Electrophoresis in a Dilute Dispersion of Colloidal Spheres

An analytical study of the electrophoretic motion of two freely-suspended, nonconducting spheres with thin electrical double layers is presented using a method of reflections. The particles may differ in radius and/or in zeta potential at the surface, and they are oriented arbitrarily relative to the direction of applied electric field. Corrections to Smoluchowski's equation due to particle interactions are determined in a power series of $1/r_{12}$ up to $O(r_{12}^{-7})$, where r_{12} is the center-to-center distance between the particles. It is found that the electrophoretic particles do not interact with one another when they have equal zeta potentials. For the specific case of spheres with identical radii, our results agree well with the exact calculations using bipolar coordinates. Based on a microscopic model, the results for two particles are used to find the effect of volume fractions of particles of each type on the mean particle velocities in a bounded dispersion. Of particular interest is the electrophoresis of a suspension of particles with arbitrary size distribution but with identical zeta potentials, in which the sole factor influencing the mean particle velocity is the volume fraction of all particles. In general, the effect of particle interactions on electrophoresis is much weaker than that on sedimentation.

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Introduction

A colloidal particle in an electrolyte solution moves through the liquid when an electric field is imposed on the particle. This motion is termed electrophoresis and has been the subject of many investigations. The electrophoretic velocity $\underline{U}^{(0)}$ of a single charged particle suspended in an unbounded fluid of viscosity η and dielectric constant ϵ_r is related to the applied electric field $\underline{E}_\infty$ by the Smoluchowski equation:

$$\underline{U}^{(0)} = \left(\frac{\epsilon\zeta}{4\pi\eta}\right)\underline{E}_\infty \qquad (1)$$

where ζ is the zeta potential of the particle surface, which is assumed uniform over distances comparable to the particle dimension. In SI units, ϵ equals $4\pi\epsilon_o\epsilon_r$, where ϵ_o is the permittivity of free space. The ratio $U^{(0)}/E_\infty$ is known as the electrophoretic mobility of the particle. The Smoluchowski equation applies to particles of any shape, provided that the local radii of curvature of the particle are much larger than the thickness of the electrical double layer surrounding the particle and that the undisturbed electric field $\underline{E}_\infty$ is constant (Morrison, 1970; Dukhin and Derjaguin, 1974; Hunter, 1981). For a nonconducting colloidal sphere, Eq. 1 holds even if $\underline{E}_\infty$ varies appreciably over length scales comparable to the particle size, with $\underline{E}_\infty$ evaluated at the position of the particle center; there is no rotational motion of the sphere (Keh and Anderson, 1985).

In many applications of electrophoresis to particle analysis or separation, colloidal particles are not isolated. So, it is important to determine if the presence of neighboring particles and/or boundaries significantly affects movement of the particles. During the past two decades, much progress has been made in the mathematical analysis concerning the applicability of Eq. 1 for charged spheres surrounded by a thin electrical double layer in a variety of systems. Through an exact representation in spherical bipolar coordinates, the electrophoretic velocity of a nonconducting sphere in the presence of a large plane surface was obtained in two special cases: the migration occurring normal to a conducting plane (Morrison and Stukel, 1970) as well as the movement being parallel to a nonconducting surface (Keh and Chen, 1988). The electrophoretic motions of a nonconducting

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sphere near a single-plane wall and inside a long pore has also been investigated using a method of reflections (Keh and Anderson, 1985). In these analyses, corrections to Smoluchowski's equation were presented for various separation distances between particle and wall. The effect of the parallel wall to the electrophoresis was found to impede the particle velocity for the case of moderate to large separations, while this velocity can be enhanced when the gap widths become small. On the contrary, the electrophoretic velocity decreases steadily as the particle approaches the normal wall and goes to zero in the limit. Another important result of these studies is that the boundary effect on electrophoresis is much weaker than for sedimentation, because the disturbance to the fluid velocity field caused by the electrophoresis sphere decays (as r^{-3}) faster than that caused by a Stokeslet (as r^{-1}) (Happel and Brenner, 1983), where r is the distance from the particle center.

On the other hand, Reed and Morrison (1976) solved the electrophoretic problem of two arbitrarily oriented spheres of equal radii using the spherical bipolar coordinates. Their results of correction to Smoluchowski's equation were presented for various separation distances as well as several values of the particles' zeta potential ratio and showed no particle interaction for the case of two spheres with identical zeta potentials. Based on a microscopic model, Anderson (1981) utilized these data for two equal-size spheres to find the concentration effect on electrophoretic mobility in a bounded, dilute dispersion; the dependence is also relatively weaker than the corresponding case of gravity settling. Since the particles in a suspension may have a wide distribution in dimension, one must determine the interactions among different particles due to differences not only in zeta potential, but also in size.

In this paper, we derive the electrophoretic velocities of two coexistent charged spheres, with radii a_1 and a_2 which could differ, as a function of their center-to-center distance r_{12} and orientation $\underline{e}$. Both spheres are free to rotate. The thin double layer assumption is employed. A method of reflections is utilized to evaluate the effects of one particle on the local electric and velocity fields experienced by the other particle. The correction to Smoluchowski's equation is sought in a power series of terms $\beta_{mn}(a_1/r_{12})^m(a_2/r_{12})^n$, and the result is obtained in Eq. 20. As in the case of spheres with identical radii, here again, the electrophoresis of two particles with equal zeta potentials shows no particle interaction. Our results compare favorably with the numerical calculations of Reed and Morrison (1976) for the special case of two spheres with identical radii. The two-particle interactions are then applied to theories of concentration effects on transport properties in dilute dispersions to obtain the effect of particle volume fractions on the mean velocities of particles of each type, and the general result is given in Eq. 28. We will demonstrate that the only factor, which affects the mean particle velocity, is the total volume fraction of particles in suspension for particles with equal zeta potentials, regardless of the distribution in particle size. For a suspension of equal-size spheres, our result agrees quite well with the result of concentration effect on electrophoresis calculated from the exact solution of two-particle interactions.

Description of the Problem for Two Particles

As shown in Figure 1, we consider the electrophoretic motion of two spherical particles of radii a_1 and a_2. They are oriented at

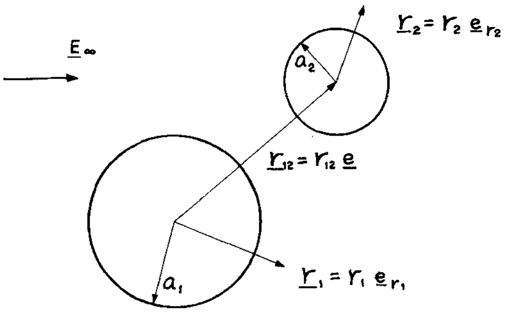

Figure 1. Electrophoretic motion of two spheres.

an arbitrary angle to an applied electric field $\underline{E}_\infty$. The particles are supposed to be sufficiently close to interact electrostatically and hydrodynamically with each other, but sufficiently distant from boundary walls for the surrounding fluid to be regarded as unbounded. Let $\underline{e}$ be the unit vector defining orientation of the two spheres and r_{12} be their center-to-center distance, hence $\underline{r}_{12} = r_{12}\,\underline{e}$ is the vector from the center of particle 1 to the center of particle 2. $\underline{E}_\infty$ is assumed to be constant over distances comparable to r_{12} and the fluid at infinity is at rest.

Since the fluid outside the thin electrical double layer is neutral, the electrostatic equation governing the electric field distribution $\underline{E}(\underline{x})$ is given by

$$\nabla \cdot \underline{E} = 0 \tag{2}$$

The boundary conditions require that the electric field far away from the two particles approach the undisturbed value and that the normal component of the current flux at each particle surface be identically zero (because the particles are nonconducting). Thus

$$\underline{e}_{r_1} \cdot \underline{E} = 0 \quad \text{at } \underline{r}_1 = a_1\underline{e}_{r_1} \tag{3a}$$

$$\underline{e}_{r_2} \cdot \underline{E} = 0 \quad \text{at } \underline{r}_2 = a_2\underline{e}_{r_2} \tag{3b}$$

$$\underline{E} \rightarrow \underline{E}_\infty \quad \text{as } r_1 \rightarrow \infty \quad \text{and} \quad r_2 \rightarrow \infty \tag{3c}$$

Here, $\underline{r}_1 = r_1\underline{e}_{r_1}$ and $\underline{r}_2 = r_2\underline{e}_{r_2}$ are the position vectors relative to the centers of particle 1 and particle 2, respectively. $\underline{e}_{r_1}$ and $\underline{e}_{r_2}$ are the corresponding unit vectors.

Due to the low velocities encountered in electrokinetic flows, the fluid motion outside the thin double layers is governed by the quasisteady Stokes equations:

$$\eta\nabla^2\underline{v} - \nabla p = \underline{0} \tag{4a}$$

$$\nabla \cdot \underline{v} = 0 \tag{4b}$$

where $\underline{v}(\underline{x})$ is the fluid velocity and $p(\underline{x})$ is the dynamic pressure. Because the electric field interacts with the double layer at the particle surface to produce a relative tangential fluid velocity at the outer edge of the double layer and the fluid is motionless far away from the particles, the boundary conditions are (Keh and

Anderson, 1985):

$$\underline{v} = \underline{U}_1 - \frac{\epsilon\zeta_1}{4\pi\eta}\underline{E} + \underline{\Omega}_1 \times \underline{r}_1 \quad \text{at } \underline{r}_1 = a_1\underline{e}_{r_1} \tag{5a}$$

$$\underline{v} = \underline{U}_2 - \frac{\epsilon\zeta_2}{4\pi\eta}\underline{E} + \underline{\Omega}_2 \times \underline{r}_2 \quad \text{at } \underline{r}_2 = a_2\underline{e}_{r_2} \tag{5b}$$

$$\underline{v} \rightarrow \underline{0} \quad \text{as } r_1 \rightarrow \infty \quad \text{and} \quad r_2 \rightarrow \infty \tag{5c}$$

where ζ_i is the zeta potential at the surface of particle $i (i = 1$ or $2)$; $\underline{U}_i$ and $\underline{\Omega}_i$ are the instantaneous translational and rotational velocities, respectively, of the particle to be determined. Equations 5a and 5b provide the coupling between the electric field and the fluid motion, and $\underline{E}$ should be determined from Eqs. 2 and 3. Note that the normal component of $\underline{E}$ vanishes at particle surfaces in accordance with the Helmholtz relation for electroosmotic flows, and the term "surface" is understood to mean outer edge of the electrical double layer.

Since the particles are freely suspended in the liquid and the "surface" of each encloses a neutral body (charged interface plus diffuse ions), the electric field produces no net force or couple on either particle. Thus, to determine the particle velocities, the requirement of zero force and zero torque exerted by the fluid on the particle surface must be fulfilled.

Solution for the Particle Velocities

For the motion of a freely-suspended, uniformly-charged sphere under an arbitrary applied electric field $\underline{E}_A(\underline{x})$ and velocity field $\underline{v}_A(\underline{x})$ in an unbounded fluid, the translational and angular velocities of the particle can be obtained by combining the generalized Smoluchowski equation and Faxen's law in the limit of $\kappa a \rightarrow \infty$ (Keh and Anderson, 1985):

$$\underline{U} = \frac{\epsilon\zeta}{4\pi\eta}(\underline{E}_A)_0 + (\underline{v}_A)_0 + \frac{1}{6}a^2(\nabla^2\underline{v}_A)_0 \tag{6a}$$

$$\underline{\Omega} = \tfrac{1}{2}(\nabla \times \underline{v}_A)_0 \tag{6b}$$

where a is the particle radius, κ is the Debye screening parameter, and subscript 0 denotes the position of the sphere center. The superposition of the electrokinetic and hydrodynamic contributions in the above equations is valid because both the governing equations and the boundary conditions in the region outside the thin double layer are linear. Note that $\underline{E}_A$ makes no contribution to the rotation of the sphere, so Eq. 6b contains only the effect of applied velocity field.

In the situation $(a_1 + a_2)/r_{12} \ll 1$, a method of reflections (Happel and Brenner, 1983; Keh and Anderson, 1985; Anderson, 1985) is used to solve the two-sphere problem. The solution of local electric and velocity fields for Eqs. 2 to 5 may be decomposed into a sum of fields, which depend on increasing powers of r_{12}^{-1}:

$$\underline{E} = \underline{E}_1^{(1)} + \underline{E}_2^{(2)} + \underline{E}_1^{(3)} + \underline{E}_2^{(4)} + \cdots \tag{7a}$$

$$\underline{v} = \underline{v}_1^{(1)} + \underline{v}_2^{(2)} + \underline{v}_1^{(3)} + \underline{v}_2^{(4)} + \cdots \tag{7b}$$

where subscripts 1 and 2 represent the reflections from particle 1 and particle 2 respectively, and the superscript (i) denotes the ith reflection from either particle surface. In these series, each set of the corresponding electric field and velocity $(\underline{E}_j^{(i)}, \underline{v}_j^{(i)})$ separately satisfies governing Eqs. 2 and 4. The advantage of this method is that the boundary-value problem may be solved to any degree of approximation by considering boundary conditions associated with only one particle surface at a time.

According to Eq. 7, the particle velocities can also be expressed in the form of a series:

$$\underline{U}_1 = \underline{U}_1^{(0)} + \underline{U}_1^{(2)} + \underline{U}_1^{(4)} + \cdots \tag{8a}$$

$$\underline{\Omega}_1 = \underline{\Omega}_1^{(0)} + \underline{\Omega}_1^{(2)} + \underline{\Omega}_1^{(4)} + \cdots \tag{8b}$$

$$\underline{U}_2 = \underline{U}_2^{(1)} + \underline{U}_2^{(3)} + \underline{U}_2^{(5)} + \cdots \tag{8c}$$

$$\underline{\Omega}_2 = \underline{\Omega}_2^{(1)} + \underline{\Omega}_2^{(3)} + \underline{\Omega}_2^{(5)} + \cdots \tag{8d}$$

where $\underline{U}_1^{(i)}$ and $\underline{\Omega}_1^{(i)}$ are related to $\underline{E}_2^{(i)}$ and $\underline{v}_2^{(i)}$ by Eq. 6 for $i = 2, 4, 6, \ldots$, while $\underline{U}_2^{(i)}$ and $\underline{\Omega}_2^{(i)}$ are related to $\underline{E}_1^{(i)}$ and $\underline{v}_1^{(i)}$ for $i = 1, 3, 5, \ldots$. Obviously, the unperturbed electric field $\underline{E}_\infty$ gives

$$\underline{U}_1^{(0)} = \frac{\epsilon\zeta_1}{4\pi\eta}\underline{E}_\infty \tag{9a}$$

$$\underline{\Omega}_1^{(0)} = \underline{0} \tag{9b}$$

The initial electric field $\underline{E}_1^{(1)}$ and velocity field $\underline{v}_1^{(1)}$, which correspond to the electrophoresis of particle 1 isolated in an unbounded fluid under $\underline{E}_\infty$, are easily obtained for $r_1 \geq a_1$ as:

$$\underline{E}_1^{(1)} = \underline{E}_\infty - \frac{1}{2}\left(\frac{a_1}{r_1}\right)^3(3\underline{e}_{r_1}\underline{e}_{r_1} - \underline{\underline{I}}) \cdot \underline{E}_\infty \tag{10a}$$

$$\underline{v}_1^{(1)} = \frac{\epsilon\zeta_1}{4\pi\eta}\left[\frac{1}{2}\left(\frac{a_1}{r_1}\right)^3(3\underline{e}_{r_1}\underline{e}_{r_1} - \underline{\underline{I}}) \cdot \underline{E}_\infty\right] \tag{10b}$$

where $\underline{\underline{I}}$ is the unit dyadic. Note that $\underline{v}_1^{(1)}$ is irrotational and satisfies Laplace's equation.

The contributions of $\underline{E}_1^{(1)}$ and $\underline{v}_1^{(1)}$ to the velocity of particle 2 are determined from Eq. 6. It is found that

$$[\underline{E}_1^{(1)}]_{\underline{r}_1 = r_{12}\underline{e}} = \underline{E}_\infty - \frac{1}{2}\left(\frac{a_1}{r_{12}}\right)^3(3\underline{e}\underline{e} - \underline{\underline{I}}) \cdot \underline{E}_\infty \tag{11a}$$

$$[\underline{v}_1^{(1)}]_{\underline{r}_1 = r_{12}\underline{e}} = \frac{\epsilon\zeta_1}{4\pi\eta}\left[\frac{1}{2}\left(\frac{a_1}{r_{12}}\right)^3(3\underline{e}\underline{e} - \underline{\underline{I}}) \cdot \underline{E}_\infty\right] \tag{11b}$$

where $\underline{r}_1 = r_{12}\underline{e}$ represents the position of the center of particle 2. Thus,

$$\underline{U}_2^{(1)} = \frac{\epsilon\zeta_2}{4\pi\eta}\underline{E}_\infty + \frac{\epsilon}{4\pi\eta}(\zeta_1 - \zeta_2)\left[\frac{1}{2}\left(\frac{a_1}{r_{12}}\right)^3(3\underline{e}\underline{e} - \underline{\underline{I}}) \cdot \underline{E}_\infty\right] \tag{12a}$$

$$\underline{\Omega}_2^{(1)} = \underline{0} \tag{12b}$$

The boundary conditions for the succeeding reflected fields from particle 2 are derived from Eqs. 3b, 3c, 5b and 5c:

$$r_2 = a_2: \underline{e}_{r_2} \cdot \underline{E}_2^{(2)} = -\underline{e}_{r_2} \cdot \underline{E}_1^{(1)} \quad (13a)$$

$$\underline{v}_2^{(2)} = -\underline{v}_1^{(1)} + \underline{U}_2^{(1)} + \underline{\Omega}_2^{(1)} \times \underline{r}_2 - \frac{\epsilon\zeta_2}{4\pi\eta}[\underline{E}_1^{(1)} + \underline{E}_2^{(2)}] \quad (13b)$$

$$r_2 \to \infty: \underline{E}_2^{(2)} \to \underline{0} \quad (13c)$$

$$\underline{v}_2^{(2)} \to \underline{0} \quad (13d)$$

The solution for the first reflected electric field from particle 2 which satisfies Eqs. 2, 13a, and 13c is furnished by (Keh and Anderson, 1985)

$$\underline{E}_2^{(2)} = \tfrac{1}{2}a_2^3 r_2^{-3}(\underline{\underline{I}} - 3\underline{e}_{r_2}\underline{e}_{r_2}) \cdot [\underline{E}_1^{(1)}]_{\underline{r}_1 = r_{12}\underline{e}} + 0[r_2^{-4}\nabla\underline{E}_1^{(1)} + r_2^{-3}\nabla\nabla\underline{E}_1^{(1)}] \quad (14)$$

where $\underline{E}_1^{(1)}$ is given in Eq. 10a.

As the governing Eq. 4 is linear, $\underline{v}_2^{(2)}$, the first reflected velocity field from particle 2 can be decomposed into two parts, $\underline{u}$ and $\underline{w}$, satisfying the following boundary conditions:

$$r_2 = a_2: \underline{u} = -\frac{\epsilon\zeta_2}{4\pi\eta}[\underline{E}_1^{(1)} + \underline{E}_2^{(2)}] + \frac{\epsilon\zeta_2}{4\pi\eta}[\underline{E}_1^{(1)}]_{\underline{r}_1 = r_{12}\underline{e}} \quad (15a)$$

$$\underline{w} = -\underline{v}_1^{(1)} + [\underline{v}_1^{(1)}]_{\underline{r}_1 = r_{12}\underline{e}} \quad (15b)$$

$$r_2 \to \infty: \underline{u} \to \underline{0} \quad (15c)$$

$$\underline{w} \to \underline{0} \quad (15d)$$

Here $\underline{u}$ is the reflected velocity to the incident electric field $\underline{E}_1^{(1)}$, while $\underline{w}$ is the disturbance caused by particle 2 to the velocity field $\underline{v}_1^{(1)}$. The summation of Eqs. 15a and 15b gives Eq. 13b since $\underline{\Omega}_2^{(1)} = \underline{0}$.

The solution for $\underline{u}$ satisfying the Stokes equations is given by (Keh and Anderson, 1985):

$$\underline{u} = \frac{\epsilon\zeta_2}{4\pi\eta}\left\{\frac{1}{2}a_2^3 r_2^{-3}(3\underline{e}_{r_2}\underline{e}_{r_2} - \underline{\underline{I}}) \cdot [\underline{E}_1^{(1)}]_{\underline{r}_1 = r_{12}\underline{e}} - \frac{5}{2}a_2^3 r_2^{-3}\underline{e}_{r_2}\underline{e}_{r_2}\underline{e}_{r_2}: [\nabla\underline{E}_1^{(1)}]_{\underline{r}_1 = r_{12}\underline{e}}\right\} + 0[r_2^{-4}\nabla\underline{E}_1^{(1)} + r_2^{-3}\nabla\nabla\underline{E}_1^{(1)}] \quad (16)$$

On the other hand, the solution for $\underline{w}$ is

$$\underline{w} = -\tfrac{5}{2}a_2^3 r_2^{-2}\underline{e}_{r_2}\underline{e}_{r_2}\underline{e}_{r_2}: [\nabla\underline{v}_1^{(1)}]_{\underline{r}_1 = r_{12}\underline{e}} - \tfrac{1}{2}a_2^3 r_2^{-2}\underline{e}_{r_2} \times (\underline{e}_x\underline{e}_y\underline{e}_z + \underline{e}_y\underline{e}_z\underline{e}_x + \underline{e}_z\underline{e}_x\underline{e}_y): [\nabla\underline{v}_1^{(1)} - (\nabla\underline{v}_1^{(1)})^T]_{\underline{r}_1 = r_{12}\underline{e}} + 0[r_2^{-4}\nabla\underline{v}_1^{(1)} + r_2^{-3}\nabla\nabla\underline{v}_1^{(1)}] \quad (17)$$

where $\underline{e}_x$, $\underline{e}_y$ and $\underline{e}_z$ are the unit vectors in Cartesian coordinates and $\underline{v}_1^{(1)}$ is expressed in Eq. 10b. The proof of Eq. 17 is provided in Appendix.

Substituting $\underline{E}_2^{(2)}$ and $\underline{v}_2^{(2)}$ into Eq. 6, we obtain the contributions to the velocity of particle 1 due to the reflected fields from particle 2:

$$[\underline{E}_2^{(2)}]_{\underline{r}_2 = -r_{12}\underline{e}} = \frac{1}{2}\frac{a_2^3}{r_{12}^3}(\underline{\underline{I}} - 3\underline{e}\underline{e}) \cdot \underline{E}_\infty + \frac{1}{4}\frac{a_1^3 a_2^3}{r_{12}^6}(\underline{\underline{I}} + 3\underline{e}\underline{e}) \cdot \underline{E}_\infty + 0(r_{12}^{-8}) \quad (18a)$$

$$[\underline{v}_2^{(2)}]_{\underline{r}_2 = -r_{12}\underline{e}} = [\underline{u} + \underline{w}]_{\underline{r}_2 = -r_{12}\underline{e}} = \frac{\epsilon\zeta_2}{4\pi\eta}\left[\frac{1}{2}\frac{a_2^3}{r_{12}^3}(3\underline{e}\underline{e} - \underline{\underline{I}}) \cdot \underline{E}_\infty - \frac{1}{4}\frac{a_1^3 a_2^3}{r_{12}^6}(3\underline{e}\underline{e} + \underline{\underline{I}}) \cdot \underline{E}_\infty + \frac{15}{2}\frac{a_1^3 a_2^3}{r_{12}^6}\underline{e}\underline{e} \cdot \underline{E}_\infty\right] - \frac{\epsilon\zeta_1}{4\pi\eta}\left[\frac{15}{2}\frac{a_1^3 a_2^3}{r_{12}^6}\underline{e}\underline{e} \cdot \underline{E}_\infty\right] + 0(r_{12}^{-8}) \quad (18b)$$

$$[\nabla^2\underline{v}_2^{(2)}]_{\underline{r}_2 = -r_{12}\underline{e}} = 0(r_{12}^{-8}) \quad (18c)$$

$$[\nabla \times \underline{v}_2^{(2)}]_{\underline{r}_2 = -r_{12}\underline{e}} = \frac{\epsilon(\zeta_1 - \zeta_2)}{4\pi\eta} \cdot \left[\frac{15}{2}\frac{a_1^3 a_2^3}{r_{12}^7}(\underline{e}_\phi\underline{e}_\theta - \underline{e}_\theta\underline{e}_\phi) \cdot \underline{E}_\infty\right] + 0(r_{12}^{-9}) \quad (18d)$$

which, when combined, give

$$\underline{U}_1^{(2)} = \frac{\epsilon(\zeta_2 - \zeta_1)}{4\pi\eta}\left[\frac{1}{2}\frac{a_2^3}{r_{12}^3}(3\underline{e}\underline{e} - \underline{\underline{I}}) \cdot \underline{E}_\infty + \frac{1}{4}\frac{a_1^3 a_2^3}{r_{12}^6}(27\underline{e}\underline{e} - \underline{\underline{I}}) \cdot \underline{E}_\infty\right] + 0(r_{12}^{-8}) \quad (19a)$$

$$\underline{\Omega}_1^{(2)} = \frac{\epsilon(\zeta_2 - \zeta_1)}{4\pi\eta}\left[\frac{15}{4}\frac{a_1^3 a_2^3}{r_{12}^7} \cdot (\underline{e}_\theta\underline{e}_\phi - \underline{e}_\phi\underline{e}_\theta) \cdot \underline{E}_\infty\right] + 0(r_{12}^{-9}). \quad (19b)$$

Here $\underline{e}$, $\underline{e}_\theta$ and $\underline{e}_\phi$ constitute the principal unit vectors in spherical coordinate system.

Obviously, $\underline{U}_1^{(4)}$ and $\underline{\Omega}_1^{(4)}$ will be of the orders $0(r_{12}^{-9})$ and $0(r_{12}^{-10})$, respectively. With the addition of Eqs. 9 and 19, the translational and angular velocities of particle 1 can be expressed as:

$$\underline{U}_1 = \frac{\epsilon\zeta_1}{4\pi\eta}\underline{E}_\infty + \frac{\epsilon(\zeta_2 - \zeta_1)}{4\pi\eta}\left[\frac{1}{2}\frac{a_2^3}{r_{12}^3}(3\underline{e}\underline{e} - \underline{\underline{I}}) + \frac{1}{4}\frac{a_1^3 a_2^3}{r_{12}^6}(27\underline{e}\underline{e} - \underline{\underline{I}})\right] \cdot \underline{E}_\infty + 0(r_{12}^{-8}) \quad (20a)$$

[The same result as this formula was also derived independently by Anderson (1984) using a similar method of reflections.]

$$\underline{\Omega}_1 = \frac{\epsilon(\zeta_2 - \zeta_1)}{4\pi\eta}\left[\frac{15}{4}\frac{a_1^3 a_2^3}{r_{12}^7}(\underline{e}_\theta\underline{e}_\phi - \underline{e}_\phi\underline{e}_\theta) \cdot \underline{E}_\infty\right] + 0(r_{12}^{-9}) \quad (20b)$$

$\underline{U}_2$ and $\underline{\Omega}_2$, the velocities of particle 2, can be obtained from the above equations by replacing ζ_1 by ζ_2, ζ_2 by ζ_1, a_1 by a_2, a_2 by a_1, $\underline{e}$ by $-\underline{e}$, and $\underline{e}_\theta \underline{e}_\phi$ by $-\underline{e}_\theta \underline{e}_\phi$. As expected, both particles will move with the velocity that would exist in the absence of the other (without rotation) for any arbitrary orientation of the particles as $r_{12} \rightarrow \infty$. In view of the neglect of inertial terms in the momentum equation of this analysis, the same result for the particle velocities would be presented if the two spheres interchange their positions with each other.

The $0(r_{12}^{-8})$ and $0(r_{12}^{-9})$ interactions in Eqs. 18–20 could be obtained by more detailed calculations of $\underline{E}_2^{(2)}$ and $\underline{v}_2^{(2)}$, but the numerical significance would be small unless the particles contact very closely. When the gap between particles approaches zero (but is still large relative to the Debye screening length), the expansion in r_{12}^{-n} may not converge, and the lubrication theory (Cooley and O'Neill, 1969; O'Neill and Majumdar, 1970b) could be a possible method to get this problem solved.

Discussion on Interactions between Particles

The interaction between two nonconducting spheres in an applied electric field, given by Eq. 20, results from three effects:

1. Each particle disturbs the local electric field experienced by the other.
2. The movement of each particle drags surrounding fluid that convects and rotates the other particle.
3. The charge on the surface of each particle causes a reverse tangential fluid velocity at the outer edge of the electrical double layer that affects the motion of the other.

The leading term of the interaction for particle translation is of $0(r_{12}^{-3})$, because both the electric and the velocity fields produced by a sphere moving in response to an applied electric field in an unbounded fluid decay like r^{-3}, as shown in Eq. 10. For spheres that allow free rotation, the leading term of the angular velocity is of $0(r_{12}^{-7})$. Thus, the interaction between particles undergoing electrophoresis is much weaker than that between sedimenting particles, since the leading terms of the translational and rotational velocities about two Stokeslets are of $0(r_{12}^{-1})$ and $0(r_{12}^{-2})$, respectively (Happel and Brenner, 1983)

In the analysis using bipolar coordinates by Reed and Morrison (1976), they assumed that two electrophoretic spheres translate without rotation. However, our derivation in the previous section shows that $\underline{U}$ obtained by taking $\underline{\Omega} = \underline{0}$ is only correct to $0(r_{12}^{-8})$ and the constraint of free particle rotation will contribute the translational velocity in the order $0(r_{12}^{-9})$. Note that the two electrophoretic spheres rotate about an axis perpendicular to both $\underline{r}_{12}$ and $\underline{E}_\infty$ in the *same* direction, which is opposite to the behavior for two spheres moving under gravity. Moreover, as far as $0(r_{12}^{-7})$ is concerned, both spheres have equal magnitudes in angular velocity.

Given the separation parameter

$$\lambda = \frac{a_1 + a_2}{r_{12}} \tag{21}$$

the ratio of particle radii a_2/a_1, the ratio of zeta potentials ζ_2/ζ_1, and the orientation of particles $\underline{e}$ relative to the applied electric field $\underline{E}_\infty$, the electrophoretic mobilities and the directions of motion of the two particles with very thin electrical double layer can be easily calculated by Eq. 20. Of special interest is the case of identical zeta potentials. When $\zeta_2/\zeta_1 = 1$, both particles move without rotation with the exact velocity they would possess if isolated for any combination of a_1, a_2 and $\underline{r}_{12}$. This remarkable result, derived from the fact that this particular flow is irrotational, is a generalization of an observation made by Reed and Morrison (1976) for two spheres of equal radii. It should be noted from Eq. 20a that the direction of electrophoresis of each particle is deflected by the other, unless the electric field is imposed either parallel or perpendicular to the line of centers of the particles.

For the specific case of two spheres with equal radii, i.e., $a_1 = a_2 = a$, our results from method of reflections can be compared with the exact calculations of Reed and Morrison (1976) using bipolar coordinates. Tables 1 and 2 give the comparisons in electrophoretic velocities of the two spheres with their line of centers parallel and perpendicular, respectively, to the applied electric

Table 1. Normalized Electrophoretic Velocities of Two Spheres with Equal Radii and Their Line of Centers Aligned with Applied Electric Field

		Asymptotic Solution		Exact Calculations	
$\frac{\zeta_2}{\zeta_1}$	$\frac{2a}{r_{12}}$	$\frac{4\pi\eta U_1}{\epsilon\zeta_1 E_\infty}$	$\frac{4\pi\eta U_2}{\epsilon\zeta_2 E_\infty}$	$\frac{4\pi\eta U_1}{\epsilon\zeta_1 E_\infty}$	$\frac{4\pi\eta U_2}{\epsilon\zeta_2 E_\infty}$
10.0	0.2	1.00906	0.99909	1.00906	0.99909
	0.4	1.07574	0.99243	1.07603	0.99240
	0.6	1.28565	0.97144	1.29596	0.97040
	0.8	1.81562	0.91844	1.97696	0.90230
0.5	0.2	0.99950	1.00101	0.99950	1.00101
	0.4	0.99579	1.00842	0.99578	1.00845
	0.6	0.98413	1.03174	0.98356	1.03289
	0.8	0.95469	1.09062	0.94572	1.10855
	0.9	0.92745	1.14510	0.89516	1.20969
−5.0	0.2	0.99396	0.99879	0.99396	0.99879
	0.4	0.94950	0.98990	0.94931	0.98986
	0.6	0.80957	0.96191	0.80269	0.96054
	0.8	0.45626	0.89125	0.34869	0.86974

Table 2. Normalized Electrophoretic Velocities of Two Spheres with Equal Radii and Their Line of Centers Normal to Applied Electric Field

		Asymptotic Solution		Exact Calculations	
$\frac{\zeta_2}{\zeta_1}$	$\frac{2a}{r_{12}}$	$\frac{4\pi\eta U_1}{\epsilon\zeta_1 E_\infty}$	$\frac{4\pi\eta U_2}{\epsilon\zeta_2 E_\infty}$	$\frac{4\pi\eta U_1}{\epsilon\zeta_1 E_\infty}$	$\frac{4\pi\eta U_2}{\epsilon\zeta_2 E_\infty}$
10.0	0.2	0.99550	1.00045	0.99550	1.00045
	0.4	0.96386	1.00361	0.96377	1.00362
	0.6	0.87686	1.01231	0.87355	1.01265
	0.8	0.70278	1.02972	0.64565	1.03544
0.5	0.2	1.00025	0.99950	1.00025	0.99950
	0.4	1.00201	0.99598	1.00201	0.99597
	0.6	1.00684	0.98632	1.00703	0.98595
	0.8	1.01651	0.96698	1.01969	0.96063
	0.9	1.02382	0.95236	1.03688	0.92625
−5.0	0.2	1.00300	1.00060	1.00300	1.00060
	0.4	1.02410	1.00482	1.02416	1.00483
	0.6	1.08209	1.01642	1.08430	1.01686
	0.8	1.19814	1.03963	1.23624	1.04725

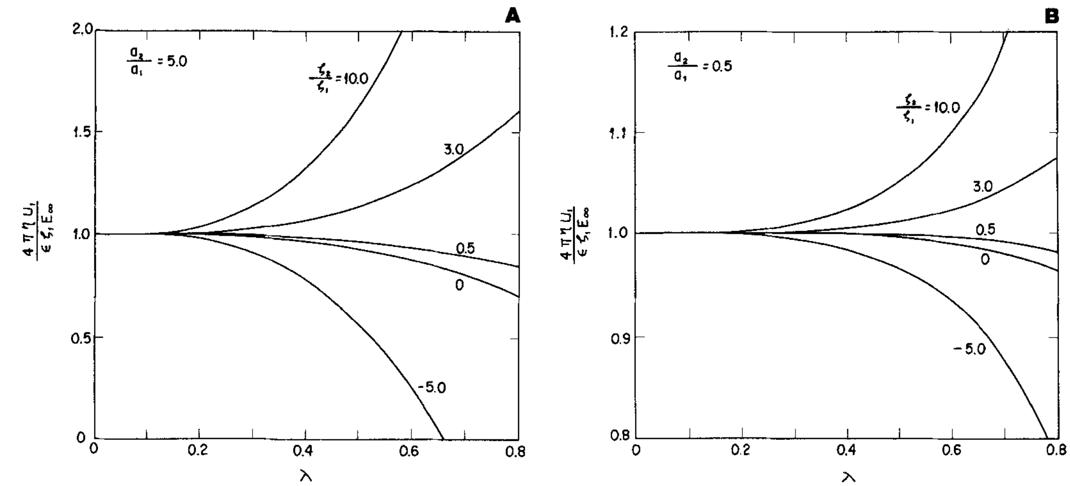

Figure 2. Normalized electrophoretic mobility of particle 1 vs. particle-particle separation variable λ with ζ_2/ζ_1 as a parameter when the two spheres move along their line of centers.

field $\underline{E}_\infty$. The results were calculated precisely following the formulae given by Reed and Morrison, while the asymptotic solution was obtained from Eq. 20a with the $0(r_{12}^{-8})$ term neglected. Here, the predictions from the asymptotic approximation for $\zeta_2/\zeta_1 = 0.5$ (or 2.0) is found to be in perfect agreement with those of the exact solution. The agreement of these two methods is quite good even for ζ_2/ζ_1 as large as 10 (the errors in velocities are less than 1% for cases $2a/r_{12} \leq 0.6$), indicating that the higher order terms such as $0(r_{12}^{-8})$ are not important unless the particles are nearly touching or their ratio in zeta potential is very large. This favorable comparison is encouraging in the sense it implies that our general result for spheres of different radii should be quite accurate for a large range of separations.

Values of the normalized translational and rotational velocities evaluated from Eq. 20 with various separation distances λ and zeta potential ratios ζ_2/ζ_1 for spheres of different radii are shown in Figures 2–4. Figures 2a and 2b are the electrophoretic velocity of particle 1 plotted for the motion of spheres along their line of centers with the ratio of radii a_2/a_1 equal to 5.0 and 0.5, respectively, while the corresponding results for the motion normal to the line of centers are depicted in Figures 3a and 3b. In Figure 4, the angular velocity of particle 1 are plotted for the motion of spheres perpendicular to their line of centers with the ratio a_2/a_1 as a parameter. For two spheres aligned with imposed electric field, the flow is axisymmetric and the angular velocities of particles vanish. The particle interaction decreases rapidly, for all values of ζ_2/ζ_1 and a_2/a_1, with increasing separation distances (i.e., decreasing λ), as illustrated in Tables 1–2 and Figures 2–4. In addition, the influence of the interaction in general is far greater on the smaller particle than on the larger one for any given values of λ and ζ_2/ζ_1.

As concluded earlier, there is no particle interaction for the case of equal zeta potentials. However, the particle interaction for a given combination of a_1, a_2 and r_{12} becomes stronger when the value of ζ_2/ζ_1 deviates further from unity. For the electrophoretic motion of two spheres parallel to their line of centers, the one with smaller zeta potential (i.e., smaller velocity) is enhanced by the motion of the other, which is retarded at the same time by the motion of the former one, if the two spheres have different zeta potentials of the same sign. For two particles

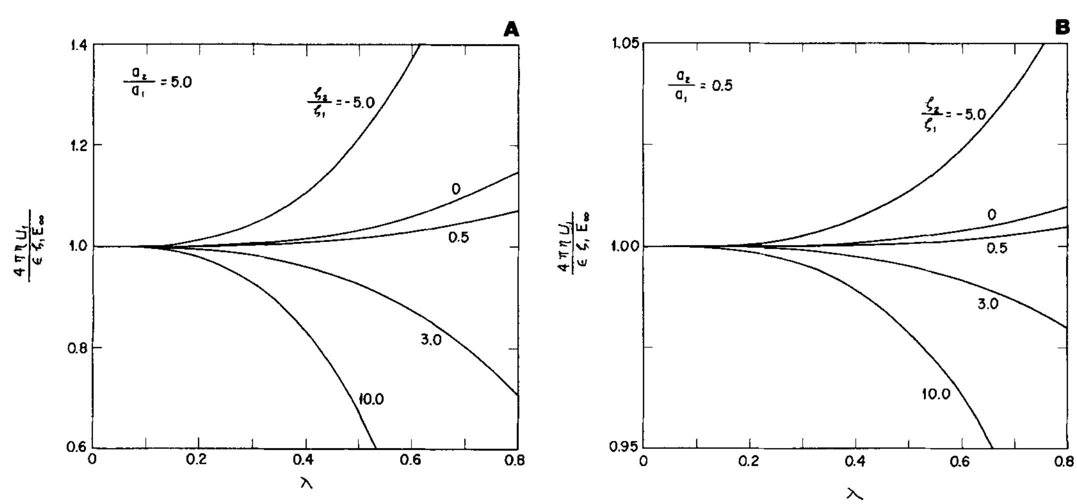

Figure 3. Normalized electrophoretic mobility of particle 1 vs. particle-particle separation variable λ with ζ_2/ζ_1 as a parameter when the two spheres move normal to their line of centers.

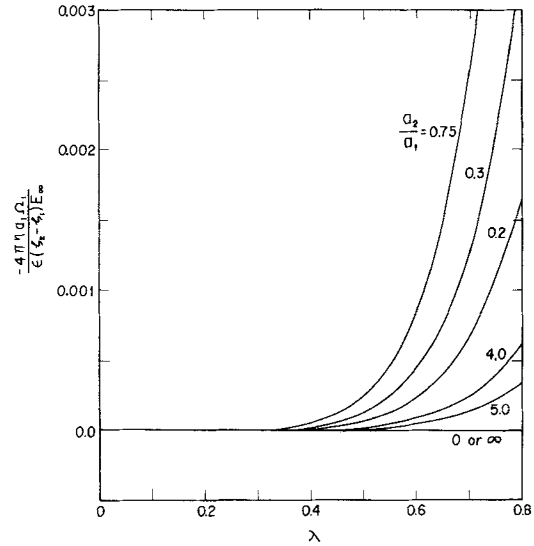

Figure 4. Normalized angular velocity of particle 1 vs. particle-particle separation variable λ with a_2/a_1 as a parameter when the two spheres move normal to their line of centers.

of different signs in zeta potential (i.e., opposite directions of velocity) aligned with applied electric field, their motions are always hindered by each other. On the other hand, for the motion of two spheres normal to their line of centers, the one with smaller zeta potential is slowed down by the motion of the other, which is speeded up simultaneously by the motion of the first one, if the two spheres have different zeta potentials of the same sign. The motions of two particles will be enhanced by each other if their line of centers is perpendicular to imposed electric field and their zeta potentials are of different signs. The particular behavior for electrophoresis is complex in contrast to the Stokes flows of two spheres (Goldman et al., 1966; Davis, 1969; O'Neill and Majumdar, 1970a).

The interaction effects between pairs of particles, obtained in the previous section, can be extended to the calculation of the average electrophoretic velocity of small particles in a statistically homogeneous dispersion acted on by an external electric field. In the following section, we obtain formulae for this average velocity that are correct to the order of first power of the volume fraction of the particles.

Concentration Dependence of Electrophoretic Velocity

In practical applications of electrophoresis, collections of colloidal particles in bounded systems are usually encountered. It is therefore necessary to determine the dependence of the electrophoretic mobility on particle concentration. For a bounded suspension subjected to an external electric field $\underline{E}_\infty$, the volume-average velocity and electric fields must obey the following:

$$\frac{1}{V}\int_V \underline{v}(\underline{x})\, d\underline{x} = \underline{0} \tag{22a}$$

$$\frac{1}{V}\int_V \underline{E}(\underline{x})\, d\underline{x} = \underline{E}_\infty \tag{22b}$$

where V denotes the entire volume of the suspension. The microscopic model of particle interactions in a dilute dispersion by Batchelor (1972) and Reed and Anderson (1980) involves both statistical and low Reynolds number hydrodynamic concepts. Based on this model incorporating with Eq. 22, the mean electrophoretic velocity of a "test" particle (subscript t), which samples all positions in a suspension, is given by a volume integral over the entire suspension:

$$\langle \underline{U}_t \rangle = \underline{U}_t^{(0)} + C\left\{ \int_V \underline{v}^*(\underline{r})[g(\underline{r}) - 1]\, d\underline{r} + \frac{a_t^2}{6}\int_V \nabla^2 \underline{v}^*(\underline{r}) g(\underline{r})\, d\underline{r} + \frac{\epsilon\zeta_t}{4\pi\eta}\int_V [\underline{E}^*(\underline{r}) - \underline{E}_\infty][g(\underline{r}) - 1]\, d\underline{r} + \int_V \underline{W}(\underline{r}) g(\underline{r})\, d\underline{r} \right\} + 0(C^2) \tag{23}$$

Here, $\underline{U}_t^{(0)} = \epsilon\zeta_t \underline{E}_\infty/4\pi\eta$, $g(\underline{r})$ is the two-particle radial distribution function, and C is the macroscopic concentration of the neighboring particles (assumed to have identical radius and zeta potential). $\underline{E}^*(\underline{r})$ and $\underline{v}^*(\underline{r})$ are the electric and velocity fields, respectively, at position $\underline{r}$ when a single neighboring sphere at the origin $\underline{0}$ move due to the applied electric field $\underline{E}_\infty$, which are expressed by Eq. 10 for $r \geq a$. Inside the neighboring sphere ($r < a$), both $\underline{E}^*$ and $\underline{v}^*$ are constant:

$$\underline{E}^* = 3/2\underline{E}_\infty \tag{24a}$$

$$\underline{v}^* = \frac{\epsilon\zeta}{4\pi\eta}\underline{E}_\infty \tag{24b}$$

$\underline{W}(\underline{r})$ is a correction function needed to account for the perturbation on $\underline{v}^*$ due to the presence of the test particle and is defined by

$$\underline{W}(\underline{r}) = \underline{U}_t^*(\underline{r}) - \underline{U}_t^{(0)} - \underline{v}^*(\underline{r}) - \frac{a_t^2}{6}\nabla^2\underline{v}^*(\underline{r}) - \frac{\epsilon\zeta_t}{4\pi\eta}[\underline{E}^*(\underline{r}) - \underline{E}_\infty] \tag{25}$$

where $\underline{U}_t^*(\underline{r})$ is the actual velocity of the test particle located at $\underline{r}$ with respect to the origin of a single neighbor at $\underline{0}$. $\underline{U}_t^*(\underline{r})$ can be computed from Eq. 20a, which is originally derived for a particle pair. Although the superscript * on the functions $\underline{E}^*$, $\underline{v}^*$ and $\underline{U}_t^*$ refers to the unbounded fluid, the effect of the suspension boundaries is accounted for in the derivation of Eq. 23. Note that the term of Faxen correction $(a_t^2\nabla^2\underline{v}^*/6)$ in Eqs. 23 and 25 equals zero, as computed from Eq. 10b.

To evaluate the volume integrals in Eq. 23, we assume that the radial distribution function has the following equilibrium value for rigid spheres without long-range pair potential:

$$g = 0 \qquad \text{if } r < a_t + a$$
$$g = 1 + 0(C) \quad \text{if } r > a_t + a \tag{26}$$

where $0(C)$ is a term proportional to the concentration of neighbors. In other words, the particles must be sufficiently small so that Brownian motion dominates any multiparticle hydrodynamic interactions that might impart microscopic structure to the suspension. It should be noted that, although the approximation of Eq. 26 may be a good one for a dispersion of identical particles, the pair-distribution function in general is nonuniform and nonisotropic, and the effects of the $0(C)$ term could be significant when the particles have different zeta potentials. The conditions under which the assumption of local equilibrium is valid for a dilute dispersion of different types of particles are discussed by Reed and Anderson (1980) and Batchelor (1982).

Given Eq. 10b or 24 for $\underline{E}^*$ and $\underline{v}^*$, Eq. 20 for $\underline{U}_t^*$ and Eq. 26 for g, the integrals in Eq. 23 are evaluated to obtain

$$\langle \underline{U}_t \rangle = \underline{U}_t^{(0)}[1 + \alpha\varphi + 0(\varphi^2)], \tag{27a}$$

with

$$\alpha = -\frac{1}{2} - \frac{\zeta}{\zeta_t} + 2\left(\frac{\zeta}{\zeta_t} - 1\right)\left(\frac{a_t}{a_t + a}\right)^3 \tag{27b}$$

where φ is the volume fraction of the neighbor particles, $(4/3)\pi a^3 C$. This result is not exact since $0(r^{-8})$ terms are neglected in $\underline{U}_t^*$; however, the error should be small. In derivation of Eq. 27, it was assumed that all neighboring particles are physically identical, even though they are allowed to differ from the test particle.

Consider now a suspension of particles that have a distribution in both zeta potential and radius. A generalization of Eq. 27 results in

$$\langle \underline{U}_i \rangle = \frac{\epsilon\zeta_i E_\infty}{4\pi\eta}\left[1 + \sum_j \alpha_{ij}\varphi_j + 0(\varphi^2)\right] \tag{28a}$$

where

$$\alpha_{ij} = -\frac{1}{2} - \frac{\zeta_j}{\zeta_i} + 2\left(\frac{\zeta_j}{\zeta_i} - 1\right)\left(\frac{a_i}{a_i + a_j}\right)^3 \tag{28b}$$

Here the subscript i denotes particles having radius a_i and zeta potential ζ_i. Obviously, the effect of type j particles on the mean electrophoretic velocity of type i particles depends on their ratios in zeta potentials and in particle radii as well as the volume fraction of type j particles. It is noted that $0(\varphi_j)$ terms can be important for large ζ_j/ζ_i. α_{ij} equals $\zeta_j/\zeta_i - 2.5$ and $-\zeta_j/\zeta_i - 0.5$ for the limiting cases of a_j/a_i approaching zero and infinity, respectively. In the application of Eq. 28 to a given dispersion of particles of different zeta potentials, the applied electric field must be sufficiently small such that the relative motions of different types of particles do not distort the equilibrium particle distribution significantly.

A particularly interesting situation arises when $\zeta_j = \zeta_i = \zeta$. Equation 28 predicts that $\alpha_{ij} = -1.5$ regardless of the difference in particle radius. Therefore, the mean particle velocity in a suspension of particles with equal zeta potentials is

$$\langle \underline{U} \rangle = \frac{\epsilon\zeta E_\infty}{4\pi\eta}[1 - 1.5\varphi + 0(\varphi^2)] \tag{29}$$

for particles of any size; the only factor influencing the particle velocity is the volume fraction of all particles. This appealing result is a generalization of an observation made by Anderson (1986) for suspensions of identical particles. Because many suspensions in practical applications are constituted from particles of the same material, it is reasonable to assume that the particles have the same zeta potential at surface, but may exhibit a size distribution. Equation 29 provides significant physical insight to be useful in interpreting quantitatively the electrophoretic data for charged particles. It should be noted that the concentration effect on electrophoresis is relatively weak in comparison with the case of gravity settling of a suspension of rigid spheres (Batchelor, 1972; Reed and Anderson, 1980; Glendinning and Russel, 1982). The $0(\varphi^2)$ term would be small except in the case of concentrated dispersions. The existing experimental data concerning the concentration effect on electrophoresis (Hauser and LeBeau, 1941; Maron et al., 1948; Zukoski and Saville, 1987) also indicate that the particle velocity decreases slightly as φ increases at small values of φ.

Anderson (1981) utilized the exact solution for the electrophoretic motion of two spheres of equal radii using bipolar coordinates (Reed and Morrison, 1976) to compute α_{ij}. The following expression results from Eq. 23:

$$\alpha_{ij} = -\frac{1}{2} - \frac{\zeta_j}{\zeta_i} + 8\int_0^1 \left[(A_\parallel + 2A_\perp - 3) + \frac{\zeta_j}{\zeta_i}(B_\parallel + 2B_\perp)\right] g(r)\lambda^{-4}\, d\lambda \tag{30}$$

where $\lambda = 2a/r$ and $A_\parallel$, $A_\perp$, $B_\parallel$, and $B_\perp$ are the mobility coefficients of the particle i defined in his Eqs. 7 and 8. [In Anderson's (1981) derivation, the mean particle effect on the average electric field of the suspension was not included, and hence the term $-1/2$ was missing (Anderson, 1986).] It is likely that he calculated these coefficients by interpolation and extrapolation from insufficient numerical values presented by Reed and Morrison (1976), the results of his Table 1 seem to contain numerical errors. We have computed these coefficients following the formulae given by Reed and Morrison and the relevant results that provide a correction to Anderson's Table 1 is described in Table

Table 3. Hydrodynamic Parameters for the Electrophoretic Velocity of a Test Particle with a Single Neighbor Present*

λ	$-(A_\parallel + 2A_\perp - 3)\lambda^{-4}$	$(B_\parallel + 2B_\perp)\lambda^{-4}$
≤0.1	<0.0010	<0.0010
0.2	0.0045	0.0045
0.3	0.0087	0.0087
0.4	0.0155	0.0155
0.5	0.0248	0.0248
0.6	0.0369	0.0369
0.7	0.0525	0.0525
0.8	0.0728	0.0728
0.9	0.0948	0.0948
0.95	0.0874	0.0874
0.96	0.0765	0.0765
0.97	0.0555	0.0555
0.98	0.0124	0.0124
0.99	−0.0984	−0.0984
0.995	−0.2553	−0.2553
1.0	−0.5151	−0.5151

*Parameters for $\lambda = 1.0$ are evaluated by extrapolation from values for $\lambda = 0.97$, 0.98, 0.99, and 0.995.

3. Using Eq. 26 for $g(r)$ and Table 3 for the accurate mobility coefficients, Eq. 30 can be integrated numerically to obtain:

$$\alpha_{ij} = -0.737 - 0.763 \frac{\zeta_j}{\zeta_i} \tag{31}$$

For the special case of $a_i = a_j$, Eq. 28 derived from the method of reflections in this work yields:

$$\alpha_{ij} = -0.75 - 0.75 \frac{\zeta_j}{\zeta_i} \tag{32}$$

In Eq. 32, the $0(r^{-8})$ terms are neglected. Compared with the exact solution (Eq. 31), Eq. 32 is sufficiently accurate. This agreement justifies the applicability of our general result, Eq. 28, for suspensions of particles with unequal radii and different zeta potentials.

Another interesting prediction of Eq. 28 arises if the surface of type i particles is neurtal. With $\zeta_i = 0$, Eq. 28 becomes:

$$\langle \underline{U}_i \rangle = \sum_j \left[-1 + 2 \left(\frac{a_i}{a_i + a_j} \right)^3 \right] \varphi_j \frac{\epsilon \zeta_j \underline{E}_\infty}{4\pi\eta} \tag{33}$$

The uncharged type i particles may have a mean velocity of finite magnitude in the same or opposite direction of applied electric field, depending on the volume fraction, zeta potential and relative size of the particles of all other types in the suspension. When the ratio a_j/a_i is greater than $2^{1/3} - 1$ ($\simeq 0.26$), type i particles get caught in the reverse fluid motion caused by the interaction between the electric field and the double layer at the surface of type j particles (Anderson, 1981). When a_j/a_i is less than this critical value, the backflow caused by the container wall against the reverse fluid motion dominates the movement of type i particles.

Particle interactions in electrophoresis were also investigated by using the cell model for a concentrated suspension (Levine and Neale, 1974). Without accounting for the statistical randomness and the boundaries of the suspension, it predicted that the particle concentration has no effect on electrophoretic mobility in the limit of thin double layer.

Acknowledgment

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Notation

a = particle radius, m
$A_\parallel, A_\perp, B_\parallel, B_\perp$ = hydrodynamic mobility coefficients
C = number density of particles in suspension, m^{-3}
$\underline{e}$ = unit vector pointing from particle 1 to particle 2
$\underline{e}_r, \underline{e}_\theta, \underline{e}_\phi$ = unit vectors of spherical coordinates
$\underline{e}_x, \underline{e}_y, \underline{e}_z$ = unit vectors of Cartesian coordinates
$\underline{E}$ = electric field, $V \cdot m^{-1}$
$E_\infty, \underline{E}_\infty$ = uniform applied electric field, $V \cdot m^{-1}$
g = two-particle radial distribution function
$\underline{\underline{I}}$ = unit dyadic
p = dynamic pressure, $N \cdot m^{-2}$
p_{-n} = solid spherical harmonic, $kg \cdot m^{-1} \cdot s^{-2}$
$\underline{r}$ = position vector relative to sphere center, m
$\underline{r}_{12}$ = vector pointing from particle 1 to particle 2, m
r_{12} = center-to-center distance between particles 1 and 2, m
$\underline{S}_m$ = mth-order polyadic surface harmonic
$\underline{u}$ = fluid velocity field specified by Eqs. 15a and 15c, $m \cdot s^{-1}$
$\underline{U}$ = electrophoretic velocity, $m \cdot s^{-1}$
$\langle \underline{U} \rangle$ = ensemble-averaged electrophoretic velocity, $m \cdot s^{-1}$
$\underline{v}$ = fluid velocity field, $m \cdot s^{-1}$
$\underline{v}_s$ = fluid velocity at particle surface, $m \cdot s^{-1}$
V = volume of the dispersion system, m^3
$\underline{w}$ = fluid velocity field specified by Eqs. 15b and 15d, $m \cdot s^{-1}$
$\underline{W}$ = correction function defined in Eq. 25, $m \cdot s^{-1}$
$\underline{x}$ = position vector, m

Greek letters

α = interaction coefficient for $0(\varphi)$
$\underline{\alpha}_m, \underline{\beta}_m, \underline{\gamma}_m$ = polyadic coefficients, $m \cdot s^{-1}$
ϵ = $4\pi\epsilon_0\epsilon_r$, $C^2 \cdot J^{-1} \cdot m^{-1}$
ϵ_0 = permittivity in vacuum, $8.854 \times 10^{-12}\ C^2 \cdot J^{-1} \cdot m^{-1}$
ϵ_r = dielectric constant of fluid
ζ = zeta potential, V
η = fluid viscosity, $kg \cdot m^{-1} \cdot s^{-1}$
κ = reciprocal Debye screening length, m^{-1}
λ = separation parameter defined in Eq. 21
Φ_{-n} = solid spherical harmonics, $m^2 \cdot s^{-1}$
χ_{-n} = solid spherical harmonics, $m \cdot s^{-1}$
φ = volume fraction of particles in suspension
Ω = angular velocity of particle, s^{-1}

Subscripts

0 = particle center
1 = particle 1
2 = particle 2
A = arbitrary applied field
i = i-type particle
j = j-type particle
R = reflected field
t = test particle

Superscripts

(0) = infinite dilution
(i) = ith reflection
* = unbounded fluid

Appendix: Velocity disturbance Caused by a Stationary Sphere in an Arbitrary Flow Field

Consider a stationary sphere of radius a positioned at the origin of spherical coordinates (r, θ, ϕ) in an unbounded fluid of viscosity η. In the absence of the sphere, the velocity field is $\underline{v}_A(\underline{r})$ such that $|a^2\nabla\nabla\underline{v}_A|$ could be comparable to $|a\nabla\underline{v}_A|$. The actual velocity field $\underline{v}(\underline{r})$ satisfies the Stokes equations, since the fluid is incompressible and the Reynolds number is small. To find the velocity disturbance caused by the sphere, $\underline{v}_R(\underline{r}) \equiv \underline{v} - \underline{v}_A$, we must solve the Stokes equations for $\underline{v}_R$ with the following boundary conditions:

$$\underline{v}_R = -\underline{v}_A \quad \text{at } r = a, \tag{A1a}$$

$$\underline{v}_R \to \underline{0} \quad \text{as } r \to \infty. \tag{A1b}$$

Note that $\underline{v}_A$ is assumed to satisfy the Stokes equations as well.

A solution for $\underline{v}_R$ can be constructed from Lamb's general solution as outlined by Brenner (1964). The velocity and pressure fields for $r > a$ are completely specified when the polyadic coefficients ($\underline{\alpha}_m$, $\underline{\beta}_m$, $\underline{\gamma}_m$) are determined at $r = a$ using the following:

$$\underline{e}_r \cdot \underline{v}_s = \sum_{m=1}^{\infty} \underline{\alpha}_m \,[\cdot]\, \underline{S}_m, \tag{A2a}$$

$$-r \nabla \cdot \underline{v}_s = \sum_{m=1}^{\infty} \underline{\beta}_m \,[\cdot]\, \underline{S}_m, \tag{A2b}$$

$$\underline{r} \cdot \nabla \times \underline{v}_s = \sum_{m=1}^{\infty} \underline{\gamma}_m \,[\cdot]\, \underline{S}_m, \tag{A2c}$$

where $\underline{v}_s = \underline{v}_R(r = a)$, the reflected velocity on the sphere surface, and $\underline{e}_r$ together with $\underline{e}_\theta$ and $\underline{e}_\phi$ are the unit vectors of spherical coordinates. The $\underline{S}_m$ are surface harmonics, which are mth-order polyadics defined by

$$\underline{S}_m = r^{m+1} \nabla^m (r^{-1}),$$
$$\underline{S}_1 = -\underline{e}_r, \quad \underline{\underline{S}}_2 = 3\,\underline{e}_r\,\underline{e}_r - \underline{\underline{I}}, \ldots \tag{A3}$$

where $\underline{\underline{I}}$ is the unit dyadic, and the symbol $[\cdot]$ represents m scalar products.

The surface velocity $\underline{v}_s$ can be expanded about the center of the sphere using Eq. A1a:

$$\underline{v}_s = -(\underline{v}_A)_0 - a\,\underline{e}_r \cdot (\nabla\,\underline{v}_A)_0 - \tfrac{1}{2} a^2 \underline{e}_r\underline{e}_r : (\nabla\nabla\,\underline{v}_A)_0 + 0(\nabla\nabla\nabla\,\underline{v}_A) \tag{A4}$$

where the subscript 0 denotes evaluation at $\underline{r} = \underline{0}$. The coefficients $\underline{\alpha}_m$, $\underline{\beta}_m$ and $\underline{\gamma}_m$ are determined by substituting Eq. A4 into Eq. A2 and comparing terms of each order. The first few coefficients are

$$\underline{\alpha}_1 = (\underline{v}_A)_0, \quad \underline{\underline{\alpha}}_2 = -\tfrac{1}{3} a (\nabla\,\underline{v}_A)_0, \tag{A5a,b}$$

$$\underline{\beta}_1 = \underline{0}, \quad \underline{\underline{\beta}}_2 = -\tfrac{1}{3} a (\nabla\,\underline{v}_A)_0, \tag{A5c,d}$$

$$\underline{\gamma}_1 = -a\,[(\nabla\,\underline{v}_A)_0 - (\nabla\,\underline{v}_A)_0^T] : (\underline{e}_x\underline{e}_y\underline{e}_z + \underline{e}_y\underline{e}_z\underline{e}_x + \underline{e}_z\underline{e}_x\underline{e}_y) \tag{A5e}$$

where $\underline{e}_x$, $\underline{e}_y$ and $\underline{e}_z$ are unit vectors of Cartesian coordinates. The velocity disturbance caused by the sphere is

$$\underline{v}_R(\underline{r}) = \nabla \times (\underline{r}\chi_{-2}) + \nabla\Phi_{-2} + \nabla\Phi_{-3} + \frac{1}{2\eta} r^2 \nabla p_{-2} + \frac{2}{\eta} \underline{r} p_{-2} + \frac{1}{2\eta} \underline{r} p_{-3} + O(r^{-3}\nabla\nabla\underline{v}_A), \tag{A6}$$

where the solid spherical harmonics

$$\chi_{-2} = \tfrac{1}{2} a^2 r^{-2} \underline{\gamma}_1 \cdot (-\underline{e}_r), \tag{A7a}$$

$$p_{-2} = \tfrac{1}{2} \eta a r^{-2} (3\underline{\alpha}_1 + \underline{\beta}_1) \cdot (-\underline{e}_r), \tag{A7b}$$

$$\Phi_{-2} = \tfrac{1}{4} a^3 r^{-2} (\underline{\alpha}_1 + \underline{\beta}_1) \cdot (-\underline{e}_r), \tag{A7c}$$

$$p_{-3} = \eta a^2 r^{-3} (4\underline{\underline{\alpha}}_2 + \underline{\underline{\beta}}_2) : (3\underline{e}_r\underline{e}_r - \underline{\underline{I}}), \tag{A7d}$$

$$\Phi_{-3} = \tfrac{1}{6} a^4 r^{-3} (2\underline{\underline{\alpha}}_2 + \underline{\underline{\beta}}_2) : (3\underline{e}_r\underline{e}_r - \underline{\underline{I}}). \tag{A7e}$$

After evaluating functions A7 from $\underline{\alpha}_1$, $\underline{\underline{\alpha}}_2$, $\underline{\beta}_1$, $\underline{\underline{\beta}}_2$ and $\underline{\gamma}_1$ given by Eq. A5 and substituting them into Eq. A6, we have

$$\begin{aligned}\underline{v}_R = &-\frac{3}{4}\frac{a}{r}(\underline{\underline{I}} + \underline{e}_r\underline{e}_r) \cdot (\underline{v}_A)_0 \\ &- \frac{1}{4}\frac{a^3}{r^3}(\underline{\underline{I}} - 3\underline{e}_r\underline{e}_r) \cdot (\underline{v}_A)_0 \\ &- \frac{5}{2}\frac{a^3}{r^2}\underline{e}_r\underline{e}_r\underline{e}_r : (\nabla\underline{v}_A)_0 \\ &+ \frac{1}{2}\frac{a^3}{r^2}(\underline{e}_x\underline{e}_y\underline{e}_z + \underline{e}_y\underline{e}_z\underline{e}_x + \underline{e}_z\underline{e}_x\underline{e}_y) \\ &: [(\nabla\underline{v}_A)_0 - (\nabla\underline{v}_A)_0^T] \\ &+ \frac{1}{2}\frac{a^5}{r^4}(2\underline{e}_r\underline{e}_r\underline{e}_r - \underline{e}_r\underline{e}_\theta\underline{e}_\theta \\ &- \underline{e}_r\underline{e}_\phi\underline{e}_\phi - \underline{e}_\theta\underline{e}_r\underline{e}_\theta - \underline{e}_\phi\underline{e}_r\underline{e}_\phi \\ &- \underline{e}_\theta\underline{e}_\theta\underline{e}_r - \underline{e}_\phi\underline{e}_\phi\underline{e}_r) : (\nabla\underline{v}_A)_0 \\ &+ O(r^{-3}\nabla\nabla\underline{v}_A).\end{aligned} \tag{A8}$$

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