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Electrophoretic motion of an arbitrary prolate body of revolution toward an infinite conducting wall

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The electrophoretic motion of an arbitrary prolate body of revolution perpendicular to an infinite conducting planar wall is investigated by a combined analytical–numerical method. The electric field is exerted normal to the conducting planar wall and parallel to the axis of revolution of the particle. The governing equations and boundary conditions are obtained under the assumption of electric double layer thin compared to the local particle curvature radius and the spacing between the particle and the boundary. The axisymmetrical electrostatic and hydrodynamic equations are solved by the method of distribution of singularities along a certain line segment on the axis of revolution inside the particle. The analytical expressions for fundamental singularities both of electrostatic and hydrodynamic equations in the presence of the infinite planar wall are derived. Employing a piecewise parabolic approximation for the density function and applying the boundary collocation method to satisfy the boundary conditions on the surface of the particle, a system of linear algebraic equations is obtained which can be solved by matrix reduction technique.

Solutions for the electrophoretic velocity of the colloidal prolate spheroid are presented for various values of a/b and a/d, where a and b are the major and minor axes of the particle respectively and d is the distance between the centre and the wall. Numerical tests show that convergence to at least four digits can be achieved. For the limiting cases of $a = b$ or $d \to \infty$, our results agree quite well with the exact solutions of electrophoresis of a sphere moving perpendicularly to an infinite planar wall or of a prolate spheroid in an unbounded fluid. As expected, owing to the effect of the wall, the electrophoretic mobility of the particle decreases monotonically for a given spheroid as it gets closer to the wall. Another important feature is that the wall effect on electrophoresis will reduce with the increase of slenderness ratio of the prolate spheroid at the same value of a/d. The boundary effect on the particle mobility and flow pattern in electrophoresis differ significantly from those of the corresponding sedimentation problem and the wall effect on the electrophoresis is much weaker than that on the sedimentation. In order to demonstrate the generality of the proposed method, the convergent results for prolate Cassini ovals are also given in the present paper.

1. Introduction

A charged particle suspended in an electrolyte solution is surrounded by an electric double layer of diffuse ions carrying a total charge equal and opposite in sign to that of the particle. When an electric field is imposed on the particle, the latter moves

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toward the electrode of opposite sign while the ions in the diffuse layer migrate in the other direction. This motion is termed electrophoresis and has been the subject of many investigations in chemical engineering and biomedical engineering such as particle characterization or separation in various colloidal and biological systems.

The electrophoretic velocity U_0 of an isolated charged particle suspended in unbounded electrolyte fluid of viscosity η and dielectric constant ϵ is related to the applied electric field E_∞ by the Smoluchowski equation

$$U_0 = \frac{\epsilon \xi E_\infty}{4\pi\eta}, \tag{1.1}$$

where ξ is the Zeta potential associated with the particle surface. The ratio U_0/E_∞ is known as the electrophoretic mobility of the particle. Equation (1.1) is valid for non-conducting particles of arbitrary shape, provided that the local radii of curvature of the particles are much larger than the thickness of the double layer surrounding the particles.

In many applications of electrophoresis, colloidal particles are not isolated and will migrate in the presence of neighbouring particles or boundaries. So it is important to modify the Smoluchowski equation to account for the effect of this on the electrophoretic velocity. In the past two decades, considerable progress has been made in this area. Reed & Morrison (1980) considered the electrophoretic problem of two arbitrarily oriented spheres of equal radii using spherical bipolar coordinates. This work was then extended by Chen & Keh (1988) and Keh & Chen (1989*a*, *b*) to the electrophoretic motion of two arbitrarily oriented, freely suspended spheres with arbitrary ratio of radii and Zeta potentials by the method of reflections and by using spherical bipolar coordinates. Utilizing the boundary collocation technique, the axisymmetric electrophoretic motion of multiple spheres along their line of centres was studied by Keh & Yang (1990) with no restriction on Zeta potential, sphere radii and distance apart. Numerical results with good convergence are calculated even if the spheres are touching.

The electrophoretic velocity of a non-conducting sphere in the vicinity of an infinite planar wall has been examined for two cases: migration normal to an infinite conducting planar wall (Morrison & Stukel 1970; Keh & Lien 1989) using bipolar coordinates; and electrophoresis parallel to an infinite non-conducting surface (Keh & Chen 1988). In both studies, modifications of the Smoluchowski equation were determined for various λ, dimensionless sphere radius with respect to the distance between the particle centre and the boundary. The parallel wall effect was found to impede the particle velocity for moderate and large separations between the sphere and the boundary, while this velocity tends to increase as the separation became small. On the other hand, the electrophoretic velocity decreases steadily when the particle approaches normal to the wall and tends to zero in the limit position when it touches the wall. Another important conclusion of these analyses is that the boundary effect on electrophoresis ($O(\lambda^3)$) is much weaker than that on sedimentation ($O(\lambda)$).

Other sphere–boundary problems that have been studied include the electrophoretic movement of a particle inside an infinite long tube or along the centreline between two large parallel plates (Keh & Anderson 1985); the electrophoresis of a colloidal cylinder parallel or perpendicular to an infinite planar wall (Keh, Kuo & Kuo 1991); the electrophoretic motion of a sphere along the axis of a circular orifice or a circular disk (Keh & Lien 1991). All previous solutions for the wall-corrected electrophoretic velocity of a particle are available only for a sphere or a circular cylinder. In this paper we will consider the axisymmetric electrophoretic motion of an arbitrary prolate body of revolution in the presence of an infinite conducting wall. The method of internal distribution of the singularities developed by Wu (1984), Yuan & Wu (1987) is adopted to solve the quasi-static electrostatic and the hydrodynamic equations. The modified Smoluchowski equation for the prolate spheroid and Cassini oval are obtained with satisfactory convergence and the electric field lines for the electrophoretic motion and streamlines for fluid motion are presented for some cases. The considerable difference between electrophoresis and sedimentation both in particle mobility and flow pattern are also explored.

The present investigation consists of five sections. In §2, the problem of electrophoretic motion of an arbitrary prolate body of revolution toward an infinite conducting planar wall is formulated. Section 2 also contains the solution scheme for this body. The elementary solutions of the electric and hydrodynamic equations representing the disturbance of a sphere are given in §3. Results of the wall-corrected Smoluchowski equation for a prolate spheroid and a Cassini oval and their flow patterns in comparison with the corresponding sedimentary motion are presented in §4. Finally, a short summary and discussion are given in §5.

2. Mathematical formulation

Consider the axisymmetric electrophoretic motion of a non-conducting arbitrary prolate particle of revolution translating toward an infinite conducting planar wall. Cylindrical and spherical coordinates (R, θ, Z) and (r, θ, ϕ) are introduced with the origin at O (figure 1). A uniform electric field $E_\infty \boldsymbol{e}_z$ is imposed on the particle, where $\boldsymbol{e}_z$ is the unit vector in the z-direction. Assume that the thickness of the double layer is much smaller than the characteristic curvature radius of the particle and the spacing between the particle and the planar wall, and the fluid outside the double layer is electrically neutral with constant conductivity. The governing equation for the electric potential distribution $\phi(\boldsymbol{x})$ is the Laplace equation

$$\nabla^2\phi = 0, \tag{2.1}$$

with the following boundary conditions on the particle surface, on the conducting planar wall and at infinity:

$$\frac{\partial \phi}{\partial n} = 0 \quad \text{at the surface,} \tag{2.2a}$$

$$\phi = -E_\infty d \quad \text{at} \quad z = d, \quad d > 0, \tag{2.2b}$$

$$\phi \sim -E_\infty z \quad \text{as} \quad r \to \infty, \tag{2.2c}$$

where $\boldsymbol{n}$ denotes the outer unit vector of the body surface. The potential on the conducting wall has been set at $-E_\infty d$ for convenience.

Once the electric field is determined, we proceed to obtain the fluid field. The Reynolds number of the fluid motion outside the thin double layer is small, so the governing equation for the stream function ψ of the present axisymmetric quasi-steady Stokes flow is

$$\mathrm{D}^2(\mathrm{D}^2\psi) = 0, \tag{2.3}$$

where the Stokes operator D^2 has the form

$$\mathrm{D}^2 = \frac{\partial^2}{\partial^2 Z} + R\frac{\partial}{\partial R}\left(\frac{1}{R}\frac{\partial}{\partial R}\right) \tag{2.4}$$

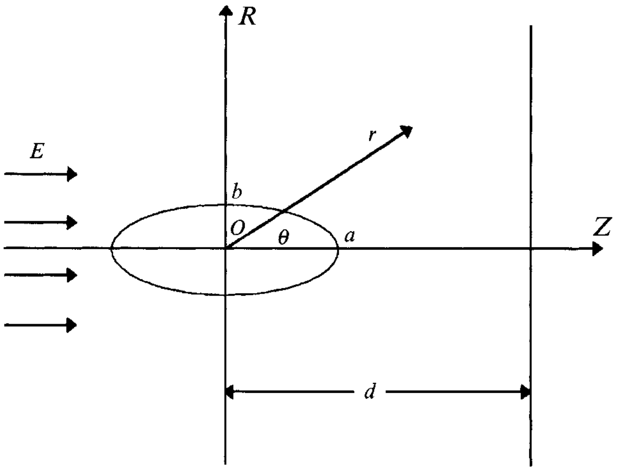


FIGURE 1. Configuration of a prolate spheroid in electrophoretic motion towards an infinite conducting wall.

in cylindrical coordinates. The stream function ψ is related to the velocity components and pressure by

$$V_z = -\frac{1}{R}\frac{\partial\psi}{\partial Z}, \quad V_R = \frac{1}{R}\frac{\partial\psi}{\partial R}, \tag{2.5a, b}$$

$$\frac{\partial P}{\partial Z} = \frac{1}{R}\frac{\partial}{\partial R}(\mathrm{D}^2\psi), \quad \frac{\partial P}{\partial R} = -\frac{1}{R}\frac{\partial}{\partial Z}(\mathrm{D}^2\psi). \tag{2.6a, b}$$

The electric field acts on the double layer of the ions at the particle surface and induces an electro-osmotic tangential velocity U_s on the surface of the particle (more precisely at the outer edge of the thin double layer) which is related to the local electric field $\boldsymbol{E}_s = -\nabla\phi$ by the Helmholtz equation for electro-osmotic flow. On account of this fact, the boundary conditions for the fluid field are

$$V = U_0 \boldsymbol{e}_z + \frac{\epsilon\xi}{4\pi\eta}\nabla\phi \quad \text{at the surface,} \tag{2.7a}$$

$$V = 0 \quad \text{at} \quad z = d, \tag{2.7b}$$

$$V \sim 0 \quad \text{as} \quad r \to \infty, \tag{2.7c}$$

where U_0 is the instantaneous electrophoretic velocity of the particle to be determined. Note that the local electric field $\nabla\phi$ must be calculated from the electrostatic equation (2.1) and boundary conditions (2.2*a–c*).

In order to determine the electrophoretic velocity U_0 of the particle, it is convenient to decompose the boundary condition (2.7*a*) on the particle surface and the total flow into two parts, using the linearity of the governing equation and boundary conditions. The first part contains (2.3), (2.7*b*), (2.7*c*) and the boundary condition on the particle surface

$$V = U_0 \boldsymbol{e}_z \tag{2.8}$$

corresponding to the fluid motion of an arbitrary prolate particle of revolution translating perpendicularly to an infinite planar wall with uniform velocity (2.8), while the second part has the same equation and boundary conditions except (2.8) which is replaced by

$$V = \frac{\epsilon\xi}{4\pi\eta}\nabla\phi \tag{2.9}$$

as the boundary condition on the particle surface. It represents the fluid flow disturbed by an infinite planar wall and a stationary arbitrary prolate particle with a tangential electro-osmotic velocity (2.9) at the particle surface layer. Once these two boundary value problems are solved, the electrophoretic velocity is readily obtained, since the net force exerted by the fluid on the particle must vanish because it is suspended freely in the fluid and the diffuse double layer encloses a neutral body. Writing the zero drag requirement we have

$$F_1 + F_2 = 0. \tag{2.10}$$

where the $F_i(i = 1,2)$ are the net force from the fluid acting on the body surface which can be obtained by the two boundary value problems (2.8) and (2.9) respectively. The original vector form of (2.10) is reduced to a scalar one since no rotation occurs and the components of the net force have only one non-zero term in the z-direction because of the symmetry of the motion. The net force of the first problem F_1 can be written in the form

$$F_1 = -6\pi\eta L U_0 \alpha = -U_0 F_1^{(0)}, \tag{2.11}$$

where $F_1^{(0)} = 6\pi\eta L\alpha$; α is correction factor to Stokes law due to the presence of the wall. Substituting (2.11) into (2.10) we have the electrophoretic velocity U_0 of the particle:

$$U_0 = F_2/F_1^{(0)}. \tag{2.12}$$

Equation (2.12) shows that only the ratio of $F_1^{(0)}$ and F_2 determines the electrophoretic mobility of the particle. Thus our main problem is to find $F_i(i = 1,2)$, which will be accomplished in the following sections.

3. Method of internal distribution of singularities in electrophoresis

In this section, we will use the method of internal distribution of singularities developed by Wu (1984) and Yuan & Wu (1987) to solve the electrophoretic equation and hydrodynamic equation describing the electrophoresis of an arbitrary prolate body of revolution moving perpendicularly toward an infinite conducting wall along its major axis. The main idea of the solution procedure may be summarized as follows. First, we obtain the analytical expressions in infinite series form for the fundamental singularity of the Laplace equation and the Stokes equation in the presence of the infinite planar wall. These two singularities will be referred to henceforth as L and S, respectively. Distributing these singularities continuously along a certain segment on the symmetry axis inside the body, two sets of integral equations result to determine the density distributions. Dividing the segment into N subsegments and approximating the density function by an interpolating polynomial at each subsegment, we are able to derive successfully the analytical expressions for the electrostatic field and the hydrodynamic field. The boundary conditions on the infinite planar wall and at infinity are automatically satisfied, and the non-slip condition on the particle surface is satisfied by the collocation technique. Hence two sets of linear algebraic equations for the density functions of L singularities and S singularities are obtained which can be solved by any matrix reduction method. We will first consider the electric potential field and then turn to the velocity field outside the particle.

3.1. *Electric potential distribution*

We will construct the elementary solution of the Laplace equation due to the disturbance of the wall and the singularity located at $R = 0$, $Z = \xi$. Since the governing equation and boundary conditions are linear for an electric field, we can write the disturbed potential ϕ for the region $z \leqslant d$ as the superposition of ϕ_w and ϕ_s:

$$\phi = \phi_w + \phi_s, \tag{3.1}$$

where ϕ_w is a solution of (2.1) in cylindrical coordinates which represents the disturbance of the wall and can be expressed as

$$\phi_w = \int_0^\infty A(k)\, J_0(kR)\, \mathrm{e}^{k(Z-\xi)}\, \mathrm{d}k, \tag{3.2}$$

where $J_0(x)$ is the Bessel function of the first kind of zero order and $A(k)$ is an unknown function of k. The second term on the right-hand side of (3.1), ϕ_s, is a solution of (2.1) in spherical coordinates representing the disturbance produced by the singularity and is given by

$$\phi_s = \sum_{n=0}^{\infty} T_n\, r^{-(n+1)}\, P_n(\cos\vartheta) = \sum_{n=0}^{\infty} T_n\, F_n^{(1)}(R, Z-\xi), \tag{3.3}$$

where $P_n(x)$ is a Legendre function of nth order, and $F_n^{(1)}(R,Z)$ is defined as

$$F_n^{(1)}(R,Z) = r^{-n-1}\, P_n(\zeta), \tag{3.4}$$

where

$$r = (R^2+Z^2)^{\frac{1}{2}} \quad \text{and} \quad \zeta = \cos\vartheta = Z/R. \tag{3.5}$$

The requirement that the potential on the wall should be zero yields

$$\int_0^\infty A(k)\, J_0(kR)\, \mathrm{e}^{k(d-\xi)}\, \mathrm{d}k = -\sum_{n=0}^{\infty} T_n\, F_n^{(1)}(R, d-\xi). \tag{3.6}$$

Applying the inverse Hankel transformation on both sides of (3.6) and using an integral formula (Erdelyi *et al.* 1954)

$$\int_0^\infty \frac{x}{(x^2+a^2)^{\mu/2}}\, P^{\gamma}_{\mu-1}\left(\frac{x}{(x^2+a^2)^{\frac{1}{2}}}\right) J_\gamma(xy)\, \mathrm{d}x = \frac{y^{\mu-2}\, \mathrm{e}^{-ay}}{\Gamma(\mu+\gamma)}, \tag{3.7}$$

$$\mathrm{Re}\,(\gamma) > -1, \quad y > 0; \quad \mathrm{Re}\,(\mu) > \tfrac{1}{2},$$

one can easily obtain

$$A(k) = -\sum_{n=0}^{\infty} T_n \frac{k^n}{n!}\, \mathrm{e}^{-2k(d-\xi)}, \tag{3.8}$$

where $P^{\gamma}_{\mu-1}$ is an associated Legendre function of order $\mu-1$ and of time γ, $\Gamma(x)$ is a Gamma function of the second kind, and a is a constant. Substituting (3.8) into (3.2) and utilizing the following integral (Erdelyi *et al.* 1954):

$$\int_0^\infty x^{\mu-\frac{1}{2}}\mathrm{e}^{-ax}(xy)^{\frac{1}{2}}\, J_0(xy)\, \mathrm{d}x = \frac{n!\, y^{\frac{1}{2}}}{(a^2+y^2)^{(n+1)/2}}\, P_n\left(\frac{a}{(a^2+y^2)^{\frac{1}{2}}}\right), \tag{3.9}$$

$$y > 0, \quad \mathrm{Re}\,(a) > 0,$$

after some algebraic manipulation, we have

$$\phi = \sum_{n=0}^{\infty} T_n[F_n^{(1)}(R, Z-\xi) - F_n^{(1)}(R, 2d-Z-\xi)], \tag{3.10}$$

$$\phi = 0 \quad \text{at} \quad z = d. \tag{3.11}$$

The components of the corresponding electric field E_z and E_R can be obtained as partial differentials of ϕ with respect to Z and R respectively, which together with ϕ are given in the following compact vector form:

$$Q(R,Z,\xi) = \sum_{n=0}^{\infty} T_n\, SE_n(R,Z,\xi), \tag{3.12}$$

where
$$Q(R,Z,\xi) = (\phi, E_Z, E_R)$$
$$SE_n(R,Z,\xi) = (SE_n^{(1)}, SE_n^{(2)}, SE_n^{(3)}),$$
$$SE_n^{(1)}(R,Z,\xi) = F_n^{(1)}(R,Z-\xi) - F_n^{(1)}(R,2d-Z-\xi), \tag{3.13a}$$
$$SE_n^{(2)}(R,Z,\xi) = (n+1)\,[F_{n+1}^{(1)}(R,Z-\xi) + F_{n+1}^{(1)}(R,2d-Z-\xi)], \tag{3.13b}$$
$$SE_n^{(3)}(R,Z,\xi) = (n+1)\,[F_{n+1}^{(3)}(R,Z-\xi) - F_{n+1}^{(3)}(R,2d-Z-\xi)], \tag{3.13c}$$
in which
$$F_n^{(3)}(R,Z) = (n+1)\,r^{-n}\frac{1}{R}I_{n+1}(\zeta), \tag{3.14}$$
where I_n is a Gegenbauer function of order n. Here we use the relationships
$$E_z = -\frac{\partial\phi}{\partial Z}, \quad E_R = -\frac{\partial\phi}{\partial R},$$
$$\frac{\partial}{\partial Z}F_n^{(1)}(R,Z) = -(n+1)\,F_{n+1}^{(1)}(R,Z),$$
$$\frac{\partial}{\partial R}F_n^{(1)}(R,Z) = -(n+1)\,F_{n+1}^{(3)}(R,Z).$$

Following the approach presented in Wu (1984), a segment of a straight line AB $(-c, c)$ inside the body is chosen, where $2c$ is the length of the line segment. If the nose and tail of the body are rounded, then their centres of curvature could be prescribed as A and B. Distributing the singularity (3.12) continuously over AB, plus the undisturbed uniform electric potential, we obtain the potential and electric field distribution as follows:
$$Q(R,Z,\xi) = (-E_\infty Z, E_\infty, 0) + \sum_{n=0}^{\infty}\int_{-c}^{c} A(\xi)\,SE_n(R,Z,\xi)\,\mathrm{d}\xi, \tag{3.15}$$
where $A(\xi)$ is an unspecified density function of singularities along AB which is to be determined by non-slip boundary conditions on the surface of the particle.

Obviously (3.15) satisfies the governing equation (2.1) and the boundary conditions on the wall (2.2*b*) and at infinity (2.2*c*). All that remains is to satisfy the condition on the surface of the body (2.2*a*). This will eventually lead to a set of integral equations to be solved for the unknown density function $A(\xi)$. Since the complexity of the kernel functions in the integral equation and the particle contour in (3.15) precludes an analytical solution, the integral equations will be solved approximately.

To this end, following the approach proposed by Yuan & Wu (1987), the segment AB is partitioned into M_E subintervals (d_{j1}, d_{j3}). With the end points d_{j1}, d_{j3} and midpoint d_{j2} of each subinterval to be chosen as interpolating points, the density function is approximated by piecewise polynomials of second order interpolating the density function at these nodal points, Truncating the infinite series at the N_Eth term, (3.15) becomes
$$Q = (-E_\infty Z, E_\infty, 0) + \sum_{j=1}^{M_E}\sum_{n=0}^{N_E}\int_{d_{j1}}^{d_{j3}} A_{nj}(\xi)\,SE_n(R,Z,\xi)\,\mathrm{d}\xi, \tag{3.16}$$
where
$$A_{nj}(\xi) = \frac{(\xi-d_{j2})(\xi-d_{j3})}{(d_{j1}-d_{j2})(d_{j1}-d_{j3})}A_{nj1} + \frac{(\xi-d_{j1})(\xi-d_{j3})}{(d_{j2}-d_{j1})(d_{j2}-d_{j3})}A_{nj2} + \frac{(\xi-d_{j2})(\xi-d_{j1})}{(d_{j3}-d_{j2})(d_{j3}-d_{j1})}A_{nj3}. \tag{3.17}$$

Here A_{njk} $(k = 1, 2, 3)$ are the corresponding values of the density function at three interpolating points. Substituting (3.17) into (3.16), after some algebraic manipulation we have

$$Q(R, Z, \xi) = (-E_\infty Z, E_\infty, 0) + \sum_{n=0}^{N_E} \sum_{m=1}^{M_E} [A_{n,2(j-1)+1} \boldsymbol{WE}_{nj1} + A_{n,2(j-1)+2} \boldsymbol{WE}_{nj2} + A_{n,2(j-1)+3} \boldsymbol{WE}_{nj3}] \tag{3.18}$$

where $\boldsymbol{WE}_{njk}$ $(k = 1, 2, 3)$ are vector functions defined as follows:

$$\boldsymbol{WE}_{njk} = (WE^{(1)}_{njk}, WE^{(2)}_{njk}, WE^{(3)}_{njk}),$$

$$WE^{(i)}_{nj1} = \frac{1}{2h^2}[d_{j2}\, d_{j3}\, TE^{(i)}_{nj1} - (d_{j2} + d_{j3})\, TE^{(i)}_{nj2} + TE^{(i)}_{nj3})], \tag{3.19a}$$

$$WE^{(i)}_{nj2} = -\frac{1}{h^2}[d_{j1}\, d_{j3}\, TE^{(i)}_{nj1} - (d_{j1} + d_{j3})\, TE^{(i)}_{nj2} + TE^{(i)}_{nj3})], \tag{3.19b}$$

$$WE^{(i)}_{nj3} = \frac{1}{2h^2}[d_{j1}\, d_{j2}\, TE^{(i)}_{nj1} - (d_{j1} + d_{j2})\, TE^{(i)}_{nj2} + TE^{(i)}_{nj3})], \tag{3.19c}$$

in which i can be either 1, 2 or 3 and

$$h = \tfrac{1}{2}(d_{j3} - d_{j1}), \tag{3.20}$$

$$TE^{(i)}_{njk}(R, Z) = \int_{d_{j1}}^{d_{j3}} \xi^{k-1}\, SE^{(i)}_n(R, Z, \xi)\, \mathrm{d}\xi \quad (i = 1, 2, 3) \quad (k = 1, 2, 3). \tag{3.21}$$

If the electric field $\boldsymbol{E}$ and the outer normal vector of the surface of the body $\boldsymbol{n}$ have the components E_z, E_R and n_Z, n_R in cylindrical coordinates, then the boundary condition on the surface of the particle (2.2a) can be written as

$$n_Z E_Z + n_R E_R = 0. \tag{3.22}$$

Hence we can substitute the last two components in (3.12) into (3.22) to yield a set of linear system of unknown coefficients A_{njk} $(k = 1, 2, 3)$. $TE^{(i)}_{njk}$ $(i = 1, 2, 3)$ can be evaluated by recurrence formulae as shown in an Appendix.†

Applying the boundary collocation technique, boundary condition (2.2a) is exactly satisfied at $(N_E + 1)(2M_E + 1)$ points on the surface of the particle. The equation (3.18) is then reduced to a system of $(N_E + 1)(2M_E + 1)$ linear algebraic equations to determine the unknown coefficients A_{njk}, which can be solved by a standard matrix inversion method, required for final determination of the approximate electric field distribution. The accuracy of the solution can be improved in principle to any degree by increasing the values of N_E and M_E.

3.2. *Fluid velocity distribution*

Once the electric field is obtained, we next turn to consider the hydrodynamic field. A procedure similar to that in §3.1 for the electric field distribution is adopted. First we write the expressions for a singularity S located at $R = 0$, $Z = \xi$ in the presence of an infinite planar wall (Yuan & Wu 1987):

$$U(R, Z, \xi) = \sum_{n=2}^{\infty} [C_n\, S^{(0)}_n(R, Z, \xi) + D_n\, S^{(e)}_n(R, Z, \xi)], \tag{3.23}$$

† The Appendix is available from the Editorial Office or the authors.

where
$$U(R,Z,\xi) = (V_z, V_R, \psi, p-p_\infty), \tag{3.24a}$$
$$S_n^{(0)}(R,Z,\xi) = (S_n^{(1)}, S_n^{(3)}, S_n^{(5)}, S_n^{(7)}), \tag{3.24b}$$
$$S_n^{(e)}(R,Z,\xi) = (S_n^{(2)}, S_n^{(4)}, S_n^{(6)}, S_n^{(8)}), \tag{3.24c}$$

where $S_n^{(i)}$ ($i = 1$–8) can be expressed as
$$S_n^{(1)}(R,Z,\xi) = F_n^{(1)}(R,Z-\xi) - F_n^{(1)}(R,2d-Z-\xi) + 2(Z-d)(n+1)\,F_{n+1}^{(1)}(R,2d-Z-\xi) \tag{3.25a}$$
$$S_n^{(2)}(R,Z,\xi) = F_n^{(2)}(R,Z-\xi) - F_n^{(2)}(R,2d-Z-\xi) - 2(n-2)(Z-d)\,F_{n-1}^{(1)}(R,2d-Z-\xi) + 2(2n-3)(Z-d)(d-\xi)\,dF_n^{(1)}(R,2d-Z-\xi), \tag{3.25b}$$
$$S_n^{(3)}(R,Z,\xi) = F_n^{(3)}(R,Z-\xi) - F_n^{(3)}(R,2d-Z-\xi) - 2(n+1)(Z-d)\,F_{n+1}^{(3)}(R,2d-Z-\xi), \tag{3.25c}$$
$$S_n^{(4)}(R,Z,\xi) = F_n^{(4)}(R,Z-\xi) - F_n^{(4)}(R,2d-Z-\xi) - 2(2n-3)(z-d)(d-\xi)\,F_n^{(3)}(R,2d-Z-\xi) + \frac{2(n-1)(n-3)}{n}(Z-d)\,F_{n-1}^{(3)}(R,2d-Z-\xi), \tag{3.25d}$$
$$S_n^{(5)}(R,Z,\xi) = F_n^{(5)}(R,Z-\xi) - F_n^{(5)}(R,2d-Z-\xi) + 2(Z-d)(n+1)\,F_{n+1}^{(5)}(R,2d-Z-\xi), \tag{3.25e}$$
$$S_n^{(6)}(R,Z,\xi) = F_n^{(6)}(R,Z-\xi) - F_n^{(6)}(R,2d-Z-\xi) - 2(n-2)(Z-d)\,F_{n-1}^{(5)}(R,2d-Z-\xi) + 2(2n-3)(Z-d)(d-\xi)\,F_n^{(5)}(R,2d-Z-\xi), \tag{3.25f}$$
$$S_n^{(7)}(R,Z,\xi) = 4(n+1)\,F_{n+1}^{(1)}(R,2d-Z-\xi), \tag{3.25g}$$
$$S_n^{(8)}(R,Z,\xi) = \frac{4n-6}{n}F_{n-1}^{(1)}(R,Z,\xi) + 4(2n-3)(d-\xi)\,F_n^{(1)}(R,2d-Z-\xi) - \frac{2(2n^2-6n+3)}{n}F_{n-1}^{(1)}(R,2d-Z-\xi), \tag{3.25h}$$

in which $F_n^{(1)}$ and $F_n^{(3)}$ are given by (3.4) and (3.14) while
$$F_n^{(2)}(R,Z) = r^{-(n-1)}[P_n(\zeta) + 2I_n(\zeta)], \tag{3.26}$$
$$F_n^{(4)}(R,Z) = (n+1)\,r^{-(n-2)}\frac{1}{R}I_{n+1}(\zeta) - 2Zr^{-(n-1)}\frac{1}{R}I_n(\zeta), \tag{3.27}$$
$$F_n^{(5)}(R,Z) = r^{-(n-1)}I_n(\zeta), \tag{3.28}$$
$$F_n^{(6)}(R,Z) = r^{-(n-3)}I_n(\zeta). \tag{3.29}$$

The singularity S is distributed continuously along AB, which is then divided into M_F subintervals with density function approximated by piecewise quadratic polynomials. Truncating the infinite series at the N_Fth terms, (3.23) can be written as
$$U(R,Z) = \sum_{j=1}^{M_F}\sum_{n=2}^{N_F}[C_{n,2(j-1)+1}\,W_{nj1}^{(Q_0)} + C_{n,2(j-1)+2}\,W_{nj2}^{(Q_0)} + C_{n,2(j-1)+3}\,W_{nj3}^{(Q_0)} + D_{n,2(j-1)+1}\,W_{nj1}^{(Q_E)} + D_{n,2(j-1)+1}\,W_{nj1}^{(Q_E)} + D_{n,2(j-1)+1}\,W_{nj1}^{(Q_E)}], \tag{3.30}$$

where $$W^{(Q_0)} = (W^{(Q1)}_{njk}, W^{(Q_3)}_{njk}, W^{(Q_5)}_{njk}, W^{(Q_7)}_{njk}) \quad (k = 1,2,3), \tag{3.31}$$

$$W^{(Q_E)}_{njk} = (W^{(Q_2)}_{njk}, W^{(Q_4)}_{njk}, W^{(Q_6)}_{njk}, W^{(Q_8)}_{njk}) \quad (k = 1,2,3), \tag{3.32}$$

$$W^{(Q_i)}_{nj1} = \frac{1}{2h^2}[d_{j2} d_{j3} T^{(i)}_{nj1} - (d_{j2}+d_{j3}) T^{(i)}_{nj2} + T^{(i)}_{nj3})], \tag{3.33a}$$

$$W^{(Q_i)}_{nj2} = -\frac{1}{h^2}[d_{j1} d_{j3} T^{(i)}_{nj1} - (d_{j1}+d_{j3}) T^{(i)}_{nj2} + T^{(i)}_{nj3})] \quad (i = 1,8), \tag{3.33b}$$

$$W^{(Q_i)}_{nj3} = \frac{1}{2h^2}[d_{j1} d_{j2} T^{(i)}_{nj1} - (d_{j1}+d_{j2}) T^{(i)}_{nj2} + T^{(i)}_{nj3})], \tag{3.33c}$$

while $$T^{(i)}_{njk}(R,Z) = \int_{d_{j1}}^{d_{j3}} \xi^{k-1} S^{(i)}_n(R,Z,\xi)\,\mathrm{d}\xi. \tag{3.34}$$

The recurrence formulae for $T^{(i)}_{njk}$ $(i = 1,\ldots,8)$ can be found in the Appendix.

As mentioned previously in §2, the hydrodynamic problem should be decomposed into two boundary value problems in order to calculate the electrophoretic mobility of the particle. The boundary condition on the surface of the particle for the second boundary value problem is now fully determined using the solutions for the electric field (3.18). By means of the collocation technique, the boundary condition (2.8) or (2.9) is applied at $(N_F-1)(2M_F+1)$ discrete points and two sets of linear algebraic equations are generated for the unknown coefficients C_{nj} and D_{nj}. The fluid velocity field is completely solved once these coefficients are evaluated. The drag force F_1 and F_2 exerted by the fluid on the particle can be determined from Happel & Brenner (1983)

$$F_i = \int_0^{\pi} \eta\pi r^3 \sin^3\vartheta \frac{\partial}{\partial r}\left(\frac{\mathrm{D}^2\psi}{r^2\sin^2\vartheta}\right) r\,\mathrm{d}\vartheta \quad (i = 1,2). \tag{3.35}$$

Substituting the expression for ψ into (3.35) and considering the orthogonality properties of Legendre and Gegenbauer functions, we obtain

$$F_i = \frac{2\pi\eta}{3}\sum_{j=1}^{m_F}[D_{2,2(j-1)+1} + D_{2,2(j-1)+2} + D_{2,2(j-1)+3}](d_{j3}-d_{j1}) \quad (i = 1,2). \tag{3.36}$$

4. Results and discussion

Consider as two examples the electrophoretic motion of a non-conducting prolate spheroid and Cassini oval translating perpendicularly to an infinite conducting planar wall.

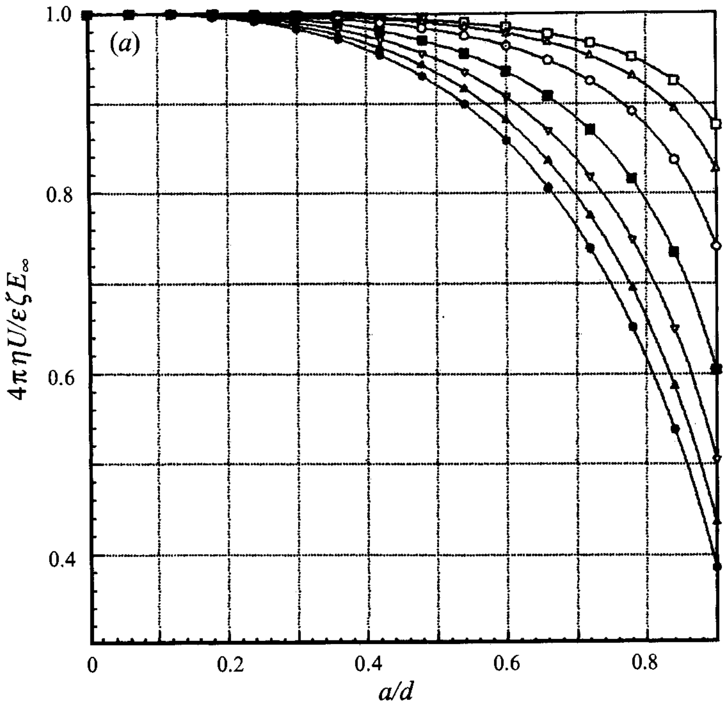
The equation for the prolate spheroid is

$$z = a\cos\vartheta, \quad R = b\sin\vartheta, \quad c = (a^2-b^2)^{\frac{1}{2}}, \quad \lambda = a/b, \tag{4.1}$$

where a and b are the major and minor axes respectively, c is the focus, ϑ is the polar angle. $(-c,0)$ and $(c,0)$ are chosen as the points A and B. Without loss of generality, we take $b = 1$.

The segment AB is partitioned into M_F subintervals with equal length and the specification of collocation points along the surface of the spheroid follows the equal-spacing principle. To avoid the singularity of the coefficient matrix at the points $\vartheta = 0, \frac{1}{2}\pi, \pi$, four closely spaced adjacent points $\vartheta = \delta, \frac{1}{2}\pi \pm \delta, \pi-\delta$ are taken instead of the above-mentioned points. δ is taken as 0.01° in our numerical computation.

The numerical results of the normalized electrophoretic mobility for various $\lambda \leqslant 3$ with spheroid-to-wall spacings a/d up to 0.9 are plotted in figure 2(a). The dynamic



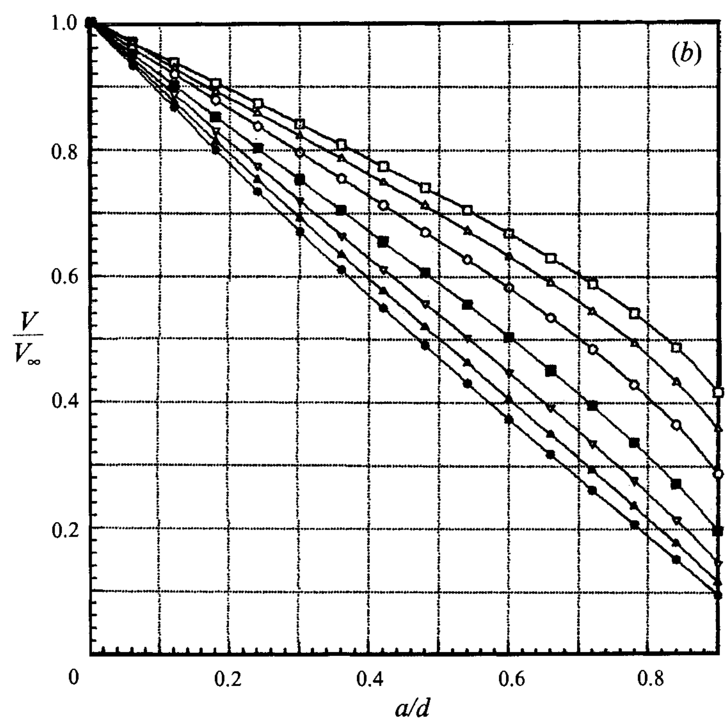


FIGURE 2. (*a*) Electrophoretic mobilities ($4\pi\eta U/\epsilon\zeta E_\infty$) and (*b*) sedimentary mobilities (V/V_∞) versus a/d for various λ for prolate spheroid. λ: □ – □, 3.0; △ – △, 2.5; ○ – ○, 2.0; ■ – ■, 1.5; ▽ – ▽, 1.25; ▲ – ▲, 1.1; ● – ●, 1.0.

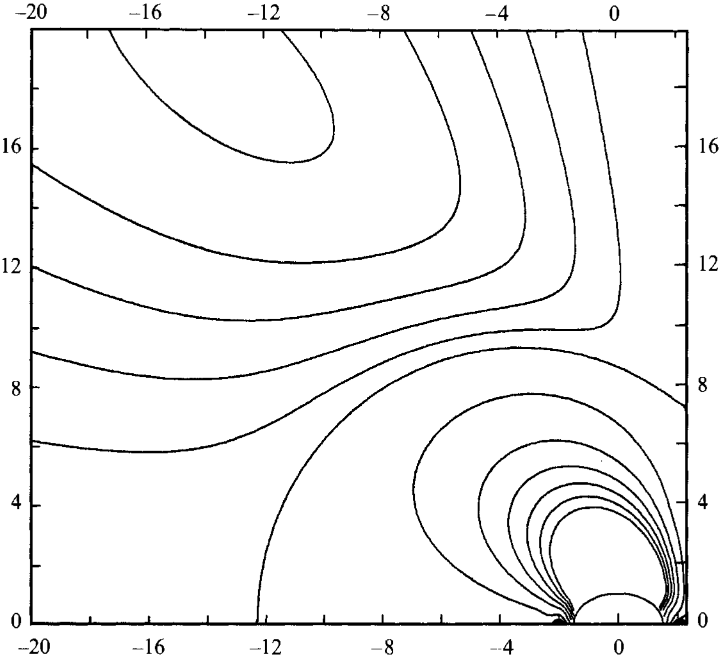
mobility for sedimentary flow is shown in figure 2(*b*) for comparison (Yuan & Wu 1987). All of the results obtained converge to at least four significant digits. For the most difficult case of $\lambda = 3$ and $a/d = 0.9$, the values of M_E, N_E, M_F and N_F are 4, 20, 4 and 16 which are sufficiently large to reach convergence. In order to test the solution accuracy, two special cases are considered where the exact solutions are available for comparison. The first is the case as $d \rightarrow \infty$ or $a/d = 0$; the present problem becomes identical to that of the electrophoretic motion of an isolated prolate spheroid in an unbounded electrolyte solution with a uniformly applied electric field. Our solutions at $d = 10$, $a/d = 0.1$ are compared with the exact solutions when $d \rightarrow \infty$ where the dimensionless electrophoretic mobility is equal to unity (Morrison 1970). Results are found to be identical to four digits. The second case is $\lambda = 1$, when the spheroid becomes a sphere. The results for this case are compared with the exact solutions for the electrophoretic motion of a sphere normal to a conducting infinite planar wall (Keh & Lien 1989). Our values agree with Keh's to four digits. The accuracy test just summarized indicates that reliable results with high accuracy can be achieved using the proposed method.

From the data and curves shown in figure 2, some interesting features can be revealed: (i) both the electrophoretic and hydrodynamic mobilities decrease monotonically when the spheroid approaches the wall; (ii) the wall effect on electrophoresis is much weaker than that on sedimentation; (iii) the wall effect on electrophoresis will reduce with the increase of slenderness ratio of the spheroid. Features (i) and (ii) are similar to the case of a sphere, while (iii) is entirely new. It demonstrates the influence of the body shape parameter of a spheroid on the electrophoresis. These three characteristics can be easily understood physically.

It is well known that the electrophoretic velocity is controlled by two main factors: viscous retardation of the fluid as the particle moves in response to the applied electric field; and the electric driving force which leads to an opposite effect. Therefore the electrophoretic velocity of the particle will always be greater than the sedimentary velocity. Moreover, the relative increment of the viscous drag due to the decrease of d/a and a/b exceeds that of the electric driving force. Hence from (2.12) the wall and shape effect on electrophoresis will increase with the decrease of d/a and a/b.

The streamlines for the electrophoretic and sedimentary motion of a colloidal prolate spheroid travelling perpendicularly towards an infinite planar wall along the axis of revolution with $a/b = 1.5$ and $d/a = 1.54$ are depicted in figure 3(*a*) and 3(*b*) respectively. From these figures we can see that the flow pattern of the electrophoretic motion differs significantly from that of the corresponding sedimentary flow. This difference can be explained by the influence of the diffuse double layer at the spheroid surface on the flow. In fact, the case of sedimentation resulting from the movement of a spheroid toward a wall, the disturbance thus induced is that of a Stokeslet, while for the electrophoretic motion, the particle is force free and thus from figure 3(*a*) and (3.14), the primary disturbance caused by the particle can be described by a potential doublelet. In other words, the disturbance to the fluid velocity field caused by an electrophoretic spheroid decays much faster (as r^{-3}) than that caused by a settling spheroid (as r^{-1}), where r is the distance from the spheroid centre.

From figure 3(*b*), the streamlines of the sedimentary flow have only one recirculation region which moves nearer to the surface of the body as it gets nearer to the wall, while for the electrophoretic motion, in addition to the inner recirculation region near the body surface, there is another outer recirculation region swirling in the opposite direction far away from the particle (see figure 3*a*). Note that the fluid field contains a stagnation point on the axis of symmetry and a circle of stagnation points on the wall.



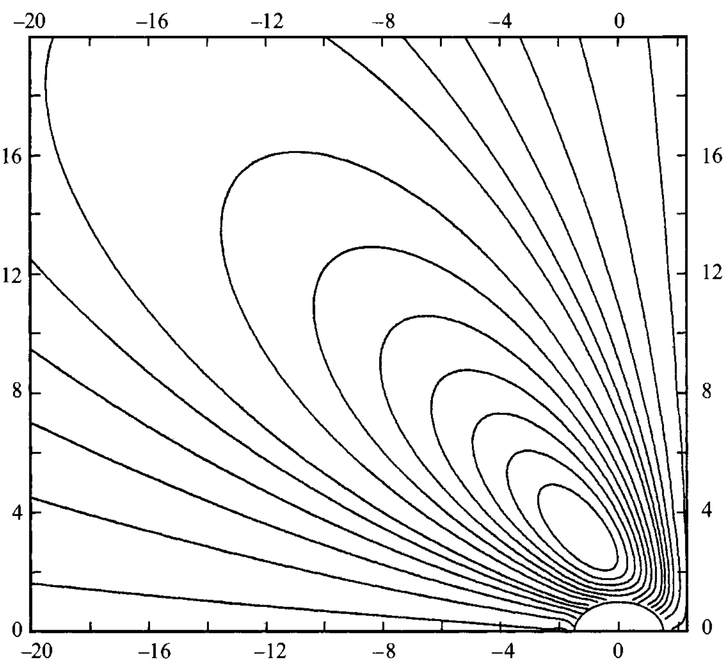


FIGURE 3. Streamlines for (*a*) electrophoretic motion and (*b*) for sedimentary motion of the prolate spheroid of $a = 1.5$, $d/a = 1.54$.

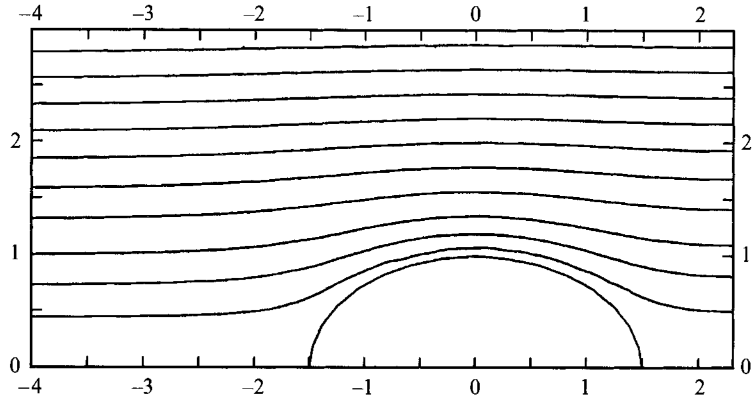


FIGURE 4. Electric field lines for the prolate spheroid with $a = 1.5$, $d/a = 1.54$.

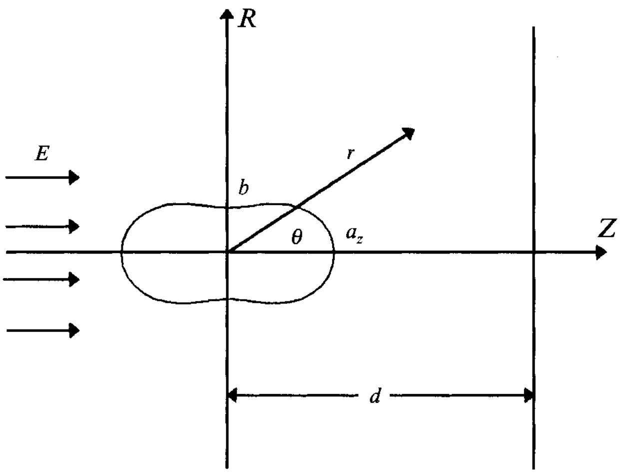


FIGURE 5. Configuration of a prolate Cassini oval in electrophoretic motion towards an infinite conducting wall.

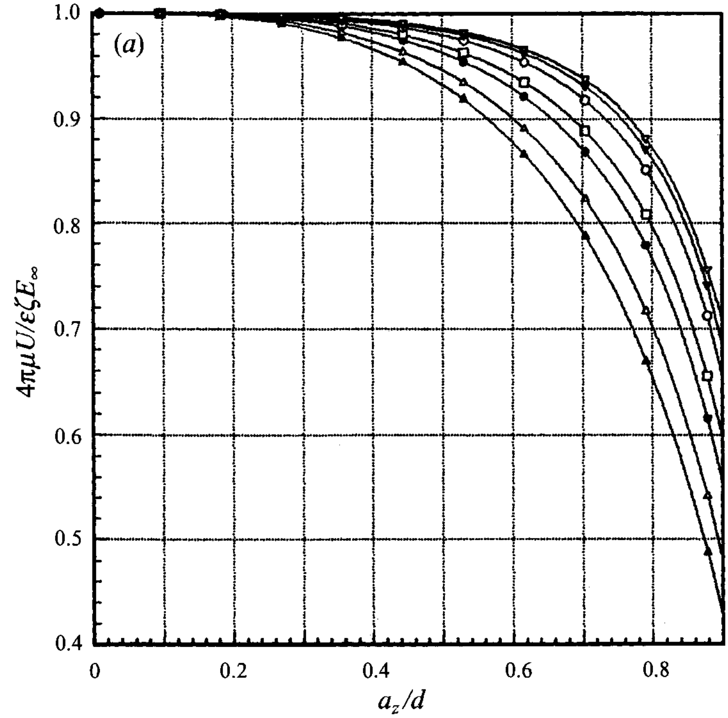
Both recirculations are divided by a separating streamline $\psi = 0$, which intersects the axis and the wall at these stagnation points. The existence of a toroidal inner circulation pattern for the electrophoretic motion corresponds to that of a potential dipole.

The electric field lines for the case shown in figure 3 are presented in figure 4. The local electric field line at the spheroid surface on the side facing the wall appears to be reduced in comparison with that on the far side.

Another example presented here to demonstrate the generality of the proposed method is a prolate Cassini oval moving perpendicularly towards an infinite conducting planar wall. The equation for a Cassini oval in polar coordinates is (figure 5)

$$\rho^2 = c^2 \cos 2\vartheta + (a^4 - c^4 \sin^2 2\vartheta)^{\frac{1}{2}} \quad (a > c > 0), \tag{4.2}$$

where ρ, ϑ are radius and polar angle respectively, c is the focus, a is a constant and $b = (a^2 - c^2)^{\frac{1}{2}}$ is the distance from the origin to the intersection point formed by the oval with the R-axis. Again we choose $b = 1$ for convenience and $(-c, 0)$, $(c, 0)$ are segment end points A and B, respectively. Collocation points are arranged similarly to those in the case of a spheroid. Convergent results to at least four significant digits are depicted in figures 6(a) and 6(b) for electrophoretic mobilities and sedimentary mobilities for



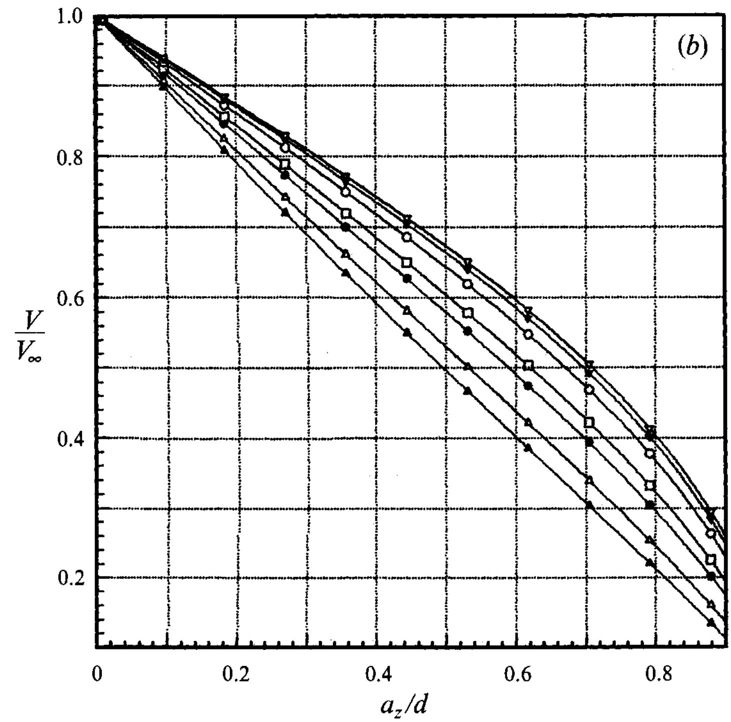


FIGURE 6. (*a*) Electrophoretic mobilities ($4\pi\eta U/\epsilon\zeta E_\infty$), and (*b*) sedimentary mobilities (V/V_∞) versus a_z/d for various c for Cassini ovals: c: ▲ – ▲, 0.3; △ – △, 0.5; ■ – ■, 0.8; □ – □, 1.0; ○ – ○, 1.5; ▼ – ▼, 2.0; ▽ – ▽, 2.5.

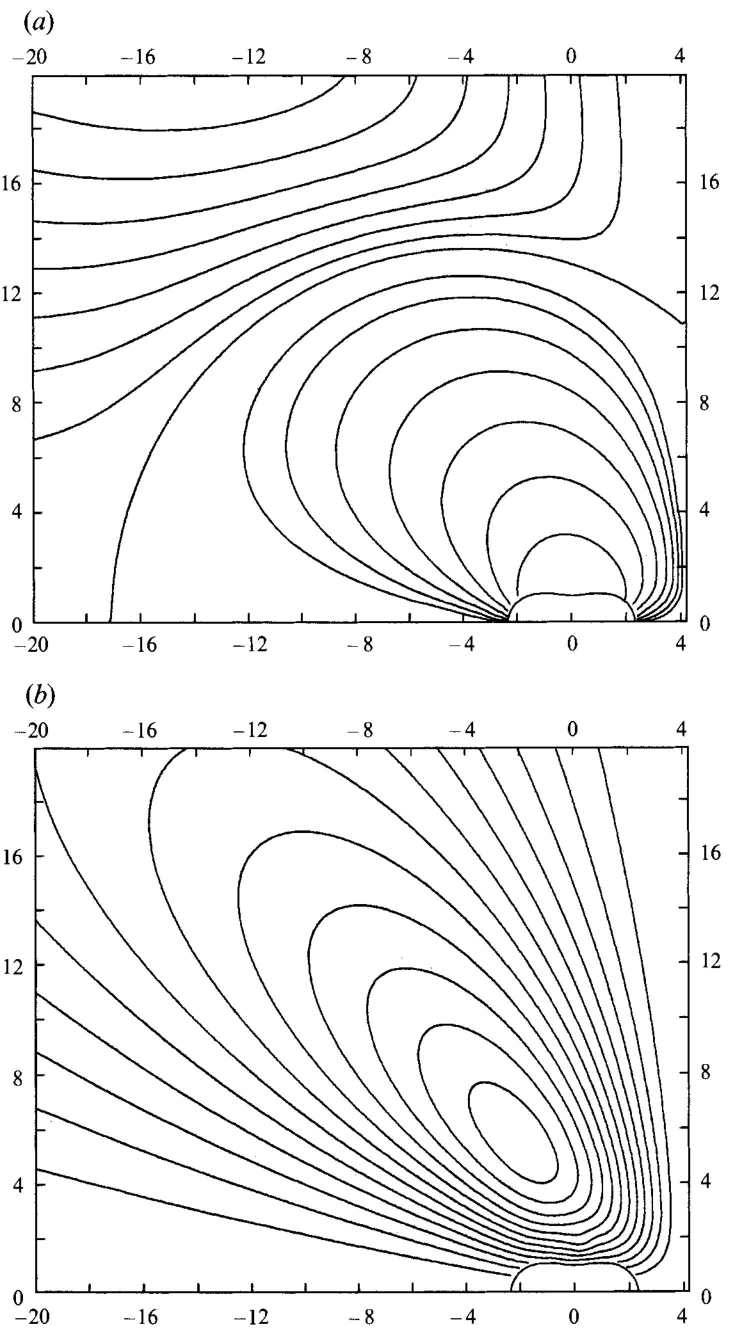


FIGURE 7. Streamlines for (*a*) electrophoretic and (*b*) sedimentary motion of the Cassini oval for $c = 1.5$, $d/a = 2.35$.

various a_z/d and c, where a_z is the distance from the origin to the intersection point at the Z-axis of the particle. The curves for the mobilities of a Cassini oval are quite similar to those of the spheroid and so the conclusions for the spheroid are also valid here. An example of flow patterns of electrophoresis and sedimentation together with the corresponding electric field lines are presented in figures 7 and 8 for a slightly concaved Cassini oval with $c = 1.5$, $d/a = 2.35$.

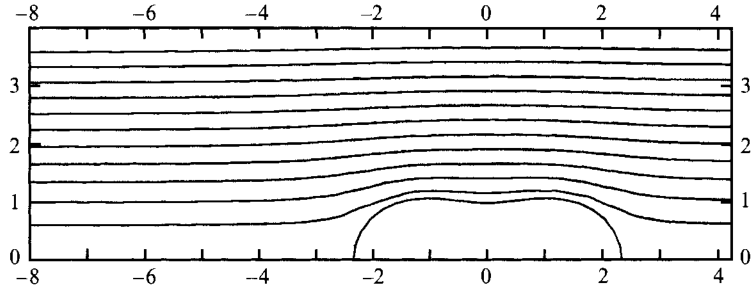


FIGURE 8. Electric field lines for the Cassini oval with $c = 1.5$, $d/a = 2.35$.

5. Concluding remarks

In the present paper, the method of internal distribution of singularities developed by Wu (1984) has been applied to obtain the solution of the problem of the electrophoretic motion of an arbitrary prolate particle of revolution towards an infinite conducting planar wall. As two examples, a prolate spheroid and a prolate Cassini oval with different shapes and various spacings from the wall are considered. The numerical results indicate that impressive convergence and accuracy characteristics can be achieved using this procedure with acceptable computational expense. Both the boundary effect and the influence of the particle shape are studied and the results are significantly different from those in the unbounded case or of a spherical particle. The most important result in this work is that the wall effect on electrophoretic mobility will reduce with the increase of slenderness ratio of the particle. It is shown that the present method is particularly suitable for non-slender bodies and needs a relatively small amount of computation compared with other methods such as the boundary integral method. Moreover, this method can be easily extended to more complex particle–particle or particle–boundary interaction problems.

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