivity of the particle. These results are important in situations where inter-particle interaction is considered, for instance, in electrokinetic deposition.

**Keywords:** Colloid, Double layer, Constant pressure irrotational Stokes flow, Short range interaction for multiple particles, Electrophoresis, Electrophoretic mobility

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## 1. Introduction

Electrophoresis, the study of the motion of small charged particles in an electrolyte due to the influence of an applied electric field, has a long history. In colloid and interface science, it has found extensive applications in the characterization of particulate dispersions, emulsions, polymeric and soft biological systems [1, 2].

Historically, it has been a century since Smoluchowski [3] published his result for the electrophoretic mobility of a colloidal particle with a thin electrical double layer. Nearly 80 years ago Overbeek [4], in his PhD thesis, extended Henry's [5] theory of the electrophoresis of a spherical colloidal particle with low surface potentials in a symmetric electrolyte to include the relaxation effect that is important at high surface potentials. Forty years ago, O'Brien & White [6] provided a comprehensive formulation of the electrokinetic problem in an electrolyte of arbitrary ionic composition. By exploiting the special symmetry of a sphere in a uniform applied electric field,  $\mathbf{E}$ , they simplified the electrokinetic equations to a set of coupled ordinary differential equations in the radial coordinate,  $r$  and developed a robust numerical scheme to solve this system of differential equations. This development facilitated the accurate estimation of the electrokinetic mobility of a solid charged sphere for all practical magnitudes of the zeta ( $\zeta$ )-potential and the sphere radius relative to the thickness of the electrical double layer.

Although the physical models of the electrophoresis of a

spherical particle considered by Overbeek [4] and by O'Brien & White [6] are identical, the O'Brien & White [6] treatment highlighted the dual length scale nature of the problem characterized by the Debye length and the particle radius. When the Debye length is small compared to the particle size, in the so-called thin double layer regime, one encounters 'stiff' differential equations that can be challenging in numerical implementations.

An important theoretical observation was made by Morrison [7] nearly half a century ago, whereby the fluid flow field around a particle undergoing electrophoretic motion is shown to be irrotational, but there have been few attempts to explore the consequences of this interesting phenomenon in the literature. Indeed, a detailed description of the flow field occurring during electrophoresis seems not to have been given to this day. In part perhaps because it has been possible to calculate the electrophoretic mobility, for instance with the O'Brien & White [6] approach, without the need to consider details of the flow field. As will be shown later, the velocity field around a particle in electrophoretic motion is unusual in the sense that it decays as  $1/r^3$  with the distance,  $r$  from the particle, rather than as  $1/r$  in the more familiar Stokes flow [8]. Associated with the fact that the velocity field is irrotational outside the double layer around the particle, the pressure field decays exponentially on the scale of the Debye length with distance from the particle rather than as  $1/r^2$  in Stokes flow. Such behaviours of the velocity and pressure fields have implications for electrokinetic studies at

finite particulate concentrations where effects due to the interactions between particles can become important [9, 10].

One objective in this paper is to demonstrate the connection between the Overbeek [4] and O'Brien & White [6] general theory of the electrophoresis of a spherical particle. From this development, we can make explicit the dual length-scale hydrodynamic features associated with a particle under electrophoretic motion and elucidate the physics principles that underpin unusual behaviour such as a more rapidly decaying velocity field, a vanishing pressure field and the presence of a fluid velocity maximum near the electrical double layer around the particle. We show that these features, that to the best of our knowledge have not been demonstrated previously, are all consequences of the fact that the particle travels at the constant electrophoretic velocity under the applied electric field that arise from the balance of the electrical forces that drives the particle and the retarding hydrodynamic drag force.

In Section 2 the governing equations are given for a general electrophoretic problem. A generalization to multi-valent systems of the formally exact solution for the electrophoresis of a spherical particle by Ohshima, Healy & White [11] is given in Section 3. The connection between this solution and the Overbeek [4] theory that appears to be absent in the literature is provided in Section 4. In Section 5 we derive general properties of the pressure and velocity that appear not to have been elucidated before. The model of Henry [5] can then be seen as a simplification of the Overbeek theory and we use it to produce numerical results to illustrate the unusual hydrodynamic behavior associated with the electrophoretic motion of a sphere in Section 6. A discussion on the force balance and its physical implications is given in Section 7 where we exhibit the cancellation between the different contributions as described by Overbeek. This is an explicit demonstration of the O'Brien & White observation that the electrophoretic mobility of a dielectric sphere is independent of its permittivity and is also independent of the form of the perturbed electrostatic potential around the sphere. The perturbed electrostatic potential governs the equal and opposite internal forces between the particle and the deformed electrical double layer and so does not affect the net force on the particle. The paper closes with concluding remarks about the implications of the present findings. Relevant details of the derivations are given in the Appendices, including a derivation of the Overbeek theory expounded in Dutch in his PhD thesis. A glossary of symbols is provided for convenience.

## 2. Governing equations

In electrophoresis, a charged colloidal particle, usually in an aqueous electrolyte, moves with constant velocity,  $U$  under the influence of a constant applied external electric field,  $E$ . In general, the magnitude of the applied field is small compared to the field within the electrical double layer around the charged particle. The physical quantity of interest is the electrophoretic mobility,  $\mu_m \equiv U/E$  that can vary with particle size, particle charge and the electrolyte composition and concentration. For particles of dimension,  $d \sim 10^{-6}$  m, velocity,  $U < 10^{-4}$  m/s [12], an order-of-magnitude estimate for the Reynolds number can be

determined as,  $Re \sim \rho_L U d / \eta \sim (10^3)(10^{-4})(10^{-6})/10^{-3} \sim 10^{-4}$  (for water with density  $\rho_L = 1000$  kg/m<sup>3</sup> and viscosity  $\eta = 10^{-3}$  Pa s). Since  $Re \ll 1$ , inertial effects can be neglected such that the Stokes model for creeping flow can be used to describe the hydrodynamics [13, 14].

The description of steady state electrokinetic phenomena also requires specification for the velocity of the solvent, the local ion number density and charge density as well as velocities or currents of ionic species that make up the electrolyte and the electrostatic potential. Here, we recapitulate the model of Overbeek [4] and of O'Brien & White [6] who derived the same governing equations for particle electrophoresis but followed different methods of solution.

### 2.1. System in an external electric field $E$

In the description given here, we assume that the coordinate system is attached to the particle under consideration and thus the flow at infinity moves in the opposite direction of the electrophoretic velocity in the laboratory frame of reference. In the presence of an external electric field,  $E$ , the local electrical chemical potential,  $\mu_i(\mathbf{x})$  of ionic species  $i$  with valence,  $z_i$  is related to the total electrostatic potential,  $\psi(\mathbf{x})$  and the local ion number density,  $n_i(\mathbf{x})$  by

$$\mu_i = \mu_i^\infty + z_i e \psi + kT \log n_i \quad (1)$$

where  $\mu_i^\infty$  is the constant reference chemical potential and  $e$  is the protonic charge. The steady state ion transport process of each ionic species,  $i$  is determined by balancing the force due to the gradient of the ionic electrical chemical potential and that due to the Stokes-Einstein drag on the ion that is proportional to the ion velocity,  $\mathbf{v}_i(\mathbf{x})$  relative to the fluid velocity,  $\mathbf{u}(\mathbf{x})$ ,

$$\lambda_i (\mathbf{v}_i - \mathbf{u}) = -\nabla \mu_i = -z_i e \nabla \psi - kT \nabla \log n_i \quad (2)$$

where  $\lambda_i$  is the ion drag coefficient. The conservation of ionic flux gives, in the steady state

$$\nabla \cdot (n_i \mathbf{v}_i) = 0. \quad (3)$$

The local volume charge density,  $\rho(\mathbf{x})$  made up of ionic species  $i$ , is given in terms of  $n_i(\mathbf{x})$  by

$$\rho = \sum_i n_i z_i e. \quad (4)$$

The Poisson equation provides the relation between the total electrostatic potential,  $\psi(\mathbf{x})$ , describing the local electric field,  $(-\nabla \psi)$ , the total volume charge density,  $\rho(\mathbf{x})$  and the ion number density,  $n_i(\mathbf{x})$ :

$$\nabla^2 \psi = -\rho/\epsilon = -(e/\epsilon) \sum_i n_i z_i \quad (5)$$

where the solvent permittivity  $\epsilon \equiv \epsilon_0 \epsilon_r$  is the product of the permittivity of free space,  $\epsilon_0$  and the relative permittivity of the solvent,  $\epsilon_r$ . Inside the particle with dielectric permittivity,  $\epsilon_p$ , the potential satisfies the Laplace equation:  $\nabla^2 \psi = 0$ .

The solvent of the electrolyte is taken to be incompressible so that the velocity field,  $\mathbf{u}$  is divergence free

$$\nabla \cdot \mathbf{u} = 0. \quad (6)$$

The momentum equation that governs the fluid velocity,  $\mathbf{u}$  and the pressure,  $p$  is described by Stokes flow in the presence of the electrostatic body force,  $(-\rho\nabla\psi)$

$$\eta \nabla^2 \mathbf{u} - \nabla p = \rho \nabla \psi, \quad (7)$$

where all inertial terms have been neglected. This equation can be derived from considering the stress tensor, see Appendix C.

## 2.2. No external field: $\mathbf{E} = \mathbf{0}$

In the absence of the external electric field,  $\mathbf{E} = \mathbf{0}$  the system is in equilibrium so the fluid and ion velocities vanish:  $\mathbf{u} = \mathbf{0}$  and  $\mathbf{v}_i = \mathbf{0}$ . With other physical variables in equilibrium distinguished by the superscript '0', the ion transport equation becomes

$$z_i e \nabla \psi^0 + kT \nabla \log n_i^0 = 0. \quad (8)$$

The integral of this result gives the mean field Boltzmann distribution for the ion number density

$$n_i^0(\mathbf{x}) = n_i^\infty \exp[-z_i e \psi^0(\mathbf{x})/kT] \quad (9)$$

with  $n_i^\infty$  representing the uniform ion density in bulk solution where  $\psi^0 = 0$ . The gradient of the Boltzmann distribution gives the identity

$$\nabla n_i^0(\mathbf{x}) = - (z_i e/kT) n_i^0(\mathbf{x}) \nabla \psi^0(\mathbf{x}) \quad (10)$$

that is useful in casting later results in physically meaningful forms. For instance, the momentum equation (7) at equilibrium becomes, using (4) and (10)

$$\begin{aligned} \nabla p^0 &= -\rho^0 \nabla \psi^0 \\ &= \epsilon (\nabla^2 \psi^0) \nabla \psi^0 \\ &= \nabla (kT \sum_i z_i n_i^0) \end{aligned} \quad (11)$$

and relates the pressure gradient to the ionic osmotic gradients.

And finally, the combination of the Poisson equation with the mean field Boltzmann distribution of ions that relate the ion density,  $n_i^0$  to the potential,  $\psi^0$  gives the Poisson-Boltzmann equation that determines the equilibrium electrostatic potential,  $\psi^0(\mathbf{x})$ :

$$\begin{aligned} \nabla^2 \psi^0 &= -\rho^0/\epsilon = -(e/\epsilon) \sum_i z_i n_i^0 \\ &= -(e/\epsilon) \sum_i z_i n_i^\infty \exp[-z_i e \psi^0/kT]. \end{aligned} \quad (12)$$

The equilibrium electrostatic potential,  $\psi^0(\mathbf{x})$  decays exponentially to zero away from the particle with the characteristic Debye length,  $1/\kappa$ , where

$$\kappa^2 \equiv (e^2/\epsilon kT) \sum_i z_i^2 n_i^\infty \quad (13)$$

that is determined by the ionic valence,  $z_i$  and the ion number density,  $n_i^\infty$  far from the particle.

It is only necessary to solve (12) to determine the potential distribution in the solvent, without the need to consider the potential inside a dielectric particle if the particle has a specified surface potential (that may even vary along the surface). On the other hand, if the particle has a specified surface charge density distribution, then in general, it will be necessary to consider the potential inside the particle in determining the potential in the solvent outside the particle.

## 2.3. The linearized electrokinetic equations

The electrokinetic transport equations are obtained by expanding the governing equations as first order perturbations in the applied external electric field,  $\mathbf{E}$ , to all equilibrium quantities. This is justified on account that the magnitude of the applied field is in practice small compared to the electric field in the electrical double layer. Hence, we can express,

$$p = p^0 + \delta p \quad (14a)$$

$$\psi = \psi^0 + \delta \psi \quad (14b)$$

$$n_i = n_i^0 + \delta n_i \quad (14c)$$

$$\mu_i = \mu_i^0 + \delta \mu_i \quad (14d)$$

$$\rho = \rho^0 + \delta \rho \quad (14e)$$

in which the perturbation terms  $\delta p$ ,  $\delta \psi$ ,  $\delta n_i$ ,  $\delta \mu_i$  and  $\delta \rho$  are of the same order as the fluid velocity,  $\mathbf{u}$ , the ion velocities,  $\mathbf{v}_i$  and the applied field,  $\mathbf{E}$ . The governing equations for the electrokinetic phenomenon are obtained by retaining such first order terms in (2), (3), (5) and (7), namely,

$$\nabla \cdot [\lambda_i n_i^0 \mathbf{u} - z_i e n_i^0 \nabla \delta \psi - kT \nabla \delta n_i - z_i e \delta n_i \nabla \psi^0] = 0 \quad (15a)$$

$$\nabla^2 \delta \psi = -\frac{1}{\epsilon} \delta \rho = -\frac{1}{\epsilon} \sum_i z_i e \delta n_i \quad (15b)$$

$$\eta \nabla^2 \mathbf{u} - \nabla \delta p = \rho^0 \nabla \delta \psi + \delta \rho \nabla \psi^0 \quad (15c)$$

where (15a) can be obtained by multiplying (2) with  $n_i$ , linearising and utilising (3).

The electrokinetic problem then entails solving the coupled equations that are linear in the perturbation quantities:  $\mathbf{u}$ ,  $\delta \psi$ ,  $\delta p$  and  $\delta n_i$  in (15). This set of equations is the common starting point of the theoretical treatment of electrokinetics. Note that these coupled equations only require the equilibrium electrostatic potential,  $\psi^0(\mathbf{x})$ , and the ion distributions,  $n_i^0(\mathbf{x})$  to be available but they do not depend whether one uses, say, the full non-linear Poisson-Boltzmann theory or the linear Debye-Hückel theory to specify these equilibrium quantities.

The theory of the electrophoretic motion of a spherical particle developed by Overbeek [4] and subsequently by O'Brien & White [6] therefore have the identical physical content and only differ in the way the equations are solved. The inherent azimuthal symmetry of the electrophoresis of a *spherical* colloidal particle under a uniform applied electric field in the  $z$ -direction implies that the unknown perturbation quantities have the general form:  $f(r, \theta) = F(r) \cos \theta$ , or  $g(r, \theta) = G(r) \sin \theta$ , where  $r$  is the radial distance from the centre of the sphere and  $\theta$  is the polar angle relative to the direction of  $\mathbf{E}$ . Thus the problem described by (15) can be reduced to a set of coupled ordinary differential equations for the unknown functions of  $r$ . This is the approach adopted by Henry and Overbeek. By further introducing ion potential functions, O'Brien & White were able to decouple this set of ordinary differential equations in order to obtain the electrophoretic mobility: one only needs to solve for a hydrodynamic function,  $h(r)$  and  $N$  ionic potential functions,  $\phi_i(r)$  where  $i = 1, \dots, N$  for  $N$  ionic species of the electrolyte.

In the following, we demonstrate the connection between the Overbeek and the O'Brien & White solutions.

### 3. The O'Brien & White solution for a sphere

#### 3.1. The first order equations in $E$

To solve the electrokinetic equations that are first order in the applied field,  $E$ , O'Brien & White [6] streamlined the analysis by introducing the ion potential,  $\varphi_i(\mathbf{x})$  in the linearization of the expression for the chemical potential (1) for the perturbed chemical potential,  $\delta\mu_i$  of ion species  $i$

$$\delta\mu_i(\mathbf{x}) = z_i e \delta\psi + kT (\delta n_i/n_i^0) \equiv -z_i e \varphi_i(\mathbf{x}). \quad (16)$$

To first order, the ion flux conservation condition (3) can now be expressed in terms of  $\varphi_i$

$$\nabla \cdot [n_i^0 (z_i e \nabla\varphi_i + \lambda_i \mathbf{u})] = 0 \quad (17)$$

to provide one equation that couples the function  $\varphi_i(\mathbf{x})$  to the velocity field,  $\mathbf{u}(\mathbf{x})$ .

To the same linear order, the Stokes equation for the fluid velocity, (7) becomes

$$\eta \nabla^2 \mathbf{u} - \nabla[\delta p - kT \sum_i \delta n_i] = - \sum_i z_i e n_i^0 \nabla\varphi_i. \quad (18)$$

Now the terms involving  $\delta p$  and  $\delta n_i$  can be eliminated by taking the curl of (18) to give

$$\eta \nabla^2 (\nabla \times \mathbf{u}) = \sum_i z_i e (\nabla\varphi_i \times (\nabla n_i^0)). \quad (19)$$

Thus (17) and (19) form a pair of equations that together determine  $\varphi_i$  and  $\mathbf{u}$ . These two functions are pivotal in the O'Brien & White solution because they are decoupled from other perturbed quantities.

The perturbed electrostatic potential,  $\delta\psi$  can be determined by the linearized version of the Poisson equation (5) in the solvent given by (15b) where the perturbed ion density,  $\delta n_i$  and hence the perturbed charged density,  $\delta\rho$  can be expressed in terms of  $\delta\psi$  and  $\varphi_i$  using (16) to give for a sphere of radius,  $a$ ,

$$r > a : \nabla^2 \delta\psi = -\frac{1}{\epsilon} \delta\rho = (e^2/\epsilon kT) \sum_i n_i^0 z_i^2 [\varphi_i + \delta\psi] \quad (20a)$$

$$r < a : \nabla^2 \delta\psi = 0. \quad (20b)$$

To first order in  $E$ , the complete electrophoresis problem is therefore determined by solving (17), (19) and (20) for the unknowns  $\varphi_i$  (17),  $\mathbf{u}$  and  $\delta\psi$  together with the following boundary conditions. More importantly, we will see that the introduction of the ion potential  $\varphi_i$  means that the electrophoretic mobility,  $U/E$  can be found by solving only (17) and (19) without the need to solve (20) for the perturbed potential,  $\delta\psi$ .

Far from the particle, we have the condition that the perturbed ion density,  $\delta n_i \rightarrow 0$  and the electrostatic potential becomes the potential that corresponds to the applied electric field,  $E$ , that is:  $\psi \rightarrow \delta\psi \rightarrow -E \cdot \mathbf{x}$ . So from (16) we have the boundary conditions:

Far from the particle,  $|\mathbf{x}| \rightarrow \infty$

$$\delta\psi(\mathbf{x}) \rightarrow -E \cdot \mathbf{x} \quad (21a)$$

$$\varphi_i(\mathbf{x}) \rightarrow E \cdot \mathbf{x} \quad (21b)$$

$$\mathbf{u}(\mathbf{x}) \rightarrow -U. \quad (21c)$$

The velocity field,  $\mathbf{u}$  in the frame of reference where the particle is stationary must be the negative of the electrokinetic velocity,  $U$  that is parallel to  $E$  in the laboratory frame.

At the solid particle surface,  $r = a$ , with outward unit normal  $\mathbf{n}$  the boundary conditions are,

$$\text{continuity of } \delta\psi(\mathbf{x}) \text{ and } \epsilon \mathbf{n} \cdot \nabla\delta\psi \quad (22a)$$

$$\nabla\varphi_i(\mathbf{x}) \cdot \mathbf{n} = 0 \quad (22b)$$

$$\mathbf{u}(\mathbf{x}) = \mathbf{0} \quad (22c)$$

since  $\delta\psi$  obeys the usual electrostatic boundary conditions, ion fluxes into the solid particle vanish and the fluid velocity relative to the solid surface is zero (the immobile hydrodynamic boundary condition).

#### 3.2. Formal solution for electrophoresis of a sphere

For a spherical solid particle with a uniform  $\zeta$  potential in a constant external electric field,  $E$ , Ohshima, Healy & White [11] derived a formal solution of the electrokinetic transport equations for a symmetric  $z : z$  electrolyte. Here we generalize their solution to an electrolyte of arbitrary composition.

In view of the boundary condition (21) on  $\varphi_i$  as  $|\mathbf{x}| \rightarrow \infty$  and by symmetry considerations, we can seek a solution of the chemical potential,  $\delta\mu_i$  or equivalently for the ion potentials,  $\varphi_i$  in the form

$$\delta\mu_i(\mathbf{x}) = -z_i e \varphi_i(\mathbf{x}) = -z_i e \phi_i(r) E \cos\theta \quad (23)$$

where the origin of the coordinate system is at the centre of the sphere, the direction of the  $z$ -axis is along  $E$  and  $\theta$  is the polar angle. The new unknown ion potential,  $\phi_i(r)$  is only a function of the radial distance,  $r$  from the centre of the sphere.

The same symmetry consideration also means that the fluid velocity,  $\mathbf{u}$  can be represented in terms of a function,  $h(r)$  that only varies with the radial coordinate,  $r$  in the form

$$\begin{aligned} \mathbf{u} &= u_r \mathbf{n}_r + u_\theta \mathbf{n}_\theta \\ &= -\frac{2}{r} h(r) E \cos\theta \mathbf{n}_r + \frac{1}{r} \frac{d}{dr} [r h(r)] E \sin\theta \mathbf{n}_\theta \end{aligned} \quad (24)$$

where  $\mathbf{n}_r$  and  $\mathbf{n}_\theta$  are unit vectors in the  $r$  and  $\theta$  directions respectively. The incompressibility condition:  $\nabla \cdot \mathbf{u} = 0$  is satisfied automatically by (24).

With the introduction of the ion potential function,  $\phi_i(r)$ , and the hydrodynamic function,  $h(r)$ , the electrokinetic transport partial differential equations for  $\varphi_i(\mathbf{x})$  (17) and  $\mathbf{u}(\mathbf{x})$  (19) become the following coupled ordinary differential equations for  $\phi_i(r)$  and  $h(r)$ :

$$\mathcal{L} [\phi_i(r)] = f_i(r) \equiv \frac{z_i e}{kT} \left( \frac{d\psi^0(r)}{dr} \right) \left( \frac{d\phi_i(r)}{dr} - \frac{2\lambda_i h(r)}{z_i e r} \right) \quad (25)$$

$$\mathcal{L} [\mathcal{L} [h(r)]] = g(r) \equiv \frac{e}{\eta r} \sum_i \frac{dn_i^0(r)}{dr} z_i \phi_i(r) \quad (26)$$

with  $\mathcal{L}$  the differential operator that follows from the identity:

$$\nabla^2 [F(r) \cos\theta] = \left[ \frac{d^2 F}{dr^2} + \frac{2}{r} \frac{dF}{dr} - \frac{2F}{r^2} \right] \cos\theta \equiv \mathcal{L} [F] \cos\theta. \quad (27)$$

The general solution of the equation

$$\mathcal{L}[F(r)] = K(r) \quad (28)$$

has homogeneous solutions:  $F(r) = r$  and  $1/r^2$  and a particular integral,

$$F(r) = -\frac{1}{3} \int_r^\infty \left( r - \frac{x^3}{r^2} \right) K(x) dx. \quad (29)$$

Notice that the differential equation for the ion potential,  $\phi_i(r)$  (25), has the gradient of the equilibrium potential,  $d\psi^0/dr$ , and the hydrodynamic function,  $h(r)$  as the inhomogeneous term on the right hand side. Whereas, the differential equation for the hydrodynamic function,  $h(r)$  (26), has the ion potential,  $\phi_i(r)$ , and the gradient of the equilibrium ion density,  $dn_i^0/dr$  (that from (10) is proportional to  $d\psi^0/dr$ ) as the inhomogeneous term on the right hand side. The origin of this term is the body force,  $(-\rho\nabla\psi)$ , in (7).

The differential equations for  $\phi_i(r)$  (25) and  $h(r)$  (26) can be integrated, using for example the Green's functions of the operators  $\mathcal{L}$  and  $\mathcal{L}^{-1}$ , to give the following formal solutions that are coupled integral equations because the functions  $f_i(r)$  and  $g(r)$  are themselves defined in terms of  $\phi_i(r)$  and  $h(r)$  in (25) and (26):

$$\begin{aligned} \phi_i(r) = & \frac{3a}{2} \left( 1 - \frac{1}{3} \int_a^\infty f_i(x) dx \right) \\ & + \frac{1}{2r^2} (2r+a)(r-a)^2 \left( 1 - \frac{1}{3} \int_a^\infty f_i(x) dx \right) \\ & + \frac{1}{3} \int_a^r \left[ r - \frac{x^3}{r^2} \right] f_i(x) dx \end{aligned} \quad (30)$$

$$\begin{aligned} h(r) = & -\frac{1}{30} \int_r^\infty (r^3 + 5x^3) g(x) dx \\ & + \frac{r}{18a} \left[ \int_a^\infty (a^3 + 2x^3) g(x) dx - \int_a^r 3ax^2 g(x) dx \right] \\ & + \frac{1}{90r^2} \left[ \int_a^\infty (5x^3a^2 - 2a^5) g(x) dx - \int_a^r 3x^5 g(x) dx \right]. \end{aligned} \quad (31)$$

These solutions are generalizations of the results of Ohshima, Healy & White [11] to a uniformly charged spherical solid particle without restrictions on the magnitude of ratio of the sphere radius to the double layer length,  $1/\kappa a$ , the  $\zeta$ -potential of the particle and the electrolyte composition. The presence of the terms  $d\psi^0/dr$  or  $dn_i^0/dr$  in  $f_i(r)$  and  $g(r)$  means that these functions decay exponentially with the Debye length,  $1/\kappa$  and become vanishingly small outside the electrical double layer around the particle,  $\kappa(r-a) \gg 1$ , thus ensuring the convergence of all integrals.

For the electrophoresis problem, we see from (21) and (22) that the boundary conditions on the functions  $\phi_i(r)$  and  $h(r)$  are

$$\frac{d\phi_i}{dr} = 0, \quad r = a \quad (32a)$$

$$\phi_i \rightarrow r, \quad r \rightarrow \infty \quad (32b)$$

$$h = 0 = \frac{dh}{dr}, \quad r = a \quad (32c)$$

$$h \rightarrow \frac{U}{2E} r \quad r \rightarrow \infty. \quad (32d)$$

The uniform velocity boundary condition at infinity (21c) is reflected in (32d) for  $h$  (see also Section 7).

The electrophoretic mobility,  $U/E$ , can be obtained from the boundary condition on  $h(r)$  as  $r \rightarrow \infty$  (32d) where the coefficient proportional to  $r$  in this limit can be obtained from (31) as

$$\mu_m \equiv \frac{U}{E} = 2 \lim_{r \rightarrow \infty} \frac{h(r)}{r} = \frac{1}{9a} \int_a^\infty (a^3 + 2x^3 - 3ax^2) g(x) dx \quad (33)$$

whereby only knowledge of the functions  $\phi_i(r)$  is required, see (26) for the relation between  $g$  and  $\phi_i$ . Hence, in the O'Brien & White [6] analysis, the mobility can be found *without* having to solve for the perturbed electrostatic potential,  $\delta\psi$ , or the perturbed ion density,  $\delta n_i$ . Since the mobility  $\mu_m = U/E$  was their primary interest, they did not explore the details of the rather unusual features of the velocity field,  $\mathbf{u}$  or the pressure.

It is easy to verify that the ion potential functions,  $\phi_i(r)$  given in (30) satisfy the required boundary condition at  $r = a$  in (32). In the limit  $r \rightarrow \infty$ ,  $\phi_i(r)$  becomes a sum of terms proportional to  $r$ . In the same large  $r$  limit, the hydrodynamic function  $h(r)$  given by (31) becomes the sum of a constant and terms proportional to  $r$  and  $1/r^2$ . As we will demonstrate below, this large  $r$  form of the hydrodynamic function  $h(r)$  has the physical implication that the velocity field outside the double layer is an unusual zero pressure Stokes flow. But before we do so, let us recall some classical results relating to the velocity and pressure field around a sphere placed in a uniform flow field at infinity.

### 3.3. Hydrodynamics of a sphere in uniform flow field

Before considering details of the pressure and velocity field in the electrophoresis problem, it is instructive to recall results of the hydrodynamic problem of Stokes flow past a sphere of radius,  $a$ , in an imposed uniform velocity field  $-U\mathbf{k}$ . For this simpler problem, the velocity,  $\mathbf{u}^S$ , has the form, similar to (24)

$$\begin{aligned} \mathbf{u}^S = & u_r^S \mathbf{n}_r + u_\theta^S \mathbf{n}_\theta \\ = & -\frac{2}{r} h^S(r) \cos \theta \mathbf{n}_r + \frac{1}{r} \frac{d}{dr} [r h^S(r)] \sin \theta \mathbf{n}_\theta \end{aligned} \quad (34)$$

with

$$h^S(r) = \frac{U}{2} \left( r + b_1 + \frac{b_2}{r^2} \right) \quad (35)$$

being the homogeneous solution of (26) with the boundary condition  $\mathbf{u}^S \rightarrow -U\mathbf{k}$  as  $r \rightarrow \infty$ . The corresponding solution for the pressure is seen to be proportional to the constant  $b_1$

$$p^S = -\frac{\eta U b_1}{r^2} \cos \theta \quad (36)$$

and the tangential stress on the sphere at  $r = a$  is proportional to the coefficient  $b_2$ :

$$\tau^S \equiv \eta \left( \frac{1}{r} \frac{\partial u_r^S}{\partial \theta} + \frac{\partial u_\theta^S}{\partial r} - \frac{u_\theta^S}{r} \right) = \frac{3\eta U b_2 \sin \theta}{a^4}. \quad (37)$$

The coefficients  $b_1$  and  $b_2$  are determined by the boundary condition at the sphere surface at  $r = a$  where the radial velocity,  $u_r^S = 0$ , because the particle is impenetrable. However, there are three cases for the boundary condition on the tangential velocity,  $u_\theta$  that are of special interest.

**3.3.1. Zero tangential velocity:**  $u_r^S = 0$ ,  $u_\theta^S = 0$  at  $r = a$

This is the boundary condition that corresponds to the Stokes problem of a solid sphere with the immobile surface velocity condition, the ‘classical’ Stokes flow [13, 14]. This gives for  $r \geq a$ ,

$$h^S(r) = \frac{U}{2} \left( r - \frac{3a}{2} + \frac{a^3}{2r^2} \right) \quad (38)$$

$$p^S(r, \theta) = \frac{3\eta a U}{2r^2} \cos \theta \quad (39)$$

$$\mathbf{u}^S = -U \cos \theta \left( 1 - \frac{3a}{2r} + \frac{a^3}{2r^3} \right) \mathbf{n}_r + U \sin \theta \left( 1 - \frac{3a}{4r} - \frac{a^3}{4r^3} \right) \mathbf{n}_\theta \quad (40)$$

where we note that the pressure decays as  $1/r^2$  and the velocity components decay as  $1/r$  towards the uniform flow as  $r \rightarrow \infty$ .

**3.3.2. Zero tangential stress:**  $u_r^S = 0$ ,  $\tau^S = 0$  at  $r = a$

The zero tangential stress boundary condition corresponds to the familiar Hadamard-Rybczynski solution [15, 16, 17] for a spherical ‘bubble’. The solutions are for  $r \geq a$ :

$$h^S(r) = \frac{U}{2} (r - a) \quad (41)$$

$$p^S(r, \theta) = \frac{\eta a U}{r^2} \cos \theta \quad (42)$$

$$\mathbf{u}^S = -U \cos \theta \left( 1 - \frac{a}{r} \right) \mathbf{n}_r + U \sin \theta \left( 1 - \frac{a}{2r} \right) \mathbf{n}_\theta. \quad (43)$$

As with the Stokes problem, the pressure decays as  $1/r^2$  and the velocity components decay as  $1/r$  towards the uniform flow as  $r \rightarrow \infty$ .

**3.3.3. Prescribed velocity:**  $u_r^S = 0$ ,  $u_\theta^S = \frac{3}{2} U \sin \theta$  at  $r = a$

When the tangential velocity at  $r = a$  is prescribed to have the value,  $u_\theta = \frac{3}{2} U \sin \theta$ , at  $r = a$  we have the solution for  $r \geq a$ ,

$$h^S(r) = \frac{U}{2} \left( r - \frac{a^3}{r^2} \right) \quad (44)$$

$$p^S(r, \theta) = 0 \quad (45)$$

$$\mathbf{u}^S = -U \cos \theta \left( 1 - \frac{a^3}{r^3} \right) \mathbf{n}_r + U \sin \theta \left( 1 + \frac{a^3}{2r^3} \right) \mathbf{n}_\theta. \quad (46)$$

Note now that the constant  $b_1$  in  $h^S(r)$  is zero and so the pressure vanishes and the velocity decays faster as  $1/r^3$  towards the constant value at infinity than the previous two cases. From (31), we see that for  $\kappa(r - a) \gg 1$ , the hydrodynamic function,  $h(r)$ , for the electrophoresis problem becomes a sum of terms in  $r$  and  $1/r^2$ , just as in (44). Thus outside the double layer, the hydrodynamic behavior is a zero pressure Stokes flow.

## 4. The Overbeek solution for a sphere

Some 40 years before the O’Brien & White [6] treatment of the electrokinetic problem detailed in the preceding section, Overbeek analysed the same theoretical model using a very different approach in his PhD thesis. His work extended that of Henry [5] which was published 10 year prior, and included what Overbeek called the relaxation effect. In essence, Henry assumed that the ionic atmosphere around the spherical colloidal particle remains in its equilibrium spherically symmetric configuration and thus omitted the distorting effects due to the motion of the particle and the electrostatic interaction between the ionic atmosphere and the applied electric field. Overbeek provided a consistent account of this effect that is important when the  $\zeta$ -potential of the particle is high, say above 50 mV.

Overbeek analysed the first order electrokinetic equations (15), detailed in Section 2, for a  $z:z$  electrolyte, but as with Henry, worked directly to solve for the first order quantities  $\mathbf{u}$ ,  $\delta\psi$ ,  $\delta n_i$  and  $\delta p$  and did not introduce the ion potential,  $\varphi_i$  (16). As we shall demonstrate, this approach is more physically perspicuous in that it allows us to deduce rather general and unusual properties of the velocity field associated with electrokinetic motion. With this approach, it is possible to identify explicitly and separate the contributions of the hydrodynamic forces and the electrical forces, and observe how the terms cancel to give a zero net force thereby resulting in a constant electrophoretic velocity for the particle, see Appendix B for details. This analysis also provides insight into why the mobility of a dielectric sphere is independent of its permittivity or the electrostatic boundary conditions. However, the numerical implementation of this theoretical approach [18] was not uniformly accurate for all parameters of interest and the development of the O’Brien & White [6] approach resolved this issue.

Here we establish equivalence of the Overbeek and O’Brien-White solutions and in particular give explicit expressions for the velocity components and the pressure.

In addition to giving an expression for the mobility, Overbeek also obtained explicit expressions for the fluid velocity,  $\mathbf{u}$ , the pressure,  $p$ , and the perturbed electrostatic potential,  $\delta\psi$ , around a spherical particle under electrophoretic motion. His solution is written in terms of 3 functions of the radial distance,  $r$  from the centre of the sphere:  $\xi(r)$ ,  $\chi(r)$  and  $R(r)$ . The mobility is expressed in terms of the function,  $\xi(r)$  as,

$$\mu_m \equiv \frac{U}{E} = -\frac{2\epsilon}{3\eta} \int_a^\infty \xi(r) dr. \quad (47)$$

The function  $\xi(r)$  has the same role as that in Henry’s theory although the particular form differs because of the omission of the relaxation effect in the Henry treatment [5]. The velocity

components  $\mathbf{u} = u_r \mathbf{n}_r + u_\theta \mathbf{n}_\theta$  are also given in terms of  $\xi(r)$ ,

$$u_r(r) = \frac{2\epsilon E \cos \theta}{3\eta} \int_a^r \left(1 - \frac{x^3}{r^3}\right) \xi(x) dx \equiv \frac{2\epsilon \zeta E \cos \theta}{3\eta} \bar{u}_r(r) \quad (48a)$$

$$u_\theta(r) = -\frac{2\epsilon E \sin \theta}{3\eta} \int_a^r \left(1 + \frac{x^3}{2r^3}\right) \xi(x) dx \equiv \frac{2\epsilon \zeta E \sin \theta}{3\eta} \bar{u}_\theta(r) \quad (48b)$$

$$w(r) \equiv (\nabla \times \mathbf{u})_\varphi = \frac{\epsilon E}{\eta} \xi(r) \sin \theta \quad (48c)$$

where  $w(r) \equiv (\nabla \times \mathbf{u})_\varphi$  in (48c) is the only non-zero component of the vorticity and is along the azimuthal  $\varphi$ -direction and we have introduced the  $\zeta$ -potential of the particle in defining the dimensionless velocities,  $\bar{u}_r(r)$  and  $\bar{u}_\theta(r)$  in (48). The derivation of the above equations can be found in Appendix B.

The pressure,  $p$  and perturbed potential,  $\delta\psi$  are given in terms of the functions  $\chi(r)$  and  $R(r)$  as follows:

$$p = -\epsilon \int_r^\infty \nabla^2 \psi^0 \frac{d\psi^0}{dx} dx - \epsilon E \chi(r) \cos \theta \quad (49a)$$

$$\delta\psi = -E R(r) \cos \theta. \quad (49b)$$

The first term for the pressure,  $p$  in (49a) is the equilibrium contribution,  $p^0$  that follows from (11) that is expressed in terms of the equilibrium electrostatic potential  $\psi^0(r)$ .

The functions  $\chi(r)$  for the perturbed pressure,  $\delta p$  and  $R(r)$  for the perturbed potential  $\delta\psi$  are related to  $\xi(r)$  by

$$\chi(r) = \left(2\frac{R(r)}{r} + \frac{dR(r)}{dr}\right) \frac{d\psi^0(r)}{dr} - 2\xi(r) \quad (50)$$

$$\xi(r) = \frac{R(r)}{r} \frac{d\psi^0(r)}{dr} + 2r \int_r^\infty \left(\frac{1}{x^2} \frac{dR(x)}{dx} - \frac{R(x)}{x^3}\right) \frac{d\psi^0(x)}{dx} dx. \quad (51)$$

The function,  $R(r)$  can be found by solving (15b). Overbeek obtained  $R(r)$  for a symmetric  $z:z$  electrolyte using a perturbation analysis that involved cumbersome algebraic manipulations that did not provide much general insight. Nonetheless, we can make the formally exact connection between the Overbeek solution and the solution of Ohshima *et al.* [11] by equating the expressions for  $u_r$  in (24) and (48a) to give

$$h(r) = -\frac{\epsilon}{3\eta} \int_a^r \left(r - \frac{x^3}{r^2}\right) \xi(x) dx \quad (52)$$

which can be used to establish, by direct substitution, the following relation between  $\xi(r)$  of Overbeek and the hydrodynamic function  $h(r)$  of Ohshima *et al.*, see also (28) and (29)

$$\xi(r) = -\frac{\eta}{\epsilon} \left[ \frac{d^2 h}{dr^2} + \frac{2}{r} \frac{dh}{dr} - 2\frac{h}{r^2} \right] \equiv -\frac{\eta}{\epsilon} \mathcal{L}[h]. \quad (53)$$

Using (31),  $\xi(r)$  can also be expressed in terms of  $g(r)$  which is defined in terms of the ion potentials,  $\phi_i(r)$ , according to (26)

$$\xi(r) = \frac{\eta}{3\epsilon} \int_r^\infty \left(r - \frac{x^3}{r^2}\right) g(x) dx \quad (54a)$$

$$= \frac{e}{3\epsilon r} \int_r^\infty \left(r - \frac{x^3}{r^2}\right) \sum_i \frac{dn_i^0(x)}{dx} z_i \phi_i(x) dx. \quad (54b)$$

This is a key relation that connects the function,  $\xi(r)$  in the Overbeek theory [4] to the ion potentials,  $\phi_i(r)$  in the O'Brien & White [6] solution.

Using (26) and (27), the inverse relationship of (54a) can be found

$$\mathcal{L} \xi(r) = -\frac{\eta}{\epsilon} \mathcal{L} [\mathcal{L}[h]] = -\frac{\eta}{\epsilon} g. \quad (55)$$

These results are important because using (54a), the Overbeek expression for electrophoretic mobility in (47) can be converted to the expression for the mobility derived by Ohshima *et al.* in (33) and thus demonstrate the equivalence of the two solutions. Furthermore, from the expression for  $\xi(r)$  in terms of the derivative of the equilibrium ion number density,  $dn_i^0/dx$  in (54b) we expect that  $\xi(r)$  decays exponentially with the Debye length,  $1/\kappa$  as  $r \rightarrow \infty$ . As we shall see in the next Section, this leads to the existence of a maximum in the tangential component of the velocity near the surface of the particle.

By employing the ion potential,  $\phi_i(r)$  of O'Brien & White, we can obtain, using (20) and (27), the equation for the function,  $R(r)$ , that determines the radial variation of the perturbed potential,  $\delta\psi$ , see (49b), for an electrolyte of general composition,

$$r > a : \mathcal{L}[R(r)] = \frac{e^2}{\epsilon kT} \sum_i n_i^0(r) z_i^2 [R(r) - \phi_i(r)] \equiv K(r) \quad (56a)$$

$$r < a : \mathcal{L}[R(r)] = 0. \quad (56b)$$

We note that the right hand side of (56a) is proportional to the perturbed charge density,  $\delta\rho$ , see (20). Using the properties of the  $\mathcal{L}$  operator in (28) and (29), the formal solution of (56) is

$$R(r) = r + \frac{B}{r^2} - \frac{1}{3} \int_r^\infty \left(r - \frac{x^3}{r^2}\right) K(x) dx, \quad r > a, \quad (57a)$$

$$= Ar, \quad r < a. \quad (57b)$$

This solution satisfies the condition  $R(r) \rightarrow r$  as  $r \rightarrow \infty$  and the requirement that  $R$  is finite at the center of the sphere,  $r = 0$ . Imposing the continuity of  $R$  and  $\epsilon(dR/dr)$  at the sphere surface,  $r = a$ , gives the constant,  $B$

$$B = \left(\frac{\epsilon - \epsilon_p}{2\epsilon + \epsilon_p}\right) a^3 + \left(\frac{\epsilon I_2 - \epsilon_p I_1}{2\epsilon + \epsilon_p}\right) a^3 \quad (58)$$

where

$$I_1 \equiv -\frac{1}{3} \int_a^\infty \left(1 - \frac{x^3}{a^3}\right) K(x) dx, \quad (59a)$$

$$I_2 \equiv -\frac{1}{3} \int_a^\infty \left(1 + \frac{2x^3}{a^3}\right) K(x) dx. \quad (59b)$$

The above results establish the equivalence of the solutions of the electrokinetic equations for a spherical particle developed by Overbeek, O'Brien & White and Ohshima *et al.* Now we can use Overbeek's solution to deduce properties of the unusual velocity and pressure field associated with the electrophoretic motion without solving the equations explicitly.

## 5. General properties of the pressure and velocity fields

Having established the equivalence between the Overbeek [4] and the O'Brien & White [6] theories, we can deduce some unusual properties of the pressure and velocity field around a spherical particle undergoing electrophoretic motion. As far as we can ascertain, these properties have not been explored in depth and this may be because the focus has been on obtaining expressions for the electrophoretic mobility.

### 5.1. The pressure field around a sphere

In most theoretical treatments, the pressure field was eliminated early in the analysis by taking the curl of the linear order form of the Stokes equation (18) to obtain (19).

From the solution of the pressure field,  $p$ , in the Overbeek solution (49a), it is possible to deduce general properties of the pressure without knowing the explicit form of  $\chi(r)$  given by (50) that is given in terms of the equilibrium potential,  $\psi^0(r)$ ,  $R(r)$  and the function,  $\xi(r)$ . The first term on the right hand side of (49a) for the pressure,  $p$  is simply the equilibrium contribution,  $p^0$  that is present even if there was no applied electric field, as shown in (11). From the relation between the function  $\xi(r)$  in the Overbeek solution to the Ohshima *et al.* [11] given in (54), we deduce that the magnitude of  $\xi(r)$  is exponentially small outside the electrical double layer because it is proportional to the derivative of the ion number density,  $dn_i^0/dx$ . Thus from (50), we see that  $\chi(r)$  is also exponentially small outside the double layer which implies that the pressure outside the double layer is zero.

Therefore outside the double layer, the hydrodynamic behavior is described by a zero pressure Stokes flow.

### 5.2. The velocity field around a sphere

We can also deduce general properties of the velocity field from the general solution given by Overbeek. Since the function  $\xi(r)$  is exponentially small outside the electrical double layer we conclude from (48c) that the vorticity,  $w(r)$  is zero outside the double layer and the flow field outside the double layer is irrotational:  $\nabla \times \mathbf{u} = \mathbf{0}$ .

The form of the velocity field,  $\mathbf{u}$ , outside the double layer and the manner it approaches the electrophoretic velocity,  $U$  in (47) can be deduced from (47), (48a) and (48b) where the expressions for the velocity components and the pressure and vorticity become, in the limit  $\kappa(r-a) \gg 1$

$$u_r \sim -U \cos \theta - \left( \frac{2\epsilon E \cos \theta}{3\eta} \int_a^\infty x^3 \xi(x) dx \right) \frac{1}{r^3} \quad (60a)$$

$$u_\theta \sim U \sin \theta - \frac{1}{2} \left( \frac{2\epsilon E \sin \theta}{3\eta} \int_a^\infty x^3 \xi(x) dx \right) \frac{1}{r^3} \quad (60b)$$

$$p \sim 0 \quad (60c)$$

$$w \sim 0. \quad (60d)$$

These equations show that the velocity decays as  $1/r^3$  outside the double layer toward the uniform flow at infinity and has the same behavior as the case of Stokes flow with a specially prescribed tangential velocity boundary condition discussed earlier

in Section 3.3.3. This asymptotic behavior has been pointed out in the literature [8] without extensive investigation. This is in stark contrast to the velocity decay in a classical Stokes sphere with the familiar immobile, no-slip boundary condition where the velocity decays as  $1/r$  given in Section 3.3.1.

The flow field in the limit of  $\kappa a \rightarrow \infty$  can also be calculated analytically, since

$$\lim_{\kappa a \rightarrow \infty} \int_a^\infty x^3 \xi(x) dx \rightarrow a^3 \int_a^\infty \xi(x) dx = -a^3 \frac{3\eta}{2\epsilon} \frac{U}{E} \quad (61)$$

where the expression (47) for the mobility  $U/E$  is used to establish the last equality. Using this result in the Overbeek solution for the velocity components (48) then gives the large  $\kappa a$  or thin double layer limiting forms for the velocity:

$$\lim_{\kappa a \rightarrow \infty} u_r(r) \rightarrow -U \cos \theta + \frac{a^3}{r^3} U \cos \theta \quad (62a)$$

$$\lim_{\kappa a \rightarrow \infty} u_\theta(r) \rightarrow U \sin \theta + \frac{a^3}{2r^3} U \sin \theta. \quad (62b)$$

These limiting results have the same form as the zero pressure Stokes flow result around a sphere with a certain prescribed tangential velocity given in Section 3.3.3. This observation provides the motivation for modeling electrophoresis in the thin double layer limit [12, 19].

Although the velocity field in (62) appears to be identical to the results obtained for a potential flow model, this is coincidental because the physics of the two models are very different. The potential flow model is valid in the limit where viscosity effects may be neglected whereas viscosity effects dominate the hydrodynamics in the electrophoresis problem in the low Reynolds number regime. In zero viscosity potential flow, the pressure is non-zero but the net force on a sphere in a uniform flow field is zero because the contribution to the stress tensor due to the pressure on the up-stream half of the sphere is exactly balanced by the pressure acting on the down-stream half of the sphere that gives rise to the well-known d'Alembert Paradox. On the other hand, in the zero pressure Stokes flow that pertains in the electrophoresis problem, the pressure is zero. Therefore, the suggestion [7] that the Bernoulli equation can be used to conclude that the pressure varies as the square of the velocity and hence decays as  $1/r^6$  is not consistent with the governing equations that describe the electrokinetic phenomenon.

From the general solution of the velocity field given by Overbeek, we can demonstrate that the radial velocity,  $u_r(r)$  (48a) changes monotonically from the surface of the sphere towards infinity, but the magnitude of the tangential velocity,  $u_\theta(r)$  (48b) exhibits a maximum near the double layer. We begin by taking the derivative of the velocity components in (48) to obtain,

$$\frac{du_r(r)}{dr} = \frac{\epsilon E \cos \theta}{\eta} \left[ \frac{2}{r^4} \int_a^r x^3 \xi(x) dx \right] \quad (63a)$$

$$\frac{du_\theta(r)}{dr} = -\frac{\epsilon E \sin \theta}{\eta} \left[ \xi(r) - \frac{1}{r^4} \int_a^r x^3 \xi(x) dx \right]. \quad (63b)$$

As we shall see the magnitude of  $\xi(r)$  decreases monotonically from the surface value  $|\xi(a)|$  to zero as  $r \rightarrow \infty$ . Thus the



derivative of the radial component of the velocity in (63a) does not change sign.

On the other hand, we know that  $\xi(r)$  decays from  $|\xi(a)|$  at  $r = a$  to zero exponentially fast outside the double layer whereas the integral in (63b) is zero at  $r = a$  and decays as  $1/r^4$  as  $r \rightarrow \infty$ . Therefore, the derivative of the tangential velocity  $du_\theta(r)/dr$  must change sign, that is, the tangential velocity,  $u_\theta$  must have a maximum in its magnitude at some position between  $r = a$  and  $r = \infty$ . This behavior is qualitatively different from familiar cases of Stokes flow results given in Section 3.3 in which the velocity profiles are all monotonic and decay much slower as  $1/r$  far from the sphere.

Before we offer numerical examples of these observations, we digress to revisit the textbook derivation of the Smoluchowski results for the mobility in the limit  $\kappa a \rightarrow \infty$  to show an important qualitative difference in the form of the velocity field in the limit  $\kappa a \gg 1$  and the velocity field near a flat surface.

### 5.3. Planar derivation of the Smoluchowski result

In this section we show that the textbook derivation of the Smoluchowski results, valid in the  $\kappa a \rightarrow \infty$ , predicts a qualitatively different form for the velocity profile to that near a sphere when  $\kappa a \gg 1$ .

The planar derivation of the Smoluchowski result assumes the particle is a flat plate at  $x = 0$  with the electrical double layer occupying the half-space,  $x > 0$ . The applied electric field is in the  $z$ -direction:  $\mathbf{E} = E\mathbf{k}$ . In the frame of reference in which the electrolyte is quiescent at  $x \rightarrow \infty$  and the flat plate moves with the electrophoretic velocity,  $U\mathbf{k}$ , the velocity field only has a non-zero  $z$ -component:  $\mathbf{u} = u_z(x)\mathbf{k}$  and by symmetry considerations, all physical quantities only vary with  $x$ .

The  $z$ -component of the Stokes equation (7) then has the form

$$\eta \frac{d^2 u_z(x)}{dx^2} = \rho(x) \frac{d\psi}{dz} = -E \rho(x) \quad (64)$$

since the  $z$ -component of the gradient of the potential is just the negative of the applied field,  $E$ . The double layer charge density,  $\rho(x)$  is related by the Poisson equation

$$\frac{d^2 \psi_s(x)}{dx^2} = -\frac{\rho(x)}{\epsilon} \quad (65)$$

to the potential  $\psi_s(x)$  due to the charged planar surface with surface potential  $\zeta = \psi_s(0)$ .

By combining (64) and (65) we have

$$\eta \frac{d^2 u_z(x)}{dx^2} = \epsilon E \frac{d^2 \psi_s(x)}{dx^2} \quad (66)$$

and a first integral gives

$$\eta \frac{du_z(x)}{dx} = \epsilon E \frac{d\psi_s(x)}{dx} \quad (67)$$

since both  $(du_z(x)/dx)$  and  $(d\psi_s(x)/dx)$  vanish in the limit  $x \rightarrow 0$ . A second integration with the boundary condition  $u_z(0) = U$  and  $\psi_s(0) = \zeta$  gives the Smoluchowski result for the mobility

$$\mu_m \equiv \frac{U}{E} = \frac{\epsilon E}{\eta} \quad (\text{Smoluchowski}). \quad (68)$$

that is applicable in the limit  $\kappa a \rightarrow \infty$ .

An important implication of this derivation is that in the large  $\kappa a$  limit, the electrical double layer is assumed to be unperturbed by the applied field,  $E$  so that we may take  $\psi_s(x)$  at the equilibrium potential,  $\psi^0(x)$ . And from (67) we conclude that the velocity profile decays monotonically from  $u_z(0) = U$  at the surface to zero as  $x \rightarrow \infty$ , in contradiction to the conclusion we deduced in Section 5.2 that the component of the velocity tangential to the surface has a maximum in its magnitude.

This apparent contradiction arises from that fact that taking a planar geometry at the start of this analysis is not consistent with the physically correct model of a thin double layer around a particle of finite curvature. The important effect of particle curvature is lost if one starts with a planar surface.

## 6. Visualisation using the Henry approximation

The omission of the relaxation effect limits the validity of the Henry approximation to the regime of low surface potentials. Nonetheless, the variations of the mobility with respect to the particle radius scaled by the Debye length,  $\kappa a$ , is predicted correctly and thus it can still provide useful and accessible physical insight into many aspects of the electrophoresis problem. We therefore use the Henry model to visualise features of the pressure and velocity field around a spherical particle in electrophoresis.

### 6.1. The Henry Approximation

Henry's solution [5] of the electrophoresis of a spherical particle can now be exhibited as a simplified version of the general Overbeek solution. Starting with (56) for the radial function,  $R(r)$  of the perturbed potential,  $\delta\psi$ , given by (49b), the Henry approximation (denoted by the superscript  $H$ ) is to assume [11],

$$R^H(r) = \phi_i^H(r). \quad (69)$$

From the derivation of (56), this approximation is tantamount to assuming that the charge density around the particle is unaffected by the applied electric field,  $\mathbf{E}$ , that is,  $\delta\rho = 0$ . Thus (56) simplifies to,

$$\mathcal{L}[R^H(r)] = 0. \quad (70)$$

The solution that satisfies the boundary conditions (32a) and (32b), together with the Overbeek expressions (50) for  $\chi(r)$  and (54) for  $\xi(r)$  are, if we assume the permittivity of the solvent is much larger than that of the particle,  $\epsilon \gg \epsilon_p$

$$R^H(r) = r + \frac{a^3}{2r^2} = \phi_i^H(r) \quad (71a)$$

$$\xi^H(r) = \left(1 + \frac{a^3}{2r^3}\right) \frac{d\psi^0(r)}{dr} - 3a^3 r \int_r^\infty \frac{1}{x^5} \frac{d\psi^0(x)}{dx} dx \quad (71b)$$

$$\chi^H(r) = 3 \frac{d\psi^0(r)}{dr} - 2 \xi^H(r) \quad (71c)$$

and are identical to results derived by Henry [5]<sup>1</sup> and Ohshima *et al.* [11]. The functions  $\xi(r)$  and  $\chi(r)$  determine the behavior of the velocity, vorticity and pressure according to (48) and from (71), we can see that they decay with the range of the electrostatic potential,  $\psi^0(r)$  that vanishes exponentially with distance from the sphere surface with the characteristic Debye length,  $1/\kappa$ . Finally, we note that the results in (71) are independent of the theory used to calculate the equilibrium potential,  $\psi^0(r)$ .

We exploit the analytical nature of the Henry solution to elucidate the general features of the velocity and pressure fields around a spherical particle during electrophoresis and to study the form of the functions  $\xi(r)$  and  $\chi(r)$ . Since Henry's theory is valid for particles with low surface potentials, we will use the Debye-Hückel expression for the equilibrium potential:

$$\psi_{DH}^0(r) = \zeta a \frac{e^{-\kappa(x-a)}}{r}. \quad (72)$$

Combining (71) and (72), we find

$$\xi^{HDH}(r) = \frac{\zeta \kappa^2}{3} \int_r^\infty \left( r - \frac{x^3}{r^2} \right) \left( \frac{a}{x^2} + \frac{\kappa a}{x} \right) \left( 1 + \frac{a^3}{2x^3} \right) e^{-\kappa(x-a)} dx \quad (73a)$$

$$\chi^{HDH}(r) = -\frac{3\zeta a}{r^2} (1 + \kappa r) e^{-\kappa(x-a)} - 2 \xi^{HDH}(r). \quad (73b)$$

The superscripts 'HDH' denote Henry's results using the Debye-Hückel expression for the equilibrium potential,  $\psi^0(r)$ . The velocity and pressure fields can then be obtained from (48). The double integrals that arise in the expressions for the velocity components can be evaluated numerically.

## 6.2. Numerical results

In Fig. 1, we can see that the dimensionless functions:  $\chi^{HDH}(r)a/\zeta$  and  $\xi^{HDH}(r)a/\zeta$  in the Overbeek solution calculated using the Henry-Debye-Hückel approximation, decay exponentially with the Debye length,  $1/\kappa$  outside the double layer for  $\kappa a$  between 1 and 100. These results provide graphical validation of the arguments used to prove the existence of a maximum in the magnitude of the tangential velocity. The short-ranged nature of the pressure field that vanishes outside the extent of the double layer is reflected by the function  $\chi(r)$ , see (49a), and that the similar short-ranged nature of  $\xi(r)$  show that outside the double layer, the vorticity vanishes and the velocity field becomes irrotational, see (48c).

In Fig. 2, the velocity profiles in the dorsal plane around a sphere at  $\kappa a = 10$  and  $\kappa a = 100$  under electrophoretic motion are shown in the reference frame in which the sphere is stationary so the fluid velocity is zero on the surface. In the upper half of the figures, the variation of the tangential velocity,  $u_\theta(r)$ , is shown as functions of the radial distance from the sphere surface at different angular positions. The tangential velocity at the

<sup>1</sup>Unfortunately, the key results given on p. 114 of Henry's paper numerous typographical errors so the expressions for  $\xi^H(r)$ ,  $\chi^H(r)$  and  $R^H(r)$  given here should be used in the general expressions due to Overbeek to obtain results for the Henry model.

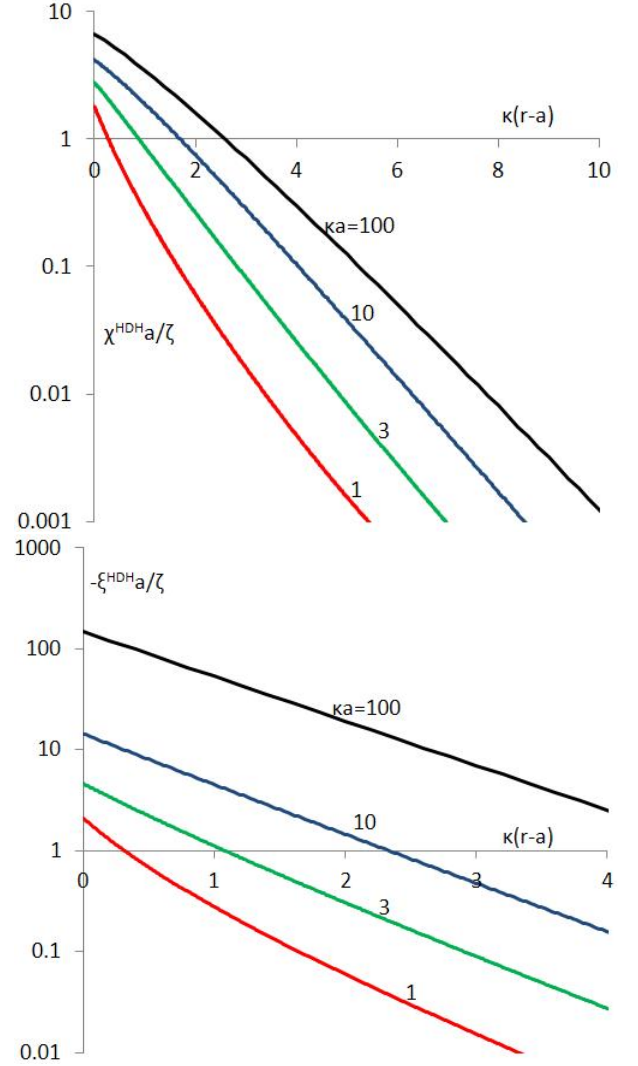


Figure 1: Variations of the functions  $\chi^{HDH}(r)a/\zeta$  and  $-\xi^{HDH}(r)a/\zeta$  in the Overbeek solution calculated using the Henry-Debye-Hückel approximation in (73) with  $\kappa(r-a)$ , for  $\kappa a$  between 1 and 100. The near exponential decaying behavior of these functions is clear on the log-linear scale.

sphere surface is zero but attains a maximum at a short distance from the surface. This maximum is larger than the uniform velocity at infinity. In the lower half of the figures, a snap shot of the velocity field around the particle is displayed and it can be seen that at  $r \sim 2a$ , the velocity has almost reached its constant uniform flow value, reflecting the faster  $1/r^3$  decay of the velocity field towards the value at infinity.

By way of contrast, the velocity field that corresponds to a classical Stokes problem of a sphere with the immobile boundary condition of zero velocity on the surface in a uniform flow field at infinity is given in Fig. 3. Here the much slower  $1/r$  decay of the velocity field towards the uniform flow at infinity is evident and the tangential velocity profile varies monotonically without a maximum.

In Fig. 4, we show the scaled normal,  $\bar{u}_r(r)$  and tangential,  $\bar{u}_\theta(r)$ , velocity components defined by (48) as functions of  $(r-a)/a$  for a sphere undergoing electrophoretic motion for

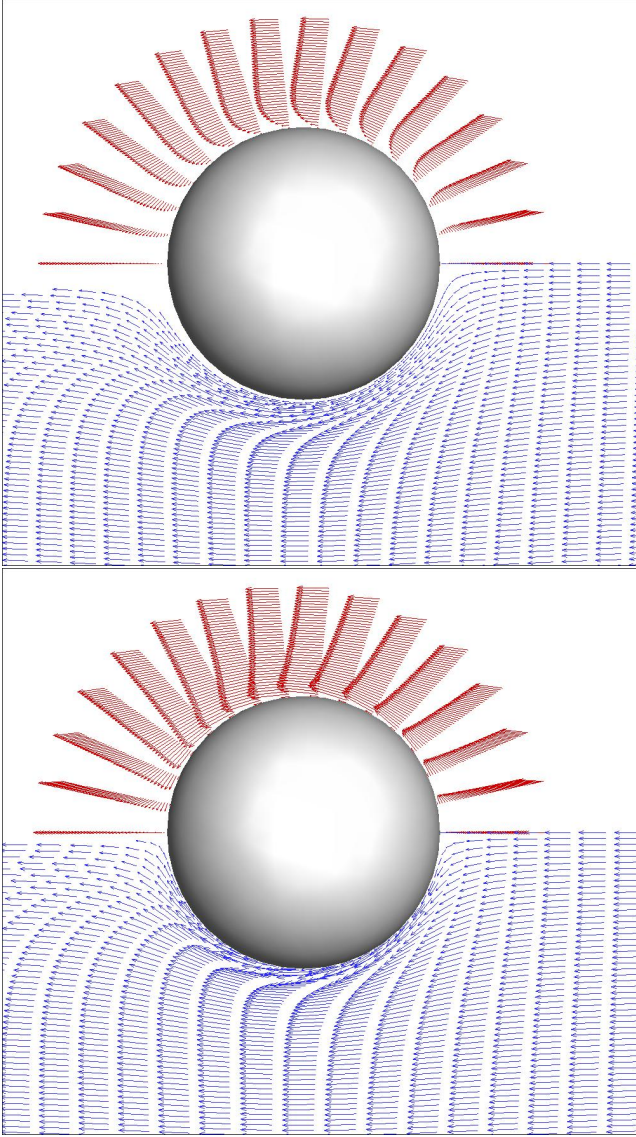


Figure 2: The velocity field around a sphere with  $\kappa a = 10$  (upper) and  $\kappa a = 100$  (lower). On the top half of each figure the instantaneous velocity is shown along radial lines where the velocity maximum is most prominent near the top of the sphere. In the lower half of each figure, a snap shot of the velocity field is given at regular intervals in time (starting from the right). The rapid  $1/r^3$  decay towards the uniform flow is evident as the velocity is close to the uniform value when  $r \sim 2a$ .

$\kappa a$  between 1 and 100. The maximum in the tangential velocity,  $\bar{u}_\theta(r)$  near the sphere is clearly evident before it approaches the constant value at infinity. In contrast, the radial velocity varies monotonically as it approaches the constant value at infinity. The variation of the position of the maximum,  $r_{max}$  and the magnitude of in the scaled tangential velocity maximum,  $\bar{u}_{\theta,max}$  with  $\kappa a$  is given in Fig. 5. The position of the maximum can be fitted to the empirical equation,

$$\left[ \frac{r_{max} - a}{a} \right] \approx \frac{1.8}{(\kappa a)^{0.79}}. \quad (74)$$

The magnitude of the scaled tangential velocity maximum asymptotes to about 2.25 as  $\kappa a \rightarrow \infty$  in comparison to the value

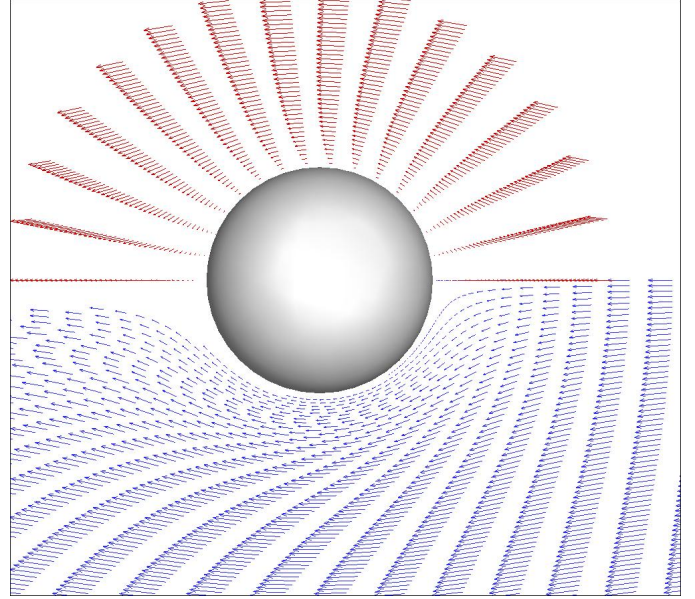


Figure 3: The classical Stokes flow field around a sphere that corresponds to the results in Section 3.3.1. The flow decays as  $1/r$  towards a uniform flow field. This is in sharp contrast to the flow field around an electrophoretically driven sphere, where the velocity decays as  $1/r^3$ , see Figs. 2 and 4. Also observe that there is no maximum velocity near the sphere as was observed in Fig. 2.

of 1.5 at  $r \rightarrow \infty$ .

As will be explained in the next section, the above general characteristics of the velocity field outside the double layer are consequences of the balance between the electrical driving force and the retarding hydrodynamic force that gives rise to a net zero force on the particle and therefore a constant electrophoretic velocity at constant applied electric fields.

## 7. The force balance and its consequences

A particle under steady electrophoretic motion has constant velocity because the electrostatic driving force due to the applied electric field on the particle and electrical double layer is exactly balanced by the hydrodynamic drag forces on the particle and ions. The net force of zero on the particle/double layer is an essential ingredient in understanding the nature of the flow outside the particle.

Both Overbeek and Henry stated that the proof of the force balance is tedious but straightforward. O'Brien and White used the reciprocity theorem by considering an integral of the total stress over a large surface that encloses the particle. Ohshima *et al.* simply noted that the force balance condition is equivalent to the absence of a constant term in the hydrodynamic  $h$ -function. Here, we provide a detailed derivation of the force balance condition and discuss the physical consequences and implications.

Outside the double layer, the right hand side of the differential equation (26) for the hydrodynamic function  $h(r)$  is zero and this equation becomes

$$\mathcal{L} [\mathcal{L} h(r)] = \frac{d}{dr} \left[ \frac{1}{r^4} \frac{d}{dr} \left( r^4 \frac{d^2 h}{dr^2} \right) \right] = 0. \quad (75)$$



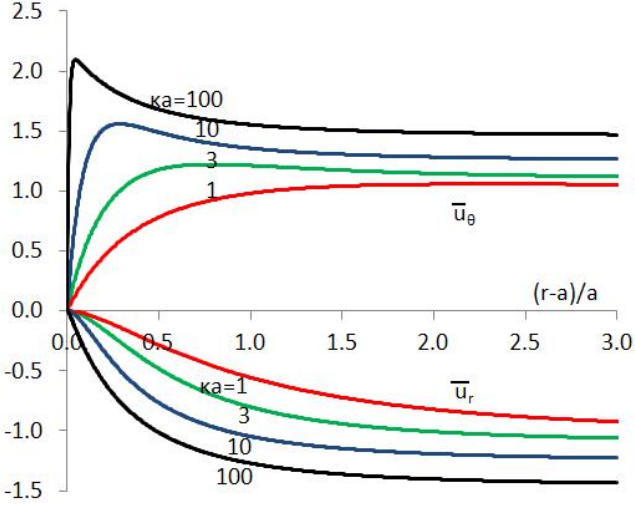


Figure 4: The scaled normal,  $\bar{u}_r(r)$  and tangential,  $\bar{u}_\theta(r)$  velocity components defined by (48) around a sphere as functions of  $(r-a)/a$  undergoing electrophoretic motion for  $\kappa a$  between 1 and 100. Note the maximum in the tangential velocity,  $\bar{u}_\theta(r)$ .

This has the general solution:  $h = c_1 r^3 + c_2/r^2 + c_3 r + c_4$ . The force can be obtained by integrating the stress tensor on a virtual sphere much larger than  $r = a + 1/\kappa$  so that it lies entirely outside the double layer. The constant  $c_1$  must be zero, because the flow field should remain finite when  $r$  tends towards infinity. The constant  $c_3 = U/(2E)$  ensures that the velocity at infinity is uniform with value  $U$ . In Appendix D, it is shown that  $c_2$  does not contribute to the force and the force depends solely on the constant  $c_4$ . If the particle experiences zero force,  $c_4$  must be zero as noted by previous workers [4, 5, 11]. In ‘classical’ Stokes flow, this can only happen for a special boundary condition, see Section 3.3.

A key physical phenomenon in electrophoretic motion of a sphere is that certain terms in the electrical and hydrodynamical forces cancel out exactly. In Overbeek’s theory, as derived in Appendix B, the total force on the sphere can be decomposed into a sum of 4 terms made up of two electrical contributions,  $F_{E1}$  and  $F_{E2}$  and two hydrodynamic contributions,  $F_{H1}$  and  $F_{H2}$  as follows:

$$F_{E1} = QE \quad (76a)$$

$$F_{E2} = -QE + \frac{QE}{3} \left( \frac{dR}{dr} + \frac{2R}{a} \right)_{r=a} \quad (76b)$$

$$F_{H1} = -6\pi\eta a U \quad (76c)$$

$$F_{H2} = -\frac{QE}{3} \left( \frac{dR}{dr} + \frac{2R}{a} \right)_{r=a} + 4\pi\epsilon E a \int_{\infty}^a \xi dx. \quad (76d)$$

Here,  $F_{E1}$ , is the force experienced by a sphere of charge  $Q$  under the influence of electric field  $E$ . The perturbed charge distribution,  $\delta\rho(r, \theta)$ , creates an additional electrostatic ‘relaxation’ force,  $F_{E2}$ , by virtue of the asymmetric charge distribution that is a function of not only the distance from the sphere center but also the polar angle,  $\theta$ . In the Henry model with  $R = R^H$ , see (71), the relaxation force,  $F_{E2}$ , vanishes identically due to the assumption that the double layer around the sphere maintains

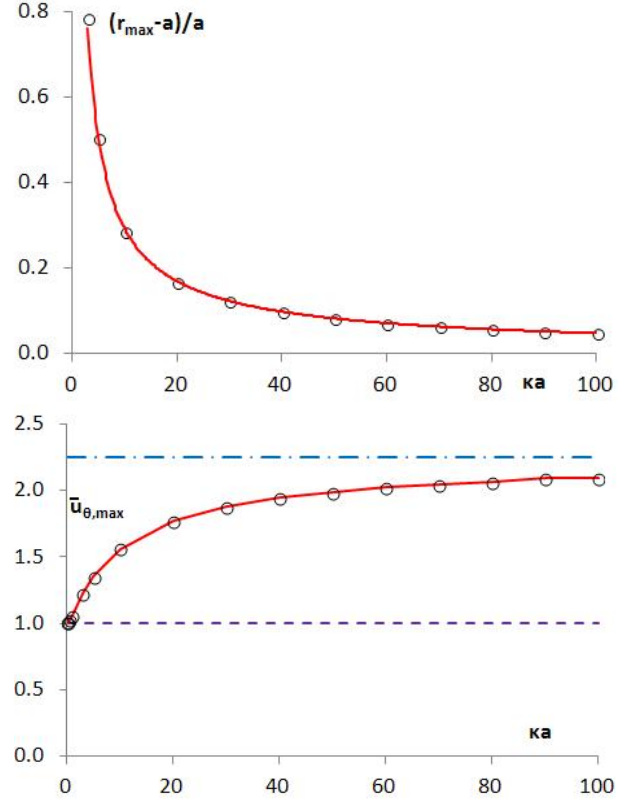


Figure 5: (Upper) Variation of the position of the maximum of the tangential velocity,  $(r_{max}-a)/a$  with scaled sphere radius,  $\kappa a$ . The line is an empirical fit given by (74). (Lower) Variation of the maximum value of the scaled tangential velocity,  $\bar{u}_{\theta,max}$ , defined by (48), with  $\kappa a$ .

spherical symmetry and is undistorted during electrophoresis. The hydrodynamic force,  $F_{H1}$ , is the classical Stokesian drag experienced by a sphere of radius  $a$  in an imposed uniform flow field at infinity;  $F_{H2}$  accounts for the additional electrophoretic drag due to the motion of the ions in the electrolyte.

Since the particle moves with constant electrophoretic velocity, the total force vanishes:

$$F_{E1} + F_{E2} + F_{H1} + F_{H2} = 0. \quad (77)$$

It is important to note that the terms involving  $R$  that represent the perturbed electrostatic potential  $\delta\psi$  in  $F_{E2}$  and  $F_{H2}$  cancel out exactly, see (49) and (76). This is the reason why O’Brien & White [6] can obtain the electrophoretic mobility without the need to solve for the perturbed electrostatic potential  $\delta\psi$  since its contribution to the force components in (76) cancel out when summed to give the total force on the sphere. The consideration of different contributions to the total force also provides a direct demonstration of the observation that mobility does not depend on the electrostatic boundary conditions and hence is independent of the permittivity of the dielectric particle [6], even though the perturbation potential,  $\delta\psi$  through  $R$ , will depend on the particle permittivity.

At this point, it is possible to connect the decomposition of forces by Overbeek highlighted in (76) to the  $U$ - and  $E$ -problems of O’Brien & White [6] who considered the forces  $F^1$  and  $F^2$  on the particle in two sub-problems as follows:

1. *U*-problem: Calculate the force,  $F^1$  on the particle fixed in a flow field  $-U$  at infinity, but in the absence of an applied electric field. The fluid velocity and perturbed potential have the limiting forms:  $u(r) \rightarrow -U$  and  $\delta\psi(r) \rightarrow 0$  as  $r \rightarrow \infty$ . By virtue of the linearity of the problem, the force will be proportional to  $U$ :  $F^1 = \alpha U$  for a determinable scalar,  $\alpha$ .  $F^1$  will correspond to the drag force experienced by a charged sphere moving through the electrolyte at a velocity of  $U$  in the absence of an external electrical field.
2. *E*-problem: Calculate the force,  $F^2$  on the particle fixed in an electric field  $E$  at infinity, but in the absence of an imposed velocity field. The fluid velocity and perturbed potential have the limiting forms:  $u(r) \rightarrow 0$  and  $\delta\psi(r) \rightarrow -\mathbf{E} \cdot \mathbf{r}$  as  $r \rightarrow \infty$ . The force,  $F^2$  is now proportional to  $E$ ,  $F^2 = \beta E$  for a determinable scalar,  $\beta$ , and describes the force experienced by a charged sphere subject to an external electric field, but fixed in position to prevent motion through the electrolyte.

O'Brien & White then evaluated the forces by integrating the stress tensor over a large surface that encloses the particle and the double layer where the only forces acting are hydrodynamic in nature. That is, the equation of motion outside the double layer is classical Stokes flow, without the body force term on the right hand side of (7), but with the boundary conditions modified to take into account the physics within the double layer.

Since we are concerned with linear electrophoresis, the superposition of the forces calculated independently in the  $U$  and  $E$  problems give rise to the total force experienced by a particle in electrophoresis, i.e.  $F^1 + F^2 = \alpha U + \beta E = 0$ , from which the mobility can be obtained as  $\mu_m = U/E = -\beta/\alpha$ .

It can be shown (see Appendix E) that the sum,

$$F^1 + F^2 = -6\pi\eta aU + 4\pi\epsilon E a \int_{\infty}^a \xi dx = 0 \quad (78)$$

that is equivalent to the force balance condition (77). We note that the first term on the right hand side of (78) is the Stokesian drag,  $F_{H1} = -6\pi\eta aU$  in (76c) whereas the second term on the right hand side of (78) is the second term of  $F_{H2}$  in (76d). As we can see in (54), the function  $\xi(r)$  can be expressed in terms of the ion potentials,  $\phi_i(r)$  that are independent of the function  $R(r)$  that characterizes the radial dependence of the perturbed electrostatic potential,  $\delta\psi(r, \theta)$ . Therefore, this is an explicit demonstration that the mobility is independent of the electrostatic boundary conditions and a consideration of the far field forces of hydrodynamic nature is sufficient to deduce the mobility of the colloidal particle.

We can understand the independence of the mobility on the electrostatic boundary conditions by noting that when considering the particle and the double layer as a combined system, which O'Brien & White did when evaluating the forces over the large surface enclosing the particle and double layer, the direct electrical force (76a), the relaxation force (76b) and the first term of the electrophoretic drag (76d) become internal forces, describing the force exerted by the electrical double layer on the particle and the equal and opposite force exerted by the particle on the double layer. These internal forces are dependent on the

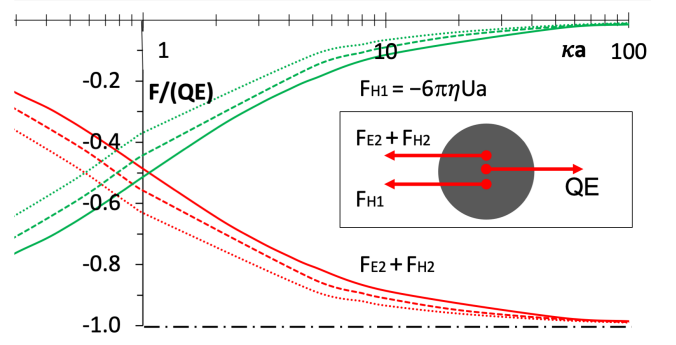


Figure 6: Variation of the Stokes drag force,  $F_{H1} = -6\pi\eta aU$  and the electrophoretic drag forces,  $[F_{E2} + F_{H2}]$  given in (76), scaled by  $F_{E1} = QE$ , with sphere radius,  $\kappa a$ . Solid lines: Henry-Debye-Hückel model that is independent of the  $\zeta$ -potential; O'Brien-White model at  $e\zeta/kT = 2$  (---) and 3 (···). An inset schematic illustrates the forces acting on the sphere, balancing the direct electrical force,  $QE$ .

electrostatic boundary conditions through the boundary conditions for  $R(r)$  in (57) but do not contribute to the electrophoretic mobility.

In Fig. 6, we exhibit the variation of the different force components in (76) with particle radius by plotting the Stokesian drag force,  $F_{H1}$  and the electrophoretic force,  $[F_{E2} + F_{H2}]$ , both scaled by the direct electrical force,  $F_{E1} = QE$ , as functions of  $\kappa a$ . We considered the univalent symmetrical electrolyte, KCl for simplicity; hence, the ion drag coefficients (2) for the potassium and chloride ions were used. The results obtained for  $e\zeta/kT = 2$  and  $e\zeta/kT = 3$  were compared with the limiting, Henry-Debye-Hückel theory that is valid at the low  $\zeta$ -potentials where the mobility is linear in  $\zeta$ . The scaled forces in the Henry-Debye-Hückel theory would hence be independent of the  $\zeta$ -potential due to the use of (72) and the Gauss's law to calculate the particle charge,  $Q$ . Moreover, at low  $\zeta$ -potentials, the relaxation force,  $F_{E2}$  from (76b) vanishes as the relaxation effect scales with  $\zeta^3$  [4] for symmetric electrolytes, thereby justifying the omission of the relaxation effect in Henry's calculations [5]. At higher  $\zeta$  potentials, such as  $e\zeta/kT = 2$  and  $e\zeta/kT = 3$ , this omission may no longer be justified and the mobility was computed using the O'Brien & White program [6]. The particle charge,  $Q$  is now calculated using the approximation for  $\psi^0$  provided by Ohshima, Healy & White in equation (49) of [20] that approximates the non-linear Poisson-Boltzmann (12) solution to higher surface potentials than (72).

In particular, we see from Fig. 6 how the magnitudes of these two force components vary with particle size while their sum always balances the direct electrical force,  $F_{E1} = QE$ . At small  $\kappa a$ , the Stokes drag force  $F_{H1} = -6\pi\eta aU$  becomes the dominant term in balancing the direct electrical force,  $F_{E1} = QE$ , but as  $\kappa a$  increases, the effect of the Stokes drag force diminishes as the electrophoretic force,  $[F_{E2} + F_{H2}]$ , dominates in cancelling the direct electrical force,  $F_{E1} = QE$ . Note that a 'cross-over' of the two forces happens near  $\kappa a \sim 1$ , and the cross-over shifts towards lower  $\kappa a$  as  $\zeta$  increases.

Thus the zero force condition not only implies the vanishing pressure outside the double layer, but it also severely changes the flow pattern and thus, the range of the hydrodynamic inter-

action. Previous works appear not to have focussed on this feature and its implications on particle-particle interactions. The velocity profile around a sphere in electrophoretic motion in Fig. 2 calculated using Henry’s model is substantially different from a classical Stokes velocity profile around a sphere where  $h = [r - 3a/2 + a^3/(2r^2)]U/(2E)$ , as shown in Section 3.3.1, with the Stokes velocity profile (40) shown in Fig. 3. When compared to the result for the velocity field around a particle in electrophoresis (60), we see that, apart from the first terms representing the constant velocity part, the velocity decays as  $1/r$  in a classical Stokes flow such as in sedimentation, as compared to  $1/r^3$  for the electrophoresis case.

A further interesting phenomenon, from a fluid dynamics perspective, is the appearance of a maximum in the tangential velocity as visualized in Section 6. This maximum is actually also a direct consequence of the  $1/r^3$  behavior of the flow field. A mass balance (see Appendix F) over a half infinite sphere illustrates that the contribution over the spherical part dies out for an electrophoretic flow. Since the velocity at the surface of the sphere is zero, in order to satisfy the continuity of material, the velocity must be greater than  $U$  somewhere between the sphere surface and infinity, resulting in a maximum. Such a maximum velocity does not appear in the velocity pattern around a Stokes flow sphere, since the velocity decays as  $1/r$  only and an integration of the half sphere at infinity will still give a contribution to the mass balance.

Morrison [7] has performed a very similar analysis, but claims that since the velocity,  $\mathbf{u}$  is irrotational outside the double layer, the Bernoulli equation should hold and since  $u \sim 1/r^3$  then  $p \sim u^2 \sim 1/r^6$ . Anderson [12], in his review cites this conclusion. However, the Anderson/Morrison Bernoulli equation assumption is incompatible with the Stokes flow assumption. Even though the flow field outside the double layer looks like a potential flow field, it is of course a viscosity dominated Stokes flow where effects due to inertia are negligible, whereas the Bernoulli pressure is due solely to inertial effects with no contribution from the viscosity. This can easily be shown, if we argue that the electrophoretic theory is based on the Stokes equation as  $\eta \nabla^2 \mathbf{u} = \nabla p$  and  $\nabla \cdot \mathbf{u} = 0$ , but since  $\nabla \times \nabla \times \mathbf{u} = \nabla(\nabla \cdot \mathbf{u}) - \nabla^2 \mathbf{u}$ , then this would be equivalent to  $\eta \nabla \times \nabla \times \mathbf{u} = -\nabla p$ . For an irrotational flow  $\nabla \times \mathbf{u} = 0$ , this would mean  $\nabla p = 0$  and the pressure outside the double layer would be a constant and not given by the Bernoulli equation. Despite this fact, the other key conclusions of Morrison [7] are indeed valid for electrophoresis.

## 8. Conclusions

The physical models of the electrophoretic motion of a spherical particle considered by Overbeek [4] and later by O’Brien & White [6] are identical although the theoretical treatments are quite different. The numerical difficulties of the dual characteristic length scale the problem encountered in using the Overbeek treatment [18] that arises when the Debye length,  $1/\kappa$ , is small compared to the particle radius,  $a$ , i.e. the thin double layer regime when  $\kappa a \gg 1$ , have been addressed by the

O’Brien & White approach. In particular, they were able to calculate the electrophoretic mobility without needing to solve for the perturbation in the electrostatic potential, the pressure or the velocity field.

In this paper, we established the equivalence between the Overbeek treatment that solved for the velocity, pressure and electrostatic potential and the O’Brien & White approach that circumvented the need to consider the velocity and the pressure. From the Overbeek result, we showed quite generally that the pressure and vorticity of the flow field vanishes exponentially fast outside the double layer so that the hydrodynamic condition outside the double layer is a zero pressure, irrotational flow. As a consequence, the velocity in the laboratory frame decays with distance as  $1/r^3$  from the sphere compared to the  $1/r$  decay in standard Stokes flow. The implication of this faster decay is that the tangential component of the velocity has a maximum near the sphere surface close to the double layer. This unusual feature of the hydrodynamic behavior clearly has implications when considering situations when particles are in close proximity whereby both electrical double layer and hydrodynamic interactions become important [9]. But as far as we are aware, such features of the hydrodynamic behavior have not been studied in details. Thus it may be fruitful to revisit the popular treatment of electrophoretic effects in the thin double layer regime [1, 12, 21] that simply models the effect of the flow inside the double layer by an effective slip velocity.

At a pedagogical level, since the velocity field outside the double layer is an irrotational, zero pressure Stokes flow, it is inconsistent to suggest that the Bernoulli equation can be used to give the pressure. We also note that the textbook derivation of the Smoluchowski results valid in the limit of  $\kappa a \rightarrow \infty$  that considers the particle as a flat plate will lead to the conclusion of a monotonic tangential velocity profile due to omission of the singular but important effect of finite surface curvature.

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## Appendix A. Glossary of symbols

As far as possible the notation of O’Brien-White [6] and Ohshima *et al.* [11] was adopted and SI units were employed. Any minor differences are noted in the text when a symbol is first defined and used.

- $a$  radius of a spherical charged colloidal particle
- $E$  constant external applied electric field vector with absolute value  $E$
- $e$  charge of a proton,  $1.602 \times 10^{-19}$  C
- $h(r)$  function used to describe the radial part of the velocity components by Ohshima *et al.* [11]
- $k$  Boltzmann’s constant,  $1.38 \times 10^{-23}$  J/K

$\mathbf{n}_r, \mathbf{n}_\theta, \mathbf{n}_\varphi$  unit vector in the  $(r, \theta, \varphi)$  - (radial, polar, azimuthal) direction of a spherical polar coordinate system centered at the sphere

$p$  pressure

$p^0$  equilibrium pressure when  $\mathbf{E} = \mathbf{0}$ , defined by (11)

$r$  radial coordinate of the spherical polar system

$R(r)$  function in the Overbeek theory used to describe the radial component of the perturbed electrostatic potential defined with:  $\delta\psi \equiv -E R(r) \cos \theta$

$T$  absolute temperature

$\mathbf{u}(\mathbf{x}) \equiv \mathbf{u}$ , velocity vector of the fluid

$\mathbf{u}^S, p^S, h^S$  velocity, pressure and hydrodynamic function in Stokes flow when  $\mathbf{E} = \mathbf{0}$  and in the absence of charges

$w \equiv (\nabla \times \mathbf{u})_\varphi = (\nabla \times \mathbf{u}) \cdot \mathbf{n}_\varphi$  component of the vorticity in the azimuthal direction

$\mathbf{x}$  general 3D position vector

$\varepsilon_r$  relative permittivity of the solvent

$\varepsilon_0$  permittivity of vacuum,  $8.852 \times 10^{-12}$  F/m

$\epsilon \equiv \varepsilon_0 \varepsilon_r$ , solvent permittivity

$\epsilon_p$  particle permittivity

$\eta$  solvent viscosity

$\theta$  polar angular coordinate of the spherical polar system, i.e. the angle between the radius vector and the electric field

$\varphi$  angle between  $r - \theta$  plane and the vertical plane in the spherical polar coordinate system

$\xi(r)$  function in the Overbeek theory, defined by (54)

$\chi(r)$  function in the Overbeek theory, defined by (50)

$z_i$  valence of ionic species  $i$

$\lambda_i$  drag coefficient of ionic species  $i$

$\mathbf{v}_i(\mathbf{x}) \equiv \mathbf{v}_i$ , velocity of ionic species  $i$

$n_i^\infty$  bulk number density of ions of type  $i$

$\kappa \equiv [(e^2/\epsilon kT) \sum_i n_i^\infty z_i^2]^{1/2}$ , Debye screening parameter

$n_i^0(\mathbf{x}) \equiv n_i^0$ , equilibrium number density of ionic species  $i$  at position  $\mathbf{x}$  given by the Poisson-Boltzmann equation, when  $\mathbf{E} = \mathbf{0}$

$\delta n_i(\mathbf{x}) \equiv \delta n_i \equiv n_i - n_i^0$   
 $\approx - (z_i e/kT) n_i^0 (\delta\psi + \varphi_i)$ , to linear order

$\varphi_i(\mathbf{x}) \equiv \varphi_i \equiv \phi_i(r)E \cos \theta$

$\mu_i^\infty$  constant reference chemical potential of ionic species  $i$

$\mu_i^0(\mathbf{x}) \equiv \mu_i^0 \equiv \mu_i^\infty + z_i e \psi^0(\mathbf{x}) + kT \log n_i^0(\mathbf{x})$ , equilibrium electrochemical potential of ionic species  $i$  when  $\mathbf{E} = \mathbf{0}$

$\mu_i(\mathbf{x}) \equiv \mu_i \equiv \mu_i^\infty + z_i e \psi(\mathbf{x}) + kT \log n_i(\mathbf{x})$ , electrochemical potential of ionic species  $i$  when  $\mathbf{E} \neq \mathbf{0}$

$\delta\mu_i(\mathbf{x}) \equiv \delta\mu_i \equiv \mu_i(\mathbf{x}) - \mu_i^0(\mathbf{x}) = -z_i e \varphi_i \equiv -z_i e \phi_i E \cos \theta$

$\rho(\mathbf{x}) \equiv \rho \equiv e \sum_i z_i n_i(\mathbf{x})$ , volume charge density at position  $\mathbf{x}$ , when  $\mathbf{E} \neq \mathbf{0}$

$\rho^0(\mathbf{x}) \equiv \rho^0 \equiv e \sum_i z_i n_i^0(\mathbf{x})$ , volume charge density at position  $\mathbf{x}$ , when  $\mathbf{E} = \mathbf{0}$

$\delta\rho(\mathbf{x}) \equiv \delta\rho \equiv \rho(\mathbf{x}) - \rho^0(\mathbf{x}) = e \sum_i z_i \delta n_i(\mathbf{x})$

$\psi^0(\mathbf{x}) \equiv \psi^0$ , equilibrium electrostatic potential at position  $\mathbf{x}$ , when  $\mathbf{E} = \mathbf{0}$ , given by the Poisson-Boltzmann equation

$\psi(\mathbf{x}) \equiv \psi$ , the total electrostatic potential whereby  $-\nabla\psi$  is the total electric field that includes contributions from the constant external field  $\mathbf{E}$ , the field due to the charged colloidal particles and perturbed ion distribution

$\delta\psi(\mathbf{x}) \equiv \delta\psi \equiv \psi(\mathbf{x}) - \psi^0(\mathbf{x})$

$\zeta$  the zeta potential of the colloidal particle (assumed to be constant everywhere on the surface)

## Appendix B. The Overbeek theory

We outline the derivation of the Overbeek theory given in his PhD thesis in Dutch [4] for the electrophoretic motion of a sphere in an electrolyte of arbitrary composition using modern notation and SI units. The governing equations of electrokinetics given in Section 2 are linearized according to (14) to give a set of coupled linear equation to first order in the perturbation quantities. Due to the axial symmetry of a sphere in an external electric field,  $\mathbf{E}$ , directed along  $\theta = 0$ , the perturbed quantities have the general form:

$$\delta f(r, \theta) = F(r) \cos \theta \quad \text{or} \quad F(r) \sin \theta. \quad (\text{B.1})$$

The problem is then reduced to solving for the function  $F(r)$  that is only a function of the distance,  $r$  from the center of the sphere.

The Poisson equation becomes

$$\rho = \rho^0 + \delta\rho = -\epsilon \nabla^2 (\psi^0 + \delta\psi) \quad (\text{B.2})$$

where the equilibrium potential,  $\psi^0(r)$  and charge density,  $\rho^0(r)$  are radially symmetric. The perturbed potential,  $\delta\psi(r, \theta)$  and the perturbed charge density,  $\delta\rho(r, \theta)$  have the form

$$\delta\psi(r, \theta) = -E R(r) \cos \theta \quad (\text{B.3a})$$

$$\delta\rho(r, \theta) = -\epsilon \nabla^2 \delta\psi = \epsilon E \mathcal{L}[R(r)] \cos \theta \quad (\text{B.3b})$$

where we have used the  $\mathcal{L}$  differential operator defined in (27) with  $R(r)$  an unknown function to be found. In the limit  $r \rightarrow \infty$ ,  $\delta\psi(r, \theta) \rightarrow -E r \cos \theta$ .

Similarly, using (11) for the equilibrium pressure,  $p^0$ , the pressure can be written as

$$p = p^0(r) + \delta p(r, \theta) \\ = - \int_{\infty}^r \rho^0 \left( \frac{d\psi^0}{dx} \right) dx - \epsilon E P(r) \cos \theta \quad (\text{B.4})$$

where  $P(r)$ , the radial function of the perturbed pressure,  $\delta p(r, \theta) \equiv -\epsilon E P(r) \cos \theta$ , is an unknown function to be found.

The perturbed pressure,  $\delta p$  can be expressed in terms of  $\delta\psi$  and  $\delta\rho$  ( $= -\epsilon \nabla^2 \delta\psi$ ) by applying the divergence operator to the momentum equation (15c) together with the incompressibility condition:  $\nabla \cdot \mathbf{u} = 0$ , to eliminate the velocity,  $\mathbf{u}$  to give

$$\nabla^2 \delta p = -\delta\rho \nabla^2 \psi^0 - \rho^0 \nabla^2 \delta\psi - \nabla \delta\rho \cdot \nabla \psi^0 - \nabla \rho^0 \cdot \nabla \delta\psi. \quad (\text{B.5})$$

This can be simplified by noting that

$$\nabla \delta\rho \cdot \nabla \psi^0 = \frac{\partial \delta\rho}{\partial r} \cdot \frac{d\psi^0}{dr} \quad (\text{B.6})$$

$$\nabla \rho^0 \cdot \nabla \delta\psi = \frac{d\rho^0}{dr} \cdot \frac{\partial \delta\psi}{\partial r} \quad (\text{B.7})$$

and using the  $\mathcal{L}$  differential operator defined in (27) to give

$$\nabla^2 \delta\psi = -E \mathcal{L}[R] \cos \theta \quad (\text{B.8})$$

$$\nabla^2 \delta p = -\epsilon E \mathcal{L}[P] \cos \theta. \quad (\text{B.9})$$

Combining these results in (B.5) gives the following relation between  $P(r)$  and  $R(r)$

$$\mathcal{L}[P] = f_1(r) \equiv 2 \mathcal{L}[R] \nabla^2 \psi^0 + \frac{d\mathcal{L}[R]}{dr} \frac{d\psi^0}{dr} + \frac{dR}{dr} \frac{d}{dr} (\nabla^2 \psi^0). \quad (\text{B.10})$$

The formal solution of this differential equation is, see (28) and (29)

$$P(r) = c_1 r + \frac{c_2}{r^2} + r \int_{\infty}^r \frac{1}{x^4} \int_{\infty}^x y^3 f_1(y) dy dx. \quad (\text{B.11})$$

For large  $r$ ,  $\delta p(r, \theta)$  and thus  $P(r)$  must vanish and consequently  $c_1 = 0$  and later, we will also find  $c_2 = 0$  as well. The integral in (B.11)

$$\chi(r) \equiv r \int_{\infty}^r \frac{1}{x^4} \int_{\infty}^x y^3 f_1(y) dy dx \quad (\text{B.12})$$

can be simplified by noting that  $\nabla^2 \psi^0(r) = \frac{1}{r^2} \frac{d}{dr} (r^2 \frac{d\psi^0}{dr})$  to give

$$\chi(r) = \frac{dR}{dr} \frac{d\psi^0}{dr} + 4r \int_{\infty}^r \left( \frac{1}{x^2} \frac{dR}{dx} - \frac{R}{x^3} \right) \frac{d\psi^0}{dx} dx. \quad (\text{B.13})$$

Thus the complete solution for the pressure  $p$  from (B.4) is

$$p = \epsilon \int_{\infty}^r \nabla^2 \psi^0 \frac{d\psi^0}{dx} dx - \epsilon E \left[ \frac{c_2}{r^2} + \chi(r) \right] \cos \theta. \quad (\text{B.14})$$

To determine the velocity field, we take the curl of the momentum equation (7) to eliminate  $p$ , and use the identity:  $\nabla \times \nabla \times \mathbf{u} = \nabla(\nabla \cdot \mathbf{u}) - \nabla^2 \mathbf{u}$  and  $\nabla \cdot \mathbf{u} = 0$  to give

$$\eta \nabla \times \nabla \times \nabla \times \mathbf{u} + \nabla \times (\delta\rho \nabla \psi^0 + \rho^0 \nabla \delta\psi) = 0. \quad (\text{B.15})$$

We now analyse the components of this equation by taking into account the symmetry of the electrophoretic problem of a sphere. In spherical polar coordinates  $(r, \theta, \varphi)$ ,  $\nabla \times \mathbf{u}$  is<sup>2</sup>

$$(\nabla \times \mathbf{u})_r = \frac{1}{r \sin \theta} \left[ -\frac{\partial}{\partial \theta} (u_\varphi \sin \theta) + \frac{\partial u_\theta}{\partial \varphi} \right] \\ (\nabla \times \mathbf{u})_\theta = \frac{1}{r} \left[ -\frac{1}{\sin \theta} \frac{\partial u_r}{\partial \varphi} + \frac{\partial}{\partial r} (r u_\varphi) \right] \quad (\text{B.16}) \\ (\nabla \times \mathbf{u})_\varphi = \frac{1}{r} \left[ -\frac{\partial}{\partial r} (r u_\theta) + \frac{\partial u_r}{\partial \theta} \right].$$

The axial symmetry of the problem means that the azimuthal component,  $u_\varphi$  must be zero, and  $\mathbf{u}$  is not a function of the azimuthal angle,  $\varphi$ . Thus the vorticity  $\mathbf{w} \equiv \nabla \times \mathbf{u}$  has no  $r$  or  $\theta$  components whereas the  $\varphi$  component is

$$(\mathbf{w})_\varphi \equiv w(r, \theta) = (\nabla \times \mathbf{u})_\varphi = \frac{1}{r} \left[ -\frac{\partial}{\partial r} (r u_\theta) + \frac{\partial u_r}{\partial \theta} \right]. \quad (\text{B.17})$$

Consequently,  $\nabla \times \mathbf{w}$  has non-zero  $r$  and  $\theta$  components, but no  $\varphi$  component and so  $\nabla \times \nabla \times \mathbf{w}$  only has a  $\varphi$  component, namely

$$[\nabla \times \nabla \times \mathbf{w}]_\varphi = -\frac{1}{r} \left\{ \frac{\partial^2 (r w)}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial \theta} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (w \sin \theta) \right] \right\}. \quad (\text{B.18})$$

Also,  $\nabla \times (\delta\rho \nabla \psi^0 + \rho^0 \nabla \delta\psi)$  is a vector with only a  $\varphi$  component, which is

$$[\nabla \times (\delta\rho \nabla \psi^0 + \rho^0 \nabla \delta\psi)]_\varphi = \frac{1}{r} \left( \frac{\partial \delta\rho}{\partial \theta} \frac{d\psi^0}{dr} - \frac{d\rho^0}{dr} \frac{\partial \delta\psi}{\partial \theta} \right). \quad (\text{B.19})$$

With these results, (B.15) now transforms into:

$$\frac{\eta}{r} \left\{ \frac{\partial^2 (r w)}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial \theta} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (w \sin \theta) \right] \right\} = \frac{1}{r} \left( \frac{\partial \delta\rho}{\partial \theta} \frac{d\psi^0}{dr} - \frac{d\rho^0}{dr} \frac{\partial \delta\psi}{\partial \theta} \right)$$

or after inserting expressions for  $\rho^0$ ,  $\delta\rho$  and  $\delta\psi$  from (B.2) and (B.3):

$$\frac{\partial^2 (r w)}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial \theta} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (w \sin \theta) \right] \\ = \frac{\epsilon E \sin \theta}{\eta} \left[ R \frac{d}{dr} \nabla^2 \psi^0 - \mathcal{L}[R] \frac{d\psi^0}{dr} \right]. \quad (\text{B.20})$$

The solution of (B.20) has the form

$$w(r, \theta) = \frac{\epsilon E}{\eta} W(r) \sin \theta \quad (\text{B.21})$$

so combining (B.20) and (B.21) gives the differential equation that determines  $W(r)$

$$\mathcal{L}[W] = f_2(r) \equiv \frac{R}{r} \frac{d}{dr} \nabla^2 \psi^0 - \frac{1}{r} \mathcal{L}[R] \frac{d\psi^0}{dr} \quad (\text{B.22})$$

with solution

$$W(r) = c_3 r + \frac{c_4}{r^2} + r \int_{\infty}^r \frac{1}{x^4} \int_{\infty}^x y^3 f_2(y) dy dx. \quad (\text{B.23})$$

<sup>2</sup>Overbeek seemed to have defined  $\nabla \times$  with a sign difference when compared to modern notation.



The integration constant  $c_3 = 0$ , since the vorticity must become zero at infinity and later on, we will see that  $c_4$  is also zero. We define  $\xi(r)$  as the integral:

$$\xi(r) \equiv r \int_{\infty}^r \frac{1}{x^4} \int_{\infty}^x y^3 \left\{ \frac{R}{y} \frac{d}{dy} \nabla^2 \psi^0 - \frac{1}{y} f_2(y) \frac{d\psi^0}{dy} \right\} dy dx \quad (\text{B.24})$$

that can be simplified using  $\nabla^2 \psi^0 = \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d\psi^0}{dr} \right)$  to give<sup>3</sup>

$$\xi(r) = \frac{R}{r} \frac{d\psi^0}{dr} - 2r \int_{\infty}^r \left( \frac{1}{x^2} \frac{dR}{dx} - \frac{R}{x^3} \right) \frac{d\psi^0}{dx} dx. \quad (\text{B.25})$$

Overbeek noted that this function fulfills the same role as the function with the same name in Henry<sup>4</sup> [5].

With the full solution for  $w(r, \theta)$  now being

$$w(r, \theta) = \frac{\epsilon E}{\eta} \left[ \frac{c_4}{r^2} + \xi(r) \right] \sin \theta, \quad (\text{B.26})$$

the only non-zero component of  $\nabla \times \mathbf{u}$ , given by (B.17) and (B.26) provides one equation for  $u_r$  and  $u_\theta$ :

$$(\nabla \times \mathbf{u})_\varphi \equiv \frac{1}{r} \left\{ -\frac{\partial}{\partial r} (r u_\theta) + \frac{\partial u_r}{\partial \theta} \right\} = \frac{\epsilon E \sin \theta}{\eta} \left( \frac{c_4}{r^2} + \xi(r) \right). \quad (\text{B.27})$$

Since by symmetry,  $u_\varphi = 0$ , a second equation for  $u_r$  and  $u_\theta$  is

$$\nabla \cdot \mathbf{u} \equiv \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 u_r) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} (u_\theta \sin \theta) = 0. \quad (\text{B.28})$$

The radial and tangential velocities have the form

$$u_r(r, \theta) = R_1(r) \cos \theta \quad \text{and} \quad u_\theta(r, \theta) = R_2(r) \sin \theta. \quad (\text{B.29})$$

Substituting this into (B.27) and (B.28), gives the following set of coupled differential equations for  $R_1(r)$  and  $R_2(r)$

$$\begin{aligned} rR_2 &= -\frac{1}{2} \frac{d}{dr} (r^2 R_1) \\ -\frac{2}{r} \frac{dR_2}{dr} - \frac{2R_2}{r^2} - \frac{2R_1}{r^2} &= \frac{2\epsilon E}{\eta} \frac{1}{r} \left[ \frac{c_4}{r^2} + \xi(r) \right]. \end{aligned}$$

The solution is (as can easily be checked by back substituting):

$$\begin{aligned} R_1(r) &= \frac{c_5}{r^3} + c_6 - \frac{\epsilon E}{\eta} \left( \frac{c_4}{r} + \frac{2}{3r^3} \int_{\infty}^r x^3 \xi dx + \frac{2}{3} \int_{\infty}^r \xi dx \right) \\ R_2(r) &= \frac{c_5}{2r^3} - c_6 + \frac{\epsilon E}{\eta} \left( \frac{c_4}{2r} - \frac{1}{3r^3} \int_{\infty}^r x^3 \xi dx + \frac{2}{3} \int_{\infty}^r \xi dx \right). \end{aligned} \quad (\text{B.31})$$

Aside from the constants  $c_2, c_4, c_5$  and  $c_6$  in equations (B.14) and (B.31), the pressure and velocity distribution are now fully determined. The constant  $c_2$  is partly determined by  $\mathbf{u}$ , since  $p$

and  $\mathbf{u}$  must also satisfy the momentum equation (7) written in the form

$$\eta \nabla \times \nabla \times \mathbf{u} + \nabla p = -\rho \nabla \psi. \quad (\text{B.32})$$

The term in  $\nabla(\cos \theta/r^2)$  in  $\nabla p$ , from (B.9) and (B.11), must be compensated by a term of the same form from  $\eta \nabla \times \nabla \times \mathbf{u}$ , since  $\rho \nabla \psi$  does not contain a term proportional to  $\nabla(\cos \theta/r^2)$ . The vector  $\eta \nabla \times \nabla \times \mathbf{u}$  has  $r$  and  $\theta$  components, thus with the help of (B.16), (B.17) and (B.26) we find<sup>5</sup>:

$$\begin{aligned} \eta(\nabla \times \nabla \times \mathbf{u})_r &= \eta(\nabla \times \mathbf{w})_r = -2\epsilon E \left[ \frac{c_4}{r^3} + \frac{\xi}{r} \right] \cos \theta \\ \eta(\nabla \times \nabla \times \mathbf{u})_\theta &= \eta(\nabla \times \mathbf{w})_\theta = -\epsilon E \left[ \frac{c_4}{r^3} - \frac{1}{r} \frac{d}{dr} (r\xi) \right] \sin \theta. \end{aligned}$$

The  $r$  and  $\theta$  components of the term  $\nabla(c_2 \epsilon E \cos \theta/r^2)$  in  $\nabla p$  are

$$\begin{aligned} c_2 \epsilon E \left( \nabla \frac{\cos \theta}{r^2} \right)_r &= -2c_2 \epsilon E \frac{\cos \theta}{r^3} \\ c_2 \epsilon E \left( \nabla \frac{\cos \theta}{r^2} \right)_\theta &= -c_2 \epsilon E \frac{\sin \theta}{r^3}. \end{aligned}$$

Then equating terms in  $\cos \theta/r^2$  and  $\sin \theta/r^2$  in (B.32) gives  $c_2 = c_4$ .

The boundary conditions for the fluid velocity and the potential:

- as  $r \rightarrow \infty$ :  $u_r \rightarrow -U \cos \theta$ ,  $u_\theta \rightarrow U \sin \theta$  and  $\psi^0 \rightarrow 0$
- at  $r = a$ :  $u_r = 0$ ,  $u_\theta = 0$  and  $\psi = \zeta$ .

can be used to determine the constants:  $c_2, c_4, c_5$  and  $c_6$ . From the conditions for  $r \rightarrow \infty$ , when applied to (B.29) and (B.31), we see that  $R_1 \rightarrow U$  and  $R_2 \rightarrow -U$ , thus

$$c_6 = -U. \quad (\text{B.33})$$

From the conditions for  $r = a$  we find from (B.31)

$$c_4 = c_2 = a \int_{\infty}^a \xi dx - \frac{3\eta a U}{2\epsilon E} = 0 \quad (\text{B.34})$$

where the last equality follows from the fact that the force on the particle (see later) and thus  $c_2 = 0 = c_4$  and

$$c_5 = -\frac{Ua^3}{2} + \frac{2\epsilon E}{3\eta} \int_{\infty}^a x^3 \xi dx + \frac{\epsilon E a^3}{3\eta} \int_{\infty}^a \xi dx. \quad (\text{B.35})$$

Finally, the complete expressions for the pressure and veloc-

<sup>3</sup>This can easiest be done by partially integrating  $\int_{\infty}^x y^3 \left\{ \frac{R}{y} \frac{d}{dy} \nabla^2 \psi^0 \right\} dy$ , by which many terms will cancel out with the terms in round brackets.

<sup>4</sup>The function  $\xi$  from Henry can be recovered by setting  $R = r + \lambda a^3/r^2$  and using  $\nabla^2 \psi^0 = \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d\psi^0}{dr} \right)$ . Henry's formula is  $\xi = \frac{d\psi^0}{dr} + \lambda a^3 r \int_{\infty}^r \frac{1}{x^4} \nabla^2 \psi^0 dx$  (page 112 of Henry).

<sup>5</sup>Note again the minus sign difference in the definition of the curl operator when compared to modern notation.

ity components are

$$p = \epsilon \int_{\infty}^r \nabla^2 \psi^0 \frac{d\psi^0}{dx} dx \quad (\text{B.36a})$$

$$+ \cos \theta \left\{ \frac{3\eta a U}{2r^2} - \epsilon E \chi - \frac{\epsilon E a}{r^2} \int_{\infty}^a \xi dx \right\}$$

$$u_r = \cos \theta \left\{ \left( -1 + \frac{3a}{2r} - \frac{a^3}{2r^3} \right) U \right. \\ \left. + \frac{2\epsilon E}{3\eta} \left( \int_{\infty}^r \xi dx + \frac{1}{r^3} \int_r^a x^3 \xi dx \right) \right. \\ \left. - \frac{\epsilon E}{\eta} \left( \frac{a}{r} - \frac{a^3}{3r^3} \right) \int_{\infty}^a \xi dx \right\} \quad (\text{B.36b})$$

$$u_{\theta} = \sin \theta \left\{ \left( 1 - \frac{3a}{4r} - \frac{a^3}{4r^3} \right) U \right. \\ \left. - \frac{2\epsilon E}{3\eta} \left( \int_{\infty}^r \xi dx - \frac{1}{2r^3} \int_r^a x^3 \xi dx \right) \right. \\ \left. + \frac{\epsilon E}{\eta} \left( \frac{a}{2r} + \frac{a^3}{6r^3} \right) \int_{\infty}^a \xi dx \right\}. \quad (\text{B.36c})$$

Overbeek then calculated separately the hydrodynamic force,  $F_H$  and the electrical force,  $F_E$ .

To calculate the *hydrodynamical* force,  $F_H$ , he divided the fluid flow into 3 components:

- a pure Stokesian flow, proportional to  $U$ , corresponding to (40),
- a second flow, directly caused in the fluid due to forces of electrical origin, that do not satisfy the boundary conditions on the boundary of the fluid and the sphere (terms with  $\chi$ ,  $\int_{\infty}^r \xi dx$  and  $\frac{1}{r^3} \int_r^a x^3 \xi dx$ ),
- and a third flow, proportional to  $\int_{\infty}^a \xi dx$ , that is not exposed to external forces, but is combined with the second flow to satisfy the boundary conditions at  $r = a$ .

The hydrodynamic force  $F_H$ , that the flow defined by (B.36) exerts on the sphere, is found by integrating the traction,  $t$ , or force per unit area in the direction of  $\theta = 0$  over the whole surface of the sphere, where <sup>6</sup>

$$t = \left( -p + 2\eta \frac{\partial u_r}{\partial r} \right)_{r=a} \cos \theta - \eta \left( \frac{\partial u_{\theta}}{\partial r} - \frac{u_{\theta}}{r} + \frac{1}{r} \frac{\partial u_r}{\partial \theta} \right)_{r=a} \sin \theta.$$

Then using (B.36) and after what Overbeek called a ‘simple but lengthy calculation’, gives

$$F_H = \int_0^{\pi} t \, 2\pi a^2 \sin \theta \, d\theta \\ = -6\pi\eta a U + \frac{4\pi\epsilon E a^2}{3} \chi(a) + \frac{8\pi\epsilon E a^2}{3} \xi(a) + 4\pi\epsilon E a \int_{\infty}^a \xi dx$$

where we have used the fact that  $u_{\theta} = 0$  and  $\partial u_r / \partial \theta = 0$  at  $r = a$ . By substituting  $\chi$  and  $\xi$  according to Eqs. (B.13) and

<sup>6</sup>The stress tensor is  $\sigma_{ij} = -p\delta_{ij} + \eta[\partial u_i / \partial x_j + \partial u_j / \partial x_i]$ . In the current case  $u_i = \frac{U_j}{U} \left\{ \frac{x_i x_j}{r^2} (R_1 + R_2) - \delta_{ij} R_2 \right\}$ .

(B.25) this will become:

$$F_H = -6\pi\eta a U + \frac{4\pi\epsilon E a}{3} \left( \frac{d\psi^0}{dr} \right)_a \left( 2R + a \frac{dR}{dr} \right)_a + 4\pi\epsilon E a \int_{\infty}^a \xi dx. \quad (\text{B.38})$$

On the right hand side we see the 3 contributions to the force

1. the classical Stokesian drag for a sphere
2. the friction due to that part of the flow that is caused directly by electrical forces, and
3. the friction due to that part of the flow that is free of external forces and is required to satisfy the boundary conditions.

The electrophoretic drag force is combination of contributions 2 and 3.

The total *electrical* force,  $F_E$ , on the sphere is the sum of the forces exerted on the sphere by the applied field,  $E$  and by the additional charge density,  $\delta\rho$

$$F_E = QE - \int_0^{\pi} \int_a^{\infty} \frac{Q \delta\rho}{4\pi\epsilon r^2} \cos \theta \, 2\pi r \sin \theta \, rd\theta \, dr$$

where  $Q$  is the total charge on the sphere and the second term on the right hand side is the integral of pair-wise Coulomb interactions between the sphere and an infinitesimal charge,  $\rho(r, \theta) [2\pi r^2 \sin \theta \, d\theta \, dr]$ , over the ion cloud surrounding the sphere <sup>7</sup> and according to (B.3),

$$\delta\rho = -\epsilon \nabla^2 \delta\psi = \epsilon E \left( \frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} - \frac{2R}{r^2} \right) \cos \theta.$$

By a simple integration we find

$$F_E = \frac{QE}{3} \left( \frac{dR}{dr} + \frac{2R}{a} \right)_{r=a}. \quad (\text{B.39})$$

To express the total charge of the sphere,  $Q$  in terms of  $\psi^0$  and  $a$ , we use the fact that this charge is equal but opposite to the total charge on the double layer. Thus,

$$Q = - \int_a^{\infty} \rho^0 4\pi r^2 dr = 4\pi\epsilon \int_a^{\infty} \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d\psi^0}{dr} \right) r^2 dr \\ = -4\pi\epsilon a^2 \left( \frac{d\psi^0}{dr} \right)_{r=a}.$$

Since the sphere under electrophoretic motion has constant velocity, the sum of all forces on the sphere must be zero, thus  $F_H + F_E = 0$ . From (B.38), (B.39) and (B.40) it then follows that

$$-6\pi\eta a U + 4\pi\epsilon E a \int_{\infty}^a \xi dx = 0.$$

This can be rearranged to give the expression for the electrophoretic mobility as,

$$\mu_m = U/E = \frac{2\epsilon}{3\eta} \int_{\infty}^a \xi dx. \quad (\text{B.41})$$

<sup>7</sup>Note that the equilibrium charge density,  $\rho^0(r) \equiv \rho(r, \theta) - \delta\rho(r, \theta)$  does not exert a net force on the sphere since the equilibrium charge distribution is spherically symmetric—the relaxation effect arises from the asymmetry in the charge distribution within the double layer.

Overbeek noted that the cancellation of  $F_E$  against the second term of  $F_H$  in (B.38) is no coincidence, but has essential meaning, since this part of  $F_H$  is exactly caused by forces that act on the charge in the fluid and this charge is equal and opposite to the charge on the sphere. This formula (B.41) is thus generally valid for the electrophoresis velocity of a sphere. We have not assumed any special assumptions concerning the functional form of  $\psi^0(r)$ , nor that of  $R(r)$ . The formulae of Henry and consequently those of Hückel and Smoluchowski, can be derived as special case from (B.41) and (B.25), by applying the appropriate form of the function  $R(r)$ .

Using (B.41), the expressions for  $u_r$  and  $u_\theta$  from (B.36) can be written more elegantly as:

$$\begin{aligned} u_r &= \frac{2\epsilon E \cos \theta}{3\eta} \int_a^r \left(1 - \frac{x^3}{r^3}\right) \xi dx \\ u_\theta &= -\frac{2\epsilon E \sin \theta}{3\eta} \int_a^r \left(1 + \frac{x^3}{2r^3}\right) \xi dx \\ p &= \epsilon \int_\infty^r \nabla^2 \psi^0 \frac{d\psi^0}{dx} dx - \epsilon E \chi \cos \theta \\ w &= (\nabla \times \mathbf{u})_\varphi = \frac{\epsilon E}{\eta} \xi \sin \theta \end{aligned}$$

with  $\chi$  in the pressure from (B.13), which can be simplified using (B.25) as:  $\chi = -2\xi + \left(\frac{2R}{r} + \frac{dR}{dr}\right) \frac{d\psi^0}{dr}$ . The above equations are the main results of Overbeek's theory as mentioned in the main text.

### Appendix C. The stress tensor of an electrophoretic system

Equation (7) that describes the momentum balance in Stokes flow with an electrostatic body force can be obtained from the following stress tensor in Cartesian tensor notation:

$$\sigma_{ij} = -p\delta_{ij} + \eta \left[ \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right] + \epsilon \left[ E_i E_j - \frac{1}{2} E_k E_k \delta_{ij} \right]. \quad (\text{C.1})$$

The first term is the isotropic pressure that has a hydrodynamic and an osmotic component and the second term is the hydrodynamic stress tensor in a Newtonian fluid of shear viscosity,  $\eta$ . The last term is the Maxwell stress tensor expressed in terms of the electric field,  $\mathbf{E}$ . Taking the divergence of (C.1), and expressing the electric field in terms of the electrostatic potential,  $\psi$ :  $E_j = -\partial\psi/\partial x_j$ , and using the continuity equation  $\partial u_j/\partial x_j = 0$ , gives

$$\frac{\partial \sigma_{ij}}{\partial x_j} = -\frac{\partial p}{\partial x_i} + \eta \frac{\partial^2 u_i}{\partial x_j^2} - \epsilon E_i \frac{\partial^2 \psi}{\partial x_j^2}. \quad (\text{C.2})$$

Since the total force on a fluid element must be zero, the divergence of the stress tensor that expresses must vanish and using the Poisson equation (5) leads directly to (7).

### Appendix D. The force on a spherical particle

In this appendix, we examine the implication on the velocity field that follows from the fact that the force on a spherical particle undergoing electrophoretic motion is zero. As shown in

Section 7, the hydrodynamic function,  $h(r)$  that holds outside the electrical double around the sphere is determined by (75) and has the general solution is  $h(r) = c_2/r^2 + c_3 r + c_4$ . The objective is to show that the constant term  $c_4$  is proportional to the force on the sphere whereas the other terms in  $h(r)$  do not contribute. The derivation of the force requires finding the stress tensor that is expressed in terms of the velocity and pressure. The analysis is carried out using Cartesian tensor notation, with the summation convention over repeating indices.

According to (24), the velocity field,  $u_i$  can be written as

$$\begin{aligned} u_i &= E_j \left[ \frac{x_i x_j}{r^2} \left\{ -\frac{h}{r} + \frac{dh}{dr} \right\} + \delta_{ij} \left\{ -\frac{h}{r} - \frac{dh}{dr} \right\} \right] \\ &= E_j \left[ \frac{x_i x_j}{r^2} \left\{ -3\frac{c_2}{r^3} - \frac{c_4}{r} \right\} + \delta_{ij} \left\{ \frac{c_2}{r^3} - 2c_3 - \frac{c_4}{r} \right\} \right]. \end{aligned} \quad (\text{D.1})$$

Upon taking the gradient of the velocity field

$$\begin{aligned} \frac{\partial u_i}{\partial x_k} &= E_j \left[ c_2 \left( -3\frac{\delta_{ik} x_j}{r^5} - 3\frac{x_i \delta_{jk}}{r^5} + 15\frac{x_i x_j x_k}{r^7} - 3\frac{\delta_{ij} x_k}{r^5} \right) \right. \\ &\quad \left. + c_4 \left( -\frac{\delta_{ik} x_j}{r^3} - \frac{x_i \delta_{jk}}{r^3} + 3\frac{x_i x_j x_k}{r^5} + \frac{\delta_{ij} x_k}{r^3} \right) \right] \end{aligned} \quad (\text{D.2})$$

we see that the term with  $c_3$  drops out since it corresponds to a uniform flow field. The term in  $c_4$  is the only one that contributes to the Laplacian of the velocity field

$$\frac{\partial^2 u_i}{\partial x_k^2} = c_4 E_j \left[ -2\frac{\delta_{ij}}{r^3} + 6\frac{x_i x_j}{r^5} \right] = -c_4 E_j \frac{\partial}{\partial x_i} \left( 2\frac{x_j}{r^3} \right) \quad (\text{D.3})$$

because the term in  $c_2$  is proportional to  $\nabla^2(1/r)$  which is identically zero.

Outside the double layer, the Stokes equation  $\nabla p = \eta \nabla^2 \mathbf{u}$  and (D.3) can be used to give the pressure,  $p = -2\eta c_4 E_j x_j / r^3$  and thus the stress tensor  $\sigma_{ij}$  outside the double layer is

$$\begin{aligned} \sigma_{ik} &= -p\delta_{ik} + \eta \left[ \frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i} \right] \\ &= c_2 \eta E_j \left[ -6\frac{\delta_{ik} x_j}{r^5} - 6\frac{x_i \delta_{jk}}{r^5} - 6\frac{x_k \delta_{ij}}{r^5} + 30\frac{x_i x_j x_k}{r^7} \right] \\ &\quad + c_4 \eta E_j \left[ 6\frac{x_i x_j x_k}{r^5} \right]. \end{aligned} \quad (\text{D.4})$$

The force on the sphere is found by integrating the traction,  $t_i = \sigma_{ik} n_k$  or the force per unit area, over a fictitious sphere that encloses the particle and its double layer:

$$\begin{aligned} t_i &= c_2 \eta \left[ -6\frac{x_j E_j n_i}{r^5} - 6\frac{E_k n_k x_i}{r^5} - 6\frac{x_k n_k E_i}{r^5} + 30\frac{x_j E_j x_k n_k x_i}{r^7} \right] \\ &\quad + c_4 \eta \left[ 6\frac{x_j E_j x_k n_k x_i}{r^5} \right]. \end{aligned} \quad (\text{D.5})$$

This can be further simplified, since on the fictitious spherical surface, the normal vector,  $\mathbf{n}$ , and the vector,  $\mathbf{x}$  are parallel and  $n_i = -x_i/r$ , thus:

$$t_i = c_2 \eta \left[ -18(x_j E_j) \frac{x_i}{r^6} + 6\frac{E_i}{r^4} \right] - c_4 \eta 6(x_j E_j) \frac{x_i}{r^4}. \quad (\text{D.6})$$

Finally the force can be obtained by integrating the traction over the whole surface of the fictitious spherical surface:

$$F_i = \int t_i dS. \quad (\text{D.7})$$

Since the force is directed along the applied electric field,  $\mathbf{E}$ , the integral for the force can be evaluated using  $x_j = r \cos \theta$ ,  $x_j E_j = Er \cos \theta$  and  $dS = 2\pi r^2 \sin \theta d\theta$  to give

$$F = c_4 (8\eta\pi E) \quad (\text{D.8})$$

where the integral of term with  $c_2$  in the traction (D.6) vanishes.

As the force on the system that comprises the particle and the double layer must be zero as argued earlier, this leads to the conclusion that  $c_4 = 0$ , or equivalently, the  $h$ -function does not contain a constant term. The fact that  $c_4 = 0$  for an electrophoretically driven sphere leads to some very unusual fluid dynamics properties, not encountered in classical Stokes hydrodynamics.

## Appendix E. The forces in the $U$ and $E$ sub-problems of O'Brien & White

O'Brien & White [6] considered the decomposition of the linear electrophoresis problem into two sub-problems, namely the  $U$  and the  $E$  problems as referred to in Section 7. In this appendix, the forces for the two sub-problems will be calculated in order to ultimately present a derivation for (78).

Physical quantities of relevance to the  $U$ -problem will be denoted by the bolded superscript '1' such as  $F^1$ ,  $\phi_i^1$  and  $\mathbf{u}^1$  representing, respectively, the force on the particle, the ion-potential function and the velocity field: all evaluated in the context of the  $U$  problem. Similarly, physical quantities evaluated in the  $E$ -problem will be differentiated with the bolded superscript '2' (not to be confused with an exponent).

### Appendix E.1. The $U$ -problem

The velocity field for the  $U$ -problem is given by modifying the classical Stokes expression from (34) with the hydrodynamic function,  $h^1(r)$ , appropriate for this problem:

$$\mathbf{u}^1 = -\frac{2}{r} h^1(r) U \cos \theta \mathbf{n}_r + \frac{1}{r} \frac{d}{dr} [r h^1(r)] U \sin \theta \mathbf{n}_\theta. \quad (\text{E.1})$$

Note that there is also a factor of  $U$  difference between (E.1) and (34), i.e.  $h^1$  and  $h$  do not share the same units. The boundary conditions of  $h^1(r)$  are now not the same as those for  $h(r)$  in (32). Indeed,  $h^1(r)$  may have a constant term at infinity as  $F^1$  need not vanish, as will be shown later. The boundary conditions for  $h^1(r)$  can be written as,

$$h^1 = 0 = \frac{dh^1}{dr}, \quad r = a \quad (\text{E.2a})$$

$$h^1 \rightarrow \frac{1}{2} r \quad r \rightarrow \infty. \quad (\text{E.2b})$$

Here, (E.2a) is equivalent to the no-slip and no ion-penetration boundary conditions and (E.2b) defines a uniform flow of  $-U$  at infinity.

The ion-potential function in the  $U$ -problem, in analogy to the ion-potential introduced in Section 3, is represented by  $\phi_i^1(r, \theta) \equiv \phi_i^1(r) U \cos \theta$ . Note that although  $\phi_i^1$  and  $\phi_i$  describe similar physical quantities (and have the same units),  $\phi_i^1$  and  $\phi_i$  from (23) do not have the same units. Both  $\phi_i^1(r)$  and  $\phi_i^1(r)$  will vanish as  $r$  tends towards infinity, since there is no applied electric field (see Section 7). However, the boundary conditions on the surface of the particle would be the same as those in (22).

The  $h^1(r)$  would satisfy an equation analogous to (26) as,

$$\mathcal{L} [\mathcal{L} [h^1(r)]] = g^1(r) \equiv \frac{e}{\eta r} \sum_i \frac{dn_i^0(r)}{dr} z_i \phi_i^1(r) \quad (\text{E.3})$$

that is true since in the  $U$  and  $E$  problem decomposition, O'Brien & White only modify the boundary conditions, and the general structure of the governing equations is left unaltered. The equation (E.3) can then be solved for  $h^1(r)$  with the boundary conditions in (E.2) to yield the following expression for the  $h^1(r)$  function:

$$\begin{aligned} h^1(r) = & -\frac{1}{30} \int_r^\infty (r^3 - 5rx^2) g^1(x) dx + \frac{r}{2} \\ & - \frac{3a}{4} \left[ 1 - \frac{2}{9a} \int_a^r x^3 g^1(x) dx \right. \\ & \quad \left. - \frac{1}{9} \int_a^\infty (a^2 - 3x^2) g^1(x) dx \right] \\ & + \frac{1}{60r^2} \left[ \int_a^\infty (5a^3 x^2 - 3a^5) g^1(x) dx \right. \\ & \quad \left. - \int_a^r 2x^5 g^1(x) dx + 15a^3 \right]. \end{aligned} \quad (\text{E.4})$$

In Appendix D, it was observed that the force acting on a particle is proportional to the constant term of the hydrodynamic function as  $r$  tends to infinity. A similar calculation can be performed, and the force  $F^1$  can be derived from (E.4) as,

$$F^1 = -6\pi\eta a U \left[ 1 - \frac{1}{9a} \int_a^\infty (a^3 + 2x^3 - 3ax^2) g^1(x) dx \right]. \quad (\text{E.5})$$

The first term in (E.5) is the Stokes drag term whereas the second term bears a close resemblance to the expression for mobility in (33). The only difference is that we are now considering the function,  $g^1(x)$ , which is only a part of the  $g(x)$  function relevant to electrophoresis.

### Appendix E.2. The $E$ -problem

The calculations for the computation of  $F^2$  is very similar to the calculations in the previous section used to compute  $F^1$ . The velocity field is now,

$$\mathbf{u}^2 = -\frac{2}{r} h^2(r) E \cos \theta \mathbf{n}_r + \frac{1}{r} \frac{d}{dr} [r h^2(r)] E \sin \theta \mathbf{n}_\theta. \quad (\text{E.6})$$

It is important to note that the velocity (and likewise the force) can now be written as proportional to the applied electric field,

E. The boundary conditions for  $h^2(r)$  are now given by,

$$h^2 = 0 = \frac{dh^2}{dr}, \quad r = a \quad (\text{E.7a})$$

$$h^2 \rightarrow \text{constant} \quad r \rightarrow \infty. \quad (\text{E.7b})$$

The boundary condition in (E.7b) for  $h^2$  is different from (32d) for  $h$ . Since far from the particle, the electrolyte is at rest relative to the particle,  $h^2(r)$  must be a constant term to leading order as  $r$  tends to infinity. The ion-potential function for the  $E$ -problem would be,  $\varphi_i^2(r, \theta) \equiv \phi_i^2(r)E \cos \theta$ . The boundary conditions for  $\phi_i^2$  would be the same as those specified for the complete electrophoresis problem in (32).

The  $h^2(r)$ , like  $h^1(r)$ , will satisfy an equation analogous to (26) with  $g^2(r)$  now defined in terms of  $\phi^2$ . The  $h^2(r)$  can thus be evaluated to yield the following result,

$$\begin{aligned} h^2(r) = & -\frac{1}{30} \int_r^\infty (r^3 - 5rx^2) g^2(x) dx \\ & - \frac{3a}{4} \left[ -\frac{2}{9a} \int_a^r x^3 g^2(x) dx - \frac{1}{9} \int_a^\infty (a^2 - 3x^2) g^2(x) dx \right] \\ & + \frac{1}{60r^2} \left[ \int_a^\infty (5a^3x^2 - 3a^5) g^2(x) dx - \int_a^r 2x^5 g^2(x) dx \right] \end{aligned} \quad (\text{E.8})$$

with the force,  $F^2$  given as,

$$F^2 = 6\pi\eta a E \left[ \frac{1}{9a} \int_a^\infty (a^3 + 2x^3 - 3ax^2) g^2(x) dx \right]. \quad (\text{E.9})$$

### Appendix E.3. Superposition

Under the assumption of linear electrophoresis, the total force acting on the particle will be,  $F^1 + F^2$ , which can be expressed as,

$$\begin{aligned} F^1 + F^2 = & -6\pi\eta a U \\ & + \frac{2\pi\eta}{3} \int_a^\infty (a^3 + 2x^3 - 3ax^2) \left( g^1(x) \frac{U}{E} + g^2(x) \right) dx. \end{aligned} \quad (\text{E.10})$$

Since the problem is linear in terms of the  $\varphi_i$  function, one can decompose,  $\varphi_i = \varphi_i^1 + \varphi_i^2$ . This would then imply that,

$$\phi_i(x) = \phi_i^1(x) \frac{U}{E} + \phi_i^2(x) \quad (\text{E.11a})$$

$$g(x) = g^1(x) \frac{U}{E} + g^2(x). \quad (\text{E.11b})$$

Hence, by comparing the second term in (E.10) to (33), we note that it is proportional to the mobility of the colloidal particle,  $\mu_m$ . Making use of the expression for mobility from Overbeek (47), equation (33) as well as the equilibrium condition,  $F^1 + F^2 = 0$ , we can obtain,

$$F^1 + F^2 = -6\pi\eta a U + 4\pi\epsilon E a \int_\infty^a \xi dx = 0. \quad (\text{E.12})$$

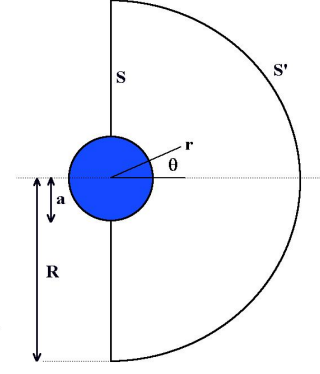


Figure F.7: A half-sphere with radius  $R$  surrounding the electrophoretic sphere with radius  $a$ . The half-sphere consists of a flat surface  $S$  at  $\theta = \pi/2$  and  $r > a$  and a (half) spherical surface  $S'$ . For an electrophoretic sphere, the surface  $S'$  does not give any contribution to the mass balance (provided  $R$  is big enough), resulting in the occurrence of a velocity maximum on  $S$ . For a 'normal' Stokes flow sphere there is a contribution on  $S'$  (even for very large  $R$ ) and hence no velocity maximum.

### Appendix F. The velocity maximum: a direct consequence of mass conservation

The velocity field for a sphere as presented in Fig. 2 not only exhibited a  $1/r^3$  behavior, but also showed a maximum  $u_\theta$  velocity, most clearly observable at  $\theta = \pi/2$ . We will now perform a mass balance on a system consisting of the sphere with radius  $a$ , a flat surface  $S$  and a hemi-spherical surface  $S'$  as illustrated in Fig. F.7 in order to explain this maximum.

Before investigating the full solution (48a, 48b), let us first investigate the limit of  $\kappa a \rightarrow \infty$ . Then  $\xi$  in (48a, 48b) decays so rapidly, that it is allowed to replace  $x$  by  $a$  and with the help of (47), the velocity of (46) is recovered. Suppose we are in a reference frame in which the sphere is moving with velocity  $U$ , then the flux entering the volume bounded by  $S$  and  $S'$  due to the moving sphere simply is  $\pi a^2 U$ . The terms in  $U \cos \theta$  and  $U \sin \theta$  in (46) are not present in this frame of reference and the total flux going through surface  $S$  (where  $\theta = \pi/2$ ) is:

$$\begin{aligned} \int_S \mathbf{u} \cdot \mathbf{n} dS = & - \int_a^\infty U \frac{a^3}{2r^3} 2\pi r dr \\ = & -a^3 U \pi \int_a^\infty \frac{1}{r^2} dr = -\pi a^2 U, \end{aligned} \quad (\text{F.1})$$

which is equal but opposite in sign to the flux generated by the moving sphere. The total flux is thus zero (as it should be). The contribution on the half spherical surface  $S'$  is zero, since  $\int_{S'} u_r dS = 0$  when  $R \rightarrow \infty$  and  $u_r$  decays as  $1/R^3$  (while the surface grows as  $R^2$ , resulting in a zero flux at large  $R$ ). Thus the contribution to the flux only originates from the surface  $S$ . This means that the  $u_\theta$  velocity must exhibit a maximum. This maximum can easily be calculated from (46) and is  $1/2U$  (or  $3/2U$  if we go back to the reference frame in which the sphere is stationary) and appears very close to  $r = a$ . For the  $\kappa a \rightarrow \infty$  limit, the double layer has a near zero thickness and thus the velocity decays from its maximum very rapidly to zero at  $r = a$ .

But will the same maximum velocity still occur for a general  $\kappa a$  value? In order to investigate this more general case, we take as the starting point Equation (48b). If we take again the frame of reference in which the sphere is moving, the flux entering the volume bounded by  $S$  and  $S'$  due to the moving sphere is still  $\pi a^2 U$ . The mass flux through surface  $S$  is given by

$$\int_S \mathbf{u} \cdot \mathbf{n} dS = - \int_a^\infty (u_\theta - U) 2\pi r dr \quad (\text{F.2})$$

The term  $u_\theta - U$  can be expressed as

$$\begin{aligned} u_\theta - U &= -\frac{2\epsilon E}{3\eta} \left[ \int_a^r \xi dx + \frac{1}{2r^3} \int_a^r x^3 \xi dx + \int_\infty^a \xi dx \right] \\ &= -\frac{2\epsilon E}{3\eta} \left[ \int_\infty^r \xi dx + \frac{1}{2r^3} \int_a^r x^3 \xi dx \right], \end{aligned} \quad (\text{F.3})$$

where (47) was used in the first equality to replace  $U$ . Then (F.2) becomes

$$\begin{aligned} \int_S \mathbf{u} \cdot \mathbf{n} dS &= \frac{4\pi\epsilon E}{3\eta} \int_a^\infty \left[ r \int_\infty^r \xi dx + \frac{1}{2r^2} \int_a^r x^3 \xi dx \right] dr \\ &= \frac{4\pi\epsilon E}{3\eta} \left\{ \left[ \frac{1}{2} r^2 \int_\infty^r \xi dx \right]_a^\infty - \int_a^\infty \frac{1}{2} r^2 \xi dr \right. \\ &\quad \left. + \left[ -\frac{1}{2r} \int_a^r x^3 \xi dx \right]_a^\infty - \int_a^\infty -\frac{1}{2x} x^3 \xi dx \right\} \end{aligned} \quad (\text{F.4})$$

where in the last equality we have used partial integration for both double integrals. The third term in the last expression is zero, and the second and last term cancel each other out. Then only the first term remains as

$$\int_S \mathbf{u} \cdot \mathbf{n} dS = -\frac{4\pi\epsilon E}{3\eta} \frac{1}{2} a^2 \int_\infty^a \xi dx = -\pi a^2 U. \quad (\text{F.5})$$

This is the same result as obtained before. The integral over the surface  $S'$  still does not give any contribution. Thus the sphere pushes a certain flux of fluid forward and exactly the opposite amount of fluid must leave through the surface  $S$ . This will automatically lead to a maximum in the velocity  $u_\theta$ . This looks apparently obvious, but this does not always need to be the case, for example, this is not the case for a classical Stokes flow sphere.

In summary, the special flow conditions around an electrophoretic sphere, the  $1/r^3$  behavior, cause a velocity maximum, something which does not occur in classical Stokes flow. This was shown here by doing a simple, (but tedious) mass balance.

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