Effects of Adsorbed Polymers on the Axisymmetric Motion of Two Colloidal Spheres

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The effects of adsorbed polymer on the slow motion of two spherical particles along the line of their centers are examined semianalytically. The particles may have unequal radii, and their surface polymer layers are allowed to differ in characteristics. The surface polymer layer on each particle is assumed to be thin relative to the radius of the particle and to the surface-to-surface distance between the particles. A method of matched asymptotic expansions in small parameters λ_i (where $i = 1$ and 2) combined with a boundary collocation technique is used to find the solution for the creeping flow field within and outside the adsorbed polymer layers, where λ_i is the ratio of the polymer-layer length scale to the radius of particle i . The results for the hydrodynamic forces exerted on the particles in a resistance problem and for the particle velocities in a mobility problem are expressed in terms of the effective hydrodynamic thicknesses (L_i) of the polymer layers, which are accurate to $O(\lambda_i^2)$. The $O(\lambda_i)$ term for L_i normalized by its value in the absence of the other particle is found to be independent of the polymer segment distribution, the hydrodynamic interactions among the segments, and the volume fraction of the segments. The $O(\lambda_i^2)$ term for L_i , however, is a sensitive function of the polymer segment distribution and the volume fraction of the segments. In general, the effects of particle interactions on the motion of polymer-coated particles can be quite significant, especially when the particles are moving in the opposite directions.

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INTRODUCTION

The increasing amount of work on the adsorption of macromolecules from solution onto solid surfaces is understandable, considering the fundamental and practical interest of the subject. One of the most spectacular effects of such adsorption is the ability of some polymers to stabilize colloidal dispersions with respect to aggregation of particles. Compared with an electrostatically stabilized dispersion, adsorption of nonionic polymers to particle surfaces has prominent

advantages in relative insensitivity to the presence of electrolytes, equal efficiency in both aqueous and nonaqueous dispersion, reversibility of flocculation, and equal efficiency at both high and low particle concentrations (1, 2). Nowadays stabilization by either natural or synthetic polymers is exploited in a diverse range of industrial products (e.g., paints, glues, inks, lubricants, detergents, pharmaceutical and food emulsions) and operative in many biological systems (such as blood and milk).

A polymer can adsorb on the surface of a colloidal particle as a result of van der Waals forces, hydrogen bonding, Coulombic (charge–charge) attraction, or dipole interactions. A balance must be struck in the affinity among the polymer, the particle surface, and the solvent. The usual result is that the polymer is tied to the surface at a number of points but for some of its length it is able to extend into the solution. Sequences of segments lying on the surface form “trains,” which are separated by “loops,” while the ends of the polymer usually protrude into the solution as “tails” (3–6).

There is no unique measure of the thickness of a surface polymer layer due to the diffuseness of the polymer chains. A convenient definition is the hydrodynamic thickness which reflects the additional viscous drag exerted by the polymer segments on the solvent motion relative to the particle. This experimentally defined length is the thickness of a totally impermeable layer that would be required on the particle surface to produce the extra viscous drag. Several methods are available for determining the hydrodynamic thickness of adsorbed polymer layers on colloidal particles, including photon correlation spectroscopy (also known as quasielastic light scattering or dynamic light scattering) (7–10), microelectrophoresis (11, 12), sedimentation (13, 14), and viscometry (15, 16). It was found both theoretically (17) and experimentally (9) that the hydrodynamic thickness of adsorbed polymer layers is usually much larger than the layer thickness determined by ellipsometry (18, 19) and by neutron scattering (20).

The steady-state motion of a single spherical particle covered by a layer of adsorbed polymers was analyzed by Anderson and Kim (21) using a method of matched asymptotic

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expansions to solve the Stokes flow equations within and outside the polymer layer. The result for the drag force exerted by the fluid on the translating particle, expressed as the hydrodynamic thickness of the adsorbed polymer layer, is accurate to $O(\lambda^2)$ where λ is the ratio of the polymer-layer characteristic thickness to the particle radius. Their calculations showed that (i) the $O(\lambda^2)$ term is negative, meaning the hydrodynamic thickness increases as the particle radius increases assuming all other conditions are constant, (ii) a free-draining model for flow through the polymer chains is a very good approximation for calculating the hydrodynamic thickness if the Stokes radius of the polymer segments is much smaller than the characteristic thickness of the polymer layer, and (iii) the presence of only a small amount of adsorbed polymer tails can make a significant contribution to the hydrodynamic thickness if the length scale of the tails exceeds the length scale of the loops by a factor of two or more. Recently, through the method of matched asymptotic expansions, the quasisteady motion of a spherical particle coated with a layer of adsorbed polymers in a concentric spherical cavity has also been examined (22).

In practical applications, many colloidal phenomena involve collaborative motion of several particles. If particles are randomly dispersed within a fluid, the most important hydrodynamic interactions are those between a pair of particles. Using a method of reflections, Anderson and Solomentssev (23) analytically solved the mobility problem of two arbitrarily oriented, identical spheres accounting for the presence of the surface layers on the particles. The mobility coefficients accurate to $O(\lambda^2)$ were determined in a power series of ξ up to $O(\xi^5)$, where ξ is the ratio of particle radius to distance between the particle centers.

For the motion of two particles with a large separation, the power-series results from one or two reflections describe the particle interactions adequately. However, when the particles are close together, higher order interactions become significant and the leading terms in the asymptotic solution result in a poor description of the particle-interaction effect. In the present work, our objective is to obtain an exact solution to the quasisteady problem of two polymer-coated spheres moving along the line of their centers to $O(\lambda^2)$. The particles may have unequal radii and their surface polymer layers may have different characteristics. The momentum equation applicable to the system is solved by using the method of matched asymptotic expansions incorporated with a boundary collocation technique (24). Our numerical results for the particle interactions compare favorably with the formulas generated analytically from the method of reflections. It is found that the hydrodynamic interactions between polymer-coated particles can be significant when the particles are almost in contact.

ANALYSIS

Consider the quasisteady motion of two spherical particles, each coated with a layer of adsorbed polymers, along

FIG. 1. Geometrical sketch of two polymer-coated spheres moving along their line of centers.

the line of their centers in an unbounded Newtonian liquid, as shown in Fig. 1. Here, (r_i, θ_i, ϕ) are the spherical coordinates measured from the center of particle i , where i equals 1 or 2. The origin of the cylindrical polar coordinate system $(\bar{w}, \phi, z)$ is taken at the center of particle 1 for convenience. The two particles, separated by a center-to-center distance d , may have arbitrary radii, R_1 and R_2 , and their surface polymer layers are allowed to differ in characteristics. The thickness of the surface polymer layer surrounding particle i is characterized by a length scale δ_i (based on loops if both loops and tails are present). In general, the length scale of a surface polymer layer depends on the molecular weight of the polymer, the amount of the polymer adsorbed, and the relative interactions among the polymer, interface, and fluid. It is assumed that $\delta_i \ll R_i$ and $\delta_1 + \delta_2 \ll d - (R_1 + R_2)$, so these two thin surface layers will not overlap with each other. The velocity of particle i equals $U_i \mathbf{e}_z$, where $\mathbf{e}_z$ is the unit vector in the z direction. The Reynolds numbers are assumed to be much smaller than unity.

The fluid velocity and dynamic pressure fields, $\mathbf{v}$ and p , are governed by the modified Stokes equations (21),

$$\nabla \cdot \{ \mu [\nabla \mathbf{v} + (\nabla \mathbf{v})^T] \} - \nabla p - \zeta \rho f [\mathbf{v} - \mathbf{v}^{(p)}] = \mathbf{0}, \quad [1a]$$

$$\nabla \cdot \mathbf{v} = 0. \quad [1b]$$

In Eq. [1a], ζ is the friction coefficient of an isolated polymer segment, ρ is the density of the polymer segments at the position in question, $\mathbf{v}^{(p)}$ is the velocity of the segments, f is a function of ρ accounting for hydrodynamic interactions among segments, and μ is the local fluid viscosity which is also a function of ρ . The density distribution of the segments in the loops and tails cannot yet be determined experimentally. Theoretical studies (5, 6) have established that the density of polymer segments in the loops decays exponentially with the distance from the surface of adsorption and the segment density in the tails can exceed the value in the bulk solution much farther from the surface. For a free-

draining model for flow through the segments $f = 1$, while segment-segment interactions cause f to increase with ρ . The effective viscosity μ in the polymer layer is not a measurable quantity. Previous calculations for an isolated sphere (21) have shown that the effects of the difference between μ and the constant bulk solvent viscosity μ_s are negligible. Therefore, we assume $\mu = \mu_s$ throughout the surface polymer layers in this work. It is understood that $\mathbf{v}^{(p)} = U_i \mathbf{e}_z$ in the surface layer surrounding the translating particle i .

Owing to the axisymmetric nature of the flow, it is convenient to introduce the Stokes stream function Ψ which satisfies Eq. [1b] and is related to the velocity components in the spherical coordinate system (r, θ, ϕ) by

$$v_r = -\frac{1}{r^2 \sin \theta} \frac{\partial \Psi}{\partial \theta}, \quad [2a]$$

$$v_\theta = \frac{1}{r \sin \theta} \frac{\partial \Psi}{\partial r}. \quad [2b]$$

Taking the curl of Eq. [1a] and applying Eqs. [1b] and [2] gives a fourth-order linear partial differential equation for Ψ ,

$$E^4 \Psi - \lambda_i^{-2} \left(\beta_i E^2 \Psi + \frac{d\beta_i}{dr} \frac{\partial \Psi}{\partial r} \right) = 0. \quad [3]$$

Here i can be either 1 or 2, and the dimensionless parameters β_i and λ_i are defined as

$$\beta_i = \frac{\delta_i^2 \zeta \rho f}{\mu_s}, \quad [4a]$$

$$\lambda_i = \frac{\delta_i}{R_i}, \quad [4b]$$

and the axisymmetric Stokesian operator E^2 is given by

$$E^2 = \frac{\partial^2}{\partial r^2} + \frac{\sin \theta}{r^2} \frac{\partial}{\partial \theta} \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \right). \quad [5]$$

In Eqs. [3] and [5], dimensionless variables are used, with r normalized by the particle radius R_i and Ψ by $U_i R_i^2$. The parameter β_i denotes the ratio of the frictional force exerted by the polymer segments on the fluid to the viscous force of the bulk fluid, and is $O(1)$ with respect to λ_i which has been assumed to be small. Equation [3] must be solved subject to the boundary conditions

$$r_i = R_i; \quad \mathbf{v} = U_i \mathbf{e}_z \quad (i = 1, 2), \quad [6a]$$

$$(\bar{\omega}^2 + z^2)^{1/2} \rightarrow \infty; \quad \mathbf{v} \rightarrow \mathbf{0}. \quad [6b]$$

The drag force (in the z direction) exerted by the fluid on the particle surface $r_i = R_i$ is (25)

$$F_i = \pi \mu_s \int_0^\pi r_i^3 \sin^3 \theta_i \frac{\partial}{\partial r_i} \left(\frac{E^2 \Psi}{r_i^2 \sin^2 \theta_i} \right) r_i d\theta_i. \quad [7]$$

In terms of the equivalent hydrodynamic thickness L_i of the adsorbed polymer layer on particle i , the drag force can be expressed by the Stokes law with a correction of the two-sphere hydrodynamic interaction,

$$F_i = -6\pi \mu_s (R_i + L_i) U_i K_i. \quad [8]$$

For the system specified by Eq. [6], the correction factor for the interaction between two “bare” spheres $K_i = -2D_{i20}/3R_i U_i$, where D_{i20} is defined by Eq. [13]. The hydrodynamic thickness L_i can be expressed as

$$L_i = A_i R_i \lambda_i (1 + B_i \lambda_i) + O(\lambda_i^3). \quad [9]$$

By combining Eqs. [7]–[9] after solving Eqs. [3] and [6] for Ψ , one can obtain dimensionless parameters A_i and B_i . Note that A_i is positive and B_i reflects the influence of curvature of the surface of particle i . Also, A_i and B_i (or L_i) are functions of the segment density distributions of the surface polymer layers and the parameters U_2/U_1 , R_2/R_1 , and $(R_1 + R_2)/d$. If the surface layer surrounding particle i is an impermeable dense film of thickness δ_i , one has $A_i = 1$ and $B_i = 0$.

Equation [3] poses a singular perturbation problem when $\lambda_i \ll 1$. In the “outer region,” in which $r_i - R_i \gg R_i \lambda_i$, one has $\beta_i = 0$, and a sufficiently general solution for the stream function is

$$\Psi^{(O)} = \sum_{i=1}^2 \sum_{n=2}^{\infty} (C_{in} r_i^{-n+1} + D_{in} r_i^{-n+3}) G_n^{-1/2}(\nu_i), \quad [10]$$

$$C_{in} = C_{in0} + C_{in1} \lambda_i + C_{in2} \lambda_i^2 + \cdots, \quad [11a]$$

$$D_{in} = D_{in0} + D_{in1} \lambda_i + D_{in2} \lambda_i^2 + \cdots, \quad [11b]$$

where $G_n^{-1/2}(\nu_i)$ is the Gegenbauer polynomial of the first kind of order n and of degree $-\frac{1}{2}$ and ν_i is used to denote $\cos \theta_i$ for brevity. The Gegenbauer polynomials are related to the Legendre polynomials via the relation

$$G_n^{-1/2}(\nu) = \frac{1}{2n-1} [P_{n-2}(\nu) - P_n(\nu)]. \quad [12]$$

A solution in the form of Eq. [10] immediately satisfies boundary condition [6b]. The unknown constants C_{imm} and D_{imm} in Eq. [11] are to be determined by matching $\Psi^{(O)}$ with the solution to Eq. [3] in the “inner regions.” The solution

of C_{in0} and D_{in0} has been obtained numerically by Gluckman *et al.* (24) who studied the axisymmetric motion of two “bare” spherical particles using the boundary collocation method.

Substituting Eq. [10] into Eq. [7] and utilizing the orthogonality properties of the Gegenbauer polynomials, we obtain the simple relation

$$F_i = 4\pi\mu_s D_{i2} \\ = 4\pi\mu_s (D_{i20} + D_{i21}\lambda_i + D_{i22}\lambda_i^2 + \cdots), \quad [13]$$

for $i = 1$ or 2 . Combination of Eqs. [8], [9], and [13] results in

$$A_i = \frac{D_{i21}}{D_{i20}}, \quad [14a]$$

$$B_i = \frac{D_{i22}}{D_{i21}}. \quad [14b]$$

Within the “inner region” near particle i , where $r_i - R_i \approx O(R_i\lambda_i)$, a solution for the stream function is sought in the form

$$\Psi_i^{(I)} = U_i \sum_{n=2}^{\infty} [\lambda_i^2 F_{in2}(y_i) + \lambda_i^3 F_{in3}(y_i) + \cdots] G_n^{-1/2}(\nu_i), \quad [15]$$

where $y_i = \lambda_i^{-1}(r_i - R_i)$. Note that this expression is used when the coordinate system (r_i, θ_i, ϕ) moves with particle i . Substituting Eq. [15] into Eqs. [3] and [6a] in the coordinate system (r_i, θ_i, ϕ) and collecting terms of equal orders in λ_i produces the following equations for $F_{imm}(y_i)$ up to $m = 3$:

$$R_i \frac{d^3 F_{in2}}{dy_i^3} - \frac{\beta_i}{R_i} \frac{dF_{in2}}{dy_i} = 0, \quad [16a]$$

$$y_i = 0: \quad F_{in2} = \frac{dF_{in2}}{dy_i} = 0; \quad [16b]$$

$$R_i \frac{d^3 F_{in3}}{dy_i^3} - \frac{\beta_i}{R_i} \frac{dF_{in3}}{dy_i} = c_{in}, \quad [17a]$$

$$y_i = 0: \quad F_{in3} = \frac{dF_{in3}}{dy_i} = 0, \quad [17b]$$

where $i = 1$ or 2 , $n = 2, 3, 4, \dots$, and c_{in} are integration constants to be determined by matching the inner and outer solutions.

The unknown boundary conditions on F_{imm} as $y_i \rightarrow \infty$ and

the constants C_{imm} and D_{imm} are to be determined by matching Eqs. [10] and [15] at equivalent orders in λ_i ,

$$\lim_{y_i \rightarrow \infty} \Psi_i^{(I)} = \lim_{y_j \rightarrow \infty} [\Psi^{(O)} + \frac{1}{2} U_i r_i^2 (1 - \nu_i^2)]_{r_i=R_i+\lambda_i y_i}. \quad [18]$$

The second term in the brackets accounts for the difference in the reference frames used for $\Psi^{(O)}$ and $\Psi_i^{(I)}$. After performing this matching we obtain the following equations for $i = 1$ or 2 :

$$0 = W_{i0}(\nu_i) + \frac{1}{2} R_i^2 (1 - \nu_i^2) U_i, \quad [19a]$$

$$0 = W_{i1}(\nu_i) + y_i X_{i0}(\nu_i) + R_i y_i (1 - \nu_i^2) U_i, \quad [19b]$$

$$\lim_{y_i \rightarrow \infty} \sum_{n=2}^{\infty} F_{in2} G_n^{-1/2}(\nu_i) U_i = W_{i2}(\nu_i) + y_i X_{i1}(\nu_i) \\ + y_i^2 Y_{i0}(\nu_i) + \frac{1}{2} y_i^2 (1 - \nu_i^2) U_i, \quad [19c]$$

$$\lim_{y_i \rightarrow \infty} \sum_{n=2}^{\infty} F_{in3} G_n^{-1/2}(\nu_i) U_i = W_{i3}(\nu_i) + y_i X_{i2}(\nu_i) \\ + y_i^2 Y_{i1}(\nu_i) + y_i^3 Z_{i0}(\nu_i), \quad [19d]$$

where the functions $W_{ik}(\nu_i)$, $X_{ik}(\nu_i)$, $Y_{ik}(\nu_i)$, and $Z_{ik}(\nu_i)$ with $k = 0, 1, 2$, and 3 are defined by Eqs. [A.1]–[A.4] in Appendix A.

With the solution of the constants C_{in0} and D_{in0} obtained numerically by using the boundary collocation technique (24), Eq. [19a] and the derivative of Eq. [19b] with respect to y_i are immediately satisfied. The constants C_{in1} and D_{in1} are to be determined by solving Eq. [19b] and the derivative of Eq. [19c] with the knowledge of C_{in0} and D_{in0} , and then the constants C_{in2} and D_{in2} are to be determined by solving Eq. [19c] and the derivative of Eq. [19d]. The useful result is obtained in the following form:

$$D_{i21} = \sum_{j=1}^2 R_j U_j \gamma_j \sum_{n=2}^{\infty} s_{ijn} b_{jn}, \quad [20a]$$

$$D_{i22} = \sum_{j=1}^2 U_j \lim_{y_j \rightarrow \infty} \sum_{n=2}^{\infty} \left[p_{ijn} \left(\frac{dF_{jn3}}{dy_j} - \frac{c_{jn}}{2R_j} y_j^2 - d_{jn} y_j \right) \right. \\ \left. + q_{ijn} \left(\frac{F_{jn2}}{R_j} + \frac{b_{jn}}{2R_j} y_j^2 - b_{jn} \gamma_j y_j \right) \right]. \quad [20b]$$

On the other hand, taking the differentiation of Eqs. [19c, d] with respect to y_i twice and solving them by utilizing the orthogonality properties of the Gegenbauer polynomials, we obtain

$$\lim_{y_j \rightarrow \infty} \frac{d^2 F_{jn2}}{dy_j^2} = -b_{jn}, \quad [21a]$$

$$\lim_{y_j \rightarrow \infty} \frac{d^2 F_{jn3}}{dy_j^2} = c_{jn} \frac{y_j}{R_j} + d_{jn}, \quad [21b]$$

for $j = 1$ or 2 . In Eqs. [20] and [21], γ_j is defined by Eq. [28a], and the dimensionless constants s_{ijn} , p_{ijn} , q_{ijn} , b_{jn} , c_{jn} , and d_{jn} , which depend on the size ratio R_2/R_1 , separation parameter $(R_1 + R_2)/d$, and velocity ratio U_2/U_1 of the particles, can be numerically determined using the boundary collocation technique. Knowing that $\beta_j = 0$ as $y_j \rightarrow \infty$, one can find that Eqs. [16a] and [17a] are consistent with Eq. [21].

If we define new variables

$$G_j = \frac{1}{b_{j2}} \frac{dF_{j22}}{dy_j}, \quad [22a]$$

$$H_j = \frac{1}{c_{j2}} \frac{dF_{j23}}{dy_j}, \quad [22b]$$

then Eqs. [16], [17], and [21] give

$$R_j \frac{d^2 G_j}{dy_j^2} - \frac{\beta_j}{R_j} G_j = 0, \quad [23a]$$

$$y_j = 0: \quad G_j = 0, \quad [23b]$$

$$y_j \rightarrow \infty: \quad \frac{dG_j}{dy_j} \rightarrow -1; \quad [23c]$$

$$R_j \frac{d^2 H_j}{dy_j^2} - \frac{\beta_j}{R_j} H_j = 1, \quad [24a]$$

$$y_j = 0: \quad H_j = 0, \quad [24b]$$

$$y_j \rightarrow \infty: \quad \frac{dH_j}{dy_j} \rightarrow \frac{y_j}{R_j} + \frac{d_{j2}}{c_{j2}}. \quad [24c]$$

Due to its linearity Eq. [24] can be decomposed into two parts, with one part given by

$$R_j \frac{d^2 H'_j}{dy_j^2} - \frac{\beta_j}{R_j} H'_j = 1, \quad [25a]$$

$$y_j = 0: \quad H'_j = 0, \quad [25b]$$

$$y_j \rightarrow \infty: \quad \frac{dH'_j}{dy_j} \rightarrow \frac{y_j}{R_j}, \quad [25c]$$

and the other in the form of Eq. [23], where

$$H_j = H'_j + \frac{d_{j2}}{c_{j2}} G. \quad [26]$$

If functions F_{jn2} and F_{jn3} , instead of F_{j22} and F_{j23} , are selected

to define the variables G_j and H_j in Eq. [22], the same equations as Eqs. [23]–[26] will be obtained.

The parameters A_i and B_i in Eq. [9] are obtained from Eqs. [14], [20], [22], and [26] as

$$A_i = \frac{1}{D_{i20}} \sum_{j=1}^2 R_j U_j \gamma_j \sum_{n=2}^{\infty} s_{ijn} b_{jn}, \quad [27a]$$

$$B_i = \frac{1}{D_{i20} A_i} \sum_{j=1}^2 R_j U_j [\Lambda'_j \sum_{n=2}^{\infty} p_{ijn} c_{jn} + \Lambda_j \sum_{n=2}^{\infty} p_{ijn} d_{jn} + \Omega_j \sum_{n=2}^{\infty} q_{ijn} b_{jn}], \quad [27b]$$

where

$$\gamma_j = \lim_{y_j \rightarrow \infty} \frac{1}{R_j} (G_j + y_j), \quad [28a]$$

$$\Lambda'_j = \lim_{y_j \rightarrow \infty} \frac{1}{R_j} \left(H'_j - \frac{y_j^2}{2R_j} \right), \quad [28b]$$

$$\Lambda_j = \lim_{y_j \rightarrow \infty} \frac{1}{R_j} (G_j - y_j), \quad [28c]$$

$$\Omega_j = \frac{1}{R_j^2} \int_0^{\infty} (G_j + y_j - R_j \gamma_j) dy_j. \quad [28d]$$

In Eq. [27], the numerical solution of D_{i20} is known (24) and the constants s_{ijn} , p_{ijn} , q_{ijn} , b_{jn} , c_{jn} , and d_{jn} can be determined by using the boundary collocation technique. After the solutions of G_j and H'_j in Eqs. [23] and [25] are obtained for given polymer segment density distributions $\rho(y_i)$ and the dependence of β_i on ρ , parameters A_i and B_i can be evaluated from Eqs. [27] and [28].

When the two particles are separated by an infinite distance (i.e., $(R_1 + R_2)/d \rightarrow 0$), the interaction between the particles vanishes. For this limiting case, $D_{i20} = -3R_i U_i / 2$, $s_{ii2} = p_{ii2} = q_{ii2} = 1$, $b_{i2} = c_{i2} = -\frac{3}{2}$, $d_{i2} = 3\gamma_{i\infty}/2$, and all the other constants s_{ijn} , p_{ijn} , q_{ijn} , b_{in} , c_{in} , and d_{in} are zero. Thus, Eq. [27] reduces to

$$A_{i\infty} = \gamma_{i\infty} = \lim_{y_i \rightarrow \infty} \frac{1}{R_i} (G_{i\infty} + y_i), \quad [29a]$$

$$B_{i\infty} = \frac{1}{R_i \gamma_{i\infty}} \lim_{y_i \rightarrow \infty} \left(H_{i\infty} - \frac{y_i^2}{2R_i} + \gamma_{i\infty} y_i \right) + \frac{1}{R_i^2 \gamma_{i\infty}} \int_0^{\infty} (G_{i\infty} + y_i - R_i \gamma_{i\infty}) dy_i. \quad [29b]$$

Here, $i = 1$ or 2 , and the subscript “ ∞ ” is used to represent the limiting case of $(R_1 + R_2)/d \rightarrow 0$. Both theoretical calcu-

lations (21) and experimental data (7, 26) showed that the value of $B_{i\infty}$ would be negative, meaning the hydrodynamic thickness of the adsorbed polymer layer increases with particle radius assuming all other conditions are constant.

The drag force exerted on particle i written by Eq. [8] can also be expressed as

$$F_i = -6\pi\mu_s(R_i + L_{i\infty})U_i K_i [1 + g_i\lambda_i + h_i\lambda_i^2 + O(\lambda_i^3)], \quad [30]$$

where

$$L_{i\infty} = A_{i\infty}R_i\lambda_i(1 + B_{i\infty}\lambda_i) + O(\lambda_i^3). \quad [31]$$

Here, the hydrodynamic thickness of the adsorbed polymer layer surrounding particle i is taken to be a constant equal to the value when the other particle is not present ($L_{i\infty}$), and the correction due to particle interactions is given by an expansion in λ_i in the brackets of Eq. [30]. A comparison between Eqs. [8] and [30] yields

$$g_i = A_i - A_{i\infty}, \quad [32a]$$

$$h_i = A_i B_i - A_{i\infty} B_{i\infty} - A_{i\infty}(A_i - A_{i\infty}). \quad [32b]$$

For a resistance problem, in which the forces acting on the particles are to be determined for the specified particle velocities, the drag force on particle i written by Eqs. [8] and [30] can also be expressed as

$$F_i = \left(1 + \frac{L_i}{R_i}\right) \sum_{j=1}^2 K_{ij} F_j^{(0)} = \left(1 + \frac{L_{i\infty}}{R_i}\right) \times [1 + g_i\lambda_i + h_i\lambda_i^2 + O(\lambda_i^3)] \sum_{j=1}^2 K_{ij} F_j^{(0)}. \quad [33]$$

Here,

$$F_j^{(0)} = -6\pi\mu_s R_j U_j, \quad [34]$$

which is the drag force on a “bare” particle j moving with velocity U_j in the absence of the other particle, and the dimensionless resistance coefficients K_{ij} for two “bare” spheres are functions of parameters R_2/R_1 and $(R_1 + R_2)/d$ only (although the factor K_i in Eq. [8] is also a function of the ratio of particle velocities).

On the other hand, for a mobility problem, in which the forces acting on the particles are prescribed and the particle velocities are to be determined, the velocity of particle i can be written as

$$\begin{aligned} U_i &= \left(1 + \frac{L_i}{R_i}\right)^{-1} \sum_{j=1}^2 M_{ij} U_j^{(0)} \\ &= [1 - A_i\lambda_i + (A_i^2 - A_i B_i)\lambda_i^2 + O(\lambda_i^3)] \sum_{j=1}^2 M_{ij} U_j^{(0)} \\ &= \left(1 + \frac{L_{i\infty}}{R_i}\right)^{-1} [1 + g_i\lambda_i + h_i\lambda_i^2 + O(\lambda_i^3)]^{-1} \sum_{j=1}^2 M_{ij} U_j^{(0)}. \end{aligned} \quad [35]$$

Here,

$$U_j^{(0)} = -\frac{1}{6\pi\mu_s R_j} F_j, \quad [36]$$

which is the velocity of a “bare” particle j subject to an applied force $-F_j$ in the absence of the other particle, and the dimensionless mobility coefficients M_{ij} for two “bare” spheres are also functions of R_2/R_1 and $(R_1 + R_2)/d$ only. The analytical and numerical solutions of coefficients K_{ij} and M_{ij} and the relations connecting K_{ij} and M_{ij} for various cases are available in the literature (27).

RESULTS AND DISCUSSION

The numerical results for the motion of two colloidal spheres, each covered by a layer of adsorbed polymers, along the line of their centers are presented in this section. The hydrodynamic parameters A_i and B_i are calculated from Eqs. [27] and [28] in which the variables G_j and H'_j can be obtained by numerically solving Eqs. [23] and [25], and the constants s_{ijn} , p_{ijn} , q_{ijn} , b_{jn} , c_{jn} , and d_{jn} are numerically determined using the boundary collocation technique. The polymer-layer properties that are required in solving the variables G_j and H'_j are β_j , which should be related to the segment density $\rho(y_j)$ by an appropriate hydrodynamic model.

Following Anderson and Kim (21), we assume that the segment density has a form of two exponentially decaying distributions,

$$\rho(y_i) = \rho_{i0}(e^{-y_i/\delta_i} + \eta_i e^{-\alpha_i y_i/\delta_i}), \quad [37]$$

where the primary distribution ($\rho_{i0}e^{-y_i/\delta_i}$) represents segments in the loops and the secondary distribution denotes the tails. α_i is the ratio of loop-to-tail length scales for the relevant surface polymer layer and is smaller than unity. It can be found from Eq. [37] that the fraction of segments contained in the tails is $\eta_i/(\eta_i + \alpha_i)$. Theories based on lattice statistics (3–6) have shown that the segment density in tails increases with the distance from the interface, then passes through a maximum, followed by an exponential de-

crease with a decay length which is about twice (or more in some cases) that of the segment density in loops. At very small distances from the interface the loops prevail over the tails, while the outer part of the adsorbed layer is completely dominated by the tails. The function form expressed by Eq. [37] is a simple and reasonable approximation for the segment density distribution as long as η and α are small (say, $\eta_i/(\eta_i + \alpha_i) \leq 0.3$ and $\alpha_i \leq 0.5$).

Substituting Eq. [37] into Eq. [4a] yields

$$\beta_i(y_i) = \beta_{i0}(e^{-y_i/\delta_i} + \eta_i e^{-\alpha_i y_i/\delta_i})f, \quad [38]$$

where

$$\beta_{i0} = \frac{\delta_i^2 \zeta \rho_{i0}}{\mu_s} = \frac{9}{2} \left(\frac{\delta_i}{a} \right)^2 \phi_{i0}, \quad [39]$$

$a (= \zeta/6\pi\mu_s)$ is the Stokes radius of each segment, and ϕ_{i0} ($= 4\pi a^3 \rho_{i0}/3$) represents the volume fraction of segments based on the segment density at the surface of particle i . For reasonable adsorption energies (i.e., not very close to the adsorption/desorption transition), ϕ_{i0} is of order (but obviously below) unity. With the assumption that $\delta_i/a \gg 1$, the typical values of β_{i0} are expected to be in the range 10–1000. The hydrodynamic parameters A_i and B_i for two polymer-coated spheres moving along the line of their centers can be evaluated for a given distribution of β_i as expressed by Eq. [38]. The Runge–Kutta–Fehlberg method (28) was employed to obtain the numerical solutions of the variables G_j and H'_j .

We first consider the motion of two geometrically identical spheres ($R_1 = R_2 = R$, $\delta_1 = \delta_2 = \delta$, $\beta_{10} = \beta_{20} = \beta_0$, $\alpha_1 = \alpha_2 = \alpha$, $\eta_1 = \eta_2 = \eta$, $A_{1\infty} = A_{2\infty} = A_\infty$, $B_{1\infty} = B_{2\infty} = B_\infty$). Two special cases of this problem warrant consideration. First, as encountered in the settling of particles, the two polymer-coated spheres are moving along the line of their centers with equal velocities in the same direction ($U_2/U_1 = 1$). Secondly, the two spheres may be traveling with equal and opposite velocities ($U_2/U_1 = -1$). In the situation of flocculation the particles approach each other, whereas the presence of equicharged particles causes the motion to be along their line of centers but in reverse directions due to the repulsive forces induced. For creeping motion, the magnitude of the force on each of the two spheres is independent of whether they are approaching or departing from each other. Note that, due to the linearity of the problem, the solution for any other pair of velocities can be obtained by linearly combining the solutions of these two special cases. Obviously, one has $A_1 = A_2 = A$, $B_1 = B_2 = B$, $g_1 = g_2 = g$, $h_1 = h_2 = h$, and $K_1 = K_2 = K$ for these two special cases.

Results of A/A_∞ and B/B_∞ for the motion of two identical

polymer-coated spheres along their line of centers with U_2/U_1 equal to 1 and -1 as functions of the separation parameter $2R/d$ are given in Table 1 for systems with no tails ($\eta = 0$) in the free-draining limit ($f = 1$). Three constant values 10, 100, and 1000 are chosen for the parameter β_0 and the values of A_∞ and B_∞ for each case are also listed in this table. Note that, although A_∞ is a function of β_0 , the ratio A/A_∞ (or g/A_∞) is independent of this parameter. For identical spheres moving with equal velocities ($U_2/U_1 = 1$), the particle interactions decrease the values of A and B (B is always negative). The ratio A/A_∞ (or g/A_∞) is a decreasing function of the separation parameter $2R/d$ for $2R/d \lesssim 0.55$ but increases with increasing $2R/d$ as $2R/d \gtrsim 0.55$. On the contrary, the ratio B/B_∞ is an increasing function of $2R/d$ for $2R/d \lesssim 0.36$ but decreases with increasing $2R/d$ as $2R/d \gtrsim 0.36$. For identical spheres approaching or moving away from each other with equal velocities ($U_2/U_1 = -1$), the particle interactions increase the value of A and the ratio A/A_∞ increases monotonically and rapidly with the increase of $2R/d$. On the other hand, the ratio B/B_∞ decreases monotonically from unity and soon becomes negative (or the value of B increases monotonically from B_∞ , which is negative, and soon becomes positive) when $2R/d$ increases from zero. Namely, for the cases of $U_2/U_1 = -1$, the hydrodynamic thickness of the adsorbed polymer layer or the surface-layer-enhanced frictional drag on each particle increases as the particle radius decreases, assuming that the separation parameter $2R/d$ and all other conditions are constant. Although the magnitude of B_∞ decreases with the increase of β_0 , the magnitude of B or B/B_∞ in general increases with the increase of β_0 for both cases. Note that, especially for the case of $U_2/U_1 = -1$, the particle interaction effects can be very significant when $2R/d$ approaches unity. For convenience in using Eqs. [8], [30], [33], and [35] to evaluate the drag force or velocity of each particle, we also list the values of K ($= K_{11} + (U_2/U_1)K_{12} = [M_{11} + (U_2/U_1)M_{12}]^{-1}$, defined by Eqs. [8], [33], and [35]) for both cases as functions of $2R/d$ in Table 1.

To seek the solution to the problem expressed by Eqs. [10] and [15] as series in powers of λ_i , we have assumed that the series in Eq. [9] converges. On the other hand, the numerical calculations for the case of $U_2/U_1 = -1$ presented in Table 1 indicate a slow convergence of Eq. [9] (viz. $A \gg 1$ and $B \gg 1$) as $2R/d$ approaches unity and β_0 is large. Under this particular situation, the perturbation solution presented here is useful only when the value of λ_i is extremely small. Indeed, additional analysis which is not limited to the assumption $\lambda_i \ll 1$ is needed to check on the validity of the expansion in λ_i introduced by Eq. [9].

Using a method of reflections, Anderson and Solomentsev (23) obtained the hydrodynamic interactions between two identical spheres accounting for the presence of the surface layers on the particles. For the axisymmetric motion of two

TABLE 1

Numerical Results of A/A_∞ and B/B_∞ for Two Identical Polymer-Coated Spheres Moving along the Line of Their Centers with Various Values of Parameters $2R/d$, β_0 , and U_2/U_1 for Systems with No Polymer Tails in the Free-Draining Limit

$\frac{2R}{d}$	A/A_∞		B/B_∞							
			$\beta_0 = 10$		$\beta_0 = 100$		$\beta_0 = 1000$		K	
	$\frac{U_2}{U_1} = 1$	$\frac{U_2}{U_1} = -1$	$\frac{U_2}{U_1} = 1$	$\frac{U_2}{U_1} = -1$	$\frac{U_2}{U_1} = 1$	$\frac{U_2}{U_1} = -1$	$\frac{U_2}{U_1} = 1$	$\frac{U_2}{U_1} = -1$	$\frac{U_2}{U_1} = 1$	$\frac{U_2}{U_1} = -1$
0	1	1	1	1	1	1	1	1	1	1
0.1	0.9307	1.0808	1.2499	0.7077	1.6937	0.1884	2.3595	-0.5907	0.9303	1.0810
0.2	0.8733	1.1746	1.4403	0.3725	2.2244	-0.7479	3.4007	-2.4287	0.8706	1.1756
0.3	0.8296	1.2863	1.5443	-0.0274	2.5166	-1.8793	3.9755	-4.6577	0.8198	1.2878
0.4	0.8011	1.4264	1.5441	-0.5431	2.5163	-3.3644	3.9748	-7.5974	0.7772	1.4242
0.5	0.7881	1.6160	1.4566	-1.2764	2.2640	-5.5176	3.4753	-11.881	0.7422	1.5967
0.6	0.7875	1.9002	1.3426	-2.4411	1.9275	-8.9978	2.8050	-18.835	0.7140	1.8283
0.7	0.7942	2.3916	1.2678	-4.5548	1.6969	-15.397	2.3407	-31.665	0.6913	2.1708
0.8	0.8028	3.4557	1.2350	-9.2079	1.5894	-29.596	2.1212	-60.186	0.6729	2.7724
0.9	0.8115	7.1185	1.2116	-24.370	1.5137	-75.985	1.9668	-153.42	0.6578	4.3331
0.95	0.8157	15.486	1.2020	-55.628	1.4825	-171.58	1.9035	-345.55	0.6512	7.1416
0.99	0.8190	—	1.1967	—	1.4656	—	1.8690	—	0.6475	15.498
			$A_\infty = 3.4570$ $B_\infty = -0.9509$		$A_\infty = 5.7596$ $B_\infty = -0.5712$		$A_\infty = 8.0622$ $B_\infty = -0.4081$			

spheres with U_2/U_1 equal to 1 and -1 considered here, their results give

$$A = A_\infty K \left[1 + 2\xi^3 + \frac{45}{4}\xi^4 + O(\xi^6) \right], \quad [40a]$$

$$A^2 - AB = K \left[A_\infty^2 - A_\infty B_\infty + \frac{1}{2}(A_\infty^2 - A_\infty B_\infty + 6\Omega_\infty) \right. \\ \left. \times \left(\frac{U_2}{U_1} \right) \xi^3 - \frac{45}{4}(A_\infty^2 + 2A_\infty B_\infty)\xi^4 + O(\xi^6) \right], \quad [40b]$$

where $\xi = R/d$ and the definition of Ω_∞ has been given by Eq. [28d]. The normalized values of A and $A^2 - AB$ calculated from the above asymptotic solution, with the $O(\xi^6)$ terms neglected, are compared with our results in Table 2. It can be found that the asymptotic formulas from the method of reflections shown in Eq. [40] agree well with the exact results as long as the particle surfaces are more than the sum of radii apart (i.e., $2R/d < 0.5$). However, accuracy begins to deteriorate, as expected, when the particles are close together.

Because many suspensions in practical applications are composed of particles of different sizes, it might be of interest to examine the interactions between two polymer-coated spheres with identical characteristics in the surface layers ($\delta_1 = \delta_2 = \delta$ and $\beta_{10} = \beta_{20} = \beta_0$) but with unequal radii. The results of $A_1/A_{1\infty}$ and $B_1/B_{1\infty}$ for the motion of two spheres along their line of centers with $\beta_0 = 100$, $U_2/U_1 =$

-1 , and various values of the size ratio R_2/R_1 are plotted versus the separation parameter $(R_1 + R_2)/d$ in Fig. 2 for systems with no tails in the free-draining limit. The parameters $A_2/A_{2\infty}$ and $B_2/B_{2\infty}$ for the case of $R_2/R_1 = \chi$ are equal to $A_1/A_{1\infty}$ and $B_1/B_{1\infty}$, respectively, for the case of $R_2/R_1 = 1/\chi$. Similar to the case of two identical polymer-coated spheres, $A_i/A_{i\infty}$ increases and $B_i/B_{i\infty}$ decreases with the increase of $(R_1 + R_2)/d$. In general, the influence of the particle interaction is more significant on the ratios $A_i/A_{i\infty}$ and $B_i/B_{i\infty}$ of the larger particle than on those of the smaller one.

We next consider the effect of tails in the surface layers of two identical polymer-coated spheres. Equations [23] and [25] are solved for G_j and H'_j in the free-draining limit over a range of η and α . For the situation of $U_2/U_1 = -1$, the results of parameters B and h as functions of the ratio $2R/d$ are plotted in Fig. 3 for typical cases of the fraction of polymer segments contained in the tails, $\eta/(\eta + \alpha)$. The curve of parameter A (or g) is not drawn since the ratio A/A_∞ is not a function of $\eta/(\eta + \alpha)$ or α and its results were presented in Table 1. It can be seen that the increase of the segment fraction in the tails or the increase of the relative length of the tails (with a decrease in α) will increase the particle interaction effect on B and h when all the other conditions are unchanged. This influence can be quite significant when the value of α is less than 0.5. It implies that the interaction between colloidal particles in the presence of adsorbed polymers is to a large extent determined by long dangling tails.

TABLE 2

The Normalized Values of A and $A^2 - AB$ for Two Identical Polymer-Coated Spheres Moving along The Line of Their Centers with Various Values of Parameters $2R/d$, β_0 , and U_2/U_1 for Systems with No Polymer Tails in the Free-Draining Limit, As Computed from Our Collocation Method (Listed in Column KK) and from Eq. [40] (Listed in Column AS)

2R/d	$(A^2 - AB)/(A_\infty^2 - A_\infty B_\infty)$							
	A/A_∞		$\beta_0 = 10$		$\beta_0 = 100$		$\beta_0 = 1000$	
	KK	AS	KK	AS	KK	AS	KK	AS
$U_2/U_1 = 1$								
0.1	0.9307	0.9307	0.9303	0.9302	0.9302	0.9302	0.9302	0.9302
0.2	0.8733	0.8733	0.8695	0.8694	0.8691	0.8690	0.8690	0.8689
0.3	0.8296	0.8301	0.8161	0.8156	0.8145	0.8137	0.8140	0.8131
0.4	0.8011	0.8037	0.7702	0.7665	0.7658	0.7608	0.7642	0.7591
0.5	0.7881	0.7982	0.7347	0.7202	0.7260	0.7069	0.7231	0.7028
0.6	0.7875	0.8176	0.7145	0.6737	0.7012	0.6473	0.6966	0.6390
0.7	0.7942	0.8673	0.7119	0.6241	0.6954	0.5766	0.6899	0.5618
0.8	0.8028	0.9528	0.7193	0.5674	0.7015	0.4885	0.6955	0.4640
0.9	0.8115	1.0812	0.7286	0.5000	0.7099	0.3765	0.7037	0.3382
0.95	0.8157	1.1637	0.7333	0.4612	0.7145	0.3094	0.7081	0.2623
0.99	0.8190	1.2396	1.1967	0.4139	1.4656	0.2495	1.8690	0.1945
$U_2/U_1 = -1$								
0.1	1.0808	1.0808	1.0811	1.0811	1.0811	1.0811	1.0811	1.0811
0.2	1.1746	1.1746	1.1764	1.1764	1.1759	1.1759	1.1758	1.1757
0.3	1.2863	1.2865	1.2900	1.2896	1.2872	1.2868	1.2862	1.2859
0.4	1.4264	1.4269	1.4286	1.4264	1.4181	1.4168	1.4145	1.4136
0.5	1.6160	1.6169	1.6031	1.5969	1.5713	1.5705	1.5606	1.5616
0.6	1.9002	1.8960	1.8312	1.8187	1.7423	1.7560	1.7124	1.7350
0.7	2.3916	2.3509	2.1359	2.1344	1.8813	1.9964	1.7955	1.9502
0.8	3.4557	3.2160	2.5013	2.6681	1.6366	2.3675	1.3458	2.2668
0.9	7.1185	5.5419	2.3178	4.0224	-2.7019	3.2698	-4.3869	3.0177
0.95	15.486	9.7025	2.2430	6.4651	-21.559	4.9249	-29.559	4.4089

We have also numerically solved for G_j and H'_j for the system with no tails in the adsorbed polymer layers considering the hydrodynamic interactions among the polymer segments. In the calculations, we follow Anderson and Kim (21) and use a combination of a modified Brinkman equation at low ϕ_i and the Blake-Kozeny equation at high ϕ_i for the expression of function $f(\phi_i)$:

$$f = 1 + 2.121\phi_i^{1/2} + 0.84\phi_i \ln \phi_i + 16.456\phi_i \quad \text{for } \phi_i < 0.29, \quad [41a]$$

$$f = \frac{8.34\phi_i}{(1 - \phi_i)^3} \quad \text{for } \phi_i > 0.29, \quad [41b]$$

where $\phi_i = (\frac{4}{3})\pi a^3 \rho(y_i)$. For two identical polymer-coated spheres, the ratio A/A_∞ (or g/A_∞) is independent of $f(\phi_i)$ (in spite of the fact that A_∞ is a weak function of δ/a) and its results are the same as those given in Table 1. In Fig. 4, the results of parameters B and h for two spheres with $U_2/U_1 = -1$ versus $2R/d$ obtained using Eq. [41] are plotted for various values of β_0 and δ/a . Although the particle inter-

action effect on B and h increases when the value of δ/a is decreased for a given value of β_0 , the hydrodynamic interactions among the polymer segments produce relatively small effects on B and h .

CONCLUDING REMARKS

The slow motion of two spherical particles coated with adsorbed polymer layers has been analyzed in this work. The analysis provides governing equations and boundary conditions which must be solved, given the polymer segment density distribution $\rho(y_i)$ and rheological parameters $\mu(y_i)$ and $\beta_i(y_i)$, to determine the parameters A_i and B_i of Eq. [9] or parameters g_i and h_i of Eq. [30]. The hydrodynamic forces exerted on the particles for a resistance problem or the particle velocities for a mobility problem correct to $O(\lambda_i^2)$ can be calculated using Eq. [33] or [35] and the results of A_i and B_i . For the exponential polymer segment distribution given by Eq. [37], the ratio A/A_∞ or g/A_∞ of two identical spheres is found to be independent of the values of β_0 , δ/a , α , and $\eta/(\eta + \alpha)$, and its results for various

FIG. 2. The normalized parameters $A_1/A_{1\infty}$ and $B_1/B_{1\infty}$ for the motion of two polymer-coated spheres with $\delta_1 = \delta_2$, $\beta_{10} = \beta_{20} = 100$, $U_2/U_1 = -1$, and various values of the size ratio R_2/R_1 as a function of the separation parameter $(R_1 + R_2)/d$ in the free-draining limit ($f = 1$).

values of $2R/d$ are listed in Table 1. The dependence of B and h on β_0 , δ/a , α , $\eta/(\eta + \alpha)$, and $R/2d$ is given in Table 1 and Figs. 3 and 4. The results indicate that the particle interaction effects on the motion of two polymer-coated particles can be significant.

Throughout the calculations in the previous section we have assumed a simple exponential decay of the polymer segment density. This could be an oversimplification since the convex nature of the surfaces of the particles might adjust the excluded volume effects among the polymer segments. A segment density of the following form was suggested (21) to allow for curvature effects on polymer distribution:

$$\rho(y_i) = \rho_{i0} \frac{e^{-y_i/\delta_i}}{1 + s(y_i/R_i)}, \quad i = 1, 2, \quad [42]$$

where s should be a positive value. For two identical polymer-coated spheres with no tails in the free-draining limit, $\beta(y)$ has the form of the above equation with ρ_{i0} replaced by β_0 . It is understood that parameters A_∞ and A (or g) are independent of the curvature coefficient s . We have numerically solved Eqs. [23] and [25] with the segment distribution given by Eq. [42] and substituted the solution of G_j and H'_j into Eq. [27b] to compute parameters B and h .

FIG. 3. The parameters B and h for the motion of two identical polymer-coated spheres with $\beta_0 = 100$ and $U_2/U_1 = -1$ as a function of $2R/d$ in the free-draining limit ($f = 1$). The solid curves are plotted for the case of $\alpha = 0.5$, and the dashed curves are plotted for the case of $\alpha = 0.25$.

FIG. 4. The parameters B and h for the motion of two identical polymer-coated spheres with $U_2/U_1 = -1$ as a function of $2R/d$. The solid curves are plotted for the case of $\beta_0 = 10$, and the dashed curves are plotted for the case of $\beta_0 = 100$. Note that $\delta/a \rightarrow \infty$ represents the free-draining limit ($f = 1$) and the two dashed curves are almost indistinguishable.

These calculations, which are plotted in Fig. 5 for the case of $U_2/U_1 = -1$, indicate that the magnitudes of B and h decrease with the increase of s for various values of $2R/d$ as one would expect.

One may wish to consider a polymer segment distribution that has the same adsorbed amount as for the exponential distribution but is uniform over a distance from the particle surface:

$$\rho(y_i) = \rho_{i0} \quad \text{if } 0 \leq y_i \leq \delta_i, \quad [43a]$$

$$\rho(y_i) = 0 \quad \text{if } y_i > \delta_i. \quad [43b]$$

For this profile in the free-draining limit, $\beta_i(y_i)$ has the form of Eq. [43] with ρ_{i0} replaced by β_{i0} and it can be shown that

$$A_{i\infty} = 1 - \beta_{i0}^{-1/2} \tanh \beta_{i0}^{1/2}, \quad [44a]$$

$$B_{i\infty} = -\frac{1}{A_{i\infty}\beta_{i0}} (1 - \operatorname{sech} \beta_{i0}^{1/2})^2. \quad [44b]$$

It can be found that the value of $A_{i\infty}$ is about six times greater

FIG. 5. The parameters B and h for the motion of two identical polymer-coated spheres with the segment density distribution given by Eq. [42], $\beta_0 = 100$, and $U_2/U_1 = -1$ as a function of $2R/d$ in the free-draining limit.

FIG. 6. The parameters B and h for the motion of two identical polymer-coated spheres with the segment density distribution given by Eq. [43], $\beta_0 = 100$, and $U_2/U_1 = -1$ as a function of $2R/d$ in the free-draining limit. The corresponding results for the exponential segment distribution are also plotted for comparison.

(if $\beta_{i0} \approx 100$) for an exponential distribution of segments than for the polymer uniformly distributed over a region of thickness δ_i . Although $A_{i\infty}$ is a function of β_{i0} for this segment distribution, the ratio $A_i/A_{i\infty}$ or $g_i/A_{i\infty}$ for the motion of two polymer-coated spheres is independent of the segment distribution, and its results have been given in Table 1 and Fig. 2. In Fig. 6, the numerical results of parameters B and h obtained using Eq. [43] as the segment distribution are plotted for the case of $U_2/U_1 = -1$. The corresponding results for the case of the exponential distribution of segments are also plotted in the same figure for comparison. It

can be seen that the particle interaction effect on B and h is weaker for the uniform distribution of segments over a distance from the particle surface than for the exponential distribution of segments.

In addition to obtaining suitable approximate solutions of the quasisteady equations of motion of two polymer-coated spheres, it is desirable to know how well the predicted effects will be realized physically. Although experimental work has lagged behind the theory in this area, considerable data for two mutually interacting “bare” spheres are now available which indicate good agreement with corresponding solutions of the creeping motion equations (25). Once the segment density distribution in the surface polymer layer $\rho(y)$ together with the dimensionless surface density parameter β_0 is determined independently, one can measure the velocities and drag forces experienced by two polymer-coated spheres falling along the line between their centers in a viscous fluid for various values of the separation parameter (29) and choose the values of λ_i to test the theoretical analysis developed in this work.

APPENDIX A

For completeness the definitions of functions $W_{ik}(\nu_i)$, $X_{ik}(\nu_i)$, $Y_{ik}(\nu_i)$, and $Z_{ik}(\nu_i)$ in Eq. [19] are listed here.

$$W_{ik}(\nu_i) = \sum_{n=2}^{\infty} \left\{ [R_i^{-n+1} C_{ink} + R_i^{-n+3} D_{ink}] G_n^{-1/2}(\nu_i) + \left(\frac{\lambda_j}{\lambda_i} \right)^k [g_{ij}^{-n+1} C_{jnk} + g_{ij}^{-n+3} D_{jnk}] G_{n0ij} \right\}, \quad [\text{A.1}]$$

$$X_{ik}(\nu_i) = \sum_{n=2}^{\infty} \left\{ -[(n-1)R_i^{-n} C_{ink} + (n-3)R_i^{-n+2} D_{ink}] \times G_n^{-1/2}(\nu_i) + \left(\frac{\lambda_j}{\lambda_i} \right)^{k+1} g_{ij}^{-n+1} [G_{n1ij} - (n-1)h_{ij}G_{n0ij}] C_{jnk} + \left(\frac{\lambda_j}{\lambda_i} \right)^{k+1} g_{ij}^{-n+3} \times [G_{n1ij} - (n-3)h_{ij}G_{n0ij}] D_{jnk} \right\}, \quad [\text{A.2}]$$

$$Y_{ik}(\nu_i) = \sum_{n=2}^{\infty} \left\{ \frac{1}{2} [n(n-1)R_i^{-n-1} C_{ink} + (n-2)(n-3)R_i^{-n+1} D_{ink}] G_n^{-1/2}(\nu_i) + \left(\frac{\lambda_j}{\lambda_i} \right)^{k+2} g_{ij}^{-n+1} \left[G_{n2ij} - (n-1)h_{ij}G_{n1ij} + (n-1) \left(\frac{n}{2} h_{ij}^2 - m_{ij} \right) G_{n0ij} \right] C_{jnk} \right\}$$

$$+ \left(\frac{\lambda_j}{\lambda_i} \right)^{k+2} g_{ij}^{-n+3} \left[G_{n2ij} - (n-3)h_{ij}G_{n1ij} \right. \\ \left. + (n-3) \left(\frac{n-2}{2} h_{ij}^2 - m_{ij} \right) G_{n0ij} \right] D_{jnk} \Big\}, \quad [\text{A.3}]$$

$$Z_{ik}(\nu_i) = \sum_{n=2}^{\infty} \left\{ -\frac{1}{6}(n-1)[n(n+1)R_i^{-n-2}C_{ink} \right. \\ + (n-2)(n-3)R_i^{-n}D_{ink}]G_n^{-1/2}(\nu_i) \\ + \left(\frac{\lambda_j}{\lambda_i} \right)^{k+3} g_{ij}^{-n+1} \left[G_{n3ij} - (n-1)h_{ij}G_{n2ij} \right. \\ + (n-1) \left(\frac{n}{2} h_{ij}^2 - m_{ij} \right) G_{n1ij} - (n-1) \\ \times \left(\frac{n(n+1)}{6} h_{ij}^3 - nh_{ij}m_{ij} + n_{ij} \right) G_{n0ij} \Big] C_{jnk} \\ + \left(\frac{\lambda_j}{\lambda_i} \right)^{k+3} g_{ij}^{-n+3} \left[G_{n3ij} - (n-3)h_{ij}G_{n2ij} \right. \\ + (n-3) \left(\frac{n-2}{2} h_{ij}^2 - m_{ij} \right) G_{n1ij} \\ - (n-3) \left(\frac{(n-1)(n-2)}{6} h_{ij}^3 \right. \\ \left. \left. - (n-2)h_{ij}m_{ij} + n_{ij} \right) G_{n0ij} \right] D_{jnk} \Big\}, \quad [\text{A.4}]$$

where $j = 3 - i$,

$$G_{n0ij} = G_n^{-1/2}(t_{ij}), \quad [\text{A.5}]$$

$$G_{n1ij} = \frac{1}{(2n-1)} \left\{ \frac{1}{2^{n-3}} \sum_{k=0}^{\langle n-2 \rangle} \right. \\ \times \frac{(-1)^k(n-k-2)!}{k!(n-2k-3)!(n-k-2)!} t_{ij}^{n-2k-2} u_{ij} - \frac{1}{2^{n-1}} \\ \times \sum_{k=0}^{\langle n \rangle} \frac{(-1)^k(n-k)!}{k!(n-2k-1)!(n-k)!} t_{ij}^{n-2k} u_{ij} \Big\}, \quad [\text{A.6}]$$

$$G_{n2ij} = \frac{1}{2(2n-1)} \left\{ \frac{1}{2^{n-3}} \sum_{k=0}^{\langle n-2 \rangle} \right. \\ \times \frac{(-1)^k(n-k-2)!}{k!(n-2k-3)!(n-k-2)!} t_{ij}^{n-2k-2} \\ \times [(n-2k-3)u_{ij}^2 + 2v_{ij}] - \frac{1}{2^{n-1}} \\ \times \sum_{k=0}^{\langle n \rangle} \frac{(-1)^k(n-k)!}{k!(n-2k-1)!(n-k)!} t_{ij}^{n-2k} \\ \times [(n-2k-1)u_{ij}^2 + 2v_{ij}] \Big\}, \quad [\text{A.7}]$$

$$G_{n3ij} = \frac{1}{6(2n-1)} \left\{ \frac{1}{2^{n-3}} \sum_{k=0}^{\langle n-2 \rangle} \right. \\ \times \frac{(-1)^k(n-k-2)!}{k!(n-2k-3)!(n-k-2)!} t_{ij}^{n-2k-2} \\ \times [(n-2k-3)(n-2k-4)u_{ij}^3 \\ + 6(n-2k-3)u_{ij}v_{ij} + 6w_{ij}] - \frac{1}{2^{n-1}} \\ \times \sum_{k=0}^{\langle n \rangle} \frac{(-1)^k(n-k)!}{k!(n-2k-1)!(n-k)!} t_{ij}^{n-2k} \\ \times [(n-2k-1)(n-2k-2)u_{ij}^3 \\ + 6(n-2k-1)u_{ij}v_{ij} + 6w_{ij}] \Big\}, \quad [\text{A.8}]$$

and

$$g_{ij} = x_{ij}^{1/2}, \quad [\text{A.9}]$$

$$h_{ij} = x_{ij}^{-1}y_{ij}, \quad [\text{A.10}]$$

$$m_{ij} = -\frac{1}{2}x_{ij}^{-2}y_{ij}^2 + \frac{1}{2}x_{ij}^{-1}, \quad [\text{A.11}]$$

$$n_{ij} = \frac{1}{2}x_{ij}^{-3}y_{ij}^3 - \frac{1}{2}x_{ij}^{-2}y_{ij}. \quad [\text{A.12}]$$

In Eqs. [A.5]–[A.8], $\langle n \rangle = 0$ if $n = 0$, $\langle n \rangle = (n-1)/2$ if n is odd, $\langle n \rangle = (n-2)/2$ if n is even, and

$$t_{ij} = x_{ij}^{-1/2}z_{ij}, \quad [\text{A.13}]$$

$$u_{ij} = \nu_i z_{ij}^{-1} - x_{ij}^{-1}y_{ij}, \quad [\text{A.14}]$$

$$v_{ij} = \frac{3}{2}x_{ij}^{-2}y_{ij}^2 - \frac{1}{2}x_{ij}^{-1} - \nu_i x_{ij}^{-1}y_{ij}z_{ij}^{-1}, \quad [\text{A.15}]$$

$$w_{ij} = -\frac{5}{2}x_{ij}^{-3}y_{ij}^3 + \frac{3}{2}x_{ij}^{-2}y_{ij} \\ + \frac{3}{2}\nu_i x_{ij}^{-2}y_{ij}^2 z_{ij}^{-1} - \frac{1}{2}\nu_i x_{ij}^{-1}z_{ij}^{-1}. \quad [\text{A.16}]$$

In Eqs. [A.9]–[A.16],

$$x_{ij} = R_i^2 + (j-i)(3-2i)d^2 - 2(j-i)R_i\nu_i d, \quad [\text{A.17}]$$

$$y_{ij} = R_i - (j-i)\nu_i d, \quad [\text{A.18}]$$

$$z_{ij} = R_i\nu_i - (j-i)d. \quad [\text{A.19}]$$

APPENDIX B: NOMENCLATURE

a	Stokes radius of a polymer segment (m)
$A_{i\infty}, B_{i\infty}$	parameters defined by Eq. [29]
A_i, B_i	parameters defined by Eq. [9]
b_{jn}, c_{jn}, d_{jn}	coefficients defined by Eq. [20]
C_{in}, D_{in}	coefficients defined by Eq. [10] (m^{n+2}/s , m^n/s)

C_{inn}, D_{inn}	coefficients defined by Eq. [11] ($m^{n+2}/s, m^n/s$)	ζ	Stokes friction coefficient of a polymer segment (kg/s)
d	center-to-center distance between two particles (m)	η_i	fraction of tails as defined by Eq. [38]
$\mathbf{e}_z$	unit vector in the z direction	θ_i, ϕ	angular spherical coordinates about particle i
f	parameter for the hydrodynamic interactions among polymer segments defined by Eq. [1a]	λ_i	δ_i/R_i
F_i	hydrodynamic force exerted on particle i (N)	Λ'_j, Λ_j	coefficients defined by Eqs. [30b, c]
F_{inn}	functions of y_i defined by Eq. [15] (m^2)	μ	viscosity inside the polymer layer (kg/m s)
$\mathbf{F}_j^{(0)}$	hydrodynamic force defined by Eq. [34] (N)	μ_s	fluid viscosity (kg/m s)
g_i, h_i	parameters defined by Eq. [30]	ν_i	$\cos \theta_i$
G_j, H_j, H'_j	functions of y_j defined by Eqs. [22]–[26] (m)	ξ	R/d
$G_n^{-1/2}$	Gegenbauer polynomials of order n and degree $-\frac{1}{2}$	ρ	polymer segment distribution (m^{-3})
K_i	particle interaction factor defined by Eq. [8]	ρ_{i0}	polymer segment density in loops at the surface of particle i (m^{-3})
K_{ij}	dimensionless resistance coefficients defined by Eq. [33]	ϕ_i	$(4/3)\pi a^3 \rho(y_i)$
L_i	effective hydrodynamic thickness of the polymer layer on particle i defined by Eq. [8] (m)	ϕ_{i0}	$(4/3)\pi a^3 \rho_{i0}$
$L_{i\infty}$	effective hydrodynamic thickness of the polymer layer on particle i defined by Eq. [31] (m)	Ψ	Stokes stream function (m^3/s)
M_{ij}	dimensionless mobility coefficients defined by Eq. [35]	$\Psi^{(o)}$	stream function in the outer region (m^3/s)
p	hydrodynamic pressure (N/m^2)	$\Psi^{(i)}$	stream function in the inner region about particle i (m^3/s)
$p_{ijn}, q_{ijn}, s_{ijn}$	coefficients defined by Eq. [20]	ϖ	radial cylindrical coordinate (m)
P_n	Legendre polynomial of order n	Ω_j	coefficients defined by Eq. [28d]
r_i	radial spherical coordinate about particle i (m)		
R_i	radius of particle i (m)		
s	curvature coefficient defined by Eq. [42]		
U_i	translational velocity of particle i (m/s)		
$\mathbf{U}_j^{(0)}$	velocity of particle j defined by Eq. [36] (m/s)		
$\mathbf{v}$	fluid velocity (m/s)		
$\mathbf{v}^{(p)}$	velocity of polymer segments (m/s)		
$W_{ik}, X_{ik}, Y_{ik}, Z_{ik}$	functions of ν_i defined by Eqs. [A.1]–[A.4] ($m^3/s, m^2/s, m/s, s^{-1}$)		
y_i	$\lambda_i^{-1}(r_i - R_i)$ (m)		
z	axial coordinate (m)		
α_i	ratio of loop-to-tail length scales for the polymer layer of particle i		
β_i	parameters defined by Eq. [4a]		
β_{i0}	parameters defined by Eq. [39]		
γ_j	coefficients defined by Eq. [28a]		
δ_i	length scale of the polymer layer surrounding particle i (m)		

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