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Electrophoresis of a colloidal sphere parallel to a dielectric plane

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An exact analytical study is presented for the electrophoretic motion of a dielectric sphere in the proximity of a large non-conducting plane. The applied electric field is parallel to the plane and uniform over distances comparable with the particle radius. The particle and plane surfaces are assumed uniformly charged and the thin-double-layer assumption is employed. The presence of the wall causes three basic effects on the electrophoretic velocity: first, an electro-osmotic flow of the suspending fluid exists owing to the interaction between the electric field and the charged wall; secondly, the electrical field lines around the particle are squeezed by the wall, thereby speeding up the particle; and thirdly, the wall enhances viscous retardation of the moving particle. In the analysis, corrections to Smoluchowski's classic equation for the electrophoretic velocity in an unbounded fluid are presented for various separation distances between the particle and the wall. Of particular interest is the electrophoresis for *small* gap widths, in which case the net effect of the plane wall is to *enhance* the particle velocity. The particle mobility can be increased by as much as 23 % when the surface-to-surface spacing is about 0.5 % of the sphere radius. For the case of moderate to large separations, the electrophoretic velocity of the particle is reduced by the wall, but this effect is much weaker than for sedimentation. In addition to the translational migration, the electrophoretic sphere rotates at the same time in the direction *opposite* to that which would occur if the sphere sedimented parallel to a plane wall. The ratio of rotational-to-translational speeds of the sphere is in general *larger* for electrophoresis than for sedimentation.

1. Introduction

When a colloidal particle suspended in an electrolyte solution is subjected to an external electric field, the particle will begin to move. This has been termed electrophoresis and used in a variety of applications. Ordinarily, the electrophoretic motion is examined in an infinite fluid in which the undisturbed electric field is constant. If the local radii of curvature of an insulating particle of arbitrary shape are large compared with the thickness of the electrical double layer, the electrophoretic velocity U_0 is given by Smoluchowski's relation (Morrison 1970; Dukhin & Derjaguin 1974; Hunter 1981):

$$U_0 = \left(\frac{\epsilon \zeta_p}{4\pi\eta}\right) E_\infty. \tag{1}$$

In this equation, ϵ is the fluid permittivity, η the fluid viscosity, ζ_p the zeta potential of the particle surface and E_∞ the applied electric field. The ratio U_0/E_∞, which equals the term in parenthesis, is known as the electrophoretic mobility of the particle.

In many applications of electrophoresis colloidal particles are not isolated and will move in the presence of neighbouring particles and/or surfaces. The coupled electrophoretic motions for two dielectric spheres in the limit $\kappa a \to \infty$ were computed by Reed & Morrison (1976), where κ is the Debye screening parameter and a is the particle radius. Considering a situation encountered in electro-deposition of colloids at metallic electrodes, Morrison & Stukel (1970) solved the problem of electrophoresis of an insulating sphere normal to a conducting plane using spherical bipolar coordinates. Recently Keh & Anderson (1985) examined electrophoretic motions of a charged non-conducting sphere in the proximity of various rigid boundaries. Using a method of reflections, they determined the particle velocity for a constant applied electric field in increasing powers of λ up to $O(\lambda^6)$, where λ is the ratio of particle radius to distance from the boundary. Their results showed that boundary effects on electrophoresis are weak for small to moderate values of λ, say $\lambda \leqslant 0.5$.

In the present paper, our objective is to obtain an exact solution to the problem of the electrophoretic motion of a single colloidal sphere parallel to a non-conducting plane. Both the particle and wall surfaces are assumed uniformly charged and the applied electric field is assumed constant over distances comparable with the particle radius. The rotation of the electrophoretic particle induced by the plane is allowed. An important assumption is that the Debye screening length is much smaller than the particle radius and the surface-to-surface spacing between the particle and the wall. Thus, the effect considered in the analysis is not due to any interaction between the double layers around the particle and adjacent to the wall.

2. Analysis

Consider the electrophoretic motion of an insulating sphere of radius a in the direction parallel to an infinite dielectric plane located at a distance b from the sphere centre. The applied electric field $E_\infty \boldsymbol{e}_x$, acting tangential to the plane wall, is assumed constant over distances comparable with the particle radius. $\boldsymbol{e}_x$ is a unit vector in Cartesian coordinates. Our purpose is to determine the correction to Smoluchowski's equation (1) for the particle due to the presence of the plane.

For conveniently satisfying the boundary conditions at solid surfaces, an orthogonal curvilinear coordinate system (ξ, Ψ, Φ) known as spherical bipolar coordinates, shown in figure 1, is utilized to solve this problem. This coordinate system is related to cylindrical polar coordinates (ρ, z, Φ), which share the same origin as the Cartesian coordinate system, by the relations (Morse & Feshbach 1953; Happel & Brenner 1983):

$$\rho = \frac{c \sin \Psi}{\cosh \xi - \cos \Psi}, \tag{2a}$$

$$z = \frac{c \sinh \xi}{\cosh \xi - \cos \Psi}, \tag{2b}$$

where c is a characteristic length in the bispherical coordinate system.

The coordinate surfaces $\xi =$ constant correspond to a family of coaxial spheres whose centres lie along the z-axis. The special case $\xi = 0$ is a sphere of infinite radius and represents the plane at $z = 0$. $\xi = \xi_0$ corresponds to the boundary of the sphere of radius $a = c \operatorname{cosech} \xi_0$, with its centre at the point $z = b = c \coth \xi_0$ and $\rho = 0$. The

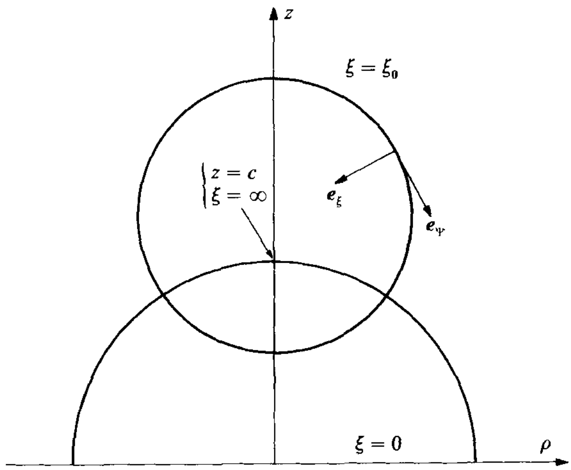

FIGURE 1. Geometrical sketch of the electrophoretic system.

relation between ξ_0 and λ, the ratio of particle radius to the distance of the particle centre from the plane wall, is

$$\lambda = a/b = \operatorname{sech}\xi_0. \tag{3}$$

To determine the electrophoretic velocity of the insulating particle near the charged plane, it is necessary to ascertain the electrical potential and fluid velocity distributions.

2.1. *Electrical potential distribution*

Since the fluid outside the thin double layer is neutral and is assumed to be of constant conductivity, the electrostatic equation governing the potential distribution $\phi(\boldsymbol{x})$ is Laplace's equation:

$$\nabla^2\phi = 0. \tag{4}$$

The boundary conditions require that the potential gradient far away from the particle approach the uniform applied electric field and that the normal component of the current flux at each surface be identically zero, since both the plane wall and the particle are insulating. Thus,

$$\boldsymbol{e}_\xi\cdot\nabla\phi = 0 \quad \text{at } \xi = 0, \tag{5a}$$

$$\boldsymbol{e}_\xi\cdot\nabla\phi = 0 \quad \text{at } \xi = \xi_0, \tag{5b}$$

$$\phi \to -E_\infty x \quad \text{as } (\rho^2+z^2)^{\frac{1}{2}} \to \infty, \tag{5c}$$

where $x = \rho\cos\Phi$.

A general solution to Laplace's equation suitable for satisfying these boundary conditions is (Morse & Feshbach 1953; Reed & Morrison 1976)

$$\phi = cE_\infty(\cosh\xi-\cos\Psi)^{\frac{1}{2}}\sum_{n=1}^{\infty}\{R_n\sinh(n+\tfrac{1}{2})\xi+S_n\cosh(n+\tfrac{1}{2})\xi\}$$
$$\times\sin\Psi P_n'(\cos\Psi)\cos\Phi-cE_\infty\sin\Psi(\cosh\xi-\cos\Psi)^{-1}\cos\Phi, \tag{6}$$

where P_n is the Legendre polynomial of order n and the prime denotes differentiation with respect to $\cos\Psi$. Boundary condition (5c) is immediately satisfied by a solution of this form.

Utilizing the expansion, which can be derived using the generating function of the Legendre polynomials,

$$(\cosh \xi - \cos \Psi)^{-\frac{3}{2}} = 2^{\frac{3}{2}} \sum_{n=0}^{\infty} \exp\left[-(n+\tfrac{1}{2})\xi\right] P'_n(\cos \Psi), \tag{7}$$

as well as the recurrence relations of the Legendre polynomials, application of the boundary conditions (5*a*) and (5*b*) yields the following relations for the coefficients:

$$R_n = 0, \tag{8a}$$

and

$$S_{n+1}(n+2)\sinh(n+\tfrac{3}{2})\xi_0 + S_{n-1}(n-1)\sinh(n-\tfrac{1}{2})\xi_0 - S_n \times \{n \sinh(n-\tfrac{1}{2})\xi_0 + (n+1)\sinh(n+\tfrac{3}{2})\xi_0\} = 2^{\frac{5}{2}} \exp\left[-(n+\tfrac{1}{2})\xi_0\right] \sinh \xi_0. \tag{8b}$$

Owing to the geometrical symmetry, this electric field is identical to that about two equal dielectric spheres when the electric field $E_\infty \boldsymbol{e}_x$ is imposed perpendicular to their line of centres. This case was solved by Reed & Morrison (1976) in the analysis of the electrophoretic motion of two spheres. Since coefficients S_n decrease as n becomes large, the recursion relation (8*b*) can be solved from the first N equations, provided that N is sufficiently large that S_{N+1} is negligible.

2.2. *Fluid velocity distribution*

With knowledge of the solution for the electric field, $\boldsymbol{E}(\boldsymbol{x}) = -\boldsymbol{\nabla}\phi$, we can now proceed to find the fluid velocity distribution. Owing to the low velocities encountered in electrokinetic flows, the fluid motion outside the thin double layer is governed by the Stokes equations:

$$\eta \nabla^2 \boldsymbol{v} - \boldsymbol{\nabla} p = \boldsymbol{0}, \tag{9a}$$

$$\boldsymbol{\nabla} \cdot \boldsymbol{v} = 0, \tag{9a}$$

where $\boldsymbol{v}(\boldsymbol{x})$ is the fluid velocity and p is the pressure.

Because the electric field interacts with the double layer at the non-conducting solid surface to produce a relative tangential fluid velocity at the outer edge of the double layer and a uniform electro-osmotic flow far away from the particle, the boundary conditions are the following (Keh & Anderson 1985):

$$\boldsymbol{v} = \frac{\epsilon \zeta_{\mathrm{w}}}{4\pi\eta} \boldsymbol{\nabla}\phi \quad \text{at } \xi = 0, \tag{10a}$$

$$\boldsymbol{v} = \boldsymbol{U} + \boldsymbol{\Omega} \times \boldsymbol{r} + \frac{\epsilon \zeta_{\mathrm{p}}}{4\pi\eta} \boldsymbol{\nabla}\phi \quad \text{at } \xi = \xi_0, \tag{10b}$$

$$\boldsymbol{v} \rightarrow \boldsymbol{v}_\infty = -\frac{\epsilon \zeta_{\mathrm{w}}}{4\pi\eta} E_\infty \boldsymbol{e}_x \quad \text{as } (\rho^2 + z^2)^{\frac{1}{2}} \rightarrow \infty, \tag{10c}$$

where ζ_{p} and ζ_{w} are the zeta potentials of the particle and of the wall respectively, $\boldsymbol{r}$ is the relative position vector about the sphere centre, and $\boldsymbol{U}$ and $\boldsymbol{\Omega}$ are respectively the translational and rotational velocities of the particle, to be determined. Equation (10) provides the coupling between the electric field and the fluid motion, and the potential distribution $\phi(\boldsymbol{x})$ is given by (6) with coefficients determined from (8). Note that the normal component of $\boldsymbol{\nabla}\phi$ vanishes at the surfaces of the particle and wall.

Since the particle 'surface' encloses a neutral body (i.e. charged interface plus diffuse ions) and the particle is freely suspended in the fluid, the electric field produces no net force or couple on the particle. Thus the force and torque exerted by the fluid on the particle surface must vanish:

$$\boldsymbol{F} = \iint_{\substack{\text{particle}\\ \text{surface}}} \boldsymbol{n}\cdot\boldsymbol{\pi}\,\mathrm{d}S = \boldsymbol{0}, \tag{11a}$$

$$\boldsymbol{T} = \iint_{\substack{\text{particle}\\ \text{surface}}} \boldsymbol{r}\times(\boldsymbol{n}\cdot\boldsymbol{\pi})\,\mathrm{d}S = \boldsymbol{0}, \tag{11b}$$

where $\boldsymbol{\pi}$ is the stress tensor and $\boldsymbol{n}$ is the unit normal to the sphere pointing into the fluid phase. After solving (9) and (10), one can evaluate $\boldsymbol{U}$ and $\boldsymbol{\Omega}$ by satisfying (11).

As both the governing equations and the boundary conditions are linear, the total flow can be decomposed into three flows. First, we consider a sphere translating parallel to the plane wall with velocity $\boldsymbol{U}$ and with no angular velocity or tangential electrokinetic velocity at the particle surface, while the plane surface and the fluid far from the particle are moving with a velocity equal to $\boldsymbol{v}_\infty$. Both $\boldsymbol{U}$ and $\boldsymbol{v}_\infty$ are in the direction parallel to $\boldsymbol{e}_x$. This flow is the Stokes flow of a sphere moving parallel to a plane and has been studied by O'Neill (1964). He found that the force and couple acting on the sphere are given by

$$\boldsymbol{F}_1 = -6\pi\eta a(\boldsymbol{U}-\boldsymbol{v}_\infty)\beta_1, \tag{12a}$$

$$\boldsymbol{T}_1 = 8\pi\eta a^2(\boldsymbol{U}-\boldsymbol{v}_\infty)\cdot\boldsymbol{e}_x\boldsymbol{e}_y\alpha_1, \tag{12b}$$

where β_1 and α_1 are the correction factors to Stoke's law due to the presence of the plane wall. These values depend upon λ, the ratio of the sphere radius to the distance of the sphere centre from the wall, and were numerically determined.

Next, we consider the fluid motion caused by the rotation of a sphere about an axis parallel to a nearby plane wall bounding a semi-infinite fluid at rest at infinity. The angular velocity at the sphere surface is $\boldsymbol{\Omega}$ which is in the direction normal to $\boldsymbol{e}_x$. The Stokes equations for this flow were solved by Dean & O'Neill (1963) and the force and couple exerted by the fluid on the sphere can be expressed as

$$\boldsymbol{F}_2 = 6\pi\eta a^2\boldsymbol{\Omega}\cdot\boldsymbol{e}_y\boldsymbol{e}_x\beta_2, \tag{13a}$$

$$\boldsymbol{T}_2 = -8\pi\eta a^3\boldsymbol{\Omega}\alpha_2, \tag{13b}$$

where the wall-correction factors β_2 and α_2 also depend upon the value of λ. Although Dean & O'Neill's theoretical analysis was legitimate, their numerical computations were incorrect, as pointed out by Goldman, Cox & Brenner (1967).

Finally, we consider the flow of a stationary sphere near a stationary plane wall with an electrokinetic tangential velocity at both solid surfaces, namely,

$$\boldsymbol{v} = \frac{\epsilon\zeta_{\mathrm{w}}}{4\pi\eta}\nabla\phi - \boldsymbol{v}_\infty \quad \text{at } \xi = 0, \tag{14a}$$

$$\boldsymbol{v} = \frac{\epsilon\zeta_{\mathrm{p}}}{4\pi\eta}\nabla\phi \qquad \text{at } \xi = \xi_0, \tag{14b}$$

$$\boldsymbol{v} \rightarrow \boldsymbol{0} \qquad \text{as } (\rho^2+z^2)^{\frac{1}{2}} \rightarrow \infty. \tag{14c}$$

Here we use the term 'surface' to mean outer edge of the double layer. Superposing this velocity field with those of wall-bounded Stokes flows caused by a translating sphere with velocity $(\boldsymbol{U}-\boldsymbol{v}_\infty)$ and by a rotating sphere with angular velocity $\boldsymbol{\Omega}$ will yield the total velocity field produced in the electrophoretic motion of a dielectric sphere parallel to a non-conducting plane wall. By obtaining expressions for the force and torque exerted on the stationary sphere, individually adding these to the forces and torques given by (12) and (13) and equating the results to zero, Smoluchowski's equation with wall corrections will result. This procedure satisfies the requirement that the applied electric field produces no net force and torque on the particle.

To find the drag and couple acting on the stationary sphere with a tangential velocity distribution, analytical techniques of the corresponding bounded Stokes' flow will be used. A general solution of (9*a*) satisfying the boundary condition (14*c*) was given by O'Neill (1964):

$$v_\rho = \frac{1}{2c} U_0[\rho Q_1 + c(V_2 + V_0)] \cos\Phi, \tag{15a}$$

$$v_z = \frac{1}{2c} U_0 [zQ_1 + 2cW_1] \cos\Phi, \tag{15b}$$

$$v_\Phi = \tfrac{1}{2} U_0 [V_2 - V_0] \sin\Phi, \tag{15c}$$

$$p = \frac{1}{c}\eta U_0 Q_1 \cos\Phi, \tag{15d}$$

where U_0 is a characteristic velocity and is taken to be $\epsilon\zeta_\mathrm{p} E_\infty/4\pi\eta$ here for convenience.

In the above equations, Q_1, V_0, V_2 and W_1 are scalar auxiliary functions of ρ and z (or of ξ and Ψ), with the following expansion forms:

$$W_1 = (\cosh\xi - \cos\Psi)^{\frac{1}{2}} \sin\Psi \sum_{n=1}^{\infty} [A_n \cosh(n+\tfrac{1}{2})\xi + B_n \sinh(n+\tfrac{1}{2})\xi]\, P'_n(\cos\Psi), \tag{16a}$$

$$Q_1 = (\cosh\xi - \cos\Psi)^{\frac{1}{2}} \sin\Psi \sum_{n=1}^{\infty} [C_n \cosh(n+\tfrac{1}{2})\xi + D_n \sinh(n+\tfrac{1}{2})\xi]\, P'_n(\cos\Psi), \tag{16b}$$

$$V_0 = (\cosh\xi - \cos\Psi)^{\frac{1}{2}} \sum_{n=0}^{\infty} [E_n \cosh(n+\tfrac{1}{2})\xi + F_n \sinh(n+\tfrac{1}{2})\xi]\, P_n(\cos\Psi), \tag{16c}$$

$$V_2 = (\cosh\xi - \cos\Psi)^{\frac{1}{2}} \sin^2\Psi \sum_{n=2}^{\infty} [G_n \cosh(n+\tfrac{1}{2})\xi + H_n \sinh(n+\tfrac{1}{2})\xi]\, P''_n(\cos\Psi). \tag{16d}$$

The coefficients of these expansions remain to be determined from the boundary conditions as well as the equation of continuity.

Substituting the solution for the electrical potential distribution, (6) and (8), as well as the solution for the fluid motion, (15) and (16), into the continuity equation (9*b*) and the boundary conditions (14*a*, *b*), it is found that the coefficients of the auxiliary functions must satisfy the following algebraic recursion formulae:†

$$\sum_{k=1}^{8} \sum_{j=n-2}^{n+2} c_{ijk} \aleph_j^{(k)} = d_i, \quad i = 1, 2, \ldots, 8, \tag{17}$$

where $\aleph_j^{(k)}$ denotes the coefficients A_j, B_j, C_j, D_j, E_j, F_j, G_j and H_j for k equal to the integers from 1 to 8 respectively; c_{ijk} and d_i are functions of ξ_0, $\zeta_\mathrm{w}/\zeta_\mathrm{p}$, and n. The

† These formulae are lengthy: the full versions are available on request from either the editor or the authors.

recurrence relations of the Legendre polynomials as well as expansions derived from the generating function of the Legendre polynomials were used to expand the boundary conditions. Because the coefficients become small with large n, simultaneous solution of (17) for the first N sets yields $8N$ coefficients, thereby determining the velocity distribution for the fluid.

The force on the sphere due to the electrokinetic fluid motion can be evaluated by direct surface integration using the first part of (11a) together with the coefficients of the auxiliary functions (16) for the velocity and pressure distributions (15), and is given by (O'Neill 1964):

$$\boldsymbol{F}_3 = 6\pi\eta a U_0 \boldsymbol{e}_x(\beta_p + \gamma\beta_w), \tag{18a}$$

with

$$\beta_p + \gamma\beta_w = -\frac{\sqrt{2}}{6}\sinh\xi_0 \sum_{n=0}^{\infty} [(E_n+F_n)+n(n+1)(C_n+D_n)], \tag{18b}$$

and $\gamma = \zeta_w/\zeta_p$. The correction factors β_p and β_w can be separately determined from (18b) by taking ζ_w and ζ_p equal to zero, in turn.

The torque about the sphere centre exerted by the fluid on the stationary sphere must be evaluated by surface integration using (11b). In the Appendix we show that, for this electrokinetic case,

$$\boldsymbol{T}_3 = -8\pi\eta a^2 U_0 \boldsymbol{e}_y(\alpha_p + \gamma\alpha_w), \tag{19a}$$

with

$$\alpha_p + \gamma\alpha_w = -\frac{\sqrt{2}}{8}\sinh^2\xi_0 \sum_{n=0}^{\infty} [n(n+1)[2A_n+2B_n+\coth\xi_0(C_n+D_n)] - (2n+1-\coth\xi_0)(E_n+F_n)]. \tag{19b}$$

The correction factors α_p and α_w can be determined in a similar way to those of β_p and β_w.

2.3. *Derivation of the particle velocity*

Since the net force and net torque acting on the electrophoretic particle must vanish to fulfill the requirement of (11), we have

$$\boldsymbol{F}_1 + \boldsymbol{F}_2 + \boldsymbol{F}_3 = \boldsymbol{0}, \tag{20a}$$

and

$$\boldsymbol{T}_1 + \boldsymbol{T}_2 + \boldsymbol{T}_3 = \boldsymbol{0}. \tag{20b}$$

Here the individual forces are presented in (12a), (13a) and (18), while the couples are given by (12b), (13b) and (19). To determine the translational velocity $\boldsymbol{U}$ and angular velocity $\boldsymbol{\Omega}$ of the particle, the above two equations must be solved simultaneously after the substitution of (12), (13), (18) and (19) into them. The results are

$$\boldsymbol{U} = \frac{1}{\alpha_1\beta_2 - \alpha_2\beta_1}\{\alpha_p\beta_2 - \alpha_2\beta_p + \gamma[(\alpha_w - \alpha_1)\beta_2 - \alpha_2(\beta_w - \beta_1)]\}\frac{\epsilon\zeta_p}{4\pi\eta}E_\infty \boldsymbol{e}_x, \tag{21a}$$

$$a\boldsymbol{\Omega} = \frac{1}{\alpha_1\beta_2 - \alpha_2\beta_1}\{\alpha_p\beta_1 - \alpha_1\beta_p + \gamma[(\alpha_w - \alpha_1)\beta_1 - \alpha_1(\beta_w - \beta_1)]\}\frac{\epsilon\zeta_p}{4\pi\eta}E_\infty \boldsymbol{e}_y. \tag{21b}$$

Numerical calculations for various values of the zeta-potential ratio γ and the dimensionless separation parameter λ find that the following relations always exist:

$$\beta_p = \beta_1 - \beta_w, \quad \alpha_p = \alpha_1 - \alpha_w. \tag{22a, b}$$

Namely, the wall-corrected electrophoretic velocity of the sphere has the following two parts:

$$U = \left(\frac{\alpha_2 \beta_p - \alpha_p \beta_2}{\alpha_2 \beta_1 - \alpha_1 \beta_2}\right) \frac{\epsilon E_\infty}{4\pi\eta} (\zeta_p - \zeta_w)\, e_x. \tag{23a}$$

$$a\Omega = -\left(\frac{\alpha_1 \beta_p - \alpha_p \beta_1}{\alpha_1 \beta_2 - \alpha_2 \beta_1}\right) \frac{\epsilon E_\infty}{4\pi\eta} (\zeta_p - \zeta_w)\, e_y. \tag{23b}$$

The result of (23*a*), that the wall does not deflect the direction of electrophoresis and the electrophoretic mobility is proportional to the zeta-potential difference between the particle and the wall, is consistent with the analytical derivation from the method of reflections assuming that the particle translates without rotation (Keh & Anderson 1985). The existence of the parallel plane causes the particle to rotate in the direction normal to the applied electric field and parallel to the wall; its magnitude is also proportional to the zeta-potential difference, as shown in (23*b*).

3. Results and discussion

The coefficients of the electrical-potential distribution (6) and the velocity field (15) and (16) have been calculated for different values of λ and γ using a digital computer. For the case of $\lambda = 0.995$, N equal to about 200 was employed such that the $(N+1)$th terms of these coefficients are negligible and increases in N do not change the calculated values appreciably. Numerical results for the wall-corrected reduced electrophoretic mobility $(\alpha_2\beta_p - \alpha_p\beta_2)/(\alpha_2\beta_1 - \alpha_1\beta_2)$ and the wall-induced non-dimensional angular velocity $-(\alpha_1\beta_p - \alpha_p\beta_1)/(\alpha_1\beta_2 - \alpha_2\beta_1)$, for various values of λ, are presented in the first, second and third columns of table 1 and depicted in figure 2. For the motion of a sphere on which a constant force Fe_x (e.g. a gravitational field) is applied parallel to a plane wall, the exact results of the translational and rotational velocities were developed using bispherical coordinates by O'Neill (1964) and Dean & O'Neill (1963). The asymptotic lubrication-theory-type solutions for small gap widths have also been obtained (O'Neill & Stewartson 1967; Goldman *et al.* 1967). The Stokes'-law correction for various separation distances was computed in the absence of external torques on the sphere and the results are given in the fourth and last columns of table 1 for a comparison.

The following important features of table 1 and figure 2 should be noted:

(i) For all $\lambda \lesssim 0.77$, the electrophoretic mobility is a monotonic decreasing function of λ; beyond this region, the mobility *increases* with increasing λ and values of $4\pi\eta/\epsilon E_\infty(\zeta_p - \zeta_w)$ *greater* than unity are observed for $\lambda \gtrsim 0.908$. This interesting phenomenon is understandable given that the wall effect on the interaction between particle and electric field tends to enhance the translational electrophoretic velocity, while the fluid dynamics are affected in a way that tends to slow down the particle (Keh & Anderson 1985). The second effect is stronger for the case $\lambda \lesssim 0.908$, and hence the net effect is a retardation of the particle velocity. For values of $\lambda \gtrsim 0.908$, the effect of the wall on the electric field is stronger than that on the viscous drag, and the net effect is to speed up the particle. The reason that the electrical force driving the motion is enhanced by the plane wall is obvious from the crowding of the electric field lines to squeeze between the particle and the wall. Note that, in the limit of $\kappa a \to \infty$, the particle velocity for the case $\lambda = 0.995$ can be as much as 23% higher than the Smoluchowski's result with the boundary being far away from the particle.

(ii) Concerning the translational velocity of the particle, the wall effect on

	electrophoresis		sedimentation	
λ	$\dfrac{4\pi\eta U}{\epsilon(\zeta_p-\zeta_w)E_\infty}$	$\dfrac{4\pi\eta a\Omega}{\epsilon(\zeta_p-\zeta_w)E_\infty}$	$\dfrac{6\pi\eta aU}{F}$	$\dfrac{6\pi\eta a^2\Omega}{F}$
0	1.000000	0	1.000000	0
0.1	0.999939	−0.000019	0.943857	0.000009
0.2	0.999532	−0.000301	0.888209	0.000123
0.3	0.998534	−0.001535	0.833155	0.000559
0.4	0.996836	−0.004922	0.778389	0.001587
0.5	0.994486	−0.012333	0.723212	0.003488
0.6	0.991723	−0.026692	0.666452	0.006540
0.65	0.990348	−0.037903	0.636911	0.008586
0.7	0.989149	−0.053007	0.606131	0.011033
0.75	0.988379	−0.073462	0.573570	0.013930
0.8	0.988532	−0.101637	0.538383	0.017339
0.85	0.990704	−0.141886	0.499101	0.021347
0.9	0.997886	−0.203891	0.452715	0.026079
0.93	1.008469	−0.261934	0.418558	0.029342
0.95	1.022313	−0.318899	0.390761	0.031720
0.97	1.050854	−0.408902	0.354974	0.034240
0.98	1.080279	−0.483419	0.330917	0.035493
0.99	1.145361	−0.618316	0.296559	0.036534
0.995	1.230600	−0.765327	0.268673	0.036638

TABLE 1. Comparison of the normalized translational and rotational velocities of a sphere moving parallel to a plane for the cases of electrophoresis and sedimentation

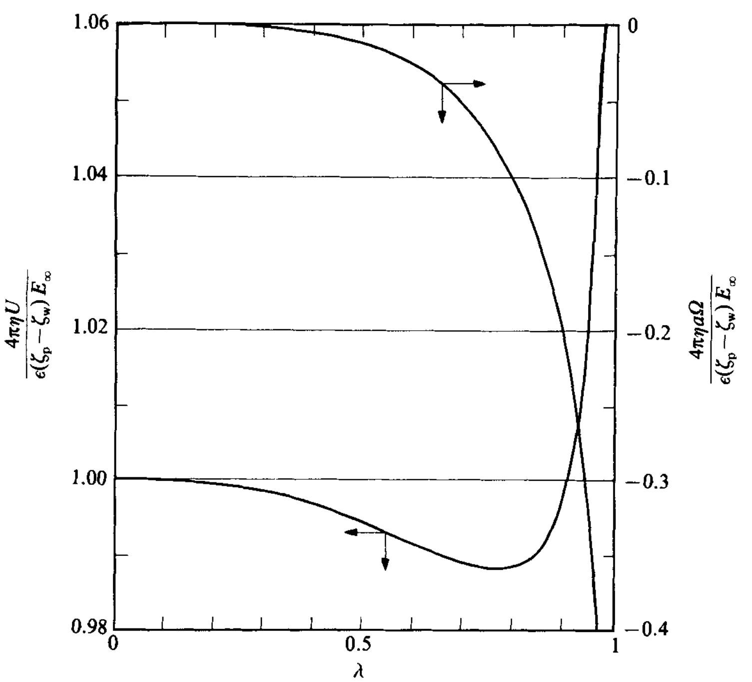

FIGURE 2. Plot of the normalized electrophoretic mobility and angular velocity versus the ratio of particle radius to distance from the wall.

electrophoresis is much weaker than for sedimentation, because the disturbance to the fluid velocity field caused by the electrophoretic particle in an unbounded fluid decays (as r^{-3}, where r is the distance from the particle centre) faster than that caused by a Stokeslet (as r^{-1}) moving under the influence of a body force (Reed & Morrison 1976; Keh & Anderson 1985). The lowest value of the non-dimensional velocity for electrophoresis is about 0.988 (only 1.2% lower than that in an unbounded fluid) which occurs as $\lambda \sim 0.77$, while the reduced mobility for a sedimenting particle in this case is as low as about 0.56.

(iii) The electrophoretic sphere will rotate about an axis which is perpendicular to the direction of applied electric field and parallel to the plane wall. It is particularly interesting that the direction of rotation is *opposite* to that which would occur if the sphere migrated in the same direction but under a body-force field. This behaviour can be explained as follows. The tangential electrokinetic velocity at the sphere 'surface' is larger for a point on the near side than for a corresponding position on the far side to the parallel plane, since the local electric field is intensified for the gap between the particle and the wall. The difference in the frictional drag between the two sides caused by the fluid adjacent to the sphere surface (or, more precisely, to the outer edge of the double layer) exerts a couple on the sphere in the direction opposite to that of the couple caused by the hydrodynamic interaction between a translating sphere and the parallel plane. The numerical results listed in the third column of table 1 show that the electrokinetic effect on the rotation of particle is *stronger* than the pure viscous effect for all values of λ; the difference in magnitude between these two effects increases when the gap thickness decreases. Generally speaking, the magnitude of particle angular velocity induced by the wall relative to a translational velocity is larger for electrophoresis than for sedimentation.

Over the past two decades, quite a few studies have been presented concerning the hydrodynamic interactions between two force-free moving particles (Reed & Morrison 1976; Meyyappan & Subramanian 1984; Anderson 1985*b*) and the migration of a single force-free particle near a parallel plane wall (Keh & Anderson 1985; Meyyappan & Subramanian 1987). All of them have assumed that the particles translate without rotation. One might question the validity of this assumption and determine if the rotation of particles significantly affects their translational velocity. The electrophoretic velocity of a sphere, assuming *no* rotation, near a parallel plane for various values of λ was calculated using the same procedures but taking $\boldsymbol{\Omega}$ equal to zero; the numerical results are listed in the first and second columns of table 2. The corresponding Stokes' law correction for a translating sphere, without rotation, is also given in the last column of table 2 to compare the wall effects. Comparing values in tables 1 and 2, we find that the assumption that the particle translates without rotation gives too *large* a correction to electrophoresis, while for sedimentation this approximation underestimates the wall correction; the error is in general larger in electrophoresis (5.8% for $\lambda = 0.99$) than in sedimentation (-1.3% for $\lambda = 0.99$).

Using a method of reflection, Keh & Anderson (1985) obtained the following power series expression in λ for the electrophoretic motion of a non-rotating sphere parallel to a plane wall:

$$\boldsymbol{U} = [1-\tfrac{1}{16}\lambda^3+\tfrac{1}{8}\lambda^5-\tfrac{31}{256}\lambda^6+O(\lambda^8)]\frac{\epsilon}{4\pi\eta}(\zeta_p-\zeta_w)E_\infty \boldsymbol{e}_x. \tag{24}$$

The coefficient inside the square brackets is listed for various values of λ in the third column of table 2. It can be found that the solution from the method of reflections shown in (24) agrees very well with the exact result even for λ values as large as 0.7,

λ	$\dfrac{4\pi\eta U}{\epsilon(\zeta_p-\zeta_w)E_\infty}$ (exact solution)	$\dfrac{4\pi\eta U}{\epsilon(\zeta_p-\zeta_w)E_\infty}$ (asymptotic solution)	$\dfrac{6\pi\eta a U}{F}$
0	1.000000	1.000000	1.000000
0.1	0.999939	0.999939	0.943857
0.2	0.999532	0.999532	0.888209
0.3	0.998535	0.998528	0.833155
0.4	0.996846	0.996784	0.778385
0.5	0.994546	0.994202	0.723195
0.6	0.991973	0.990570	0.666391
0.65	0.990825	0.998207	0.636803
0.7	0.990031	0.985325	0.605947
0.75	0.989979	0.981744	0.573267
0.8	0.991416	0.977216	0.537891
0.85	0.995969	0.971410	0.498309
0.9	1.007962		0.451426
0.93	1.024169		0.416799
0.95	1.044453		0.388559
0.97	1.084734		0.352137
0.98	1.125057		0.327629
0.99	1.211846		0.292631
0.995	1.322681		0.264265

TABLE 2. The normalized electrophoretic mobility (as computed from the exact bipolar coordinate solution and the asymptotic method-of-reflection solution) and Stokes mobility for the motion of a sphere translating *without* rotation parallel to a plane

the error in this case still being less than 0.5%. However, the exciting result that the particle mobility increases when the gap between the particle and the wall gets small is not predicted by the asymptotic expression up to $O(\lambda^6)$.

4. Concluding remarks

The electrophoretic velocity of a dielectric sphere parallel to a charged non-conducting plane in the limit $\kappa a \to \infty$ is obtained in this work. For an open system with no pressure gradients far from the particle, a net electro-osmotic flow is allowed to occur and the direction of particle motion, either translation or rotation, is determined by the difference in zeta potentials $(\zeta_p - \zeta_w)$. The wall effect on electrophoresis is to slow the particle velocity for large separation distances, but this retardation is much weaker than for sedimentation. Peculiarly, the electrophoretic velocity of the particle can be enhanced by the neighbouring plane when the gap widths become small, as shown in figure 2. This behaviour is understandable because the wall affects the electrical force and the viscous force in opposite directions and competition between these two forces determines whether the net wall effect is to speed up or to slow down the particle motion. A scientific implication of this result is that a planar surface can stabilize a particle, with strong viscous forces preventing it from moving perpendicular to the planar surface (Maude 1961; Brenner 1961; Cox & Brenner 1967), yet allow it relative freedom in electrophoretic motion parallel to the surface.

Throughout this work we have assumed that $\kappa a \to \infty$ with ζ_p and ζ_w constant on the solid/fluid interfaces. The fluid velocity field for electro-osmotic flows induced by non-uniformly charged walls can be complicated (Anderson & Idol 1985), and dielectrophoresis may occur when ζ_p is not uniform (Anderson 1985*a*). For the electrophoresis of spherical particles of finite κa in unbounded fluids, analytic expressions and numerical results to correct Smoluchowski's relation have been obtained (O'Brien & Hunter 1981; O'Brien & White 1978).

Similar to electrophoresis, another example of 'phoretic motion' is the thermocapillary migration of fluid particles in a second fluid possessing a temperature gradient. The coupled thermocapillary motions of two gas bubbles (Meyyappan & Subramanian 1984) and two fluid droplets (Anderson 1985*b*) have been analysed, and, more recently, the effect of a plane surface on thermal migration of a gas bubble was studied (Meyyappan & Subramanian 1987). Their results showed that the thermocapillary mobility of a bubble parallel to a plane decreases as a strictly monotonic function with λ; this effect is also weaker than for a bubble in motion due to a body force. A comparison between their computations and our results reveals that the wall effect is in general even weaker in electrophoresis than in thermocapillary motions.

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Appendix: Torque exerted on a sphere with arbitrary surface tangential velocity distribution

A particular solution of the Stokes equations for a steady motion of fluid of constant density and viscosity flowing around a sphere referred to spherical coordinates (r, θ, Φ) with the centre of the sphere as origin is (Dean & O'Neill 1963)

$$v_r = U_0 V_r \cos\Phi, \quad v_\theta = U_0 V_\theta \cos\Phi, \quad v_\Phi = U_0 V_\Phi \sin\Phi. \qquad \text{(A 1}\,a, b, c)$$

Here we take the characteristic velocity U_0 equal to $\epsilon\zeta_p E_\infty/4\pi\eta$, the electrophoretic velocity of a particle in an unbounded fluid of viscosity η and dielectric constant ϵ, consistent with (15).

Substituting (A 1) into the first part of (11*b*) in which

$$\boldsymbol{\pi} = -p\boldsymbol{I} + \eta[\nabla \boldsymbol{v} + (\nabla \boldsymbol{v})^{\mathrm{T}}]$$

with $\boldsymbol{I}$ being the unit dyadic, we obtain the couple exerted by the fluid on the sphere about the centre:

$$\boldsymbol{T} = \boldsymbol{e}_y \pi\eta a^3 U_0 \int_0^\pi \left[\frac{1}{a}\frac{\partial V_r}{\partial\theta} + \frac{\cot\theta}{a} V_r + \frac{\partial V_\theta}{\partial r} - \cos\theta\frac{\partial V_\Phi}{\partial r} - \frac{1}{a} V_\theta + \frac{\cos\theta}{a} V_\Phi\right]_{r=a} \sin\theta \,\mathrm{d}\theta. \qquad \text{(A 2)}$$

Since the sphere is stationary and the electro-osmotic velocity of the fluid at the particle 'surface' is tangential as given by (14*b*), we have

$$V_r = 0, \quad \frac{\partial V_r}{\partial\theta} = 0 \quad \text{at } r = a. \qquad \text{(A 3)}$$

Therefore, the first two terms in the brackets of (A 2) vanish.

If V_θ and V_Φ are expressed in terms of the auxiliary functions for the cylindrical components of fluid velocity given in (15), (A 2) becomes

$$\boldsymbol{T} = \boldsymbol{e}_y \pi\eta a^3 U_0 \int_0^\pi \frac{1}{c}\left[\cos\theta\frac{\partial}{\partial r}(\tfrac{1}{2}\rho Q_1 + cV_0) - \sin\theta\frac{\partial}{\partial r}(\tfrac{1}{2}zQ_1 + cW_1) - \frac{\cos\theta}{a}(\tfrac{1}{2}\rho Q_1 + cV_0) + \frac{\sin\theta}{a}(\tfrac{1}{2}zQ_1 + cW_1)\right]_{r=a} \sin\theta\, \mathrm{d}\theta. \quad \text{(A 4)}$$

Substituting (16) into the above equation and using relations between spherical and bipolar coordinates as well as integral expansions derived from the generating function of the Legendre polynomials, we obtain the following expression for the torque exerted on the sphere in terms of the coefficients A_n, B_n, ..., etc:

$$\boldsymbol{T} = \boldsymbol{e}_y \sqrt{2}\pi\eta a^2 U_0 \sinh^2\xi_0 \sum_{n=0}^{\infty} \{n(n+1)[2A_n + 2B_n + \coth\xi_0(C_n + D_n)] - (2n+1-\coth\xi_0)(E_n + F_n)\}. \quad \text{(A 5)}$$

This formula is equivalent to (19).

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