Boundary Effects on Diffusiophoresis and Electrophoresis: Motion of a Colloidal Sphere Normal to a Plane Wall

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A combined analytical–numerical study of the diffusiophoresis and electrophoresis of a rigid sphere in a uniform applied field perpendicular to a plane wall is presented. The range of the interaction between the solute species and the solid surfaces is assumed to be small relative to the particle’s radius and to the spacing between the particle and the wall, but the polarization of the diffuse species in the thin particle–solute interaction layer is allowed. A slip velocity of fluid and normal fluxes of solute species at the outer edge of the thin diffuse layer are used as the boundary conditions for the fluid domain outside the diffuse layer. Through the use of a collocation method along with these boundary conditions, a set of conservative equations governing the system is solved in the quasisteady state situation and the effects of a plane wall on diffusiophoresis and electrophoresis are calculated for various cases. For the cases of diffusiophoresis in a nonelectrolyte gradient and of electrophoresis, the particle velocity decreases monotonically with the decrease of the distance of the particle center from the wall. For the case of diffusiophoresis in an electrolyte gradient, however, the boundary effect is a complicated function of the properties of the particle and ions, and it no longer varies monotonically with the separation distance for some situations. © 1996

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1. INTRODUCTION

The transport behavior of small particles in a continuous medium at low Reynolds numbers is of much fundamental and practical interest. In general, driving forces for motions of colloidal particles include concentration gradients of the particles themselves (diffusion), bulk velocities of the disperse medium (convection), and gravitational or centrifugal fields (sedimentation). Problems of the colloidal transport induced by these well-known driving forces have been treated extensively in the past. Another category of driving forces for the locomotions of colloidal particles, which has commanded less attention, involves a nonuniform imposed

field (such as electrical potential, temperature, or solute concentration) that interacts with the surface of each particle. A good review of particle motions associated with this mechanism, known as “phoretic motions,” was given by Anderson (1).

Perhaps the most familiar example of the various phoretic motions of colloidal particles is electrophoresis, which results from the interaction between an applied electric field and the electrical double layer surrounding a charged particle. The electrophoretic velocity U_0 of a single nonconducting particle suspended in an unbounded fluid is related to the uniformly applied electric field E^∞ by the well-known Smoluchowski equation (2–4),

$$U_0 = \frac{\epsilon\zeta}{4\pi\eta} E^\infty. \quad [1.1]$$

Here, $\epsilon/4\pi$ is the fluid permittivity, η is the fluid viscosity, and ζ is the zeta potential associated with the particle surface.

Another example of phoretic motions is called “diffusiophoresis” (4), which is the migration of a solid particle in response to the macroscopic concentration gradient of a molecular solute; the solute can be nonionic or ionic. The particle moves toward or away from regions of higher solute concentration, depending on long-range interactions between the solute molecules and the particle. In an unbounded solution with a constant concentration gradient ∇n^∞ , the diffusiophoretic velocity of a particle is

$$U_0 = \frac{kT}{\eta} L^* K \nabla n^\infty \quad [1.2]$$

for the case of a nonionic solute (5), and

$$U_0 = \frac{\epsilon\zeta}{4\pi\eta} \frac{kT}{Ze} \frac{\nabla n^\infty}{n^\infty(\mathbf{0})} \left[\frac{D_2 - D_1}{D_2 + D_1} + \frac{4kT}{Ze\zeta} \ln \cosh\left(\frac{Ze\zeta}{4kT}\right) \right] \quad [1.3]$$

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for the case of a symmetric electrolyte solute (6). Here, L^* is a characteristic length for the range of particle–solute interactions, K is the Gibbs adsorption length characterizing the strength of the adsorption (K and L^* are defined by Eqs. [3.3a] and [3.3d]), $n^\infty(\mathbf{0})$ is the macroscopic solute concentration measured at the particle center $\mathbf{0}$ in the absence of the particle, D_1 and D_2 are the diffusion coefficients of the anion and cation, respectively, Z is the absolute value of the valences of the ions, e is the charge of a proton, k is the Boltzmann constant, and T is the absolute temperature.

Equations [1.1]–[1.3] indicate that the electrophoretic and diffusiophoretic velocities of a particle are independent of particle size and shape. However, their validity is based on the assumptions that the local radii of curvature of the particle are much larger than the thickness of the particle–solute interaction layer at the particle surface and the effect of the polarization (relaxation effect) of the diffuse solute species in the interfacial layer due to nonuniform “osmotic” flow is negligible. Recently, important advances have been made in the evaluation of the phoretic velocity of colloidal particles relaxing these assumptions.

When the double-layer distortion from equilibrium was taken as a perturbation, O’Brien and White (7) obtained a numerical solution for the electrophoretic velocity of a dielectric sphere of radius a in an unbounded solution which was applicable to arbitrary values of ζ and κa ; κ^{-1} is the Debye screening length (equal to $(\epsilon kT/8\pi Z^2 e^2 n^\infty)^{1/2}$). On the other hand, Dukhin and Derjaguin (4) obtained an analytical expression for the electrophoretic mobility of a spherical particle with a thin but polarized double layer in a solution of a symmetric electrolyte. Later, O’Brien (8) generalized this analysis to the case of electrophoresis of a charged sphere in a solution containing an arbitrary combination of electrolytes. The result for the electrophoretic velocity in a symmetric electrolyte solution can be analytically expressed as (9)

$$\mathbf{U}_0 = \frac{\epsilon \zeta}{4\pi \eta} \mathbf{E}^\infty \left[\frac{1}{3} (2 + c_1 + c_2) + \frac{4kT}{3Ze\zeta} (c_1 - c_2) \ln \cosh \left(\frac{Ze\zeta}{4kT} \right) \right] \quad [1.4]$$

with

$$c_1 = \frac{1}{2a^2 \Delta} (a^2 + a\beta_{22} + 3a\beta_{12} - 2a\beta_{11} + 2\beta_{12}\beta_{21} - 2\beta_{11}\beta_{22}), \quad [1.5a]$$

$$c_2 = \frac{1}{2a^2 \Delta} (a^2 + a\beta_{11} + 3a\beta_{21} - 2a\beta_{22} + 2\beta_{12}\beta_{21} - 2\beta_{11}\beta_{22}), \quad [1.5b]$$

and

$$\Delta = \frac{1}{a^2} (a^2 + a\beta_{11} + a\beta_{22} + \beta_{11}\beta_{22} - \beta_{12}\beta_{21}), \quad [1.6]$$

where β_{11} , β_{12} , β_{21} , and β_{22} are relaxation coefficients defined by Eq. [2.6] or [4.3]. If $|\zeta|$ is small and κa is large, the interaction between the diffuse counterions and the particle surface is weak and the polarization of the double layer is also weak. In the limit of

$$(\kappa a)^{-1} \exp \left(\frac{Ze|\zeta|}{2kT} \right) \rightarrow 0, \quad [1.7]$$

$c_1 = c_2 = 0.5$ ($\beta_{11}/a = \beta_{12}/a = \beta_{21}/a = \beta_{22}/a = 0$) and Eq. [1.4] reduces to the Smoluchowski equation [1.1].

For the case of diffusiophoretic motion of a colloidal sphere with a thin but polarized particle–solute interaction layer in a gradient of nonelectrolyte solute, the formula for the particle velocity has been analytically derived (10),

$$\mathbf{U}_0 = \frac{kT}{\eta} L^* K \left(1 + \frac{\beta}{a} \right)^{-1} \nabla n^\infty, \quad [1.8]$$

where the definition of β is given by Eq. [2.6] or [3.2]. For a strongly adsorbing solute, relaxation parameter β/a can be much greater than unity. In the limit of $\beta/a \rightarrow 0$ (very weak adsorption), the polarization of the diffuse solute in the interfacial region vanishes and Eq. [1.8] reduces to Eq. [1.2].

On the other hand, Prieve and Roman (11) obtained a numerical solution for the diffusiophoretic migration of a dielectric sphere in concentration gradients of symmetric electrolytes (KCl or NaCl) over a broad range of ζ and κa using the method of O’Brien and White (7). Recently, analytical expressions for the diffusiophoretic velocity of a colloidal sphere with a thin but polarized double layer in an unbounded solution have also been derived (12, 13). The result for the diffusiophoretic velocity in a symmetric electrolyte solution is (13)

$$\mathbf{U}_0 = \frac{\epsilon \zeta}{4\pi \eta} \frac{kT}{Ze} \frac{\nabla n^\infty}{n^\infty(\mathbf{0})} \left[\frac{2}{3} \left(\frac{D_2 - D_1}{D_2 + D_1} + b_1 - b_2 \right) + \frac{8kT}{3Ze\zeta} (1 + b_1 + b_2) \ln \cosh \left(\frac{Ze\zeta}{4kT} \right) \right], \quad [1.9]$$

where

$$b_1 = \frac{D_2}{D_2 + D_1} c_1 - \frac{3}{2a\Delta} \beta_{12}, \quad [1.10a]$$

$$b_2 = \frac{D_1}{D_2 + D_1} c_2 - \frac{3}{2a\Delta} \beta_{21}, \quad [1.10b]$$

and c_1 , c_2 and Δ are defined by Eqs. [1.5] and [1.6]. In the limiting situation as given in Eq. [1.7], Eq. [1.9] reduces to Eq. [1.3].

It could be found from Eqs. [1.4], [1.8], and [1.9] that the effect of polarization of the diffuse layer is to decrease the particle velocity. The reason for this consequence is that the transport of the solute inside the particle-solute interaction layer reduces the field along the particle surface. Although Eqs. [1.4] and [1.9] are derived for the solution of a symmetric electrolyte, they can also be applied to the solution containing an arbitrary electrolyte using O'Brien's (8) reasoning that only the most highly charged counterions play a dominant role in the ionic fluxes along the particle surface.

In practical applications of diffusiophoresis and electrophoresis, particles are not isolated and the surrounding fluid is externally bounded by solid walls. Thus, it is important to determine if the presence of neighboring boundaries significantly affects the movement of particles. In the limiting case that Eqs. [1.1]–[1.3] are applicable, the normalized velocity field of the immense fluid that is dragged by a particle during diffusiophoresis is the same as for electrophoresis of the particle (1); thus, the boundary effects on electrophoresis, which have been investigated extensively in the past (14–17), can be utilized to interpret those in diffusiophoresis. An important result of these investigations is that the boundary effects on diffusiophoresis and electrophoresis are much weaker than on sedimentation, because the disturbance to the fluid velocity field caused by a phoretic sphere decays faster (as r^{-3}) than that caused by a stokeslet (as r^{-1}), where r is the distance from the particle center.

When the polarization effect of solute species in the diffuse layers adjacent to the solid surfaces is considered, the boundary effects on diffusiophoresis can be quite different from those on electrophoresis, due to the fact that the particle size and some other unique factors are involved in each transport mechanism (13). Until now, the boundary effects on diffusiophoresis or electrophoresis of particles with polarization of the diffuse layer have not been studied. In this work we present a common analysis of the diffusiophoretic (in gradients of nonelectrolytes or electrolytes) and electrophoretic motions of a colloidal sphere perpendicular to an infinite plane wall. The polarized diffuse layers are assumed to be thin compared to the radius of the particle and to the gap thickness between the particle and the wall. The quasisteady-state equations of conservation applicable to each system are solved by a combined analytical-numerical method using the boundary-collocation technique. The particle velocities are obtained with good convergence for various cases. In the limiting case of Eq. [1.7] or $\beta/a \rightarrow 0$, our results are in excellent agreement with those obtained in previous analyses for electrophoresis (16, 17).

2. BASIC EQUATIONS

Consider the diffusiophoretic or electrophoretic motion of a rigid particle of arbitrary shape in the vicinity of a solid boundary in a liquid solution containing M chemical species (ionic or nonionic). The layer of interaction between the solute species and each fluid/solid interface is assumed to be thin in comparison with the radii of curvature of the interface and the spacing between the particle and the boundary. Hence, the fluid phase can be divided into two regions: an "inner" region defined as the interaction layer adjacent to the interface and an "outer" region defined as the remainder of the fluid.

In the outer region, the equations of conservation of the solute species and fluid momentum can be expressed by the Laplace's equation (13),

$$\nabla^2 \mu_m = 0, \quad m = 1, 2, \dots, M, \quad [2.1]$$

and the Stokes equations,

$$\eta \nabla^2 \mathbf{v} - \nabla p = \mathbf{0}, \quad [2.2a]$$

$$\nabla \cdot \mathbf{v} = 0. \quad [2.2b]$$

In Eq. [2.1], μ_m is the modified chemical potential energy of species m defined as

$$\mu_m = \mu_m^0 + kT \ln n_m + \Phi_m, \quad [2.3]$$

where μ_m^0 is a constant at a given temperature; n_m is the concentration of species m ; and Φ_m represents all kinds of potential energy, resulting from van der Waals forces, electrical forces, etc., for the interaction between type- m species and the fluid/solid interface. In Eqs. [2.2], $\mathbf{v}$ is the fluid velocity field and p is the dynamic pressure.

The governing equations [2.1] and [2.2] in the outer region ought to satisfy the following boundary conditions at the fluid/solid interface obtained by solving for the fluid velocity and the modified chemical potentials of the solute species in the inner region and using a matching procedure to ensure a continuous solution in the whole fluid phase (8, 13),

$$\mathbf{n} \cdot \nabla \mu_m = - \sum_{i=1}^M \beta_{mi} \mathbf{I} : \nabla_s \nabla_s \mu_i, \quad [2.4]$$

$$\mathbf{v} = \mathbf{v}^* - \frac{1}{\eta} \sum_{m=1}^M n_m^\infty \nabla_s \mu_m \int_0^\infty y_n [\exp(-\Phi_m^0/kT) - 1] dy_n, \quad [2.5]$$

with

$$\begin{aligned} \beta_{mi} = & \delta_{mi} \int_0^\infty [\exp(-\Phi_m^0/kT) - 1] dy_n \\ & + \frac{kT}{\eta D_m} n_i^\infty \int_0^\infty [\exp(-\Phi_m^0/kT) - 1] \\ & \times \int_0^{y_n} \int_{y_n}^\infty [\exp(-\Phi_m^0/kT) - 1] dy_n'' dy_n' dy_n. \quad [2.6] \end{aligned}$$

In Eqs. [2.4]–[2.6], Φ_m^0 is the equilibrium potential energy of species m ; y_n is the distance measured from the interface along $\mathbf{n}$, which is the unit vector outwardly normal to the interface; n_m^∞ is the local bulk concentration of species m ; $\mathbf{I}$ is the unit dyadic; $\nabla_s = (\mathbf{I} - \mathbf{nn}) \cdot \nabla$ represents the gradient operator along the interface; δ_{mi} denotes the Kronecker delta, which is unity if i equals m and zero otherwise; and $\mathbf{v}^*$ is the velocity of the interface, equal to zero for the fixed solid boundary and $\mathbf{U} + \boldsymbol{\Omega} \times \mathbf{r}$ for a particle translating at velocity $\mathbf{U}$ at a reference point and rotating at angular velocity $\boldsymbol{\Omega}$, where $\mathbf{r}$ is the position vector on the particle surface measured from the reference point. To obtain Eqs. [2.5] and [2.6], it has been assumed that the equilibrium concentration of any species is related to its equilibrium potential energy by the Boltzmann distribution.

The modified chemical potentials in the outer region far away from the particle approach the undisturbed values:

$$\mu_m \rightarrow \mu_m^0 + kT \ln n_m^\infty + \Phi_m^\infty. \quad [2.7]$$

In Eq. [2.7], $\Phi_m^\infty = 0$ for the case of nonionic diffusio-phoresis and $\nabla \Phi_m^\infty = -z_m e \mathbf{E}^\infty$ for the cases of ionic diffusio-phoresis (in which $\mathbf{E}^\infty$ is an induced electric field given by Eq. [4.1]) and electrophoresis, where z_m is the valence of type- m ions. If there is no “osmotic” flow generated by the fixed solid boundary, one has the condition $\mathbf{v} \rightarrow \mathbf{0}$ far from the particle.

Because there is no effective external field exerted beyond the outer edge of the particle–solute interaction layer, the particle (plus its adjacent diffuse layer of solute species) is force and torque free. With this constraint, one can calculate the particle velocities $\mathbf{U}$ and $\boldsymbol{\Omega}$ after solving Eqs. [2.1] and [2.2] for the modified chemical potentials and the fluid velocity. For a spherical particle in an unbounded solution, the electrophoretic and diffusio-phoretic velocities can be determined through the above procedure and the results are given by Eqs. [1.4], [1.8], and [1.9]. There is no rotational motion of the isolated sphere due to the axial symmetry.

3. DIFFUSIOPHORESIS NORMAL TO A PLANE WALL IN A NONELECTROLYTE GRADIENT

In this section we consider the diffusio-phoretic motion of a spherical particle of radius a in a solution of a nonelectro-

FIG. 1. Geometrical sketch for the diffusio-phoretic motion of a spherical particle perpendicular to a plane wall.

lyte solute ($M = 1$) in the direction normal to an infinite plane wall located at a distance d from the particle center, as shown in Fig. 1. Here, (ρ, ϕ, z) and (r, θ, ϕ) denote the circular cylindrical and the spherical coordinates, respectively, and the origin of coordinates is chosen at the particle center. The concentration gradient of the solute far away from the particle, ∇n^∞ , is a constant along the axial direction (n^∞ is a linear function of z only). It is assumed that $a|\nabla n^\infty|/n^\infty(\mathbf{0}) \ll 1$ and $L/a^* \ll 1$, where L is the characteristic thickness of the particle-solute interaction layer (which is approximately the molecular dimension of the solute) and a^* is the smaller of a and $d - a$. The interaction between the solute molecules and the particle surface is described by the potential energy $\Phi(y_n)$, which decays to zero when $y_n/L \gg 1$. Our purpose is to determine the correction to Eq. [1.8] for the particle velocity due to the presence of the plane wall.

Before determining the diffusio-phoretic velocity for the particle, the modified chemical potential and velocity fields in the surrounding fluid must be solved.

3.1. Modified Chemical Potential Distribution

The modified chemical potential energy μ of the solute obeys Laplace's equation (Eq. [2.1]) and is subject to the following boundary conditions at the surfaces (or, more precisely, at the outer edges of the thin particle-solute interaction layers) of the particle and the plane wall and far away from the particle according to Eqs. [2.4] and [2.7],

$$\frac{\partial \mu}{\partial r} = -\beta \left[\nabla^2 - \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) \right] \mu \quad \text{at } r = a,$$

[3.1a]

$$\mu = \mu^0 + kT \ln n^\infty \quad \text{at } z = d, \quad [3.1b]$$

$$\mu \rightarrow \mu^0 + kT \ln n^\infty \quad \text{as } r \rightarrow \infty \text{ and } z \leq d. \quad [3.1c]$$

In Eq. [3.1a], the relaxation coefficient

$$\beta = (1 + \nu \text{Pe})K, \quad [3.2]$$

with

$$K = \int_0^\infty [\exp(-\Phi(y_n)/kT) - 1] dy_n, \quad [3.3a]$$

$$\nu = (L^* K^2)^{-1} \int_0^\infty \left\{ \int_0^\infty [\exp(-\Phi(y'_n)/kT) - 1] dy'_n \right\}^2 dy_n, \quad [3.3b]$$

$$\text{Pe} = \frac{kT}{\eta D} L^* K n^\infty(\mathbf{0}), \quad [3.3c]$$

and

$$L^* = K^{-1} \int_0^\infty y_n [\exp(-\Phi(y_n)/kT) - 1] dy_n. \quad [3.3d]$$

Here, D is the solute diffusion coefficient, Pe is the Peclet number, and νPe accounts for the effect of convection on the solute distribution just outside the adsorption layer. The concentration at the plane wall has been set equal to a constant to allow a uniform solute gradient in the axial direction far away from the particle.

Since the governing equation and boundary conditions are linear, one can write the chemical potential distribution as the superposition

$$\mu = \mu^0 + kT \ln n^\infty + \mu_w + \mu_s. \quad [3.4]$$

Here, μ_w is a Fourier–Bessel integral solution of Laplace's equation in the cylindrical coordinates that represents the disturbance produced by the plane wall and is given by

$$\mu_w = \int_0^\infty \omega R(\omega) J_0(\omega \rho) e^{\omega z} d\omega, \quad [3.5]$$

where J_0 is the Bessel function of the first kind of order zero and $R(\omega)$ is an unknown function of ω . The last term on the right-hand side of Eq. [3.4], μ_s , is a solution of Laplace's equation in spherical coordinates representing the disturbance generated by the particle and is given by an infinite series in harmonics,

$$\mu_s = \sum_{n=0}^{\infty} T_n r^{-(n+1)} P_n(\cos \theta), \quad [3.6]$$

where P_n is the Legendre polynomial of order n and T_n are the unknown coefficients to be determined. Note that a solution of μ in the form given by Eqs. [3.4]–[3.6] immediately satisfies boundary condition [3.1c].

A brief conceptual description of the solution procedure to determine $R(\omega)$ and T_n is given below to help the readers follow the mathematical development. At first, boundary condition [3.1b] is exactly satisfied on the plane wall by using a Hankel transform. This permits the unknown function $R(\omega)$ to be determined in terms of the coefficients T_n . Then boundary condition [3.1a] on the particle surface can be satisfied by making use of the collocation method and the solution of the collocation matrix provides numerical values for the coefficients T_n .

Substitution of the solution μ given by Eqs. [3.4]–[3.6] into the boundary condition [3.1b] and application of the Hankel transform on the variable ρ lead to a solution for $R(\omega)$ in terms of the unknown coefficients T_n . After the substitution of this solution into Eq. [3.5], the resulting chemical potential field is given by

$$\mu = \mu^0 + kT \ln n^\infty + \sum_{n=0}^{\infty} T_n [B_n''(\rho, z) - B_n''(\rho, 2d - z)], \quad [3.7]$$

where the function $B_n''(\rho, z)$ is defined by Eq. [A.12] in the Appendix. Eq. [3.7] provides an exact solution for the chemical potential distribution and the unknown coefficients T_n must be determined from the remaining boundary condition [3.1a] on the particle surface. Utilizing the relation

$$\frac{\partial}{\partial r} = \sin \theta \frac{\partial}{\partial \rho} + \cos \theta \frac{\partial}{\partial z}, \quad [3.8]$$

one can apply boundary condition [3.1a] to [3.7] to yield

$$\begin{aligned} \sum_{n=0}^{\infty} T_n \left[\left(\frac{2\beta}{r} - 1 \right) \alpha_n'(\rho, z) + \frac{\beta}{r} \gamma_n'(\rho, z) \right] \\ = \frac{kT |\nabla n^\infty|}{n^\infty(\mathbf{0})} \left(\frac{2\beta}{r} - 1 \right) z \quad \text{at } r = a. \end{aligned} \quad [3.9]$$

Here, the functions $\alpha_n'(\rho, z)$ and $\gamma_n'(\rho, z)$ are defined by Eqs. [A.1] and [A.2].

To satisfy the condition [3.9] exactly along the entire surface of the particle would require the solution of the entire infinite array of unknown coefficients T_n . However, the collocation technique (17–19) enforces the boundary condition at a finite number of discrete points on the semicircular generating arc of the particle and truncates the infinite series in Eq. [3.7] into a finite one. If the spherical boundary is

approximated by satisfying condition [3.1a] at N_c discrete points on its generating arc, the infinite series in Eq. [3.7] is truncated after N_c terms, resulting in a system of N_c simultaneous linear algebraic equations in the truncated form of Eq. [3.9]. This matrix equation can be solved to yield the N_c unknown coefficients T_n required in the truncated form of Eq. [3.7] for the chemical potential distribution. The accuracy of the truncation technique can be improved to any degree by taking a sufficiently large value of N_c . Naturally, as $N_c \rightarrow \infty$ the truncation error vanishes.

3.2. Fluid Velocity Distribution

With knowledge of the solution for the modified chemical potential distribution in the fluid phase, we can now proceed to find the flow field. The velocity distribution for the fluid outside the thin particle-solute interaction layer is governed by the Stokes equations (Eqs. [2.2]) or the following quasi-steady fourth-order differential equation for axisymmetric slow viscous flow,

$$E^4\Psi = E^2(E^2\Psi) = 0, \quad [3.10]$$

where the Stokes stream function Ψ is related to the velocity components in cylindrical coordinates by

$$v_\rho = \frac{1}{\rho} \frac{\partial \Psi}{\partial z}, \quad [3.11a]$$

$$v_z = -\frac{1}{\rho} \frac{\partial \Psi}{\partial \rho}, \quad [3.11b]$$

and the operator E^2 has the form

$$E^2 = \rho \frac{\partial}{\partial \rho} \left(\frac{1}{\rho} \frac{\partial}{\partial \rho} \right) + \frac{\partial^2}{\partial z^2}. \quad [3.12]$$

The boundary conditions for the velocity field, resulting from Eq. [2.5] and the fact that the fluid is motionless far away from the particle, are

$$\mathbf{v} = U\mathbf{e}_z - \frac{1}{\eta} n^\infty(\mathbf{0}) L^* K \nabla_s \mu \quad \text{at } r = a, \quad [3.13a]$$

$$\mathbf{v} = \mathbf{0} \quad \text{at } z = d, \quad [3.13b]$$

$$\mathbf{v} \rightarrow \mathbf{0} \quad \text{as } r \rightarrow \infty \text{ and } z \leq d, \quad [3.13c]$$

where $\mathbf{e}_z$ is the unit vector in the axial direction and U is the instantaneous diffusiophoretic velocity to be determined. There will be no rotation of the particle due to the axial symmetry. In Eq. [3.13a], $\nabla_s \mu$ can be obtained from the chemical potential distribution given by Eq. [3.7] with coefficients T_n determined from Eq. [3.9].

The stream function is linearly composed of two parts:

$$\Psi = \Psi_w + \Psi_s. \quad [3.14]$$

Here Ψ_w is a solution of Eq. [3.10] in cylindrical coordinates that represents the disturbance produced by the plane wall and is given by a Fourier-Bessel integral,

$$\Psi_w = \int_0^\infty \rho J_1(\omega \rho) [X(\omega) + zY(\omega)] e^{\omega z} d\omega, \quad [3.15]$$

where J_1 is the Bessel function of the first kind of order one and $X(\omega)$ and $Y(\omega)$ are unknown functions of ω . The second part of Ψ , denoted by Ψ_s , is a solution of Eq. [3.10] in spherical coordinates representing the disturbance generated by the particle and is given by

$$\Psi_s = \sum_{n=2}^{\infty} (B_n r^{-n+1} + D_n r^{-n+3}) G_n^{-1/2}(\cos \theta), \quad [3.16]$$

where $G_n^{-1/2}$ is the Gegenbauer polynomial of the first kind of order n and degree $-1/2$; B_n and D_n are unknown constants. Note that boundary condition [3.13c] is immediately satisfied by a solution of the form given by Eqs. [3.14]–[3.16].

As was the case with the solution for the modified chemical potential distribution, the determination of $X(\omega)$, $Y(\omega)$, B_n and D_n will be undertaken by a two-step procedure. First, boundary condition [3.13b] is exactly satisfied on the plane wall by a Hankel transform; then, boundary condition [3.13a] is satisfied numerically at collocation points on the particle surface. Application of boundary condition [3.13b] to Eqs. [3.14]–[3.16] using Eq. [3.11] leads to a solution for $X(\omega)$ and $Y(\omega)$ in terms of the unknown coefficients B_n and D_n . This solution is substituted back into Eq. [3.15], leading to a new expression for the stream function. Presented below is the result for the velocity components,

$$v_\rho = \sum_{n=2}^{\infty} [B_n \beta'_n(\rho, z) + D_n \delta'_n(\rho, z)], \quad [3.17a]$$

$$v_z = \sum_{n=2}^{\infty} [B_n \beta''_n(\rho, z) + D_n \delta''_n(\rho, z)], \quad [3.17b]$$

where the functions β'_n , δ'_n , β''_n , δ''_n are defined by Eqs. [A.4]–[A.7].

The only boundary condition that remains to be satisfied is that on the particle surface. Substituting Eq. [3.7] into Eq. [3.13a] one obtains

$$v_\rho = -\frac{1}{\eta} L^* K n^\infty(\mathbf{0}) \frac{z}{(\rho^2 + z^2)} \left[\sum_{n=0}^{\infty} T_n \alpha''_n(\rho, z) - \rho \right], \quad [3.18a]$$

$$v_z = U + \frac{1}{\eta} L^* K n^\infty(\mathbf{0}) \frac{\rho}{(\rho^2 + z^2)} \left[\sum_{n=0}^{\infty} T_n \alpha_n''(\rho, z) - \rho \right], \quad [3.18b]$$

at $r = a$. The definition of $\alpha_n''(\rho, z)$ is given by Eq. [A.3]. Here the first N_c coefficients T_n have been determined through the procedure given in the previous subsection. Application of these boundary conditions to Eqs. [3.17] can be accomplished by utilizing the collocation technique presented for the solution of the modified chemical potential field. At the particle surface, boundary conditions [3.18] are applied at N_v discrete points (values of θ) and the infinite series in Eqs. [3.17] are truncated after N_v terms. This generates a set of $2N_v$ linear algebraic equations for the $2N_v$ unknown coefficients B_n and D_n . The fluid velocity field is completely solved once these coefficients are determined.

3.3. Velocity of the Particle

The drag force exerted by the fluid on the spherical boundary $r = a$ can be determined from (20)

$$F = \eta \pi \int_0^\pi r^3 \sin^3 \theta \frac{\partial}{\partial r} \left(\frac{E^2 \Psi}{r^2 \sin^2 \theta} \right) r d\theta. \quad [3.19]$$

Substitution of Eqs. [3.14]–[3.16] into the above integral and application of the orthogonality properties of the Gegenbauer polynomials result in the simple relation

$$F = 4\pi\eta D_2. \quad [3.20]$$

This shows that only the coefficient D_2 contributes to the drag force on the particle.

Since the diffusiophoretic particle is freely suspended in the fluid, the net force exerted by the fluid on the surface of the particle must vanish. From Eq. [3.20], we have $D_2 = 0$. The diffusiophoretic velocity U of the particle is to be obtained by satisfying this constraint. The normalized particle velocity U/U_0 will be a function of the relaxation parameter β/a and the separation parameter a/d , where U_0 is the diffusiophoretic velocity of the particle in the absence of the plane wall and is given by Eq. [1.8]. By the linearity of the problem, the same value of the normalized diffusiophoretic velocity is predicted for a given combination of β/a and a/d whether the particle is approaching the plane wall or receding from it.

3.4. Results and Discussion

The solution for the diffusiophoretic motion of a colloidal sphere normal to a plane wall in a nonelectrolyte gradient, using the boundary collocation technique, will be presented in this section. The system of linear algebraic equations to

be solved for unknown coefficients T_n is constructed from Eq. [3.9], while that for B_n and D_n is composed of Eqs. [3.17] and [3.18]. The details of the collocation scheme used for this work were given in Keh and Lien (1991). The numerical calculations were performed by using a DEC 3000/600 workstation.

Numerical values of the wall-corrected reduced diffusiophoretic mobility for a sphere moving perpendicular to a plane wall in a nonelectrolyte gradient for various values of the parameters β/a and a/d are presented in Table 1 and depicted in Fig. 2. All of the results obtained under this collocation scheme converge to at least five significant figures. The accuracy of the truncation technique is principally a function of the relative spacing a/d . For the difficult case of $a/d = 0.995$, the number of collocation points $N_c = 140$ and $N_v = 160$ are sufficiently large to achieve this convergence. As expected, the particle will move with the velocity that would exist in the absence of the wall, given by Eq. [1.8], as $a/d = 0$. The diffusiophoretic velocity then steadily decreases as the particle approaches the wall (with increasing a/d), going to zero at the limit. It can be seen that the retardation effect produced by the wall is a monotonic decreasing function of β/a . For the case of $\beta/a = 0$, the diffusiophoretic mobility of the sphere is identical to the prediction by ignoring the polarization effect of the diffuse layers (16, 17).

4. DIFFUSIOPHORESIS NORMAL TO A PLANE WALL IN AN ELECTROLYTE GRADIENT

We now consider the axisymmetric diffusiophoretic motion of a colloidal sphere of radius a in a solution of symmet-

TABLE 1
The Normalized Diffusiophoretic Mobility of a Colloidal Sphere Moving Perpendicular to a Plane Wall in a Nonelectrolyte Solute Gradient

a/d	U/U ₀		
	$\beta/a = 0.1$	$\beta/a = 1.0$	$\beta/a = 10$
0	1	1	1
0.1	0.99941	0.99957	0.99972
0.2	0.99532	0.99655	0.99778
0.3	0.98425	0.98845	0.99264
0.4	0.96251	0.97269	0.98277
0.5	0.92564	0.94614	0.96636
0.6	0.86739	0.90437	0.94076
0.7	0.77800	0.83997	0.90133
0.8	0.64028	0.73827	0.83840
0.9	0.41854	0.56121	0.72453
0.95	0.25031	0.40497	0.61603
0.99	0.06144	0.16596	0.41482
0.995	0.03188	0.10876	0.35021

FIG. 2. Plots of the normalized diffusiophoretic mobility of a spherical particle in the direction perpendicular to a plane wall versus the separation parameter for various values of the relaxation parameter β/a .

rically charged, binary electrolyte ($M = 2$) toward an infinite plane wall whose distance from the particle is d . The concentration gradient ∇n^∞ of the electrolyte is a constant along the axial direction ($n_1^\infty = n_2^\infty = n^\infty$, where subscripts 1 and 2 refer to the anion and cation, respectively). Again we assume $a|\nabla n^\infty|/n^\infty(\mathbf{0}) \ll 1$. The thickness of the electrical double layer (similar to the particle-solute interaction layer in the previous section), which is characterized by the Debye length κ^{-1} , is assumed to be much smaller than the radius of the particle and the gap width between the particle and the plane wall. However, the effect of polarization of the diffuse layer will be taken into account. The interaction between the diffuse ions and the charged surfaces of the particle and the wall is dominated by the electrical energies $\Phi_m = z_m e \Phi_e$, where z_m is the valence of ions m ($m = 1$ or 2 ; $-z_1 = z_2 = Z$) and Φ_e is the electrical potential. The objective here is to determine the correction to Eq. [1.9] for the particle due to the presence of the wall.

Since n^∞ is not uniform, it is required that the total fluxes of cations and anions are equal in order to have no current arising from the diffusive fluxes of the solute ions in an electrically neutral solution. So an electric field arises spontaneously due to the difference in mobilities of the cation and the anion (6),

$$\mathbf{E}^\infty = -\nabla \Phi_e^\infty = \frac{kT}{Ze} \left(\frac{D_2 - D_1}{D_2 + D_1} \right) \nabla \ln n^\infty. \quad [4.1]$$

Because all the governing equations and boundary conditions are linear, diffusiophoresis in electrolytes can be con-

sidered a linear combination of two effects: (1) “chemi-phoresis” due to the nonuniform adsorption of counterions over the surface of the particle, which is analogous to diffusiophoresis in nonelectrolytes considered in the previous section; (2) “electrophoresis” due to the macroscopic electric field generated by the gradient of electrolyte concentration given by Eq. [4.1]. In Eq. [1.3] for the diffusiophoretic velocity of a particle with an unpolarized double layer, the first term in the brackets results from the contribution of electrophoresis, while the other term represents the chemi-phoretic contribution.

4.1. Modified Chemical Potential Distributions

The modified chemical potentials (also termed electrochemical potentials (21)) of the ions outside the double layers satisfy Laplace’s equation [2.1] and are subject to the boundary conditions (according to Eqs. [2.4] and [2.7])

$$\frac{\partial \mu_m}{\partial r} = - \sum_{i=1}^2 \beta_{mi} \left[\nabla^2 - \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) \right] \mu_i \quad \text{at } r = a, \quad [4.2a]$$

$$\mu_m = \mu_m^0 + kT \ln n^\infty + z_m e \Phi_e^\infty \quad \text{at } z = d, \quad [4.2b]$$

$$\mu_m \rightarrow \mu_m^0 + kT \ln n^\infty + z_m e \Phi_e^\infty \quad \text{as } r \rightarrow \infty \text{ and } z \leq d, \quad [4.2c]$$

where $m = 1$ or 2 . Analytical expressions of the relaxation coefficients β_{mi} for a symmetric electrolyte can be obtained as (9, 13)

$$\beta_{11} = \frac{1}{\kappa} \left[4 \left(1 + \frac{3f_1}{Z^2} \right) \exp(\bar{\zeta}) \sinh \bar{\zeta} - \frac{12f_1}{Z^2} (\bar{\zeta} + \ln \cosh \bar{\zeta}) \right], \quad [4.3a]$$

$$\beta_{12} = \frac{-1}{\kappa} \left(\frac{12f_1}{Z^2} \right) \ln \cosh \bar{\zeta}, \quad [4.3b]$$

$$\beta_{21} = \frac{-1}{\kappa} \left(\frac{12f_2}{Z^2} \right) \ln \cosh \bar{\zeta}, \quad [4.3c]$$

$$\beta_{22} = \frac{1}{\kappa} \left[-4 \left(1 + \frac{3f_2}{Z^2} \right) \exp(-\bar{\zeta}) \sinh \bar{\zeta} + \frac{12f_2}{Z^2} (\bar{\zeta} - \ln \cosh \bar{\zeta}) \right], \quad [4.3d]$$

where $\bar{\zeta} = Ze\zeta/4kT$ and $f_m = \epsilon(kT)^2/6\pi\eta e^2 D_m$; ζ is the zeta potential of the particle surface. Note that the plane

wall must be a conducting one to allow the electrolyte concentration and the electrical potential to be constant on it.

Similarly to the analysis to obtain Eq. [3.7] in the previous section, the solution for the modified chemical potentials that satisfies the boundary condition [4.2b] at the plane wall and the far-field condition [4.2c] is given by

$$\begin{aligned} \mu_m = & \mu_m^0 + kT \ln n^\infty - \frac{z_m}{Z} \left(\frac{D_2 - D_1}{D_2 + D_1} \right) \frac{kT |\nabla n^\infty|}{n^\infty(\mathbf{0})} z \\ & + \sum_{n=0}^{\infty} T_{mn} [B_n''(\rho, z) - B_n''(\rho, z)], \quad [4.4] \end{aligned}$$

where $m = 1$ or 2 and T_{1n} and T_{2n} are unknown coefficients to be determined by using the boundary condition [4.2a] on the particle surface. In addition to the contribution of the undisturbed solute distribution to μ_m , a contribution due to the induced electric field given by Eq. [4.1] is also included in Eq. [4.4]. Substituting Eq. [4.4] into Eq. [4.2a] with the help of Eq. [3.8] yields

$$\begin{aligned} & \sum_{n=0}^{\infty} T_{1n} \left[\left(\frac{2\beta_{11}}{r} - 1 \right) \alpha_n'(\rho, z) + \frac{\beta_{11}}{r} \gamma_n'(\rho, z) \right] \\ & + \sum_{n=0}^{\infty} T_{2n} \frac{\beta_{12}}{r} [2\alpha_n'(\rho, z) + \gamma_n'(\rho, z)] \\ & = \frac{kT |\nabla n^\infty|}{n^\infty(\mathbf{0})} \left[\left(1 - \frac{2\beta_{11}}{r} - \frac{2\beta_{12}}{r} \right) \right. \\ & \quad \left. + \left(1 - \frac{2\beta_{11}}{r} + \frac{2\beta_{12}}{r} \right) \left(\frac{D_2 - D_1}{D_2 + D_1} \right) \right] z, \quad [4.5a] \end{aligned}$$

$$\begin{aligned} & \sum_{n=0}^{\infty} T_{1n} \frac{\beta_{21}}{r} [2\alpha_n'(\rho, z) + \gamma_n'(\rho, z)] \\ & + \sum_{n=0}^{\infty} T_{2n} \left[\left(\frac{2\beta_{22}}{r} - 1 \right) \alpha_n'(\rho, z) + \frac{\beta_{22}}{r} \gamma_n'(\rho, z) \right] \\ & = \frac{kT |\nabla n^\infty|}{n^\infty(\mathbf{0})} \left[\left(1 - \frac{2\beta_{21}}{r} - \frac{2\beta_{22}}{r} \right) \right. \\ & \quad \left. + \left(-1 - \frac{2\beta_{21}}{r} + \frac{2\beta_{22}}{r} \right) \left(\frac{D_2 - D_1}{D_2 + D_1} \right) \right] z \quad [4.5b] \end{aligned}$$

at $r = a$, where $\alpha_n'(\rho, z)$ and $\gamma_n'(\rho, z)$ have been defined by Eqs. [A.1] and [A.2].

Now, the collocation technique described in the previous

section can be used. The infinite series in solution [4.4] and boundary conditions [4.5] are truncated after N_c terms and the truncated form of Eqs. [4.5] is applied at N_c discrete points (values of θ) along the particle surface. This generates a system of $2N_c$ linear algebraic equations for $2N_c$ unknown coefficients T_{1n} and T_{2n} . Once these coefficients are determined, the solution for the electrochemical potential fields is completely known.

4.2. Fluid Velocity Distribution

Having obtained the modified chemical potential distributions in the fluid phase, we can now take up the solution of the flow field. The velocity distribution for the fluid outside the thin double layers is governed by the same equation as Eq. [3.10] and obeys boundary condition [3.13b] at the plane wall and condition [3.13c] at infinity. The boundary condition on the particle surface becomes (9, 13)

$$\begin{aligned} \mathbf{v} = & U \mathbf{e}_z - \frac{\epsilon}{2\pi\eta} \frac{kT}{(Ze)^2} [(\bar{\zeta} + \ln \cosh \bar{\zeta}) \nabla_s \mu_1 \\ & + (-\bar{\zeta} + \ln \cosh \bar{\zeta}) \nabla_s \mu_2] \quad \text{at } r = a. \quad [4.6] \end{aligned}$$

The velocity components v_ρ and v_z for the fluid flow satisfying Eqs. [3.10], [3.13b], and [3.13c] can be expressed by Eqs. [3.17], and the unknown coefficients B_n and D_n should be determined from boundary condition [4.6] now. Substitution of Eq. [4.4] into Eq. [4.6] leads to

$$\begin{aligned} v_\rho = & -\frac{\epsilon\zeta}{4\pi\eta} \frac{1}{Ze} \frac{z}{(\rho^2 + z^2)} \left\{ \frac{1}{2} \sum_{n=0}^{\infty} (T_{1n} - T_{2n}) \alpha_n''(\rho, z) \right. \\ & - \frac{kT |\nabla n^\infty|}{n^\infty(\mathbf{0})} \left(\frac{D_2 - D_1}{D_2 + D_1} \right) \rho + \frac{4kT}{Ze\zeta} \ln \cosh \left(\frac{Ze\zeta}{4kT} \right) \\ & \times \left[\frac{1}{2} \sum_{n=0}^{\infty} (T_{1n} + T_{2n}) \alpha_n''(\rho, z) - \frac{kT |\nabla n^\infty|}{n^\infty(\mathbf{0})} \rho \right] \Big\}, \quad [4.7a] \end{aligned}$$

$$\begin{aligned} v_z = & U + \frac{\epsilon\zeta}{4\pi\eta} \frac{1}{Ze} \frac{\rho}{(\rho^2 + z^2)} \left\{ \frac{1}{2} \sum_{n=0}^{\infty} (T_{1n} - T_{2n}) \alpha_n''(\rho, z) \right. \\ & - \frac{kT |\nabla n^\infty|}{n^\infty(\mathbf{0})} \left(\frac{D_2 - D_1}{D_2 + D_1} \right) \rho + \frac{4kT}{Ze\zeta} \ln \cosh \left(\frac{Ze\zeta}{4kT} \right) \\ & \times \left[\frac{1}{2} \sum_{n=0}^{\infty} (T_{1n} + T_{2n}) \alpha_n''(\rho, z) - \frac{kT |\nabla n^\infty|}{n^\infty(\mathbf{0})} \rho \right] \Big\}, \quad [4.7b] \end{aligned}$$

TABLE 2
The Normalized Diffusiophoretic Mobility of a Dielectric Sphere Moving Perpendicular to a Plane Wall in a Concentration Gradient of Symmetric Electrolytes for the Case $f_1 = 0.2$ and $\kappa a = 100$

$\zeta e/kT$	a/d	U/U_0					
		$D_2 - D_1 = 0$			$(D_2 - D_1)/(D_2 + D_1) = -0.2$		
		$Z = 1$	$Z = 2$	$Z = 3$	$Z = 1$	$Z = 2$	$Z = 3$
2	0.2	0.99542	0.99575	0.99649	0.99900	0.99629	0.99718
	0.4	0.96340	0.96616	0.97224	0.99363	0.97066	0.97803
	0.6	0.87088	0.88114	0.90332	0.98667	0.89819	0.92487
	0.8	0.65020	0.67774	0.73635	0.97061	0.72431	0.79431
	0.9	0.43157	0.46989	0.55377	0.86353	0.53351	0.63469
	0.95	0.26107	0.29872	0.38678	0.64904	0.35809	0.46680
	0.99	0.06415	0.08142	0.13325	0.20075	0.10512	0.17289
	0.995	0.03314	0.04341	0.07836	0.10741	0.05692	0.10345
	0.999	0.0068	0.0093	0.0206	0.0228	0.0124	0.0279
5	0.2	0.99628	1.00286	0.99401	0.99697	0.94469	0.99440
	0.4	0.97053	1.02471	0.95170	0.97634	0.54463	0.95489
	0.6	0.89716	1.09373	0.82756	0.91883	-0.65639	0.83917
	0.8	0.72012	1.24760	0.53172	0.77856	-3.45318	0.56328
	0.9	0.53023	1.32572	0.25688	0.61143	-5.66735	0.30540
	0.95	0.36136	1.27559	0.06941	0.44068	-6.56694	0.12688
	0.99	0.11668	0.89325	-0.09369	0.15405	-5.35463	-0.03745
	0.995	0.06661	0.71943	-0.10654	0.08961	-4.41782	-0.05452
	0.999	0.0164	0.4096	-0.1000	0.0226	-2.5812	-0.0582
8	0.2	0.99891	0.99445	0.99497	1.00328	0.99465	0.99497
	0.4	0.99215	0.95532	0.95957	1.02829	0.95696	0.95962
	0.6	0.97530	0.84076	0.85622	1.10736	0.84673	0.85639
	0.8	0.92796	0.56756	0.60962	1.28087	0.58380	0.61009
	0.9	0.84043	0.31182	0.37668	1.35480	0.33682	0.37738
	0.95	0.71257	0.13417	0.21138	1.26913	0.16381	0.21218
	0.99	0.39361	-0.03137	0.04536	0.78093	-0.00210	0.04611
	0.995	0.28754	-0.04945	0.02208	0.58261	-0.02173	0.02277
	0.999	0.1295	-0.0554	0.0035	0.2693	-0.0331	0.0040

at $r = a$, where $\alpha_n''(\rho, z)$ has been defined by Eq. [A.3]. To use the collocation technique, the infinite series in Eqs. [3.17] are truncated after N_v terms and the boundary conditions [4.7] (in which the coefficients T_{1n} and T_{2n} are determined through the procedure given in the previous subsection) are applied at N_v discrete points along the particle surface. The resulting system of $2N_v$ linear algebraic equations can be solved to yield the $2N_v$ unknown coefficients B_n and D_n . The velocity distribution is completely determined once these coefficients are obtained.

4.3. Velocity of the Particle

Because the diffusiophoretic particle is freely suspended in the fluid, the drag force exerted on the particle, which is still given by Eq. [3.20], vanishes. By satisfying this requirement, the particle velocity is determined. Due to the linearity of the diffusiophoretic problem, the particle migration velocity U can be expressed as

$$U = U^c + U^e \quad [4.8]$$

where U^c and U^e denote the corresponding chemiphoretic and electrophoretic velocities, respectively. U^c can be determined from the same procedure by setting $D_1 = D_2$ in Eq. [4.4] for μ_m . U^e can also be determined similarly by taking the second term on the right-hand side of Eq. [4.4] as a constant.

4.4. Results and Discussion

In this subsection, we present the solution for the diffusiophoretic motion of a dielectric sphere normal to a conducting plane in a constant gradient of a symmetric electrolyte. To use the boundary collocation technique, Eqs. [4.5] are applied to solve the coefficients T_{1n} and T_{2n} for μ_1 and μ_2 , and Eqs. [3.17] and [4.7] are applied to solve coefficients B_n and D_n for the velocity field. The diffusiophoretic velocity of the particle has been calculated for

FIG. 3. Plots of the normalized diffusio-phoretic mobility of a spherical particle in the direction perpendicular to a plane wall versus the separation parameter with $f_1 = 0.2$ and $\kappa a = 100$: (a) $D_2 - D_1 = 0$ and $\zeta e/kT = 5$; (b) $(D_2 - D_1)/(D_2 + D_1) = -0.2$ and $\zeta e/kT = -5$.

various values of $(D_2 - D_1)/(D_2 + D_1)$, f_1 , Z , $\zeta e/kT$, κa , and a/d . Part of the numerical results of the normalized diffusio-phoretic mobility as a function of the separation parameter a/d are presented in Table 2 and depicted in Fig. 3 (with $f_1 = 0.2$, $\kappa a = 100$, $Z = 1, 2$, and 3). All the data in Table 2 are at least convergent to the digits as shown. Only the results at positive zeta potentials are displayed when $D_1 = D_2$ since the induced electric field given by Eq. [4.1] vanishes and the particle velocity, which is due to the chemi-phoretic effect only, is an even function of zeta potential. It can be seen that the diffusio-phoretic mobility of the particle is not necessarily a monotonic function of a/d . For some cases, the particle will reverse the direction of diffusio-phoresis and the magnitude of its normalized velocity can be dramatically varied when the separation distance is decreased. In general, no theoretical rule could appropriately predict the boundary effect on diffusio-phoresis. The fact that both the chemi-phoretic and the electrophoretic effects (which react differently to the neighboring wall) contribute to the particles' movement is responsible for this complexity. Although it is difficult to obtain convergent results of the particle velocity for situations of very small separation distance ($a/d > 0.999$), both the physical reasoning and the numerical tendency indicate that $U/U_0 \rightarrow 0$ as $a/d \rightarrow 1$. Note that the electrolytes associated with $(D_2 - D_1)/(D_2 + D_1) = 0$ and -0.2 in Table 2 and Fig. 3 are very close to the aqueous solutions of KCl and NaCl, respectively.

In Figs. 4 and 5, the normalized diffusio-phoretic mobility of a particle moving perpendicular to a plane wall is

plotted versus κa in the range from 10^2 to 10^6 for cases of $(D_2 - D_1)/(D_2 + D_1) = 0$ and -0.2 , respectively (with $a/d = 0.6$). It is evident that, as κa becomes very large, the diffusio-phoretic mobility of the sphere will approach the value calculated by ignoring the polarization effect of the double layers (shown by a dashed line in each figure). From Figs. 4a and 5a for the case $Z = 1$, the boundary effect is weakened steadily (the value of U/U_0 is getting close to unity) as κa becomes small gradually. A novel result is that, as shown in Figs. 4b, 4c, 5b, and 5c for $Z = 2$ and $Z = 3$, there can be a maximum and a minimum of the normalized particle mobility occurring at some κa for the representative cases of $\zeta e/kT = -5, 5$, and 8 . If the particle is charged more highly or the counterions have a larger magnitude of valence, the locations of these maximal boundary effects will shift toward larger κa ; that means larger values of κa are required to make the assumption of $\kappa a \rightarrow \infty$ valid. Because the direction of diffusio-phoresis of an isolated particle can reverse with the variation of $\zeta e/kT$ or κa (11–13), these extremes arise at combinations of $\zeta e/kT$ and κa in which the magnitude of U_0 is very small.

5. ELECTROPHORESIS NORMAL TO A PLANE WALL

Considered in this section is the axisymmetric electrophoretic motion of a charged particle of radius a toward an infinite plane wall whose distance from the particle is d . The applied electric field is uniform and equal to $E^\infty \mathbf{e}_z$. The bulk concentrations of all ions n_m^∞ beyond the electrical double layers are constant. It is assumed that $\kappa a \gg 1$ and $\kappa(d$

FIG. 4. Plots of the normalized diffusioelectric mobility of a spherical particle in the direction perpendicular to a plane wall versus the ratio of the particle radius to the Debye length with $a/d = 0.6$ and $f_1 = f_2 = 0.2$ ($D_2 - D_1 = 0$): (a) $Z = 1$; (b) $Z = 2$; (c) $Z = 3$.

$-a) \gg 1$, but the effect of double layer relaxation is incorporated. The potential energy Φ_m of ionic species m is equal to $z_m e \Phi_e$. For simplicity, only one symmetric electrolyte in the liquid phase ($M = 2$; $-z_1 = z_2 = Z$; $n_1^\infty = n_2^\infty = n^\infty$, where subscripts 1 and 2 denote anion and cation, respectively) will be considered. Now the object is to obtain the correction to Eq. [1.4] for the particle due to the presence of the wall.

5.1. Modified Chemical Potential Distributions

Outside the double layers, the electrochemical potentials of the ions satisfy Laplace's equation [2.1] and the

boundary conditions [4.2] (with $\Phi_e^\infty = -E^\infty z$). Similar to Eqs. [3.7] and [4.4], the solution for the electrochemical potentials that satisfies Eqs. [4.2b] and [4.2c] can be expressed as

$$\mu_m = \mu_m^0 + kT \ln n^\infty - z_m e E^\infty z + \sum_{n=0}^{\infty} T_{mn} [B_n''(\rho, z) - B_n''(\rho, 2d - z)], \quad [5.1]$$

where $m = 1$ or 2 and T_{1n} and T_{2n} are unknown coefficients to be determined from the boundary condition [4.2a].

FIG. 5. Plots of the normalized diffusio-phoretic mobility of a spherical particle in the direction perpendicular to a plane wall versus the ratio of the particle radius to the Debye length with $a/d = 0.6$, $(D_2 - D_1)/(D_2 + D_1) = -0.2$, and $f_1 = 0.2$: (a) $Z = 1$; (b) $Z = 2$; (c) $Z = 3$.

Substituting Eq. [5.1] into Eq. [4.2a] with the help of Eq. [3.8] results in

$$\begin{aligned} & \sum_{n=0}^{\infty} T_{1n} \left[\left(\frac{2\beta_{11}}{r} - 1 \right) \alpha'_n(\rho, z) + \frac{\beta_{11}}{r} \gamma'_n(\rho, z) \right] \\ & + \sum_{n=0}^{\infty} T_{2n} \frac{\beta_{12}}{r} [2\alpha'_n(\rho, z) + \gamma'_n(\rho, z)] \\ & = ZeE^{\infty} \left(1 - \frac{2\beta_{11}}{r} + \frac{2\beta_{12}}{r} \right) z, \end{aligned} \quad [5.2a]$$

$$\begin{aligned} & \sum_{n=0}^{\infty} T_{1n} \frac{\beta_{21}}{r} [2\alpha'_n(\rho, z) + \gamma'_n(\rho, z)] \\ & + \sum_{n=0}^{\infty} T_{2n} \left[\left(\frac{2\beta_{22}}{r} - 1 \right) \alpha'_n(\rho, z) + \frac{\beta_{22}}{r} \gamma'_n(\rho, z) \right] \\ & = ZeE^{\infty} \left(-1 - \frac{2\beta_{21}}{r} + \frac{2\beta_{22}}{r} \right) z, \end{aligned} \quad [5.2b]$$

at $r = a$. As described in the previous sections, we can use the collocation technique to solve the first N_c sets of the coefficients T_{1n} and T_{2n} .

TABLE 3

The Normalized Electrophoretic Mobility of a Dielectric Sphere Moving Perpendicular to a Plane Wall in a Solution of Symmetric Electrolytes for the Case $f_1 = f_2 = 0.2$ and $\kappa a = 100$

$\zeta e/kT$	a/d	U/U_0		
		$Z = 1$	$Z = 2$	$Z = 3$
2	0.2	0.99511	0.99528	0.99565
	0.4	0.96076	0.96224	0.96529
	0.6	0.86075	0.86633	0.87748
	0.8	0.62218	0.63725	0.66684
	0.9	0.39379	0.41460	0.45672
	0.95	0.22716	0.24713	0.29083
	0.99	0.05222	0.06084	0.08574
	0.995	0.02666	0.03169	0.04829
	0.999	0.0054	0.0066	0.0119
5	0.2	0.99557	0.99639	0.99557
	0.4	0.96460	0.97135	0.96454
	0.6	0.87502	0.89916	0.87433
	0.8	0.66040	0.72497	0.65886
	0.9	0.44731	0.54830	0.45240
	0.95	0.28047	0.40387	0.30114
	0.99	0.07873	0.19900	0.13336
	0.995	0.04327	0.14864	0.10354
	0.999	0.0100	0.0774	0.0687
8	0.2	0.99630	0.99538	0.99500
	0.4	0.97057	0.96295	0.95980
	0.6	0.89645	0.86854	0.85707
	0.8	0.71721	0.64315	0.61194
	0.9	0.53339	0.42831	0.38026
	0.95	0.38067	0.27270	0.21565
	0.99	0.16313	0.10610	0.04967
	0.995	0.11205	0.07869	0.02613
	0.999	0.0464	0.0496	0.0063

5.2. Fluid Velocity Distribution

Same as the case of diffusiophoresis considered in the previous section, the velocity distribution for the fluid outside the double layers is governed by Eqs. [3.10], [4.6], [3.13b], and [3.13c]. The solution for the velocity components v_ρ and v_z that satisfies boundary condition [3.13b] and [3.13c] is still given by Eqs. [3.17], and the coefficients B_n and D_n are to be determined by using condition [4.6]. Substituting Eq. [5.1] into Eq. [4.6], one obtains

$$v_\rho = -\frac{\epsilon\zeta}{4\pi\eta} \frac{1}{Ze} \frac{z}{(\rho^2 + z^2)} \times \left[\sum_{n=0}^{\infty} (T_{1n} - T_{2n}) \alpha_n''(\rho, z) - 2ZeE^\infty \rho + \frac{kT}{Ze\zeta} \times \ln \cosh\left(\frac{Ze\zeta}{4kT}\right) \sum_{n=0}^{\infty} (T_{1n} + T_{2n}) \alpha_n''(\rho, z) \right], \quad [5.3a]$$

$$v_z = U + \frac{\epsilon\zeta}{4\pi\eta} \frac{1}{Ze} \frac{\rho}{(\rho^2 + z^2)} \times \left[\sum_{n=0}^{\infty} (T_{1n} - T_{2n}) \alpha_n''(\rho, z) - 2ZeE^\infty \rho + \frac{kT}{Ze\zeta} \times \ln \cosh\left(\frac{Ze\zeta}{4kT}\right) \sum_{n=0}^{\infty} (T_{1n} + T_{2n}) \alpha_n''(\rho, z) \right], \quad [5.3b]$$

at $r = a$. The coefficients B_n and D_n can be solved by the substitution of the truncated form of Eqs. [3.17] into Eqs. [5.3] using the collocation technique presented in the previous sections.

5.3. Velocity of the Particle

Similar to the cases of diffusiophoresis considered in the previous sections, the electrophoretic particle is freely suspended in the fluid, and the drag force exerted on the particle, which is expressed by Eq. [3.20], equals zero. The electrophoretic velocity of the particle can be determined by satisfying this constraint. This particle velocity is the same as the electrophoretic velocity U^e obtained in the previous section with the substitution of Eq. [4.1].

5.4. Results and Discussion

The solution for the electrophoresis of a charged sphere normal to a conducting plane in a symmetric electrolyte will be presented in this subsection. To use the collocation technique, Eqs. [5.2] are applied to solve the coefficients T_{1n} and T_{2n} for μ_1 and μ_2 , and Eqs. [3.17] and [5.3] are applied to solve B_n and D_n for the flow field. The electrophoretic velocity of the particle has been calculated for various values of $f_1, f_2, Z, \zeta e/kT, \kappa a$, and a/d . Part of the numerical results of the normalized electrophoretic mobility as a function of a/d are listed in Table 3. It can be seen that the electrophoretic velocity of the particle is a monotonic decreasing function of a/d and vanishes as $a/d = 1$.

Figure 6 is drawn to show the effect of the plane wall on the electrophoretic sphere versus the particle's zeta potential for three cases of κa when the separation parameter a/d is kept constant. When $Z = 1$, as illustrated in Fig. 6a, the normalized electrophoretic mobility of the particle is a monotonic increasing function of the nondimensional zeta potential $\zeta e/kT$ ranging from 0 to 8. Also, the value of U/U_0 is larger with smaller κa . However, when $Z = 2$ or 3 as shown in Figs. 6b and 6c, a maximum of U/U_0 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 Fig. 7, the normalized electrophoretic mobility of the

FIG. 6. Plots of the normalized electrophoretic mobility of a spherical particle in the direction perpendicular to a plane wall versus the dimensionless zeta potential with $a/d = 0.6$ and $f_1 = f_2 = 0.2$: (a) $Z = 1$; (b) $Z = 2$; (c) $Z = 3$.

particle is plotted versus κa for three cases of $\zeta e/kT$ with $a/d = 0.6$. It is shown that the electrophoretic mobility of the particle will approach the value calculated in the limit of Eq. [1.7] (indicated by a dashed line) for each case as long as the value of κa approaches infinity. From Fig. 7a for the case $Z = 1$, the boundary effect is weakened steadily as κa becomes small gradually. However, as shown in Figs. 7b and 7c for $Z = 2$ and 3 respectively, there can be a maximum of U/U_0 at some κa for the representative cases of $\zeta e/kT = 5$ and 8. This observation can also be predicted from Figs. 6b and 6c. If the particle is charged more highly or the counterions have a larger magnitude of valence, the locations of these maxima will shift toward larger κa .

6. SUMMARY

Three problems of similar physical and mathematical structures are studied in this work: the diffusiophoresis of a sphere normal to a plane in a nonelectrolyte solute gradient, the diffusiophoresis of a sphere normal to a plane in an electrolyte solute gradient, and the electrophoresis of a sphere normal to a plane in an external electric field. Although the region of the interaction between the solute species and the solid surfaces is taken to be small relative to the particle dimension and to the spacing between the particle and the wall, the assumptions allow for polarization of the mobile species in the diffuse layer. The method devel-

FIG. 7. Plots of the normalized electrophoretic mobility of a spherical particle in the direction perpendicular to a plane wall versus the ratio of the particle radius to the Debye length with $a/d = 0.6$ and $f_1 = f_2 = 0.2$: (a) $Z = 1$; (b) $Z = 2$; (c) $Z = 3$.

oped for treating the electrokinetic equations in the limit of thin double layer (4, 8) is used to obtain the equations of conservation and the boundary conditions in the “outer” region applicable to the problems.

A semianalytical procedure with the boundary collocation technique has been used to solve the modified chemical potential energy field and the velocity field in the fluid phase. The migration velocity of the particle perpendicular to the plane wall is calculated for various cases. For the case of diffusiophoresis in a nonelectrolyte gradient, the particle mobility decreases monotonically as the particle approaches the wall and goes to zero in the limit. The larger the polarization effect in

the diffuse layer (or the value of β/a) is, the weaker the boundary effect on the diffusiophoresis is. For the case of diffusiophoresis in an electrolyte gradient, the interaction between the particle and the wall is a complicated function of the properties of the particle and ions, and it no longer varies monotonically with the extent of separation for some situations. For the case of electrophoresis, the particle mobility decreases monotonically with the decrease in the separation distance between the particle and the wall, but it is not a simple function of the particle’s and ions’ properties. No general rule can make an adequate prediction for such complicated phenomena present in electrophoresis and ionic diffusiophoresis.

APPENDIX

For the purpose of conciseness the definitions of some functions in Sections 3–5 are listed here:

$$\alpha'_n(\rho, z) = \rho[A_n(\rho, z) - A_n(\rho, 2d - z)] \\ - (n + 1)z[B''_{n+1}(\rho, z) + B''_{n+1}(\rho, 2d - z)], \quad [\text{A.1}]$$

$$\gamma'_n(\rho, z) = \rho^2[C_n(\rho, z) - C_n(\rho, 2d - z)] \\ - 2(n + 1)\rho z[A_{n+1}(\rho, z) + A_{n+1}(\rho, 2d - z)] \\ + (n + 1)(n + 2)z^2[B''_{n+2}(\rho, z) - B''_{n+2}(\rho, 2d - z)], \quad [\text{A.2}]$$

$$\alpha''_n(\rho, z) = z[A_n(\rho, z) - A_n(\rho, 2d - z)] \\ + (n + 1)\rho[B''_{n+1}(\rho, z) + B''_{n+1}(\rho, 2d - z)], \quad [\text{A.3}]$$

$$\beta'_n(\rho, z) = B'_n(\rho, z) - B'_n(\rho, 2d - z) \\ + 2(n + 1)(d - z)B'_{n+1}(\rho, 2d - z), \quad [\text{A.4}]$$

$$\delta'_n(\rho, z) = D'_n(\rho, z) - D'_n(\rho, 2d - z) \\ - (2/n)(n - 1)(n - 3)(d - z)B'_{n-1}(\rho, 2d - z) \\ + 2(2n - 3)d(d - z)B'_n(\rho, 2d - z), \quad [\text{A.5}]$$

$$\beta''_n(\rho, z) = B''_n(\rho, z) - B''_n(\rho, 2d - z) \\ - 2(n + 1)(d - z)B''_{n+1}(\rho, 2d - z), \quad [\text{A.6}]$$

$$\delta''_n(\rho, z) = D''_n(\rho, z) - D''_n(\rho, 2d - z) \\ + 2(n - 2)(d - z)B''_{n-1}(\rho, 2d - z) \\ - 2(2n - 3)d(d - z)B''_n(\rho, 2d - z), \quad [\text{A.7}]$$

where

$$A_n(\rho, z) = \frac{nz^2 - (n + 1)\rho^2}{\rho(\rho^2 + z^2)^{(n+3)/2}} P_n \left[\frac{z}{(\rho^2 + z^2)^{1/2}} \right] \\ - \frac{nz}{\rho(\rho^2 + z^2)^{(n+2)/2}} P_{n-1} \left[\frac{z}{(\rho^2 + z^2)^{1/2}} \right], \quad [\text{A.8}]$$

$$C_n(\rho, z) = [-(n + 1)(\rho^2 + z^2) - n\rho^{-2}z^2(\rho^2 + z^2) \\ + (n + 1)(n + 3)\rho^2 - 2n(n + 2)z^2 \\ + n^2\rho^{-2}z^4] \cdot \frac{1}{(\rho^2 + z^2)^{(n+5)/2}} P_n \left[\frac{z}{(\rho^2 + z^2)^{1/2}} \right]$$

$$+ [n(2n + 3)z - n(2n - 1)\rho^{-2}z^3 \\ + n\rho^{-2}z(\rho^2 + z^2)] \cdot \frac{1}{(\rho^2 + z^2)^{(n+4)/2}} P_{n-1} \left[\frac{z}{(\rho^2 + z^2)^{1/2}} \right] \\ + \frac{n(n - 1)z^2}{\rho^2(\rho^2 + z^2)^{(n+3)/2}} P_{n-2} \left[\frac{z}{(\rho^2 + z^2)^{1/2}} \right], \quad [\text{A.9}]$$

$$B'_n(\rho, z) = \frac{n + 1}{\rho(\rho^2 + z^2)^{n/2}} G_{n+1}^{-1/2} \left[\frac{z}{(\rho^2 + z^2)^{1/2}} \right], \quad [\text{A.10}]$$

$$D'_n(\rho, z) = \frac{n + 1}{\rho(\rho^2 + z^2)^{(n-2)/2}} G_{n+1}^{-1/2} \left[\frac{z}{(\rho^2 + z^2)^{1/2}} \right] \\ - \frac{2z}{\rho(\rho^2 + z^2)^{(n-1)/2}} G_n^{-1/2} \left[\frac{z}{(\rho^2 + z^2)^{1/2}} \right], \quad [\text{A.11}]$$

$$B''_n(\rho, z) = \frac{1}{(\rho^2 + z^2)^{(n+1)/2}} P_n \left[\frac{z}{(\rho^2 + z^2)^{1/2}} \right], \quad [\text{A.12}]$$

$$D''_n(\rho, z) = \frac{2}{(\rho^2 + z^2)^{(n-1)/2}} G_n^{-1/2} \left[\frac{z}{(\rho^2 + z^2)^{1/2}} \right] \\ + \frac{1}{(\rho^2 + z^2)^{(n-1)/2}} P_n \left[\frac{z}{(\rho^2 + z^2)^{1/2}} \right]. \quad [\text{A.13}]$$

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

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