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ELECTROPHORESIS OF DUMBBELL-LIKE COLLOIDAL PARTICLES

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Abstract—A theoretical analysis of the dynamics of dumbbell-like colloidal particles moving by electrophoresis is presented. The dumbbell consists of two rigid spheres of arbitrary radii connected by an infinitesimally thin, rigid rod. Each sphere has a uniform but arbitrary zeta potential and is surrounded by a thin electrical double layer, as defined in the Helmholtz limit. The analysis utilizes the linearity of the governing electrokinetic equations to reduce the problem to subproblems for which the solutions already exist or are easily derived. Translational and angular velocities of the nonuniformly charged dumbbell are obtained by utilizing rigid-body mechanics, solutions for the electrophoresis of two freely suspended spheres and solutions for the components of the grand resistance matrix for two spheres translating and rotating with arbitrary velocities. The results, which depend linearly on the zeta potentials of the spheres, are presented in the form of four dimensionless functions, two to describe the translation, one to describe the rotation and one to locate the "center" of the dumbbell. These four functions depend only on the spheres' radii and the distance between the centers of the spheres. Sample calculations are presented to illustrate features of the electrophoretic motion of doublets that could be formed by heterocoagulation or bridging mechanisms. Estimates of angular velocities indicate that only modest fields might be required to align a suspension of doublets, even when the suspension undergoes shear flow.

Key Words: electrophoresis, zeta potential, dumbbell

INTRODUCTION

Electrophoresis provides a means to characterize and separate colloidal species on the basis of surface charge or more correctly, surface potential with respect to the bulk fluid. Smoluchowski's equation relates the particle velocity $\mathbf{U}$ to the applied electric field $\mathbf{E}_\infty$ and the zeta potential ζ associated with the particle's surface:

$$\mathbf{U} = \frac{\epsilon\zeta}{4\pi\eta}\mathbf{E}_\infty, \qquad [1]$$

where η and ϵ are the viscosity and dielectric constant of the fluid, respectively. The assumptions used to derive [1] are: (i) the particle is rigid and nonconducting; (ii) the local mean radius of curvature $\bar{R}$ is much larger than the Debye screening length κ^{-1} of the solution ($\kappa\bar{R} \to \infty$); (iii) the surrounding fluid is unbounded; and (iv) the zeta potential is uniform over the particle surface. Morrison (1970) showed that [1] holds for particles of arbitrary shape and that no particle rotation occurs, given the above assumptions. A boundary-layer analysis of the double layer by Dukhin & Derjaguin (1974) and O'Brien (1983) has shown that the effects of double-layer polarization may be neglected when

$$\kappa\bar{R}\left[\cosh\left(\frac{ze\zeta}{2kT}\right)\right]^{-1} \gg 1, \qquad [2]$$

where z is the charge number of the counterion with the largest absolute valency in the electrolyte, e is the charge on one proton, T is the fluid temperature and k is Boltzmann's constant. Theories have been developed to account for zeta potential variations over the surface of spherical (Anderson 1985) and nonspherical (Fair & Anderson 1989; Teubner 1982) particles, assuming (i), (ii) and (iii) are valid assumptions.

Interest in the development of theories to describe the electrophoresis of suspensions has resulted in several approaches to multiparticle systems, including the use of capillary tube models, unit cell models, lattice models or periodically constricted tubes (Kozak & Davis 1989). Another approach has been to examine the electrophoresis of two interacting particles and then attempt to describe the concentration effects in terms of the two-sphere description (Anderson 1981; Chen & Keh 1988). This approach considers the effects of electric field and hydrodynamic interactions on the electrophoretic velocity of a particle because of its proximity to another particle. Typically, these theories have been directed toward suspensions in which flocculation or coagulation is absent. In many suspensions, especially heterogeneous suspensions, coagulation occurs to form aggregates which would be expected to affect the behavior of the suspension as a whole. An aggregate formed by heterocoagulation or bridging represents an interesting system for which both nonuniform charge effects and "particle interactions" must be accounted. Here, the term "particle interactions" refers to interactions between particles which compose a single aggregate.

A theory for the electrophoresis of nonuniformly charged ellipsoidal particles (Fair & Anderson 1989) suggests that a particle with nonuniform charge and nonspherical shape has interesting dynamics in an electric field. For example, an oblate or prolate spheroid having a nonzero dipole moment of the zeta potential tends to align with the electric field, in contrast to the zero rotation predicted for uniformly charged particles (Morrison 1970). Furthermore, a quadrupole moment of the zeta potential distribution on a spheroid causes the translational velocity to depend on the particle's orientation with respect to the applied field. Since the Brownian mobility of micron-sized particles in liquids is small, the application of an electric field to a suspension of single particles and multiparticle aggregates might significantly influence the microscopic structure through alignment of the particles and through the distribution of their translational velocities. If the electrokinetic effects are comparable to the hydrodynamic effects, electric fields might influence the rheology of the suspension.

In an attempt to understand and model the electrophoresis of aggregates formed in a heterogeneous suspension, we have chosen to study the most elementary aggregate, a doublet formed by heterocoagulation or bridging of two different colloidal particles in the suspension. The objective of this work is to provide a theory for the electrophoretic mobility of a doublet modelled as a dumbbell composed of two spheres of arbitrary sizes connected by an infinitesimally thin, rigid rod of arbitrary length. Since the connecting rod is thin, we assume that it does not affect the electric field or the velocity field and only serves to insure the rigid-body motion of the dumbbell. Each sphere is rigid and nonconducting with a uniform but arbitrary zeta potential. We also invoke the thin double-layer assumption with the understanding that the magnitudes of the zeta potentials are sufficiently small to neglect polarization effects, as required by [2].

In this paper we develop a solution for the dumbbell problem which satisfies the electrokinetic equations in the limit of thin double layers. We utilize the linearity of the governing equations to divide the problem into two subproblems for which the solutions already exist or are easily obtained. The first subproblem ("free" problem) is the electrophoresis of two freely suspended spheres without the connecting rod. The second subproblem ("connector" problem) involves the Stokes-flow resistance of two spheres translating and rotating such that the force, torque and rigid-body motion constraints on the dumbbell are satisfied.

DYNAMICS OF A DUMBBELL IN AN ELECTRIC FIELD

The system under consideration is a dumbbell composed of two charged spheres with thin double layers, labelled 1 and 2 with radii a_1 and a_2 and zeta potentials ζ_1 and ζ_2 as shown in figure 1. The sphere centers are separated by a distance l and the orientation of the dumbbell is defined by a unit vector $\mathbf{e}$ directed from the center of sphere 1 toward the center of sphere 2. An applied electric field $\mathbf{E}_\infty$ causes the dumbbell to translate with velocity $\mathbf{U}_o$ and rotate with angular velocity $\mathbf{\Omega}$. The velocity $\mathbf{U}_o$ refers to the translational velocity of a point "o" on the dumbbell designated as the center or "origin". For low to moderate applied electric fields, $\mathbf{U}_o$ and $\mathbf{\Omega}$ are linearly proportional to $\mathbf{E}_\infty$. Assuming no inertial effects, the quasi-steady fluid velocity must satisfy the Stokes

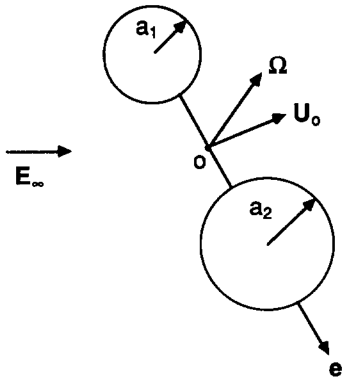

Figure 1. Charged colloidal dumbbell in an applied electric field. The rigid connecting rod is assumed to be infinitesimally thin relative to the size of the spheres; l is the distance between the centers of the spheres.

equations, modified by the inclusion of the electrical stress which results from interactions of the applied electric field with the charged fluid in the thin double layer:

$$\eta \nabla^2 \mathbf{v} - \nabla p + \nabla \cdot \tau^e = 0, \quad [3a]$$

$$\nabla \cdot \mathbf{v} = 0; \quad [3b]$$

on S^p: $$\mathbf{v} = \mathbf{U}_o + \mathbf{\Omega} \times \mathbf{r}_o, \quad [3c]$$

$r \to \infty$: $$\mathbf{v} \to 0, \quad [3d]$$

where $\mathbf{v}$ is the fluid velocity, p is the pressure, $\mathbf{r}_o$ is the position vector measured from the origin, S^p denotes the particle surface and τ^e is the electrical stress tensor. In principle, we should also apply [3c] to the surface of the connecting rod in addition to the surfaces of the spheres; however, we assume it is sufficiently thin, compared to a_1 and a_2, to have no effect on the fluid dynamics. For a fluid with a spatially uniform dielectric constant, $\nabla \cdot \tau^e = \rho_e \mathbf{E}$, where $\rho_e(\mathbf{r}_o)$ is the charge density within the diffuse double layer. The force and torque acting on a boundary which encompasses the particle and its thin double layer are zero, since the region enclosed by the boundary represents a body with no net charge. These two additional relationships are necessary to solve for $\mathbf{U}_o$ and $\mathbf{\Omega}$. On this boundary the contributions to the force and torque from the electrical stress are negligible because $\rho_e(\mathbf{r}_o)$ essentially zero outside the boundary. Since $\kappa a_i \to \infty$, the boundary appears to coincide with the particle surface on length scales $O(a_i)$, which enables us to evaluate contributions to the force and torque from the stress tensor over a known surface in space defined by the particle's surface rather than an imaginary boundary. This approach has been used previously to determine electrophoretic velocities of compact particles (Anderson 1985; Fair & Anderson 1989).

Since the force acting on a rigid body is independent of the choice of origin, the constraint that the net force is zero on the dumbbell can be expressed in terms of the forces acting on the two spheres:

$$\mathbf{F}_1 + \mathbf{F}_2 = 0. \quad [4]$$

Though the torque acting on a rigid body usually depends on the choice of origin, for a force-free dumbbell the torque is independent of the choice of origin. To prove this we first express the total torque about the dumbbell's origin in terms of the forces and torques acting on each sphere:

$$\mathbf{T}_o = \mathbf{T}_1 + \mathbf{T}_2 + \mathbf{r}_{o1} \times \mathbf{F}_1 + \mathbf{r}_{o2} \times \mathbf{F}_2, \quad [5]$$

where $\mathbf{r}_{oi}$ is the position vector for the center of sphere i relative to the origin of the dumbbell and $\mathbf{T}_i$ is the torque on sphere i about its center. Using [4] to eliminate $\mathbf{F}_1$ gives

$$\mathbf{T}_o = \mathbf{T}_1 + \mathbf{T}_2 + (\mathbf{r}_{o2} - \mathbf{r}_{o1}) \times \mathbf{F}_2, \quad [6]$$

which is independent of the choice of the origin since $(\mathbf{r}_{o2} - \mathbf{r}_{o1}) = l\mathbf{e}$. The constraint that the torque acting on the dumbbell is zero becomes

$$\mathbf{T}_1 + \mathbf{T}_2 + l\mathbf{e} \times \mathbf{F}_2 = 0. \quad [7]$$

Rather than attempting to solve [3] along with [4] and [7] directly for $\mathbf{U}_o$ and $\boldsymbol{\Omega}$ given τ^e, it is more convenient to utilize the linearity of the governing equations to divide the problem into a "free" part and a "connector" part, such that superposition of the solutions for these two subproblems yields the solution to the dumbbell problem:

$$\mathbf{U}_i = \mathbf{U}_i^f + \mathbf{U}_i^c, \quad [8a]$$

$$\boldsymbol{\Omega}_i = \boldsymbol{\Omega}_i^f + \boldsymbol{\Omega}_i^c, \quad [8b]$$

$$\mathbf{F}_i = \mathbf{F}_i^f + \mathbf{F}_i^c, \quad [8c]$$

$$\mathbf{T}_i = \mathbf{T}_i^f + \mathbf{T}_i^c, \quad [8d]$$

$$\mathbf{v} = \mathbf{v}^f + \mathbf{v}^c \quad [8e]$$

and

$$p = p^f + p^c, \quad [8f]$$

where subscripts $i = 1, 2$ refer to quantities evaluated at the centers of the spheres. The "free" part (superscript f) considers two freely suspended spheres moving by electrophoresis. The "connector" part (superscript c) considers two interacting spheres in Stokes flow such that superposition with the "free" part gives the rigid-body motion of the dumbbell governed by [3], [4] and [7]. Both the "free" and "connector" parts can be considered from the perspective of parallel and perpendicular orientations of the director $\mathbf{e}$ with respect to the direction of the applied field $\mathbf{E}_\infty$.

THE "FREE" PROBLEM

The "free" case considers the motion of two spheres, each of which are free to translate and rotate in response to the electric field. $\mathbf{v}^f$ and p^f must satisfy [3a] and [3b] along with the following boundary conditions:

on S_1^p: $$\mathbf{v}^f = \mathbf{U}_1^f + \boldsymbol{\Omega}_1^f \times \mathbf{r}_1, \quad [9a]$$

on S_2^p: $$\mathbf{v}^f = \mathbf{U}_2^f + \boldsymbol{\Omega}_2^f \times \mathbf{r}_2, \quad [9b]$$

$r \to \infty$: $$\mathbf{v}^f \to 0, \quad [9c]$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are position vectors with origins at the respective sphere centers. The net force and torque on *each* sphere are zero because the spheres are not connected. The solution of this problem must account for the perturbations to the electric field and velocity field caused by the proximity of the two spheres. The governing equations can be solved by dividing the fluid into an "inner" and an "outer" region and using a matching procedure to ensure a continuous solution, whereby the solution obtained for the "inner" region supplies a boundary condition for "outer" region (Anderson 1985).

The "inner' region encompasses the thin double layer where the fluxes of charge and fluid are locally one-dimensional and parallel to the particle's surface. Poisson's equation relates the electrical potential to the charge density. The solution for the flow in the "inner" region gives the Helmholtz expression for the fluid velocity at the outer edge of the double layer relative to the local velocity of the particle's surface:

$$\mathbf{v}_i^s = -\frac{\epsilon\zeta_i}{4\pi\eta}\,\mathbf{E}_i^s. \quad [10]$$

$\mathbf{E}_i^s$ is the local electric field on the surface of sphere i found by solving Laplace's equation in the "outer" region:

$$\nabla^2 \Phi = 0; \quad [11a]$$

on S_1^{p+}: $$\mathbf{n}\cdot\nabla\Phi = 0, \quad [11b]$$

on S_2^{p+}: $$\mathbf{n}\cdot\nabla\Phi = 0, \quad [11c]$$

$r \to \infty$: $$-\nabla\Phi \to \mathbf{E}_\infty, \quad [11d]$$

on S_i^{p+}: $$\mathbf{E}_i^s = -\nabla\Phi, \quad [11e]$$

where $\mathbf{n}$ is the unit normal to the dumbbell surface pointing into the fluid. S_i^{p+} denotes the surface which coincides with the outer edge of the double layer around sphere i. Since the double layers are thin, S_i^{p+} and S_i^p (the actual surface of the sphere) are indistinguishable on the scale of a_i.

The "outer" region consists of the fluid external to the outer edge of the thin double layer. In this region ρ_e is essentially zero and the electrical stress tensor is negligible. The equations and boundary conditions which govern the flow are:

$$\eta \nabla \mathbf{v}^f - \nabla p^f = 0, \tag{12a}$$

$$\nabla \cdot \mathbf{v}^f = 0; \tag{12b}$$

$$\text{on } S_1^{p+}: \quad \mathbf{v}^f = \mathbf{U}_1^f + \mathbf{\Omega}_1^f \times \mathbf{r}_1 + \mathbf{v}_1^s \tag{12c}$$

$$\text{on } S_2^{p+}: \quad \mathbf{v}^f = \mathbf{U}_2^f + \mathbf{\Omega}_2^f \times \mathbf{r}_2 + \mathbf{v}_2^s \tag{12d}$$

$$r \to \infty: \quad \mathbf{v}^f \to 0, \tag{12e}$$

where $\mathbf{v}_i^s$ is the "slip" velocity given by [10]. Requiring that

$$\mathbf{F}_1^f = \mathbf{F}_2^f = 0 \tag{13}$$

and

$$\mathbf{T}_1^f = \mathbf{T}_2^f = 0 \tag{14}$$

provides closure to solve for the translational and angular velocities of the spheres.

The velocities of the two "free" spheres undergoing electrophoresis can be expressed as follows:

$$\mathbf{U}_1 = \frac{\epsilon}{4\pi\eta}[(\zeta_1 + (\zeta_2 - \zeta_1)A_1)\mathbf{ee} + (\zeta_1 + (\zeta_2 - \zeta_1)B_1)(\mathbf{I} - \mathbf{ee})] \cdot \mathbf{E}_\infty, \tag{15a}$$

$$\mathbf{U}_2 = \frac{\epsilon}{4\pi\eta}[(\zeta_2 + (\zeta_1 - \zeta_2)A_2)\mathbf{ee} + (\zeta_2 + (\zeta_1 - \zeta_2)B_2)(\mathbf{I} - \mathbf{ee})] \cdot \mathbf{E}_\infty, \tag{15b}$$

$$a_1 \mathbf{\Omega}_1 = \frac{\epsilon}{4\pi\eta}(\zeta_2 - \zeta_1)C_1 \mathbf{e} \times \mathbf{E}_\infty \tag{15c}$$

and

$$a_2 \mathbf{\Omega}_2 = \frac{\epsilon}{4\pi\eta}(\zeta_2 - \zeta_1)C_2 \mathbf{e} \times \mathbf{E}_\infty, \tag{15d}$$

where $\mathbf{I}$ is the unit dyadic. Two solutions are currently available for the dimensionless parameters $(A_1, A_2, B_1, B_2, C_1, C_2)$. The first (Chen & Keh 1988) is based on a method of reflections; the results are reproduced in appendix A correct through $O(l^{-7})$. The second (Keh & Chen 1989a, b) was obtained by utilizing bispherical coordinates. For the range of separation distances from $(a_1 + a_2)/l = 0.99$ to $(a_1 + a_2)/l = 0.2$, A_1 and A_2 were evaluated for three size ratios $(a_1/a_2 = 1, 0.5, 0.2)$ and B_1, B_2, C_1 and C_2 for two size ratios $(a_1/a_2 = 1, 0.5)$. These results suggest that the solution obtained by the method of reflections holds for moderate to large separation distances but becomes increasingly inaccurate as the separation distance decreases, especially for the angular velocities. The solution using bispherical coordinates indicates that the smaller sphere rotates increasingly faster than the larger sphere as the separation distance decreases, while the method-of-reflections solution predicts that the spheres have the same angular velocities. The direction of rotation is the same for both spheres, unlike the case of two sedimenting spheres (Chen & Keh 1988; Keh & Chen 1989b). We note that the solution obtained by Reed & Morrison (1976) for the electrophoresis of two equal-sized spheres using bispherical coordinates does not apply since the spheres were not allowed to rotate freely.

THE "CONNECTOR" PROBLEM

The "connector" problem involves solving for four unknown translational and angular velocities that yield a solution to the original dumbbell problem when they are combined with the results of the "free" case. The fluid dynamics must satisfy the classical Stokes equations:

$$\eta \nabla^2 \mathbf{v}^c - \nabla p^c = 0, \qquad [16a]$$

$$\nabla \cdot \mathbf{v}^c = 0; \qquad [16b]$$

on S_1^p: $$\mathbf{v}^c = \mathbf{U}_1^c + \mathbf{\Omega}_1^c \times \mathbf{r}_1, \qquad [16c]$$

on S_2^p: $$\mathbf{v}^c = \mathbf{U}_2^c + \mathbf{\Omega}_2^c \times \mathbf{r}_2, \qquad [16d]$$

$r \to \infty$: $$\mathbf{v}^c \to 0. \qquad [16e]$$

Since the forces and torques acting on the spheres in the "free" case are zero, [4] and [7] can be expressed in terms of the "connector" forces and torques using [8c] and [8d] to give

$$\mathbf{F}_1^c + \mathbf{F}_2^c = 0 \qquad [17]$$

and

$$\mathbf{T}_1^c + \mathbf{T}_2^c + l\mathbf{e} \times \mathbf{F}_2^c = 0. \qquad [18]$$

These relationships supply two of the four vector constraints required to close the problem. The other constraints result from the consideration of the rigid-body mechanics of the dumbbell. The angular velocity of a rigid body is independent of the choice of origin giving, as the third constraint,

$$\mathbf{\Omega}_2^c - \mathbf{\Omega}_1^c = \mathbf{\Omega}_1^f - \mathbf{\Omega}_2^f. \qquad [19]$$

The final constraint utilizes the standard rigid-body description of the velocity at point $\mathbf{x}$ on the dumbbell:

$$\mathbf{U}(\mathbf{x}) = \mathbf{U}_o + \mathbf{\Omega} \times \mathbf{r}_{ox}, \qquad [20]$$

where r_{ox} is the position of $\mathbf{x}$ relative to the origin. Applying [20] with $\mathbf{x}$ at the center of each sphere and eliminating $\mathbf{U}_o$ gives

$$\mathbf{U}_2 - \mathbf{U}_1 = \mathbf{\Omega} \times (\mathbf{r}_{o2} - \mathbf{r}_{o1}). \qquad [21]$$

Using the fact that $\mathbf{\Omega} = \mathbf{\Omega}_1 = \mathbf{\Omega}_2$ and substituting [8a] and [8b] into the above expression gives the final constraint:

$$\mathbf{U}_2^c - \mathbf{U}_1^c - \mathbf{\Omega}_1^c \times l\mathbf{e} = \mathbf{U}_1^f - \mathbf{U}_2^f + \mathbf{\Omega}_1^f \times l\mathbf{e}. \qquad [22]$$

Therefore, the two-sphere hydrodynamics problem must be solved such that $\mathbf{U}_1^c$, $\mathbf{U}_2^c$, $\mathbf{\Omega}_1^c$ and $\mathbf{\Omega}_2^c$ satisfy [17]–[19] and [22], with the velocities of the "free" problem known.

The force and torque on each of the spheres obtained from a solution of [16] can be expressed in terms of the translational and angular velocities using the grand resistance matrix formalism of Brenner & O'Neill (1972):

$$\begin{bmatrix} \mathbf{F}_1^c \\ \mathbf{F}_2^c \\ \mathbf{T}_1^c \\ \mathbf{T}_2^c \end{bmatrix} = -\eta \mathbf{R} \begin{bmatrix} \mathbf{U}_1^c \\ \mathbf{U}_2^c \\ \mathbf{\Omega}_1^c \\ \mathbf{\Omega}_2^c \end{bmatrix}, \qquad [23]$$

where $\mathbf{R}$ is the grand resistance matrix for two spheres. $\mathbf{R}$ is a 4×4 matrix whose elements are dyadic resistance coefficients with the following general form:

$$\mathbf{R}_{jk} = \mathbf{R}_{jk}^p \mathbf{ee} + R_{jk}^n (\mathbf{I} - \mathbf{ee}) + R_{jk}^s \hat{\epsilon} \cdot \mathbf{e}, \qquad [24]$$

where $\hat{\epsilon}$ is the permutation triadic ($\hat{\epsilon} = -\mathbf{I} \times \mathbf{I}$) and $\mathbf{I}$ is the unit dyadic. The resistance scalars ($R_{jk}^p, R_{jk}^n, R_{jk}^s$) are functions of the radii of the spheres and the separation distance.

In this paper we used the results of Jeffrey & Onishi (1984a) that are valid for arbitrarily-sized spheres and arbitrary separation distances. They provide three solutions for each of the components: a method-of-reflections solution; an asymptotic solution for nearly touching spheres; and a composite solution which combines the results from the method of reflections with those from the asymptotic solution. In appendix A we list the expressions for the resistance scalars that were obtained by the method of reflections. The composite solution represents the singular terms which appear in the asymptotic solution more efficiently than the series solution obtained by the method of reflections. We solved the recurrence relationships given by Jeffrey & Onishi (1984a) using the corrections given in appendix B and retained terms through $O(l^{-50})$ for each series in the composite solution. To test the accuracy of the composite solution we numerically evaluated the expressions for the scalar resistances and obtained good agreement with the tabulated results of Davis (1969), obtained using bispherical coordinates. As a further check we computed the components of the grand resistance matrix for a dumbbell using the two-sphere grand resistance matrix and found excellent agreement with the tabulated results of Adler (1981), obtained using bispherical coordinates. Appendix C outlines the method utilized by both Adler (1981) and ourselves to obtain the grand resistance matrix for a dumbbell using the two-sphere grand resistance matrix.

We obtained an analytical solution for the "connector" velocities in terms of the "free" velocities and the scalar components of **R** by using [23] and solving [17]–[19] and [22] simultaneously; the details are given elsewhere (Fair 1990). Rather than give the explicit solution for the "connector" velocities here, in the next section we give the final results for the dumbbell obtained by combining the "free" and "connector" velocities.

RESULTS

Since the governing equations and constraints are independent of the location of the origin of the dumbbell, the origin is arbitrary and only affects the presentation of the results for the translational velocity. We place the origin at the center of hydrodynamic stress of the dumbbell to enable our results to be used directly in the determination of the effects of particle orientation on the average translational velocity of an ensemble of dumbbells or on the time-averaged translational velocity of an individual dumbbell. The center of hydrodynamic stress is the unique point for bodies of revolution at which there is no coupling between translation and rotation (Happel & Brenner 1973); i.e. the force on the body depends only upon the translational velocity at that point and the torque about the point depends only upon the rotational velocity. For the dumbbell this point lies along the line connecting the centers of the spheres a distance lX_{01} from the center of sphere 1. Appendix C outlines the procedure used to determine X_{01} using the grand resistance matrix for two spheres.

The electrophoretic motion of the dumbbell is obtained by combining the results of the "free" and "connector" problems:

$$\mathbf{U}_o = (1 - X_{01})(\mathbf{U}_1^f + \mathbf{U}_1^c) + X_{01}(\mathbf{U}_2^f + \mathbf{U}_2^c) \quad [25a]$$

and

$$\mathbf{\Omega} = \mathbf{\Omega}_1^f + \mathbf{\Omega}_1^c = \mathbf{\Omega}_2^f + \mathbf{\Omega}_2^c. \quad [25b]$$

Substitution of the "free" and "connector" velocities into [25] leads to the following expressions:

$$\mathbf{U}_o = \frac{\epsilon}{4\pi\eta}[M^p\mathbf{ee} + M^n(\mathbf{I} - \mathbf{ee})] \cdot \mathbf{E}_\infty \quad [26a]$$

and

$$\mathbf{\Omega} = \frac{\epsilon}{4\pi\eta}\left(\frac{\zeta_2 - \zeta_1}{l}\right) N\mathbf{e} \times \mathbf{E}_\infty, \quad [26b]$$

where M^p and M^n can be conveniently expressed as linear functions of the zeta potentials:

$$M^p = [\zeta_1(1 - K^p) + \zeta_2 K^p] \quad [26c]$$

and

$$M^n = [\zeta_1(1 - K^n) + \zeta_2 K^n]. \quad [26d]$$

The dimensionless parameters K^p, K^n and N are functions of the resistance scalars (see [24]) and the "free" velocity parameters (see [15]), and therefore, depend only on a_1/a_2 and $(a_1+a_2)/l$:

$$K^p = \frac{(R_{11}^p + R_{21}^p)A_1 + (R_{12}^p + R_{22}^p)(1-A_2)}{R_{11}^p + R_{12}^p + R_{21}^p + R_{22}^p}, \qquad [27a]$$

$$N = \frac{h_1h_6 - h_4h_3 - h_3h_5 + h_2h_6}{h_1h_5 - h_4h_2} + 1 - B_1 - B_2 \qquad [27b]$$

and

$$K^n = B_1 + \frac{h_3h_5 - h_2h_6}{h_1h_5 - h_4h_2} + X_{o1}N, \qquad [27c]$$

where

$$X_{o1} = \frac{l(R_{21}^n + R_{22}^n) - (R_{31}^s + R_{32}^s + R_{41}^s + R_{42}^s)}{l(R_{11}^n + R_{12}^n + R_{21}^n + R_{22}^n)}, \qquad [27d]$$

$$h_1 = R_{11}^n + R_{21}^n - \left(\frac{R_{13}^s + R_{23}^s + R_{14}^s + R_{24}^s}{l}\right), \qquad [27e]$$

$$h_2 = R_{12}^n + R_{22}^n + \left(\frac{R_{13}^s + R_{23}^s + R_{14}^s + R_{24}^s}{l}\right), \qquad [27f]$$

$$h_3 = (R_{13}^s + R_{23}^s + R_{14}^s + R_{24}^s)\left(\frac{B_1 + B_2 - 1}{l}\right) + (R_{13}^s + R_{23}^s)\frac{C_1}{l} + (R_{14}^s + R_{24}^s)\frac{C_2}{l}, \qquad [27g]$$

$$h_4 = -R_{31}^s - R_{41}^s - R_{23}^s - R_{24}^s + lR_{21}^n - \left(\frac{R_{33}^n + R_{34}^n + R_{43}^n + R_{44}^n}{l}\right), \qquad [27h]$$

$$h_5 = -R_{32}^s - R_{42}^s + R_{23}^s + R_{24}^s + lR_{22}^n + \left(\frac{R_{33}^n + R_{34}^n + R_{43}^n + R_{44}^n}{l}\right) \qquad [27i]$$

and

$$h_6 = \left[(R_{33}^n + R_{34}^n + R_{43}^n + R_{44}^n + lR_{23}^s + lR_{24}^s)\left(\frac{B_1 + B_2 - 1}{l}\right) + (R_{33}^n + R_{43}^n + lR_{23}^s)\frac{C_1}{l} + (R_{34}^n + R_{44}^n + lR_{24}^s)\frac{C_2}{l}\right]. \qquad [27j]$$

In the limit $(a_1+a_2)/l \to 0$, there is no interaction between the spheres except that required by the connecting rod, and using the relations given in appendix A, we obtain

$$K^p = K^n = \left(1 + \frac{a_1}{a_2}\right)^{-1}, \qquad [28a]$$

$$N = 1 \qquad [28b]$$

and

$$X_{o1} = \left(1 + \frac{a_1}{a_2}\right)^{-1}. \qquad [28c]$$

For the special case when $\zeta_1 = \zeta_1$, Smoluchowski's equation holds with $\Omega = 0$ for all values of a_1/a_2 and $(a_1+a_2)/l$.

The additional fore–aft symmetry imparted to the dumbbell when $a_1 = a_2$ provides a means to obtain a solution for this special case. The center of hydrodynamic stress is at the midpoint between the spheres ($X_{o1} = 1/2$). The original problem, defined by [3] and the zero force and torque constraints, can be split into two problems, one symmetric and one anti-symmetric with respect to the zeta potentials of the spheres. The symmetric problem gives both spheres the same potential, equal to $(\zeta_1+\zeta_2)/2$. Smoluchowski's result applies to this case:

$$\mathbf{U}_o^{sym} = \frac{\epsilon}{4\pi\eta}\left(\frac{\zeta_1 + \zeta_2}{2}\right)\mathbf{E}_\infty; \qquad \Omega^{sym} = 0. \qquad [29]$$

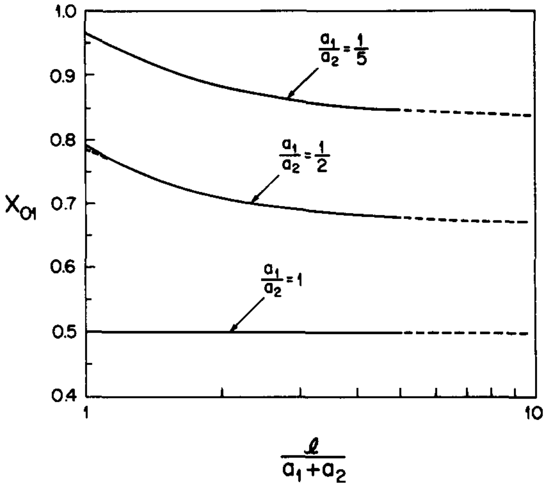

Figure 2. The distance from the center of sphere 1 to the center of hydrodynamic stress for a dumbbell, normalized by the distance between the centers of the spheres. Dashed lines indicate the method-of-reflections solution and solid lines indicate the solution listed in table 1.

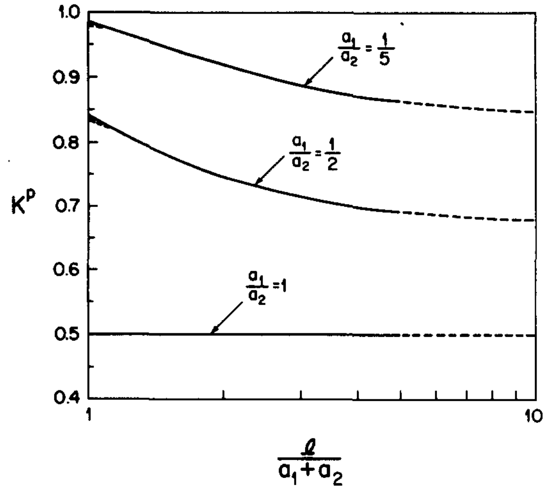

Figure 3. K^p, as defined by [26] and [27], vs the dimensionless center-to-center distance. Dashed lines indicate the method-of-reflections solution and solid lines indicate the solution listed in table 1.

For the antisymmetric case, with the zeta potentials equal in magnitude but opposite in sign, we obtain

$$\mathbf{U}_o^{\text{anti}} = 0. \tag{30}$$

By adding these solutions together we have

$$K^p = K^n = \tfrac{1}{2}. \tag{31}$$

Since Ω^{anti} cannot be deduced easily, we cannot obtain the rotational parameter N for this special case without following the complete procedure described previously.

Figure 2 shows how the center of hydrodynamic stress "o" varies with the separation between the spheres and the ratio of their radii. Figures 3–5 are plots of K^p, K^n and N constructed using the numerical results listed in table 1. These numerical values were calculated using the composite solution for the scalar resistances (Jeffrey & Onishi 1984a) and the parameters for the "free" velocities tabulated by Keh & Chen (1989a, b). The method-of-reflections results correct to $O(l^{-7})$, obtained using the expressions for "free" velocities and the resistance scalars given in appendix A,

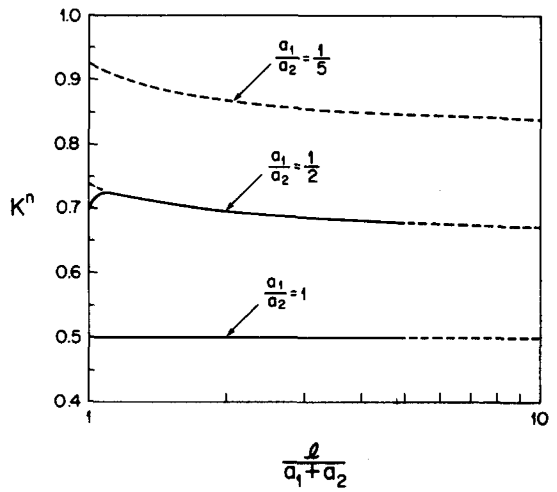

Figure 4. K^n, as defined by [26] and [27], vs the dimensionless center-to-center distance. Dashed lines indicate the method-of-reflections solutions and solid lines indicate the solution listed in table 1.

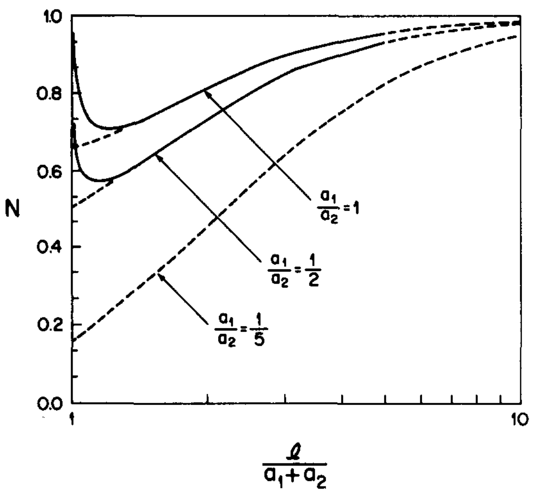

Figure 5. N, as defined by [26] and [27], vs the dimensionless center-to-center distance. Dashed lines indicate the method-of-reflections solution and solid lines indicate the solution listed in table 1.

Table 1. Numerical values of the dimensionless parameters defined in [26] and [27] and plotted in figures 2–5[a]

a_1/a_2	$(a_1+a_2)/l$	K^p	K^n	N	X_{01}
	0.20	0.8638			0.8486
	0.40	0.8995			0.8694
	0.60	0.9359			0.8978
	0.80	0.9656			0.9319
0.20	0.90	0.9767			0.9491
	0.95	0.9813			0.9572
	0.97	0.9830			0.9603
	0.98	0.9838			0.9618
	0.99	0.9845			0.9634
	0.20	0.6925	0.6784	0.9339	0.6792
	0.40	0.7266	0.6907	0.8017	0.6970
	0.60	0.7665	0.7035	0.6755	0.7224
	0.80	0.8060	0.7172	0.5861	0.7552
0.50	0.90	0.8245	0.7234	0.5715	0.7734
	0.95	0.8334	0.7230	0.5928	0.7826
	0.97	0.8369	0.7195	0.6231	0.7863
	0.98	0.8386	0.7155	0.6540	0.7882
	0.99	0.8403	0.7072	0.7197	0.7900
	0.20	0.5000	0.5000	0.9557	0.5000
	0.40	0.5000	0.5000	0.8632	0.5000
	0.60	0.5000	0.5000	0.7712	0.5000
	0.80	0.5000	0.5000	0.7123	0.5000
1.00	0.90	0.5000	0.5000	0.7206	0.5000
	0.95	0.5000	0.5000	0.7648	0.5000
	0.97	0.5000	0.5000	0.8128	0.5000
	0.98	0.5000	0.5000	0.8585	0.5000
	0.99	0.5000	0.5000	0.9512	0.5000

[a]These results were computed using the composite solution of Jeffrey & Onishi (1984a) through $O(l^{-50})$ for the resistance coefficients and the tabulated results of Keh & Chen (1988a, b) for the "free" velocities.

are also plotted in figures 2–5. At small separation distances, the method-of-reflections results underestimate the magnitudes of the parameters for the "free" velocities and, consequently, the results for K^n and N do not give the correct behavior at these separations. The method-of-reflections results for K^p show excellent agreement at all separation distances with the results listed in table 1.

In many systems of interest, the separation distance between the spheres may be small as a result of tethering by polymer bridges or by coagulation into a primary or secondary minimum of the energy profile. Our results for small separations and extrapolations to the case of touching spheres provide a model for these systems. The results for K^p are readily extrapolated to the case of touching spheres, but it is difficult to accurately extrapolate the results for K^n and N, except for K^n for equal-sized spheres. This difficulty arises because the curves for N and K^n have large slopes when the spheres are nearly touching. Nonetheless, we have extrapolated the curves in figures 2–5 to the limit $(a_1+a_2)/l \to 1$ with the results listed in table 2.

To more accurately describe the behavior of a dumbbell with a small separation distance, the results of an asymptotic solution of the "free" case for nearly touching spheres could be combined with existing results for the two-sphere grand resistance matrix using the procedure developed in this paper. The exact solution for the case when the spheres touch requires the use of a tangent sphere coordinate system. This analysis has been performed for the case when **e** is parallel with

Table 2. Extrapolations of the curves in figures 2–5 to $(a_1+a_2)/l \to 1$[a]

a_1/a_2	K^p	K^n	N	X_{01}
0.20	0.9852			0.9650
0.50	0.8420	0.6979	0.7938	0.7918
1.00	0.5000	0.5000	1.0553	0.5000

[a]Linear extrapolations were performed using the slope at $(a_1+a_2)/l = 0.99$, obtained by a cubic-spline fit.

$\mathbf{E}_\infty$ for equal-sized spheres with the result that $K^p = 1/2$, in agreement with the result predicted by the symmetry arguments leading to [31] (Fair 1990).

At small separation distances the double layers of the spheres may overlap. This overlap would result in interactions of the double layers, a situation assumed not to exist in deriving the solutions for the "free" case used in this paper. These double-layer interactions would occur over a small surface area of the dumbbell and might be expected to produce local effects of $O((\kappa a_i)^{-1})$. If this assertion is correct, such effects would be small for dumbbells with thin double layers and the behavior predicted by our model should represent real systems.

ELECTROSTATIC ALIGNMENT OF DUMBBELLS

While the translational velocity is certainly of interest in conventional electrophoresis, whether for purposes of charge characterization or particle separation, rotational motion is the more striking result because Smoluchowski's theory for particles of *uniform* zeta potential predicts *no* rotation. The consequences of rotation depend on the relative strength of the electrophoretic alignment vs Brownian motion or the shear rate of the suspending fluid.

The rotary Péclet number is a dimensionless parameter which quantifies the degree of alignment achieved by an applied electric field despite the randomizing effect of Brownian motion:

$$\mathrm{Pe_r} \equiv \frac{|\Omega|}{D^r}, \qquad [32]$$

where D^r is the rotational diffusion coefficient about an axis perpendicular to $\mathbf{e}$. When $\mathrm{Pe_r} > 1$, the particles are strongly aligned. D^r can be expressed in terms of the resistance of the dumbbell to rotation and fluid properties:

$$D_r = \frac{kT}{\eta K^r}, \qquad [33]$$

where K^r is a resistance scalar of the grand resistance matrix for a dumbbell $\mathbf{R}^d$ (see appendix C) for rotation about an axis perpendicular to $\mathbf{e}$ which passes through the center of hydrodynamic stress. K^r can be written in terms of the resistance scalars of $\mathbf{R}$:

$$\begin{aligned} K^r = [&(lX_{01})^2(R^n_{11} + R^n_{12} + R^n_{21} + R^n_{22}) - (lX_{01})(R^s_{13} + R^s_{14} + R^s_{23} + R^s_{24}) \\ &+ (lX_{01})(R^s_{31} + R^s_{32} + R^s_{41} + R^s_{42}) - (l^2X_{01})(R^n_{12} + R^n_{21} + 2R^n_{22}) \\ &+ l^2(R^n_{22}) + l(R^s_{23} + R^s_{24} - R^s_{32} - R^s_{42}) + (R^n_{33} + R^n_{34} + R^n_{43} + R^n_{44})]. \end{aligned} \qquad [34]$$

The $\mathrm{Pe_r}$ for the electrophoretic alignment can be expressed in general terms by

$$\mathrm{Pe_r} = \left[\frac{3\epsilon|\zeta_2 - \zeta_1|E_\infty}{2kT}\left(\frac{la_1a_2}{a_1+a_2}\right)\right] H \sin\theta, \qquad [35]$$

where θ is the solid angle between $\mathbf{e}$ and $\mathbf{E}_\infty$. H is a dimensionless parameter, plotted in figure 6, which depends on the separation distance and the ratio of the spheres' radii:

$$H = NK^r\left(\frac{a_1 + a_2}{6\pi l^2 a_1 a_2}\right), \qquad [36]$$

such that $H \to 1$ as $l/(a_1 + a_2) \to \infty$. In an aqueous solution at 25°C with an applied field of 1000 V/m, dumbbells ($a_1 = 0.5\ \mu$m, $a_2 = 0.5\ \mu$m, $l = 1.01\ \mu$m) whose spheres differ in zeta potential by kT/e have $\mathrm{Pe_r} < 1$ only if $\theta < 2°$, indicating that the dumbbells are almost completely aligned.

The ability of an applied electric field to orient dumbbells when the suspension is under shear ($\dot\gamma$ = shear rate) is determined by the expression

$$\left[\frac{\epsilon(\zeta_2 - \zeta_1)N}{4\pi\eta l}\right]\frac{E_\infty}{\dot\gamma}, \qquad [37]$$

which is the ratio of the characteristic magnitude of the angular velocity caused by the electric field to that due to fluid vorticity. To obtain a sense of the field required to align the particles, we

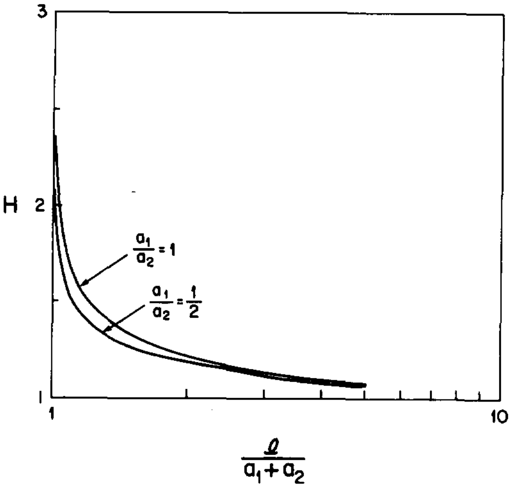

Figure 6. H, obtained using [36] and the values listed in table 1, vs the dimensionless center-to-center distance.

consider micron-sized dumbbells ($l = 1\ \mu$m) in water at 25°C, with the two spheres differing in zeta potential by kT/e. Taking $N = 1$ for the purpose of this order-of-magnitude estimate, the criterion for alignment of the dumbbells, which is derived by requiring the expression in [37] to greatly exceed unity, is

$$E_\infty \gg 50\dot{\gamma}, \qquad [38]$$

where E_∞ is in V/m and $\dot{\gamma}$ is in s^{-1}. This calculation indicates that only modest electric fields are needed to align these types of particles, even when the shear rate is rather large (say, 100–1000 s^{-1}). Since orientation of nonspherical particles affects rheological properties, one might hope to adjust the rheology of a suspension of dipolar dumbbells by controlling the magnitude and direction of the electric field.

SUMMARY

Our method of constructing a solution for the electrophoretic mobility coefficients for charged dumbbells utilizes published results for the two-sphere hydrodynamics of electrophoresis and Stokes flow. The translational and rotational mobilities for electrophoresis of a rigid dumbbell can be calculated directly from [27] and the method-of-reflections values for the scalar resistance coefficients found in appendix A; figures 3–5 show that this calculation is accurate except when the two spheres of the dumbbell almost touch. To extend the calculations to small separation distances for values of a_1/a_2 not considered here, one would need to solve the "free" problem of electrophoresis in a manner similar to Keh & Chen (1989a, b). We have estimated the mobility coefficients for the case of *touching* spheres by extrapolating our numerical calculations in a reasonable but still arbitrary manner to $l/a_1 + a_2) \rightarrow 1$; these values are listed in table 2.

The motion of heterogeneous colloids, whether single particles of nonuniform surface charge, such as clay, or aggregates formed by single particles of different surface charge, has received little attention. Our analysis shows that even a small difference in the zeta potential between the two spheres of a dumbbell would couple with the applied electric field to align the dumbbell. Order-of-magnitude estimates indicate that rather modest electric fields are necessary to control the alignment of micron-sized dumbbells, even when the suspension is sheared, if the difference in zeta potentials of the spheres is of order kT/e. Such alignment should be detectable by optical and rheological measurements, thereby pointing toward an experimental route for evaluating the quantitative accuracy of the assumptions on which the analysis presented here is based.

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APPENDIX A

Method-of-reflections Solution for "Free" Problem Parameters and the Scalar Components of **R**

Chen & Keh (1988) provide a method-of-reflections solution for the dimensionless parameters in [15]:

$$A_1 = (a_3^2)l^{-3} + \left(\frac{13a_1^3a_2^3}{2}\right)l^{-6} + O(l^{-8}), \qquad [A.1]$$

$$A_2 = (a_1^3)l^{-3} + \left(\frac{13a_1^3a_2^3}{2}\right)l^{-6} + O(l^{-8}), \qquad [A.2]$$

$$B_1 = \left(\frac{-a_2^3}{2}\right) l^{-3} + \left(\frac{-a_1^3 a_2^3}{4}\right) l^{-6} + O(l^{-8}), \qquad [A.3]$$

$$B_2 = \left(\frac{-a_1^3}{2}\right) l^{-3} + \left(\frac{-a_1^3 a_2^3}{4}\right) l^{-6} + O(l^{-8}), \qquad [A.4]$$

$$C_1 = \left(\frac{15 a_1^4 a_2^3}{4}\right) l^{-7} + O(l^{-9}) \qquad [A.5]$$

and

$$C_2 = \left(\frac{15 a_1^3 a_2^4}{4}\right) l^{-7} + O(l^{-9}). \qquad [A.6]$$

The method-of-reflections results for the scalar components of the grand resistance matrix **R** were extracted from the work of Jeffrey & Onishi (1984a) and are listed below using the notation of [24]. The resistance scalars not listed are all zero except for those associated with rotation about **e** ($R^p_{33}, R^p_{34}, R^p_{43}, R^p_{44}$) which are not required for the analysis in this paper.

$$R^p_{11} = 6\pi a_1 \left[1 + \left(\frac{9a_1 a_2}{4}\right) l^{-2} + \left(-\frac{3a_1^3 a_2}{2} + \frac{81 a_1^2 a_2^2}{16} + \frac{9 a_1 a_2^3}{4}\right) l^{-4} + \left(\frac{a_1^5 a_2}{4} + \frac{27 a_1^4 a_2^2}{16} + \frac{281 a_1^3 a_2^3}{64} + \frac{81 a_1^2 a_2^4}{8} + \frac{9 a_1 a_2^5}{4}\right) l^{-6} + O(l^{-8}) \right], \qquad [A.7]$$

$$R^p_{22} = 6\pi a_2 \left[1 + \left(\frac{9a_1 a_2}{4}\right) l^{-2} + \left(-\frac{3a_1 a_2^3}{2} + \frac{81 a_1^2 a_2^2}{16} + \frac{9 a_1^3 a_2}{4}\right) l^{-4} + \left(\frac{a_1 a_2^5}{4} + \frac{27 a_1^2 a_2^4}{16} + \frac{281 a_1^3 a_2^3}{64} + \frac{81 a_1^4 a_2^2}{8} + \frac{9 a_1^5 a_2}{4}\right) l^{-6} + O(l^{-8}) \right], \qquad [A.8]$$

$$R^p_{12} = -6\pi a_1 \left[\left(\frac{3a_2}{2}\right) l^{-1} + \left(-\frac{a_1^2 a_2}{2} + \frac{27 a_1 a_2^2}{8} - \frac{a_2^3}{2}\right) l^{-3} + \left(\frac{9 a_1^3 a_2^2}{4} + \frac{243 a_1^2 a_2^3}{32} + \frac{9 a_1 a_2^4}{4}\right) l^{-5} + \left(\frac{9 a_1^5 a_2^2}{4} + \frac{405 a_1^4 a_2^3}{32} + \frac{1515 a_1^3 a_2^4}{128} + \frac{405 a_1^2 a_2^5}{32} + \frac{9 a_1 a_2^6}{4}\right) l^{-7} + O(l^{-9}) \right], \qquad [A.9]$$

$$R^p_{21} = -6\pi a_2 \left[\left(\frac{3a_1}{2}\right) l^{-1} + \left(-\frac{a_1 a_2^2}{2} + \frac{27 a_1^2 a_2}{8} - \frac{a_1^3}{2}\right) l^{-3} + \left(\frac{9 a_1^2 a_2^3}{4} + \frac{243 a_1^3 a_2^2}{32} + \frac{9 a_1^4 a_2}{4}\right) l^{-5} + \left(\frac{9 a_1^2 a_2^5}{4} + \frac{405 a_1^3 a_2^4}{32} + \frac{1515 a_1^4 a_2^3}{128} + \frac{405 a_1^5 a_2^2}{32} + \frac{9 a_1^6 a_2}{4}\right) l^{-7} + O(l^{-9}) \right], \qquad [A.10]$$

$$R^n_{11} = 6\pi a_1 \left[1 + \left(\frac{9a_1 a_2}{16}\right) l^{-2} + \left(\frac{3a_1^3 a_2}{8} + \frac{81 a_1^2 a_2^2}{256} + \frac{9 a_1 a_2^3}{8}\right) l^{-4} + \left(\frac{a_1^5 a_2}{16} + \frac{27 a_1^4 a_2^2}{32} + \frac{1241 a_1^3 a_2^3}{4096} + \frac{81 a_1^2 a_2^4}{64} + \frac{9 a_1 a_2^5}{8}\right) l^{-6} + O(l^{-8}) \right], \qquad [A.11]$$

$$R^n_{22} = 6\pi a_2 \left[1 + \left(\frac{9a_1 a_2}{16}\right) l^{-2} + \left(\frac{3a_1 a_2^3}{8} + \frac{81 a_1^2 a_2^2}{256} + \frac{9 a_1^3 a_2}{8}\right) l^{-4} + \left(\frac{a_1 a_2^5}{16} + \frac{27 a_1^2 a_2^4}{32} + \frac{1241 a_1^3 a_2^3}{4096} + \frac{81 a_1^4 a_2^2}{64} + \frac{9 a_1^5 a_2}{8}\right) l^{-6} + O(l^{-8}) \right], \qquad [A.12]$$

$$R^{n}_{12} = -6\pi a_1\left[\left(\frac{3a_2}{4}\right)l^{-1} + \left(\frac{a_1^2a_2}{4} + \frac{27a_1a_2^2}{64} + \frac{a_2^3}{4}\right)l^{-3} + \left(\frac{63a_1^3a_2^2}{64} + \frac{243a_1^2a_2^3}{1024} + \frac{63a_1a_2^4}{64}\right)l^{-5}\right.$$
$$\left. + \left(\frac{9a_1^5a_2^2}{8} + \frac{1053a_1^4a_2^3}{1024} + \frac{19083a_1^3a_2^4}{16384} + \frac{1053a_1^2a_2^5}{1024} + \frac{9a_1a_2^6}{8}\right)l^{-7} + O(l^{-9})\right], \quad \text{[A.13]}$$

$$R^{n}_{21} = -6\pi a_2\left[\left(\frac{3a_1}{4}\right)l^{-1} + \left(\frac{a_1a_2^2}{4} + \frac{27a_1^2a_2}{64} + \frac{a_1^3}{4}\right)l^{-3} + \left(\frac{63a_1^2a_2^3}{64} + \frac{243a_1^3a_2^2}{1024} + \frac{63a_1^4a_2}{64}\right)l^{-5}\right.$$
$$\left. + \left(\frac{9a_1^2a_2^5}{8} + \frac{1053a_1^3a_2^4}{1024} + \frac{19083a_1^4a_2^3}{16384} + \frac{1053a_1^5a_2^2}{1024} + \frac{9a_1^6a_2}{8}\right)l^{-7} + O(l^{-9})\right], \quad \text{[A.14]}$$

$$R^{s}_{31} = -R^{s}_{13} = -4\pi a_1^2\left[\left(\frac{9a_1^2a_2}{8}\right)l^{-3} + \left(\frac{3a_1^4a_2}{8} + \frac{81a_1^3a_2^2}{128} + \frac{9a_1^2a_2^3}{8}\right)l^{-5}\right.$$
$$\left. + \left(\frac{189a_1^5a_2^2}{128} + \frac{8409a_1^4a_2^3}{2048} + \frac{243a_1^3a_2^4}{128} + \frac{9a_1^2a_2^5}{8}\right)l^{-7} + O(l^{-9})\right], \quad \text{[A.15]}$$

$$R^{s}_{32} = -R^{s}_{23} = 4\pi a_1^2\left[\left(\frac{3a_1a_2}{2}\right)l^{-2} + \left(\frac{27a_1^2a_2^2}{32}\right)l^{-4}\right.$$
$$\left. + \left(\frac{108a_1^4a_2^2}{64} + \frac{243a_1^3a_2^3}{512} + \frac{9a_1^2a_2^4}{8}\right)l^{-6} + O(l^{-8})\right], \quad \text{[A.16]}$$

$$R^{s}_{41} = -R^{s}_{14} = -4\pi a_2^2\left[\left(\frac{3a_1a_2}{2}\right)l^{-2} + \left(\frac{27a_1^2a_2^2}{32}\right)l^{-4}\right.$$
$$\left. + \left(\frac{108a_1^2a_2^4}{64} + \frac{243a_1^3a_2^3}{512} + \frac{9a_1^4a_2^2}{8}\right)l^{-6} + O(l^{-8})\right], \quad \text{[A.17]}$$

$$R^{s}_{42} = -R^{s}_{24} = 4\pi a_2^2\left[\left(\frac{9a_1a_2^2}{8}\right)l^{-3} + \left(\frac{3a_1a_2^4}{8} + \frac{81a_1^2a_2^3}{128} + \frac{9a_1^3a_2^2}{8}\right)l^{-5}\right.$$
$$\left. + \left(\frac{189a_1^2a_2^5}{128} + \frac{8409a_1^3a_2^4}{2048} + \frac{243a_1^4a_2^3}{128} + \frac{9a_1^5a_2^2}{8}\right)l^{-7} + O(l^{-9})\right], \quad \text{[A.18]}$$

$$R^{n}_{33} = 8\pi a_1^3\left[1 + \left(\frac{3a_1^3a_2}{4}\right)l^{-4} + \left(\frac{27a_1^4a_2^2}{64} + 4a_1^3a_2^3\right)l^{-6} + O(l^{-8})\right], \quad \text{[A.19]}$$

$$R^{n}_{44} = 8\pi a_2^3\left[1 + \left(\frac{3a_1a_2^3}{4}\right)l^{-4} + \left(\frac{27a_1^2a_2^4}{64} + 4a_1^3a_2^3\right)l^{-6} + O(l^{-8})\right], \quad \text{[A.20]}$$

$$R^{n}_{34} = 8\pi a_1^3\left[\left(\frac{a_2^3}{2}\right)l^{-3} + \left(\frac{9a_1a_2^4}{16}\right)l^{-5} + \left(\frac{9a_1^3a_2^4}{16} + \frac{81a_1^2a_2^5}{256} + \frac{9a_1a_2^6}{16}\right)l^{-7} + O(l^{-9})\right] \quad \text{[A.21]}$$

and

$$R^{n}_{43} = 8\pi a_2^3\left[\left(\frac{a_1^3}{2}\right)l^{-3} + \left(\frac{9a_1^4a_2}{16}\right)l^{-5} + \left(\frac{9a_1^4a_2^3}{16} + \frac{81a_1^5a_2^2}{256} + \frac{9a_1^6a_2}{16}\right)l^{-7} + O(l^{-9})\right]. \quad \text{[A.22]}$$

APPENDIX B

Corrections for Calculation of Resistance Scalars

We used three corrections to obtain the resistance scalars from the work of Jeffrey & Onishi (1984a). First, their [4.9], which is part of a set of recurrence relations, has a sign error in one of the subscripts and should read

$$V_{npq} = P_{npq} + \frac{2n}{(n+1)(2n+3)} \sum_{s=1}^{q} \binom{n+s}{n+1} P_{s(q-s)(p-n-1)}. \qquad [B.1]$$

With this correction our expressions for f_k agree exactly with the expressions they list under their [4.14]. The other two corrections apply to the functions g_4 and g_5 used in their [7.15] to calculate Y^C_{12}. These functions should be

$$g_4 = \frac{\lambda^2}{10}(1+\lambda)^{-1} \qquad [B.2]$$

and

$$g_5 = \frac{1}{500}\lambda(43 - 24\lambda + 43\lambda^2)(1+\lambda)^{-1}. \qquad [B.3]$$

Also note that g_5 has been corrected by a factor of 2 to agree with the asymptotic expressions given by Jeffrey & Onishi (1984b) using their [2.27] and [4.2].

APPENDIX C

Evaluation of X_{ol}

To determine the location of the center of hydrodynamic stress for a dumbbell designated by the subscript "o", we first develop expressions for the force and torque in terms of the grand resistance matrix for two spheres. The total force on the dumbbell $\mathbf{F}^d$ is simply the sum of the forces on the spheres:

$$\mathbf{F}^d = \mathbf{F}_1 + \mathbf{F}_2. \qquad [C.1]$$

The total torque about the origin of the dumbbell is

$$\mathbf{T}^d_o = \mathbf{T}_1 + \mathbf{T}_2 + \mathbf{r}_{o1} \times \mathbf{F}_1 + \mathbf{r}_{o2} \times \mathbf{F}_2, \qquad [C.2]$$

where $\mathbf{F}_i$ and $\mathbf{T}_i$ are the hydrodynamic force and torque on sphere i. These two relationships can be expressed more compactly as

$$\begin{pmatrix} \mathbf{F}^d \\ \mathbf{T}^d_o \end{pmatrix} = \mathbf{D}_o \begin{bmatrix} \mathbf{F}_1 \\ \mathbf{F}_2 \\ \mathbf{T}_1 \\ \mathbf{T}_2 \end{bmatrix}, \qquad [C.3]$$

where $\mathbf{D}_o$ depends on the origin through its dependence on $\mathbf{r}_{oi}$. Rigid-body mechanics require

$$\mathbf{U}_i = \mathbf{U}^d_o + \mathbf{\Omega}^d \times \mathbf{r}_{oi} \qquad [C.4]$$

and

$$\mathbf{\Omega}_i = \mathbf{\Omega}^d, \qquad [C.5]$$

where $\mathbf{U}^d_o$ and $\mathbf{\Omega}^d$ are arbitrary and $\mathbf{U}_i$ is evaluated at the center of sphere i. The above can be written more compactly as

$$\begin{bmatrix} \mathbf{U}_1 \\ \mathbf{U}_2 \\ \mathbf{\Omega}_1 \\ \mathbf{\Omega}_2 \end{bmatrix} = \mathbf{G}_o \begin{pmatrix} \mathbf{U}^d_o \\ \mathbf{\Omega}^d_o \end{pmatrix}, \qquad [C.6]$$

where $\mathbf{G}_o$ depends on the choice of origin through its dependence on $\mathbf{r}_{oi}$. The grand resistance matrix for a dumbbell $\mathbf{R}^d$ relates the forces and torques to the translational and angular velocity of the dumbbell:

$$\begin{pmatrix} \mathbf{F}^d \\ \mathbf{T}^d_o \end{pmatrix} = -\eta \mathbf{R}^d \begin{pmatrix} \mathbf{U}^d_o \\ \Omega^d \end{pmatrix}. \qquad [C.7]$$

We can express $\mathbf{R}^d$ in terms of $\mathbf{R}$ by using the formalism of [23] and by combining [C.3], [C.6] and [C.7]:

$$\mathbf{R}^d = \mathbf{D}_o \mathbf{R} \mathbf{G}_o. \qquad [C.8]$$

We define X_{o1} to be the normalized distance from the origin to the center of sphere 1 such that

$$\mathbf{r}_{o1} = -X_{o1} l \mathbf{e} \qquad [C.9a]$$

and

$$\mathbf{r}_{o2} = (1 - X_{o1}) l \mathbf{e}. \qquad [C.9b]$$

By substituting [C.9] into the expressions for $\mathbf{D}_o$ and $\mathbf{G}_o$ and using [C.8], we can express $\mathbf{R}^d$ in terms of X_{o1}. X_{o1} is found in terms of the resistance scalars of $\mathbf{R}$ by requiring $\mathbf{R}^d$ to be diagonal, so that the rotational and translational motions are uncoupled at the origin:

$$X_{o1} = \frac{l(R^n_{21} + R^n_{22}) - (R^s_{31} + R^s_{32} + R^s_{41} + R^s_{42})}{l(R^n_{11} + R^n_{12} + R^n_{21} + R^n_{22})}. \qquad [C.10]$$

Figure 2 shows X_{o1} as a function of the distance between the centers of the spheres and the ratio of their sizes.