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Axisymmetric electrophoresis of multiple colloidal spheres

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A study of the electrophoretic motion of a chain of colloidal spheres along the line through their centres is presented. The spheres may differ in radius and in zeta potential and they are allowed to be unequally spaced. Also, the spheres can be either freely suspended in the fluid or linked by infinitesimally thin rods with arbitrary lengths. The fluid can contain an arbitrary combination of general electrolytes. Although the thin-double-layer assumption is employed, the polarization effect of the mobile ions in the diffuse layer is taken into account. A slip velocity of fluid and normal fluxes of ions at the outer edge of the double layer can be derived and used as the boundary conditions for the fluid domain outside the thin double layer. Using a collocation technique along with these boundary conditions, a set of electrokinetic equations governing this problem is solved in the quasi-steady state and the particle interaction effects are computed for various cases. The most important discovery is that a group of particles with the same zeta potential will interact with one another, unlike the no-interaction results obtained in previous investigations assuming that the double layer is infinitesimally thin. For most situations, the particle interaction among the spheres is a complicated function of the properties of the spheres and ions. Also, it no longer varies monotonically with the extent of separation for some cases. The phenomena cannot be predicted systematically by a simple general rule.

1. Introduction

When a charged particle is placed in an electrolyte solution, it is balanced by a surrounding cloud of diffuse ions carrying a net charge equal but opposite to that of the particle. The combination of the fixed charge on the solid surface and the adjacent mobile ions is termed an electrical double layer. If an external electric field is imposed on such a system, the particle will move toward the electrode of opposite sign, while the diffuse counterions migrate in the reverse direction, the motion well known as electrophoresis. The electrophoretic velocity $U^{(0)}$ of the particle can be related to the applied field $\boldsymbol{E}_\infty$ by the Smoluchowski equation

$$U^{(0)} = \frac{\epsilon\zeta}{4\pi\eta}\boldsymbol{E}_\infty. \tag{1.1}$$

Here, ζ is the zeta potential on the shear plane of the particle, ϵ is the dielectric constant of the solution, and η is the fluid viscosity. Equation (1.1) can be applied

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to a non-conducting particle of arbitrary shape; however, its validity is based on the following assumptions:

(i) the zeta potential is uniform over the particle surface;

(ii) the local radius of curvature of the particle is much larger than the thickness of the double layer, i.e. $\kappa L \rightarrow \infty$, where κ^{-1} is the Debye screening length and L is the characteristic length of the particle;

(iii) the ion concentrations are not affected by the imposed field, that is, the cloud of diffuse ions is at equilibrium.

In fact, the equilibrium distribution of the ions inside the double layer would be distorted when an external electric field is imposed. This so-called polarization of the double layer becomes significant when the zeta potential is large. O'Brien & White (1978) studied the electrophoretic motion of a spherical particle when the applied field is not strong. Taking the double-layer distortion as a perturbation, their work involving numerical calculations was applicable to a broad range of ζ and κL. On the other hand, Dukhin & Derjaguin (1974) obtained an analytical mobility expression for a charged sphere with a thin but polarized double layer in a symmetric electrolyte solution. Later, O'Brien (1983) extended their analysis to explore this locomotion for the case of an arbitrary combination of general electrolytes. The advantage of Dukhin & Derjaguin's theory is that a 'slip velocity' at the outer boundary of the diffuse layer has been derived, so the only region one needs to take into account is the neutral fluid phase outside the double layer. It was found that the effect of polarization of the double layer is to impede the particle's movement. One reason for this outcome is that the back field resulting from the polarization of the diffuse ions has a tendency to resist the imposed field. The electrophoresis of a spheroid with a thin distorted double layer has also been studied by Dukhin & Shilov (1980) and O'Brien & Ward (1988). They found that this polarization effect would even change the direction of the spheroid's migration, making it no longer parallel to the applied field.

In most real electrophoresis situations, collections of particles are encountered. Thus, it is important to examine how the presence of its neighbours affects the movement of a particle. Recently, much progress has been made in the mathematical analysis of the particle interactions in electrophoresis of dielectric spheres with an extremely thin double layer, i.e. $\kappa L \rightarrow \infty$. Chen & Keh (1988) utilized a method of reflections to analytically solve the problem of electrophoretic motion of two arbitrarily oriented spheres with arbitrary ratios of radii and zeta potentials. Corrections to Smoluchowski's equation due to particle interactions were determined in a power series in r_{12}^{-1} up to $O(r_{12}^{-7})$, where r_{12} is the centre-to-centre distance between the spheres. Another approach to investigate the two-sphere motion is to utilize spherical bipolar coordinates. By this means, the electrophoretic mobilities of two non-rotating spheres with equal sizes were first computed by Reed & Morrison (1976), and recently this work was extended to the situation of two arbitrary freely suspended spheres (Keh & Chen 1989*a*, *b*). Later a third routine employed to solve this problem was the multipole collocation technique, which can be used to examine the motion of a collection of more than two arbitrary spheres. It can also allow the calculation of the electrophoretic mobilities of a group of spheres separated by any distance, including when they are touching (Keh & Yang 1990, 1991). One of the common conclusions from the above articles is that there is no particle interaction as long as all spheres have the same zeta potential.

Until now, the interactions among particles with polarization of the double layer have not been investigated. The object of the present work is to study the axisymmetric electrophoretic motion of multiple spheres, which are surrounded by distorted clouds of diffuse ions, directed along their line of centres. It is assumed that the thickness of the double layer is small but the value of κL is still finite. The spheres may differ in radius and in zeta potential and they are allowed to be unequally spaced. Also, the fluid solution can be composed of more than one kind of general electrolyte. By using a multipole truncation (or collocation) technique, a set of electrokinetic equations is solved semianalytically in the quasi-steady state. The spheres' velocities are obtained with good convergence for various cases. In the limiting case of $\kappa L \rightarrow \infty$, our results are in excellent agreement with those obtained in previous analyses (Keh & Chen 1989*a*; Keh & Yang 1990).

This paper is presented in five sections. In §2, we adopt O'Brien's (1983) theory and follow the same procedure to briefly restate the derivation of the slip velocity at the outer edge of the double layer. In addition to the derivation of some analytical formulae for the case of a symmetric electrolyte, we make a slight modification to the calculation of the electrophoretic velocity by a numerical integration following the numerical solution of the Poisson–Boltzmann equation for the case of general electrolytes. Then, the multipole collocation technique is employed to solve the electrokinetic equations for the axisymmetric motion of N spheres located on a straight line through their centres in §3. In §4, we exhibit the results for the electrophoretic motion of an isolated sphere, of two free spheres, of three free spheres, and of a rigid dumbbell. Finally, a short summary of this work is given in §5.

2. Electrophoresis of a dielectric particle

Consider the electrophoretic motion of a non-conducting particle in an unbounded quiescent fluid. The particle is charged uniformly on the surface and the thickness of the electrical double layer is assumed to be small compared to the particle dimension. The bulk number densities of all ions in the electrolyte solution beyond the double layer are constant. In spite of the assumption of a thin double layer, the electric-field-induced polarization of ionic distribution in the double layer will still be considered. The gravitational effect is ignored. Our aim in this section is to analyse such a system and to introduce how the polarization of the diffuse layer influences the electrophoretic mobility of the particle, which can no longer be predicted properly by the Smoluchowski equation.

2.1. *Electrokinetic equations*

To calculate the electrophoretic mobility of a charged particle, in general, it is necessary to determine the ionic concentration, electrical potential and fluid velocity distributions in the electrolyte solution. When there is no chemical reaction occurring among the ions and the system is in a steady state, the conservation of all M ionic species requires that

$$\nabla \cdot \boldsymbol{J}_m = 0, \quad m = 1, 2, \ldots, M, \tag{2.1}$$

where $\boldsymbol{J}_m$ is the density flux of the mth type of ion. If the electrolyte solution is dilute, this flux of density is given by (O'Brien 1986)

$$\boldsymbol{J}_m = n_m \boldsymbol{v} - n_m D_m \nabla \mu_m / kT, \tag{2.2}$$

with the electrochemical potential energy of the mth species of ion, μ_m, defined as

$$\mu_m = \mu_m^0 + kT \ln n_m + e z_m \Phi. \tag{2.3}$$

Here, $\boldsymbol{v}$ is the fluid velocity; Φ is the electrical potential; n_m, D_m and z_m are the number density, diffusion coefficient and valence of type-m ions, respectively; k is the Boltzmann constant; T is the absolute temperature; e is the charge of a proton; μ_m^0 is a constant. The first term on the right-hand side of (2.2) represents the convection of the ions by the fluid and the second term indicates both the diffusion and the electrically induced migration of the ions.

Because the Reynolds number for the electrophoretic motion is so low that the inertial effect is negligible, the fluid flow field satisfies the modified Stokes equations

$$\eta \nabla^2 \boldsymbol{v} - \nabla p = \rho_e \nabla \Phi, \quad \nabla \cdot \boldsymbol{v} = 0, \tag{2.4a, b}$$

where η and p are the fluid viscosity and pressure distribution respectively, and $\rho_e = \sum_{m=1}^{M} e z_m n_m$ denotes the charge density of the fluid.

If the intensity of the applied electric field is not high, the ionic number densities and the electrical potential deviate very slightly from those at equilibrium. Hence, we can express them as

$$n_m = n_m^0 + \delta n_m, \quad \Phi = \Phi^0 + \delta \Phi, \tag{2.5a, b}$$

where Φ^0 and n_m^0 are the equilibrium electrical potential and ionic number densities, respectively, that satisfy the Boltzmann distribution; the small quantities δn_m and $\delta \Phi$ refer to related perturbations. By combining (2.1)–(2.5) and ignoring the products of the small quantities, a set of electrokinetic equations for the fields μ_m and $\boldsymbol{v}$ can be obtained (O'Brien & White 1978; O'Brien 1983):

$$n_m^0 \nabla^2 \mu_m + \nabla n_m^0 \cdot \nabla \mu_m = \frac{kT}{D_m} \nabla n_m^0 \cdot \boldsymbol{v}, \quad m = 1, 2, \ldots, M, \tag{2.6a}$$

$$\eta \nabla^2 (\nabla \times \boldsymbol{v}) = \sum_{m=1}^{M} \nabla n_m^0 \times \nabla \mu_m. \tag{2.6b}$$

Beyond the double layer (the 'inner' region) surrounding the particle, or in the 'outer' region, no ionic concentration gradients ∇n_m^0 occur and the fluid is electrically neutral. The electrokinetic equations (2.6) become

$$\nabla^2 \mu_m = 0, \quad m = 1, 2, \ldots, M, \tag{2.7a}$$

$$\nabla^2 (\nabla \times \boldsymbol{v}) = \mathbf{0}. \tag{2.7b}$$

Since matched expansions for electrochemical potentials and fluid velocity in both regions can be constructed for the case of a thin double layer, the usual strategy is to solve (2.7) for μ_m and $\boldsymbol{v}$ and the solution obtained for the inner region supplies boundary conditions for the outer region.

2.2. *Boundary conditions at the outer edge of the thin double layer*

Since the double-layer thickness on a lengthscale κ^{-1} (the Debye length) is much smaller than the particle dimension L (the shape of the particle can be arbitrary), we may regard the double layer as a structure composed of a charged plane interface and an adjacent diffuse cloud of ions. From the equation of continuity (2.4b), it is quite apparent that the ratio of tangential to normal fluid velocities in the double layer is of $O(\kappa L)$. This implies that the flow within the diffuse layer is primarily tangential to the particle surface. It could be shown from (2.6a) that μ_m is constant across the double layer, which means that the double layer is in local (but not global) equilibrium. By integrating (2.6*b*) over the double layer, the tangential fluid velocity relative to the particle surface within the double layer can be derived (O'Brien 1983):

$$\boldsymbol{v} = -\frac{1}{\eta}\sum_{m=1}^{M} \boldsymbol{\nabla}_{\mathrm{s}}\mu_m \int_0^{y}\int_{y'}^{\infty} (n_m^0 - n_m^\infty)\,\mathrm{d}y''\,\mathrm{d}y', \tag{2.8}$$

where y (or y'') is the perpendicular distance from the particle surface, n_m^∞ is the constant bulk number density of type-m ions, and $\boldsymbol{\nabla}_{\mathrm{s}} = (\boldsymbol{I}-\boldsymbol{nn})\cdot\boldsymbol{\nabla}$ ($\boldsymbol{n}$ is the unit normal to the solid surface pointing into the fluid phase and $\boldsymbol{I}$ is the unit dyadic) denotes the gradient tangential to the particle surface. At the outer edge of the diffuse cloud ($y \rightarrow \infty$), a 'slip velocity' results:

$$\boldsymbol{v}_{\mathrm{s}} = -\frac{1}{\eta}\sum_{m=1}^{M} \boldsymbol{\nabla}_{\mathrm{s}}\mu_m \int_0^{\infty} y(n_m^0 - n_m^\infty)\,\mathrm{d}y. \tag{2.9}$$

This slip velocity comes from the tangential gradients $\boldsymbol{\nabla}_{\mathrm{s}}\mu_m$ which vary with position along the particle surface.

When the electric field sweeps double-layer ions across the particle surface, there may be some portions of the surface where the net tangential ion fluxes will be negative and consequently normal ion influxes occur just beyond the double layer. Over the other parts of the surface, however, the net tangential ion fluxes are positive, thus some ions in the double layer will be expelled out into the bulk electrolyte solution to prevent accumulation of the ions. Using this, it can be shown that at the outer edge of the double layer (O'Brien 1983)†

$$\boldsymbol{n}\cdot\boldsymbol{\nabla}\mu_m = -z_m \sum_{k=1}^{M} \frac{\beta_{mk}}{z_k} L \nabla_{\mathrm{s}}^2 \mu_k, \quad m = 1,2,\ldots,M, \tag{2.10}$$

with

$$\beta_{mk} = \frac{1}{\kappa L}\left\{\delta_{mk}\int_0^{\kappa t} \exp(-z_m\bar{\Phi}^0)\,\mathrm{d}\bar{y} \right.$$
$$\left. +\tfrac{3}{2} f_m \frac{z_k}{z_m}\bar{n}_k^\infty \int_0^{\kappa t} (\exp(-z_m\bar{\Phi}^0)-1)\int_0^{\bar{y}}\int_{\bar{y}'}^{\infty} [\exp(-z_k\bar{\Phi}^0)-1]\,\mathrm{d}\bar{y}''\,\mathrm{d}\bar{y}'\,\mathrm{d}\bar{y}\right\}, \tag{2.11}$$

where $\nabla_{\mathrm{s}}^2 = (\boldsymbol{I}-\boldsymbol{nn}):\boldsymbol{\nabla\nabla}$ is the surface Laplacian operator; the non-dimensionalized variables (denoted by an overbar) are $\bar{y} = \kappa y$, $\bar{\Phi}^0 = \Phi^0 e/kT$, and

$$\bar{n}_k^\infty = n_k^\infty \Big/ \sum_{m=1}^{M} z_m^2 n_m^\infty; \quad f_m = \epsilon(kT)^2/6\pi\eta e^2 D_m$$

is the dimensionless drag coefficient of ion m; t is the thickness of the double layer; δ_{mk} denotes the Kronecker delta which is unity if m equals k, and zero otherwise. As $\kappa L \rightarrow \infty$, β_{mk} approaches zero, and hence the terms on the right-hand side of (2.10) vanish. This indicates that there is no ion flux normal to the surface just beyond the double layer, the same boundary conditions as that employed in the derivation of the Smoluchowski equation.

Because the errors in the derivation of (2.11) are $O(1/\kappa L)$, the integrals in this equation must be large (i.e. the zeta potential of the particle must be high such that

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† There is a certain arbitrariness in the way some integrals are evaluated in the O'Brien methodology. Formula (2.11) is somewhat different from his result. In the Appendix, we show the derivation of (2.11) and include a short discussion.

the ratio $\exp(e|z_m\zeta|/2kT)/\kappa L$ is $O(1)$) to allow the neglect of these errors. Even so, (2.11) can in fact be applied for any zeta potential since at low zeta potential the coefficient β_{mk} itself is an $O(1/\kappa L)$ quantity and the effects of the double-layer polarization become unimportant. In §4.1, the results of the electrophoretic mobility for a spherical particle with an *arbitrary* zeta potential and a large value of κL obtained using (2.11) are found to be in good agreement with the 'exact' (numerical) calculations by O'Brien & White (1978).

For a symmetric two-species electrolyte with the absolute value of valence Z, an analytical solution for Φ^0 is available. Thus, all values of β_{mk} defined by (2.11) can be calculated analytically. In the Appendix, we show that

$$\beta_{11} = \frac{1}{\kappa L}\left[4\left(1+\frac{3f_1}{Z^2}\right)\exp(\bar{\zeta})\sinh\bar{\zeta}-\frac{12f_1}{Z^2}(\bar{\zeta}+\ln\cosh\bar{\zeta})\right], \tag{2.12a}$$

$$\beta_{12} = \frac{1}{\kappa L}\left(\frac{12f_1}{Z^2}\right)\ln\cosh\bar{\zeta}, \tag{2.12b}$$

$$\beta_{21} = \frac{1}{\kappa L}\left(\frac{12f_2}{Z^2}\right)\ln\cosh\bar{\zeta}, \tag{2.12c}$$

$$\beta_{22} = \frac{1}{\kappa L}\left[-4\left(1+\frac{3f_2}{Z^2}\right)\exp(-\bar{\zeta})\sinh\bar{\zeta}+\frac{12f_2}{Z^2}(\bar{\zeta}-\ln\cosh\bar{\zeta})\right], \tag{2.12d}$$

where $\bar{\zeta} = Ze\zeta/4kT$; ζ is the zeta potential of the particle. The subscripts 1 and 2 for m or k of the variables denote the anion and cation, respectively. Note that the errors in (2.12) are still $O(1/\kappa L)$, like those in (2.11).

If the fluid solution does not contain only one type of symmetric electrolyte but consists of an arbitrary combination of ions, it is impossible to evaluate β_{mk} analytically because there is no analytical expression for Φ^0. However, this difficulty could be overcome by utilizing an asymptotic solution of Φ^0 for the case when the particle is charged highly. In addition, it could be argued that only the most highly charged counterions play a major role in the ionic flux normal to the particle surface (O'Brien 1983), that is, boundary condition (2.10) may be approximated by

$$\boldsymbol{n}\cdot\nabla\mu_m = -\lambda L\left[\nabla_s^2\mu_m+\frac{3f_m}{2\alpha^2}\sum_k{}' \bar{n}_k^\infty \nabla_s^2\mu_k\right] \quad \text{for } z_m = z_\sigma, \tag{2.13a}$$

$$\boldsymbol{n}\cdot\nabla\mu_m = 0 \quad \text{otherwise}, \tag{2.13b}$$

with

$$\lambda = [\exp(e|z_\sigma\zeta|/2kT)-1]/\alpha\kappa L \tag{2.14a}$$

and

$$\alpha = |z_\sigma|\,(\textstyle\sum_k{}' \bar{n}_k^\infty/2)^{\frac{1}{2}}. \tag{2.14b}$$

Here the subscript σ refers to the counterions with the highest charge, and $\sum_k'$ denotes summation over all of those ionic species, for which $z_m = z_\sigma$. If there is merely one kind of counterion with the largest absolute valence, the boundary condition (2.13) could be simplified as

$$\boldsymbol{n}\cdot\nabla\mu_m = -\beta_{mm}L\nabla_s^2\mu_m, \quad m = 1,2,\ldots,M, \tag{2.15}$$

with

$$\beta_{mm} = \left(\frac{2}{\bar{n}_m^\infty}\right)^{\frac{1}{2}}\left(1+\frac{3f_m}{z_m^2}\right)\frac{\exp(e|z_m\zeta|/2kT)-1}{|z_m|\kappa L} \quad \text{if } z_m = z_\sigma, \tag{2.16a}$$

$$\beta_{mm} = 0 \quad \text{otherwise}. \tag{2.16b}$$

To check the validity of the approximate boundary condition (2.13) or (2.15), we compare the magnitudes of all β_{mk} for a symmetric electrolyte. For example, if the particle is charged positively, it is found from (2.12) that β_{11} is at least one order of magnitude larger than the others, which are no more than $O(10^{-2})$. Hence, the estimation that only the most highly charged counterions dominate the normal ion flux, whereas the effect from the others may be negligible, appears reasonable.

2.3. *Electrophoresis of an isolated particle*

We now consider the electrophoresis of a single particle when a uniform electric field $\boldsymbol{E}_\infty$ is applied. In the fluid phase outside the thin double layer, the electrochemical potentials μ_m satisfy Laplace's equation (2.7*a*) and the velocity field is governed by the Stokes equations or (2.7*b*).

The potential gradient far away from the particle approaches the applied electric field and the fluid is motionless there. Thus, μ_m and $\boldsymbol{v}$ must obey

$$|\boldsymbol{r}| \rightarrow \infty: \quad \nabla\mu_m \rightarrow -ez_m \boldsymbol{E}_\infty, \quad \boldsymbol{v} \rightarrow \boldsymbol{0}, \tag{2.17a, b}$$

where $\boldsymbol{r}$ is the position vector from the particle centre. At the particle 'surface', μ_m is subject to boundary condition (2.10) or (2.13) and $\boldsymbol{v}$ is given by the following according to (2.9):

$$\boldsymbol{v} = \boldsymbol{U} + \boldsymbol{\Omega} \times \boldsymbol{r} - \frac{1}{\eta} \sum_{m=1}^{M} \nabla_s \mu_m \int_0^\infty y(n_m^0 - n_m^\infty)\,\mathrm{d}y, \tag{2.18}$$

where $\boldsymbol{U}$ and $\boldsymbol{\Omega}$ are the translational and angular velocities of the electrophoretic particle to be determined. Here the particle 'surface' means the outer edge of the diffuse layer.

Since the surface encloses a neutral body (charged interface plus diffuse ions), the particle is force and torque free, that is

$$\boldsymbol{F} = \iint_{\substack{\text{particle}\\ \text{surface}}} \boldsymbol{n}\cdot\boldsymbol{\pi}\,\mathrm{d}S = \boldsymbol{0}, \tag{2.19a}$$

$$\boldsymbol{T} = \iint_{\substack{\text{particle}\\ \text{surface}}} \boldsymbol{r} \times (\boldsymbol{n}\cdot\boldsymbol{\pi})\,\mathrm{d}S = \boldsymbol{0}, \tag{2.19b}$$

where $\boldsymbol{\pi}$ is the fluid stress tensor. With the constraints above, one can compute $\boldsymbol{U}$ and $\boldsymbol{\Omega}$ after solving (2.7) for the electrochemical potentials and the fluid velocity.

If the particle is a sphere, the velocities $\boldsymbol{U}$ and $\boldsymbol{\Omega}$ can be determined through the above procedure, and the results are (O'Brien 1983)

$$\boldsymbol{U} = -\frac{\epsilon kT}{6\pi\eta e} \boldsymbol{E}_\infty \sum_{m=1}^{M} (1+c_m)\, z_m \bar{n}_m^\infty \int_0^\infty \bar{y}[\exp(-z_m \bar{\Phi}^0) - 1]\,\mathrm{d}\bar{y}, \tag{2.20a}$$

$$\boldsymbol{\Omega} = \boldsymbol{0} \tag{2.20b}$$

with

$$c_m = \frac{1}{2} - \frac{3\lambda}{(2+2\lambda)}\left[1 + \frac{3f_m}{z_m^2(1+\lambda W_\sigma)}\right] \quad \text{for } z_m = z_\sigma, \tag{2.21a}$$

$$c_m = \tfrac{1}{2} \qquad \text{otherwise,} \tag{2.21b}$$

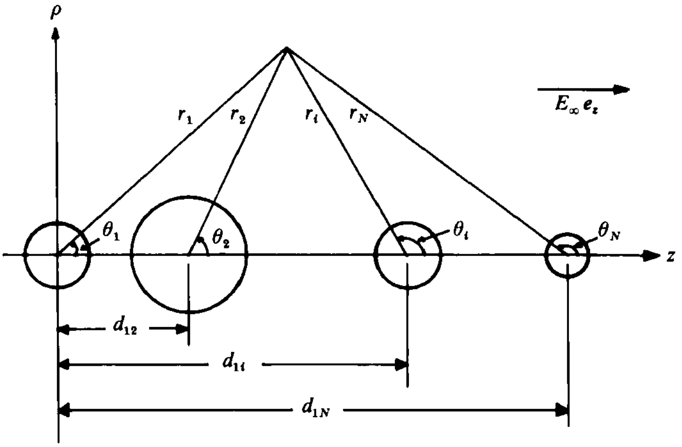

FIGURE 1. Geometrical sketch of the electrophoretic motion of multiple spheres.

where
$$W_\sigma = 1 + \frac{3 \sum_k' \bar{n}_k^\infty f_k}{z_\sigma^2 \sum_k' \bar{n}_k^\infty}. \tag{2.22}$$

Of course, the particle dimension L is equal to its radius a now. The equilibrium electrical potential $\bar{\Phi}^0$ can be obtained by solving the Poisson–Boltzmann equation by the numerical Runge–Kutta method, and then the integral in (2.20*a*) can be calculated numerically.

If the zeta potential of the sphere is small and $\kappa a \rightarrow \infty$, the polarization of the double layer is weak enough that there are hardly any ion fluxes in the normal direction. In this case, $\lambda \rightarrow 0$ and each c_m is equal to 0.5. In fact, the following relation always holds for a planar surface:

$$\sum_{m=1}^{M} z_m \bar{n}_m^\infty \int_0^\infty \bar{y}[\exp(-z_m \bar{\Phi}^0) - 1]\, d\bar{y} = -\frac{e\zeta}{kT}, \tag{2.23}$$

which could be derived from the integration of the Poisson–Boltzmann equation. Therefore, (2.20*a*) is reduced to the Smoluchowski equation (1.1) and the slip velocity (2.9) at the outer edge of the diffuse layer becomes the simple Helmholtz expression for electro-osmotic flow.

Specifically, if only a symmetric electrolyte exists in the fluid surrounding the sphere, boundary condition (2.10) with the values of β_{mk} provided in (2.12), instead of (2.13), will be used. Then, c_1 and c_2 in (2.21) are given by

$$c_1 = (\tfrac{1}{2} + \tfrac{1}{2}\beta_{22} - \tfrac{3}{2}\beta_{12} - \beta_{11} + \beta_{12}\beta_{21} - \beta_{11}\beta_{22})/\Delta, \tag{2.24a}$$
$$c_2 = (\tfrac{1}{2} + \tfrac{1}{2}\beta_{11} - \tfrac{3}{2}\beta_{21} - \beta_{22} + \beta_{12}\beta_{21} - \beta_{11}\beta_{22})/\Delta, \tag{2.24b}$$

where
$$\Delta = 1 + \beta_{11} + \beta_{22} + \beta_{11}\beta_{22} - \beta_{12}\beta_{21}. \tag{2.25}$$

The integral in (2.20*a*) can be analytically computed as follows:

$$\int_0^\infty \bar{y}[\exp(\pm Z\bar{\Phi}^0) - 1]\, d\bar{y} = \pm 4\bar{\zeta} + 4 \ln \cosh \bar{\zeta}, \tag{2.26}$$

and the particle velocity is analytically expressed as

$$U = \frac{\epsilon\zeta}{4\pi\eta} \boldsymbol{E}_\infty \left[\frac{1}{3}(2+c_1+c_2) + \frac{4kT}{3Ze\zeta}(c_1-c_2)\ln\cosh\left(\frac{Ze\zeta}{4kT}\right)\right]. \tag{2.27}$$

If we assume $f_1 = f_2 = f$, and neglect the small quantities of $\beta_{11}\beta_{22}$ and $\beta_{12}\beta_{21}$, (2.27) can be reduced to

$$U = \frac{\epsilon\zeta}{4\pi\eta} \boldsymbol{E}_\infty \left[1 - 4\frac{W\sinh^2\bar{\zeta} + (1 - W + (2\bar{\zeta})^{-1}\sinh 2\bar{\zeta})\ln\cosh\bar{\zeta}}{\kappa a + 8W\sinh^2\bar{\zeta} + 8(1-W)\ln\cosh\bar{\zeta}}\right], \tag{2.28}$$

where

$$W = 1 + 3f/Z^2. \tag{2.29}$$

This result is just that derived by Dukhin & Derjaguin (1974)†.

3. Analysis for the electrophoresis of multiple spheres

In this section, we consider the axisymmetric electrophoretic motion of N colloidal spheres located along the z-axis as shown in figure 1. The ambient fluid is unbounded and the externally imposed electric field $E_\infty \boldsymbol{e}_z$ is uniform. Here, $\boldsymbol{e}_z$ is a unit vector in the circular cylindrical coordinate system (ρ, ϕ, z) with the origin taken at the centre of the first sphere for convenience. The zeta potentials and radii of the spherical particles may differ from one another and the gap widths between two neighbouring particles need not be identical. The electrolyte solution contains M different types of ion but, for simplicity, only one corresponding kind of counterion with the highest charge for each particle. It is assumed that the thickness of the double layer is much smaller than the particles' radii. However, the effect of polarization of the diffuse cloud described in the previous section will be taken into account. The purpose is to determine how the electrophoretic velocity of each particle is affected by the presence of the others.

3.1. *Electrochemical potential distributions*

Because the bulk ionic concentrations outside the double layers are uniform, the electrochemical potentials obey Laplace's equation (2.7*a*) and are subject to the following boundary conditions according to (2.15), (2.16) and (2.17*a*):

$$\frac{\partial\mu_m}{\partial r_i} = -\beta_{mmi} a_1 \nabla_s^2 \mu_m \quad \text{at} \quad r_i = a_i, \tag{3.1a}$$

$$\boldsymbol{\nabla}\mu_m \rightarrow -ez_m E_\infty \boldsymbol{e}_z \qquad \text{as} \quad (\rho^2 + z^2)^{\frac{1}{2}} \rightarrow \infty, \tag{3.1b}$$

with

$$\beta_{mmi} = \left(\frac{2}{\bar{n}_m^\infty}\right)^{\frac{1}{2}} \left(1 + \frac{3f_m}{z_m^2}\right) \frac{\exp(e|z_m\zeta_i|/2kT) - 1}{|z_m|\kappa a_1} \quad \text{if } m = \sigma_i, \tag{3.2a}$$

$$\beta_{mmi} = 0 \qquad \text{otherwise}, \tag{3.2b}$$

for $i = 1, 2, \ldots, N$ and $m = 1, 2, \ldots, M$. Here, a_i is the radius of sphere i (more precisely, the distance from the sphere centre to the outer edge of the diffuse layer surrounding the sphere), (r_i, θ_i, ϕ) are spherical coordinates measured from the centre of particle i, and index σ_i denotes the most highly charged counterions for sphere i.

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† There are printing errors in the numerator of (93) in Dukhin & Derjaguin's article, p. 307.

A general solution to (2.7a) suitable for satisfying (3.1) is (Keh & Yang 1990)

$$\mu_m = \mu_m^0 + kT \ln n_m^{\infty} - ez_m E_{\infty} z + ez_m E_{\infty} \sum_{j=1}^{N} \sum_{n=0}^{\infty} A_{mjn} r_j^{-(n+1)} P_n(q_j), \tag{3.3}$$

for $m = 1, 2, \ldots,$ or M, where P_n is the Legendre polynomial of order n and q_j denotes $\cos\theta_j$. This solution form satisfies (3.1b) immediately and the coefficients A_{mjn} will be determined using (3.1a). In order to apply (3.3), r_j and q_j must be written in terms of a single coordinate system:

$$r_j = [\rho^2 + (z - d_{1j})^2]^{\frac{1}{2}}, \tag{3.4a}$$

$$q_j = (z - d_{1j})/[\rho^2 + (z - d_{1j})^2]^{\frac{1}{2}}, \tag{3.4b}$$

where d_{ij} is the distance between the centres of particles i and j (so $d_{ii} = 0$).

With the aid of the relations

$$\frac{\partial}{\partial r_i} = (1 - q_i^2)^{\frac{1}{2}} \frac{\partial}{\partial \rho} + q_i \frac{\partial}{\partial z}, \tag{3.5a}$$

$$\begin{aligned} \nabla_s^2 &= \nabla^2 - \frac{1}{r_i^2} \frac{\partial}{\partial r_i}\left(r_i^2 \frac{\partial}{\partial r_i}\right) \\ &= \nabla^2 - (1 - q_i^2) \frac{\partial^2}{\partial \rho^2} - q_i^2 \frac{\partial^2}{\partial z^2} - 2(1 - q_i^2)^{\frac{1}{2}} q_i \frac{\partial^2}{\partial \rho\, \partial z} - \frac{2}{r_i}(1 - q_i^2)^{\frac{1}{2}} \frac{\partial}{\partial \rho} - \frac{2q_i}{r_i} \frac{\partial}{\partial z}, \end{aligned} \tag{3.5b}$$

we introduce μ_m in (3.3) into the boundary condition (3.1a) to obtain

$$\begin{aligned} &\sum_{j=1}^{N} \sum_{n=0}^{\infty} A_{mjn} \left\{ \beta_{mmi} a_1 [q_i^2 (n+1) G_{n+1}(r_j, q_j) - (1 - q_i^2) H_{n+1}(r_j, q_j) \right. \\ &\qquad \left. + 2q_i (1 - q_i^2)^{\frac{1}{2}} (n+1) F_{n+1}(r_j, q_j)] + \left(1 + \frac{2\beta_{mmi} a_1}{r_i}\right) [(1 - q_i^2)^{\frac{1}{2}} F_n(r_j, q_j) + q_i G_n(r_j, q_j)] \right\} \\ &= \left(1 - \frac{2\beta_{mmi} a_1}{r_i}\right) q_i \quad \text{at} \quad r_i = a_i, \end{aligned} \tag{3.6}$$

where

$$F_n(r_j, q_j) = -r_j^{-(n+2)} (1 - q_j^2)^{\frac{1}{2}} P'_{n+1}(q_j), \tag{3.7a}$$

$$G_n(r_j, q_j) = -r_j^{-(n+2)} (n+1) P_{n+1}(q_j), \tag{3.7b}$$

$$H_n(r_j, q_j) = -r_j^{-(n+2)} \{[(n+1) - (n+2) q_j^2] P'_n(q_j) + q_j (1 - q_j^2) P''_n(q_j)\}, \tag{3.7c}$$

for $i = 1, 2, \ldots, N$ and $m = 1, 2, \ldots, M$. The prime on $P_n(q_j)$ means differentiation with respect to q_j.

If the fluid contains only one symmetric electrolyte, boundary condition (3.1a) is replaced by

$$r_i = a_i: \quad \frac{\partial \mu_1}{\partial r_i} = -\beta_{11} a_1 \nabla_s^2 \mu_1 + \beta_{12} a_1 \nabla_s^2 \mu_2, \tag{3.8a}$$

$$\frac{\partial \mu_2}{\partial r_i} = \beta_{21} a_1 \nabla_s^2 \mu_1 - \beta_{22} a_1 \nabla_s^2 \mu_2, \tag{3.8b}$$

where β_{11}, β_{12}, β_{21} and β_{22} are given by (2.12). Following the same procedure to obtain (3.6) produces

$$\begin{aligned}\sum_{j=1}^{N}\sum_{n=0}^{\infty} A_{1jn}\Big\{&\beta_{11}a_1[q_i^2(n+1)\,G_{n+1}(r_j,q_j)-(1-q_i^2)\,H_{n+1}(r_j,q_j)\\&+2q_i(1-q_i^2)^{\frac{1}{2}}(n+1)\,F_{n+1}(r_j,q_j)]+\left(1+\frac{2\beta_{11}a_1}{r_i}\right)[(1-q_i^2)^{\frac{1}{2}}F_n(r_j,q_j)+q_i\,G_n(r_j,q_j)]\Big\}\\&+A_{2jn}\,\beta_{12}\,a_1\Big\{q_i^2(n+1)\,G_{n+1}(r_j,q_j)-(1-q_i^2)\,H_{n+1}(r_j,q_j)\\&+2q_i(1-q_i^2)^{\frac{1}{2}}(n+1)\,F_{n+1}(r_j,q_j)+\frac{2}{r_i}[(1-q_i^2)^{\frac{1}{2}}F_n(r_j,q_j)+q_i\,G_n(r_j,q_j)]\Big\}\\=&\left[1-\frac{2a_1}{r_i}(\beta_{11}+\beta_{12})\right]q_i,\end{aligned} \qquad (3.9a)$$

$$\begin{aligned}\sum_{j=1}^{N}\sum_{n=0}^{\infty} A_{2jn}\Big\{&\beta_{22}a_1[q_i^2(n+1)\,G_{n+1}(r_j,q_j)-(1-q_i^2)\,H_{n+1}(r_j,q_j)\\&+2q_i(1-q_i^2)^{\frac{1}{2}}(n+1)\,F_{n+1}(r_j,q_j)]+\left(1+\frac{2\beta_{22}a_1}{r_i}\right)[(1-q_i^2)^{\frac{1}{2}}F_n(r_j,q_j)+q_i\,G_n(r_j,q_j)]\Big\}\\&+A_{1jn}\,\beta_{21}\,a_1\Big\{q_i^2(n+1)\,G_{n+1}(r_j,q_j)-(1-q_i^2)\,H_{n+1}(r_j,q_j)\\&+2q_i(1-q_i^2)^{\frac{1}{2}}(n+1)\,F_{n+1}(r_j,q_j)+\frac{2}{r_i}[(1-q_i^2)^{\frac{1}{2}}F_n(r_j,q_j)+q_i\,G_n(r_j,q_j)]\Big\}\\=&\left[1-\frac{2a_1}{r_i}(\beta_{21}+\beta_{22})\right]q_i,\quad \text{at } r_i=a_i,\quad \text{for } i=1,2,\ldots,\text{ or } N.\end{aligned} \qquad (3.9b)$$

To satisfy boundary condition (3.1*a*) exactly along the entire semicircular generating arc of each sphere would require the solution of the entire infinite array of unknown coefficients A_{mjn}. However, the multipole collocation method allows one to truncate the infinite series in (3.3) into a finite one with K terms,

$$\mu_m=\mu_m^0+kT\ln n_m^\infty-ez_mE_\infty z+ez_mE_\infty\sum_{j=1}^{N}\sum_{n=0}^{K-1}A_{mjn}\,r_j^{-(n+1)}P_n(q_j), \qquad (3.10)$$

and then to enforce the boundary condition (3.6) at K discrete points on the generating arc of each sphere (Gluckman, Pfeffer & Weinbaum 1971; Keh & Yang 1990). As a result, for N spheres in the chain, this yields a set of KN simultaneous linear algebraic equations for the KN unknown coefficients A_{mjn} (for each value of m) of the truncated solution (3.10):

$$\begin{aligned}\sum_{j=1}^{N}\sum_{n=0}^{K-1} A_{mjn}\Big\{&\beta_{mmi}\,a_1[q_{iki}^2(n+1)\,G_{n+1}(r_{jki},q_{jki})-(1-q_{iki}^2)\,H_{n+1}(r_{jki},q_{jki})\\&+2q_{iki}(1-q_{iki}^2)^{\frac{1}{2}}(n+1)\,F_{n+1}(r_{jki},q_{jki})]\\&+\left(1+\frac{2\beta_{mmi}\,a_1}{r_{iki}}\right)[(1-q_{iki}^2)^{\frac{1}{2}}F_n(r_{jki},q_{jki})+q_{iki}\,G_n(r_{jki},q_{jki})]\Big\}\\=&\left(1-\frac{2\beta_{mmi}\,a_1}{r_{iki}}\right)q_{iki},\end{aligned} \qquad (3.11)$$

where $i = 1, 2, \ldots, N$; $k = 1, 2, \ldots, K$; r_{jki} and q_{jki} denote the values of r_j and q_j at the position of the kth point on the generating arc of particle i. This matrix equation can be solved by any standard matrix reduction technique to yield the A_{mjn} coefficients in (3.10) for the electrochemical potential distributions μ_m. In general, the larger the value of K, the more accurate the result will be by this truncation technique. Naturally, the truncation error vanishes as $K \to \infty$.

Similarly, boundary condition (3.8) for the case of fluid containing only one symmetric electrolyte can also be applied using the truncation method to generate a set of $2KN$ algebraic equations for coefficients A_{1jn} and A_{2jn}. However, A_{1jn} and A_{2jn} are coupled here, unlike any A_{mjn} in (3.11) which is independent of the others with different values of m.

3.2. *Fluid velocity distribution*

Knowing the electrochemical potential distributions in the fluid phase, we can now take up the solution of the fluid velocity field. Because the fluid outside the thin double layers is neutral, the velocity field is governed by the quasi-steady fourth-order differential equation for axisymmetric creeping flow,

$$\mathrm{E}^4\Psi = \mathrm{E}^2(\mathrm{E}^2\Psi) = 0, \tag{3.12}$$

where Ψ is the Stokes stream function, and the operator E^2 has the following form in spherical coordinates (r, θ, ϕ):

$$\mathrm{E}^2 = \frac{\partial^2}{\partial r^2} + \frac{\sin\theta}{r^2}\frac{\partial}{\partial\theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}. \tag{3.13}$$

The velocity components in circular cylindrical coordinates are expressed by

$$v_\rho = \frac{1}{\rho}\frac{\partial\Psi}{\partial z}, \quad v_z = -\frac{1}{\rho}\frac{\partial\Psi}{\partial\rho}. \tag{3.14a, b}$$

The boundary conditions for the fluid velocity beyond the double layers surrounding the spheres, resulting from (2.17*b*) and (2.18), are

$$\boldsymbol{v} = U_i \boldsymbol{e}_z - \frac{1}{\eta}\sum_{m=1}^{M} \boldsymbol{\nabla}_{\mathrm{S}}\mu_m \int_0^\infty y_i(n^0_{mi} - n^\infty_m)\,\mathrm{d}y_i \quad \text{at} \quad r_i = a_i, \tag{3.15a}$$

$$\boldsymbol{v} \to \boldsymbol{0} \quad \text{as} \quad (\rho^2 + z^2)^{\frac{1}{2}} \to \infty, \tag{3.15b}$$

for $i = 1, 2, \ldots, N$. Here n^0_{mi} denotes the equilibrium number density of ion m within the double layer surrounding sphere i, y_i is the perpendicular distance from the surface of sphere i, and U_i is the instantaneous electrophoretic velocity of sphere i to be determined. The spheres will not rotate owing to the axial symmetry of the fluid motion. $\boldsymbol{\nabla}_{\mathrm{S}}\mu_m$ can be calculated from the electrochemical potential distribution (3.10) with A_{mjn} determined by (3.11). The integral in (3.15*a*) must be evaluated numerically except for the special case of a symmetric electrolyte.

The general solution of (3.12) for Ψ, which satisfies boundary condition (3.15*b*) immediately, is (Gluckman *et al.* 1971; Keh & Yang 1990)

$$\Psi = \sum_{j=1}^{N}\sum_{n=2}^{\infty} [B_{jn} r_j^{-n+1} + C_{jn} r_j^{-n+3}]\, G_n^{-\frac{1}{2}}(q_j), \tag{3.16}$$

where $G_n^{-\frac{1}{2}}(q_j)$ is the Gegenbauer polynomial of order n and degree $-\frac{1}{2}$. Unknown coefficients B_{jn} and C_{jn} are to be determined from (3.15*a*).

Substituting (3.3) and (3.16) into boundary condition (3.15*a*) and using the formulae (3.14) as well as the recurrence relations of the Legendre and Gegenbauer polynomials, it is shown that the coefficients B_{jn} and C_{jn} must fulfil the following set of equations for $i = 1, 2, \ldots, N$:

$$\sum_{j=1}^{N} \sum_{n=2}^{\infty} [B_{jn} S_n(r_j, q_j) + C_{jn} T_n(r_j, q_j)]$$

$$= U_i - \frac{eE_\infty}{\eta} \sum_{m=1}^{M} z_m \int_0^\infty y_i (n_{mi}^0 - n_m^\infty)\,\mathrm{d}y_i \left\{ \sum_{j=1}^{N} \sum_{n=0}^{\infty} A_{mjn} [(1-q_i^2)\, G_n(r_j, q_j) \right.$$

$$\left. - q_i (1-q_i^2)^{\frac{1}{2}} F_n(r_j, q_j)] - (1-q_i^2) \right\}, \tag{3.17a}$$

$$\sum_{j=1}^{N} \sum_{n=2}^{\infty} [B_{jn} S_n^*(r_j, q_j) + C_{jn} T_n^*(r_j, q_j)]$$

$$= -\frac{eE_\infty}{\eta} \sum_{m=1}^{M} z_m \int_0^\infty y_i (n_{mi}^0 - n_m^\infty)\,\mathrm{d}y_i \left\{ \sum_{j=1}^{N} \sum_{n=0}^{\infty} A_{mjn} [q_i^2 F_n(r_j, q_j) \right.$$

$$\left. - q_i (1-q_i^2)^{\frac{1}{2}} G_n(r_j, q_j)] + q_i (1-q_i^2)^{\frac{1}{2}} \right\}, \tag{3.17b}$$

at $r_i = a_i$, where

$$S_n(r_j, q_j) = -r_j^{-n-1} P_n(q_j), \tag{3.18a}$$

$$T_n(r_j, q_j) = -r_j^{-n+1} [P_n(q_j) + 2G_n^{-\frac{1}{2}}(q_j)], \tag{3.18b}$$

$$S_n^*(r_j, q_j) = -r_j^{-n-1} (n+1)\,(1-q_j^2)^{-\frac{1}{2}} G_{n+1}^{-\frac{1}{2}}(q_j), \tag{3.18c}$$

$$T_n^*(r_j, q_j) = -r_j^{-n+1} (1-q_j^2)^{-\frac{1}{2}} [(n+1)\, G_{n+1}^{-\frac{1}{2}}(q_j) - 2q_j\, G_n^{-\frac{1}{2}}(q_j)]. \tag{3.18d}$$

Similar to the previous subsection, we could utilize the multipole truncation technique to reserve finite terms as below to approximate the infinite-series solution (3.16):

$$\Psi = \sum_{j=1}^{N} \sum_{n=2}^{K'+1} [B_{jn} r_j^{-n+1} + C_{jn} r_j^{-n+3}]\, G_n^{-\frac{1}{2}}(q_j). \tag{3.19}$$

If the truncated solutions (3.10) and (3.19) are used for the electrochemical potentials and the velocity field and introduced into boundary condition (3.15*a*) satisfied at K' points along the generating arc of each of the N particles, then a set of $2NK'$ linear algebraic equations is generated:

$$\sum_{j=1}^{N} \sum_{n=2}^{K'+1} [B_{jn} S_n(r_{jki}, q_{jki}) + C_{jn} T_n(r_{jki}, q_{jki})]$$

$$= U_i - \frac{eE_\infty}{\eta} \sum_{m=1}^{M} z_m \int_0^\infty y_i (n_{mi}^0 - n_m^\infty)\,\mathrm{d}y_i \left\{ \sum_{j=1}^{N} \sum_{n=0}^{K-1} A_{mjn} [(1-q_{iki}^2)\, G_n(r_{jki}, q_{jki}) \right.$$

$$\left. - q_{iki} (1-q_{iki}^2)^{\frac{1}{2}} F_n(r_{jki}, q_{jki})] - (1-q_{iki}^2) \right\}, \tag{3.20a}$$

$$\sum_{j=1}^{N} \sum_{n=2}^{K'+1} [B_{jn} S_n^*(r_{jki}, q_{jki}) + C_{jn} T_n^*(r_{jki}, q_{jki})]$$

$$= -\frac{eE_\infty}{\eta} \sum_{m=1}^{M} z_m \int_0^\infty y_i (n_{mi}^0 - n_m^\infty)\,\mathrm{d}y_i \left\{ \sum_{j=1}^{N} \sum_{n=0}^{K-1} A_{mjn} [q_{iki}^2 F_n(r_{jki}, q_{jki}) \right.$$

$$\left. - q_{iki} (1-q_{iki}^2)^{\frac{1}{2}} G_n(r_{jki}, q_{jki})] - q_{iki} (1-q_{iki}^2)^{\frac{1}{2}} \right\}, \tag{3.20b}$$

where $i = 1, 2, \ldots, N$ and $k = 1, 2, \ldots, K'$. The $2NK'$ unknown coefficients B_{jn} and C_{jn} could be easily calculated in terms of the particle velocities U_i by simultaneous solution of the above equations.

3.3. *Velocities of free spheres*

The drag force exerted by the fluid on each particle surface $r_i = a_i$ can be determined from (Happel & Brenner 1983)

$$F_i = \eta\pi \int_0^\pi r_i^3 \sin^3\theta_i \frac{\partial}{\partial r_i}\left(\frac{\mathrm{E}^2\Psi}{r_i^2\sin^2\theta_i}\right) r_i\, \mathrm{d}\theta_i. \tag{3.21}$$

Substituting (3.16) or (3.19) into the above integral and utilizing the orthogonality properties of the Gegenbauer polynomials yields the simple relation

$$F_i = 4\pi\eta C_{i2}. \tag{3.22}$$

This means that only the first multipole contributes to the drag force on each particle.

Because the particles are freely suspended in the fluid and the 'surface' of each encompasses a neutral body, no net drag force from the fluid acts on the particles. From (3.22), it is apparent that

$$C_{i2} = 0 \quad \text{for} \quad i = 1, 2, \ldots, N. \tag{3.23}$$

The electrophoretic velocities U_i of the N spheres can be determined by solving the above N equations simultaneously and expressed as

$$U_i = M_i U_{i0}, \tag{3.24}$$

where U_{i0} is the electrophoretic velocity of particle i when it is isolated from the others. The derivation of U_{i0} has been discussed in §2.3. The mobility parameters M_i depend on the relative positions, sizes and zeta potentials of the particles as well as the bulk concentrations, valences and diffusivities of the ions.

3.4. *Velocity of a rigid cluster of spheres*

We now consider the electrophoretic motion of a rigid cluster of N spheres. The spheres are all located along the z-axis and are connected through their centres with rigid rods of arbitrary lengths. The connecting rods are assumed to be infinitesimally thin compared to the sphere sizes; hence they make neither electrostatic nor hydrodynamic contributions but only serve to ensure the rigid-body motion of the cluster. Here, our object is to explore the electrophoresis of aggregates formed by flocculation or bridging of colloidal particles in a suspension.

The difference between the case here and that of free spheres in the previous subsection is that the N spheres in the chain translate at the same speed U_0, the electrophoretic velocity of the cluster, and the drag force on each individual particle no longer vanishes but the total force on the entire cluster disappears, that is,

$$\boldsymbol{F} = \sum_{i=1}^{N} \boldsymbol{F}_i = \boldsymbol{0}. \tag{3.25}$$

Utilizing (3.22), the requirement of $U_i = U_0$ and the relation above, U_0 can be determined straightforwardly.

4. Results and discussion

In this section, we present our results for the axisymmetric electrophoretic motions of a single sphere, of two free spheres, of three free spheres, and of a rigid cluster of spheres. The details of the collocation scheme used for this work were given

		$\frac{4\pi\eta U}{\epsilon E_\infty \zeta}$					
		$Z=1$		$Z=2$		$Z=3$	
κa	$\frac{\zeta e}{kT}$	A	B	A	B	A	B
100	1.0	0.984	0.993	0.973	0.981	0.950	0.958
	3.0	0.910	0.929	0.739	0.746	0.433	0.435
	5.0	0.751	0.765	0.316	0.316	0.114	0.115
	7.0	0.525	0.525	0.129	0.130	0.07	0.068
200	1.0	0.992	0.997	0.986	0.990	0.974	0.978
	3.0	0.952	0.962	0.844	0.849	0.574	0.575
	5.0	0.851	0.862	0.433	0.433	0.135	0.135
	7.0	0.664	0.669	0.158	0.158	0.07	0.069
400	1.0	0.996	0.998	0.993	0.995	0.987	0.989
	3.0	0.975	0.981	0.913	0.916	0.715	0.717
	5.0	0.917	0.925	0.578	0.579	0.173	0.173
	7.0	0.788	0.795	0.210	0.209	0.07	0.071

TABLE 1. The electrophoretic velocity of a single sphere in a solution containing only one symmetric electrolyte of valence Z with $f = 0.4$, as computed from (2.20) (listed in column A) and (2.27) (listed in column B)

by Keh & Yang (1990). To avoid superfluity, only the fluid containing one symmetric electrolyte will be considered.

4.1. *A single sphere*

The electrophoretic velocity of an isolated sphere can be evaluated using (2.20) for the general case, or (2.27) for the special situation when the fluid contains only one symmetric electrolyte. A comparison of the results calculated for various cases of symmetric electrolyte, with the dimensionless ionic drag coefficients $f_1 = f_2 = f = 0.4$, from the two formulae is illustrated in table 1. Although (2.20) generates a slightly smaller electrophoretic velocity value than (2.27) does for the case of a not-too-high zeta potential, the agreement between them is very good. Thus, our judgment that only the normal flux of the most highly charged counterions needs to be considered is quite reasonable.

From (2.27) or (2.28), it is easily found that the particle mobility is affected by four factors: ζ, Z, f and κa. As shown in figure 2, in which the diagonal represents the prediction by the Smoluchowski equation (1.1), the electrophoretic mobility is reduced owing to the polarization of the double layer. The non-equilibrium distribution of the ions within the double layer results in a back field and tangential osmotic pressure gradients which reduce the driving force for fluid flow (O'Brien & Ward 1988). When ζ increases, the concentration of counterions in the diffuse layer becomes high and, consequently, the normal fluxes of these ions are significant, so that the deviation of the mobility results from (1.1) becomes more apparent. In addition, if the counterion carries a higher charge, the movement of the particle will be slowed down more significantly. From figure 2, it can also be seen that when the thickness of the double layer decreases, that is κa becomes larger, the results will get closer to what (1.1) predicts. This is understandable because as κa becomes larger it

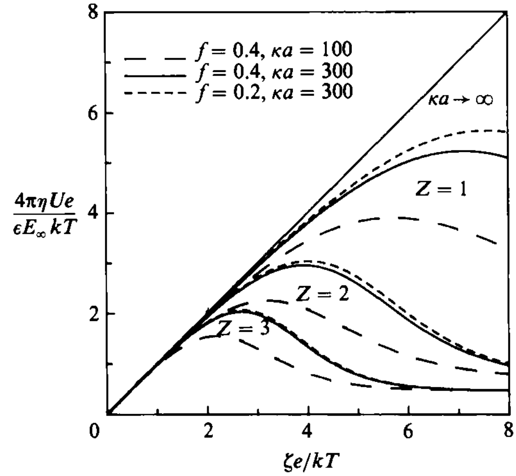

FIGURE 2. Plots of the normalized electrophoretic mobility of an isolated sphere versus the dimensionless zeta potential $\zeta e/kT$ for different values of κa and f.

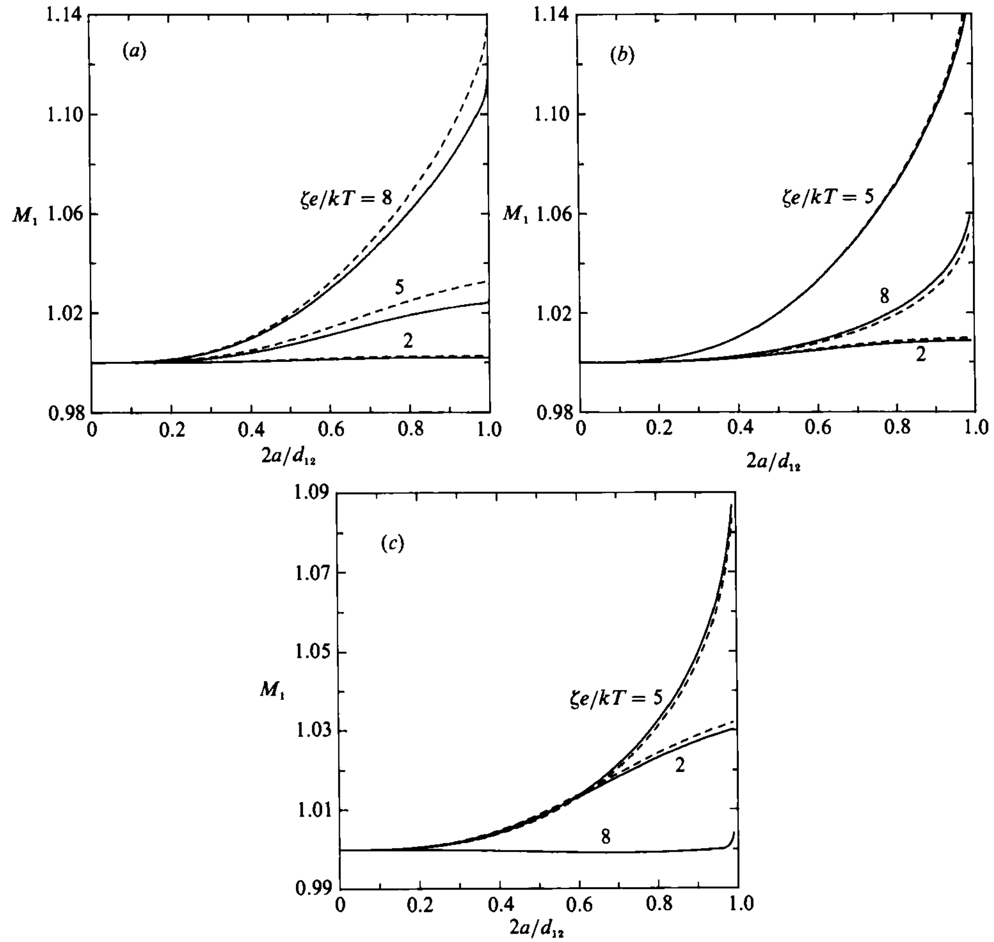

FIGURE 3. Plots of the mobility parameters of two identical spheres ($M_1 = M_2$) versus the separation parameter $2a/d_{12}$ with $\kappa a = 100$ and $f = 0.2$ (solid curves) or $f = 0.4$ (dashed curves): (a) $Z = 1$, (b) $Z = 2$, (c) $Z = 3$.

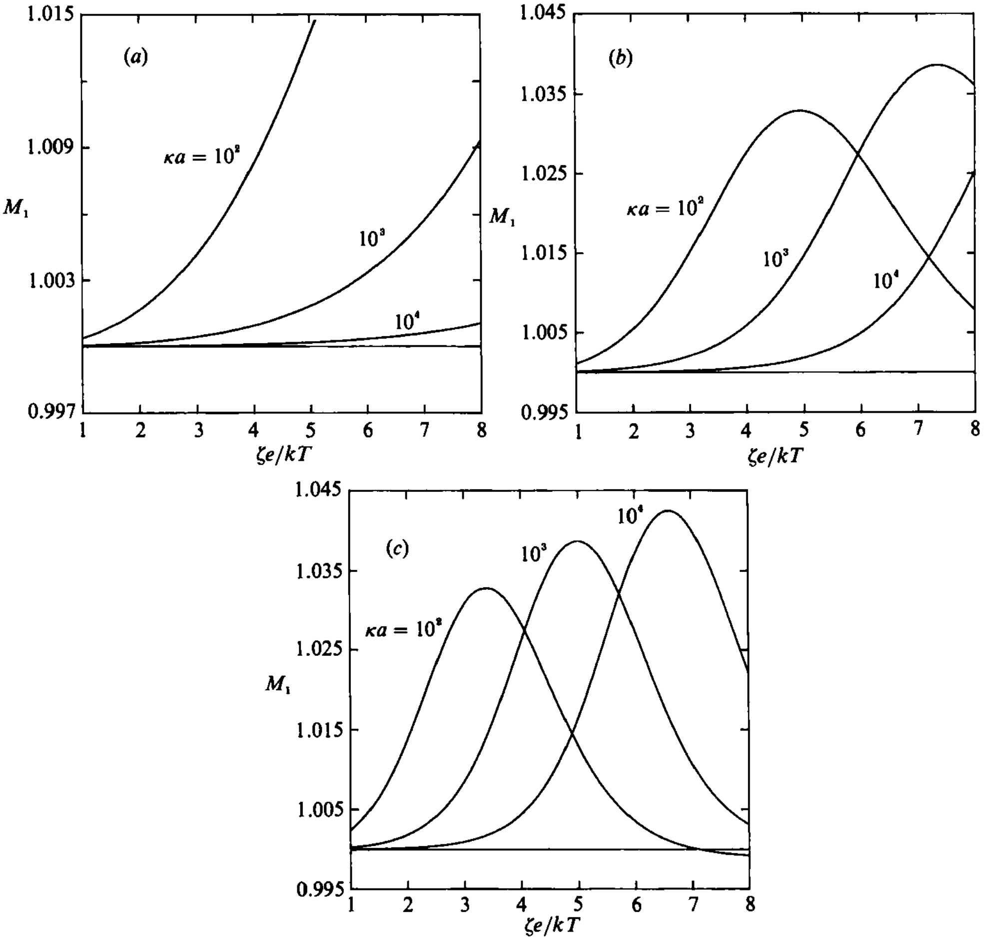

FIGURE 4. Plots of the mobility parameters of two identical spheres versus the dimensionless zeta potential $\zeta e/kT$ with $2a/d_{12} = 0.6$ and $f = 0.4$: (*a*) $Z = 1$, (*b*) $Z = 2$, (*c*) $Z = 3$.

approaches the traditional assumption of $\kappa a \rightarrow \infty$ for the electrophoretic problems. The effect of the last factor, f, on the particle's mobility is shown in figure 2 for the cases of $f = 0.2$ and 0.4 (representing the bounds for most realistic aqueous systems). The mobility is lessened as the ionic drag coefficient becomes large, but its influence is of less importance.

We have also evaluated the electrophoretic mobility of a spherical particle in an aqueous solution of KCl using (2.27) for various values of κa ($\geqslant 100$) and ζ (large or small); the results are in quite good agreement with the numerical values of O'Brien & White (1978).

4.2. *Two identical free spheres*

Numerical results, obtained by using the collocation technique, for two identical spheres ($a_1 = a_2 = a$, $\zeta_1 = \zeta_2 = \zeta$) undergoing electrophoresis along their line of centres are presented in this subsection. Here we only consider the special case that the fluid consists of a single type of symmetric electrolyte. In other words, (3.9) is applied to solve the unknown coefficients A_{1jn} and A_{2jn} in (3.3) for μ_m. The most important discovery is that, unlike the conclusions of the previous studies in which the effects of polarization of diffuse ions were ignored (Reed & Morrison 1976; Chen

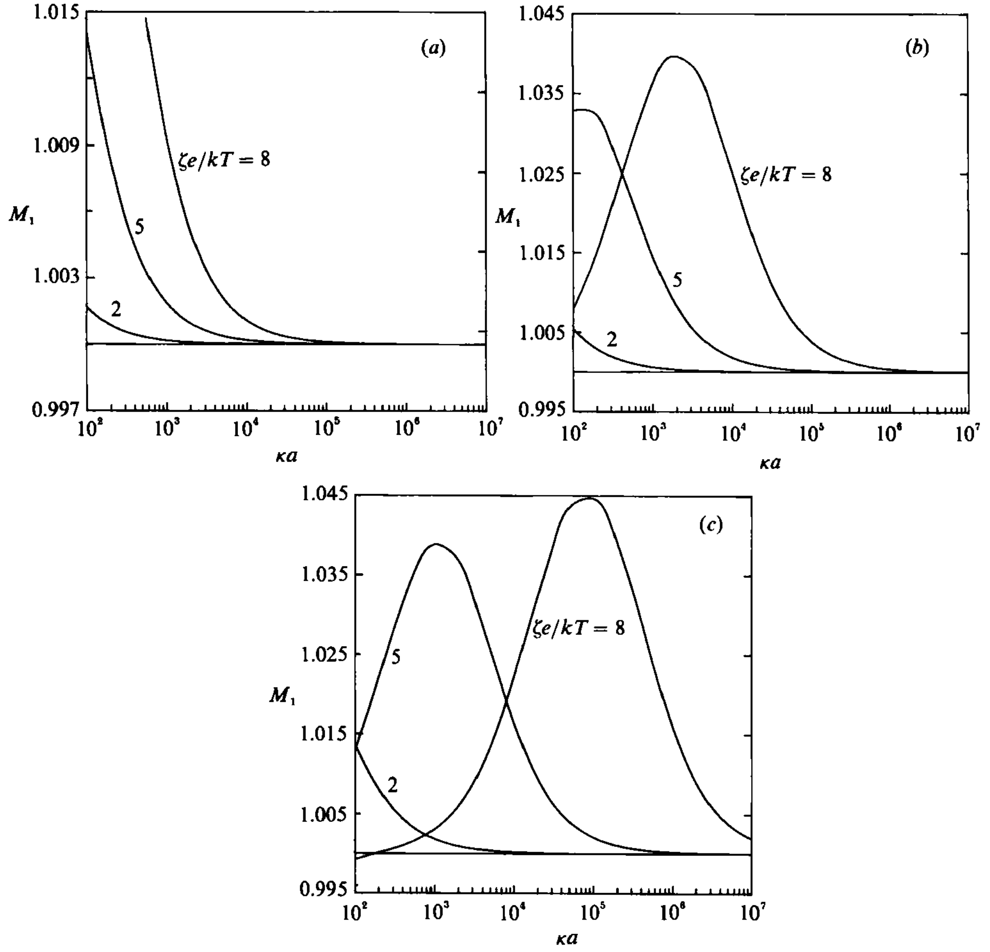

FIGURE 5. Plots of the mobility parameters of two identical spheres versus the ratio of the sphere radius to the Debye length κa with $2a/d_{12} = 0.6$ and $f = 0.4$: (a) $Z = 1$, (b) $Z = 2$, (c) $Z = 3$.

& Keh 1988; Keh & Chen 1989*a*), interactions exist between the two spheres even though they have equal zeta potentials on the surface.

It is evident, as shown in figure 3(*a–c*), that the mobility parameter $M_1 (= M_2)$, indicating the extent of particle interaction, is a function of the separation parameter $2a/d_{12}$. The ionic drag coefficient ($f_1 = f_2 = f$ is assumed) affects the particle interaction slightly. In particular, the two curves for $f = 0.2$ and $f = 0.4$ nearly coincide for the cases when $Z = 1$ and $\zeta e/kT = 2$ in figure 3(*a*), $Z = 2$ and $\zeta e/kT = 5$ in figure 3(*b*) and $Z = 3$ and $\zeta e/kT = 8$ in figure 3(*c*). In general, the two spheres are speeded up by each other when they get closer except when the particles have a large zeta potential and the counterions carry a high charge. As shown in figure 3(*c*), when $\zeta e/kT = 8$ and $Z = 3$, the movement of the two particles is slowed down and there exists a minimum in their electrophoretic velocity at about $2a/d_{12} = 0.7$.

Figure 4 is drawn to show the interaction effect between the two spheres versus the particles' zeta potential when the separation parameter $2a/d_{12}$ is kept constant. When $Z = 1$, as illustrated in figure 4(*a*), the mobility parameter of each particle is a monotonic increasing function of the non-dimensional zeta potential $\zeta e/kT$ ranging

			$Z=1$		$Z=2$		$Z=3$	
$\frac{\zeta_1 e}{kT}$	$\frac{\zeta_2 e}{kT}$	$\frac{2a}{d_{12}}$	M_1	M_2	M_1	M_2	M_1	M_2
1	5	0.2	1.0034	0.9993	1.0021	0.9997	1.0015	1.0007
		0.4	1.0279	0.9939	1.0164	0.9968	1.0117	1.0043
		0.6	1.1036	0.9753	1.0561	0.9837	1.0375	1.0070
		0.8	1.3217	0.9164	1.1490	0.9341	1.0819	0.9890
		0.9	1.6076	0.8387	1.2441	0.8734	1.0994	0.9825
		0.95	1.8853	0.7645	1.3096	0.8304	1.0763	1.0297
		0.99	2.2685	0.6632	1.3383	0.8101	0.9524	1.2414
		1.0	2.4107	0.6259	1.3203	0.8207	0.8506	1.4116
3	6	0.2	1.0013	0.9999	1.0015	1.0013	1.0013	1.0017
		0.4	1.0101	0.9991	1.0114	1.0096	1.0102	1.0127
		0.6	1.0339	0.9931	1.0361	1.0259	1.0331	1.0382
		0.8	1.0866	0.9653	1.0762	1.0413	1.0733	1.0805
		0.9	1.1413	0.9278	1.0919	1.0631	1.0960	1.1317
		0.95	1.1839	0.8974	1.0763	1.1208	1.0943	1.2136
		0.99	1.2163	0.8739	0.91	1.47	0.9981	1.5629
		1.0	1.2185	0.8723	0.84	1.61	0.719	1.852
5	−5	0.2	0.9983	0.9983	0.9990	0.9990	1.0004	1.0004
		0.4	0.9857	0.9857	0.9915	0.9915	1.0030	1.0030
		0.6	0.9442	0.9442	0.9664	0.9664	1.0095	1.0095
		0.8	0.8139	0.8139	0.8791	0.8791	1.0058	1.0058
		0.9	0.6293	0.6293	0.7303	0.7303	0.9268	0.9268
		0.95	0.4337	0.4337	0.5384	0.5384	0.7414	0.7414
		0.99	0.1274	0.1274	0.1713	0.1713	0.2559	0.2559
		1.0	0.000	0.000	0.000	0.000	0.000	0.000
8	−8	0.2	0.9988	0.9988	1.0006	1.0006	1.0009	1.0009
		0.4	0.9899	0.9899	1.0050	1.0050	1.0081	1.0081
		0.6	0.9603	0.9603	1.0171	1.0171	1.0289	1.0289
		0.8	0.8610	0.8610	1.0282	1.0282	1.0632	1.0632
		0.9	0.7025	0.7025	0.9617	0.9617	1.0158	0.0158
		0.95	0.5106	0.5106	0.7781	0.7781	0.8335	0.8335
		0.99	0.1609	0.1609	0.2721	0.2721	0.2916	0.2916
		1.0	0.000	0.000	0.000	0.000	0.000	0.000

TABLE 2. The mobility parameters M_1 and M_2 for the axisymmetric electrophoresis of two freely suspended spheres with $a_1 = a_2 = a$ for the case $f = 0.4$ and $\kappa a = 100$

from 1 to 8. Also, the spheres translate faster with smaller κa. However, when $Z = 2$ or 3 as shown in figures 4(*b*) and 4(*c*), a maximum of the particle velocity exists for some cases. When κa increases, the maximum occurs at a larger zeta potential. Note that these maxima for the cases with $Z = 3$ take place at smaller zeta potentials than those with $Z = 2$.

In figure 5, it is shown that there is no particle interaction in electrophoresis for each case as long as the value of κa approaches infinity. This result is in accordance with the situation considered earlier using the Helmholtz relation, instead of (2.8), to express the 'slip velocity' at the particle surfaces (Reed & Morrison 1976). From figure 5(*a*) for the case $Z = 1$, the particle interaction is weakened steadily as κa becomes large gradually. A novel result is that, as shown in figures 5(*b*) and 5(*c*) for $Z = 2$ and 3 respectively, there can be a maximum of the particle interaction occurring at some κa for the representative cases of $\zeta e/kT = 5$ and 8. This

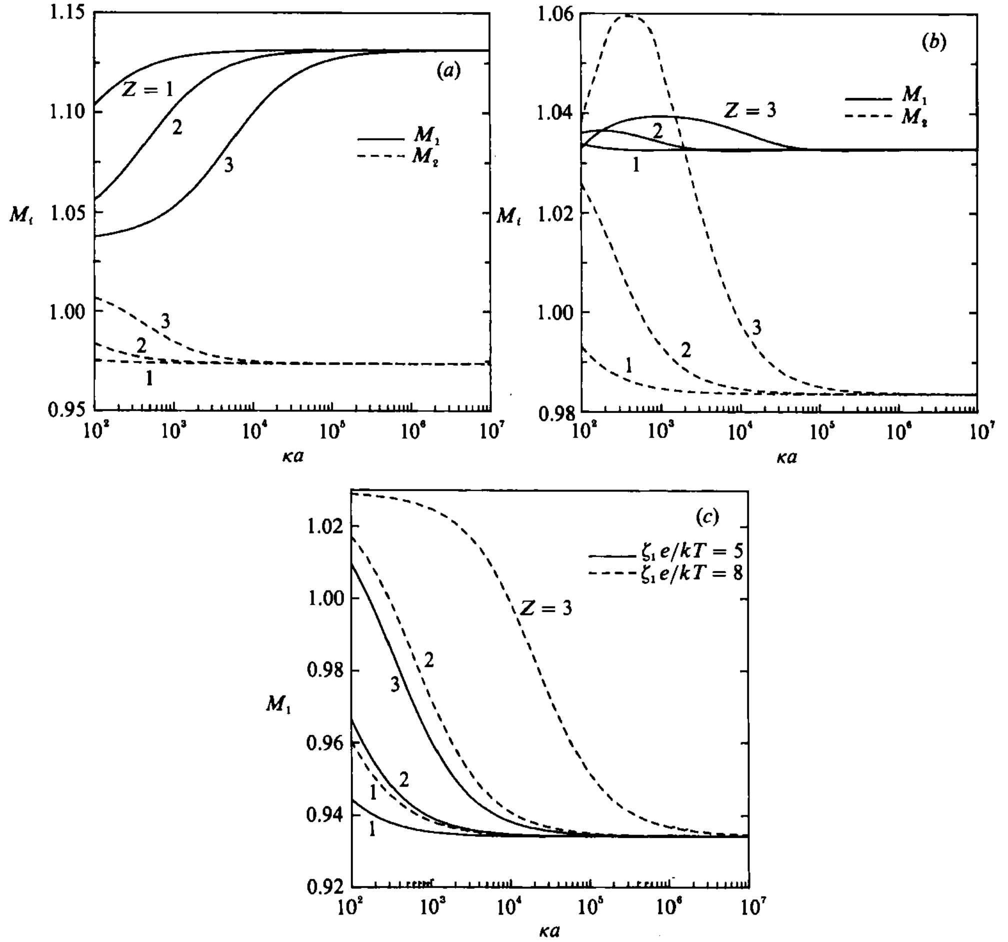

FIGURE 6. Plots of the mobility parameters of two equal-sized spheres versus the ratio of sphere radius to the Debye length κa with $2a/d_{12} = 0.6$ and $f = 0.4$: (a) $\zeta_1 e/kT = 1$ and $\zeta_2 e/kT = 5$, (b) $\zeta_1 e/kT = 3$ and $\zeta_2 e/kT = 6$, (c) $\zeta_1 e/kT = -\zeta_2 e/kT = 5$ or 8 ($M_1 = M_2$).

observation can also be predicted from figures 4(b) and 4(c). If the particles are charged more highly or the counterions have a larger magnitude of valence, the locations of these maximal interactions will shift toward larger κa, that means larger values of κa are required to make the assumption of $\kappa a \rightarrow \infty$ valid.

4.3. *Two arbitrary free spheres*

In this subsection, we first present the results for two spheres of the same size ($a_1 = a_2 = a$) having different zeta potentials. The values of mobility parameters at various particle separations are illustrated in table 2, in which all the results are at least convergent to the digits as shown. In figure 6(a–c), plots of the mobility parameters M_1 and M_2 versus κa are drawn for $2a/d_{12} = 0.6$. It is evident that as κa becomes very large, the electrophoretic mobility of each sphere will approach the value calculated by ignoring the polarization effect of the double layer (Keh & Chen 1989a). When the two particles have the zeta potentials of the same electrical sign, the numerical results for the case $Z = 1$ are consistent with the general intuition for the axisymmetric electrophoretic motion that the particle with the larger velocity would be slowed down by the other, which at the same time is accelerated by the

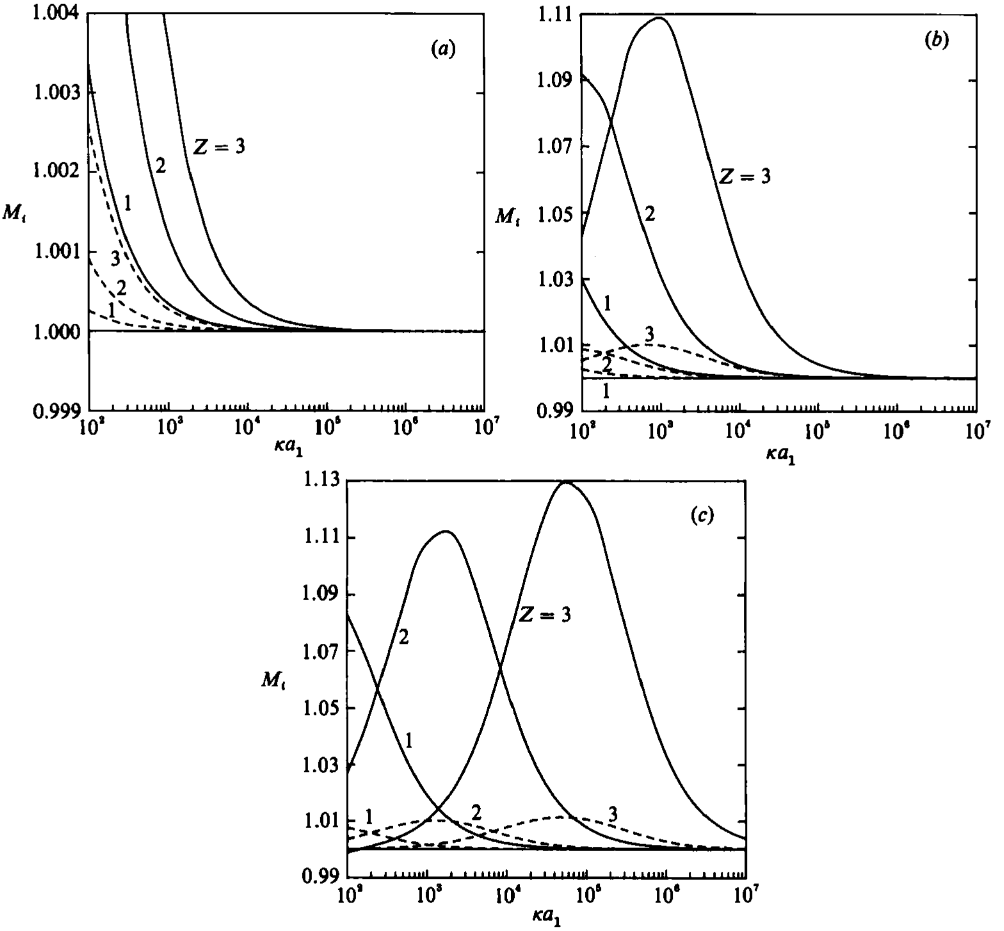

FIGURE 7. Plots of the mobility parameters M_1 (solid curves) and M_2 (dashed curves) of two unequal-sized spheres with the same zeta potential versus the ratio of the radius of sphere 1 to the Debye length κa_1 for the case of $a_2/a_1 = 2$, $(a_1+a_2)/d_{12} = 0.6$ and $f = 0.4$: (*a*) $\zeta e/kT = 2$, (*b*) $\zeta e/kT = 5$, (*c*) $\zeta e/kT = 8$.

former. However, no theoretical rule could appropriately predict the particle interaction for the cases of $Z = 2$ and 3. For the case of two touching spheres ($2a/d_{12} = 1$), they migrate as a single particle and their electrophoretic velocities are identical. If the pair of spheres are charged oppositely but with equal magnitudes of zeta potential, they will translate at the same speed but in opposite directions along their line of centres. Whether the particle velocities are increased or decreased depends on the combination of ζ, Z, f, κa and $2a/d_{12}$, as illustrated in table 2 and figure 6(*c*). When these two spheres touch, they act like a neutral body and both of them will be motionless.

Since many dispersions in practical applications are constituted from particles of the same material, it might be of interest to examine the interactions between two identically charged spheres ($\zeta_1 = \zeta_2 = \zeta$) with unequal sizes. The results for the interaction parameters for spheres with $a_2/a_1 = 2$ and $(a_1+a_2)/d_{12} = 0.6$ are depicted versus κa_1 in figure 7 (*a*–*c*). It is understood that, although the two spheres possess the same zeta potential, they will move at different speeds even if situated very far apart. In general, the influence of the particle interaction is more significant on the smaller one than on the larger. In can also be seen that the shift of the locations of the maximal particle interactions is like that for a pair of identical spheres. Again, whether the particle interaction enhances or retards the electrophoretic velocity of each sphere depends on the combination of parameters for each case.

4.4. *Three free spheres*

The utilization of the multipole collocation technique for solving the three-particle problem becomes more difficult than for the case of two spheres. The presence of the third sphere results in an increase in the number of unknown coefficients to be determined for μ_m and Ψ, so that a longer computing time is needed. Therefore, we only consider the simplest case in this subsection: three spheres having equal radii ($a_1 = a_2 = a_3 = a$) and zeta potentials ($\zeta_1 = \zeta_2 = \zeta_3 = \zeta$) separated at the same spacing on a straight line ($d_{12} = d_{23}$). The values of the mobility parameters M_1 ($= M_3$) and M_2 as a function of $2a/d_{12}$ are listed in table 3. For the cases of $\zeta e/kT = 5$ and 8, we could not obtain a convergent solution when the three spheres all touch; thus, only the results for $2a/d_{12} \leqslant 0.99$ are presented. As expected, the velocity of the middle sphere is affected more by the particle interaction than are those at each side of it.

It may be of interest to see the difference between two-particle and three-particle interaction effects on the electrophoretic velocities. A comparison between table 3 and figure 3, shows that the existence of the third sphere enhances the two-particle interaction effect on both sphere 1 and sphere 2.

4.5. *A rigid cluster of spheres*

The velocity of a linear rigid cluster of spheres undergoing axisymmetric electrophoresis can be determined by the procedure described in §3.4. For conciseness, here we only consider the motion of a dumbbell, along the line connecting the centres of its two spheres. The results for the electrophoretic mobility of the dumbbell, expressed in terms of the dimensionless form U_0/U_{10}, versus the separation parameter $(a_1+a_2)/d_{12}$ are exhibited in table 4. The last column in table 4 represents results neglecting the polarization effects of the ions in double layers, for comparison. Generally speaking, the polarization effects on the electrophoresis of a rigid dumbbell can be quite large under appropriate conditions.

For the simplest case that its two spheres are identical both in radius and in zeta potential, the dumbbell will move at the same speed as that of either of these two spheres suspended freely and separated by the same distance as discussed in §4.2. When the two spheres of a dumbbell are of the same size but unequal zeta potentials, the contribution of each particle to the mobility of the dumbbell is no longer equivalent, as show in the first five rows of table 4. As the two spheres get closer, the influence on the dumbbell's velocity of the sphere with larger U_{i0} seems to become more important. This discovery differs from the deduction of previous studies, in which the diffuse-layer polarization effect is ignored, that a dumbbell composed of two equal-sized spheres will just translate at the mean undisturbed velocity of the two spheres (Fair & Anderson 1990; Keh & Yang 1991).

In a suspension of colloidal particles of the same material, all the particles should have identical zeta potentials. Since flocculation by bridging of different-sized particles can occur usually, it might be important to examine the electrophoretic motion of such a dumbbell. Listed in the second five rows of table 4 are the electrophoretic velocity results for the case of a rigid dumbbell composed of two spheres with $a_2/a_1 = 2$, $\kappa a_1 = 100$ and $\zeta_1 e/kT = \zeta_2 e/kT = 5$. As expected, the larger

		$Z=1$		$Z=2$		$Z=3$	
$\frac{\zeta e}{kT}$	$\frac{2a}{d_{12}}$	M_1	M_2	M_1	M_2	M_1	M_2
2	0.2	1.0001	1.0002	1.0003	1.0005	1.0007	1.0013
	0.4	1.0007	1.0012	1.0023	1.0039	1.0055	1.0094
	0.6	1.0021	1.0032	1.0067	1.0105	1.0169	1.0266
	0.8	1.0033	1.0044	1.0116	1.0155	1.0324	1.0440
	1.0	1.0039	1.0039	1.0147	1.0147	1.0477	1.0477
5	0.2	1.0007	1.0013	1.0015	1.0027	1.0006	1.0010
	0.4	1.0057	1.0097	1.0121	1.0207	1.0046	1.0079
	0.6	1.0175	1.0273	1.0408	1.0645	1.0162	1.0256
	0.8	1.0331	1.0450	1.0977	1.1343	1.0427	1.0587
	0.99	1.0475	1.0490	1.2347	1.2424	1.1417	1.1462
8	0.2	1.0015	1.0027	1.0003	1.0006	1.0000	0.9999
	0.4	1.0120	1.0205	1.0028	1.0047	0.9996	0.9994
	0.6	1.0396	1.0625	1.0099	1.0156	0.9991	0.9986
	0.8	1.0907	1.1247	1.0266	1.0365	0.9991	0.9988
	0.99	1.1910	1.1972	1.0916	1.0946	1.0014	1.0015

TABLE 3. The mobility parameters M_1 ($=M_3$) and M_2 for the axisymmetric electrophoresis of three identical spheres ($a_1=a_2=a_3=a$ and $\zeta_1=\zeta_2=\zeta_3=\zeta$) suspended freely with equal spacings ($d_{12}=d_{23}$) for the case $f=0.4$ and $\kappa a=100$

				U_0/U_{10} (with polarization)			U_0/U_{10} (without polarization)
$\frac{a_2}{a_1}$	$\frac{\zeta_1 e}{kT}$	$\frac{\zeta_2 e}{kT}$	$\frac{a_1+a_2}{d_{12}}$	$Z=1$	$Z=2$	$Z=3$	
1	1	5	0.2	2.4262	1.3051	0.8022	3.000
			0.4	2.4281	1.3099	0.8084	3.000
			0.6	2.4302	1.3193	0.8221	3.000
			0.8	2.4257	1.3258	0.8389	3.000
			1.0	2.4107	1.3203	0.8506	3.000
2	5	5	0.2	1.0887	1.2593	1.1191	1.000
			0.4	1.0957	1.2802	1.1288	1.000
			0.6	1.1061	1.3136	1.1448	1.000
			0.8	1.1163	1.3571	1.1683	1.000
			0.99	1.1226	1.4186	1.220	1.000
2	4	−1	0.2	0.1070	−0.0235	−0.5236	0.1344
			0.4	0.0629	−0.0744	−0.6000	0.0917
			0.6	0.0110	−0.1348	−0.6910	0.0419
			0.8	−0.0414	−0.1970	−0.7833	−0.0075
			1.0	−0.0897	−0.2558	−0.8680	−0.0536

TABLE 4. The dimensionless electrophoretic velocity of a rigid dumbbell U_0/U_{10} along the line connecting two spheres for the case $f=0.4$ and $\kappa a_1=100$

sphere dominates the motion of the dumbbell and its influence becomes more important when the two spheres are less separated. Also, the tendency that the interaction effect is strong for the case of $Z=2$ and weak for $Z=1$ is consistent with the results of figure 7(*b*) for two free spheres with $\zeta e/kT=5$.

An interesting case is the electrophoresis of a neutral dumbbell (with zero area-averaged zeta potential, i.e. the ratio ζ_2/ζ_1 equal to $-a_1^2/a_2^2$). In the third five rows of table 4, we show the dumbbell mobility versus $(a_1+a_2)/d_{12}$ for the case $\zeta_1 e/kT = 4$, $\zeta_2 e/kT = -1$ and $a_2/a_1 = 2$. It can be seen that, as before, the larger sphere will increasingly dominate the dumbbell's movement as the distance between the two spheres decreases. For most situations, the neutral dumbbell moves in the same direction as that of the larger sphere when isolated, especially for the cases $Z = 2$ and 3. This observation is qualitatively consistent with that in Fair & Anderson (1990) and Keh & Yang (1991).

5. Conclusions

In this paper the electrophoretic motion of colloidal spheres with thin but distorted electrical double layers is studied. Not only the movement of an isolated sphere but also the interactions among a finite assemblage of spheres moving along their line of centres have been examined. The governing equations in the 'outer' region can be solved by applying the boundary conditions provided by the solution for the 'inner' region and using a matching procedure to ensure a continuous solution in the whole fluid phase. There are four factors influencing the mobility of a particle: the zeta potential at the surface, the ratio of the particle dimension to the Debye length, the valences of ions in solution and the ionic drag coefficients. The polarization of the diffuse ions will hinder the electrophoretic velocity of the sphere compared to what the Smoluchowski equation predicts.

For the axisymmetric electrophoresis of multiple spheres or a rigid dumbbell freely suspended in the fluid, a combined analytical–numerical procedure with the multipole collocation technique has been used to solve the electrochemical potential distributions and the velocity field for the fluid around the spheres. The most important discovery is that particle interactions actually exist among spheres with identical zeta potentials in an unbounded fluid as long as κa is finite. In addition, the particle interaction is no longer a simple monotonic function of both the spheres' and ions' properties as well as the separation distance for some cases. No general rule can make an adequate prediction for such a complicated phenomenon. This novel result should be noted by both theoreticians and experimentalists in relevant fields.

Appendix

We begin by deriving (2.11) which can then be used to obtain (2.12) by the analytical integration over the double layer for the system in which the fluid comprises only a single kind of symmetric electrolyte.

We take a slab-shaped control volume lying on the particle surface, which is just a portion of the double layer with thickness t ($\ll L$). Integrating both sides in (2.6*a*) over the entire control volume and using the divergence theorem yields (O'Brien 1983)

$$\iint_{\substack{\text{control}\\ \text{surface}}} \left[n_m^0 \nabla \mu_m - \frac{kT}{D_m}(n_m^0 - n_m^\infty)\, \boldsymbol{v} \right] \cdot \mathrm{d}\boldsymbol{S} = 0. \tag{A 1}$$

The second term in the integral is replaced by $kTn_m^0\, \boldsymbol{v}/D_m$ in O'Brien's article. Both of them are correct because $\nabla n_m^0 = \nabla(n_m^0 - n_m^\infty)$ when all bulk ionic concentrations n_m^∞ are uniform. We can substitute $\boldsymbol{v}$ in (2.8) into (A 1), and then follow the same procedure as that employed by O'Brien to obtain (2.10) and (2.11).

For a symmetric electrolyte with absolute value of valence Z, the one-dimensional Poisson–Boltzmann equation,

$$\frac{\mathrm{d}^2\bar{\Phi}^0}{\mathrm{d}\bar{y}^2}=\frac{1}{Z}\sinh Z\bar{\Phi}^0, \tag{A 2}$$

possesses an analytical solution:

$$\bar{\Phi}^0=\frac{2}{Z}\ln\left[\frac{1+\gamma\exp(-\bar{y})}{1-\gamma\exp(-\bar{y})}\right], \tag{A 3}$$

$$\gamma=\tanh\bar{\zeta}, \tag{A 4}$$

where $\bar{\zeta}=Ze\zeta/4kT$ and ζ is the zeta potential associated with the solid surface. One can substitute $\bar{\Phi}^0$ in (A 3) into (2.11) to evaluate the integrals. The upper limit κt in the integration, which represents the outer edge of the double layer, may be regarded as infinity from the viewpoint of the boundary-layer concept, so that the parameters β_{mk} can be computed and expressed by

$$\beta_{11}=\frac{1}{\kappa L}\left[\kappa t+4\left(1+\frac{3f_1}{Z^2}\right)\exp(\bar{\zeta})\sinh\bar{\zeta}-\frac{12f_1}{Z^2}(\bar{\zeta}+\ln\cosh\bar{\zeta})\right], \tag{A 5a}$$

$$\beta_{12}=\frac{1}{\kappa L}\left[\kappa t+\left(\frac{12f_1}{Z^2}\right)\ln\cosh\bar{\zeta}\right], \tag{A 5b}$$

$$\beta_{21}=\frac{1}{\kappa L}\left[\kappa t+\left(\frac{12f_2}{Z^2}\right)\ln\cosh\bar{\zeta}\right], \tag{A 5c}$$

$$\beta_{22}=\frac{1}{\kappa L}\left[\kappa t-4\left(1+\frac{3f_2}{Z^2}\right)\exp(-\bar{\zeta})\sinh\bar{\zeta}+\frac{12f_2}{Z^2}(\bar{\zeta}-\ln\cosh\bar{\zeta})\right]. \tag{A 5d}$$

We adopt (2.11) rather than the corresponding formula originally derived by O'Brien (1983) because some divergent integrations of infinite series can be avoided (Anderson & Prieve 1991). Since there is no definite boundary for a double layer and we have assumed $t/L \ll 1$, the κt terms in the above equations may be safely neglected. Then, (A 5) is reduced to (2.12).

REFERENCES

Anderson, J. L. & Prieve, D. C. 1991 Diffusiophoresis caused by gradients of strongly adsorbing solutes. *Langmuir* **7**, 403.

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

Dukhin, S. S. & Derjaguin, B. V. 1974 Electrokinetic phenomena. In *Surface and Colloid Science* (ed. E. Matijevic), vol. 7. Wiley.

Dukhin, S. S. & Shilov, V. N. 1980 Kinetic aspects of electrochemistry of disperse systems. Part II. Induced dipole moment and the non-equilibrium double layer of a colloid particle. *Adv. Colloid Interface Sci.* **13**, 153.

Fair, M. C. & Anderson, J. L. 1990 Electrophoresis of dumbbell-like colloidal particles. *Intl J. Multiphase Flow* **16**, 663.

Gluckman, M. J., Pfeffer, R. & Weinbaum, S. 1971 A new technique for treating multiparticle slow viscous flow: axisymmetric flow past spheres and spheroids. *J. Fluid Mech.* **50**, 705.

Happel, J. & Brenner, H. 1983 *Low Reynolds Number Hydrodynamics*. Martinus Nijhoff.

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

KEH, H. J. & CHEN, S. B. 1989*b* Particle interactions in electrophoresis – II. Motion of two spheres normal to their line of centres. *J. Colloid Interface Sci.* **130**, 556.

KEH, H. J. & YANG, F. R. 1990 Particle interactions in electrophoresis – III. Axisymmetric motion of multiple spheres. *J. Colloid Interface Sci.* **139**, 105.

KEH, H. J. & YANG, F. R. 1991 Particle interactions in electrophoresis – IV. Motion of arbitrary three-dimensional clusters of spheres. *J. Colloid Interface Sci.* **145**, 362.

O'BRIEN, R. W. 1983 The solution of the electrokinetic equations for colloidal particles with thin double layers. *J. Colloid Interface Sci.* **92**, 204.

O'BRIEN, R. W. 1986 Electroosmosis in porous materials. *J. Colloid Interface Sci.* **110**, 477.

O'BRIEN, R. W. & WARD, D. N. 1988 The electrophoresis of a spheroid with a thin double layer. *J. Colloid Interface Sci.* **121**, 402.

O'BRIEN, R. W. & WHITE, L. R. 1978 Electrophoretic mobility of a spherical colloidal particle. *J. Chem. Soc. Faraday Trans. II* **74**, 1607.

REED, L. D. & MORRISON, F. A. 1976 Hydrodynamic interaction in electrophoresis. *J. Colloid Interface Sci.* **54**, 117.