

Particle Interactions in Electrophoresis

V. Motion of Multiple Spheres with Thin but Finite Electrical Double Layers

HUAN JANG KEH¹ AND JONG BIN CHEN

Department of Chemical Engineering, National Taiwan University, Taipei 106-17, Taiwan, Republic of China

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The electrophoretic motion of an arbitrary finite cluster of colloidal spheres is considered. The spheres are allowed to differ in size and in zeta potential at the surface. Also, the spheres can be either freely suspended in the fluid or linked by infinitesimally thin rods to form a rigid aggregate. The fluid can contain an arbitrary combination of general electrolytes. Although the electrical double layers surrounding the particles are assumed small relative to the particles' radii, the polarization of the mobile ions in the diffuse layer induced by the applied electric field is taken into account. A slip velocity of the fluid and normal fluxes of ions at the outer edge of the double layer are 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 limit and the particle interaction effects are computed for various cases. It is found that particles with the same zeta potential will interact with one another, unlike the no-interaction results obtained in previous studies 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, and it no longer varies monotonically with the extent of separation for some cases. Our numerical results for the interaction between two identical spheres are also used to evaluate the effect of the volume fraction of particles on the average electrophoretic velocity in a bounded suspension. For various situations, this average velocity is reduced as the particle concentration is increased. © 1993 Academic Press, Inc.

1. INTRODUCTION

A colloidal particle, when placed in an electrolyte solution, can be driven to move by the application of an electric field that interacts with the electrical double layer surrounding the particle. This motion is called electrophoresis and has been the subject of many investigations. The electrophoretic velocity $U^{(0)}$ of the particle is related to the applied electric field E_∞ by Smoluchowski's equation (1, 2),

$$U^{(0)} = \frac{\epsilon \zeta}{4\pi\eta} E_\infty. \quad [1.1]$$

Here, $\epsilon/4\pi$ is the permittivity of the solution, η is the fluid viscosity, and ζ is the zeta potential on the shear plane at the particle surface. Equation [1.1] can be applied to an isolated dielectric particle of arbitrary shape and size. However, its validity is based on two key assumptions, that the local radii of curvature of the particle are much larger than the thickness of the double layer at the particle surface and that the polarization of diffuse ions in the double layer due to the nonuniform electroosmotic flow is negligible. Recently, important advances have been made in the calculation of the electrophoretic velocity of colloidal particles, relaxing these assumptions.

Taking the double-layer distortion from equilibrium as a perturbation, O'Brien and White (3) obtained a numerical solution for the electrophoretic velocity of a nonconducting sphere of radius a over a broad range of ζ and κa ; κ^{-1} is the Debye screening length. On the other hand, Dukhin and Derjaguin (2) obtained an analytical expression for the electrophoretic mobility of a spherical particle with thin but polarized double layer in a solution of symmetrically charged, binary electrolyte. Later, O'Brien (4) generalized this analysis to the case of electrophoretic motion in a solution composed of an arbitrary combination of electrolytes. The advantage of this theory is that a "slip velocity" and normal ionic fluxes at the outer edge of the diffuse layer have been derived, so the only region one needs to take into account is the neutral fluid phase outside the double layer. The results of these studies (2–4) have shown that the effect of polarization of the double layer is to hinder the electrophoretic velocity. One reason for this consequence is that the back field resulting from the polarization of the diffuse ions is liable to counterbalance the applied electric field. If ζ is small and κa is large, the interaction between the diffuse ions and the inside charge at the particle surface is weak and the polarization of the double layer is slight. In the limit of

$$\frac{1}{\kappa a} \exp\left(\frac{e|z_\sigma \zeta|}{2k_B T}\right) \rightarrow 0, \quad [1.2]$$

¹ To whom correspondence should be addressed.

where z_e is the valence of the counterions with the highest charge, e is the charge of a proton, and $k_B T$ is the thermal energy, the electrophoretic velocity of the particle can be accurately predicted by the Smoluchowski equation [1.1].

In practical applications of electrophoresis, multiple particle systems are more important than the single particle situation; the later condition represents only the limiting case at low dispersed phase hold-up. In dispersions, particle interactions can be of primary importance. Recently, much progress has been made in the theoretical analysis of the particle interactions in electrophoresis of insulating spheres with extremely thin double layers, i.e., $\kappa a \rightarrow \infty$. Chen and Keh (5) utilized a method of reflections to solve analytically the problem of electrophoresis of two arbitrarily oriented spheres with arbitrary ratios of radii and of zeta potentials. Another approach to examining this two-sphere motion is to use spherical bipolar coordinates. By this means, the electrophoretic mobilities of two nonrotating spheres with identical radii were first computed by Reed and Morrison (6), and later this work was extended to the situations of two arbitrary freely suspended spheres (7, 8). The third routine employed to solve this problem was the boundary collocation technique, which could be used to calculate the electrophoretic velocities for a collection of two or more arbitrary spheres (9, 10). One of the common conclusions from these investigations for the case $\kappa a \rightarrow \infty$ is that there is no particle interaction as long as all spheres have the same zeta potential.

In view of the fact that the polarization of the double layers surrounding the particles may significantly influence the behavior of particle interactions in electrophoresis, Chen and Keh (11) studied the axisymmetric electrophoretic motion of a string of spheres of arbitrary radii and zeta potentials with thin double layers along their line of centers using a boundary collocation technique. The most important discovery was that the particles with the same zeta potential will interact with one another, unlike the no-interaction results obtained in previous investigations (5–10) assuming that the double layers are infinitesimally thin. The present work is an extension of that of Chen and Keh (11) to the situation of the electrophoretic motion of multiple spheres in an arbitrary configuration. Again, the spheres may differ in radius and in zeta potential and the polarization of diffuse ions in the double layers, which are small in thickness but still have finite values in κa , is allowed. Also, the fluid solution can contain more than one kind of general electrolyte. By using the boundary collocation method, a set of electrokinetic equations is solved semianalytically in the quasi-steady state. The particle velocities are obtained with good convergence for various cases. The solution method for the electrophoresis of freely suspended spheres is also employed to examine the electrophoretic motion of a three-dimensional rigid cluster composed of N arbitrary spheres connected by thin rods of arbitrary lengths through their centers. The interaction effects between two spheres are also used to find the mean electro-

phoretic velocity in a bounded dispersion of colloidal particles. In the limiting case of $\kappa a \rightarrow \infty$, our results are in excellent agreement with those obtained in a previous analysis of this series (10).

2. ELECTROPHORESIS OF A CHARGED PARTICLE

We consider the electrophoretic motion of a dielectric particle in an unbounded quiescent fluid which contains M ionic species. The bulk densities of all ions n_m^∞ ($m = 1, 2, \dots, M$) in the electrolyte solution beyond the electrical double layer are constant. The thickness of the double layer is assumed to be much smaller than the particle dimension. The inside charge is uniformly fixed to the particle; that is, no conductance or charge polarization occurs inside the particle when the external field is applied. In spite of the assumption of a thin double layer, the electric field induced polarization of ionic distributions in the double layer will still be considered. Our purpose in this section is to introduce how the polarization of the diffuse layer influences the electrophoretic mobility of the particle.

2.1. Electrokinetic Equations

To calculate the electrophoretic velocity of a particle, in general, it is necessary to determine the electrical potential, ionic concentration, and fluid velocity distributions in the electrolyte solution. Conservation of all ionic species, which do not react with one another, at a steady state requires that

$$\nabla \cdot \mathbf{J}_m = 0, \quad m = 1, 2, \dots, M, \quad [2.1]$$

where \mathbf{J}_m is the density flux of the m th type of ion. If the solution is dilute, this flux is given by

$$\mathbf{J}_m = n_m \mathbf{v} - n_m \frac{D_m}{k_B T} \nabla \mu_m, \quad [2.2]$$

with the electrochemical potential energy of the m th species of ion μ_m defined as (12)

$$\mu_m = \mu_m^0 + k_B T \ln n_m + e z_m \Phi. \quad [2.3]$$

Here, \mathbf{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; and μ_m^0 is a constant. Since the Reynolds numbers of electrophoretic motions are very small, the inertial effect on the fluid momentum balance can be ignored. Thus, the fluid flow is governed by the modified Stokes equations

$$\eta \nabla^2 \mathbf{v} - \nabla p = \sum_{m=1}^M e z_m n_m \nabla \Phi, \quad [2.4]$$

$$\nabla \cdot \mathbf{v} = 0, \quad [2.5]$$

where p is the fluid pressure.

If the intensity of the external electric field is not high, the deviation in the ionic number densities and the electrical potential from equilibrium is so slight that the perturbation theory can be utilized to linearize the governing equations. It has been found that the electrochemical potential energy fields and the fluid velocity satisfy the set of electrokinetic equations (3, 4),

$$n_m^0 \nabla^2 \mu_m + \nabla n_m^0 \cdot \nabla \mu_m = \frac{k_B T}{D_m} \nabla n_m^0 \cdot \mathbf{v}, \quad m = 1, 2, \dots, M, \quad [2.6]$$

$$\eta \nabla^2 (\nabla \times \mathbf{v}) = \sum_{m=1}^M \nabla n_m^0 \times \nabla \mu_m. \quad [2.7]$$

Here, n_m^0 is the equilibrium number density of the m th species of ion, which is related to the equilibrium electrical potential Φ^0 by the Boltzmann distribution

$$n_m^0 = n_m^\infty \exp\left(-\frac{z_m e \Phi^0}{k_B T}\right). \quad [2.8]$$

Beyond the double layer (the "inner" region) surrounding the particle, or in the "outer" region, no ionic density gradients ∇n_m^0 occur and Eqs. [2.6] and [2.7] reduce to

$$\nabla^2 \mu_m = 0, \quad m = 1, 2, \dots, M, \quad [2.9]$$

$$\nabla^2 (\nabla \times \mathbf{v}) = 0. \quad [2.10]$$

Because matched expansions of μ_m and \mathbf{v} in both inner and outer regions can be constructed for the case of a thin double layer, the usual strategy is to solve Eqs. [2.5], [2.9], and [2.10] for μ_m and \mathbf{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 a Thin Double Layer

Because the thickness of the double layer is much smaller than the particle dimension, this inner region can be regarded as a thin flat layer on the scale of Debye length κ^{-1} . This implies that the fluid flow within the diffuse layer is primarily tangential to the solid surface from using the equation of continuity [2.5]. By the match of solutions between the inner and outer regions, it can be found that, at the outer boundary of the double layer, an apparent slip velocity parallel to the particle surface and normal gradients of the electrochemical potential energies occur (4, 11),

$$\mathbf{v}_s = -\frac{1}{\eta} \sum_{m=1}^M \nabla_s \mu_m \int_0^\infty y_n (n_m^0 - n_m^\infty) dy_n, \quad [2.11]$$

$$\mathbf{n} \cdot \nabla \mu_m = -\sum_{k=1}^M \beta_{mk} \nabla_s^2 \mu_k, \quad m = 1, 2, \dots, M, \quad [2.12]$$

with

$$\begin{aligned} \beta_{mk} = & \delta_{mk} \int_0^\infty \left[\exp\left(-\frac{z_m e \Phi^0}{k_B T}\right) - 1 \right] dy_n \\ & + \frac{k_B T}{\eta D_m} n_k^\infty \int_0^\infty \left[\exp\left(-\frac{z_m e \Phi^0}{k_B T}\right) - 1 \right] \\ & \times \int_0^{y_n} \int_{y_n'}^\infty \left[\exp\left(-\frac{z_k e \Phi^0}{k_B T}\right) - 1 \right] dy_n'' dy_n' dy_n. \end{aligned} \quad [2.13]$$

Here, y_n (or y_n'') is the perpendicular distance from the particle surface, \mathbf{n} is the unit vector normal to the solid surface pointing toward the fluid phase, δ_{mk} is the Kronecker delta, $\nabla_s = (\mathbf{I} - \mathbf{nn}) \cdot \nabla$ is the gradient tangential to the particle surface (\mathbf{I} is the unit dyadic), and $\nabla_s^2 = \nabla_s \cdot \nabla_s$ is the surface Laplacian operator.

If the fluid solution contains only one type of symmetric electrolyte ($M = 2$) with the absolute value of valence Z , the equilibrium electrical potential Φ^0 , which is obtained by solving the one-dimensional Poisson-Boltzmann equation, has the well-known expression

$$\Phi^0 = \frac{2k_B T}{Ze} \ln \left[\frac{1 + \tanh \bar{\zeta} \exp(-\kappa y)}{1 - \tanh \bar{\zeta} \exp(-\kappa y)} \right], \quad [2.14]$$

where $\bar{\zeta} = Ze\zeta/4k_B T$ and ζ is the zeta potential at the particle surface. Thus, all values of β_{mk} defined by Eq. [2.13] can be calculated analytically, with the result

$$\beta_{11} = \frac{1}{\kappa} \left[4 \left(1 + \frac{3f_1}{Z^2} \right) \exp(\bar{\zeta}) \sinh \bar{\zeta} - \frac{12f_1}{Z^2} (\bar{\zeta} + \ln \cosh \bar{\zeta}) \right], \quad [2.15a]$$

$$\beta_{12} = \frac{1}{\kappa} \left[-\frac{12f_1}{Z^2} \ln \cosh \bar{\zeta} \right], \quad [2.15b]$$

$$\beta_{21} = \frac{1}{\kappa} \left[-\frac{12f_2}{Z^2} \ln \cosh \bar{\zeta} \right], \quad [2.15c]$$

$$\begin{aligned} \beta_{22} = & \frac{1}{\kappa} \left[-4 \left(1 + \frac{3f_2}{Z^2} \right) \exp(-\bar{\zeta}) \sinh \bar{\zeta} \right. \\ & \left. + \frac{12f_2}{Z^2} (\bar{\zeta} - \ln \cosh \bar{\zeta}) \right]. \end{aligned} \quad [2.15d]$$

In the above equations,

$$f_m = \frac{\epsilon (k_B T)^2}{6\pi\eta e^2 D_m}, \quad m = 1, 2, \dots, M, \quad [2.16]$$

which is the dimensionless drag coefficient of ion m . The subscripts 1 and 2 for m or k of the variables in Eqs. [2.15a]–[2.15d] refer to the anion and cation, respectively.

For the case of a solution consisting of an arbitrary combination of general electrolytes, it is impossible to evaluate β_{mk} analytically because there is no analytical solution available for Φ^0 . Nonetheless, this can be overcome by the utilization of an asymptotic solution for Φ^0 for the case when the particle is highly charged. Also, a reasoning is that only the most highly charged counterions play a major role in the ionic fluxes normal to the particle surface (4); that is, boundary condition [2.12] might be approximated by

$$\mathbf{n} \cdot \nabla \mu_m = -\lambda \left[\nabla_s^2 \mu_m + \frac{3f_m}{4\alpha^2 I} \sum_k' n_k^\infty \nabla_s^2 \mu_k \right] \quad \text{for } z_m = z_\sigma, \quad [2.17a]$$

$$\mathbf{n} \cdot \nabla \mu_m = 0 \quad \text{otherwise,} \quad [2.17b]$$

with

$$\lambda = \frac{1}{\alpha\kappa} \left[\exp\left(\frac{e|z_\sigma \zeta|}{2k_B T}\right) - 1 \right] \quad [2.18a]$$

and

$$\alpha = \frac{|z_\sigma|}{2} \left(\frac{1}{I} \sum_k' n_k^\infty \right)^{1/2}. \quad [2.18b]$$

Here, I is the ionic strength in the bulk solution, the subscript σ denotes the counterions with the highest charge, and the symbol \sum_k' represents summation over all those ionic species (for which $z_m = z_\sigma$).

2.3. Electrophoretic Velocity of an Isolated Particle

We now consider the electrophoresis of a single particle when a constant external electric field \mathbf{E}_∞ is imposed. In the fluid phase outside the thin double layer, the electrochemical potential energies μ_m satisfy Laplace's equation [2.9] and the velocity field \mathbf{v} is governed by the Stokes equations [2.10] and [2.5]. The boundary conditions far away from the particle are

$$|\mathbf{r}| \rightarrow \infty: \quad \nabla \mu_m \rightarrow -z_m e \mathbf{E}_\infty, \quad [2.19a]$$

$$\mathbf{v} \rightarrow \mathbf{0}, \quad [2.19b]$$

where \mathbf{r} is the position vector with origin at the particle center. At the particle "surface" (outer edge of the diffuse layer), μ_m is subject to boundary condition [2.12] or [2.17] and \mathbf{v} is given (according to [2.11]) by

$$\mathbf{v} = \mathbf{U} + \boldsymbol{\Omega} \times \mathbf{r}$$

$$-\frac{1}{\eta} \sum_{m=1}^M \nabla_s \mu_m \int_0^\infty y_n (n_m^0 - n_m^\infty) dy_n, \quad [2.20]$$

where \mathbf{U} and $\boldsymbol{\Omega}$ are the translational and angular velocities of the electrophoretic particle to be determined. Because the particle surface encloses a neutral body (charged interface plus diffuse ions), the particle is force and torque free. With this constraint, one can calculate \mathbf{U} and $\boldsymbol{\Omega}$ after solving Eqs. [2.5], [2.9], [2.10], [2.12], [2.19], and [2.20] for μ_m and \mathbf{v} .

When the particle is a sphere of radius a , its translational and angular velocities, which can be determined through the above procedure, are (4)

$$\mathbf{U} = -\frac{2e}{3\eta} \mathbf{E}_\infty \sum_{m=1}^M (1 + c_m) z_m n_m^\infty \times \int_0^\infty y_n \left[\exp\left(-\frac{z_m e \Phi^0}{k_B T}\right) - 1 \right] dy_n, \quad [2.21a]$$

$$\boldsymbol{\Omega} = \mathbf{0}, \quad [2.21b]$$

with

$$c_m = \frac{1}{2} - \frac{3\lambda}{2(a + \lambda)} \left[1 + \frac{3f_m a}{z_m^2 (a + W_\sigma \lambda)} \right] \quad \text{for } z_m = z_\sigma, \quad [2.22a]$$

$$c_m = \frac{1}{2} \quad \text{otherwise,} \quad [2.22b]$$

where

$$W_\sigma = 1 + \frac{3 \sum_k' f_k n_k^\infty}{z_\sigma^2 \sum_k' n_k^\infty}. \quad [2.23]$$

The equilibrium electrical potential Φ^0 can be obtained by solving the Poisson–Boltzmann equation by the Runge–Kutta method, and then the integral in Eq. [2.21a] can be computed numerically. If the zeta potential of the sphere is small and κa is large so that the limit of Eq. [1.2] is approached, there are hardly any ion fluxes in the direction normal to the particle surface and the polarization of the double layer is negligible. In this situation, Eq. [2.11] for the slip velocity at the outer edge of the diffuse layer becomes the simple Helmholtz expression for electroosmotic flow, $\lambda/a \rightarrow 0$, each c_m is equal to $\frac{1}{2}$, and Eq. [2.21a] reduces to the Smoluchowski equation [1.1].

If the spherical particle is undergoing electrophoresis in the fluid containing only one symmetric electrolyte ($M = 2$), c_1 and c_2 in Eq. [2.21a] become

$$c_1 = \frac{1}{2a^2\Delta} (a^2 + a\beta_{22} + 3a\beta_{12} - 2a\beta_{11} + 2\beta_{12}\beta_{21} - 2\beta_{11}\beta_{22}), \quad [2.24a]$$

$$c_2 = \frac{1}{2a^2\Delta} (a^2 + a\beta_{11} + 3a\beta_{21} - 2a\beta_{22} + 2\beta_{12}\beta_{21} - 2\beta_{11}\beta_{22}), \quad [2.24b]$$

where

$$\Delta = \frac{1}{a^2} (a^2 + a\beta_{11} + a\beta_{22} + \beta_{11}\beta_{22} - \beta_{12}\beta_{21}), \quad [2.25]$$

and β_{11} , β_{12} , β_{21} , and β_{22} are given by Eq. [2.15]. In this case, the integral in Eq. [2.21a] can be calculated analytically and the electrophoretic velocity can be expressed in a simple closed form (11),

$$\mathbf{U} = \frac{\epsilon\zeta}{4\pi\eta} \mathbf{E}_\infty \left[\frac{1}{3} (2 + c_1 + c_2) + \frac{4k_B T}{3Ze\zeta} (c_1 - c_2) \ln \cosh\left(\frac{Ze\zeta}{4k_B T}\right) \right]. \quad [2.26]$$

3. ANALYSIS FOR THE ELECTROPHORESIS OF MULTIPLE SPHERES

We consider the electrophoretic motion of N spherical particles in an immense fluid in an arbitrary three-dimensional configuration as shown in Fig. 1. The Cartesian coordinate system (x, y, z) with the unit vectors \mathbf{e}_x , \mathbf{e}_y , and \mathbf{e}_z is established so that the constant applied electric field \mathbf{E}_∞ equals $E_\infty \mathbf{e}_x$ and the center of the i th sphere locates at the position (b_i, c_i, d_i) with $b_1 = c_1 = d_1 = 0$. The radii and zeta

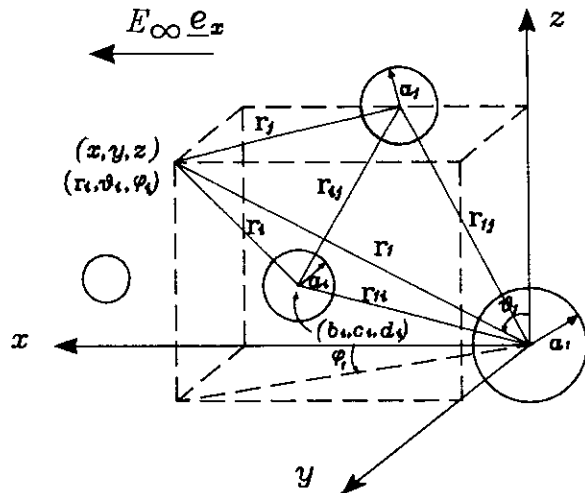


FIG. 1. Geometrical sketch of the electrophoretic motion of multiple spheres.

potentials of the particles may differ from one another. The fluid solution contains M different types of ion but, for simplicity, only one corresponding kind of counterion with the highest charge for each particle. The thickness of the electrical double layers is assumed to be small relative to the radius of each sphere and to the surface-to-surface spacing between any two particles. Nevertheless, the effect of polarization in the diffuse layer described in the previous section will be taken into account. The objective is to determine how the electrophoretic velocity of each sphere is affected by the presence of the other ones.

3.1. Electrochemical Potential Distributions

Since the bulk ionic concentrations outside the double layers are uniform, the electrochemical potential energies obey Laplace's equation [2.9] and are subject to the boundary conditions (according to Eqs. [2.17]–[2.19a])

$$\frac{\partial \mu_m}{\partial r_i} = -\beta_{mni} \nabla_s^2 \mu_m \quad \text{at } r_i = a_i, \quad [3.1]$$

$$\nabla \mu_m \rightarrow -ez_m E_\infty \mathbf{e}_x \quad \text{as } (x^2 + y^2 + z^2)^{1/2} \rightarrow \infty, \quad [3.2]$$

with

$$\beta_{mni} = 2 \left(\frac{I}{n_m^\infty} \right)^{1/2} \left(1 + \frac{\epsilon k_B^2 T^2}{2\pi\eta D_m e^2 z_m^2} \right) \times \frac{\exp(e|z_m \zeta_i|/2k_B T) - 1}{|z_m| \kappa} \quad \text{if } m = \sigma_i, \quad [3.3a]$$

$$\beta_{mni} = 0 \quad \text{otherwise}, \quad [3.3b]$$

for $i = 1, 2, \dots, N$ and $m = 1, 2, \dots, M$. Here, (r_i, θ_i, ϕ_i) represent spherical coordinates measured from the center of particle i , a_i is the radius of particle i , and index σ_i denotes the most highly charged counterions for particle i .

The fundamental solution of the Laplace equation that can describe an arbitrary disturbance caused by a sphere includes the solid spherical harmonic functions. For N spheres dispersed in the electrochemical potential fields, the general solution to Eq. [2.9] can be expressed by a superposition of this fundamental solution in the spherical coordinates as written from N different origins (sphere centers),

$$\begin{aligned} \mu_m = & \mu_m^0 + k_B T \ln n_m^\infty - ez_m E_\infty x \\ & + ez_m E_\infty \sum_{j=1}^N \sum_{n=0}^{\infty} \sum_{k=0}^n r_j^{-(n+1)} P_n^k(q_j) \\ & \times [R_{mjkn} \cos(k\phi_j) + S_{mjkn} \sin(k\phi_j)], \quad [3.4] \end{aligned}$$

for $m = 1, 2, \dots, M$, where P_n^k is the associated Legendre function of order k and degree n and q_j denotes $\cos \theta_j$ for brevity. This solution form satisfies boundary condition [3.2]

immediately and the coefficients R_{mjkn} and S_{mjkn} will be determined using [3.1]. It is understood that $S_{mjkn} = 0$ if $k = 0$.

In order to express the electrochemical potential fields [3.4] in terms of a single coordinate system, it is necessary to perform a transformation between the coordinates (r_j, q_j, ϕ_j) of an arbitrary position relative to the j th sphere and the coordinates (r_i, q_i, ϕ_i) of the position relative to the i th sphere. The formulas for this transformation of coordinates were provided in Part IV (10). With the aid of these formulas and the relation

$$\nabla_s^2 = \frac{1}{r_i^2} \frac{\partial}{\partial q_i} \left[\left(1 - q_i^2 \right) \frac{\partial}{\partial q_i} \right] + \frac{1}{r_i^2 (1 - q_i^2)} \frac{\partial^2}{\partial \phi_i^2}, \quad [3.5]$$

we introduce μ_m in Eq. [3.4] into the boundary condition [3.1] to obtain

$$\begin{aligned} & \sum_{j=1}^N \sum_{n=0}^{\infty} \sum_{k=0}^n \{ R_{mjkn} [R'_{jkn}(a_i, q_i, \phi_i) + \beta_{mmi} R''_{jkn}(a_i, q_i, \phi_i)] \\ & + S_{mjkn} [S'_{jkn}(a_i, q_i, \phi_i) + \beta_{mmi} S''_{jkn}(a_i, q_i, \phi_i)] \} \\ & = \left(1 - \beta_{mmi} \frac{2}{a_i} \right) \sqrt{1 - q_i^2} \cos \phi_i, \quad [3.6] \end{aligned}$$

where $i = 1, 2, \dots, N$, $m = 1, 2, \dots, M$,

$$\begin{aligned} R''_{jkn}(r_i, q_i, \phi_i) = & \frac{1}{r_i^2} \left\{ -2q_i \left[-(n+1)r_j^{-(n+2)} \cos(k\phi_j) \frac{\partial r_j}{\partial q_i} - r_j^{-(n+1)} k \sin(k\phi_j) \frac{\partial \phi_j}{\partial q_i} \right] \right. \\ & + [(n+1)(n+2)r_j^{-(n+3)} \cos(k\phi_j)] \left[(1 - q_i^2) \left(\frac{\partial r_j}{\partial q_i} \right)^2 + \frac{1}{(1 - q_i^2)} \left(\frac{\partial r_j}{\partial \phi_i} \right)^2 \right] \\ & + [-(n+1)r_j^{-(n+2)} \cos(k\phi_j)] \left[(1 - q_i^2) \frac{\partial^2 r_j}{\partial q_i^2} + \frac{1}{(1 - q_i^2)} \frac{\partial^2 r_j}{\partial \phi_i^2} \right] \\ & + [-r_j^{-(n+1)} k^2 \cos(k\phi_j)] \left[(1 - q_i^2) \left(\frac{\partial \phi_j}{\partial q_i} \right)^2 + \frac{1}{(1 - q_i^2)} \left(\frac{\partial \phi_j}{\partial \phi_i} \right)^2 \right] \\ & + [-r_j^{-(n+1)} k \sin(k\phi_j)] \left[(1 - q_i^2) \frac{\partial^2 \phi_j}{\partial q_i^2} + \frac{1}{(1 - q_i^2)} \frac{\partial^2 \phi_j}{\partial \phi_i^2} \right] \\ & + [2(n+1)r_j^{-(n+2)} k \sin(k\phi_j)] \left[(1 - q_i^2) \frac{\partial r_j}{\partial q_i} \frac{\partial \phi_j}{\partial q_i} + \frac{1}{(1 - q_i^2)} \frac{\partial r_j}{\partial \phi_i} \frac{\partial \phi_j}{\partial \phi_i} \right] \} P_n^k(q_j) \\ & + \frac{1}{r_i^2} \left\{ -2q_i r_j^{-(n+1)} \cos(k\phi_j) \frac{\partial q_j}{\partial q_i} \right. \\ & + [-2(n+1)r_j^{-(n+2)} \cos(k\phi_j)] \left[(1 - q_i^2) \frac{\partial r_j}{\partial q_i} \frac{\partial q_j}{\partial q_i} + \frac{1}{(1 - q_i^2)} \frac{\partial r_j}{\partial \phi_i} \frac{\partial q_j}{\partial \phi_i} \right] \\ & + [-2r_j^{-(n+1)} k \sin(k\phi_j)] \left[(1 - q_i^2) \frac{\partial q_j}{\partial q_i} \frac{\partial \phi_j}{\partial q_i} + \frac{1}{(1 - q_i^2)} \frac{\partial q_j}{\partial \phi_i} \frac{\partial \phi_j}{\partial \phi_i} \right] \\ & + [r_j^{-(n+1)} \cos(k\phi_j)] \left[(1 - q_i^2) \frac{\partial^2 q_j}{\partial q_i^2} + \frac{1}{(1 - q_i^2)} \frac{\partial^2 q_j}{\partial \phi_i^2} \right] \} \frac{dP_n^k(q_j)}{dq_j} \\ & + \frac{1}{r_i^2} [r_j^{-(n+1)} \cos(k\phi_j)] \left[(1 - q_i^2) \left(\frac{\partial q_j}{\partial q_i} \right)^2 + \frac{1}{(1 - q_i^2)} \left(\frac{\partial q_j}{\partial \phi_i} \right)^2 \right] \frac{d^2 P_n^k(q_j)}{dq_j^2}, \quad [3.7a] \end{aligned}$$

$$\begin{aligned} S''_{jkn}(r_i, q_i, \phi_i) = & \frac{1}{r_i^2} \left\{ -2q_i \left[-(n+1)r_j^{-(n+2)} \sin(k\phi_j) \frac{\partial r_j}{\partial q_i} + r_j^{-(n+1)} k \cos(k\phi_j) \frac{\partial \phi_j}{\partial q_i} \right] \right. \\ & + [(n+1)(n+2)r_j^{-(n+3)} \sin(k\phi_j)] \left[(1 - q_i^2) \left(\frac{\partial r_j}{\partial q_i} \right)^2 + \frac{1}{(1 - q_i^2)} \left(\frac{\partial r_j}{\partial \phi_i} \right)^2 \right] \\ & + [-(n+1)r_j^{-(n+2)} \sin(k\phi_j)] \left[(1 - q_i^2) \frac{\partial^2 r_j}{\partial q_i^2} + \frac{1}{(1 - q_i^2)} \frac{\partial^2 r_j}{\partial \phi_i^2} \right] \end{aligned}$$

$$\begin{aligned}
 & + [-r_j^{-(n+1)} k^2 \sin(k\phi_j)] \left[(1 - q_i^2) \left(\frac{\partial \phi_j}{\partial q_i} \right)^2 + \frac{1}{(1 - q_i^2)} \left(\frac{\partial \phi_j}{\partial \phi_i} \right)^2 \right] \\
 & + [r_j^{-(n+1)} k \cos(k\phi_j)] \left[(1 - q_i^2) \frac{\partial^2 \phi_j}{\partial q_i^2} + \frac{1}{(1 - q_i^2)} \frac{\partial^2 \phi_j}{\partial \phi_i^2} \right] \\
 & + [-2(n+1)r_j^{-(n+2)} k \cos(k\phi_j)] \left[(1 - q_i^2) \frac{\partial r_j}{\partial q_i} \frac{\partial \phi_j}{\partial q_i} \frac{1}{(1 - q_i^2)} \frac{\partial r_j}{\partial \phi_i} \frac{\partial \phi_j}{\partial \phi_i} \right] \Big\} P_n^k(q_j) \\
 & + \frac{1}{r_i^2} \left\{ -2q_i r_j^{-(n+1)} \sin(k\phi_j) \frac{\partial q_j}{\partial q_i} \right. \\
 & + [-2(n+1)r_j^{-(n+2)} \sin(k\phi_j)] \left[(1 - q_i^2) \frac{\partial r_j}{\partial q_i} \frac{\partial q_j}{\partial q_i} + \frac{1}{(1 - q_i^2)} \frac{\partial r_j}{\partial \phi_i} \frac{\partial q_j}{\partial \phi_i} \right] \\
 & + [2r_j^{-(n+1)} k \cos(k\phi_j)] \left[(1 - q_i^2) \frac{\partial q_j}{\partial q_i} \frac{\partial \phi_j}{\partial q_i} + \frac{1}{(1 - q_i^2)} \frac{\partial q_j}{\partial \phi_i} \frac{\partial \phi_j}{\partial \phi_i} \right] \\
 & + [r_j^{-(n+1)} \sin(k\phi_j)] \left[(1 - q_i^2) \frac{\partial^2 q_j}{\partial q_i^2} \frac{1}{(1 - q_i^2)} \frac{\partial^2 q_j}{\partial \phi_i^2} \right] \Big\} \frac{dP_n^k(q_j)}{dq_j} \\
 & + \frac{1}{r_i^2} [r_j^{-(n+1)} \sin(k\phi_j)] \left[(1 - q_i^2) \left(\frac{\partial q_j}{\partial q_i} \right)^2 + \frac{1}{(1 - q_i^2)} \left(\frac{\partial q_j}{\partial \phi_i} \right)^2 \right] \frac{d^2 P_n^k(q_j)}{dq_j^2}, \quad [3.7b]
 \end{aligned}$$

and $R'_{jkn}(r_i, q_i, \phi_i)$ and $S'_{jkn}(r_i, q_i, \phi_i)$ were defined in Part IV (10).

To satisfy boundary condition [3.6] exactly along the entire surface of each sphere would require the solution of the entire infinite array of unknown coefficients R_{mjkn} and S_{mjkn} . However, the boundary collocation method (10, 13) enforces the boundary condition at a finite number of discrete points on the surface of each sphere and truncates the infinite series [3.4] into a finite one:

$$\begin{aligned}
 \mu_m = & \mu_m^0 + k_B T \ln n_m^\infty - ez_m E_\infty x + ez_m E_\infty \\
 & \times \sum_{j=1}^N \sum_{k=0}^{K-1} \sum_{n=k}^{k+L-1} r_j^{-(n+1)} P_n^k(q_j) [R_{mjkn} \cos(k\phi_j) \\
 & + S_{mjkn} \sin(k\phi_j)], \quad [3.8]
 \end{aligned}$$

where $m = 1, 2, \dots$, or M ; K and L are positive integer numbers. This solution form leaves a total of $MNL(2K - 1)$ unknown constants R_{mjkn} and S_{mjkn} ($S_{mj0n} = 0$) to be determined. To generate the equations needed to evaluate these unknown constants, we multiply the truncated form of Eq. [3.6] by the function sets $\cos(k'\phi_i)$ and $\sin(k'\phi_i)$, integrate with respect to ϕ_i from 0 to 2π , and utilize the orthogonality properties of these functions in this interval to obtain

$$\begin{aligned}
 \sum_{j=1}^N \sum_{k=0}^{K-1} \sum_{n=k}^{k+L-1} \left\{ R_{mjkn} \int_0^{2\pi} [R'_{jkn}(a_i, q_i, \phi_i) \right. \\
 \left. + \beta_{mmi} R''_{jkn}(a_i, q_i, \phi_i)] \cos(k'\phi_i) d\phi_i \right.
 \end{aligned}$$

$$\begin{aligned}
 & + S_{mjkn} \int_0^{2\pi} (S'_{jkn}(a_i, q_i, \phi_i) \\
 & + \beta_{mmi} S''_{jkn}(a_i, q_i, \phi_i)] \cos(k'\phi_i) d\phi_i \Big\} \\
 = & \begin{cases} \left(1 - \beta_{mmi} \frac{2}{a_i} \right) \pi \sqrt{1 - q_i^2} & (k' = 1) \\ 0 & (k' = 0, 2, 3, \dots, K-1), \end{cases} \quad [3.9a]
 \end{aligned}$$

$$\begin{aligned}
 & \sum_{j=1}^N \sum_{k=0}^{K-1} \sum_{n=k}^{k+L-1} \left\{ R_{mjkn} \int_0^{2\pi} [R'_{jkn}(a_i, q_i, \phi_i) \right. \\
 & + \beta_{mmi} R''_{jkn}(a_i, q_i, \phi_i)] \sin(k'\phi_i) d\phi_i \\
 & + S_{mjkn} \int_0^{2\pi} [S'_{jkn}(a_i, q_i, \phi_i) \\
 & + \beta_{mmi} S''_{jkn}(a_i, q_i, \phi_i)] \sin(k'\phi_i) d\phi_i \Big\} \\
 = & 0 \quad (k' = 1, 2, \dots, K-1), \quad [3.9b]
 \end{aligned}$$

where $m = 1, 2, \dots, M$ and $i = 1, 2, \dots, N$. The above equations can be satisfied at L discrete values of θ_i (rings) along the surface of each sphere i to result in a set of $MNL(2K - 1)$ linear algebraic equations, which can be solved by any standard matrix-reduction method to determine the equal-number unknown constants. Note that the definite integrals in Eqs. [3.9] for each collocation ring must be performed numerically.

For the special case with planar symmetry, i.e., the centers of all the spheres lie in the plane $y = 0$, the coefficients S_{mjkn} are all zero and Eq. [3.9b] becomes trivial. Thus, the number of unknown coefficients (R_{mjkn} only) is reduced to $MNLK$ and they can be solved by an equal number of collocation equations in the form of Eq. [3.9a]. Furthermore, there are two special cases which can be deduced from the planar case: a string of spheres oriented parallel to the applied electric field (the centers of all spheres lie along the x -axis) and a string of spheres oriented perpendicular to the applied field (the centers of all spheres lie on the z -axis). The electrochemical potential distributions for the former case are axisymmetric about the x -axis and were solved in a previous analysis (11). For the configuration of a finite chain of spheres located on the z -axis, we have $\phi_i = \phi$, $b_i = c_i = 0$ ($i = 1, 2, \dots, N$), and Eq. [3.6] can be simplified to yield

$$\sum_{j=1}^N \sum_{n=1}^{\infty} R_{mj1n} [G_{j11n}(a_i, q_i) + \beta_{m11} H_{j11n}(a_i, q_i)] \\ = \left(1 - \beta_{m11} \frac{2}{a_i}\right) \sqrt{1 - q_i^2}, \quad [3.10]$$

where $m = 1, 2, \dots, M$, $i = 1, 2, \dots, N$, the function $G_{jikn}(r_i, q_i)$ was defined in Part IV (10),

$$H_{jikn}(r_i, q_i) = r_j^{-(n+5)} \left\{ \left[(n+1)(n+3)d_{ij}^2(1 - q_i^2) \right. \right. \\ + 2(n+1)d_{ij}q_i \frac{r_j^2}{r_i} - \frac{k^2 r_j^4}{r_i^2(1 - q_i^2)} \left. \right] P_n^k(q_j) \\ + \left[2(n+2)d_{ij}(1 - q_i^2)(d_{ij}q_j - r_j) \right. \\ + 2 \frac{r_j^2}{r_i} q_i(d_{ij}q_j - r_j) + q_j(1 - q_i^2)d_{ij}^2 \left. \right] \frac{dP_n^k(q_j)}{dq_j} \\ + \left. \left[(1 - q_i^2)(d_{ij}q_j - r_j)^2 \right] \frac{d^2 P_n^k(q_j)}{dq_j^2} \right\} \quad [3.11]$$

with $d_{ij} = d_i - d_j$, and the dependence on ϕ factors out. Instead of using Eq. [3.9], one can apply the truncated form of boundary condition [3.10] at L discrete values of θ_i along the surface of each of the N spheres for this special case. This generates a set of MNL linear algebraic equations which can be solved for the MNL unknown constants R_{mj1n} .

If the fluid contains only one symmetrically charged, binary electrolyte ($M = 2$), boundary condition [3.1] is replaced by

$$r_i = a_i: \quad \frac{\partial \mu_1}{\partial r_i} = -\beta_{11} \nabla_s^2 \mu_1 - \beta_{12} \nabla_s^2 \mu_2, \quad [3.12a]$$

$$\frac{\partial \mu_2}{\partial r_i} = -\beta_{21} \nabla_s^2 \mu_1 - \beta_{22} \nabla_s^2 \mu_2, \quad [3.12b]$$

where β_{11} , β_{12} , β_{21} , and β_{22} are given by Eqs. [2.15]. For the case of a string of N spheres oriented normal to the applied field, one can follow the same procedure leading to Eq. [3.10] to obtain

$$\sum_{j=1}^N \sum_{n=1}^{\infty} \{ R_{1j1n} [G_{j11n}(a_i, q_i) + \beta_{111} H_{j11n}(a_i, q_i)] \\ + R_{2j1n} \beta_{12} H_{j11n}(a_i, q_i) \} \\ = \left[1 - (\beta_{111} + \beta_{12}) \frac{2}{a_i} \right] \sqrt{1 - q_i^2}, \quad [3.13a]$$

$$\sum_{j=1}^N \sum_{n=1}^{\infty} \{ R_{1j1n} \beta_{21} H_{j11n}(a_i, q_i) + R_{2j1n} [G_{j11n}(a_i, q_i) \\ + \beta_{22} H_{j11n}(a_i, q_i)] \} \\ = \left[1 - (\beta_{21} + \beta_{22}) \frac{2}{a_i} \right] \sqrt{1 - q_i^2}, \quad [3.13b]$$

where $i = 1, 2, \dots$, or N . Similarly, the above boundary conditions can also be applied using the truncation method to generate a set of $2NL$ algebraic equations for unknown coefficients R_{1j1n} and R_{2j1n} . Note that R_{1j1n} and R_{2j1n} are coupled here, unlike any R_{mj1n} in Eq. [3.10] 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. Since the fluid outside the thin double layers is neutral and the Reynolds numbers encountered in electrophoretic motions are low, the velocity field is governed by the Stokes equations [2.5] and [2.10]. The boundary conditions for the fluid velocity beyond the double layers surrounding the spheres, resulting from Eqs. [2.20] and [2.19b], are

$$\mathbf{v} = \mathbf{U}_i + \boldsymbol{\Omega}_i \times \mathbf{r}_i - \frac{1}{\eta} \sum_{m=1}^M \nabla_s \mu_m \int_0^{\infty} y_i (n_{mi}^0 - n_m^{\infty}) dy_i \\ \text{at } r_i = a_i, \quad [3.14a]$$

$$\mathbf{v} \rightarrow \mathbf{0} \quad \text{as } (x^2 + y^2 + z^2)^{1/2} \rightarrow \infty, \quad [3.14b]$$

for $i = 1, 2, \dots$, or N . Here n_{mi}^0 is 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 $\mathbf{U}_i (= U_{ix} \mathbf{e}_x + U_{iy} \mathbf{e}_y + U_{iz} \mathbf{e}_z)$ and $\boldsymbol{\Omega}_i (= \Omega_{ix} \mathbf{e}_x + \Omega_{iy} \mathbf{e}_y + \Omega_{iz} \mathbf{e}_z)$ are the instantaneous translational and rotational velocities, respectively, of sphere i to be determined. $\nabla_s \mu_m$ can be calculated from the electrochemical potential distribution [3.8] with coefficients R_{mjkn} and S_{mjkn} determined by Eqs. [3.9]. The integral in Eq. [3.14a] must be evaluated

numerically except for the special case of a symmetric electrolyte.

The general solution of the Stokes equations, which satisfies boundary condition [3.14b] immediately, can be expressed in terms of the spherical coordinates originating at the center of the i th sphere (10, 13),

$$\mathbf{v} = v_{r_i} \mathbf{e}_{r_i} + v_{\theta_i} \mathbf{e}_{\theta_i} + v_{\phi_i} \mathbf{e}_{\phi_i}, \quad [3.15]$$

where \mathbf{e}_{r_i} , \mathbf{e}_{θ_i} , and \mathbf{e}_{ϕ_i} are the unit vectors in the spherical coordinate system (r_i, θ_i, ϕ_i) ,

$$\begin{bmatrix} v_{r_i} \\ v_{\theta_i} \\ v_{\phi_i} \end{bmatrix} = \sum_{j=1}^N \sum_{n=1}^{\infty} \sum_{k=0}^n \left\{ A_{jkn} \begin{bmatrix} A_{jkn}^{(1)} \\ A_{jkn}^{(2)} \\ A_{jkn}^{(3)} \end{bmatrix} + B_{jkn} \begin{bmatrix} B_{jkn}^{(1)} \\ B_{jkn}^{(2)} \\ B_{jkn}^{(3)} \end{bmatrix} + \cdots + F_{jkn} \begin{bmatrix} F_{jkn}^{(1)} \\ F_{jkn}^{(2)} \\ F_{jkn}^{(3)} \end{bmatrix} \right\}, \quad [3.16]$$

and $A_{jkn}^{(1)}$, $A_{jkn}^{(2)}$, $A_{jkn}^{(3)}$, $B_{jkn}^{(1)}$, \dots , and $F_{jkn}^{(3)}$ are functions of (r_i, q_i, ϕ_i) which have been defined in Part IV (10). Unknown coefficients A_{jkn} , B_{jkn} , \dots , and F_{jkn} are to be determined by using Eq. [3.14a].

Utilizing the collocation technique presented in the previous subsection for the solution of the electrochemical potential fields, we can apply the boundary condition [3.14a] to Eq. [3.15] to yield

$$\sum_{j=1}^N \sum_{k=0}^{K^*-1} \sum_{\substack{n=k \\ n \neq 0}}^{k+L^*-1} [A_{jkn} A_{jkn}^{(1)} + B_{jkn} B_{jkn}^{(1)} + \cdots + F_{jkn} F_{jkn}^{(1)}]_{r_i=a_i} = U_{ix} \sqrt{1-q_i^2} \cos \phi_i + U_{iy} \sqrt{1-q_i^2} \sin \phi_i + U_{iz} q_i, \quad [3.17a]$$

$$\begin{aligned} & \sum_{j=1}^N \sum_{k=0}^{K^*-1} \sum_{\substack{n=k \\ n \neq 0}}^{k+L^*-1} [A_{jkn} A_{jkn}^{(2)} + B_{jkn} B_{jkn}^{(2)} + \cdots + F_{jkn} F_{jkn}^{(2)}]_{r_i=a_i} \\ &= U_{ix} q_i \cos \phi_i + U_{iy} q_i \sin \phi_i - U_{iz} \sqrt{1-q_i^2} \\ & - a_i (\Omega_{ix} \sin \phi_i - \Omega_{iy} \cos \phi_i) + \frac{1}{\eta} \sum_{m=1}^M \frac{\sqrt{1-q_i^2}}{a_i} \frac{\partial \mu_m}{\partial q_i} \Big|_{r_i=a_i} \\ & \quad \times \int_0^{\infty} y_i (n_{mi}^0 - n_{mi}^{\infty}) dy_i, \quad [3.17b] \end{aligned}$$

$$\begin{aligned} & \sum_{j=1}^N \sum_{k=0}^{K^*-1} \sum_{\substack{n=k \\ n \neq 0}}^{k+L^*-1} [A_{jkn} A_{jkn}^{(3)} + B_{jkn} B_{jkn}^{(3)} + \cdots + F_{jkn} F_{jkn}^{(3)}]_{r_i=a_i} \\ &= -U_{ix} \sin \phi_i + U_{iy} \cos \phi_i - a_i (\Omega_{ix} q_i \cos \phi_i \\ & + \Omega_{iy} q_i \sin \phi_i - \Omega_{iz} \sqrt{1-q_i^2}) - \frac{1}{\eta} \sum_{m=1}^M \frac{1}{a_i \sqrt{1-q_i^2}} \frac{\partial \mu_m}{\partial \phi_i} \Big|_{r_i=a_i} \\ & \quad \times \int_0^{\infty} y_i (n_{mi}^0 - n_{mi}^{\infty}) dy_i, \quad [3.17c] \end{aligned}$$

where $i = 1, 2, \dots$, or N . Multiplying Eqs. [3.17] by the function sets $\cos(k' \phi_i)$ ($k' = 0, 1, 2, \dots, K^* - 1$) and $\sin(k' \phi_i)$ ($k' = 1, 2, \dots, K^* - 1$), integrating with respect to ϕ_i from 0 to 2π , and utilizing the orthogonality properties of these functions in this interval allow one to obtain $3(2K^* - 1)$ equations which are similar in form to Eqs. [3.9]. These equations can be satisfied at L^* discrete values of θ_i along the surface of each of the N spheres to produce a set of $3NL^*(2K^* - 1)$ linear algebraic equations, which can be solved for the equal-number unknown constants A_{jkn} , B_{jkn} , \dots , and F_{jkn} ($B_{j0n} = D_{j0n} = F_{j0n} = 0$) in terms of the particle velocities U_i and Ω_i . Once these coefficients are determined, the fluid velocity field is completely solved.

For the case of planar symmetry, i.e., the centers of all the spheres lie in the plane $y = 0$, $U_{iy} = \Omega_{ix} = \Omega_{iz} = 0$, the coefficients A_{jkn} , D_{jkn} , and F_{jkn} are all zero and the integration of Eqs. [3.17] after multiplication by $\sin(k' \phi_i)$ with respect to ϕ_i from 0 to 2π is trivial. Thus, the number of unknown coefficients is reduced to $3NL^*K^*$ and they are determined by an equal number of collocation equations. Similar to the previous subsection, two special cases can be deduced from the planar case. The fluid velocity field about a chain of spheres undergoing electrophoresis along their line of centers is axially symmetric and was solved by employing the Stokes stream function (11). For the case of a chain of spheres oriented normal to the applied electric field (the centers of all spheres lie on the z -axis), we have $\phi_i = \phi$, $b_i = c_i = 0$, $U_{iz} = 0$ ($i = 1, 2, \dots, N$), and Eqs. [3.17] can be simplified to

$$\sum_{j=1}^N \sum_{n=1}^{L^*} [B_{j1n} B_{j1n}^{(1)} + C_{j1n} C_{j1n}^{(1)} + E_{j1n} E_{j1n}^{(1)}]_{r_i=a_i} = U_{ix} \sqrt{1-q_i^2} \cos \phi, \quad [3.18a]$$

$$\begin{aligned} & \sum_{j=1}^N \sum_{n=1}^{L^*} [B_{j1n} B_{j1n}^{(2)} + C_{j1n} C_{j1n}^{(2)} + E_{j1n} E_{j1n}^{(2)}]_{r_i=a_i} \\ &= U_{ix} q_i \cos \phi + a_i \Omega_{iy} \cos \phi \\ & + \frac{1}{\eta} \sum_{m=1}^M \frac{\sqrt{1-q_i^2}}{a_i} \frac{\partial \mu_m}{\partial q_i} \Big|_{r_i=a_i} \\ & \quad \times \int_0^{\infty} y_i (n_{mi}^0 - n_{mi}^{\infty}) dy_i, \quad [3.18b] \end{aligned}$$

$$\begin{aligned} & \sum_{j=1}^N \sum_{n=1}^{L^*} [B_{j1n} B_{j1n}^{(3)} + C_{j1n} C_{j1n}^{(3)} + E_{j1n} E_{j1n}^{(3)}]_{r_i=a_i} \\ &= -U_{ix} \sin \phi - a_i \Omega_{iy} q_i \sin \phi \\ & - \frac{1}{\eta} \sum_{m=1}^M \frac{1}{a_i \sqrt{1-q_i^2}} \frac{\partial \mu_m}{\partial \phi} \Big|_{r_i=a_i} \\ & \quad \times \int_0^{\infty} y_i (n_{mi}^0 - n_{mi}^{\infty}) dy_i. \quad [3.18c] \end{aligned}$$

In the above equations, the angular derivatives of the electrochemical potential distributions at the particle surfaces can be computed by using Eqs. [3.8] and [3.10] (or [3.13] if the fluid solution contains only one symmetric electrolyte) with the facts that $R_{mjkn} = 0$ if $k \neq 1$ and $S_{mjkn} = 0$ and the dependence on ϕ will all factor out. The $3NL^*$ unknown constants B_{j1n} , C_{j1n} , and E_{j1n} could be easily calculated in terms of the particle velocities U_{ix} and Ω_{iy} by simultaneous solution of a set of $3NL^*$ algebraic equations generated by Eqs. [3.18].

3.3. Velocities of Free Spheres

The drag force exerted by the fluid on the i th sphere and the hydrodynamic torque experienced by the sphere about its center are (10, 13)

$$\mathbf{F}_i = -4\pi(E_{i11}\mathbf{e}_x + F_{i11}\mathbf{e}_y + E_{i01}\mathbf{e}_z) \quad [3.19a]$$

and

$$\mathbf{T}_i = -8\pi\eta(A_{i11}\mathbf{e}_x + B_{i11}\mathbf{e}_y + A_{i01}\mathbf{e}_z), \quad [3.19b]$$

respectively. The six coefficients in the above equations for each of the N spheres are known from the solution of Eqs. [3.17].

Because the particles are freely suspended in the fluid and the "surface" of each encompasses a neutral body, no net drag force or torque from the fluid acts on the particles including the diffuse layers. From Eqs. [3.19], it is apparent that

$$A_{i01} = A_{i11} = B_{i11} = E_{i01} = E_{i11} = F_{i11} = 0, \quad [3.20]$$

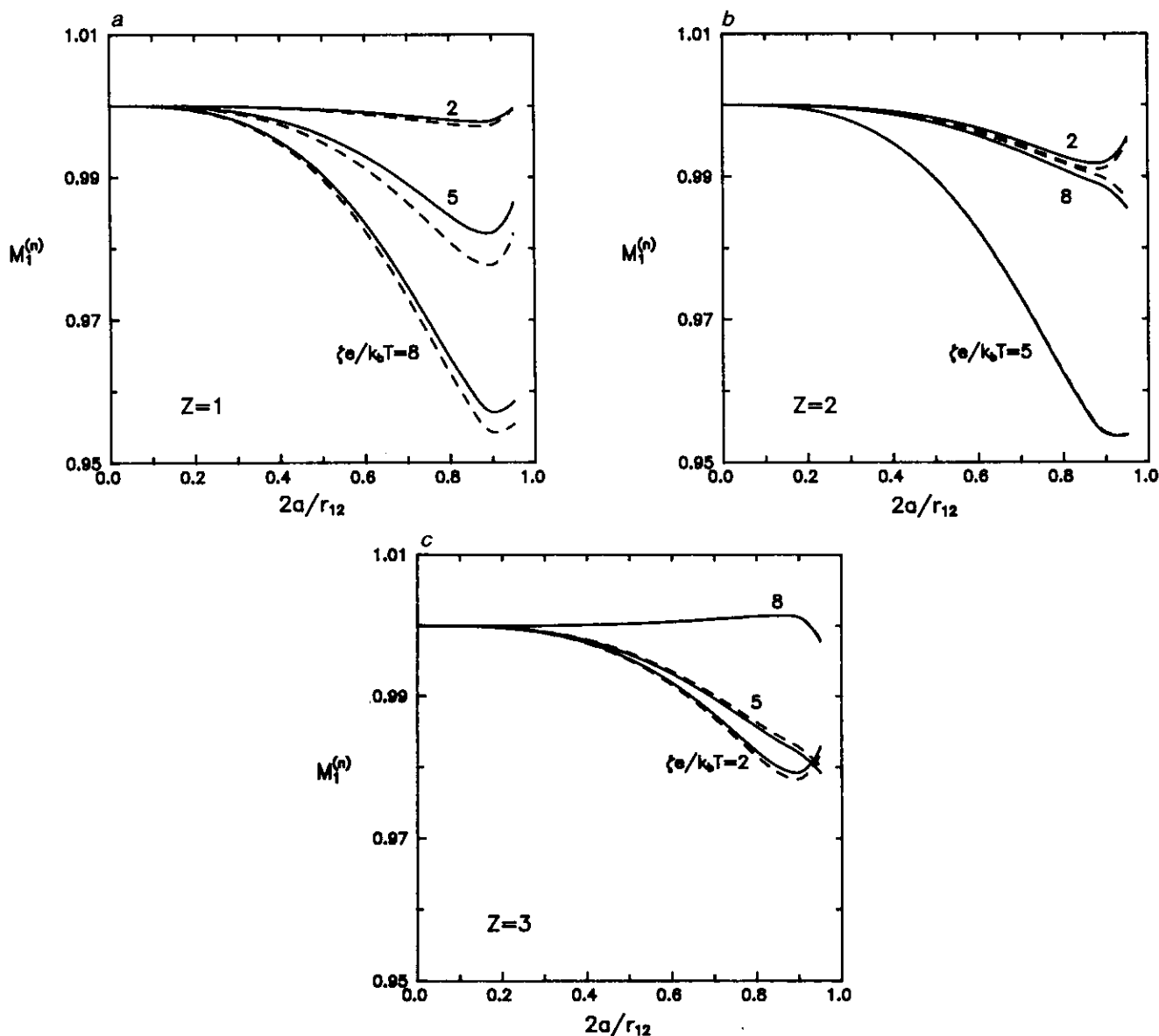


FIG. 2. Plots of the translational mobility parameters of two identical spheres undergoing electrophoresis normal to their line of centers ($M_1^{(n)} = M_2^{(n)}$) versus the separation parameter $2a/r_{12}$ with $\kappa a = 100$ and $f = 0.2$ (solid curves) or $f = 0.4$ (dashed curves): (a) $Z = 1$, (b) $Z = 2$, (c) $Z = 3$.

for $i = 1, 2, \dots, \text{or } N$. The translational and angular velocities \mathbf{U}_i and $\mathbf{\Omega}_i$ of the N spheres ($6N$ components in total) can be determined by solving the above $6N$ equations simultaneously. The result for the i th sphere can be expressed as

$$\mathbf{U}_i = \mathbf{M}_i \cdot \mathbf{U}_{i\infty}, \quad [3.21a]$$

$$\mathbf{\Omega}_i = \frac{1}{a_i} \mathbf{N}_i \cdot \mathbf{U}_{i\infty}, \quad [3.21b]$$

where $\mathbf{U}_{i\infty}$ is the electrophoretic velocity of sphere i when it is isolated from the others. The derivation of $\mathbf{U}_{i\infty}$ has been discussed in Subsection 2.3. The dimensionless mobility

tensors \mathbf{M}_i and \mathbf{N}_i depend on the relative positions, sizes, and zeta potentials of the particles as well as on the bulk concentrations, valences, and diffusivities of the ions.

For the special case of a string of coaxial spheres oriented arbitrarily with respect to the applied electric field, Eqs. [3.21] become

$$\mathbf{U}_i = [M_i^{(p)} \mathbf{e}\mathbf{e} + M_i^{(n)} (\mathbf{I} - \mathbf{e}\mathbf{e})] \cdot \mathbf{U}_{i\infty}, \quad [3.22a]$$

$$\mathbf{\Omega}_i = \frac{1}{a_i} N_i \mathbf{e} \times \mathbf{U}_{i\infty}, \quad [3.22b]$$

where \mathbf{e} is the unit vector directed from the center of sphere 1 toward the centers of the other spheres.

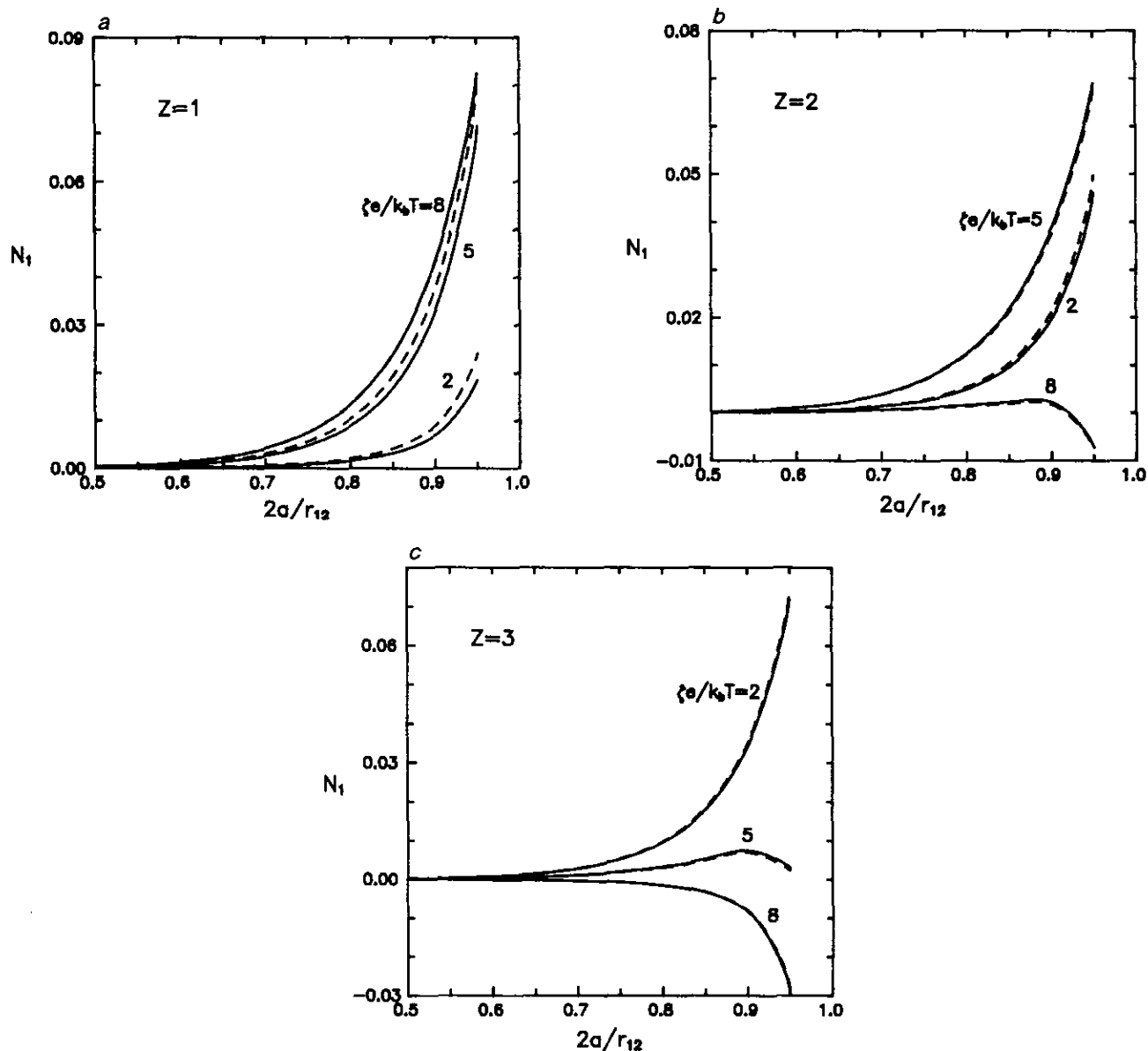


FIG. 3. Plots of the rotational mobility parameters of two identical spheres undergoing electrophoresis normal to their line of centers ($N_1 = -N_2$) versus the separation parameter $2a/r_{12}$ with $\kappa a = 100$ and $f = 0.2$ (solid curves) or $f = 0.4$ (dashed curves): (a) $Z = 1$, (b) $Z = 2$, (c) $Z = 3$.

3.4. Velocities of a Rigid Cluster of Spheres

We now consider the electrophoresis of a rigid cluster of N spheres connected through their centers 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 objective 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 rotate at the same angular velocity Ω , which is also the angular

velocity of the rigid cluster, and the translational velocity of each sphere in the cluster can be written as

$$\mathbf{U}_i = \mathbf{U}_0 + \Omega \times \mathbf{r}_{0i}, \quad i = 1, 2, \dots, N, \quad [3.23]$$

where \mathbf{U}_0 refers to the translational velocity of a point on the cluster designated as the origin and \mathbf{r}_{0i} is the position vector of the center of sphere i measured from the origin. After the substitution of Eq. [3.23] and the relation $\Omega_i = \Omega$ into Eqs. [3.17] or [3.18], the set of unknown coefficients $\{A_{jkn}, B_{jkn}, \dots, F_{jkn}\}$ or $\{B_{j1n}, C_{j1n}, E_{j1n}\}$ can be solved in terms of the components of the cluster velocities \mathbf{U}_0 and Ω by using the same collocation technique.

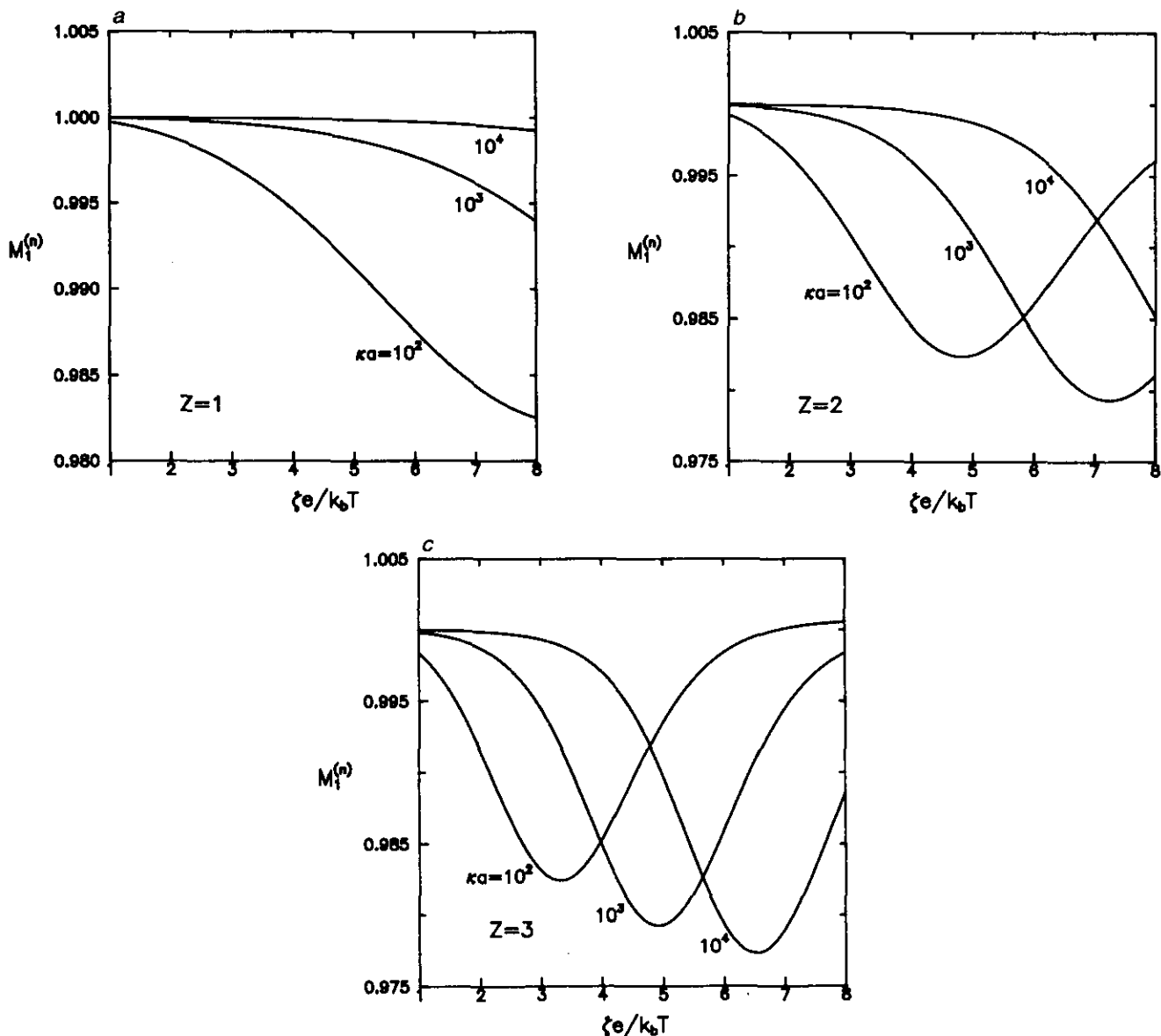


FIG. 4. Plots of the translational mobility parameters of two identical spheres undergoing electrophoresis normal to their line of centers versus the dimensionless zeta potential $\zeta e/k_B T$ with $2a/r_{12} = 0.6$ and $f = 0.4$: (a) $Z = 1$, (b) $Z = 2$, (c) $Z = 3$.

To determine U_0 and Ω the requirement that the net force and net torque exerted by the fluid on the rigid cluster are zero is needed. Application of this constraint to Eq. [3.19] yields (10)

$$\sum_{j=1}^N E_{i1j} = 0, \quad [3.24a]$$

$$\sum_{i=1}^N F_{i1j} = 0, \quad [3.24b]$$

$$\sum_{i=1}^N E_{i0j} = 0, \quad [3.24c]$$

$$\sum_{i=1}^N (2\eta A_{i1j} + y_{0i} E_{i0j} - z_{0i} F_{i1j}) = 0, \quad [3.24d]$$

$$\sum_{i=1}^N (2\eta B_{i1j} + z_{0i} E_{i1j} - x_{0i} E_{i0j}) = 0, \quad [3.24e]$$

$$\sum_{i=1}^N (2\eta A_{i0j} + x_{0i} F_{i1j} - y_{0i} E_{i1j}) = 0, \quad [3.24f]$$

where x_{0i} , y_{0i} , and z_{0i} are the Cartesian components of vector r_{0i} . The translational and rotational velocities U_0 and Ω (each having three components) can be obtained by solving the above six equations simultaneously.

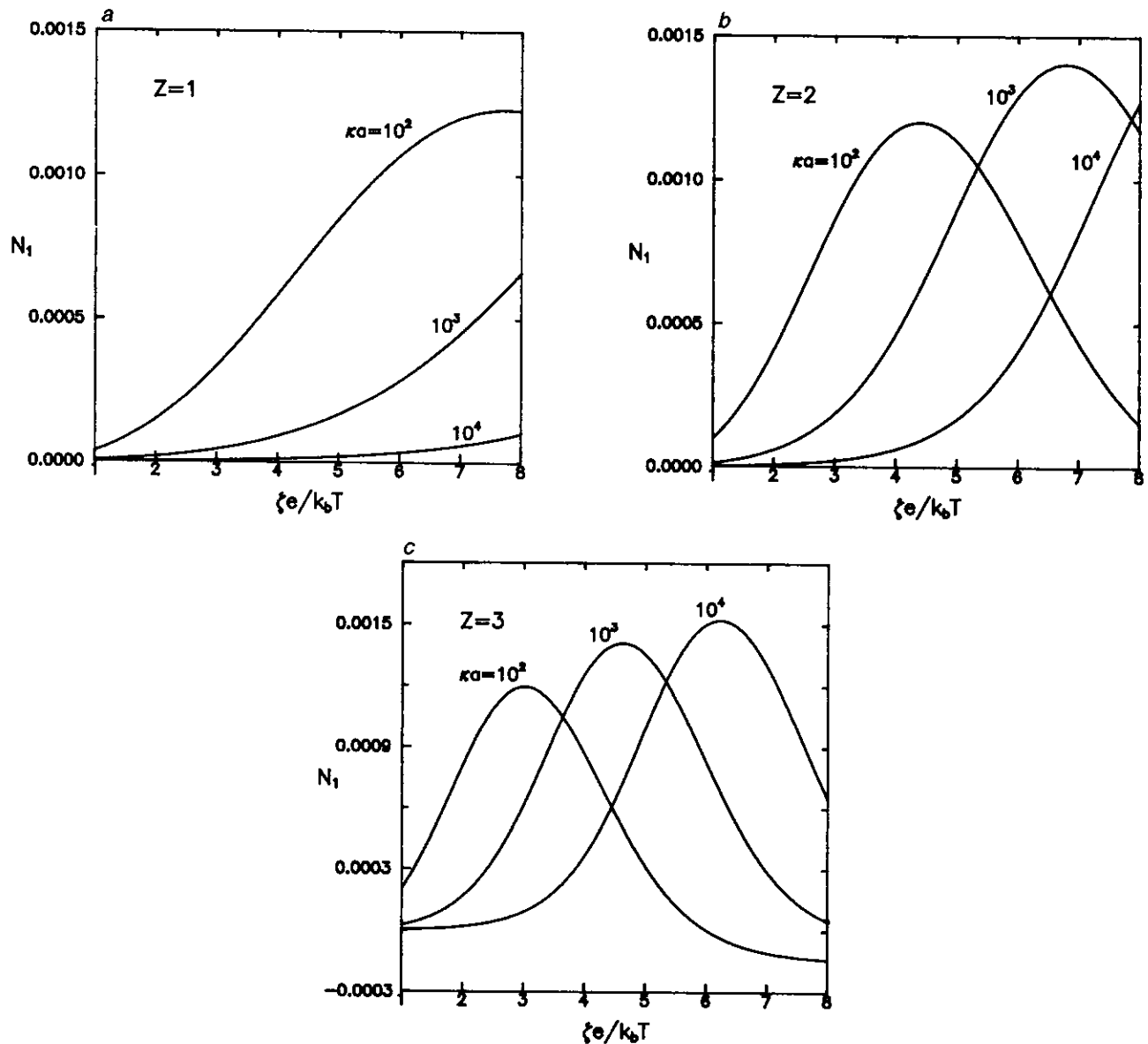


FIG. 5. Plots of the rotational mobility parameters of two identical spheres undergoing electrophoresis normal to their line of centers versus the dimensionless zeta potential $\zeta e/k_B T$ with $2a/r_{12} = 0.6$ and $f = 0.4$: (a) $Z = 1$, (b) $Z = 2$, (c) $Z = 3$.

4. RESULTS AND DISCUSSION

The electrophoretic velocity of an isolated sphere can be evaluated using Eq. [2.21a] for the general case, or Eq. [2.26] for the special situation when the fluid contains only one symmetric electrolyte. The numerical results for the axisymmetric electrophoretic motions of two or three free spheres and of a rigid dumbbell (cluster of two spheres), resulting from using the boundary collocation method, have already been obtained (11). In this section, we present our results for the electrophoretic motions of two free spheres, of three coaxial free spheres, and of a rigid dumbbell normal to their lines of sphere centers. The details of the collocation scheme used for this work were given in Part IV (10). To avoid

superfluity, only the fluid containing one symmetric electrolyte will be considered. In other words, Eq. [3.13] is applied to solve the unknown constants R_{1j1n} and R_{2j1n} in Eq. [3.4] for μ_m . Because of governing equations and boundary conditions concerning the problem of electrophoresis of coaxial spheres oriented at an arbitrary angle with respect to the applied electric field are linear, the general solution can be obtained as a superposition of the individual components provided by the previous study (11) and this work.

4.1. Two Identical Free Spheres

In this subsection, we present the particle interaction results, obtained by using the collocation technique, for the

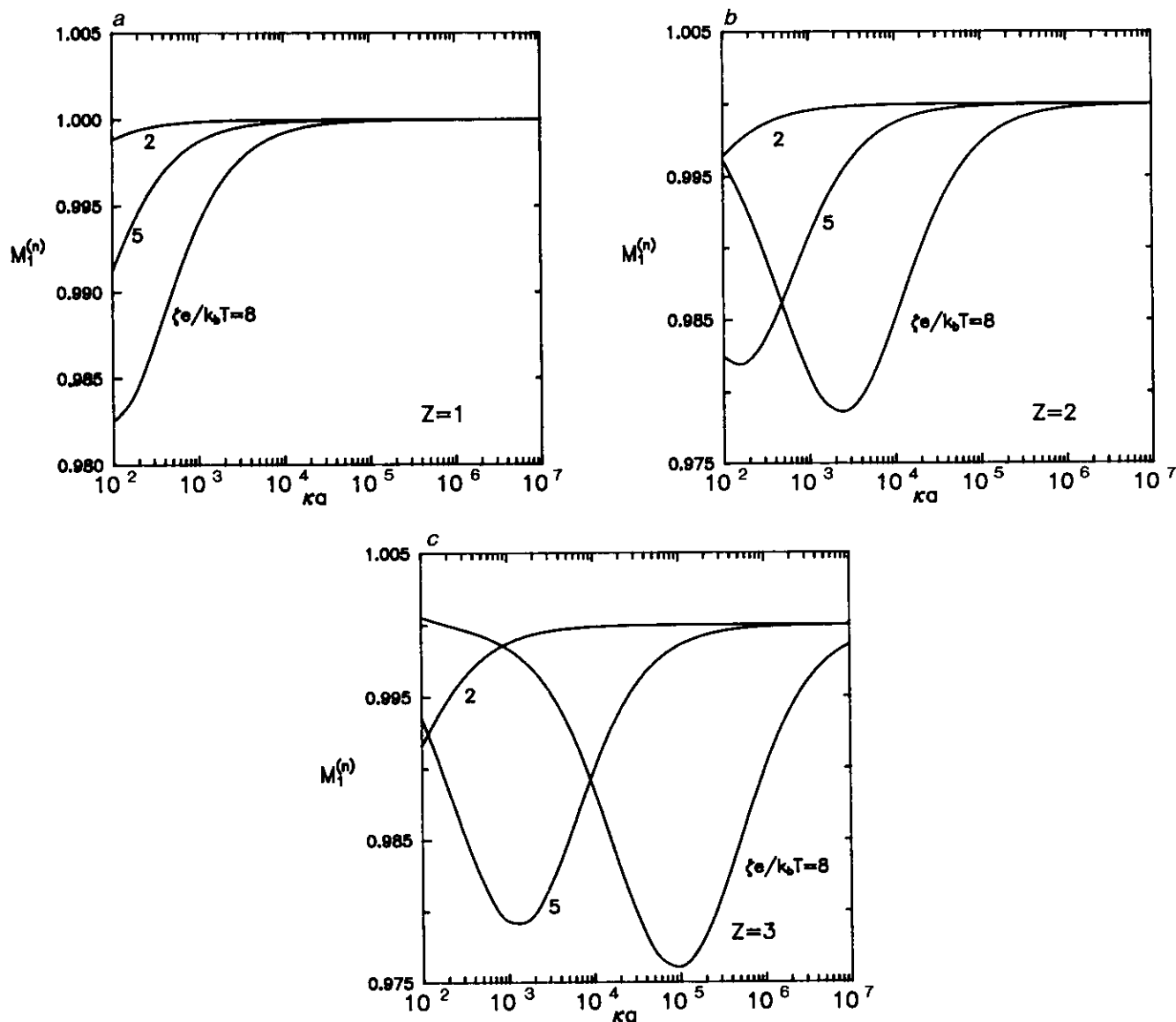


FIG. 6. Plots of the translational mobility parameters of two identical spheres undergoing electrophoresis normal to their line of centers versus the ratio of the sphere radius to the Debye length κa with $2a/r_{12} = 0.6$ and $f = 0.4$: (a) $Z = 1$, (b) $Z = 2$, (c) $Z = 3$.

electrophoresis of two identical spheres ($a_1 = a_2 = a$ and $\zeta_1 = \zeta_2 = \zeta$) perpendicular to their line of centers. Unlike the conclusions of the previous studies in which the effects of polarization of diffuse ions were neglected (5-10), interactions exist between the two spheres even though they have equal zeta potentials on the surface.

The mobility parameters $M_1^{(n)}$ ($=M_2^{(n)}$) and N_1 ($=-N_2$), which indicate the extent of particle interactions as defined by Eqs. [3.22], are plotted as a function of the separation parameter $2a/r_{12}$ with $\kappa a = 100$ in Figs 2 and 3, respectively. It is assumed that the drag coefficients of the anion and cation are equal ($f_1 = f_2 = f$) and the cases $f = 0.2$ and $f = 0.4$ are selected because they represent the bounds for most realistic aqueous systems. It can be seen that the ionic drag

efficient only weakly affects the particle interaction, especially for the cases when $Z = 2$ and $Z = 3$. In general, the translational velocities of the two spheres undergoing electrophoresis normal to their line of centers are reduced and their angular velocities are enhanced by the proximity of each other except when the particles have a large zeta potential and the counterions carry a high charge. The particle velocities for a given case of ζ and Z are not necessarily a monotonic function of $2a/r_{12}$. Note that the two electrophoretic spheres rotate in the opposite directions and these directions for the case of large $\zeta e/k_B T$ and Z can be reversed when their gap thickness is varied, as shown in Figs. 3b and 3c.

Figures 4 and 5 are drawn to show the interaction effects between the two spheres versus the particles' zeta potential

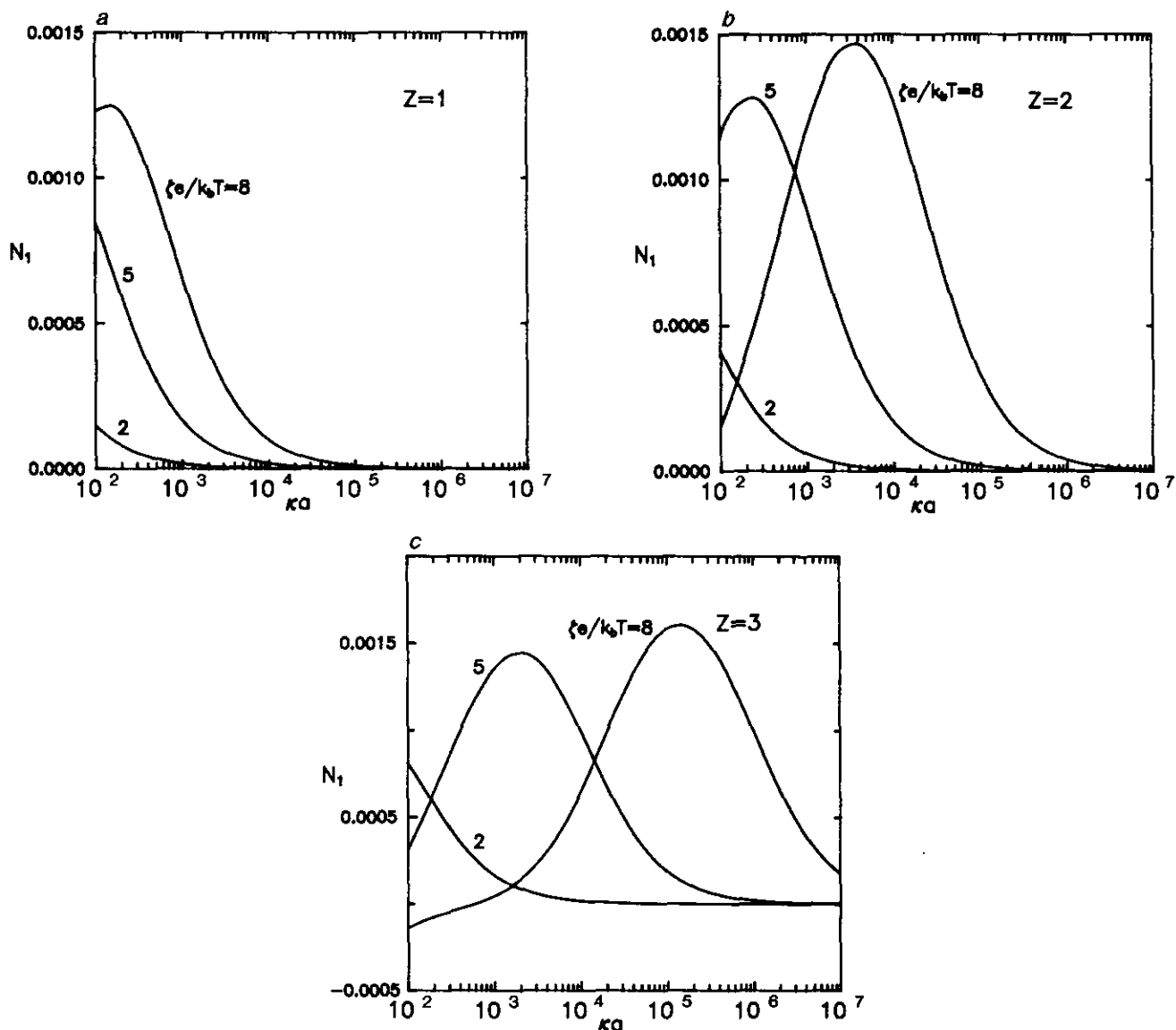


FIG. 7. Plots of the rotational mobility parameters of two identical spheres undergoing electrophoresis normal to their line of centers versus the ratio of the sphere radius to the Debye length κa with $2a/r_{12} = 0.6$ and $f = 0.4$: (a) $Z = 1$, (b) $Z = 2$, (c) $Z = 3$.

for three cases of κa when the separation parameter $2a/r_{12}$ is kept constant. When $Z = 1$, the translational mobility parameter of each sphere is a monotonic decreasing function and the magnitude of the rotational mobility parameter is a monotonic increasing function of the nondimensional zeta potential $\zeta e/k_B T$ ranging from 1 to 7.5, as illustrated in Figs. 4a and 5a. Also, the spheres translate slower and rotate faster with smaller κa . However, when $Z = 2$ or 3, a minimum of the translational velocity and a maximum of the angular velocity of the particles exist for some cases, as shown in Figs. 4b, 4c, 5b, and 5c. When κa increases, the minimum or the maximum occurs at a larger zeta potential. Note that these extremes for the cases with $Z = 3$ take place at smaller zeta potentials than those with $Z = 2$.

In Figs. 6 and 7, the mobility parameters are plotted versus κa for $\kappa a \geq 100$. 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 Eq. [2.11], to express the "slip velocity" at the particle surfaces (5, 8). From Figs. 6a and 7a for the case $Z = 1$, the particle interaction is weakened steadily as κa becomes large gradually. A novel result is that, as shown in Figs. 6b, 6c, 7b, and 7c for $Z = 2$ and 3, there can be a minimum of the translational velocity and a maximum of the angular velocity of the spheres occurring at some κa for the representative cases of $\zeta e/k_B T = 5$ and 8. If the particles are charged more highly or the counterions have a larger magnitude of valence, the locations of these maximal particle interactions will shift toward larger κa ; that means larger values of κa are required to make the assumption of $\kappa a \rightarrow \infty$ valid.

4.2. Two Arbitrary Free Spheres

In this subsection, we first present the results of mobility parameters $M_1^{(n)}$, $M_2^{(n)}$, N_1 , and N_2 for the electrophoresis

TABLE 1
The Mobility Parameters $M_1^{(n)}$ and $M_2^{(n)}$ for the Electrophoresis of Two Freely Suspended Spheres Normal to Their Line of Centers with $a_1 = a_2 = a$ for the Case of $f = 0.4$ and $\kappa a = 100$

$\frac{\zeta_1 e}{k_B T}$	$\frac{\zeta_2 e}{k_B T}$	$\frac{2a}{r_{12}}$	Z = 1		Z = 2		Z = 3	
			$M_1^{(n)}$	$M_2^{(n)}$	$M_1^{(n)}$	$M_2^{(n)}$	$M_1^{(n)}$	$M_2^{(n)}$
1	5	0.2	0.9983	1.0004	0.9990	1.0002	0.9993	0.9997
		0.4	0.9864	1.0029	0.9918	1.0013	0.9940	0.9974
		0.6	0.9531	1.0098	0.9719	1.0047	0.9796	0.9920
		0.8	0.8791	1.0260	0.9307	1.0145	0.9510	0.9901
		0.9	0.8073	1.0453	0.8967	1.0311	0.9295	1.0086
		0.95	0.7476	1.0672	0.8715	1.0533	0.9137	1.0412
		0.99	0.6151	1.1197	1.1510	1.2429	-0.1033	-0.0563
3	6	0.2	0.9994	1.0000	0.9993	0.9993	0.9993	0.9991
		0.4	0.9949	1.0003	0.9942	0.9948	0.9948	0.9933
		0.6	0.9825	1.0010	0.9803	0.9833	0.9828	0.9785
		0.8	0.9577	1.0049	0.9547	0.9688	0.9618	0.9569
		0.9	0.9394	1.0145	0.9382	0.9744	0.9500	0.9529
		0.95	0.9299	1.0296	0.9294	0.9943	0.9448	0.9598
		0.99	0.9010	1.0593	0.8616	0.9570	0.9124	0.9188
5	-5	0.2	1.0008	1.0008	1.0005	1.0005	0.9998	0.9998
		0.4	1.0068	1.0068	1.0040	1.0040	0.9985	0.9985
		0.6	1.0234	1.0234	1.0132	1.0132	0.9940	0.9940
		0.8	1.0603	1.0603	1.0304	1.0304	0.9795	0.9795
		0.9	1.0982	1.0982	1.0421	1.0421	0.9565	0.9565
		0.95	1.1330	1.1330	1.0479	1.0479	0.9285	0.9285
		0.99	1.1963	1.1963	1.0506	1.0506	0.8687	0.8687
		1.0	1.39	1.39	1.02	1.02	0.68	0.68
8	-8	0.2	1.0006	1.0006	0.9997	0.9997	0.9995	0.9995
		0.4	1.0047	1.0047	0.9975	0.9975	0.9960	0.9960
		0.6	1.0160	1.0160	0.9907	0.9907	0.9855	0.9855
		0.8	1.0384	1.0384	0.9707	0.9707	0.9571	0.9571
		0.9	1.0567	1.0567	0.9421	0.9421	0.9194	0.9194
		0.95	1.0697	1.0697	0.9088	0.9088	0.8775	0.8775
		0.99	1.0869	1.0869	0.8390	0.8390	0.7917	0.7917
		1.0	1.13	1.13	0.54	0.54	0.52	0.52

of two spheres of the same size ($a_1 = a_2 = a$) having different zeta potentials. The values of the translational and rotational mobility parameters for several representative cases of zeta potentials at various particle separations are illustrated in Tables 1 and 2, respectively, in which all the results are at least convergent to the digits as shown. In Figs. 8 and 9, the corresponding plots of these mobility parameters versus κa are drawn for $\kappa a \geq 100$ and $2a/r_{12} = 0.6$. It is evident that as κa becomes very large, the translational and rotational velocities of each of the two spheres undergoing electrophoresis normal to their line of centers will approach the values calculated by ignoring the polarization effect of the double layer (8, 10). When the two spheres with finite κa have the zeta potentials of the same electrical sign, the numerical results for the case $Z = 1$ show that the particle with larger zeta potential would be speeded up by the other, which at the same time is slowed down by the former, consistent with the tendency exhibited when $\kappa a \rightarrow \infty$ (5, 8). However, for

the cases of $Z = 2$ and 3, the translational velocity of the particle with the larger zeta potential can be reduced by the other if the value of κa is not very high. When the two spheres are charged oppositely but with equal magnitudes of zeta potential, they will translate at the same speed but in opposite directions. Whether the particle velocities are increased or decreased depends on the combination of ζ , Z , f , κa , and $2a/r_{12}$. Note that the two electrophoretic spheres always rotate in the same direction when $\kappa a \rightarrow \infty$. If the value of κa is not very high, the two spheres can rotate in opposite directions, as illustrated in Figs. 9a and 9b.

Because many suspensions in practical applications are composed of 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 translational and rotational mobility parameters for spheres with $a_2/a_1 = 2$ and $(a_1 + a_2)/r_{12} = 0.6$ are depicted versus κa_1 in Figs. 10 and 11, respectively. It is understood

TABLE 2
The Mobility Parameters N_1 and N_2 for the Electrophoresis of Two Freely Suspended Spheres Normal to Their Line of Centers with $a_1 = a_2 = a$ for the Case of $f = 0.4$ and $\kappa a = 100$

$\frac{\zeta_1 e}{k_B T}$	$\frac{\zeta_2 e}{k_B T}$	$\frac{2a}{r_{12}}$	Z = 1		Z = 2		Z = 3	
			N_1	N_2	N_1	N_2	N_1	N_2
1	5	0.2	-9.09E-7	-8.67E-8	-3.26E-8	-3.00E-7	3.08E-7	1.67E-8
		0.4	-1.11E-4	-4.80E-5	-6.54E-6	-6.92E-5	2.55E-5	-1.30E-4
		0.6	-2.00E-3	-9.88E-4	1.48E-5	-1.46E-3	5.98E-4	-2.76E-3
		0.8	-1.42E-2	-1.05E-2	3.55E-3	-1.60E-2	7.62E-3	-3.08E-2
		0.9	-2.38E-2	-3.50E-2	1.90E-2	-5.29E-2	2.48E-2	-9.92E-2
		0.95	-1.18E-2	-7.44E-2	4.15E-2	-1.05E-1	4.09E-2	-1.85E-1
		0.99	-3.55E-2	-1.72E-1	1.42	-9.71E-1	-4.12	5.95
3	6	0.2	4.80E-8	-3.10E-7	3.19E-7	-8.44E-7	5.65E-7	-1.72E-6
		0.4	9.24E-6	-5.02E-5	3.84E-5	-1.23E-4	3.55E-5	-1.10E-4
		0.6	3.01E-4	-1.07E-3	8.45E-4	-2.57E-3	7.49E-4	-2.23E-3
		0.8	5.80E-3	-1.21E-2	9.74E-2	-2.80E-2	8.06E-3	-2.30E-2
		0.9	2.60E-2	-4.20E-2	3.09E-2	-8.89E-2	2.40E-2	-6.88E-2
		0.95	6.19E-2	-8.84E-2	5.55E-2	-1.67E-1	4.03E-2	-1.19E-1
		0.99	6.36E-2	-1.49E-1	-1.59E-1	1.41E-1	-6.39E-2	1.14E-1
5	-5	0.2	5.62E-7	-5.62E-7	1.97E-7	-1.97E-7	-4.46E-7	4.46E-7
		0.4	8.31E-5	-8.31E-5	3.80E-5	-3.80E-5	-2.88E-5	2.88E-5
		0.6	1.62E-3	-1.62E-3	7.04E-4	-7.04E-4	-6.27E-4	6.27E-4
		0.8	1.49E-2	-1.49E-2	5.40E-3	-5.40E-3	-7.73E-3	7.73E-3
		0.9	4.18E-2	-4.18E-2	1.15E-2	-1.15E-2	-2.79E-2	2.79E-2
		0.95	7.48E-2	-7.48E-2	1.48E-2	-1.48E-2	-5.86E-2	5.86E-2
		0.99	1.48E-1	-1.48E-1	1.54E-2	-1.54E-2	-1.32E-1	1.32E-1
1.0	4.01E-1	-4.01E-1	-2.11E-2	2.11E-2	-3.79E-1	3.79E-1		
8	-8	0.2	3.07E-7	-3.07E-7	-1.01E-6	1.01E-6	-1.38E-6	1.38E-6
		0.4	4.99E-5	-4.99E-5	-4.03E-5	4.03E-5	-5.82E-5	5.82E-5
		0.6	9.45E-4	-9.45E-4	-8.45E-4	8.45E-4	-1.20E-3	1.20E-3
		0.8	7.89E-3	-7.89E-3	-9.88E-3	9.88E-3	-1.33E-2	1.33E-2
		0.9	1.93E-2	-1.93E-2	-3.43E-2	3.43E-2	-4.46E-2	4.46E-2
		0.95	3.02E-2	-3.02E-2	-7.03E-2	7.03E-2	-8.95E-2	8.95E-2
		0.99	4.82E-2	-4.82E-2	-1.56E-1	1.56E-1	-1.94E-1	1.94E-1
1.0	1.02E-1	-1.02E-1	-5.44E-1	5.44E-1	-5.54E-1	5.54E-1		

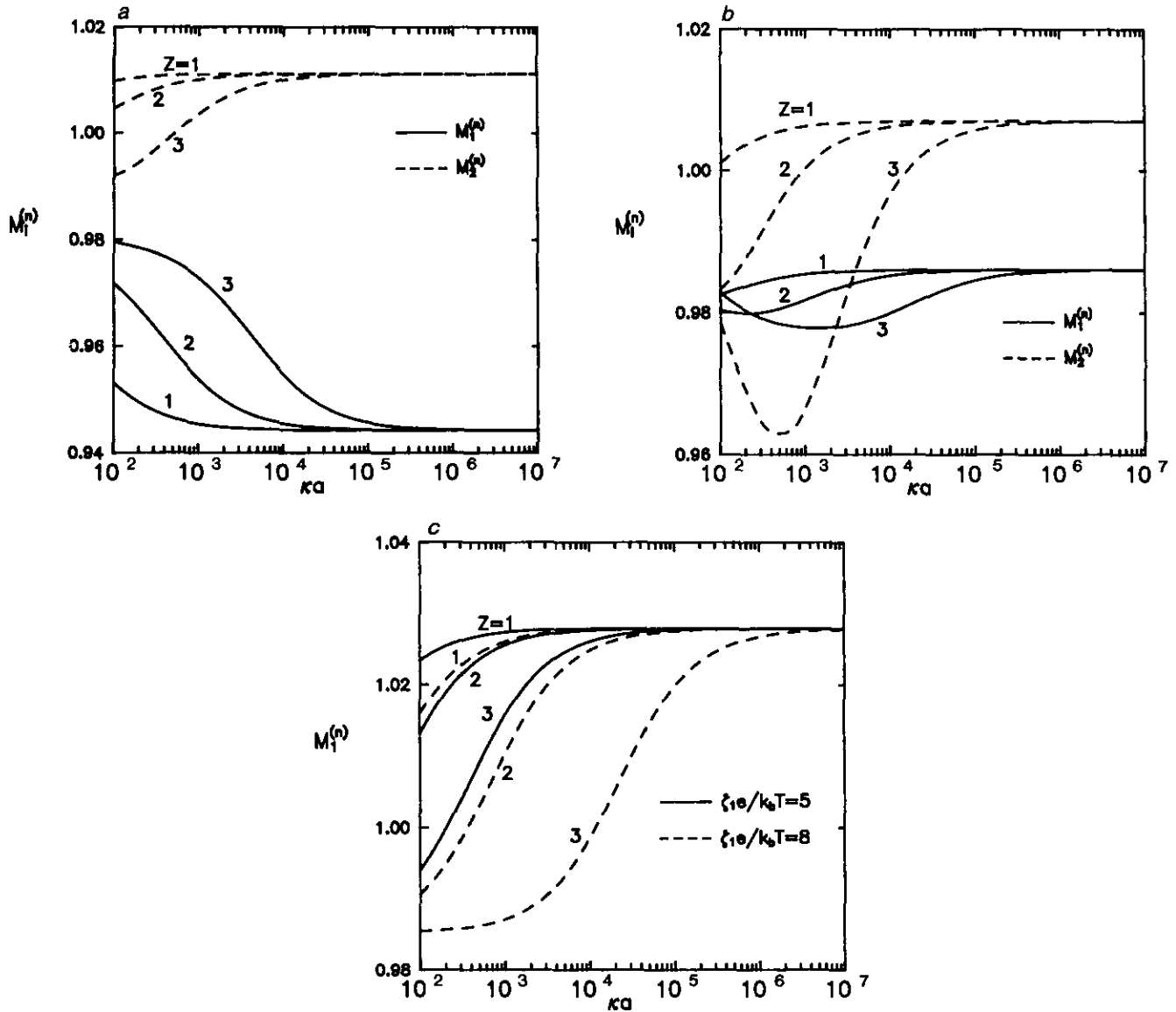


FIG. 8. Plots of the translational mobility parameters of two equal-sized spheres undergoing electrophoresis normal to their line of centers versus κa with $2a/r_{12} = 0.6$ and $f = 0.4$: (a) $\zeta_1 e/k_B T = 1$ and $\zeta_2 e/k_B T = 5$, (b) $\zeta_1 e/k_B T = 3$ and $\zeta_2 e/k_B T = 6$, (c) $\zeta_1 e/k_B T = -\zeta_2 e/k_B T = 5$ or 8 ($M_1^{(n)} = M_2^{(n)}$).

that, although the two spheres possess the same zeta potential, they will translate at different speeds even if situated very far apart. In general, the translational velocity of the larger sphere is enhanced by the motion of the smaller one, which is retarded at the same time by the larger one. The two electrophoretic spheres rotate in the opposite directions, which are the same as those for a pair of identical spheres. It can be seen that the shift of the locations of the maximal particle interactions is also like that for two identical spheres.

4.3. Three Free Spheres

The number of relevant parameters involved in the general problem of three spheres is quite great. Also, the utilization

of the boundary collocation technique for solving the three-sphere problem becomes more difficult than for the case of two spheres. 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 ($r_{12} = r_{23}$). The values of the mobility parameters $M_1^{(n)}$ ($=M_3^{(n)}$), $M_2^{(n)}$, and N_1 ($=-N_3$) for the case of $f = 0.4$ and $\kappa a = 100$ as a function of $\zeta e/k_B T$ and $2a/r_{12}$ are listed in Table 3. As expected, the translational velocity of the middle sphere is affected more by the particle interaction than are those at each side of it. Note that the middle sphere does not rotate in this symmetric configuration.

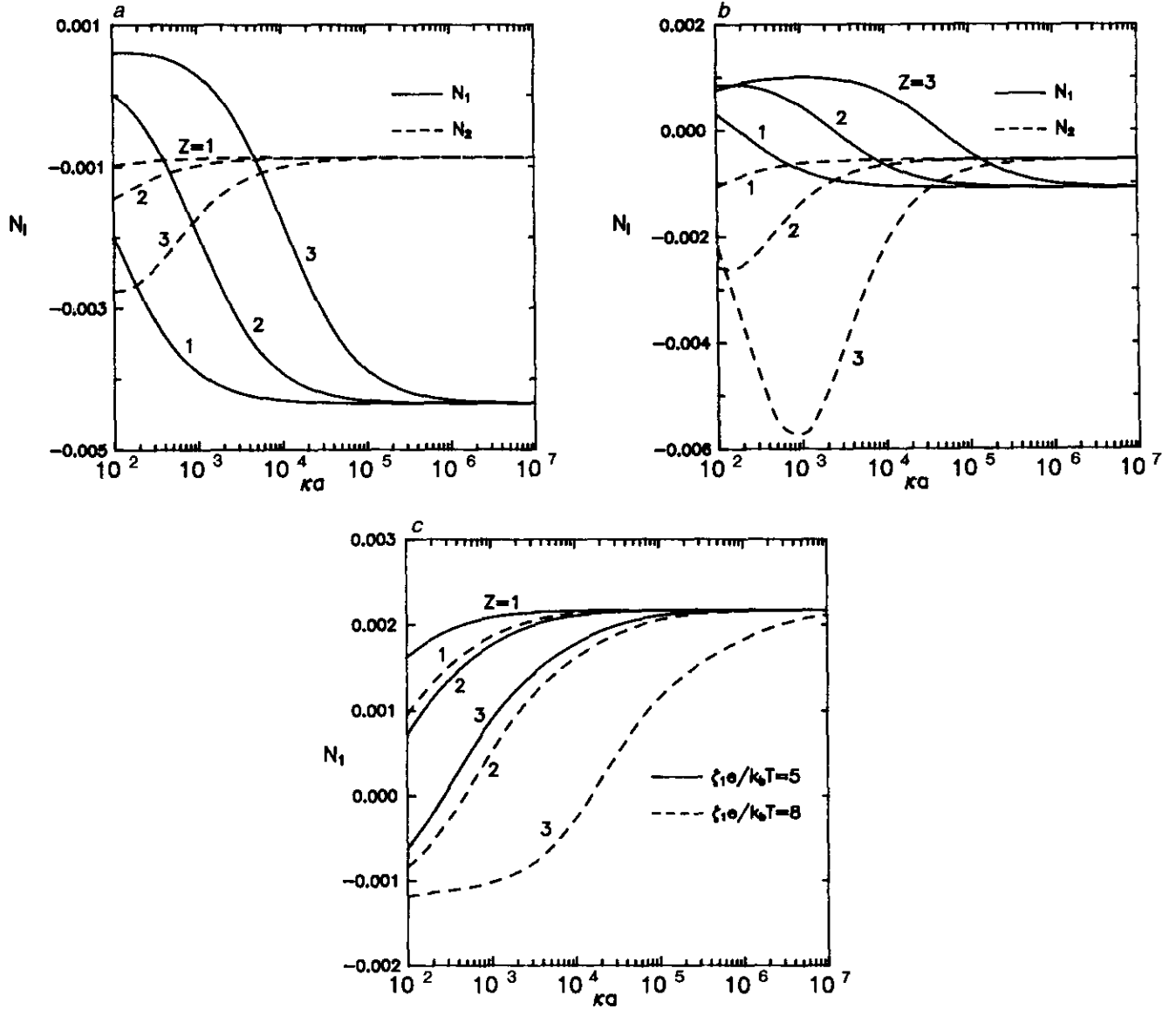


FIG. 9. Plots of the rotational mobility parameters of two equal-sized spheres undergoing electrophoresis normal to their line of centers versus κa with $2a/r_{12} = 0.6$ and $f = 0.4$: (a) $\zeta_1 e/k_B T = 1$ and $\zeta_2 e/k_B T = 5$, (b) $\zeta_1 e/k_B T = 3$ and $\zeta_2 e/k_B T = 6$, (c) $\zeta_1 e/k_B T = -\zeta_2 e/k_B T = 5$ or 8 ($N_1 = N_2$).

It may be of interest to see how the existence of a third coaxial sphere affects the electrophoretic velocities of two neighboring spheres. The difference between two-sphere and three-sphere interaction effects on the electrophoretic mobilities in the direction of their line of centers has been compared in a previous study (11). A comparison between Table 3 and Figs. 2 and 3 shows that the presence of the third sphere enhances the translation, while reducing the rotation, of both sphere 1 and sphere 2 during the electrophoresis normal to the line through the sphere centers.

4.4. A Rigid Cluster of Spheres

The translational and angular velocities of a rigid cluster of spheres undergoing electrophoresis can be determined by

the procedure described in Subsection 3.4. For conciseness, here we only consider the motion of a dumbbell, the cluster composed of two spheres connected by an infinitesimally thin, rigid rod. Although the angular velocity Ω of the rigid dumbbell is independent of the location of its origin, the choice of the origin will affect the presentation of results for the translational velocity U_0 . We follow the previous studies on the electrophoresis of a dumbbell with $\kappa a \rightarrow \infty$ (10, 14) to place the origin of the dumbbell at its center of hydrodynamic stress.

The results for the translational and angular velocities of a rigid dumbbell undergoing electrophoresis normal to the line through the sphere centers, expressed in terms of the dimensionless forms $U_0/U_{1\infty}$ and $\Omega r_{12} U_{1\infty}$ (where $U_0 =$

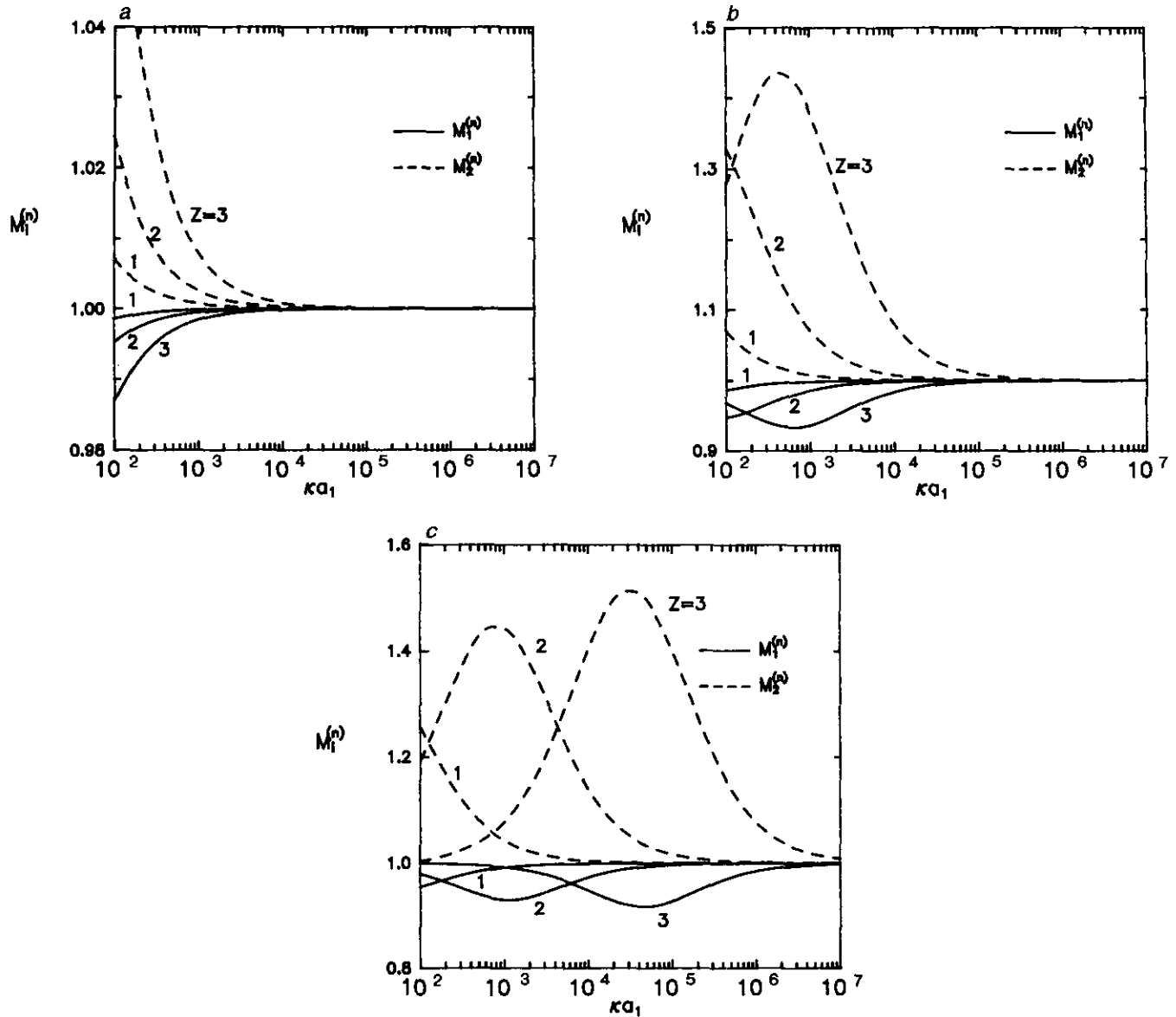


FIG. 10. Plots of the translational mobility parameters $M_1^{(n)}$ (solid curves) and $M_2^{(n)}$ (dashed curves) of two unequal-sized spheres with the same zeta potential versus κa_1 for the case of $a_2/a_1 = 2$, $(a_1 + a_2)/r_{12} = 0.6$ and $f = 0.4$: (a) $\zeta e/k_B T = 2$, (b) $\zeta e/k_B T = 5$, (c) $\zeta e/k_B T = 8$.

$U_0 \mathbf{e}_x$, $\boldsymbol{\Omega} = \boldsymbol{\Omega} \times \mathbf{e}_x$ and $\mathbf{U}_{1\infty} = U_{1\infty} \mathbf{e}_x$), versus the separation parameter $(a_1 + a_2)/r_{12}$ for various cases, are exhibited in Table 4. The last column in Table 4 represents results neglecting the polarization effects of the ions in diffuse layer, 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 of the electrophoretic motion of a dumbbell having two identical spheres perpendicular to its connecting rod, the dumbbell will move without rotation at the same velocity as that of either of these two spheres suspended freely and separated by the same distance, as discussed in Subsection 4.1. When the two spheres of a dumb-

bell are of the same radius but unequal zeta potentials, the effect of polarization of the diffuse layer is to reduce its translational and rotational velocities, as illustrated in the 10 rows with $a_2/a_1 = 1$ in Table 4. The magnitudes of these velocities decrease with the increase of the separation parameter $2a/r_{12}$.

Since flocculation by bridging of particles having identical zeta potentials but different sizes can occur in a suspension of colloidal particles of the same material, it might be important to investigate the electrophoretic motion of such a dumbbell. Results of the translational and angular velocities for the case of a rigid dumbbell composed of two spheres with $a_2/a_1 = 2$, $\kappa a_1 = 100$, and $\zeta_1 e/k_B T = \zeta_2 e/k_B T = 5$ un-

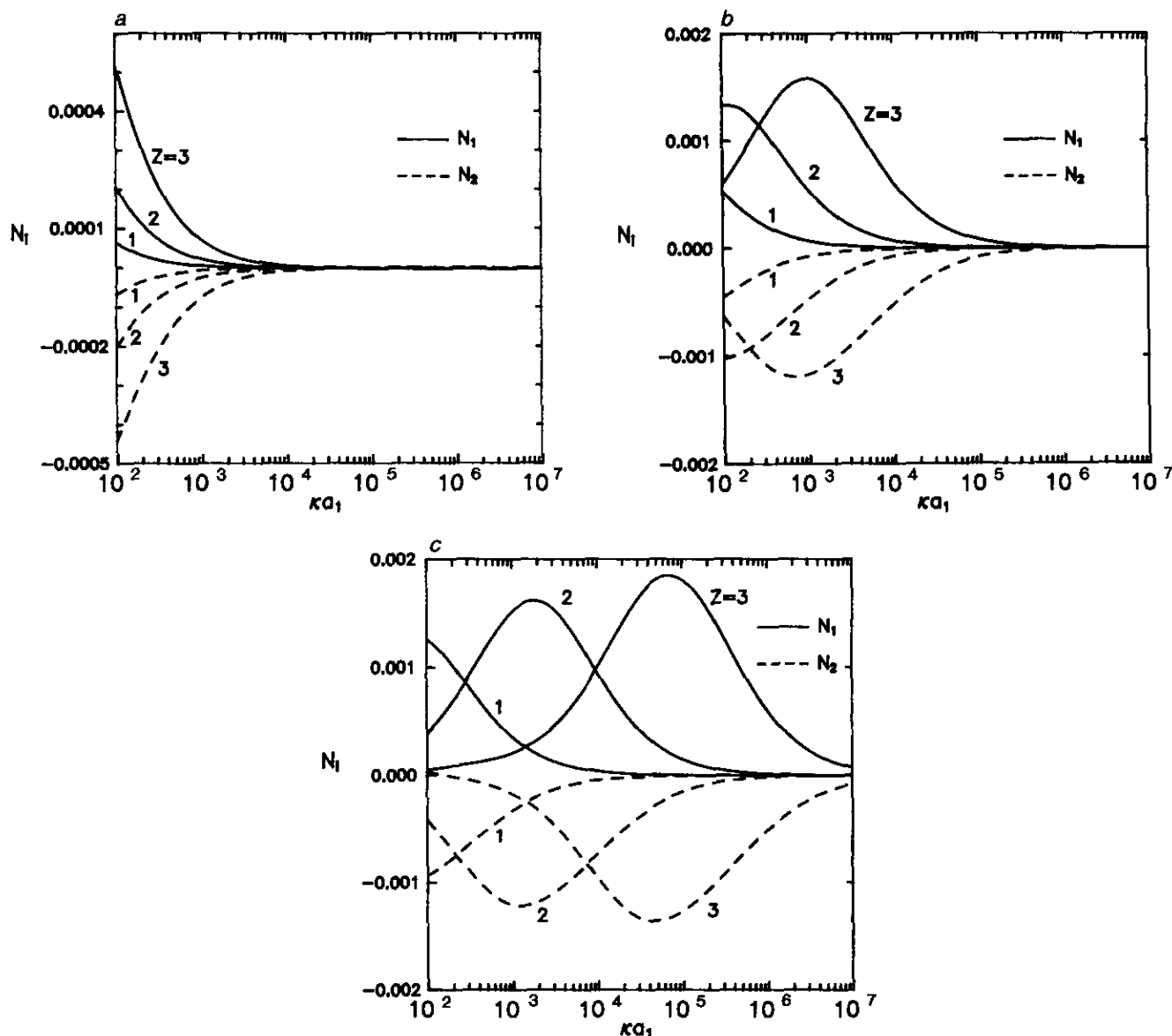


FIG. 11. Plots of the rotational mobility parameters N_1 (solid curves) and N_2 (dashed curves) of two unequal-sized spheres with the same zeta potential versus κa_1 for the case of $a_2/a_1 = 2$, $(a_1 + a_2)/r_{12} = 0.6$ and $f = 0.4$: (a) $\zeta e/k_B T = 2$, (b) $\zeta e/k_B T = 5$, (c) $\zeta e/k_B T = 8$.

dergoing electrophoresis normal to its connecting rod are also listed in Table 4. As expected, the motion of the dumbbell is dominated by the larger sphere. The tendency that the two-sphere interaction effect is strong for the case of $Z = 2$ and weak for $Z = 1$ is consistent with the results of Figs. 10b and 11b for two free spheres with $\zeta e/k_B T = 5$.

An interesting case is the electrophoresis of a neutral dumbbell (with the ratio ζ_2/ζ_1 equal to $-a_1^2/a_2^2$). In Table 4, we also present the translational and rotational mobilities of a neutral dumbbell with $\zeta_1 e/k_B T = 4$, $\zeta_2 e/k_B T = -1$, and $a_2/a_1 = 2$ undergoing transverse electrophoresis. It can be seen that the larger sphere will increasingly dominate the dumbbell's migration, and the magnitude of the dumbbell's

angular velocity is reduced as the distance between the two spheres decreases. This observation is qualitatively consistent with that of previous studies in which the double-layer polarization effect is excluded (10, 14). Note that the neutral dumbbell migrates in the same direction as that of the larger sphere when isolated for the cases $Z = 2$ and 3, while it moves in the opposite direction for the case of $Z = 1$.

4.5. Concentration Dependence of Electrophoretic Velocity

The interaction effects between pairs of particles can be used to determine how the average electrophoretic velocity of a dilute dispersion is affected by the volume fraction ϕ of

TABLE 3

The Mobility Parameters $M_1^{(n)}$ ($=M_2^{(n)}$), $M_2^{(n)}$, and N_1 ($=-N_3$) for the Electrophoresis of Three Coaxial Identical Spheres ($a_1 = a_2 = a_3 = a$ and $\zeta_1 = \zeta_2 = \zeta_3 = \zeta$) Suspended Freely with Equal Spacings ($r_{12} = r_{23}$) for the Case of $f = 0.4$ and $\kappa a = 100$

$\frac{\zeta e}{k_B T}$	$\frac{2a}{r_{12}}$	Z = 1			Z = 2			Z = 3		
		$M_1^{(n)}$	$M_2^{(n)}$	N_1	$M_1^{(n)}$	$M_2^{(n)}$	N_1	$M_1^{(n)}$	$M_2^{(n)}$	N_1
2	0.2	1.0000	0.9999	-2.21E-6	0.9999	0.9997	-3.43E-8	0.9996	0.9994	-2.03E-8
	0.4	0.9996	0.9993	1.64E-6	0.9988	0.9979	6.47E-6	0.9971	0.9950	1.32E-5
	0.6	0.9987	0.9977	9.44E-5	0.9958	0.9928	2.52E-3	0.9903	0.9831	4.71E-4
	0.8	0.9966	0.9949	1.73E-3	0.9896	0.9844	4.40E-3	0.9765	0.9635	7.72E-3
	0.99	0.993	1.033	7.83E-2	0.9686	0.469	-8.53E-1	0.9313	-0.333	-2.17
5	0.2	0.9996	0.9993	-1.60E-8	0.9992	0.9987	6.55E-7	0.9997	0.9995	2.52E-6
	0.4	0.9971	0.9948	1.39E-5	0.9940	0.9893	2.03E-5	0.9977	0.9960	1.39E-4
	0.6	0.9899	0.9826	4.95E-4	0.9802	0.9651	5.97E-4	0.9927	0.9871	1.43E-4
	0.8	0.9756	0.9622	8.17E-3	0.9554	0.9261	8.79E-3	0.9843	0.9730	2.03E-3
	0.99	0.9546	1.167	3.96E-1	0.9228	0.9429	1.01E-1	0.9797	1.1783	3.70E-1
8	0.2	0.9992	0.9987	2.15E-7	0.9998	0.9997	3.00E-8	1.0000	1.0000	5.37E-6
	0.4	0.9940	0.9894	2.10E-5	0.9986	0.9976	1.31E-5	1.0002	1.0003	6.26E-6
	0.6	0.9801	0.9651	6.59E-4	0.9957	0.9923	5.66E-5	1.0007	1.0012	-1.07E-4
	0.8	0.9547	0.9258	9.91E-3	0.9908	0.9840	8.25E-4	1.0020	1.0028	-1.35E-3
	0.99	0.9180	0.8936	2.12E-2	0.9868	0.9467	-5.43E-2	1.0107	1.2250	3.68E-1

the particles. For a bounded suspension of identical spheres, the mean electrophoretic velocity can be expressed as (5, 10, 15)

$$\langle \mathbf{U} \rangle = \mathbf{U}_\infty [1 + \alpha \varphi + \mathbf{O}(\varphi^2)], \quad [4.1]$$

with

$$\alpha = -1.5 + 8 \int_0^1 [M_1^{(p)} + 2M_1^{(n)} - 3] \lambda^{-4} d\lambda, \quad [4.2]$$

where $\lambda = 2a/r_{12}$, \mathbf{U}_∞ is the electrophoretic velocity of an isolated sphere given by Eq. [2.21a] or [2.26], and the two-particle mobility parameters $M_1^{(p)}$ and $M_1^{(n)}$ are defined by Eq. [3.22a] for the case of two identical spheres. When $\kappa a \rightarrow \infty$, $M_1^{(p)} = M_1^{(n)} = 1$ (there is no particle interaction in electrophoresis of identical spheres) and Eq. [4.2] gives $\alpha = -1.5$.

The collocation results of $M_1^{(n)}$ in Eq. [4.2] as a function of λ for various values of κa , $\zeta e/k_B T$, and Z were presented in Subsection 4.1, while the corresponding numerical solutions of $M_1^{(p)}$ were obtained in a previous study (11). Thus, the integration in Eq. [4.2] can be performed numerically using these data, and the results of the coefficient α for various cases of identical particles and symmetric electrolyte are listed in Table 5. Note that, in each case, α is negative and the average electrophoretic velocity becomes lower when the volume fraction of the spheres in the suspension is increased. When $Z = 1$, the α values for all cases of different κa and $\zeta e/k_B T$ deviate little from the value of -1.5 for the limiting

situation of $\kappa a \rightarrow \infty$. However, when $Z = 2$ or 3, the magnitude of α increases monotonically with the increase of $\zeta e/k_B T$ for a given value of κa and can be much greater than 1.5 for the cases of large $\zeta e/k_B T$.

Particle interactions in electrophoresis have also been studied by using a unit cell model for a concentrated suspension of spheres with thin but finite double layers (16, 17). Without accounting for the statistical randomness and the boundaries of the suspension, this model also predicts that the average electrophoretic mobility decreases with an increase of the particle concentration.

5. CONCLUSIONS

The electrophoretic motion of an assemblage of colloidal spheres with thin but distorted electrical double layers is studied in this paper. The spheres may differ in radius and in zeta potential, and they are allowed to be arranged in any configuration in three-dimensional space. Not only the particle interactions among free spheres but also the movement of a rigid cluster of connected spheres has 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 and the interactions among particles: the ratio of the particle dimension to the Debye length, the zeta potential at the particle surface, the valences of ions in solution, and the ionic drag coefficients.

A combined analytical-numerical procedure with the

TABLE 4
 The Dimensionless Translational and Rotational Velocities of a Rigid Dumbbell Undergoing Electrophoresis Normal to the Line Connecting Two Spheres for the Case of $f = 0.4$ and $\kappa a_1 = 100$

$\frac{a_2}{a_1}$	$\frac{\xi_1 e}{k_B T}$	$\frac{\xi_2 e}{k_B T}$	$\frac{a_1 + a_2}{r_{12}}$	$U_0/U_{1\infty}$ (with polarization)			$U_0/U_{1\infty}$ (without polarization)
				Z = 1	Z = 2	Z = 3	
1	1	5	0.2	2.4257	1.3040	0.8007	3.0000
			0.4	2.4246	1.3013	0.7974	3.0000
			0.6	2.4213	1.2939	0.7885	3.0000
			0.8	2.4136	1.2792	0.7718	3.0000
			0.99	2.3964	1.2544	0.7600	3.0000
2	5	5	0.2	1.1416	1.5647	1.3397	1.0000
			0.4	1.1430	1.5705	1.3432	1.0000
			0.6	1.1426	1.5693	1.3427	1.0000
			0.8	1.1394	1.5594	1.3378	1.0000
			0.99	1.1323	1.5456	1.3329	1.0000
2	4	-1	0.2	0.1249	-0.0041	-0.5012	0.1520
			0.4	0.1090	-0.0222	-0.5279	0.1366
			0.6	0.0928	-0.0404	-0.5540	0.1207
			0.8	0.0755	-0.0596	-0.5803	0.1038
			0.99	0.0552	-0.0839	-0.6121	0.0849

$\frac{a_2}{a_1}$	$\frac{\xi_1 e}{k_B T}$	$\frac{\xi_2 e}{k_B T}$	$\frac{a_1 + a_2}{r_{12}}$	$\Omega r_{12}/U_{1\infty}$ (with polarization)			$\Omega r_{12}/U_{1\infty}$ (without polarization)
				Z = 1	Z = 2	Z = 3	
1	1	5	0.2	2.7256	0.5823	-0.3790	3.8227
			0.4	2.4629	0.5300	-0.3366	3.4525
			0.6	2.1982	0.4819	-0.2867	3.0777
			0.8	1.9865	0.4491	-0.2366	2.7757
			0.99	1.8396	0.4299	-0.1895	2.5708
2	5	5	0.2	0.1952	0.7788	0.4685	0
			0.4	0.1682	0.6711	0.4038	0
			0.6	0.1428	0.5698	0.3430	0
			0.8	0.1230	0.4900	0.2955	0
			0.99	0.1095	0.4244	0.2579	0
2	4	-1	0.2	-1.2048	-1.3823	-2.0667	-1.1674
			0.4	-1.0340	-1.1861	-1.7727	-1.0020
			0.6	-0.8691	-0.9964	-1.4879	-0.8423
			0.8	-0.7365	-0.8431	-1.2568	-0.7142
			0.99	-0.6355	-0.7222	-1.0757	-0.6186

TABLE 5
 The Results of Coefficient α (Defined by Eq. [4.2]) for Various Values of κa , $\xi e/k_B T$, and Z with $f = 0.4$

κa	$\frac{\xi e}{k_B T}$	α		
		Z = 1	Z = 2	Z = 3
10^2	2	-1.48	-1.59	-1.58
	5	-1.60	-1.67	-2.07
	8	-1.56	-2.13	-2.79
10^3	2	-1.47	-1.47	-1.49
	5	-1.49	-1.65	-1.58
	8	-1.53	-1.78	-2.61
10^4	2	-1.46	-1.48	-1.47
	5	-1.47	-1.49	-1.57
	8	-1.45	-1.67	-2.28

boundary collocation technique has been used to solve the electrochemical potential distributions and the velocity field for the fluid around the electrophoretic spheres. It has been found 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.

The interaction effects between pairs of spheres have also been employed to find the average electrophoretic velocity in a bounded suspension of colloidal particles. This average velocity is decreased for various cases as the concentration of the particles in the suspension is increased.

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