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A BOUNDARY COLLOCATION METHOD FOR THE MOTION OF TWO SPHEROIDS IN STOKES FLOW: HYDRODYNAMIC AND COLLOIDAL INTERACTIONS

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Abstract—The dynamics of two non-Brownian spheroidal particles in low Reynolds number flows are studied. The boundary least squares–collocation method is developed based on the singularity solution for Stokes flow. This method allows the solution of the mobility problem for two spheroidal particles suspended in an arbitrary flow field to be obtained directly, at a modest computational cost. The method was tested with several model problems and the results were in good agreement with known results for various limiting cases. The method is then applied to the trajectory calculation for two spheroidal particles with additional long-range colloidal interactions. The classical DLVO theory is used with the Derjaguin approximation. Several examples for the motion of two oblate spheroids in a shear flow are shown.

Key Words: boundary collocation method, Stokes flow, DVLO theory, spheroids, hydrodynamic interaction

INTRODUCTION

Over the last two decades interactions between spheres in shear flow have been studied in great detail, both theoretically and experimentally, by several researchers (Curtis & Hocking 1970; van de Ven & Mason 1976a, b; Arp & Mason 1977a, b; Zeichner & Schowalter 1977; Takamura *et al.* 1981a, b; Adler 1981a–c). Their results have played an important role in understanding the stability and coagulation of colloidal suspensions in shear flow (Schowalter 1982, 1984; van de Ven 1982). Progress in this research area has been made possible through the availability of accurate information on the hydrodynamic interaction between spheres (Lin *et al.* 1970; Batchelor & Green 1972).

Although some polymer colloids consist of perfect spheres, most colloidal suspensions contain nonspherical particles. Moreover, some rheological properties of suspensions result specifically, only from nonsphericity of the particle shapes, e.g. clay suspensions (van Olphen 1977). So far theoretical studies on the motion of two nonspherical particles in shear flow are almost nonexistent, mainly because of the difficulties in determining the hydrodynamic interaction between nonspherical particles. The objective of this study is to develop a numerical method with which one can determine the dynamics of ellipsoidal particles, in particular prolate (rod shape) and oblate (disk shape) spheroids in arbitrary flow fields.

HYDRODYNAMIC INTERACTIONS

Governing equations

The motion of small colloidal particles immersed in an unbounded fluid is usually characterized by a small particle Reynolds number. The velocity field $\mathbf{u}$ and the pressure field p then satisfy the Stokes equation and the equation of continuity for incompressible flow:

$$-\nabla p + \mu \nabla^2 \mathbf{u} = 0 \quad \text{and} \quad \nabla \cdot \mathbf{u} = 0. \qquad [1a, b]$$

Here μ is the viscosity of the fluid. Each particle centered at $\mathbf{x}_c^{(\alpha)}$ is in a rigid-body motion with translational velocity $\mathbf{U}^{(\alpha)}$ and rotational velocity $\mathbf{\Omega}^{(\alpha)}$,

$$\mathbf{u}|_{\partial B^{(\alpha)}} = \mathbf{U}^{(\alpha)} + \mathbf{\Omega}^{(\alpha)} \times (\mathbf{x} - \mathbf{x}_c^{(\alpha)}). \qquad [2]$$

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We use the superscript (α) to label the particles and ∂B denotes the surface of the particle. The fluid velocity approaches an undisturbed linear flow field far from the particles,

$$\mathbf{u}|_{r\to\infty} = \mathbf{U}^{\infty} + \boldsymbol{\Omega}^{\infty} \times \mathbf{x} + \mathbf{E}^{\infty} \cdot \mathbf{x}. \qquad [3]$$

The ambient field is a superposition of uniform stream, a vorticity and a rate-of-strain field.

Determination of the Stokes solutions is difficult, in general, for multiparticle systems. Since the Stokes equations are separable only in a few orthogonal coordinate systems, not many analytical solutions are available except for the particles whose geometry fits in a coordinate surface of one of those coordinate systems: e.g. two parallel cylinders (Raasch 1961), two spheres (Lin *et al.* 1970) and two touching spheres (Nir & Acrivos 1973). Thus, we usually solve the Stokes problems for multiparticle systems using an approximate method where the solution satisfies the governing equations and boundary conditions either asymptotically or on the average.

Boundary methods

In many Stokes problems of practical interest, we do not need to solve for the flow field around the suspended particles, but seek to find only the motion of and certain moments of the stress distribution on the particles. Thus, spatial numerical schemes which require the discretization of the entire medium are not efficient for this purpose. Moreover, since the nature of the momentum transport in Stokes flows is entirely diffusive, any disturbance produced by boundaries decays very slowly. Thus, the integration domain for spatial numerical schemes would have to be made very large relative to the particle size. For instance, a translating sphere in Stokes flow produces the disturbance velocity field which decays like r^{-1}, while the analogous problem in potential flow shows the r^{-3} type decay. Therefore, even in the situation in which the solutions for the full Navier–Stokes equations show negligible interactions between two separate boundaries, the solutions for the Stokes equations may show significant hydrodynamic interactions.

Alternatively, we may use the *boundary method* in which we express the Stokes solutions as a sum of fundamental singularity solutions (Green's functions) of the Stokes equations and seek to determine their density by using the boundary conditions on the particle surface. Since we can represent a single particle as a collection of point singularities, the boundary method, in principle, can be readily applied to the multiparticle system.

As a general solution to the Stokes equations, we may use the single-layer velocity representation (Youngren & Acrivos 1975) or slender-body theory (Cox 1970), if applicable. In this case we have to determine the unknown Stokeslet density in such a way that the no-slip boundary condition would be satisfied on the surface of each particle. We then calculate the total hydrodynamic force and torque, respectively, by integrating the density of the Stokeslet distribution and its first-order moment about the particle center. Obviously, we can only solve the resistance problem using this representation. In order to solve the mobility problem we have to solve the resistance problem first and then determine the motion of each particle by inversion of the linear relations between the force moments and the particle velocities. In other words, we calculate the force and torque acting on each particle due to a set of mutually perpendicular translational and rotational motions of a given particle, and then choose the correct linear combination of the particle velocities in such a way that the given conditions for the hydrodynamic force and torque are satisfied for each particle. For example, in sedimentation the hydrodynamic force is balanced by the gravity force and the net torque is set to zero.

A direct method for the mobility problem

There are three major disadvantages in using the single-layer velocity representation (and the slender-body theory in a similar context) in solving the mobility problem. First, these equations are Fredholm integral equations of the first-kind and thus ill-posed.† Second, the method is not a direct one, especially for problems with ambient flow. Third, the singular behavior of the hydrodynamic force and torque at small separations between two particles makes the inversion process to the mobility solution unstable. In contrast with the resistance problem, the mobility problem is inherently stable since the translational and rotational velocities of particles remain finite

†But they may be recast as second-kind equations (Power & Miranda 1987; Karrila & Kim 1989; Karrila *et al.* 1989).

at all separations. Thus, it is natural to seek a simple, direct method which could provide more accurate results for the mobility problems for the multiparticle system.

A drawback of the single-layer velocity representation applied to the mobility problem stems from the fact that we do not know how to distribute Stokeslets from the given conditions for the total hydrodynamic force and torque until we solve the complete problem. However, there are velocity representations in which Stokeslets (and other singularities) are distributed *a priori* before we solve the given Stokes problem, e.g. the multipole expansion solution. With these velocity representations, we only have to determine the strength (tensor quantity) of singularities, and that is readily accomplished using the boundary conditions. (The boundary conditions furnish a set of linear equations which contain the strength of singularities on each particle and the particle velocities as the unknowns.) Since the hydrodynamic force and torque acting on each particle are proportional to the strength of Stokeslets and rotlets, we can solve either the resistance problem or the mobility problem directly from these linear equations.

Obviously, the key to this direct method is the information on the spatial distribution of Stokeslets and rotlets. The velocity representation which has the simplest spatial distribution for these singularities is the multipole expansion about the particle center. Although the point distribution at the particle center is a natural choice for spherical particles [see Yoon & Kim (1987) for the mobility problem for two spheres], it is not an efficient way to distribute singularities for nonspherical particles. For very slender or flat particles, we need to include many higher order singularities in the multipole expansion expression to obtain reasonable results.

In contrast with the multipole expansion solution, the singularity solution (Chwang & Wu 1975; Kim 1986; Kim & Arunachalam 1987) is more appropriate for nonspherical particles since singularities are distributed over the internal region which resembles the particle shape. This area (or line) distribution of singularities makes the singularity solution converge faster than the multipole expansion solution when we truncate both representations at the same order (i.e. the same number of unknowns to be determined).

Singularity solutions for ellipsoids

The singularity solution for the Stokes flow around ellipsoids has been derived by Kim & Arunachalam (1987). We may use either the ellipsoidal harmonic representation or the integral representation. We use the former since it is more efficient for our computational purposes.

The velocity field around two ellipsoidal particles, with the semi-axes ($a \geqslant b \geqslant c$), immersed in an ambient field $\mathbf{u}^{\infty}$, is given by

$$u_i(\mathbf{x}) = u_i^{\infty}(\mathbf{x}) + \sum_{\alpha=1}^{2} \sum_{n=1}^{\infty} P^{(\alpha)}_{jk_1 \ldots k_{n-1}} C_{ijk_1 \ldots k_{n-1}}(\mathbf{x} - \mathbf{x}_c^{(\alpha)}), \qquad [4]$$

where

$$C_{ijk_1 \ldots k_{n-1}} = \frac{\partial}{\partial x_{k_1}} \cdots \frac{\partial}{\partial x_{k_{n-1}}} \left(\delta_{ij} G_{n-1} - x_j \frac{\partial G_{n-1}}{\partial x_i} + \frac{a_j^2}{2n} \frac{\partial^2 G_n}{\partial x_i \partial x_j} \right).$$

Here the G_ns are ellipsoidal harmonics, the solution of the Laplace equation in ellipsoidal coordinates, and are defined as

$$G_n = \int_{\lambda}^{\infty} \left(\frac{x^2}{a^2+t} + \frac{y^2}{b^2+t} + \frac{z^2}{c^2+t} - 1 \right)^n \frac{\mathrm{d}t}{\Delta(t)}, \quad \Delta(t) = \sqrt{(a^2+t)(b^2+t)(c^2+t)},$$

where λ is the positive root of the cubic equation for t,

$$\frac{x^2}{a^2+t} + \frac{y^2}{b^2+t} + \frac{z^2}{c^2+t} - 1 = 0. \qquad [5]$$

The three roots of [5] generate the ellipsoidal coordinates system. The largest root λ corresponds to the "radial" coordinate variable and on the ellipsoid surface $\lambda = 0$.

Here $\mathbf{C}$ contains the information on the spatial distribution of singularities and $\mathbf{P}$ represents their strength. The force and torque exerted on each particle are related to the strengths of the Stokeslets and Stokes dipoles as

$$F_i^{(\alpha)} = -16\pi\mu P_i^{(\alpha)} \quad \text{and} \quad T_i^{(\alpha)} = \tfrac{32}{3}\pi\mu\epsilon_{ijk} P_j^{(\alpha)}. \qquad [6a, b]$$

The no-slip boundary conditions at the surfaces of both particles furnish the following equations:

$$\sum_{\alpha=1}^{2}\sum_{n=1}^{\infty} P^{(\alpha)}_{jk_1\ldots k_{n-1}} C_{ijk_1\ldots k_{n-1}}(\mathbf{x}-\mathbf{x}^{(\alpha)}_c)|_{\partial B^{(1)}} = U^{(1)}_i + \epsilon_{ipq}\Omega^{(1)}_p(x_q - x^{(1)}_{cq})|_{\partial B^{(1)}} - u^{\infty}_i|_{\partial B^{(1)}} \quad [7a]$$

and

$$\sum_{\alpha=1}^{2}\sum_{n=1}^{\infty} P^{(\alpha)}_{jk_1\ldots k_{n-1}} C_{ijk_1\ldots k_{n-1}}(\mathbf{x}-\mathbf{x}^{(\alpha)}_c)|_{\partial B^{(2)}} = U^{(2)}_i + \epsilon_{ipq}\Omega^{(2)}_p(x_q - x^{(2)}_{cq})|_{\partial B^{(2)}} - u^{\infty}_i|_{\partial B^{(2)}}. \quad [7b]$$

Equations [7a, b] are a system of linear equations for $\mathbf{P}^{(\alpha)}$, $\mathbf{U}^{(\alpha)}$ and $\mathbf{\Omega}^{(\alpha)}$. In the resistance problem, the r.h.s. of [7a, b] is given and we can determine $\mathbf{P}^{(\alpha)}$, and thus the force and torque on each ellipsoid. In the mobility problem, $P^{(\alpha)}_i$ and the antisymmetric part of $P^{(\alpha)}_{ij}$ are given so that we can determine $\mathbf{U}^{(\alpha)}$ and $\mathbf{\Omega}^{(\alpha)}$.

Least squares–collocation method

We may solve [7a, b] using any variation of the method of weighted residuals: Galerkin method, collocation method and subdomain method. Because of its simplicity the collocation method has been favored by several researchers (Gluckman *et al.* 1971; Ganatos *et al.* 1978; Kim & Mifflin 1985). However, the solution of the boundary collocation method is generally sensitive to the choice of the collocation points. In order to make the solution less sensitive to the choice of the collocation points we use the least squares approach. In this method we choose more collocation points than unknowns, so the number of equations in [7a, b] is greater than the number of unknowns, and determine the solution which minimizes the sum of the squares of the residuals. In our study the least squares solution is obtained using F04JGF in the NAG FORTRAN library,† a least squares routine based on the QR decomposition.

Interaction between ellipsoid and Stokeslet

In order to test the new boundary method we compare numerical and analytical results for the problem of the interaction between a single stationary ellipsoid and a Stokeslet. This type of analysis is relevant in all two-particle interaction problems in Stokes flow (and in particular to our discussion in section 3 of two spheroids in shear flow) because the particle–particle interaction can be viewed as that between a single test particle and a collection of point singularities distributed in such a way to mimic the effects of the second particle. Because of the linearity of the governing equations, this approach gauges the discretization errors of the numerical method.

Consider an oblate spheroid placed at the origin

$$\frac{x^2+y^2}{a^2}+\frac{z^2}{c^2}=1, \quad a>c.$$

A Stokeslet with the strength $\mathbf{f}$ is located at $(0, 0, R)$. Without loss of generality, we consider two cases: axisymmetric (only f_z is nonzero) and asymmetric (only f_y is nonzero) problems. In the axisymmetric problem we calculate the force exerted on the spheroid (only its z component is nonzero), while in the asymmetric problem we calculate both the force (y component) and torque (x component) on the spheroid. Exact expressions for the nondimensionalized force and torque on the oblate spheroid are given by (Yoon 1989)

$$F_z/f_z = \frac{(k^2-c^2)\cot^{-1}(R/k)+a^2kR/(R^2+k^2)}{(k^2-c^2)\cot^{-1}(c/k)+ck}, \quad [8]$$

$$F_y/f_y = \frac{(a^2+2k^2)\cot^{-1}(R/k)-a^2kR/(R^2+k^2)}{(a^2+2k^2)\cot^{-1}(c/k)-ck} \quad [9]$$

and

$$T_x/(f_yR) = \frac{(k^2-c^2)\cot^{-1}(R/k)+\dfrac{2k^3c^2/R-k^3R+kc^2R)}{(R^2+k^2)}}{(k^2-c^2)\cot^{-1}(c/k)+ck}. \quad [10]$$

Here k denotes $\sqrt{a^2-c^2}$.

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We choose the collocation points in such a way that they are evenly spaced, in the oblate spheroidal coordinates (η, ϕ), over the surface. In the cartesian coordinates these collocation points are given by

$$x(\eta_i, \phi_j) = a\sqrt{1-\eta_i^2}\cos(\phi_j),$$
$$y(\eta_i, \phi_j) = a\sqrt{1-\eta_i^2}\sin(\phi_j),$$
$$z(\eta_i, \phi_j) = c\eta_i,$$

where

$$\eta_i = -1 + \frac{2}{N_e+1} i, \qquad i = 1, \ldots, N_e,$$

$$\phi_j = \frac{2\pi}{N_p}(j-1), \qquad j = 1, \ldots, N_p.$$

The results for an oblate spheroid of aspect ratio 10 are shown in figure 1. The number of collocation points is 1000 ($N_e = 200$, $N_p = 5$) and we truncate the singularity solution after the octupole moments, i.e. retain only P_i, P_{ij}, P_{ijk} and P_{ijkl} as the unknowns. The exact solutions and numerical results are shown as solid and broken lines, respectively. Our numerical results are in good agreement with the exact solutions even when the Stokeslet is very close to the spheroid. We found that an increase in N_p does not affect the results because of the axisymmetric nature of the problem. However, in order to obtain accurate results for higher order multipole moments, N_p should be increased accordingly to capture the high frequency behavior of those moments. For instance, with $N_p = 3$ we cannot obtain the correct value for the torque, regardless of the choice of N_e, even though the corresponding results for the force are reasonably accurate.

Mobility functions for two approaching spheroids

As another test, we calculate mobility functions for two approaching oblate spheroids for which analytic results are available in two limiting cases—the far-field (widely-separated) and near-field (almost-touching) geometries. We consider two different configurations (edge–edge and face–face modes) in which the fore–aft mirror symmetry about the midplane perpendicular to the line of centers exists. We apply a unit force on each oblate spheroid along their line of centers (but in opposite directions) so that they approach each other, and we calculate the translational velocity of each spheroid.

As in Kim & Mifflin (1985), we may define mobility functions for translational velocities and applied forces along the line of centers, by

$$\begin{pmatrix} U^{(1)} \\ U^{(2)} \end{pmatrix} = \frac{1}{\mu} \begin{pmatrix} x_{11}^a & x_{12}^a \\ x_{12}^a & x_{11}^a \end{pmatrix} \begin{pmatrix} F_{ex}^{(1)} \\ F_{ex}^{(2)} \end{pmatrix}.$$

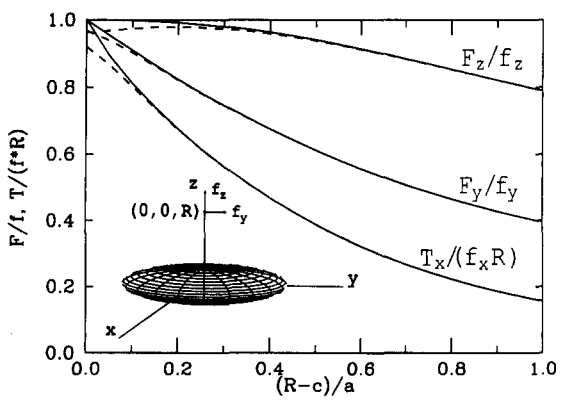

Figure 1. The force and torque on an oblate spheroid ($c/a = 0.1$) due to a Stokeslet located on the axis of revolution. The singularity solution is truncated after the octupole moments and the number of collocation points is 1000 ($N_e = 200$, $N_p = 5$). The exact solutions are shown as solid lines.

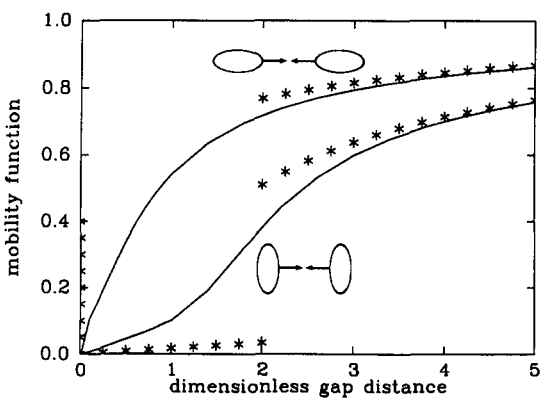

Figure 2. The mobility function for oblate spheroids ($c/a = 0.1$) in EE and FF modes. The singularity solution is truncated after the octupole moments and the number of collocation points is 20 for each spheroid. The asymptotic results are shown as asterisks.

In this particular example we compute $x_{11}^a - x_{12}^a$. When the center-to-center separation R is large, the mobility function approaches that of a single, isolated spheroid. We nondimensionalize $x_{11}^a - x_{12}^a$ such that it approaches unity at large R. We denote this nondimensional mobility function as $\hat{x}_{11}^a - \hat{x}_{12}^a$.

Using the method of reflections, we obtain the asymptotic expressions for $\hat{x}_{11}^a$ and $\hat{x}_{12}^a$. The results for the edge–edge(EE) and face–face(FF) cases are given by:

$$\hat{x}_{11}^a(\mathrm{EE}) = 1 - \frac{1}{(1+2e^2)\tau - e\sqrt{1-e^2}}\left[\frac{\frac{3}{2}}{(3-2e^2)\tau - 3e\sqrt{1-e^2}}\right.$$
$$\times\left[1 - \left(\frac{k}{R}\right)\sin^{-1}\left(\frac{2k}{R}\right) - \sqrt{1-4\left(\frac{k}{R}\right)^2}\right]^2$$
$$\left. + \frac{\frac{1}{3}}{3\tau - e(3+2e^2)\sqrt{1-e^2}}\left\{1 - \left[1+2\left(\frac{k}{R}\right)^2\right]\sqrt{1-4\left(\frac{k}{R}\right)^2}\right\}^2\right]\left(\frac{R}{a}\right)^4,$$

$$\hat{x}_{12}^a(\mathrm{EE}) = \frac{1}{(1+2e^2)\tau - e\sqrt{1-e^2}}\left[(1+2e^2)\sin^{-1}\left(\frac{2k}{R}\right) + \frac{2}{e}\left(\frac{R}{a}\right)\right.$$
$$\left.\times\left\{-\frac{2}{3} + \left[\frac{2}{3} + \frac{1}{3}\left(\frac{k}{R}\right)^2\right]\sqrt{1-4\left(\frac{k}{R}\right)^2}\right\}\right];$$

and

$$\hat{x}_{11}^a(\mathrm{FF}) = 1 - \left[\frac{\frac{3}{16}}{e\sqrt{1-e^2} + (2e^2-1)\tau}\right]\left[\frac{1}{-3e\sqrt{1-e^2} + (3-2e^2)\tau}\right]$$
$$\times\left\{\left(\frac{R}{a}\right)^2\ln\left[1+4\left(\frac{k}{R}\right)^2\right] - 4e\left(\frac{R}{a}\right)\cot^{-1}\left(\frac{R}{2k}\right) + 4e^2\right\}^2,$$

$$\hat{x}_{12}^a(\mathrm{FF}) = \frac{1}{e\sqrt{1-e^2} + (2e^2-1)\tau}\left[\frac{1-e^2}{2e}\left\{\left(\frac{R}{a}\right)\ln\left[1+4\left(\frac{k}{R}\right)^2\right]\right.\right.$$
$$\left.\left. - 2e\cot^{-1}\left(\frac{R}{2k}\right)\right\} + e^2\cot^{-1}\left(\frac{R}{2k}\right)\right].$$

Here e is the eccentricity (k/a) of the spheroid and $\tau = \tan^{-1}(e/\sqrt{1-e^2})$. These results are accurate to $O(R^{-4})$.

The asymptotic expressions for $\hat{x}_{11}^a - \hat{x}_{12}^a$ at the near-field limit can be obtained using the result of Cox (1974). Corresponding expressions which contain only the leading order term are given by

$$\hat{x}_{11}^a - \hat{x}_{12}^a(\mathrm{EE}) = \frac{8(a^2+c^2)}{3c^3}\left[\frac{e^3}{-e\sqrt{1-e^2} + (1+2e^2)\tau}\right]d$$

and

$$\hat{x}_{11}^a - \hat{x}_{12}^a(\mathrm{FF}) = \frac{8c^2}{3a^3}\left[\frac{e^3}{e\sqrt{1-e^2} + (2e^2-1)\tau}\right]d.$$

Here d denotes the minimum gap distance between spheroids.

Numerical results for oblate spheroids of aspect ratio 10 are shown in figure 2. The singularity solution is truncated at the octupole terms and 20 collocation points are used on each spheroid. The asymptotic results at the near-field and far-field limits are also shown as asterisks. Our results are in good agreement with the asymptotic results for the far-field. It is known that the asymptotic solution for the near-field limit has an extremely small domain of validity, but even there, our method captures the correct behavior of the mobility function. Finally, the computational costs are quite modest—about 1 min on a MicroVax II for each configuration of the spheroids.

COLLOIDAL INTERACTIONS

DLVO theory

In addition to hydrodynamic interactions, there always exist other long-range interactions between particles suspended in most colloidal systems. According to the classical DLVO theory (Derjaguin & Landau 1941; Verwey & Overbeek 1948) there are two major long-range colloidal interactions: van der Waals attractions and electric double-layer repulsions (or attractions between particles with different surface charges). Both are electromagnetic in nature. Other short-range ($d < 10$ nm) colloidal forces, e.g. solvation and steric forces (Israelachvili 1985), may also exist, however, in this study we only consider long-range colloidal interactions based on the DLVO theory.

When the center-to-center distance R between two particles is larger than their size ($\sim 1\ \mu$m), hydrodynamic forces induced by the motion of the second particle show the R^{-1} (or R^{-2} for force-free particles) distance dependence. On the other hand, van der Waals attractions fall with distance as R^{-7} (or as R^{-8} with a retardation), while electric double-layer repulsions decay exponentially. Thus, in the far-field limit the hydrodynamic interaction is predominant over colloidal interactions. In fact, van der Waals attractions and electric double-layer repulsions are rarely important beyond 1 μm from the surface of the particle.

In the near-field limit the behavior of each of the interactions is quite different. When the gap distance between two particles is d, hydrodynamic forces diverge as d^{-1} (or as $\ln d$), while van der Waals attractions diverge as d^{-2}. Electric double-layer repulsions remain finite at contact. Thus, as two particles approach each other closely, van der Waals attractions dominate lubrication forces and the two particles eventually coagulate unless there exists a substantial energy barrier between them.

In the intermediate range ($d < 1\ \mu$m), each of the interactions can be important and the behavior of colloids depends on a delicate balance among these interactions. Before we discuss the DLVO theory applied to nonspherical particles, it is useful to introduce relevant dimensionless groups (Zeichner & Schowalter 1977):

$$N_R = \frac{\epsilon \psi^{(1)2} a}{A}, \quad N_F = \frac{6\pi\mu a^3 G}{A}, \quad \Psi = \frac{\psi^{(2)}}{\psi^{(1)}}.$$

Here ϵ denotes the dielectric constant of the medium, a the length scale of the particle (the major semi-axis for ellipsoids), A the Hamaker constant, $\psi^{(\alpha)}$ the surface potential of each particle and G the shear rate. The first dimensionless group represents the ratio of electric double-layer forces and van der Waals forces, while the second one represents the ratio of hydrodynamic forces and van der Waals forces.

Derjaguin approximation

The original DLVO theory considered the case of interacting spheres. However, one can readily extend the approximation method of Derjaguin (1934), which was originally used for the derivation of electric double-layer repulsions between two spheres, to more general cases.

Consider two particles almost in contact (at a single point), with the minimum gap distance d. We take the local cartesian coordinates system with the point of minimum separation as origin and with the z-axis in the direction of the normal to the surface. Then, according to White (1983) the interaction energy between two particles is given by

$$V(d) = \frac{2\pi}{\Lambda} \int_d^\infty W(h)\, \mathrm{d}h, \qquad [11]$$

where

$$\Lambda = \left[\left(\frac{1}{R_x^{(1)}} + \frac{1}{R_x^{(2)}} \right) \left(\frac{1}{R_y^{(1)}} + \frac{1}{R_y^{(2)}} \right) + \sin^2\phi \left(\frac{1}{R_x^{(1)}} - \frac{1}{R_y^{(1)}} \right) \left(\frac{1}{R_x^{(2)}} - \frac{1}{R_y^{(2)}} \right) \right]^{1/2}.$$

Here $R_i^{(\alpha)}$ denotes the principal radii of curvature of the particle surface at the point of minimum separation and ϕ is the angle between the principal axes of curvature of the two surfaces. Note that the particle shape only affects the coefficient of the interaction energy. The interaction energy

$W(h)$ is for a unit area on the surface of one halfspace interacting with the whole area on the surface of another halfspace, with h denoting the gap between the halfspaces. The Derjaguin approximation is valid for any type of interaction, whether attractive or repulsive, as long as the range of the interaction and the separation d is much less than the smallest radius of curvature of the system.

The corresponding force between the two particles is therefore

$$F(d) = -\frac{\partial V}{\partial d} = \frac{2\pi}{A} W(d). \qquad [12]$$

Thus, the interaction energy and the resulting force can be readily derived from $W(h)$. Expressions for $W(h)$ for van der Waals attractions and electric double-layer repulsions (Hogg *et al.* 1966) are given by

$$W_A(h) = -\frac{A}{12\pi h^2} \qquad [13]$$

and

$$W_R(h) = \frac{\epsilon\kappa}{8\pi}\left[(\psi^{(1)2} + \psi^{(2)2})(1 - \coth \kappa h) + \frac{2\psi^{(1)}\psi^{(2)}}{\sinh \kappa h}\right]. \qquad [14]$$

Here κ is the reciprocal of the Debye length, the characteristic thickness of the electric double layer.

Using [13] and [14], expressions for the total energy and the total colloidal force for colloidal interactions are given by

$$V_C(d) = \frac{3\pi\mu a^2 G}{N_F A}\left\{-\frac{a}{3d} + \frac{N_R}{2}\left[(1 + \Psi^2)\ln(1 - e^{-2\kappa d}) + c \ln\left(\frac{1 + e^{-\kappa d}}{1 - e^{-\kappa d}}\right)\right]\right\} \qquad [15]$$

and

$$F_C(d) = \frac{3\pi\mu a G}{N_F A}\left\{-\frac{a^2}{3d^2} + \frac{N_R \kappa a}{2}\left[(1 + \Psi^2)(1 - \coth \kappa d) + \frac{2\Psi}{\sinh \kappa d}\right]\right\}. \qquad [16]$$

Trajectory analysis

The motion of non-Brownian rigid particles is governed by Newton's laws of motion,

$$\mathbf{F}_H^{(\alpha)} + \mathbf{F}_C^{(\alpha)} = 0 \qquad [17a]$$

and

$$\mathbf{T}_H^{(\alpha)} + \mathbf{T}_C^{(\alpha)} = 0, \qquad [17b]$$

in which the subscripts H and C represent contributions from hydrodynamic and colloidal interactions, respectively. We neglect the rates of change of the linear and angular momenta of each particle ($\alpha = 1, 2$).

If V_C is the interaction energy of the two particles system, the generalized forces ($\mathbf{F}_C^{(\alpha)}$, $\mathbf{T}_C^{(\alpha)}$) on each particle can be obtained by differentiating V_C with respect to the generalized coordinates of the system, ($\mathbf{x}_C^{(1)}$, $\mathbf{x}_C^{(2)}$, $\boldsymbol{\theta}^{(1)}$, $\boldsymbol{\theta}^{(2)}$):

$$\mathbf{F}_C^{(\alpha)} = -\frac{\partial V_C}{\partial \mathbf{x}_C^{(\alpha)}} \qquad [18a]$$

and

$$\mathbf{T}_C^{(\alpha)} = -\frac{\partial V_C}{\partial \boldsymbol{\theta}^{(\alpha)}}. \qquad [18b]$$

Here $\boldsymbol{\theta}^{(\alpha)}$ denotes the orientation of each particle. Because of their anisotropic shape, the direction of $\mathbf{F}_C^{(\alpha)}$ between two nonspherical particles is not that of the center-to-center vector, $\mathbf{x}_C^{(1)} - \mathbf{x}_C^{(2)}$, but normal to the particle surfaces at the point of minimum separation. Also, nonspherical particles rotate as they attract or repel each other, in order for the interaction energy to be minimized.

If we assume that the steady hydrodynamic forces (and torques) at each instant of time, the translational and rotational velocities of both particles at each instant can be determined by

solving [7a, b]. We first calculate $\mathbf{F}_C^{(\alpha)}$ and $\mathbf{T}_C^{(\alpha)}$ using the DLVO theory described in the previous section. For $\mathbf{F}_C^{(\alpha)}$ we use the explicit expression [16], while for $\mathbf{T}_C^{(\alpha)}$ we use the centered difference form of [18b],

$$\frac{\partial V_C}{\partial \theta_i^{(\alpha)}} \simeq \left[\frac{V_C(\theta_i^{(\alpha)} + \Delta\theta) - V_C(\theta_i^{(\alpha)} - \Delta\theta)}{2\Delta\theta}\right].$$

We then specify the values for $P_i^{(\alpha)}$ and the antisymmetric part of $P_{ij}^{(\alpha)}$ using [6a, b] and [17a, b], and solve the least squares–collocation solutions of [7a, b] to obtain the translational and rotational velocities of both particles. Using the quasi-steady-states approximation, in which the velocities of both particles at each configuration are assumed to reach their steady-state values instantaneously [see Czarnecki (1985) and Dukhin & Lyklema (1987) on the applicability of the DLVO theory under dynamic conditions], we can determine the trajectory and orientation of each particle starting from any initial configuration.

As an illustration we consider the motion of two freely-moving oblate spheroids ($c/a = 0.4$) suspended in shear flow,

$$\mathbf{u}^\infty = (0, gz, 0).$$

In our example the following values are used for the DLVO interaction energy:

$$N_F = 20, \quad N_R = 60, \quad \kappa a = 20, \quad \Psi = 1.$$

With these values, the interaction–distance curve has a substantial energy barrier, and therefore, the colloidal suspension is stable. The trajectory of the center of mass and the orientation of each spheroid are shown in figures 3 and 4. Here the axes of revolution of both spheroids remain on the yz-plane throughout. We scale time and length with the shear rate G and the major semi-axis of the oblate spheroid, respectively. The initial orientations affect the trajectory of the center of mass because of the nonspherical shape. As two oblate spheroids approach one another in a shear flow, electric double-layer repulsions (and lubrication forces) force them across fluid streamlines. This phenomena is known as the secondary electroviscous effect of colloidal suspensions.

SUMMARY AND CONCLUSIONS

We have developed a boundary collocation method for the mobility problems for two spheroidal particles suspended in arbitrary Stokes flow. The method can be extended to other shapes for which a general solution which forms a complete basis set for Stokes flow is available.

The method was tested with several model problems in which analytical results were available. Reasonably accurate solutions were obtained with computational times much less than other boundary-integral methods, and we expect this to be a general conclusion for problems in which the shape of each particle fits a coordinate system possessing a convenient basis set. We also illustrate the combined use of the DLVO theory and hydrodynamics to study the trajectory of two disk-like particles in shear flow. We presented the case in which electric double-layer repulsions prevent the collision (and possible coagulation) of spheroids.

In order to study the stability condition of suspensions of spheroidal particles, we need to perform many trajectory calculations with different values for N_R and N_F [Zeichner & Schowalter

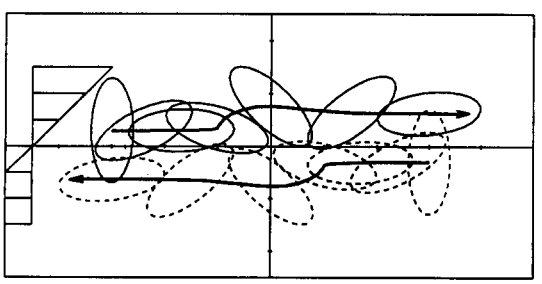

Figure 3. The motion of two oblate spheroids ($c/a = 0.4$) in a shear flow ($N_F = 20$, $N_R = 60$, $\kappa a = 20$, $\Psi = 1$).

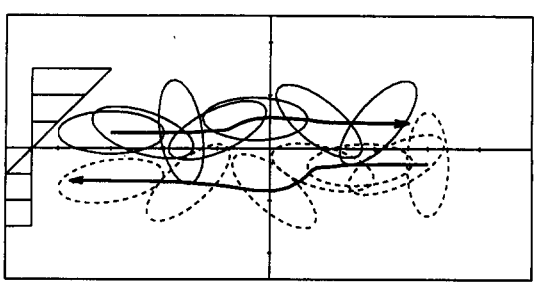

Figure 4. The motion of two oblate spheroids ($c/a = 0.4$) in a shear flow ($N_F = 20$, $N_R = 60$, $\kappa a = 20$, $\Psi = 1$).

(1977) for spheres]. For spherical particles this does not cause any difficulties, since all information on hydrodynamic interactions can be stored in three mobility functions (Batchelor & Green 1972) and these functions can be readily obtained to any desired accuracy in advance. For spheroidal particles, more variables are required to describe the configuration. Moreover, unlike the case of spheres, the "initial" orientation plays a role. Thus, a large number of trajectory calculations over the whole range of system parameters is needed in order to draw any conclusions regarding the average behavior of the suspension. Only the most efficient numerical scheme can be used for this purpose. At the same time the numerical scheme should be accurate, especially at the near-field where the outcome of an encounter between spheroids is mostly determined. This is indeed a difficult task for nonspherical particles, in general, and in this work we suggest the boundary collocation method as a promising candidate.

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