Pergamon

Int. J. Multiphase Flow Vol. 21, No. 4, pp. 705–714, 1995
Copyright © 1995 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0301-9322/95 \$9.50 + 0.00

0301-9322(95)00002-X

ELECTROPHORESIS OF TWO ARBITRARY AXISYMMETRIC PROLATE PARTICLES

KE-LI SUN and WANG-YI WU†

Department of Mechanics, Peking University, Beijing, 100871, People's Republic of China

(Received 9 October 1994; in revised form 26 December 1994)

Abstract—The electrophoretic motion of two freely-suspended, non-conducting arbitrary coaxial prolate particles of revolution with thin electrical double layers is investigated using the method of internal distribution of singularities. Corrections to the Smoluchowski equation due to particle interactions are determined. The electrophoretic mobilities of two prolate spheroid particles are calculated for different distances of two particles, various ratios of zeta potentials and a variety of parameters of particle shape. It is also found that the electrophoretic particles in our problem do not interact with one another when they have equal surface zeta potentials.

Key Words: electrophoresis, prolate particle

1. INTRODUCTION

A charged particle suspended in an electrolyte solution is covered by an electrical double layer of diffuse ions having a total charge, equal and opposite in sign, to that of the particle. The charged particle moves through the liquid when an electric field is exerted on the particle. This motion is termed electrophoresis, which is an interesting subject in chemical and biomedical engineering and has been applied to particle characterization or separation in a variety of colloidal and biological systems. Determination of electrophoretic velocity is one of the main topics in electrophoresis. For a single charged particle suspended in an unbounded electrolyte fluid of viscosity η and dielectric constant ϵ, the electrophoretic velocity U_0 is evaluated by the well-known Smoluchowski equation:

$$U_0 = \frac{\epsilon\zeta}{4\pi\eta} E_\infty$$

where ζ is the zeta potential of the particle surface and E_∞ is the applied constant electrical field. The ratio U_0/E_∞ is known as the electrophoretic mobility of the particle. The Smoluchowski equation holds for non-conducting particles of any shape, providing the local radii of curvature of the particle are much larger than the thickness of the electrical double layer covering the particles.

Colloidal particles encountered in practice are often not isolated and will migrate in the presence of neighbouring particles or boundaries, so it is necessary to determine how they affect the movement of particles and therefore modify the Smoluchowski equation. Using spherical bipolar co-ordinates, Reed & Morrison (1976) studied the electrophoresis of two arbitrarily oriented spheres with equal radii. Their results were presented for various distances apart as well as for several values of zeta potential ratio and it is shown that no interaction exists for the case of two spheres with identical zeta potentials. Utilizing these data for two equal-sized spheres, Anderson (1981) considered the concentration effect on electrophoretic mobility in a bounded, dilute dispersion; the dependence is rather weaker than that of gravity settling. The aforementioned work was extended by Chen & Keh (1988) and Keh & Chen (1989a,b) to the electrophoretic motion of two arbitrarily oriented spheres with arbitrary ratios of radii and zeta potentials by the method of reflection using the spherical bipolar co-ordinates. The axisymmetric electrophoretic motion of multipole spheres along their line of centre was calculated by Keh & Yang (1990) by making use

†To whom correspondence should be addressed.

of the multipole method and the boundary collocation technique, provided there was no restriction on zeta potential, sphere radii or distance apart.

All previous solutions for corrected electrophoretic velocity are available only for spheres. In this paper we will study the axisymmetric electrophoretic motion of two freely suspended and non-conducting arbitrary coaxial prolate bodies of revolution along their common axis of revolution. The two particles can differ both in size and in shape. The method of internal distribution of singularities developed by Wu (1984) is adopted to solve the electrostatic and the hydrodynamic equations. The modified Smoluchowski equation for the prolate spheroid is obtained with satisfactory convergence for different particle shapes, zeta potentials and distances apart.

The mathematical description of the problem will be presented in section 2, while in section 3 the method of internal distribution of singularities will be considered. Finally in section 4 the convergence and accuracy of the method will be examined and the covergent numerical results of the electrophoretic mobilities for different parameters are given in detail.

2. MATHEMATICAL DESCRIPTION

Consider the axisymmetric electrophoretic motion of two non-conducting and freely suspended arbitrary coaxial prolate particles of revolution. Cylindrical and spherical co-ordinates (R, θ, z) and (r, θ, ϕ) are introduced with the origin at O_1 (figure 1). z_0 is the distance between the centres of the two particles. A uniform electric field $E_\infty \mathbf{e}_z$ is imposed on the particles along their common axis of revolution. Assume that the thickness of the double layer is much smaller than the characteristic curvature radius of the particle and the fluid outside the thin double layer is electrically neutral with constant conductivity. The co-ordinates can be non-dimensionalized by taking L_1, the characteristic length of particle 1, as the reference length. The electric potential ϕ_e and electric stream function ψ_e, which are related to the local electric field $\mathbf{E(x)}$ by the following relationships can then be introduced:

$$\mathbf{E(x)} = -E_\infty \nabla \phi_e, \quad E_z = -\frac{\partial \phi_e}{\partial z} = -\frac{1}{R}\frac{\partial \psi_e}{\partial R}, \quad E_R = -\frac{\partial \phi_e}{\partial R} = \frac{1}{R}\frac{\partial \psi_e}{\partial z} \qquad [1]$$

where E_R, E_z are the dimensionless components of $\mathbf{E}$ in the R and z directions. The governing equation for the electric stream function $\psi_e(\mathbf{x})$ is given by the following equations and boundary conditions:

$$E^2 \psi_e = 0 \qquad [2]$$

$$\psi_e = 0 \quad \text{on } S_1 \qquad [3a]$$

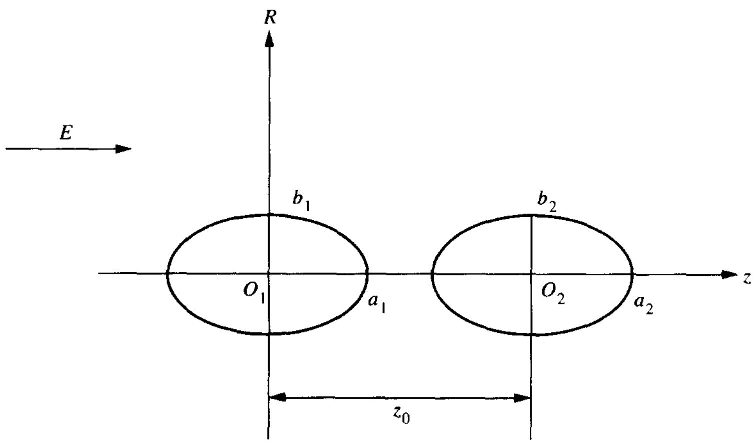

Figure 1. Configuration of two arbitrary axisymmetric prolate particles in electrophoretic motion.

$$\psi_e = 0 \quad \text{on } S_2 \tag{3b}$$

$$\psi_e \to -\frac{R^2}{2} \quad \text{as} \quad r \to \infty \tag{3c}$$

where S_1, S_2 refer to the surfaces of the two particles. The Stokes operator E^2 in the cylindrical co-ordinates has the form

$$E^2 = R\frac{\partial}{\partial R}\left(\frac{1}{R}\frac{\partial}{\partial R}\right) + \frac{\partial^2}{\partial z^2} \tag{4}$$

Once the electric field is determined, we turn to consider the fluid field. Since the Reynolds number of the fluid flow is small, the stream function ψ' of the axisymmetric steady Stokes flow is governed by

$$E^2(E^2\psi') = 0 \tag{5}$$

The stream function ψ' is related to the velocity components by

$$v_z = \frac{1}{R}\frac{\partial\psi'}{\partial R}, \quad v_R = -\frac{1}{R}\frac{\partial\psi'}{\partial z} \tag{6}$$

The electric field acts on the double layer of the ions at the particle surfaces and induces electro-osmotic tangential velocities $\mathbf{U}_s$ on the surfaces of the particles which are related to the local electric field $\mathbf{E}_s = -E_\infty \nabla\phi$ by the Helmholtz equation for electro-osmotic flow:

$$\mathbf{U}_s = -\frac{\epsilon\zeta}{4\pi\eta}\mathbf{E}_s$$

On account of this fact, the boundary conditions for the fluid field are

$$\mathbf{V}' = U_1'\mathbf{e}_z + \frac{\epsilon\zeta_1 E_\infty}{4\pi\eta}\nabla\phi_e \quad \text{on } S_1 \tag{7a}$$

$$\mathbf{V}' = U_2'\mathbf{e}_z + \frac{\epsilon\zeta_2 E_\infty}{4\pi\eta}\nabla\phi_e \quad \text{on } S_2 \tag{7b}$$

$$\mathbf{V}' = 0 \quad \text{as} \quad r \to \infty \tag{7c}$$

where U_1', U_2' are the instantaneous electrophoretic velocities of the two particles to be determined, ζ_1, ζ_2 are the zeta potentials of the particle surfaces S_1 and S_2, respectively. Note that the local electric field $\nabla\phi_e$ will be calculated from the electrostatic equation [2], boundary conditions [3a–c] and the relationships [1].

Non-dimensionalizing [5] and boundary conditions [7a–c] by taking $\epsilon\zeta_1 E_\infty/4\pi\eta$ as the characteristic velocity, we have

$$E^2(E^2\psi) = 0 \tag{8}$$

$$\mathbf{V} = \mathrm{U}_1\mathbf{e}_z + \nabla\phi_e \quad \text{on } S_1 \tag{9a}$$

$$\mathbf{V} = \mathrm{U}_2\mathbf{e}_z + \xi\nabla\phi_e \quad \text{on } S_2 \tag{9b}$$

$$\mathbf{V} = 0 \quad \text{as} \quad r \to \infty \tag{9c}$$

where the physical quantities without prime refer to the non-dimensional quantity and

$$\xi = \frac{\zeta_2}{\zeta_1} \tag{10}$$

$$U_1 = \frac{U_1'}{\dfrac{\epsilon\zeta_1 E_\infty}{4\pi\eta}} = \lambda_1 \tag{11}$$

$$U_2 = \frac{U_2'}{\dfrac{\epsilon\zeta_1 E_\infty}{4\pi\eta}} = \lambda_2\frac{\zeta_2}{\zeta_1} = \lambda_2\xi \tag{12}$$

here we define

$$\lambda_1 = \frac{U_1'}{\frac{\epsilon\zeta_1 E_\infty}{4\pi\eta}}, \quad \lambda_2 = \frac{U_2'}{\frac{\epsilon\zeta_2 E_\infty}{4\pi\eta}}$$

as the non-dimensional electrophoretic mobilities of particles 1 and 2, respectively.

In order to determine the electrophoretic velocities U_1 and U_2 of the particles, it is convenient to decompose the boundary condition [9a,b] and the total flow into four parts using the linearity of the governing equation and the boundary conditions. Let

$$\mathbf{V} = U_1\mathbf{V}_1 + U_2\mathbf{V}_2 + \mathbf{V}_3 + \xi\mathbf{V}_4, \quad \psi = U_1\psi_1 + U_2\psi_2 + \psi_3 + \xi\psi_4 \tag{13}$$

here $\psi_1, \psi_2, \psi_3, \psi_4$ and $\mathbf{V}_1, \mathbf{V}_2, \mathbf{V}_3, \mathbf{V}_4$, satisfy

$$E^2(E^2\psi_i) = 0 \quad i = 1, 2, 3, 4 \tag{14}$$

$$\mathbf{V}_1 = \mathbf{e}_z, \quad \mathbf{V}_2 = 0, \quad \mathbf{V}_3 = \nabla\phi_e, \quad \mathbf{V}_4 = 0 \quad \text{on } S_1 \tag{15a}$$

$$\mathbf{V}_1 = 0, \quad \mathbf{V}_2 = \mathbf{e}_z, \quad \mathbf{V}_3 = 0, \quad \mathbf{V}_4 = \nabla\phi_e \quad \text{on } S_2 \tag{15b}$$

$$\mathbf{V}_i = 0 \quad \text{as} \quad r \to \infty \quad i = 1, 2, 3, 4 \tag{15c}$$

Once these four boundary value problems are solved, the electrophoretic velocities as well as the mobilities are readily obtained, since the net forces exerted by the fluid on the freely suspended particles must disappear. Writing the zero drag requirement for the two particles we have

$$\begin{cases} U_1F_{11} + U_2F_{12} + F_{13} + \xi F_{14} = 0 \\ U_1F_{21} + U_2F_{22} + F_{23} + \xi F_{24} = 0 \end{cases} \tag{16}$$

where the F_{1i} and F_{2i} $(i = 1, 2, 3, 4)$ are the net forces acting on the particle surfaces S_1 and S_2 obtained from the four boundary value problems. Equation [16] is a system of linear algebraic equations to determine the dimensionless electrophoretic velocities U_1 and U_2, which can be expressed as:

$$U_1 = e_1 + f_1\xi, \; U_2 = e_2 + f_2\xi \tag{17}$$

where

$$e_1 = \Delta_{11}/\Delta, \quad f_1 = \Delta_{12}/\Delta, \quad e_2 = \Delta_{21}/\Delta, \quad f_2 = \Delta_{22}/\Delta,$$

$$\Delta_{11} = F_{12}F_{23} - F_{13}F_{22} \quad \Delta_{12} = F_{12}F_{24} - F_{14}F_{22}$$

$$\Delta_{21} = F_{13}F_{21} - F_{11}F_{23} \quad \Delta_{22} = F_{14}F_{21} - F_{11}F_{24} \quad \Delta = F_{11}F_{22} - F_{12}F_{21} \tag{18}$$

In the case of $\xi = 1$, we can prove that the dimensionless velocities and the non-dimensional electrophoretic mobilities of the two particles are identical and equal to unity, i.e.

$$U_1 = U_2 = \lambda_1 = \lambda_2 = 1$$

Therefore, both particles move as if they were isolated and the Smoluchowski equation holds exactly for these particles.

In fact, it is easy to verify that when $\xi = 1$, $\mathbf{V} = \mathbf{e}_z - \mathbf{E}/E_\infty$ and $U_1 = U_2 = 1$ are the solutions of [8] with the boundary conditions [9a–c]. Such flow causes no drag force to the particles because it is a potential flow.

Considering that $U_1 = U_2 = 1$ while $\xi = 1$, we have from [17]

$$e_1 + f_1 = 1, \quad e_2 + f_2 = 1$$

and

$$U_1 = e_1 + (1 - e_1)\xi, \quad U_2 = e_2 + (1 - e_2)\xi \tag{19}$$

The non-dimensional mobilities λ_1 and λ_2 of the two particles can be calculated by means of [11] and [12]

$$\lambda_1 = e_1 + (1 - e_1)\xi, \quad \lambda_2 = \frac{e_2}{\xi} + (1 - e_2) \qquad [20]$$

Thus our main problem is to find F_{1i} and F_{2i} $(i = 1, 2, 3, 4)$, which will be accomplished in the following section.

3. METHOD OF INTERNAL DISTRIBUTION OF SINGULARITIES IN ELECTROPHORESIS

In this section, the method of internal distribution of singularities developed by Wu (1984) is employed to solve the electrostatic equation and hydrodynamic equation describing the electrophoresis of two arbitrary coaxial prolate particles of revolution.

3.1. Electrical field

Since the electric field and the inviscid potential axisymmetric flow past an axisymmetric body have the same governing equation and boundary conditions, the method of internal distribution of singularities presented in Chen & Wu (1988) is utilized. The fundamental singularity to electric field at $z = \bar{\xi}$ and $R = 0$ can be written as:

$$Q'(R, z, \bar{\xi}) = \sum_{n=2}^{\infty} B_n SE_n(R, z, \bar{\xi}) \qquad [21]$$

where

$$Q'(R, z, \bar{\xi}) = (\psi_e, E_z, E_R) \qquad [22]$$

$$SE_n(R, z, \bar{\xi}) = (F_n^{(3)}(R, z - \bar{\xi}), \quad F_n^{(1)}(R, z - \bar{\xi}), \quad F_n^{(5)}(R, z - \bar{\xi})) \qquad [23]$$

and

$$F_n^{(1)}(R, z) = r^{-(n+1)} P_n(\bar{\zeta}), \quad F_n^{(3)}(R, z) = r^{-(n-1)} C_n^{-1/2}(\bar{\zeta}),$$
$$F_n^{(5)}(R, z) = (n + 1) r^{-n} C_{n+1}^{-1/2}(\bar{\zeta}) \qquad [24]$$

$$r = (R^2 + z^2)^{1/2} \quad \text{and} \quad \bar{\zeta} = \cos\theta = \frac{z}{r} \qquad [25]$$

here P_n is the Legendre polynomial of order n, $C_n^{-1/2}$ is the Gegenbauer function of the first kind of order n and degree $-1/2$.

Following the approach presented in Wu (1984), a segment of straight line $A_iB_i(-c_i, c_i)$ $(i = 1, 2)$ inside each particle is chosen, where $2c_i$ is the length of the line segment. If the nose and tail of the particle are rounded, their centres of curvature could be prescribed as A and B. Distributing the singularity [21] continuously over AB, plus the undisturbed uniform electric field, we obtain:

$$Q(R, z) = (-R^2/2, 1, 0) + \sum_{n=2}^{\infty} \left[\int_{-c_1}^{c_1} B_n^{(1)}(\bar{\xi}) SE_n(R, z, \bar{\xi})\, d\bar{\xi} + \int_{-c_2}^{c_2} B_n^{(2)}(\bar{\xi}) SE_n(R, z - z_0, \bar{\xi})\, d\bar{\xi} \right] \qquad [26]$$

where $B_n^{(1)}(\bar{\xi})$ and $B_n^{(2)}(\bar{\xi})$ are the unspecified density functions of the singularities along AB which are to be determined by satisfying boundary conditions on the surfaces of the particles.

Obviously [26] satisfies the governing equation [2] and the boundary condition at infinity [3c]. All that remains is to satisfy the conditions [3a] and [3b] on the surfaces of the particles. This will eventually lead to a set of integral equations to be solved for the unknown density functions $B_n^{(1)}(\bar{\xi})$ and $B_n^{(2)}(\bar{\xi})$.

Since the complexity of the kernel functions in the integral equation precludes an analytical solution, the integral equations will be solved approximately.

To this end, following the approach proposed by Chen & Wu (1988), the segment A_iB_i is partitioned into M subintervals (dj_1, dj_3). With the end points dj_1, dj_3 and midpoint dj_2 of each subinterval to be chosen as interpolating points, the density functions are approximated by piecewise polynomials of second order interpolating the density function at these nodal points. Truncating the infinite series at the Nth term, [26] becomes

$$Q(R,z)=(-R^2/2,1,0)+\sum_{j=1}^{m}\sum_{n=2}^{N+1}\left[\int_{dj_1}^{dj_3} B_{nj}^{(1)}(\bar{\xi})SE_n(R,z,\bar{\xi})\,d\bar{\xi}+\int_{dj_2}^{dj_3} B_{nj}^{(2)}(\bar{\xi})SE_n(R,z-z_0,\bar{\xi})\,d\bar{\xi}\right] \quad [27]$$

where

$$B_{nj}(\bar{\xi})=\frac{(\bar{\xi}-dj_2)(\bar{\xi}-dj_3)}{(dj_1-dj_2)(dj_1-dj_3)}B_{nj1}+\frac{(\bar{\xi}-dj_1)(\bar{\xi}-dj_3)}{(dj_2-dj_1)(dj_2-dj_3)}B_{nj2}+\frac{(\bar{\xi}-dj_2)(\bar{\xi}-dj_1)}{(dj_3-dj_2)(dj_3-dj_1)}B_{nj3} \quad [28]$$

Here B_{njk} ($k = 1, 2, 3$) are the corresponding values of the density function at the three interpolating points. Substituting [28] into [27], after some algebraic manipulation we have

$$Q(R,z)=(-R^2/2,1,0)+\sum_{j=1}^{m}\sum_{n=2}^{N+1}\sum_{k=1}^{3}[B_{n,2(j-1)+k}^{(1)}WE_{njk}(R,z)+B_{n,2(j-1)+k}^{(2)}WE_{njk}(R,z-z_0)] \quad [29]$$

where

$$WE_{njk}=(G_{njk}^{(3)},G_{njk}^{(1)},G_{njk}^{(5)}) \quad [30]$$

$$G_{njk}^{(i)}=\sum_{l=1}^{3}q_{lk}G_{nl}^{(i)}(R,z) \quad i=1,3,5 \quad [31]$$

$$q_{1k}=\frac{(z-dj_2)(z-dj_3)(z-dj_1)}{z-dj_k}\frac{(-1)^{k-1}H_k}{H_1H_2H_3}$$

$$q_{2k}=\{(z-dj_k)-[(z-dj_1)+(z-dj_2)+(z-dj_3)]\}\frac{(-1)^{k-1}H_k}{H_1H_2H_3} \quad k=1,2,3 \quad [32]$$

$$q_{3k}=\frac{(-1)^{k-1}H_k}{H_1H_2H_3}$$

$$H_1=dj_3-dj_2,\quad H_2=dj_3-dj_1,\quad H_3=dj_2-dj_1 \quad [33]$$

$$G_{nl}^{i}(r,z)=\int_{dj_1}^{dj_3}(z-\bar{\xi})^{l-1}F_n^{(i)}(R,z-\bar{\xi})\,d\bar{\xi} \quad i=1,3,5 \quad [34]$$

$G_{nl}^{(i)}$ can be evaluated by a recurrence formula as shown in Chen & Wu (1988).

Applying the collocation technique, boundary conditions [3a] and [3b] are exactly satisfied at $N(2M + 1)$ points on each surface of the two particles. Equation [29] is then reduced to a system of $2N(2M + 1)$ linear algebraic equations to determine the unknown coefficient $B_{nj}^{(1)}$, $B_{nj}^{(2)}$, which can be solved by a standard matrix inversion method. The accuracy of the solution can be improved in principle to any degree by increasing the values of N and M. Therefore the electric field distribution is finally determined, which provides the necessary data for further consideration of the fluid velocity distribution.

3.2. Fluid velocity field

Once the electric field was obtained, we now proceed to consider the hydrodynamic field. A procedure similar to that in section 3.1 for the electric field is adopted. First, the expressions for a singularity of Stokes flow [5] located at $R = 0$, $z = \bar{\xi}$ can be written as follows (Wu 1984):

$$U(R,z,\bar{\xi})=\sum_{n=2}^{\infty}C_nS_n(R,z,\bar{\xi})+D_nT_n(R,z,\bar{\xi}) \quad [35]$$

where

$$U(R,z,\bar{\xi})=(\psi,v_z,v_R) \quad [36]$$

$$S_n(R,z,\bar{\xi})=(F_n^{(3)}(R,z-\bar{\xi}),F_n^{(1)}(R,z-\bar{\xi}),F_n^{(5)}(R,z-\bar{\xi})) \quad [37]$$

Table 1. Comparison of the present results with exact solutions ($\zeta = 10$)

		$z_0 = 10$	$z_0 = 5$	$z_0 = 3.3$	$z_0 = 2.5$
λ_1	Present	1.00906	1.07603	1.29595	1.97699
	Exact	1.00906	1.07603	1.29596	1.97696
λ_2	Present	0.99909	0.99240	0.97040	0.90230
	Exact	0.99909	0.99240	0.97040	0.90230

$$T_n(R, z, \bar{\xi}) = (F_n^{(4)}(R, z - \bar{\xi}), F_n^{(2)}(R, z - \bar{\xi}), F_n^{(6)}(R, z - \bar{\xi})) \quad [38]$$

and

$$F_n^{(2)}(R, z) = r^{-(n-1)}(P_n(\bar{\zeta}) + 2C_n^{-1/2}(\bar{\zeta})) \quad [39a]$$

$$F_n^{(4)}(R, z) = r^{-(n-3)}C_n^{-1/2}(\bar{\zeta}) \quad [39b]$$

$$F_n^{(6)}(R, z) = (n+1)r^{-(n-2)}\frac{1}{R}C_{n+1}^{-1/2}(\bar{\zeta}) - 2\frac{z}{R}r^{-(n-1)}C_n^{-1/2}(\bar{\zeta}) \quad [39c]$$

The singularities are distributed continuously along AB, which is then divided into M subintervals with the density function approximated by piecewise quadratic polynomials. Truncating the infinite series at the Nth terms, [35] can be written as

$$U(R, z) = \sum_{j=1}^{M}\sum_{n=2}^{N+1}\sum_{k=1}^{3} [C_{n,2(j-1)+k}^{(1)} W_{njk}(R, z) + D_{n,2(j-1)+k}^{(1)} \times WW_{njk}(R, z) + C_{n,2(j-1)+k}^{(2)} W_{njk}(R, z - z_0) + D_{n,2(j-1)+k}^{(2)} \times WW_{njk}(R, z - z_0)] \quad [40]$$

where

$$W_{njk} = (G_{njk}^{(3)}, G_{njk}^{(1)}, G_{njk}^{(5)}) \quad [41a]$$

$$WW_{njk} = (G_{njk}^{(4)}, G_{njk}^{(2)}, G_{njk}^{(6)}) \quad [41b]$$

the definition of $G_{njk}^{(i)}$ was given in [31]–[34].

As mentioned previously in section 2, the hydrodynamic problem shoud be decomposed into four boundary value problems in order to calculate the electrophoretic mobility of the two particles. The boundary conditions on the surfaces of the particles for the third and fourth boundary value problem are now fully determined using the electric field [1]. By means of the collocation technique,

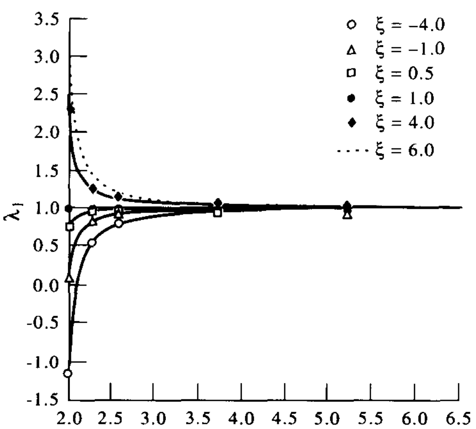

Figure 2. Non-dimensional electrophoretic mobility λ_1 of particle 1 vs z_0 for various ξ with $a_2 = 1, b_1 = b_2 = 1/1.5$.

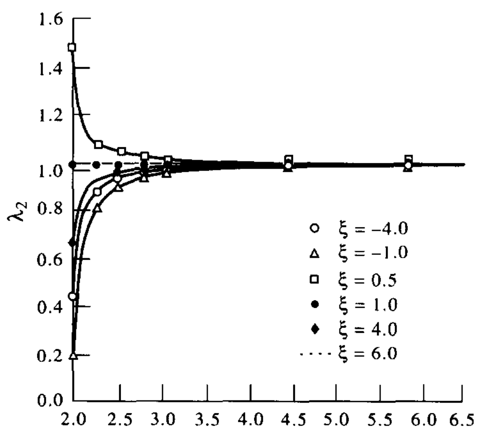

Figure 3. Non-dimensional electrophoretic mobility λ_2 of particle 2 vs z_0 for various ξ with $a_2 = 1, b_1 = b_2 = 1/1.5$.

the boundary conditions [15a] and [15b] are applied at $N(2M+1)$ discrete points at each surface of the two particles, which leads to a set of linear algebraic equations for the unknown coefficients $C_{nj}^{(1)}, D_{nj}^{(1)}, C_{nj}^{(2)}$ and $D_{nj}^{(2)}$. The fluid field is completely solved once these coefficients are evaluated. The drag forces F_1 and F_2 exerted by the fluid on particles 1 and 2 can be determined from Happel & Brenner (1983)

$$F_i = \int_0^\pi \eta\pi r^3 \sin^3\theta \frac{\partial}{\partial r}\left(\frac{E^2\psi}{r^3\sin^3\theta}\right) r\, d\theta \quad i = 1, 2 \tag{42}$$

Substituting the expression for ψ into [42] and considering the orthogonality properties of Legendre and Gegenbauer functions, we have

$$F_i = \frac{2\pi}{3}\sum_{j=1}^{M}\left(D_{2,2(j-1)+1}^{(i)} + 4D_{2,2(j-1)+2}^{(i)} + D_{2,2(j-1)+3}^{(i)}\right)(dj_3 - dj_1) \quad i = 1, 2 \tag{43}$$

4. RESULTS AND DISCUSSION

Consider, as an example, the axisymmetric electrophoretic motion of two freely suspended and non-conducting coaxial prolate spheroids, with their common axis parallel to the direction of an applied electric field.

Suppose the equations of the two prolate spheroids are

$$\frac{z^2}{a_1^2} + \frac{R^2}{b_1^2} = 1 \tag{44}$$

and

$$\frac{(z-z_0)^2}{a_2^2} + \frac{R^2}{b_2^2} = 1 \tag{45}$$

where a_1, a_2 and b_1, b_2 are the major and minor axes, respectively, z_0 is the distance between the two particle centres. The origin of the co-ordinates is chosen at the centre of particle 1. Without loss of generality, we take $a_1 = 1$. In other words, a_1 is selected as a reference length. The foci of the spheroids are chosen as points A and B.

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

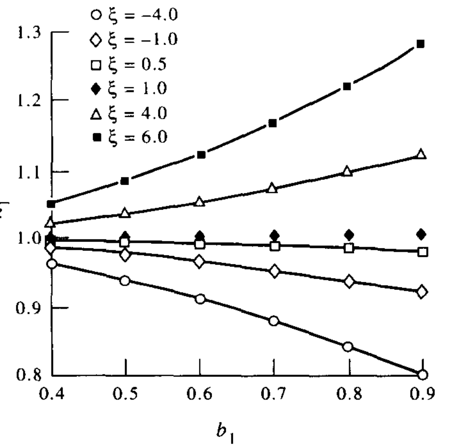

Figure 4. Non-dimensional electrophoretic mobility λ_1 of particle 1 vs b_1 for various ξ with $z_0 = 3, a_2 = 1, b_1 = b_2$.

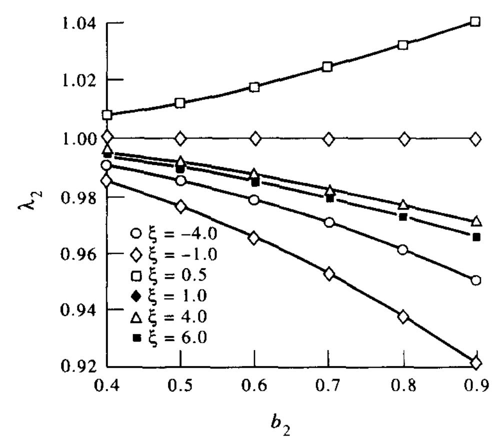

Figure 5. Non-dimensional electrophoretic mobility λ_2 of particle 2 vs b_2 for various ξ with $z_0 = 3, a_2 = 1, b_1 = b_2$.

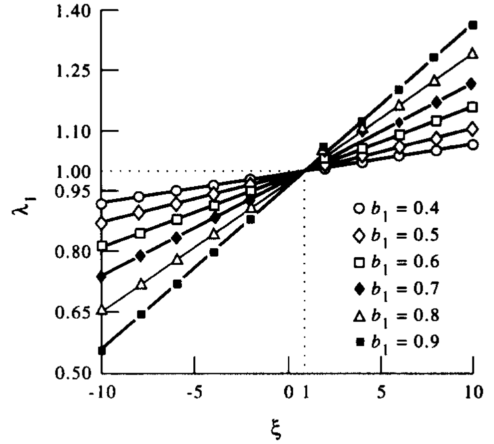

Figure 6. Non-dimensional electrophoretic mobility λ_1 of particle 1 vs ξ for various b_1 with $z_0 = 3, a_2 = 1, b_1 = b_2$.

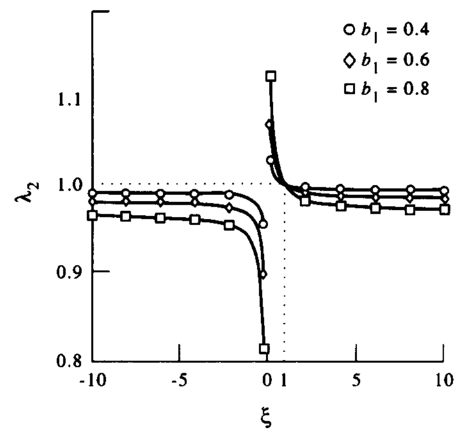

Figure 7. Non-dimensional electrophoretic mobility λ_2 of particle 2 vs ξ for various b_1 with $z_0 = 3, a_2 = 1, b_1 = b_2$.

We shall first test the convergence and accuracy of the method. All of the results obtained converge to at least four significant digits. As a test of the convergence characteristic of the method, a specific case of two spheres with equal radii, i.e. $a_1 = a_2 = b_1 = b_2 = 1$, is calculated, the solutions are compared in table 1 with the exact solutions given by Reed & Morrison (1976). Our results of the mobility agree with exact results to five digits even for the difficult case of $\xi = 10$ and $z_0 = 2.5$. The accuracy test indicates that reliable results with high accuracy can be achieved using the proposed method.

Equations [19] and [20] show that the main factors affecting the dimensionless electrophoretic velocities and mobilities are the ratio of the zeta potentials ξ and the distance between the centres z_0 of the two particles and the parameters a_2, b_1, b_2 of the particle shapes. In this paper, the effects of these factors on mobilities were studied by the above-mentioned semi-analytical and semi-numerical method.

The effect of z_0 on λ_1 and λ_2 for various $\xi(-4, -1, 0.5, 1, 4, 6)$ with $a_2 = 1$ and $b_1 = b_2 = 1/1.5$ are given in figures 2 and 3. The results indicate that when z_0 is small, λ_1 and λ_2 are obviously different from 1 and they tend to 1 rapidly as $z_0 \rightarrow \infty$. This means that the interaction becomes stronger when the particles become closer and decreases sharply with the increase of z_0. The numerical results also suggest that as $z_0 > 5$, the interaction is weak enough to be neglected. In this case the particles can be treated as isolated and Smoluchowski's equation holds with high accuracy. Figure 2 shows that the presence of particle 2 will enhance the velocity of particle 1 as $\xi > 1$ and will weaken it as $\xi < 1$. In the meantime, figure 3 demonstrates that particle 2 will migrate faster

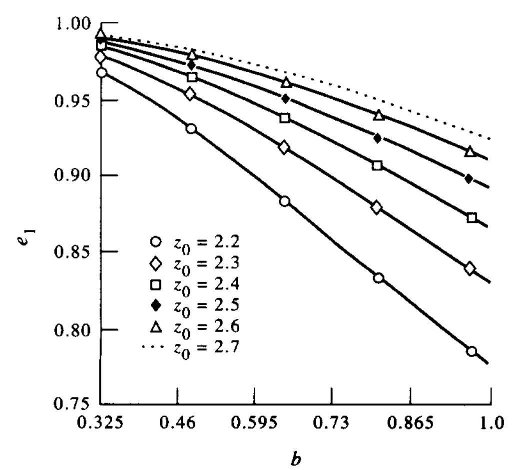

Figure 8. Coefficient e_1 vs b for various z_0 with $a_2 = 1, b_1 = b_2 = b$.

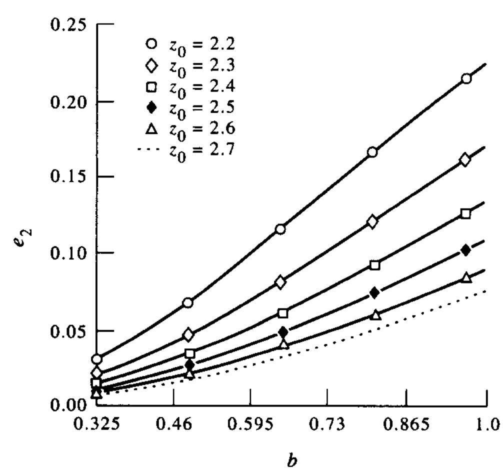

Figure 9. Coefficient e_2 vs b for various z_0 with $a_2 = 1, b_1 = b_2 = b$.

than an isolated particle in the range of $0 < \xi < 1$ and will move slower when $\xi < 0$ or $\xi > 1$. In the case of $\xi = 1$, as was proved in section 2, $\lambda_1 = \lambda_2 = 1$, the two particles move as if they were isolated and Smoluchowski's equation holds exactly.

The curves of λ_1 and λ_2 versus b_1 for various ξ with $a_2 = 1, b_2 = b_1$ and $z_0 = 3.0$ are depicted in figures 4 and 5, which indicate that with fixed ξ and z_0, the interaction will strengthen with increase of b.

It can be seen from [19] and [20] that the dimensionless velocities $U_1 = \lambda_1$ and $U_2 = \xi\lambda_2$ are linear functions of ξ. The non-dimensional electrophoretic mobilities λ_1 and λ_2 versus ξ for various b_1 with $a_2 = 1, b_2 = b_1$ and $z_0 = 3.0$ are plotted in figures 6 and 7. In fact, λ_1 and λ_2 are totally determined by the coefficients e_1 and e_2 which are functions of a_1, a_2, b_1, b_2 and z_0. Figures 8 and 9 demonstrate the effect of $b(b_1 = b_2 = b)$ on e_1 and e_2 with different z_0.

In conclusion, for the case of two freely suspended and non-conducting particles, Smoluchowski's equation needs to be corrected by virtue of the presence of the neighbouring particle. The factors that affect the strength of the interaction are the parameters of the particle shape, the ratio ξ of the zeta potentials and the distance z_0 between the two particles. The dimensionless electrophoretic velocities $U_1 = \lambda_1$ and $U_2 = \xi\lambda_2$ calculated by [19] and [20] are linear functions of ξ. When the distance between two particles is more than five times larger than the characteristic length of the particle, the interacation is weak enough to be neglected.

REFERENCES

Anderson, J. L. 1981 Concentration dependence of electrophoretic mobility. *J. Colloid Interface Sci.* **82,** 248.

Chen, S. B. & Keh, H. J. 1988 Electrophoresis in a dilute dispersion of colloidal spheres. *AIChE J.* **34,** 1075.

Chen, L. L. & Wu, W. Y. 1988 A singularity distribution method to treat the irrotational flow. *Adv. Hydrodyn.* **3,** 70.

Happel & Brenner 1983 *Low Reynolds Number Hydrodynamics.* Nijhoff, The Netherlands.

Keh, H. J. & Chen, S. B. 1989a Particle interactions in electrophoresis. Part 1. Motion of two spheres along their line of centers. *J. Colloid Interface Sci.* **130,** 542.

Keh, H. J. & Chen, S. B. 1989b Particle interactions in electrophoresis. Part 2. Motion of two spheres normal to their line of centers. *J. Colloid Interface Sci.* **130,** 556.

Keh, H. J. & Yang, F. R. 1990 Particle interactions on electrophoresis. Part 3. Axisymmetric motion of multiple spheres. *J. Colloid Interface Sci.* **139,** 105.

Reed, L. D. & Morrison, B. A. 1976 Hydrodynamic interaction in electrophoresis. *J. Colloid Interface Sci.* **54,** 117.

Wu, W. Y. 1984 A new approach of treating the Stokes flow of nonslender prolate arbitrary axisymmetric body. *Scient. Sin. A* **27,** 730.