Yoon, H., and H. W. Blanch, "Competition for Double Growth Limiting Nutrients in Continuous Culture," *J. Appl. Chem. Biotech.*, **27**, 260 (1977).

Yoon, H., G. Klinzing and H. W. Blanch, "Competition for Mixed Substrates by Microbial Populations," *Biotech. Bioeng.*, **19**, 1193 (1977).

Manuscript received August 2, 1979; revision received November 2, and accepted December 10, 1979

Hindered Settling of a Suspension at Low Reynolds Number

C. C. REED and JOHN L. ANDERSON

Carnegie-Mellon University
Pittsburgh, Pennsylvania 15213

The purpose of this paper is to analyze how the settling velocity of a dispersion of spherical particles (that is, drops of arbitrary viscosity) depends on concentration. The procedure used entirely avoids the divergent integrals which previous workers in this field have been forced to deal with and yields explicit formulas for the sedimentation velocity. These formulas, accurate to first order in the particle volume fraction, depend on both the physical characteristics of the particles (size, buoyant density, viscosity ratio) as well as on any long range forces (for example, electrical double layer repulsions or van der Waals attraction) which may exist between particles. Sample calculations are given for globular proteins subject to double layer repulsions and for micron size colloids which experience van der Waals attractions in addition to the electrostatics. In the latter case, it is shown how the Hamaker constant can be extracted from sedimentation data. The analysis is extended to more concentrated suspensions by assuming that the hydrodynamic interactions among particles are pairwise additive; comparison with published data shows this analysis to be reasonably accurate, even for dense suspensions, without any adjustable parameters.

SCOPE

The question addressed in this paper is: How does the presence of other particles dispersed in a Newtonian fluid influence the settling velocity of a typical particle? The problem is to find α_{ij} of Equation (2) and then to extend the model to include higher-order concentration effects. By particle we mean a spherical drop of arbitrary viscosity that is sufficiently small to be in the Stokes flow regime ($Re << 1$). The driving force for the settling is an externally controlled body force due to, say, gravity or centrifugal acceleration. We begin the analysis by developing a virial expansion of the concentration effect and focus on the first-order coefficient which represents the summation of hydrodynamic interactions between pairs of particles. Evaluation of this coefficient is made possible by utilizing constraints on the suspension, such as incompressibility (zero volume flow), which have been recognized by Batchelor (1972) and others (for example, Pyun and Fixman, 1964) as necessary to use the velocity fields generated by particles in an unbounded fluid when computing the average hydrodynamic interactions between particles in a bounded fluid. The results of the first-order analysis for concentration effects in a polydisperse suspension [Equations (24) and (41)] clearly show how physical properties such as drop viscosity, density and size must be accounted for and, further, how important a factor the microscopic spatial distribution of particles is to the settling rate of the suspension. In our analysis this microscopic distribution is assumed to be controlled by local equilibria.

Although the virial expansion described in Appendix C represents a formal method to include C^2 and higher-order concentration effects, it is not useful at present because the n particle hydrodynamic problem is not completely solved for $n \geq 3$. Instead, we extend the analysis to more concentrated suspensions by assuming pairwise additivity of the hydrodynamic interactions and by preaveraging the interactions among all particles except the typical one (called the test particle). The hindered settling rate of the suspension is then determined by allowing the test particle to sample positions within the suspension without perturbing it. Published experimental data for the settling of dense suspensions are compared with the results of this model to test the accuracy of this reasonable, although still ad hoc, preaveraging step in the analysis.

CONCLUSIONS AND SIGNIFICANCE

The first-order hindrance coefficient α_{ij} [see Equation (2)] is given approximately by Equation (43) if all particles have the same density. Its value is greatest for rigid particles ($\lambda = 1.5$) and smallest for gas bubbles ($\lambda = 1.0$); larger neighbors ($a_j > a_i$) tend to hinder the settling of type i particles more than do smaller neighbors. Contrary to intuition, repulsive forces acting between particles, which cause greater average separations between particles than in the case of a uniform distribution, result in a greater hindrance to settling. This surprising result is explained by noting that at large separations a pair of settling particles experience more of each other's (retarding) backflow generated by the boundaries of the suspension,

---

C. C. Reed is at the Department of Applied Mathematics, Rochester Institute of Technology, Rochester, New York 14623.

0001-1541-80-3497-0816-$01.45.

whereas at close separations the pair pulls each other faster because of the solvent drag in the vicinity of each particle. Extension of our analysis to more concentrated monodisperse suspensions gives a relationship between settling velocity and particle concentration [Equation (54)] containing no adjustable parameters that agrees remarkably well with published data for suspensions of inert particles as dense as 40% by volume solids. We propose that this extension [Equation (50)], which only involves binary parameters, can be used to model the settling of dense polydisperse suspensions of viscous drops and rigid particles.

Relatively few theoretical models of hindered settling at low Reynolds number conditions have been published, and Batchelor (1972) reviews the subtle aspects of the more important works. Especially lucid is his discussion of the cell model (Happel and Brenner, 1965) and why it leads to the incorrect result predicting that the hindrance effect goes as the cube root of the particle volume fraction (ϕ). Batchelor derives the formulas necessary to compute the $0(\phi)$ hindrance effect for a monodisperse suspension of rigid spheres which are uniformly distributed at the microscopic scale; his numerical integrations give

$$<\underline{U}> = [1 - 6.55\phi + 0(\phi^2)]\, \underline{U}_0 \tag{1}$$

In this paper we derive definite integrals from which the linear coefficients α_{ij} are easily computed if one knows the appropriate physical parameters (density, size, pair potential) for the particles

$$<\underline{U}> = \left[1 + \sum_j \alpha_{ij}\phi_j\right] \underline{U}_{i0} \tag{2}$$

Equation (2) has an error of $0(\phi^2)$ associated with it. The procedure used in doing these calculations is based on a virial expansion of multiple particle effects, and it avoids the divergent integrals which previous workers have dealt with. Throughout this paper we assume that the local (microscopic) distribution of particles is unperturbed from its equilibrium state. In the first section, the statistical analysis for rigid particles is presented, and the results obtained here are then used in the second section to evaluate α_{ij} for various types of rigid particles. Some of these calculations emphasize the importance of the Debye-Hückel screening of interparticle electrostatics in aqueous systems. The above analysis can also be used in reverse; that is, measurements of first-order concentration effects on the settling rate at low Reynolds number can be used to derive microscopic information about particle interactions, as suggested by Goldstein and Zimm (1971). This application of the theory is illustrated in the second section. The third section deals with the settling of fluid drops, and the effect of drop viscosity on α_{ij} is examined. In this section we derive an approximate analytical expression for α_{ij} [Equation (43)] involving drop viscosity and size. Finally, we develop an extension of the analysis to suspensions of high concentration, the basis of which is an assumption of pairwise hydrodynamic interactions. Without any adjustable parameters, this model agrees very well with published data for the settling of dense monodisperse suspensions of rigid particles.

ANALYSIS: HINDERED SETTLING OF RIGID SPHERES AT LOW CONCENTRATIONS

The system consists of a dilute dispersion of N identical, rigid, spherical particles falling under the action of an external force through a bounded Newtonian fluid. Particle velocities are assumed low enough such that inertial effects are negligible. The macroscopic concentration of particles (C) is uniform and equal to N/V, and the container dimension $V^{1/3}$ is much larger than the particle radius (a); hence, the settling velocities should be independent of boundary configuration. In the analysis that follows, we introduce a test particle into the dispersion and ask how, on the average, the sedimentation velocity of this test particle is affected by the presence of the N original particles which we shall henceforth refer to as neighbors. The test particle need not be of the same type as the N neighbors; for instance, its radius (a_t) and density (ρ_t) may be different. It is this arbitrary nature of the test particle that allows us to obtain results applicable to one and multicomponent dispersions almost simultaneously.

There are two essential physical concepts which underlie the analysis. The first is the diluteness of the dispersion as measured by the volume fraction ϕ of the N neighbors. If $\phi << 1$, then the influence of the neighbors on the test particle can be added in a hierarchy of two-body (test particle plus one neighbor), three-body (test particle plus two neighbors), etc., interactions, as shown in Appendix C. Since the two-body interactions produce a correction of $0(\phi)$, three-body interactions produce a correction of $0(\phi^2)$, etc., a virial expansion results for the effect of the N neighbors on the mean sedimentation velocity ($<\underline{U}_t>$) of the test particle:

$$<\underline{U}_t> = [1 + \alpha\phi + \beta\phi^2 + \ldots]\, \underline{U}_{t0} \tag{3}$$

The brackets around $\underline{U}_t$ means that an average has been taken over many placements of the test particle at arbitrary positions within the dispersion; such an average over essentially an infinite number of realizations of the system is called an ensemble average and should produce the result detectable by a macroscopic observer, as long as the actual number of test particles in the system is large enough so that statistical deviations from the ensemble averaged velocity are negligible. Implicit in ensemble averages is an assumption of local equilibrium in the microscopic distribution of particles, independent of how the dispersion was initially formed. This assumption demands that the particles exhibit some Brownian motion, and the criterion for its validity is examined in Appendix B.

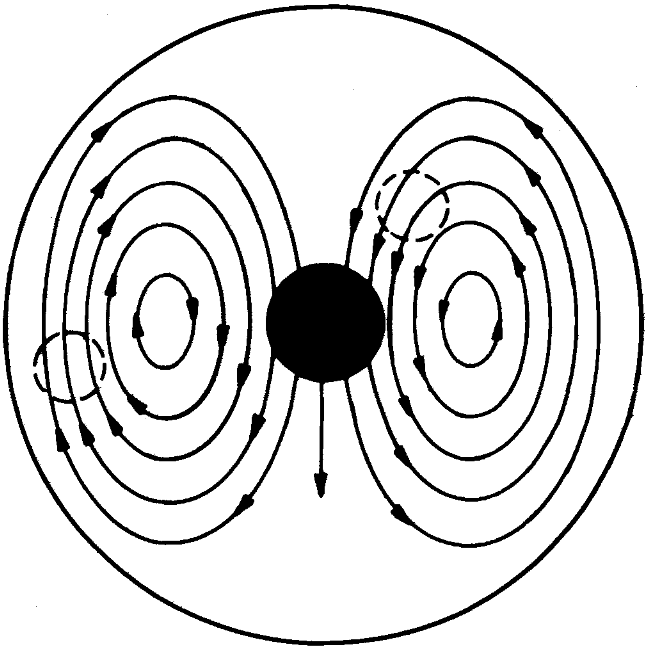

Figure 1. Fluid streamlines for particle motion in a bounded system. When a test particle (dashed circle) is near a neighbor, it experiences the neighbor's downflow and settles more rapidly. When it is far from the neighbor, it feels the neighbor's backflow (caused by the container walls) and settles more slowly.

The second important physical concept is backflow, which occurs in a bounded fluid but not in an unbounded fluid. A moving particle drags some fluid near its surface with it, and in a bounded system this downflow of particle plus fluid must be compensated for by a reverse flow of fluid elsewhere in the container, as illustrated in Figure 1. This figure demonstrates an important facet of hydrodynamic interactions in bounded fluids, namely, that the microscopic distribution among particles couples to the hydrodynamic interaction. For example, if two particles are, on the average, close to one another, then they will each be caught in the other's downflow and hence will settle faster than if each were to fall by itself in an unbounded fluid. Conversely, a bias toward large separations, perhaps resulting from a mutual repulsion between the particles, results in a hindered sedimentation, since each particle sees the other's backflow most of the time. The importance of the container boundary, therefore, is indirect in that it creates this backflow condition.

The position at which the test particle is introduced in the dispersion is denoted by $\underline{x}$, and the relative position of each of the N original particles is $\underline{r}_j = \underline{R}_j - \underline{x}$. The configuration of the dispersion is described by the set of relative position vectors $\underline{\xi}_N = (\underline{r}_1, \underline{r}_2, \ldots \underline{r}_N)$, meaning that particle number 1 is at $\underline{r}_1$ from the test particle, particle 2 is at $\underline{r}_2$, etc.; thus, each particle is distinctly labeled, but all N of them are identical physically. $\underline{U}_t(\underline{\xi}_N)$ is the velocity of the test particle in the presence of a given configuration of neighbors, and $P(\underline{\xi}_N|\underline{x})$ is the probability density of that configuration, given the presence of a test particle at $\underline{x}$. The normalization for the probability density function is

$$\int_V P(\underline{\xi}_N|\underline{x})\, d\underline{\xi}_N = 1 \tag{4}$$

where $d\underline{\xi}_N$ represents the product of N volume differentials $d\underline{r}_1\, d\underline{r}_2 \ldots d\underline{r}_N$, and the integral sign in (4) actually means N such integrals over the container volume V. The ensemble average velocity of the test particle is

$$<\underline{U}_t> = \int_V \underline{U}_t(\underline{\xi}_N)\, P(\underline{\xi}_N|\underline{x})\, d\underline{\xi}_N \tag{5}$$

The above integral cannot be evaluated directly, but a cluster expansion technique (Appendix C) can be used to arrive at a virial expression such as Equation (3). If we are concerned only with terms up to $0(C)$, the appropriate expansion is

$$<\underline{U}_t> = \underline{U}_{t0} + C \int_V \underline{\Delta}_1(\underline{r})\, g^{(2)}(\underline{r})\, d\underline{r} + 0(C^2) \tag{6}$$

where $\underline{U}_{t0}$ is the test particle velocity in the absence of the other N particles and is given by Stokes law

$$\underline{U}_{t0} = (6\pi\mu a_t)^{-1}\, \underline{F}_t \tag{7}$$

$g^{(2)}(\underline{r})$ is the two-particle (radial) distribution function; the product $C\, g^{(2)}(\underline{r})d\underline{r}$ is the probability of finding any of the N neighbors in the volume element $d\underline{r}$ located at $\underline{r}$, given a test particle at the origin. $\underline{\Delta}_1$ is the perturbation to the velocity of the test particle when one and only one neighbor is at $\underline{r}$:

$$\underline{\Delta}_1 = \underline{U}_t(\underline{r}) - \underline{U}_{t0} \tag{8}$$

Essentially, then, Equation (6) says that the effect of all N neighbors on the test particle can be calculated by summing all binary interactions independently, without including the interactions among the neighbors themselves (see final section), if only a correction to $0(C)$ is desired.

The next step would seem to be substitution of Equation (8) into (6), but a problem arises in that $\underline{U}_t(\underline{r})$ is not known for two particles falling in a bounded fluid. That is, $\underline{U}_t(\underline{r})$ is practically equal to the velocity of the test particle in an unbounded fluid for small values of $r \sim 0(a)$, but the range of integration in (6) is over the entire fluid volume. Also, far from the test particle, the backflow generated by the presence of the container walls is inmportant. In other words, it is physically incorrect to assume that $[\underline{U}_t(\underline{r})]_{\text{bounded}} = [\underline{U}_t(\underline{r})]_{\text{unbounded}}$ over the entire range of test particle-neighbor separation, and it is precisely this assmption which gives rise to the divergent integrals encountered by previous investigators. To overcome this difficulty, we follow Batchelor's advice and add zero to $\underline{\Delta}_1$ in a physically meaningful way:

$$\underline{\Delta}_1 = \underline{v}(\underline{0}, \underline{r}) + \frac{a_t^2}{6}[\nabla_x^2 \underline{v}]_{\underline{x}=\underline{0}} + \underline{W}(\underline{0}, \underline{r}) \tag{9}$$

where

$$\underline{W}(\underline{0}, \underline{r}) \equiv \underline{U}_t(\underline{r}) - \underline{U}_{t0} - \underline{v}(\underline{0}, \underline{r}) - \frac{a_t^2}{6}[\nabla_x^2 \underline{v}]_{\underline{x}=\underline{0}} \tag{10}$$

Here $\underline{v}(\underline{x}, \underline{R})$ is the velocity at $\underline{x}$ which would be produced by the settling of a single neighbor, located at $\underline{R}$ in the bounded fluid, if the test particle and the other $N - 1$ neighbors were not present. The ∇_x^2 operator refers to the coordinate $\underline{x}$ describing the location of the test particle, which is arbitrary because all positions are equal in an average sense, except those regions adjacent to the boundaries (the volume of these regions contributes negligibly to the total system volume). From now on we consider $\underline{x}$ to be the origin $(\underline{0})$ of the coordinate system. Substituting (9) into (6), we get

$$<\underline{U}_t> = \underline{U}_{t0} + C\left\{\int_V \underline{v}(\underline{0}, \underline{r})\, g^{(2)}(\underline{r})d\underline{r} + \frac{a_t^2}{6}\int_V [\nabla_x^2 \underline{v}]_{\underline{x}=0}\, g^{(2)}(\underline{r})d\underline{r} + \int_V \underline{W}(\underline{0}, \underline{r})\, g^{(2)}(\underline{r})d\underline{r}\right\} + 0(C^2) \tag{11}$$

The first integral on the right side of (11) is evaluated by realizing that the mean velocity at any point $(\underline{x} = \underline{0})$ in a bounded fluid must be zero:

$$\int_V \underline{v}(\underline{0}, \underline{r})d\underline{r} = \underline{0} \tag{12}$$

This constraint allows the first integral in (11) to be written as

$$\int_V \underline{v}(\underline{0}, \underline{r})\, [g^{(2)}(\underline{r}) - 1]\, d\underline{r} = \int_V \underline{v}_\infty(\underline{r}, \underline{0})\, [g^{(2)}(\underline{r}) - 1]\, d\underline{r} \tag{13}$$

where two important changes have been made. First, the velocity field $\underline{v}_\infty$ generated by a particle in an unbounded fluid was substituted for the velocity field $\underline{v}$ in a bounded fluid because $[g^{(2)}(\underline{r}) - 1]$ converges rapidly to zero for $r >> 0(a)$, and the local velocity field in the vicinity of the moving particle is unperturbed by the presence of the container boundaries. Second, the integration variable was switched to the coordinate describing the location of the test particle, a valid change because $\underline{v}_\infty$ is an even function of the position $\underline{r}$.

To evaluate the second integral in (11), we use the following constraint, valid for a rigid particle, which is proved in Appendix A:

$$\int_{r>a} [\nabla_x^2 \underline{v}]_{x=0}\, d\underline{r} = 4\pi a \underline{U}_0 \tag{14}$$

$\underline{U}_0$ is the unhindered settling velocity of the single neighbor given by Stokes' law

$$\underline{U}_0 = (6\pi\mu a)^{-1}\, \underline{F} \tag{15}$$

The second integral can thus be written as

$$\frac{2}{3}\pi a_t^2 a \underline{U}_0 + \frac{a_t^2}{6}\int_{r>a} \nabla^2 \underline{v}_\infty(\underline{r}, \underline{0})\, [g^{(2)}(\underline{r}) - 1]\, d\underline{r} \tag{16}$$

where, again, the unbounded fluid velocity field was substituted for the bounded one because of the convergence of $g^{(2)}$ to unity, and the integration variable was changed to the coordinate describing the position of the test particle. The integration over $r < a$ is zero because $g^{(2)}(\underline{r})$ is zero in this region. The third integral in (11) is computed directly because $\underline{W}$ goes as r^{-4} for $r >> 0(a)$, and hence its value in an unbounded fluid $(\underline{W}_\infty)$ can be substituted with negligible error in the vicinity of the test particle; $\underline{W}_\infty$ is calculated from Equation (10) using the values of $\underline{U}_t$ and $\underline{v}$ for an unbounded fluid.

To evaluate the above integrals, the radial distribution function describing the two-particle configurational probability must be known. If the local conditions about a test particle can be assumed to be at an equilibrium state, then the Boltzmann expression is sufficient to describe the distribution with an error of only $0(C)$ (Hill, 1956; Reed and Gubbins, 1973):

$$\begin{aligned} r \le 2a: &\quad g^{(2)} = 0 \\ r > 2a: &\quad g^{(2)} = \exp\left[-E(r)/kT\right] \end{aligned} \tag{17}$$

The conditions under which the assumption of local equilibrium is valid are examined in Appendix B. The hydrodynamic distortion of the equilibrium two-particle distribution function produces an effect of $0(\gamma^2)$ on the interaction coefficient α, where γ is the distortion parameter defined by Equation (B7). If the physical conditions of the system are such that $|\gamma| < 1$, then the dynamics of the sedimentation process should have a negligible effect on the interaction coefficient. If the test particle and neighbor are the same type (a one-component system), there is no distortion ($\gamma = 0$), and the local equilibrium assmption of Equation (17) is exact in the steady state.

After substituting Equations (13), (16) and (17) into (11) and subsequently rearranging the range of integrations, one obtains

$$\begin{aligned} <\underline{U}> = \underline{U}_{t0} + C \Bigg\{ &- \int_{r<\sigma} \underline{v}_\infty(\underline{r}, \underline{0})\, d\underline{r} + \frac{2}{3}\pi a_t^2 a \underline{U}_0 \\ &- \frac{a_t^2}{6} \int_{a<r<\sigma} \nabla^2 \underline{v}_\infty(\underline{r}, \underline{0})\, d\underline{r} + \int_{r>\sigma} \underline{W}_\infty(\underline{r}, \underline{0})\, d\underline{r}, \\ &+ \int_{r>\sigma} \left[\underline{v}_\infty(\underline{r}, \underline{0}) + \frac{a_t^2}{6} \nabla^2 \underline{v}_\infty(\underline{r}, \underline{0}) + \underline{W}_\infty(\underline{r}, \underline{0})\right] \\ &\left[\exp\left(-E(r)/kT\right) - 1\right] d\underline{r} \Bigg\} + 0(C^2) \end{aligned} \tag{18}$$

where $\sigma \equiv a_t + a$, the closest possible distance between a neighbor and the test particle. The first four expressions between the brackets depend only on the physical characteristics of the system (particle size and density), while the final integral also depends on the physico-chemical interactions $[E(r)]$ between particles.

Evaluation of the Unbounded Velocity Fields

A single rigid particle (neighbor) of radius a which translates without rotation at $\underline{U}_0$ in an unbounded fluid, when no other particles are present, generates the following velocity field at position $\underline{r}$ from its center (Batchelor, 1967):

$$\begin{aligned} r < a: &\quad \underline{v}_\infty = \underline{U}_0 \\ r > a: &\quad \underline{v}_\infty = \left[\frac{3}{4}\left(\frac{a}{r}\right) + \frac{1}{4}\left(\frac{a}{r}\right)^3\right]\underline{U}_0 \\ &\quad + \left[\frac{3}{4}\left(\frac{a}{r}\right) - \frac{3}{4}\left(\frac{a}{r}\right)^3\right] \underline{e}\,\underline{e} \cdot \underline{U}_0 \end{aligned} \tag{19}$$

The Laplacian of this field can be expressed as

$$\begin{aligned} r < a: &\quad \nabla^2 \underline{v}_\infty = 0 \\ r > a: &\quad \nabla^2 \underline{v}_\infty = \frac{3}{2}\left(\frac{a}{r^3}\right)\left[\underline{\underline{I}} - 3\underline{e}\,\underline{e}\right] \cdot \underline{U}_0 \end{aligned} \tag{20}$$

where $\underline{e} = \underline{r}/r$, the unit vector pointing radially from the center of the particle. The velocity of a test particle whose center is at $\underline{r}$, when a single neighbor is at $\underline{0}$, can be expressed in terms of a linear combination of the forces acting on each particle:

$$\underline{U}_{t\infty}(\underline{r}) = \underline{\underline{A}} \cdot \underline{U}_{t0} + \underline{\underline{B}} \cdot \underline{U}_0 \tag{21}$$

$\underline{U}_{t0}$ and $\underline{U}_0$ are related through the Stokes equation to the forces acting on each of the two particles. The symmetry about the line of centers ($\underline{e}$) allows the mobility dyadics to be expressed as follows (Batchelor, 1976):

$$\underline{\underline{A}} = A_\parallel(r)\underline{e}\,\underline{e} + A_\perp(r)\left[\underline{\underline{I}} - \underline{e}\,\underline{e}\right] \tag{22a}$$

$$\underline{\underline{B}} = B_\parallel(r)\underline{e}\,\underline{e} + B_\perp(r)\left[\underline{\underline{I}} - \underline{e}\,\underline{e}\right] \tag{22b}$$

Using the above relations, some of the integrals in (18) can be fully evaluated. Furthermore, in the remaining integrals, the angular integrations can be performed. A change of integration variable from r to $\omega \equiv (a + a_t)/r$ transforms the infinite range to a finite one. Finally, we assume that the external force acting on each particle is proportional to its buoyant mass:

$$\underline{F}_t = \frac{4}{3}\pi a_t^3 \Delta\rho_t \underline{b} \tag{23a}$$

$$\underline{F} = \frac{4}{3}\pi a^3 \Delta\rho\, \underline{b} \tag{23b}$$

By combining Equations (7) and (15) with (23), and then substituting (19) to (22) into (18), we obtain

TABLE 1. VALUES OF $-[(A_\parallel + 2A_\perp - 3)\omega^{-4}]$

ω a_j/a_i =	0.25	0.50	1.00	2.00	4.00
0	0.0240	0.0926	0.234	0.370	0.384
0.1	0.0136	0.0984	0.234	0.400	0.374
0.2	0.0126	0.0971	0.232	0.416	0.375
0.3	0.0138	0.0922	0.228	0.420	0.384
0.4	0.0147	0.0854	0.223	0.419	0.407
0.5	0.0151	0.0781	0.219	0.451	0.444
0.6	0.0151	0.0703	0.215	0.415	0.504
0.7	0.0146	0.0642	0.213	0.431	0.566
0.8	0.0139	0.0616	0.216	0.471	0.642
0.9	0.0152	0.0675	0.232	0.528	0.751
1.0	0.0228	0.102	0.443	0.790	1.30

NOTE: $\omega \equiv \dfrac{a_i + a_j}{r}$

Subscript j corresponds to the neighbor particle, i to the test particle. Particles are rigid. These values were taken from calculations by Cooley and O'Neill (1969*a*, 1969*b*) and by O'Neill and Majumdar (1970). The following asymptotic formula is valid as $\omega \to 0$ (Batchelor, 1976):

$$[(A_\parallel + 2A_\perp - 3)\omega^{-4}] = \frac{-(15/4)}{(a_j/a_i)(1 + a_i/a_j)^4} + 0(\omega^2)$$

TABLE 2. VALUES OF $[(B_\parallel + 2B_\perp - 3\omega/(1 + a_i/a_j))\omega^{-4}]$

ω a_j/a_i =	0.25	0.50	1.00	2.00	4.00
0	—	—	—	—	—
0.1	—	—	—	—	—
0.2	—	—	—	—	—
0.3	—	—	—	—	—
0.4	—	−0.04	0.08	—	—
0.5	0.02	−0.05	0.05	—	—
0.6	−0.02	0.02	0.05	—	—
0.7	−0.02	0.02	0.04	0.02	—
0.8	−0.02	0.04	0.06	0.04	—
0.9	0.01	0.05	0.10	0.09	0.05
1.0	0.05	0.12	0.21	0.25	0.21

NOTE: $\omega = \dfrac{a_i + a_j}{r}$

Subscript j corresponds to the neighbor particle, i to the test particle. Particles are rigid. These values were taken from the calculations by Cooley and O'Neill (1969*a*, 1969*b*) and by Spielman (1970). The — in any column means that the accuracy of the literature calculations was not sufficient to give a reasonable number (significant figures were lost on previous calculations). These values are probably very close to zero. The following asymptotic formula is valid as $\omega \to 0$ (Batchelor, 1976):

$$\left[\left(B_\parallel + 2B_\perp - \frac{3\omega}{1 + a_i/a_j}\right)\omega^{-4}\right] = 0(\omega^3) = K\,\omega^3$$

The list below gives the average of K at $\omega = 0.9$ and $\omega = 1.0$ using the above table:

a_j/a_i	K
0.25	0.03
0.50	0.09
1.00	0.17
2.00	0.19
3.00	0.14

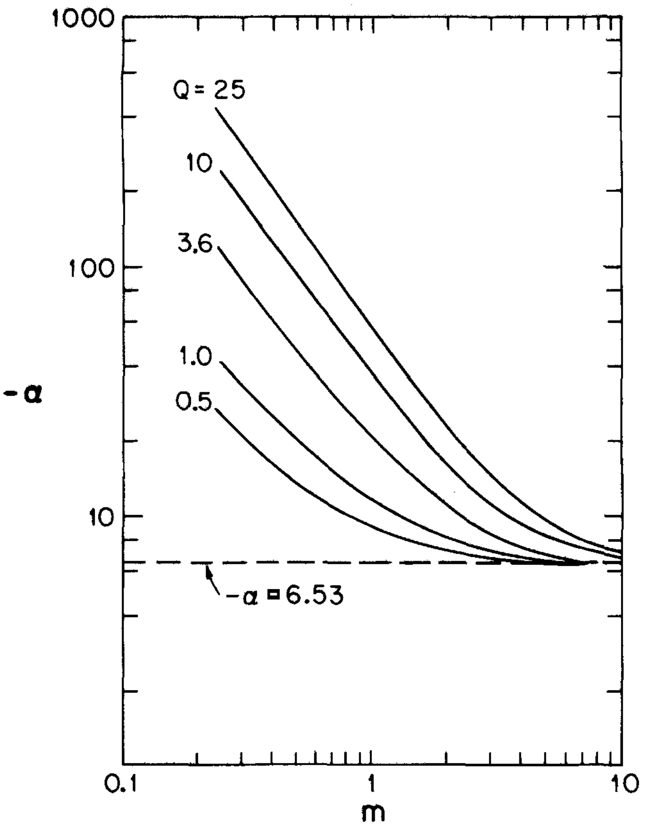

Figure 2. First-order hindrance coefficient for small charged particles of radius a whose pair potential is given by Equation (27).

$$<\underline{U}_t> = [1 + \alpha\phi]\,\underline{U}_{t0} \tag{24a}$$

$$\begin{aligned}\alpha = &- \left[1 + 3\left(\frac{a}{a_t}\right) + \left(\frac{a}{a_t}\right)^2\right]\frac{\Delta\rho}{\Delta\rho_t}\\ &+ \left(1 + \frac{a_t}{a}\right)^3 \int_0^1 \left\{[A_\parallel + 2A_\perp - 3] + \left(\frac{\Delta\rho}{\Delta\rho_t}\right)\right.\\ &\left.\left(\frac{a}{a_t}\right)^2 \left[B_\parallel + 2B_\perp - \frac{3\omega}{(1 + a_t/a)}\right]\right\} \omega^{-4}\, d\omega\\ &+ \left(1 + \frac{a_t}{a}\right)^3 \int_0^1 \left\{[A_\parallel + 2A_\perp - 3] + \left(\frac{\Delta\rho}{\Delta\rho_t}\right)\right.\\ &\left.\left(\frac{a}{a_t}\right)^2 [B_\parallel + 2B_\perp]\right\} [\exp(-E/kT) - 1]\, \omega^{-4}\, d\omega\end{aligned} \tag{24b}$$

Because we have allowed the test particle to be arbitrary in its size and density, the above relationship is really the desired multicomponent result to be used in Equation (2). The coefficients α_{ij} are thus given by (24*b*) if one understands that the subscript j corresponds to the neighbor (unsubscripted in the above analysis), while i corresponds to the test particle (subscripted t in the above analysis). Values of the hydrodynamic interaction parameters $A_\parallel$, $A_\perp$, $B_\parallel$ and $B_\perp$ as a function of the two-particle separation were obtained from the literature and are listed in Tables 1 and 2. Given the buoyant density and diameter ratios for type i and j particles, as well as the interaction energy (E), one can numerically compute the integrals in (24*b*) necessary to evaluate α_{ij}. Becuase there is some uncertainty in Table 2, it seems prudent to use Batchelor's (1976) asymptotic relation:

$$\left[B_\parallel + 2B_\perp - \frac{3\omega}{1 + a_i/a_j}\right]\omega^{-4} = K\,\omega^3 \text{ as } \omega \to 0 \tag{25}$$

Here the constant K is evaluated by averaging the numerical results for the left-hand side of (25) at $\omega = 0.9$ and 1.0, and (25) is used over the full range of ω. Values of K are listed at the bottom of Table 2.

RESULTS: RIGID PARTICLES

Numerical integrations of the terms in (24*b*) were performed to obtain the coefficient α_{ij} appearing in (2). Because of a loss in significant figures when computing the hydrodynamic parameters appearing in Tables 1 and 2 from the appropriate literature calculations, there is an uncertainty in the α_{ij} values reported here of about ± .05. Equation (25) was used in lieu of the uncertain parameters in Table 2.

We first consider a suspension of particles which only interact by a hard sphere potential; that is, there is no long range energy ($E = 0$), and the dispersion is uniform on a microscopic scale for $r > \sigma_{ij}$. In this case, the last integral in (24*b*) contributes nothing to the settling rate. For a one-component system (that is, only one type of particle), the only coefficient of interest is α_{ii} which we compute to be -6.53. This agrees with Batchelor's determination shown in Equation (1).

The coupling between the long range pair potential energy, which controls the microscopic distribution, and hydrodynamic interactions occurs in the final integral of (24*b*). If particles repel one another ($E > 0$), then on the average they see each other's backflow, and α_{ii} is more negative than -6.53 (that is, the hindrance is greater). On the other hand, an attractive potential ($E < 0$) causes a pseudo pairing in which the particles are, more often than not, experiencing the downflow produced by each other. For a one-component system we use the hydrodynamic parameters calculated by Goldman et al. (1966) for the average velocity of a pair of identical rigid spheres falling through a quiescent, unbounded fluid; their calculations are well fit by the folowing polynomial:

$$\mathcal{K} \equiv [A_\parallel + 2A_\perp - 3] + [B_\parallel + 2B_\perp] = 1.4861\,\omega + 0.08823\,\omega^2 - 0.21110\,\omega^3 \tag{26a}$$

so that

$$\alpha_{ii} = -6.53 + 8\int_0^1 \mathcal{K}\,[\exp(E/kT) - 1]\,\omega^{-4}\,d\omega \tag{26b}$$

In Figure 2 are plotted values of α_{ii} computed from (26) assuming an electrostatic repulsion between particles given by

$$\frac{E}{kT} = \frac{Q}{\left(1 + \frac{m}{2}\right)^2}\,\frac{\exp[-ms]}{1 + s} \tag{27}$$

where

$$m = 2\kappa a, \qquad Q = \frac{(qe)^2}{2a\epsilon kT}, \qquad s \equiv \omega^{-1} - 1$$

This potential represents double layer interactions of charged spheres when the Debye length parameter (κ^{-1}) is of order the sphere radius (Stitger and Hill, 1959). We have chosen values of Q and m that would be reasonable for a globular protein such as serum albumin ($a \approx 3.6$ nm, $Q = .1\,q^2$, where q is the net charge number of the molecule) in aqueous solution ($m = 24\sqrt{I_S}$, where I_S is the ionic strength in units of kg mole · m^{-3}). This figure clearly shows that the reduction of settling velocity is substantial when $m \leq 2$. Electroviscous effects on the particle mobilities have been neglected in our calculations, and although these are usually small, they may introduce a non-negligible correction when $m < 1$. To our knowledge there exist no analyses of electroviscous effects on two-particle hydrodynamic interactions.

Our calculations of the hindrance factor for a one-component dispersion of colloidal particles are shown in Figure 3. The pair potential in this case was assumed to be due to electrostatic repulsion (E_R) and van der Waals attraction (E_A):

$$E = E_R + E_A \tag{28}$$

The expression for E_R was derived by Hogg et al. (1966) using the diffuse double layer model and assuming large values of m:

$$E_R = \frac{\epsilon a \psi_0^2}{2} \ln\left[1 + \exp(-ms)\right] \qquad (29)$$

where

$$\psi_0 = \frac{2kT}{e} \sinh^{-1}\left[\frac{2\pi e \kappa^{-1}\sigma_0}{\epsilon kT}\right]$$

The attractive potential between two identical spheres resulting from dispersion interactions (neglecting retardation effects) can be expressed as

$$E_A = \frac{-H}{12}\left\{(s^2 + 2s)^{-1} + (s^2 + 2s + 1)^{-1} + 2\ln\left[\frac{(s^2 + 2s)}{(s^2 + 2s + 1)}\right]\right\} \qquad (30)$$

where H is the Hamaker constant (Hamaker, 1937). Thus, the free parameters in the pair potential are the Hamaker constant (H), the Debye parameter (κ), the particle radius (a) and the surface charge (σ_0).

The curves in Figure 3 were computed specifically for particles 0.26 μm in radius, $\sigma_0 = 0.05$ Coul/m^2 (typical of stabilized latexes, see van den Hull and Vanderhoff, 1970), in aqueous solution at 25°C. The solution ionic strength is denoted by I_S, and for these solutions $\kappa = 3.3\sqrt{I_S}$, where κ is expressed as nm^{-1} and I_S as kg mol · m^{-3}. Because $E_A \rightarrow -\infty$ as $s \rightarrow 0$, a Born repulsion barrier 0.5 nm thick was included to prevent contact:

$$E \rightarrow +\infty \quad \text{for} \quad s < 0.00096$$

Some calculations were performed with a 0.75 nm Born barrier, and they agree closely with the corresponding calculations using a 0.5 nm barrier, indicating the arbitrariness of this parameter is not too significant. As Figure 3 shows, we predict $H \sim 4 \times 10^{-21}$J for the polystyrene latexes used in the experiments by Cheng and Schachman (1955), in agreement with the similar calculations of Goldstein and Zimm (1971). This value of the Hamaker constant is in fair agreement with those values determined by thermodynamic or static means. Perhaps the measurement of hindered settling rates will find application to the determination of pair potential parameters for macromolecular and colloidal systems.

Given the pair potential as well as the ratio of diameter and buoyant densities, one can easily compute the multicomponent hindrance coefficient α_{ij} using Equations (24) and (25) and Tables 1 and 2. We have done this for purely hard sphere potentials ($E_{ij} = 0$ to study the effect of size and density differences, and the results are listed in Table 3. As both $\Delta\rho_j/\Delta\rho_i$ and a_j/a_i increase, so does the degree of hindrance. The density effect is a direct result of the increased velocity of the neighbor. On the other hand, the size effect is the result of two opposite influences as observed in Equation (24*b*). The first term on the right side of this equation, which represents the influence of backflow retarding the settling of the test particles, goes as $(a_j/a_i)^2$ as one would expect for a straight velocity effect ($U_{j0} \sim a_j^2$), while the second term goes as $(a_i/a_j)^3$. The net numerical effect of these two opposing influences is that the magnitude of α_{ij} increases with a_j/a_i. Following the lower left to upper right diagonals of Table 3, one sees that a doubling of a_j/a_i or $\Delta\rho_j/\alpha\Delta\rho_i$ has an equivalent effect on α_{ij}.

HINDERED SETTLING OF FLUID DROPS

The approach used to evaluate the hindrance parameter α_{ij} for a suspension of drops follows essentially the same line of reasoning as for rigid particles. The drops are assumed to be small enough so that interfacial tension maintains their spherical shape; it is also assumed that there is no coalescence, and Marangoni stresses are not important. Low Reynolds number conditions prevail, and hence inertial terms are neglected.

An important hydrodynamic parameter is

$$\lambda \equiv \frac{1 + (3/2)(\overline{\mu}/\mu)}{1 + \overline{\mu}/\mu} \qquad (31)$$

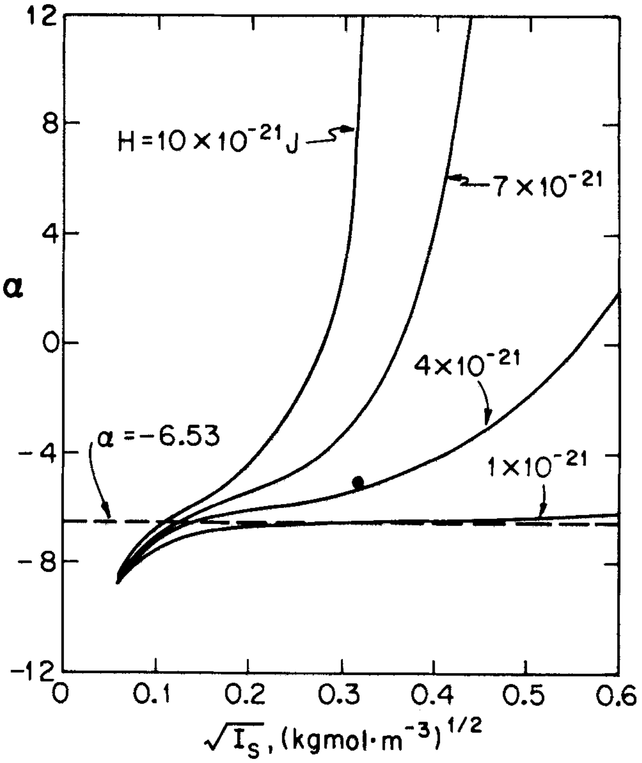

Figure 3. First-order hindrance coefficient for particles of radius 0.26μm and surface charge density 0.05 Coul/m^2 in water at 25 deg. The pair potential is given by Equations (28) to (30) with a Born barrier of 5 Å. The filled circle is the experimental result of Cheng and Schachman (1955), $\alpha = -5.06$.

A rigid sphere has $\lambda = 3/2$, while for a gas bubble $\lambda = 1$. If $r >> 0(a)$, then the additional velocity of a test drop placed at $\underline{x} = \underline{0}$ induced by a neighbor at $\underline{r}$ is calculated by the analogue of Faxen's law derived for drops by Hetsroni et al. (1971). This additional velocity is

$$\underline{v}(\underline{0}, \underline{r}) + \frac{a_t^2(\lambda - 1)}{2\lambda}\left[\nabla_x^2 \underline{v}(\underline{x}, \underline{r})\right]_{\underline{x}=\underline{0}} \qquad (32)$$

Thus, $\underline{\Delta}_1$ of Equation (6) is again given by (9) and (10) except that the prefactor of the $\nabla_x^2\underline{v}$ terms is $a_t^2(\lambda - 1)/2\lambda$ instead of $a_t^2/6$. The same arguments developed between Equations (11) to (18) are utilized, except that (14) and (15) are replaced by the following (see Appendix A):

$$\int_{r>a} [\nabla_x^2 \underline{v}(\underline{x}, \underline{r})_{\underline{x}=\underline{0}}\, d\underline{r} = \frac{8}{3}\pi a \lambda\, \underline{U}_0 \qquad (A8)$$

$$\underline{U}_0 = (4\pi\mu a\lambda)^{-1}\, \underline{F} \qquad (33)$$

The analogue to (18) becomes

$$<\underline{U}_t> = \underline{U}_{t0} + C\left\{-\int_{r<\sigma} \underline{v}_\infty(\underline{r}, \underline{0})d\underline{r} + \frac{4}{3}\pi a_t^2 a(\lambda - 1)\underline{U}_0 - \frac{a_t^2(\lambda - 1)}{2\lambda}\int_{a<r<\sigma} \nabla^2 \underline{v}_\infty(\underline{r}, \underline{0})d\underline{r} + \int_{r>\sigma} \underline{W}_\infty(\underline{r}, \underline{0})d\underline{r}\right.$$

TABLE 3. VALUES OF α_{ij}[SEE EQUATION (2)]*

a_j/a_i	$(\Delta\rho_j/\Delta\rho_i) \rightarrow$ 0.25	0.50	1.00	2.0	4.0
0.25	−2.31	−2.76	−3.62	−5.38	−8.88
0.50	−2.83	−3.48	−4.78	−7.38	−12.6
1.00	−3.02	−4.18	−6.53	−11.2	−20.5
2.0	−4.11	−6.70	−11.9	−22.2	−43.0
4.0	−8.00	−15.0	−28.9	−56.8	−113.

---

* Purely hard sphere particle interactions ($E_{ij} = 0$). Particles are rigid.

$$+ \int_{r>\sigma} \left[\underline{v}_\infty(\underline{r}, \underline{0}) + \frac{a_t^2(\lambda - 1)}{2\lambda} \nabla^2 \underline{v}_\infty(\underline{r}, \underline{0}) + \underline{W}_\infty(\underline{r}, \underline{0}) \right] [\exp(- E(r)/kT) - 1] \, d\underline{r} \Big\} + 0(C^2) \qquad (34)$$

where $\underline{W}_\infty$ is given by (10) when the unbounded velocities are used, but the prefactor before the $[\nabla_x^2 \underline{v}]_{\underline{x}=\underline{0}}$ term is $a_t^2(\lambda - 1)/2\lambda$.

The external velocity field at $\underline{r}$ in the continuous fluid ($r > a$) generated by a drop of radius a and internal viscosity $\bar{\mu}$, which is located at $\underline{0}$ and translating at the steady velocity $\underline{U}_0$ given by (33), is conveniently expressed as (Batchelor, 1967)

$$\underline{v}_\infty = \left[\frac{\lambda}{2} \left(\frac{a}{r} \right) + \frac{1}{2} (\lambda - 1) \left(\frac{a}{r} \right)^3 \right] \underline{U}_0 + \left[\frac{\lambda}{2} \left(\frac{a}{r} \right) - \frac{3}{2} (\lambda - 1) \left(\frac{a}{r} \right)^3 \right] \underline{e} \; \underline{e} \cdot \underline{U}_0 \qquad (35)$$

$$\nabla^2 \underline{v}_\infty = \frac{\lambda a}{r^3} [\underline{\underline{I}} - 3 \, \underline{e} \; \underline{e}] \cdot \underline{U}_0 \qquad (36)$$

The field inside the drop ($r < a$) is not needed because we only require its average value which equals $\underline{U}_0$. If we combine (34) to (36) and restrict our attention to a monodisperse suspension ($a_t = a$, $\Delta\rho_t = \Delta\rho$, $\bar{\mu}_t = \bar{\mu}$), we obtain

$$<\underline{U}> = [1 + \alpha\phi] \, \underline{U}_0 + 0(\phi^2) \qquad (37a)$$

$$\alpha = - 2 [1 + \lambda] + 8 \int_0^1 [\mathscr{K} - \lambda\omega] \omega^{-4} \, d\omega + 8 \int_0^1 \mathscr{K} [\exp(-E/kT) - 1] \, \omega^{-4} \, d\omega \qquad (37b)$$

where, as before

$$\mathscr{K} \equiv [A_\parallel + 2A_\perp - 3] + [B_\parallel + 2B_\perp]$$

and the mobility coefficients have the same meaning as those appearing in (21) to (22), except now we are concerned with two spherical drops settling in an unbounded fluid. Equation (37*b*) is identical to (24*b*) if we set $\lambda = 3/2$, the value for a rigid drop.

The necessary hydrodynamic information to calculate α from (37*b*) is contained in the parameter $\mathscr{K}$. Wacholder and Weihs (1972) published their calculations for $A_\parallel + B_\parallel$ (that is, translation of two drops parallel to the line between centers) as a function of separation and $\bar{\mu}/\mu$. We were unable to find calculations of ($A_\perp + B_\perp$) in the literature. Fortunately, the dominant contribution to $\mathscr{K} - \lambda\omega$ is from $A_\parallel + B_\parallel$, and a reasonable estimate of the first integral in (37*b*) can be made by splitting the integrand as follows:

$$\mathscr{K} - \lambda\omega = \Lambda_\parallel + \Lambda_\perp \qquad (38a)$$

$$\Lambda_\parallel = A_\parallel + B_\parallel - 1 - \frac{\lambda}{2} \omega + \frac{(\lambda - 1)}{4} \omega^3 \qquad (38b)$$

$$\Lambda_\perp = 2[A_\perp + B_\perp - 1] - \frac{\lambda}{2} \omega - \frac{(\lambda - 1)}{4} \omega^3 \qquad (38c)$$

The $0(\omega)$ and $0(\omega^3)$ terms result from the contributions of $\underline{v}_\infty$ and $\nabla^2 \underline{v}_\infty$ to the parallel and perpendicular components of $\underline{W}_\infty$. For rigid particles ($\lambda = 3/2$), the calculations of Goldman et al. (1966), or equivalently Tables 1 and 2, can be used to obtain

$$8 \int_0^1 \Lambda_\parallel \, \omega^{-4} \, d\omega = - 1.43 \qquad (39a)$$

$$8 \int_0^1 \Lambda_\perp \, \omega^{-4} \, d\omega = - 0.10 \qquad (39b)$$

The dominance of (39*a*) suggests the following extrapolation to fluid particles:

$$8 \int_0^1 (\mathscr{K} - \lambda\omega) \omega^{-4} = d\omega \approx \left(\frac{1.53}{1.43} \right) \int_0^1 \Lambda_\parallel \, \omega^{-4} \, d\omega \qquad (40)$$

We have computed α for microscopically uniform dispersions ($E = 0$) using Equations (37) and (40) and values of $\Lambda_\parallel$ obtained from the paper by Wacholder and Weihs; the results are presented in Table 4. As one might guess from intuition, the hindrance parameter decreases in magnitude as the drop viscosity decreases. The values of α in Table 4 are slightly different from those calculated by Wacholder (1973) because he used an improper asymptotic expression for ($A_\perp + B_\perp$).*

TABLE 4. HINDRANCE COEFFICIENTS (α) FOR A MONODISPERSE SUSPENSION OF FLUID DROPS*

λ	$\bar{\mu}/\mu$	α
1.00	0	−4.54
1.17	.5	−5.17
1.25	1.0	−5.50
1.42	5.0	−6.18
1.50	∞	−6.53

* No long range energy between drops (E = 0).

The extension of (37) to a suspension of drops differing in size and density is straightforward beginning with Equations (34) to (36). For example, if we consider only variations in size, the linear coefficient appearing in (2) is

$$\alpha_{ij} = - \left[1 + 2\lambda \frac{a_j}{a_i} + \left(\frac{a_j}{a_i} \right)^2 \right] + \left[1 + \left(\frac{a_i}{a_j} \right) \right]^3 \int_0^1 \left\{ [A_\parallel + 2A_\perp - 3] + \left(\frac{a_j}{a_i} \right)^2 \left[B_\parallel + 2B_\perp - \frac{2\lambda\omega}{(1 + a_i/a_j)} \right] \right\} \omega^{-4} \, d\omega$$
$$+ \left[1 + \left(\frac{a_i}{a_j} \right) \right]^3 \int_0^1 \left\{ [A_\parallel + 2A_\perp - 3] + \left(\frac{a_j}{a_i} \right)^2 [B_\parallel + 2B_\perp] \right\} [\exp(- E_{ij}/kT) - 1] \, \omega^{-4} \, d\omega \qquad (41)$$

For $\lambda = 3/2$ (rigid drops), the above formula is the same as Equation (24*b*), since $a_i = a_t$, $a_j = a$, and $\Delta\rho = \Delta\rho_t$. Because calculations relating the mobility coefficients (A, B) to drop separation are incomplete for $\lambda < 3/2$, we utilize the following asymptotic formulas which we derived using a reflection technique suggested by Batchelor (1976):

$$A_\parallel = 1 - \frac{\lambda(3\lambda - 2)}{(1 + a_j/a_i)^4} (a_j/a_i)^3 \omega^4 + 0(\omega^6)$$

$$A_\perp = 1 + 0(\omega^6)$$

$$B_\parallel = \frac{\lambda\omega}{1 + a_i/a_j} - \frac{(\lambda - 1) \left[1 + \left(\frac{a_i}{a_j} \right)^2 \right] \omega^3}{(1 + a_i/a_j)^3} + 0(\omega^7)$$

$$B_\perp = \frac{\lambda\omega}{2(1 + a_i/a_j)} + \frac{(\lambda - 1) \left[1 + \left(\frac{a_i}{a_j} \right)^2 \right] \omega^3}{2(1 + a_i/a_j)^3} + 0(\omega^7) \qquad (42)$$

Substituting these expressions into (41) and neglecting the terms of order ω^6 and higher, we obtain the following equation for microscopically uniform suspensions ($E_{ij} = 0$):

$$- \alpha_{ij} \approx 1 + 2\lambda(a_j/a_i) + (a_j/a_i)^2 + \frac{\lambda(3\lambda - 2)}{1 + a_j/a_i} \qquad (43)$$

An idea of the accuracy of this expression can be obtained by considering rigid particles of the same size; Equation (43) predicts $\alpha_{ii} = - 6.88$, whereas the correct value is $- 6.53$, an error of only 5%.

In many systems, surfactants adsorb to the surface of drops and cause Marangoni stresses which affect the hydrodynamics.

---

* Equation (2.8) of Wacholder's paper is in error because it contains terms of $0(\omega^4)$ and $0(\omega^5)$, whereas Equation (42) here shows that ($A_\perp + B_\perp$) should not have these terms.

The analysis of this section neglected such complications, but the results [Equations (41) and (43)] could still be used to model contaminated suspensions by defining λ to include the hydrodynamic contribution of Marangoni stresses. Adsorption of surfactants tends to increase the drag force experienced by a single drop [for example, see Levich (1962)] and thus causes the drop to appear more solidlike. If F/U_0 is known for drops of given size and material, then an equivalent λ would be defined by Equation (33) to be used in Equation (41) and all subsequent relations. Such a correction for Marangoni effects is probably qualitatively valid, but an assessment of its quantitative accuracy is not possible because the two-drop hydrodynamic problem associated with surfactant adsorption/desorption has not been solved (to our knowledge).

SEDIMENTATION RATES OF CONCENTRATED SUSPENSIONS

The virial expansion developed in Appendix C provides a formal technique for extending the analysis to higher particle concentrations. The practical utility of this expansion is somewhat limited, however, because the general n particle hydrodynamic problem has not been worked out for $n > 2$. A more promising approach is to preaverage the hydrodynamic interactions among all the neighbors, ignoring the presence of the test particle, and then average the interaction of the test particle with each neighbor separately. The mathematics are only tractable if the test particle-neighbor hydrodynamic interactions are assumed pairwise additive, and if it is assumed that the presence of the test particle has negligible effect on the ensemble average of the neighbor-neighbor interactions.

As before, the test particle is introduced at position $\underline{x} = \underline{0}$ in the suspension. Let $\underline{\Delta}_1^*(\underline{r}_j; \underline{\xi}_{N-1})$ be the change in the settling velocity of the test particle due to neighbor j at $\underline{r}_j$; the configuration $\underline{\xi}_{N-1}$ of the $N - 1$ other neighbors appears in the argument of $\underline{\Delta}_1^*$ because the velocity of neighbor j depends on this configuration even when the test particle is not there. The mean effect of these pseudo binary interactions between the test particle and each neighbor is obtained by summing over j and ensemble averaging over $\underline{\xi}_{N-1}$:

$$<\underline{U}> = \underline{U}_{t0} + \int_V \cdots \int_V \sum_{j=1}^{n} \underline{\Delta}_1^*(\underline{r}_j; \underline{\xi}_{N-1}) \\ P(\underline{r}_j \mid \underline{0}) P(\underline{\xi}_{N-1} \mid \underline{r}_j, \underline{0}) d\underline{\xi}_{N-1} d\underline{r}_j \qquad (44)$$

The pseudo binary interaction is decomposed into three terms as in Equation (9):

$$\underline{\Delta}_1^*(\underline{r}_j; \underline{\xi}_{N-1}) = \underline{v}(\underline{0}, \underline{r}_j; \underline{\xi}_{N-1}) \\ + \frac{(\lambda - 1)a_t^2}{2\lambda} [\nabla_x \underline{v}]_{\underline{x}=\underline{0}} + \underline{W}(\underline{0}, \underline{r}_j; \underline{\xi}_{N-1}) \qquad (45)$$

The pairwise additive assumption for the hydrodynamic interactions between test particle and neighbors occurs in $\underline{W}$:

$$\underline{W} = \underline{U}_t(\underline{r}_j; \underline{\xi}_{N-1}) - \underline{U}_{t0} - \underline{v}(\underline{0}, \underline{r}_j; \underline{\xi}_{N-1}) \\ - \frac{(\lambda - 1)}{2\lambda} a_t^2 [\nabla_x \underline{v}]_{\underline{x}=\underline{0}} \qquad (46)$$

that is, the only effect of $\underline{\xi}_{N-1}$ is to alter the velocity ($\underline{v}$) of the neighbor in the absence of the test particle, but it has no effect on $\underline{U}_t(\underline{r}_j)$ other than that. A second assumption which is needed is that

$$P(\underline{\xi}_{N-1} \mid \underline{r}_j, \underline{0}) \approx P(\underline{\xi}_{N-1} \mid \underline{r}_j) \qquad (47)$$

that is, the conditional probability of $\underline{\xi}_{N-1}$ given neighbor j at $\underline{r}_j$ is about the same whether or not the test particle is at $\underline{x} = \underline{0}$.

Applying (45) and (47) to (44) and integrating over $\underline{\xi}_{N-1}$ for each j, and realizing that all neighbors are statistically the same, we get an expression nearly identical to Equation (11):

$$<\underline{U}_t> = \underline{U}_{t0} + C \left\{ \int_V <\underline{v}(\underline{0}, \underline{r})>_{N-1} g^{(2)}(r, C) d\underline{r} \right. \\ + \frac{(\lambda - 1)}{2\lambda} a_t^2 \int_V [\nabla_x^2 <\underline{v}(\underline{x}, \underline{r})>_{N-1}]_{\underline{x}=\underline{0}} g^{(2)}(r, C) d\underline{r} \\ \left. + \int_V <\underline{W}(\underline{0}, \underline{r})>_{N-1} g^{(2)}(r, C) d\underline{r} \right\} \qquad (48)$$

where the brackets $< >_{N-1}$ mean an ensemble average over the configuration of the $N - 1$ neighbors given a single neighbor at $\underline{r}$ in the absence of the test particle:

$$<\underline{v}(\underline{0}, \underline{r})>_{N-1} = \int_V \cdots \int_V \underline{v}(\underline{0}, \underline{r}; \underline{r}_2, \underline{r}_3, \ldots \underline{r}_N) \\ P(\underline{r}_2, \underline{r}_3, \ldots \underline{r}_N \mid \underline{r}) d\underline{r}_2 d\underline{r}_3 \ldots d\underline{r}_N \qquad (49)$$

Subsequent manipulations of (48) are the same as those following Equation (11) except that $<\underline{U}>$ replaces $\underline{U}_0$ (that is, interactions among the neighbors changes their mean velocity) and the long range part of $g^{(2)}$ (for $r > \sigma$) is a function of C and hence is not necessarily given by (17). Assuming (for convenience) that the density of all particles is the same, the mean settling velocity of the test particle (subscript i) is

$$\Omega_i = 1 + \sum_{j=1}^{n} [\zeta_{ij}\Omega_j + \iota_{ij}] \phi_j \\ \Omega_i = <U_i>/U_{i0} \qquad (50)$$

$$\zeta_{ij} = -\left[1 + 2\lambda\left(\frac{a_j}{a_i}\right) + \left(\frac{a_j}{a_i}\right)^2\right] \\ + \left(1 + \frac{a_i}{a_j}\right)^3 \left(\frac{a_j}{a_i}\right)^2 \\ \left\{\int_0^1 \left(B_\parallel + 2B_\perp - \frac{2\lambda\omega}{1 + a_i/a_j}\right) \omega^{-4} d\omega \right. \\ \left. + \int_0^1 (B_\parallel + 2B_\perp) [g_{ij}^{(2)}(r, \phi_1, \phi_2, \ldots \phi_n) - 1] \omega^{-4} d\omega \right\} \qquad (51a)$$

$$\iota_{ij} = \left(1 + \frac{a_i}{a_j}\right)^3 \int_0^1 (A_\parallel + 2A_\perp - 3) \\ g_{ij}^{(2)}(r, \phi_1, \phi_2, \ldots \phi_n) \omega^{-4} d\omega \qquad (51b)$$

The coefficients ζ_{ij} and ι_{ij} are binary in the hydrodynamic sense because the interaction parameters ($A_\parallel$, $A_\perp$, $B_\parallel$, $B_\perp$) depend only on the relative separation between a single type i and type j particle and the physical properties of the two types of particles. However, these coefficients are multicomponent through the configurational statistics in that $g_{ij}^{(2)}$ depends on the concentration of all types of particles. Equation (50) represents a set of n equations which must, in general, be solved to obtain each hindered settling ratio Ω_i; these equations are obviously nonlinear in the volume fractions ϕ_j.

To test the accuracy of Equation (50), consider a monodisperse suspension of rigid particles ($\lambda = 1.5$) which interact only through a hard sphere potential ($E = 0$):

$$\frac{<U>}{U_0} = \Omega = \frac{1 + \iota\phi}{1 - \zeta\phi} \qquad (52)$$

From Tables 1 and 2, the coefficients are evaluated from (51a) and (51b):

$$\zeta = -4.70 + 8 \int_0^1 (B_\parallel + 2B_\perp) [g^{(2)}(r, \phi) - 1] \omega^{-4} d\omega \qquad (53a)$$

$$\iota = -1.83 + 8 \int_0^1 (A_\parallel + 2A_\perp - 3)[g^{(2)}(r, \phi) - 1] \omega^{-4} d\omega \qquad (53b)$$

Our preliminary calculations using values of $g^{(2)}(r, \phi)$ published by Oden and Henderson (see Reed and Gubbins, 1973, Appendix M) indicate that if (52) is expanded in powers of ϕ, the integrals in (53a) and (53b) account collectively for only about 25% of the order ϕ^2 coefficient. To maintain simplicity, we neglect the integrals in (53) so that (52) becomes

$$\frac{<U>}{U_0} \approx \frac{1 - 1.83\phi}{1 + 4.70\phi} \qquad (54)$$

This expression probably overestimates the hindrance effect (underestimates $<U>/U_0$) to a small extent because the integral terms of (53) have been neglected.

A fair amount of data for hindered settling of identical rigid particles at low Reynolds numbers has been published (Richardson and Zaki, 1954; Maude and Whitmore, 1958; Hanratty and Bandukwala, 1958; Chong et al., 1979). These data are basically in very good agreement and are well fit by the empirical expression

$$\frac{<U>}{U_0} = k_1(1 - \phi)^p \tag{55}$$

where $p \approx 4.6$ and $k_1 \approx 0.95$. An interesting observation by nearly all these experimenters is that (55) is only a good fit of the data when $\phi > 0.05$; below this concentration, Equation (55) overestimates the observed value of $<U>$. In Table 5, our theoretical model [as represented by Equation (54)] is compared with (55), and the agreement is quite good, especially considering that there are no adjustable parameters in the theory. This agreement suggests that Equation (50) may, in fact, be a reasonable representation of a polydisperse suspension; unfortunately, published data (for example, Richardson and Shabi, 1960) are too sparse to rigorously evaluate our model, and the interpretation of measurements on settling zones in such suspensions is not straightforward (Mizra and Richardson, 1979). Reasonable estimates of ζ_{ij} and ι_{ij} can be made using Equations (42) for the hydrodynamic interaction parameters needed in (51) and neglecting concentration effects on $g_{ij}^{(2)}$:

$$\zeta_{ij} \approx -\left[1 + 2\lambda\left(\frac{a_j}{a_i}\right) + \left(\frac{a_j}{a_i}\right)^2\right] \tag{56a}$$

$$\iota_{ij} \approx -\frac{\lambda(3\lambda - 2)}{1 + a_j/a_i} \tag{56b}$$

For a monodisperse suspension of rigid particles, these approximations yield, when substituted into (52):

$$\frac{<U>}{U_0} \approx \frac{1 - 1.88\phi}{1 + 5.0\phi} \tag{57}$$

a good approximation to the more precise Equation (54). Calculations using the above expression, shown in Table 5, are in fair agreement with the experimental results.

TABLE 5. COMPARISON BETWEEN EXPERIMENTAL DATA [EQUATION (55)] AND THE THEORETICAL MODEL [EQUATIONS (54) OR (57)] FOR A MONODISPERSE SUSPENSION OF RIGID SPHERES

	$<U>/U_0$		
ϕ	Equation (55)	Equation (54)	Equation (57)
0.05	0.75 (0.79)*	0.74	0.72
0.10	0.59 (0.62)	0.56	0.54
0.20	0.34 (0.36)	0.33	0.31
0.30	0.18(0.20)	0.19	0.17
0.40	0.091(0.096)	0.093	0.080

---

* The values in parentheses were calculated from the Vand-Hawksley equation

$$\frac{<U>}{U_0} = (1 - \phi)^2 \exp\left[\frac{-2.5\phi}{1 - \frac{39}{64}\phi}\right]$$

which fits very well the data published by Hanratty and Bandukwala (1958).

One heuristic approach to modeling dense suspensions involves the concept of consistent field; the effect of particle concentration is reflected by changes in the apparent macroscopic material properties of the solvent (for example, Barnea and Mizrahi, 1973, 1975). The Vand-Hawksley model for settling of a suspension (see Table 5), which is based on a consistent field model, seems to work very well for suspensions of rigid spherical particles having $\phi > 0.05$ (Hanratty and Bandukwala, 1958). It can be shown, however, that this model is fundamentally incorrect as $\phi \rightarrow 0$. Consider rigid spheres of density ρ_s in a solvent of density ρ and viscosity μ. The macroscopic density and viscosity of the suspension depend on ϕ:

$$<\rho> = \phi\rho_s + (1 - \phi)\rho$$
$$<\mu> = \mu\,[1 + 2.5\phi + 0(\phi)^2] \tag{58}$$

In the Vand-Hawksley model an additional correction $(1 - \phi)^{-1}$ is made for the relative velocity between solvent and particles. (We do not understand the rationale for this correction.) The use of (58) and this velocity correction leads to the following limiting expression for hindered settling of the particles:

$$\frac{<U>}{U_0} = 1 - 4.5\phi + 0(\phi^2) \tag{59}$$

whereas the fundamentally correct model discussed in this paper predicts the first-order coefficient is -6.5. Furthermore, the consistent field model cannot account for the effect of pair potentials $[E(r)]$ between particles, as illustrated in Figures 2 and 3, because $<\rho>$ and $<\mu>$ are independent of microscopic particle distribution when only $0(\phi)$ effects are considered. The fact that the limiting form of the Vand-Hawksley Equation (59) is incorrect suggests that its success at larger ϕ is, in some respects, fortuitous.

Consistent field models also run into problems when applied to polydisperse suspensions. Suppose a suspension contains two types of rigid particles differing only in size, say, with $a_1/a_2 = 0.5$. Again, limiting our attention to dilute systems where $0(\phi^2)$ terms are negligible, the coefficients appearing in Equation (2) are obtained from Table 3:

$$\begin{aligned} \alpha_{11} &= -6.53 \qquad \alpha_{12} = -11.9 \\ \alpha_{21} &= -4.78 \qquad \alpha_{22} = -6.53 \end{aligned} \tag{60}$$

The Vand-Hawksley model would use Equations (58) to characterize the suspension with $\phi = \phi_1 + \phi_2$ and possibly $(1 - \phi)^{-1}$ to correct for relative velocity changes with concentration, with the result

$$\alpha_{11} = \alpha_{12} = \alpha_{21} = \alpha_{22} = -4.5 \tag{61}$$

an answer drastically different from (60). Thus, the consistent field model seems incapable of accounting for effects of polydispersity in a suspension.

SUMMARY

An important assumption in the theoretical development is that the particle configurational probability at the microscopic level is determined by equilibrium phenomena. A small value of the distortion parameter γ, as determined by Equation (B7), should provide a reasonable indication that thermal (Brownian) forces, rather than the hydrodynamics, dominate the (statistically stationary) relative configuration of particles.

Equation (43) provides a useful approximation for the coefficients α_{ij} which determine first-order concentration effects [see Equation (2)] in suspensions where the particles interact only through hard sphere potentials. Table 3 gives more accurate values of α_{ij} as a function of size and density differences between type i and j rigid particles, while Table 4 shows α_{ii} as a function of particle-to-solvent viscosity. Possible effects of long range pair potentials on α_{ij} are illustrated in Figures 2 and 3 for electrostatic repulsion between the particles, and these effects can be calculated given any pair potential $E_{ij}(r)$ by using Equation (41), with Tables 1 and 2 for rigid particles ($\lambda = 1.5$) or Equation (42) for drops ($1.0 \le \lambda < 1.5$). The two-particle analysis is extended to denser suspensions by preaveraging hydrodynamic interactions among neighbors before averaging interactions between one neighbor and the test particle. The resulting expression, Equation (50), provides a reasonable estimate of hindrance effects at high particle concentrations, as seen in Table 5. If concentration effects on the two-particle distribution function $[g_{ij}^{(2)}]$ can be ignored, as appears to be the case from Table 5, then Equations (56) can be used to compute (approximately) the complete set of binary coefficients needed in (50) when the particles only interact via hard sphere potentials. The effect of long range pair potentials (E_{ij}) on ζ_{ij} and ι_{ij} can be approximated by substituting Equation (17) for $g_{ij}^{(2)}$in the appropriate integrands of (51*a*) and (51*b*).

ACKNOWLEDGMENT

We are grateful to Professor Morton Gurtin of the Mathematics Department at Carnegie-Mellon University for helping us prove Equation (A8). We thank Cornell University and Carnegie-Mellon University for financial support.

APPENDIX A: MEAN VALUE OF $\nabla_x^2 \underline{v}(\underline{x}, \underline{R})$ IN A BOUNDED FLUID

$\underline{v}(\underline{x}, \underline{R})$ is the velocity at $\underline{x}$ caused by a single drop of radius a located at $\underline{R}$ in a fluid bounded by rigid container walls. This drop experiences a body force $\underline{F}$, so that when it is far from the container boundary it translates at a steady velocity $\underline{U}_0$ given by (33). There are no other drops in the fluid for the purpose of this calculation.

Let V^* denote the volume bounded by the surface $r = a$ and by an imaginary outer surface past which the particle is excluded because of its dimension (that is, the shortest distance from this outer boundary to the container wall equals a, and hence if the drop is on the outer surface it will just touch the container wall). The quantity of interest is related to the deviatoric stress dyadic $\underline{\underline{\sigma}}'(\underline{x}, \underline{R})$ by

$$\mu \nabla_x^2 \underline{v} = \nabla_x \cdot \underline{\underline{\sigma}}' \tag{A1}$$

Because the container is so large compared to the scale of the drop, the mean value of $\underline{\underline{\sigma}}'$ over V^* should be independent of the choice of $\underline{x}$, as long as it is not too cose to the outer surface, so that

$$\int_{V^*} \underline{\underline{\sigma}}'(\underline{x}, \underline{R}) d\underline{R} = \text{constant} \tag{A2}$$

$$\nabla_x \cdot \int_{V^*} \underline{\underline{\sigma}}'(\underline{x}, \underline{R}) d\underline{R} = 0 \tag{A3}$$

To avoid complications arising because V^* depends on $\underline{x}$, we use the relative coordinate $\underline{r}$

$$\underline{r} = \underline{R} - \underline{x} \tag{A4}$$

and hence

$$\int_{r>a} \nabla_x \cdot \underline{\underline{\sigma}}'(\underline{x}, \underline{x} + \underline{r}) d\underline{r} = 0 \tag{A5}$$

where the outer limit of integration is the container boundary. Let ∇_1 be the gradient operator with respect to $\underline{x}$ holding $\underline{x} + \underline{r}$ constant and ∇_2 the operator with respect to $\underline{x} + \underline{r}$. Equation (A5) can then be written as

$$\int_{r>a} \nabla_1 \cdot \underline{\underline{\sigma}}' d\underline{r} + \int_{r>a} \nabla_2 \cdot \underline{\underline{\sigma}}' \, d\underline{r} = \underline{0} \tag{A6}$$

The first integral in (A6) is our objective since $\nabla_1 = \nabla_x$. The second integral can be evaluated by using the divergence theorem:

$$\int_{r>a} \nabla_2 \cdot \underline{\underline{\sigma}}' d\underline{p} = \int_{r=a} \underline{n} \cdot \underline{\underline{\sigma}}' ds + \int_{\substack{\text{outer}\\ \text{surface}}} \underline{n} \cdot \underline{\underline{\sigma}}' ds \tag{A7}$$

When the drop is on the outer surface, it touches the rigid container boundary and hence must be stationary no matter what the value of the force applied to it. The stress at $\underline{x}$ is, therefore, zero when $\underline{r}$ is on the outer surface, so that the second integral on the right side of (A7) is zero. The first integral (over $r = a$) is the expression for the total force acting on the drop by the deviatoric stress in the continuous fluid, which is $-(8\pi/3)\mu a \lambda \underline{U}_0$, where μ is the viscosity of the fluid outside the drop. Combining these results with (A1) and (A5) to (A7), we get the desired quantity:

$$\int_{r>a} \nabla_x^2 \underline{v} d\underline{r} = \frac{8\pi}{3} \mu a \lambda \underline{U}_0 \tag{A8}$$

If the drop is a rigid particle, then $\lambda = 3/2$, and (A8) agrees with what Batchelor (1972) obtained by integrating $\underline{\underline{\sigma}}'$ over $r < a$ (that is, over the interior of the particle).

APPENDIX B: DISTORTION OF THE EQUILIBRIUM TWO-PARTICLE DISTRIBUTION FUNCTION

In a dispersion containing two different types of particles, the applied external field ($\underline{b}$) tends to distort the microscopic distribution of neighbors about a test particle. To visualize this effect, consider a binary system of rigid particles of types 1 and 2 which may differ in size or density, but only interact through a hard sphere potential. Before the external field is turned on, an observer located on a test particle of type 1 would see a uniform distribution of type 2 particles [$g^{(2)} = 1$]. Consider the situation that type 2 particles are more massive than type 1 particles. When the field is turned on, parallel to the z axis, the type 2 particles will translate faster than type 1, with the result that their time averaged local concentration will increase [$g^{(2)} > 1$] at θ = 180 deg but decrease [$g^{(2)} < 1$] at θ = 0 deg. Brownian motion tends to force $g^{(2)}$ back toward unity on both sides of the test particle. At steady conditions, Brownian diffusion balances the polarization effects on either size of the test particle caused by the unequal sedimentation rates between the test particle and the neighbors.

At steady conditions, the flux of neighbors relative to the position of the test particle is constant, and hence the divergence of the flux is zero:

$$\nabla \cdot [g^{(2)} (\underline{U}^* - \underline{U}_t^*)] = 0 \tag{B1}$$

$\underline{U}^*$ and $\underline{U}_t^*$ are the average microscopic velocities of neighbor and test particle, respectively. These velocities respond to the forces resulting from the external field ($\underline{F}$), interparticle energy (E) and Brownian forces of the solvent [$- kT\nabla \ln g^{(2)}$]:

$$\begin{aligned} \underline{F}_t^* &= \underline{F}_t + \underline{e} \frac{dE}{dr} + kT\nabla \ln g^{(2)} \\ \underline{F}^* &= \underline{F} - \underline{e} \frac{dE}{dr} - kT\nabla \ln g^{(2)} \end{aligned} \tag{B2}$$

The gradient operator in (B2) refers to the interparticle separation vector $\underline{r}$. The velocities are linear functions of these forces

$$\begin{aligned} \underline{U}_t^* &= \underline{\underline{A}}^* \cdot \underline{F}_t^* + \underline{\underline{B}}^* \cdot \underline{F}^* \\ \underline{U}^* &= \underline{\underline{C}}^* \cdot \underline{F}_t^* + \underline{\underline{D}}^* \cdot \underline{F}^* \end{aligned} \tag{B3}$$

where the mobility dyadics are functions of $\underline{r}$. Combining (B2) and (B3) and defining $G \equiv g^{(2)} \exp(E/kT)$, we get a flux equation:

$$\begin{aligned} g^{(2)}(\underline{U}^* - \underline{U}_t^*) = - kT \, [(\underline{\underline{A}}^* + \underline{\underline{D}}^*) - (\underline{\underline{B}}^* + \underline{\underline{C}}^*)] \\ \cdot \exp(- E/kT)\nabla G + [(\underline{\underline{D}}^* - \underline{\underline{B}}^*) \cdot \underline{F} \\ - (\underline{\underline{A}}^* - \underline{\underline{C}}^*) \cdot \underline{F}_t] \exp(- E/kT) G \end{aligned} \tag{B4}$$

Substitution of this expression into (B1) results in a conservation equation which can, in principle, be solved for $G(\underline{r})$ subject to the following boundary conditions:

$$\begin{aligned} r = \sigma: &\quad \underline{e} \cdot (\underline{U}^* - \underline{U}_t^*) = 0 \\ r \rightarrow \infty: &\quad \underline{U}^* - \underline{U}_t^* \rightarrow \underline{U}_0 - \underline{U}_{t0} \end{aligned} \tag{B5}$$

where $\underline{U}_0$ and $\underline{U}_{t0}$ are computed from the external forces using Stokes formula. Note that if the neighbors are identical to the test particle ($\underline{F} = \underline{F}_t$, and $a = a_t \rightarrow \underline{\underline{D}}^* = \underline{\underline{A}}^*$ and $\underline{\underline{C}}^* = \underline{\underline{B}}^*$), then the solution to (B1) and (B4) is $G = 1$, implying no distortion of the equilibrium distribution. Any distortion arises because of a difference in the physical properties (a, $\Delta\rho$) between the two types of particles.

To estimate the effect of an external field on $g^{(2)}$, we simplify the mathematics by neglecting hydrodynamic interactions between the particles:

$$\begin{aligned} \underline{\underline{A}}^* &\rightarrow A^* \underline{\underline{I}} \qquad & \underline{\underline{D}}^* &\rightarrow D^* \underline{\underline{I}} \\ \underline{\underline{B}}^* &\rightarrow \underline{\underline{0}} \qquad & \underline{\underline{C}}^* &\rightarrow \underline{\underline{0}} \end{aligned}$$

Also, we consider only hard sphere interparticle potentials ($E = 0$ for $r > \sigma$). The external forces are colinear and define the z axis of a coordinate system centered on the test particle. Letting $p \equiv r/\sigma$, Equations (B1), (B4) and conditions (B5) are combined to give

$$\frac{1}{p^2}\left[\frac{\partial}{\partial p} \frac{(p^2 \partial g^{(2)})}{\partial p} + \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \frac{(\sin\theta \, \partial g^{(2)}}{\partial\theta}\right] = \gamma \left[\cos\theta \frac{\partial g^{(2)}}{\partial p} - \frac{\sin\theta}{p} \frac{\partial g^{(2)}}{\partial\theta}\right] \tag{B6}$$

$$\gamma = \frac{\sigma[(D^*/A^*) F - F_t]}{[(D^*/A^*) + 1]kT} \tag{B7}$$

γ is a distortion parameter which is the ratio of the difference in sedimentation forces to the thermal force acting on the particles. As

$\gamma \to 0$, the thermal force dominates to establish an equilibrium microscopic distribution.

Equation (B6) is easily solved to $0(\gamma)$ by a regular expansion:

$$g^{(2)} = 1 - \left(\frac{\gamma}{2}\right)\frac{\cos\theta}{p^2} + 0(\gamma^2) \tag{B8}$$

If this expression replaces the Boltzmann (equilibrium) factor in the integrand of the final term in Equation (18), and the mobility dyadics shown in (21) and (22) are also substituted, the first-order term ($\cos\theta$) integrates to zero over the angles. Thus, the error associated with approximating the radial distribution function by its equilibrium value is $0(\gamma^2)$, at least in the absence of long range interparticle energies. In terms of the physical properties of the system, the distortion parameter is computed from

$$\gamma = [a_t a^3 \Delta\rho - a_t^3 a \Delta\rho]\frac{(4\pi/3)b}{kT} \tag{B9}$$

To safely ignore nonequilibrium effects, the requirement $|\gamma| < 1$ must be met. In the ultracentrifugation of compact macromolecules with $a_t \sim a \sim 10^{-6}$ cm, $b \leq 10^8$ cm/s^2 and $|\Delta\rho - \Delta\rho_t| \sim 0.1$ g/cm^3, the equilibrium distribution prevails at room temperature since $\gamma \sim 10^{-3}$. For colloidal size particles ($a \sim 1.0\ \mu$m) having the same density difference, however, the external field must be less than or equal to 10^3 cm/s^2, or the earth's gravitational acceleration, to keep $\gamma < 1$.

APPENDIX C: DEVELOPMENT OF A VIRIAL EXPANSION FOR CONCENTRATION EFFECTS

The rather difficult problem of computing the effect of N particles on the settling velocity of a test particle placed at position $\underline{x} = \underline{0}$ in the dispersion can be simplified to a series of zero-neighbor, single-neighbor, two-neighbor, etc., interactions by a cluster expansion technique similar to that used in the statistical thermodynamic description of gases leading to a virial equation of state. The mean settling velocity of the test particle is given by the ensemble average denoted by Equation (5). Define the disturbances ($\underline{\Delta}$) to the velocity of the test particle by

$$\begin{aligned}
&\underline{\Delta}_1(\underline{r}_1) = \underline{U}_t(\underline{r}_1) - \underline{U}_{t0}\\
&\underline{\Delta}_2(\underline{r}_1, \underline{r}_2) = \underline{U}_t(\underline{r}_1, \underline{r}_2) - \underline{U}_{t0} - \underline{\Delta}_1(\underline{r}_1) - \underline{\Delta}_1(\underline{r}_2)\\
&\underline{\Delta}_3(\underline{r}_1, \underline{r}_2, \underline{r}_3) = \underline{U}_t(\underline{r}_1, \underline{r}_2, \underline{r}_3) - \underline{U}_{t0} - \underline{\Delta}_2(\underline{r}_1, \underline{r}_2)\\
&\qquad - \underline{\Delta}_2(\underline{r}_2, \underline{r}_3) - \underline{\Delta}_2(\underline{r}_1, \underline{r}_3) - \underline{\Delta}_1(\underline{r}_1)\\
&\qquad - \underline{\Delta}_1(\underline{r}_2) - \underline{\Delta}_1(\underline{r}_3)
\end{aligned} \tag{C1}$$

where $\underline{U}_t(\underline{r}_1, \underline{r}_2, \ldots \underline{r}_m)$ is the velocity of the test particle when neighbor 1 is at $\underline{r}_1, \ldots$, and neighbor m is at $\underline{r}_m$ from the test particle; and $\underline{U}_{t0}$ is the velocity of the test particle when there are no neighbors. Suppose there are only three neighbors; then

$$\begin{aligned}
\underline{U}_t(\underline{r}_1, \underline{r}_2, \underline{r}_3) &= \underline{U}_{t0} + \underline{\Delta}_1(\underline{r}_1) + \underline{\Delta}_1(\underline{r}_2)\\
&+ \underline{\Delta}_1(\underline{r}_3) + \underline{\Delta}_2(\underline{r}_1, \underline{r}_2) + \underline{\Delta}_2(\underline{r}_2, \underline{r}_3)\\
&+ \underline{\Delta}_2(\underline{r}_1, \underline{r}_3) + \underline{\Delta}_3(\underline{r}_1, \underline{r}_2, \underline{r}_3)
\end{aligned}$$

More generally, for N neighbors

$$\begin{aligned}
\underline{U}_t(\underline{\xi}_N) = \underline{U}_{t0} &+ \sum_{j=1}^{N} \underline{\Delta}_1(\underline{r}_j)\\
&+ \sum_{j=1}^{N-1}\sum_{k>j}^{N} \underline{\Delta}_2(\underline{r}_j, \underline{r}_k)\\
&+ \sum_{j=1}^{N-2}\sum_{k>j}^{N-1}\sum_{l>k}^{N} \underline{\Delta}_3(\underline{r}_j, \underline{r}_k, \underline{r}_l)\\
&+ \ldots\ldots
\end{aligned} \tag{C2}$$

The disturbances $\underline{\Delta}$ represent a hierarchy of interactions; that is, $\underline{\Delta}_1$ is the binary hydrodynamic interaction between one neighbor and the test particle, $\underline{\Delta}_2$ is the effect of three particle interactions (two neighbors plus test particle) which includes the neighbor-neighbor interaction, etc.

The importance of (C2) is that it allows the ensemble average in Equation (5) to be expanded as a power series in particle concentration. Setting $\underline{x} = \underline{0}$ arbitrarily as the position of the test particle, the ensemble average of the first term of (C2) is

$$\int_V \underline{U}_{t0}\, P(\underline{\xi}_N|\underline{0})d\underline{\xi}_N = \underline{U}_{t0}\int_V P(\underline{\xi}_N|\underline{0})d\underline{\xi}_N = \underline{U}_{t0} \tag{C3}$$

since $\underline{U}_{t0}$ is a constant and $P(\underline{\xi}_N|\underline{0})$ is normalized when integrated over $d\underline{\xi}_N$. Now look at the integral of the second term of (C2):

$$\int_V \left[\sum \underline{\Delta}_1(\underline{r}_j)\right] P(\underline{\xi}_N|\underline{0})d\underline{\xi}_N = \sum_{j=1}^{N} \int_V \underline{\Delta}_1(\underline{r}_j)\, P(\underline{r}_j|\underline{0})d\underline{r}_j \int_V P(\underline{\xi}_{N-1}|\underline{r}_j, \underline{0})d\underline{\xi}_{N-1}$$

$P(\underline{\xi}_{N-1}|\underline{r}_j, \underline{0})$ is the conditional probability density function that the $N - 1$ neighbors (not including particle j) are at

$$\underline{\xi}_{N-1} = (\underline{r}_1, \underline{r}_2, \ldots \underline{r}_{j-1}, \underline{r}_{j+1}, \ldots \underline{r}_N)$$

given particle j is at $\underline{r}_j$ and the test particle is at $\underline{0}$. This conditional probability is normalized when integrated over $d\underline{\xi}_{N-1}$, so that the ensemble average of the second term in (C2) becomes

$$\sum_{j=1}^{N} \int_V \underline{\Delta}_1(\underline{r}_j)\; P(\underline{r}_j|\underline{0})d\underline{r}_j$$

Since the neighbors are all identical, each integral above is the same no matter what the value of j. Furthermore, the conditional probability is written in terms of the two-particle radial distribution function as

$$P(\underline{r}, \underline{0}) = \frac{C}{N}\, g^{(2)}(\underline{r}) \tag{C4}$$

where the concentration of neighbors is taken as a constant independent of position. Thus, the ensemble average of the second term of (C2) which involves $\underline{\Delta}_1$ is proportional to C, while the ensemble average of the third term is proportional to C^2, etc. The result of this averaging is Equation (6).

A formal expression of the ensemble average of the $\underline{\Delta}_2$ terms in (C2) can be obtained by similar manipulations of the conditional probability. Defining the three particle distribution function $g^{(3)}$ by

$$P(\underline{r}_1, \underline{r}_2|\underline{0}) = \frac{C^2}{N^2}\, g^{(3)}(\underline{r}_1, \underline{r}_2)$$

the final expansion to $0(C^2)$ is

$$\begin{aligned}
<\underline{U}_t> = \underline{U}_{t0} &+ C\int_V \underline{\Delta}_1(\underline{r})\, g^{(2)}(\underline{r})\, d\underline{r}\\
&+ \frac{C^2}{2}\int\int_V \underline{\Delta}_2(\underline{r}_1, \underline{r}_2)\; g^{(3)}(\underline{r}_1, \underline{r}_2)d\underline{r}_1 d\underline{r}_2 + 0(C^3)
\end{aligned} \tag{C5}$$

as long as $N >> 1$ and all neighbors are identical. It is important to note that $g^{(2)}$ and $g^{(3)}$ are functions of C except at dilute conditions, and Δ_2 accounts for hydrodynamic interactions between the neighbors (subscripts 1 and 2).

NOTATION

a = particle radius, m
$\underline{\underline{A}}, \underline{\underline{B}}, \underline{\underline{C}}, \underline{\underline{D}}$ = hydrodynamic mobility dyadics, Equations (22) and (B3), asterisk denotes a dimensional quantity
$\underline{b}$ = acceleration of particles, m · s^{-2}
C = macroscopic concentration, m^{-3}
$E(r)$ = long range potential energy between two particles, J
e = charge on an electron, = 4.8×10^{-10} esu
$\underline{e}$ = unit vector pointing radially from the center of a particle
$\underline{F}$ = external force on particle, N
$g^{(2)}$ = two-particle radial distribution function
$g^{(3)}$ = three-particle distribution function
H = Hamaker constant, J
$\underline{\underline{I}}$ = idemfactor dyadic
I_S = ionic strength, kg mole · m^{-3}
K = constant appearing in Equation (25)
k = Boltzmann's constant, 1.38×10^{-23} J/°K
m = electrostatic interaction parameter, Equation (27)
N = number of particles in system
$P(\underline{\xi}_N|\underline{x})$ = normalized conditional probability density function for the configuration $\underline{\xi}_N$ of N neighbors given a test particle at $\underline{x}$, m^{-3N}
Q = electrostatic interaction parameter, Equation (27)
q = net charge number of particle
$\underline{R}$ = position of a neighbor in a laboratory fixed frame of reference, m
$\underline{r}$ = position relative to the test particle, $\underline{R} - \underline{x}$, m

s = dimensionless surface-to-surface separation, Equation (27)
T = temperature, °K
$\underline{U}(\underline{\xi}_N)$ = settling velocity of a particle having N neighbors, $m \cdot s^{-1}$
$<\underline{U}>$ = ensemble averaged settling velocity, $m \cdot s^{-1}$
$\underline{U}_0$ = unbounded settling velocity if $N = 0$, given by Stokes' law, $m \cdot s^{-1}$
V = volume of system, m^3
$\underline{v}(\underline{x}, \underline{R})$ = velocity field at $\underline{x}$ produced by a neighbor (at $\underline{R}$) settling through a bounded fluid when no other particles are present, $m \cdot s^{-1}$
$\underline{W}(\underline{0}, \underline{r})$ = part of $\underline{\Delta}_1$ defined by Equation (10), $m \cdot s^{-1}$
$\underline{x}$ = position of test particle, taken as the origin ($\underline{x} = \underline{0}$) in the calculations, m

Greek Letters

α = first-order interaction coefficient, Equation (2) or (3)
β = second-order interaction coefficient, Equation (3)
γ = distortion parameter, Equation (B7) and (B9)
$\underline{\Delta}_1(\underline{r})$ = perturbation of test particle velocity due to presence of a single neighbor at $\underline{r}$ from it, defined by Equation (8), $m \cdot s^{-1}$
ϵ = dielectric constant of continuous fluid
ζ = hindrance factor for concentrated suspensions [see Equation (50)]
$\mathscr{K}$ = orientation averaged hydrodynamic mobility coefficient for a pair of identical spheres falling through unbounded fluid, Equation (26*a*)
κ = Debye screening parameter, m^{-1}
$\Lambda_{\|}$, $\Lambda_{\perp}$ = hydrodynamic mobility coefficients for a pair of identical liquid drops falling through unbounded fluid, Equation (38)
λ = viscosity parameter, Equation (31)
μ = viscosity of continuous fluid, $kg \cdot m^{-1} \cdot s^{-1}$
$\overline{\mu}$ = viscosity of drop, $kg \cdot m^{-1} \cdot s^{-1}$
ι = hindrance factor for concentrated suspensions [see Equation (50)]
$\underline{\xi}_N$ = configuration ($\underline{r}_1$, $\underline{r}_2$, . . ., $\underline{r}_N$) of N neighbors about a test particle
$d\underline{\xi}$ = $d\underline{r}_1 \, d\underline{r}_2 \, . \, . \, . \, . \, d\underline{r}_N$, m^{3N}
ρ = density of particle or drop, $kg \cdot m^{-3}$
$\Delta\rho$ = particle density minus fluid density, $kg \cdot m^{-3}$
σ = $a + a_t$, m
σ_0 = surface charge, $esu \cdot m^{-2}$
$\underline{\sigma}'$ = deviatoric stress dyadic, $N \cdot m^{-2}$
$\overline{\phi}$ = volume fraction
ψ_0 = surface potential for electrostatic double layer, $J^{1/2} \cdot m^{-1/2}$
Ω = $<U>/U_0$
ω = σ/r

Subscripts

i, t = test particle
j = neighbor (also, no subscript)
∞ = unbounded fluid (no container walls)
0 = infinite dilution (no particle interactions)
$\|$ = parallel to line of center
$\perp$ = perpendicular to line of center

LITERATURE CITED

Barnea, E., and J. Mizrahi, "A Generalized Approach to the Fluid Dynamics of Particulate Systems. Part I. General Correlation for Fluidization and Sedimentation of Solid Multiparticle Systems," *Chem. Eng. J.*, **5**, 171 (1973).

———., "A Generalized Approach to the Fluid Dynamics of Particulate Systems. Part II. Sedimentation and Fluidization of Clouds of Spherical Liquid Drops," *Can. J. Chem. Eng.*, **53**, 461 (1975).

Batchelor, G. K., *An Introduction to Fluid Dynamics*, pp. 230-238, Cambridge University Press, England (1967).

———., "Sedimentation in a Dilute Dispersion of Spheres," *J. Fluid Mech.*, **52**, 245 (1972).

———., "Brownian Diffusion of Particles with Hydrodynamic Interaction," *J. Fluid Mech.*, **74**, 1 (1976).

Cheng, P., and J. Schachman, "Studies on the Validity of the Einstein Viscosity Law and Stokes' Law of Sedimentation," *J. Polymer Sci.*, **16**, 19 (1955).

Chong, Y. S., D. A. Ratkowsky and N. Epstein, "Effect of Particle Shape on Hindered Settling in Creeping Flow," *Powder Technol.*, **23**, 55 (1979).

Cooley, M. D. A., and M. E. O'Neill, "On the Slow Motion of Two Spheres in Contact Along Their Line of Centers Through a Viscous Fluid," *Proc. Camb. Phil. Soc.*, **66**, 407 (1969*a*).

———., "On the Slow Motion Generated in a Viscous Fluid by the Approach of a Sphere to a Plane Wall or Stationary Sphere," *Mathematika*, **16**, 37 (1969*b*).

Goldman, A. J., R. G. Cox and H. Brenner, "The Slow Motion of Two Identical Arbitrarily Oriented Spheres through a Viscous Fluid," *Chem. Eng. Sci.*, **21**, 1151 (1966).

Goldstein, B., and B. H. Zimm, "Effect of Concentration and Intermolecular Forces on the Sedimentation of Polystyrene Spheres," *J. Chem. Phys.*, **54**, 4408 (1971).

Hamaker, H. C., "The London-van der Waals Attraction Between Spherical Particles," *Physica*, **4**, 1058 (1937).

Hanratty, T. J., and A. Bandukwala, "Fluidization and Sedimentation of Spherical Particles," *AIChE J.*, **3**, 293 (1958).

Happel, J., and H. Brenner, *Low Reynolds Number Hydrodynamics*, Chapt. 6 and 8, Prentice-Hall, Englewood Cliffs, N. J. (1965).

Hetsroni, G., E. Wacholder and S. Haber, "The Hydrodynamic Resistance of a Fluid Sphere Submerged in Stokes Flows," *Z. Ang. Math. Mech.*, **51**, 45 (1971).

Hill, T. L., *Statistical Mechanics*, McGraw-Hill, New York (1956).

Hogg, R., T. W. Healy and D. W. Fuerstenau, "Mutual Coagulation of Colloidal Dispersions," *Trans. Faraday Soc.*, **62**, 1638 (1966).

Levich, V. G., *Physicochemical Hydrodynamics*, Prentice-Hall, Englewood Cliffs, N. J. (1962).

Maude, A. D., and R. L. Whitmore, "A Generalized Theory of Sedimentation," *Br. J. Appl. Phys.*, **9**, 477 (1958).

Mizra, S., and J. F. Richardson, "Sedimentation of Suspensions of Particles of Two or More Sizes," *Chem. Eng. Sci.*, **34**, 447 (1979).

O'Neill, M. E., and S. R. Majumdar, "Asymmetrical Slow Viscous Fluid Motions Caused by the Translation or Rotation of Two Spheres. Part I. The Determination of Exact Solutions for any Values of the Ratio of Radii and Separation Parameters," *Z. Angew. Math. Phys.*, **21**, 164 (1970).

Pyun, C. W., and M. Fixman, "Frictional Coefficient of Polymer Molecules in Solution," *J. Chem. Phys.*, **41**, 937 (1964).

Reed, C. C., "Mathematical Concepts in the Transport of Interacting Particles," Ph.D. thesis, Cornell Univ., Ithaca, N. Y. (1978).

Reed, T. M., and K. E. Gubbins, *Applied Statistical Mechanics*, McGraw-Hill, New York (1973).

Richardson, J. F., and F. A. Shabi, "The Determination of Concentration Distribution in a Sedimenting Suspension Using Radioactive Solids," *Trans. Inst. Chem. Engrs.*, **38**, 33 (1960).

Richardson, J. F. and W. N. Zaki, "Sedimentation and Fluidization: Part I," *ibid.*, **32**, 35 (1954).

Spielman, L. A., "Viscous Interactions in Brownian Coagulation," *J. Colloid Interface Sci.*, **33**, 562 (1970).

Stitger, D., and T. L. Hill, "Theory of the Donnan Membrane Equilibrium. II. Calculation of the Osmotic Pressure and of the Salt Distribution in a Donnan System with Highly Charged Colloid Particles," *J. Phys. Chem.*, **63**, 551 (1959).

van der Hull, H. J., and J. W. Vanderhoff, "Clean Monodisperse Latexes as Model Colloids," in *Proceedings ACS Symposium on Polymer Colloids, Chicago*, R. M. Fitch, ed., Plenum Press (1970).

Wacholder, E., and D. Weihs, "Slow Motion of a Fluid Sphere in the Vicinity of Another Sphere or a Plane Boundary," *Chem. Eng. Sci.*, **27**, 1817 (1972).

Wacholder, E., "Sedimentation in a Dilute Emulsion," *ibid.*, **28**, 1447 (1973).

Manuscript received September 19, 1978; revision received February 9, and accepted February 29, 1980.