CELL AND PARTICLE INTERACTIONS AND AGGREGATION DURING ELECTROPHORETIC MOTION

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ABSTRACT

The stability and pairwise aggregation rates of small spherical particles under the collective effects of buoyancy-driven motion and electrophoretic migration are analyzed. The particles are assumed to be non-Brownian, with thin double-layers and different zeta potentials. The particle aggregation rates may be enhanced or reduced, respectively, by parallel and antiparallel alignments of the buoyancy-driven and electrophoretic velocities. For antiparallel alignments, with the buoyancy-driven relative velocity exceeding the electrophoretic relative velocity between two widely-separated particles, there is a "collision-forbidden region" in parameter space due to hydrodynamic interactions; thus, the suspension becomes stable against aggregation.

INTRODUCTION

Colloidal suspensions play important roles in many engineering fields, including materials processing, environmental engineering, chemical engineering, and biotechnology. An important goal in many such processes is to predict the conditions for which a suspension is stable against aggregation, or the particle aggregation rate for an unstable suspension. In an unstirred suspension, buoyancy-driven relative particle motion may result in aggregation of particles with different sizes or density. In addition, most colloidal particles are charged and so migrate in an applied electric field. In a heterogeneous suspension, electrophoretic relative motion and aggregation of particles with different electric charges or ζ-potentials may occur [1,2].

Gravity-induced particle aggregation has been studied by Melik and Fogler [3] and Davis [4], who employed trajectory analyses to predict pairwise particle collision rates. Recently, Nichols, Loewenberg and Davis [5] analyzed the stability criteria and pairwise aggregation rates for electrophoretic motion of colloidal spheres with differing zeta potentials and thin, unpolarized electric double layers. Their results indicate that hydrodynamic interactions generally have a weaker effect on the collision rate for electrophoretic motion than for gravity motion. As a result, the collision efficiencies for electrophoresis generally exceed those for buoyancy-driven motion by an order of magnitude. In these studies, the effects of gravity motion and electrophoretic migration were examined independently. However, gravity and electrophoresis may act simultaneously in some applications. One example is the separation of slowly sedimenting suspensions, for which an electric field may be employed to accelerate the initial formation of aggregates; once the aggregates become large enough, gravity will play a more important role.

Stability criteria and aggregation rates of charged particles in a dilute colloidal suspension under the collective action of gravity and an electric field are considered in this work. Of particular interest are the cases of parallel and antiparallel alignment of the undisturbed gravity and electrophoretic velocities, as these may lead to greatly increased or reduced aggregation rates, respectively.

THEORETICAL DEVELOPMENT

A dilute colloidal suspension containing spherical particles dispersed in an isothermal fluid of Newtonian viscosity μ and density ρ is considered. For dilute suspensions, the probability of a third particle influencing

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the relative motion of two particles is small, and so the analysis is restricted to binary interaction of two spherical particles of radii a_1 and a_2, densities ρ_1 and ρ_2, and zeta potentials ζ_1 and ζ_2, respectively. The particles are assumed to be small enough so that inertia may be neglected, but sufficiently large that Brownian motion is negligible. These assumptions are valid for sedimenting particles of approximately 1 µm - 50 µm in radii [4]. For electrophoretic motion, these assumptions are valid over a broader range of 0.1 µm - 1 cm in radius [2,5]. This study is also restricted to particles with moderate surface potentials and thin electric double layers.

The velocity of each particle is linearly dependent on gravity, the electric field, and the interparticle forces. Moreover, the relative velocity $V_{12} = U_2 - U_1$ can be decomposed into motion along and normal to the line of centers:

$$V_{12} = V_{12}^{G,o} \cdot \left[\frac{rr}{r^2} L^G(s) + \left(I - \frac{rr}{r^2} \right) M^G(s) \right] + V_{12}^{E,o} \cdot \left[\frac{rr}{r^2} L^E(s) + \left(I - \frac{rr}{r^2} \right) M^E(s) \right] - \frac{a_1 a_2}{6\pi\mu a_1 a_2} \frac{rr}{r^2} G(s) \cdot \nabla\Phi_{12} \quad , \quad (1)$$

where r is the vector from the center of particle 1 to the center of particle 2, I is the unit second-order tensor, $s = 2r/(a_1 + a_2)$ is the dimensionless separation between particle centers, and $\Phi_{12}(r)$ is interparticle force potential.

The relative velocity for two widely separated particles due to gravity is given by the Stokes formula:

$$V_{12}^{G,o} \equiv U_2^{G,o} - U_1^{G,o} = \frac{2(\rho_1 - \rho)a_1^2(1 - \lambda^2\gamma)}{9\mu} g \quad , \quad (2)$$

where $\lambda = a_2/a_1$ is the particle size ratio, $\gamma = (\rho_2 - \rho)/(\rho_1 - \rho)$ is the buoyant density ratio, and g is the gravitational acceleration vector. By contrast, the electrophoretic relative velocity of two widely separated particles is independent of their sizes, shapes, and densities [5]:

$$V_{12}^{E,o} \equiv U_2^{E,o} - U_1^{E,o} = \frac{\varepsilon\zeta_1(\beta - 1)}{\mu} E \quad , \quad (3)$$

where $\beta = \zeta_2/\zeta_1$ is the ratio of zeta potentials, and E is the applied electric field.

The interparticle force acts only along the line of centers and is given by $-\nabla\Phi_{12}$, with the total interparticle potential assumed to be the sum of the individual attractive and repulsive contributions by DLVO theory. The attractive van der Waals potential for spheres close together is [5]:

$$\Phi_A = -\frac{A a_1 a_2}{6(a_1 + a_2)h}\left[1 - \frac{5.32h}{\lambda_L} \ln\left(1 + \frac{\lambda_L}{5.32h} \right) \right] \quad , \quad (4)$$

where h is the separation between particles surfaces, λ_L is the London retardation wavelength, of approximately 0.1 µm, and A is the Hamaker constant, which is typically of order $10^{-19} - 10^{-21}$ J. The electrostatic repulsive potential due to thin overlapping double layers and modest surface potentials is [5]:

$$\Phi_R = \frac{\varepsilon a_1 a_2(\zeta_1^2 + \zeta_2^2)}{4(a_1 + a_2)}\left[\frac{2\zeta_1\zeta_2}{\zeta_1^2 + \zeta_2^2} \ln\left(\frac{1 + \exp(-\kappa h)}{1 - \exp(-\kappa h)} \right) + \ln(1 - \exp(-2\kappa h)) \right] \quad , \quad (5)$$

where κ is the reciprocal double-layer thickness, which increases with the ionic strength of the surrounding fluid. The above expression is valid for constant surface potentials $\kappa a > 10$, and $\zeta < 60$ mV.

The relative mobility functions for motion along the line of centers (L^G, L^E, and G) and motion normal to the line of centers (M^G and M^E) describe the effects of hydrodynamic interactions between two spherical particles in creeping flow. L^E, M^E and G depend only on the size ratio, λ, and the dimensionless distance between centers, s,

and are unchanged when λ is replaced by λ^{-1}. L^G and M^G also depend on the buoyant density ratio, γ, and are unchanged when λ and γ are replaced by λ^{-1} and γ^{-1}, respectively.

For the electrophoretic relative mobilities, L^E and M^E, a far-field reflection solution [6], a boundary collocation solution [7,8], and a near-field lubrication solution [2] are used in this study. The relative mobility G and the buoyancy-driven relative mobilities, L^G and M^G, are taken from [9]. The relative mobilities approach unity when the particles are far apart, indicating the absence of hydrodynamic interactions. As the two particles approach each other, the mobilities decrease due to hydrodynamic interactions. For widely separated particles, the relative mobility functions for particles in buoyancy-driven motion depart from unity as $1/r$. In contrast, electrophoretic motion of charged particles and their neutralizing double layers has a force-free nature , and the mobility functions have a weaker departure, as $1/r^3$. As the separation between two particles vanishes, the mobilities along the line of centers approach zero, whereas the mobilities normal to the line of centers tend to finite limits. For particles in close approach, the electrophoretic relative mobilities are much larger than the buoyancy-driven mobilities due to electrically-driven convection in the electrical double-layer, which facilitates the removal of fluid from the near-contact region that separates two approaching particles, a phenomenon called "electro-osmotic fluid withdrawal" [2].

Decomposing the relative velocity into components along and normal to the line of centers yields:

$$V_r = -\left[L^G(s) + V_{12}^{E,o}L^E(s)/V_{12}^{G,o}\right]\cos\theta - \frac{G(s)}{N_A}\left(f_A(s) - N_R f_R(s)\right) , \tag{6}$$

$$V_\theta = \left[M^G(s) + V_{12}^{E,o}M^E(s)/V_{12}^{G,o}\right]\sin\theta , \tag{7}$$

where θ is the angle from $V_{12}^{G,o}$ to r, and V_r and V_θ are the components of the relative velocity along and perpendicular to the line of centers, respectively, made dimensionless by $V_{12}^{G,o} = \left|V_{12}^{G,o}\right|$, and $V_{12}^{E,o} = V_{12}^{E,o} \cdot V_{12}^{G,o}/V_{12}^{G,o}$. The parameter $N_A = 6\pi V_{12}^{G,o}a^2/A$ represents the ratio of gravitational and van der Waals forces, where $a = (a_1 + a_2)/2$ is the average radius. The function $f_A(s)$ is the dimensionless van der Waals force deduced from equation (4). The parameter $N_R = \varepsilon\varsigma_1^2 a/A$ describes the characteristic strength of electrostatic repulsion relative to van der Waals attraction. The function $f_R(s)$ is the dimensionless electrostatic repulsion from equation (5).

By restricting our attention to electric fields which are parallel or antiparallel to the gravity vector, the pairwise aggregation rate per unit volume of the dispersion may be expressed as a collision cross-section times the flux of particle pairs:

$$J_{12} = n_1 n_2 \pi (a_1 + a_2)^2 V_{12}^o E_{12} , \tag{8}$$

where n_1 and n_2 are the number of particles of types 1 and 2, respectively, per unit volume, $V_{12}^o = \left|V_{12}^{G,o} + V_{12}^{E,o}\right|$ is the magnitude of the relative velocity of two isolated particles, and E_{12} is the collision efficiency. The collision efficiency is unity when the particles move in rectilinear motion without interactions; values differing form unity account for hydrodynamic and interparticle interactions. The collision efficiency is related to the critical parameter, $E_{12} = \sigma_c^2/(a_1 + a_2)^2$, where σ_c is the critical impact parameter defined such that particle aggregation occurs if the initial horizontal offset is $\sigma \le \sigma_c$, as shown in Figure 1.

Following earlier work for collisions induced individually by gravity [3,4] and electrophoresis [5], the relative trajectories of two particles are determined by integrating the relative trajectory equation, which results from dividing (6) by (7):

$$\frac{ds}{d\tau} = -s\frac{\left[L^G + V_{12}^{E,o}L^E/V_{12}^{G,o}\right]\cos\theta + \left[G(f_A - N_R f_R)/N_A\right]}{\left[M(s) + V_{12}^{E,o}M^E/V_{12}^{G,o}\right]\sin\theta} , \tag{9}$$

where $\tau = 2V_{12}^o t/(a_1 + a_2)$ is the dimensionless time. The critical impact parameter is determined by integrating equation (9) backwards from a critical point where $\theta = \pi$ and $V_r = 0$, as described previously for gravity [4] and electrophoresis [5] acting independently.

RESULTS AND DISCUSSION

When a colloidal suspension is said to be stable, it usually means that electrostatic or other repulsive forces prevent the particles from aggregating. When the electrophoretic and gravitational velocities of charged colloidal particles are in opposite directions, however, there may be a purely hydrodynamic stability against aggregation. Consider, for example, the dimensionless relative velocity along the line of centers for the case $V_{12}^{G,o}/V_{12}^{E,o} = -2.5$, $\lambda = 0.5$, and $\gamma = 1$, illustrated in Figure 2. For this case, the relative motion due to gravity exceeds that due to electrophoresis when the two spheres are well separated, and so the faster-moving sphere approaches the slower-moving one. As the spheres become closer together, hydrodynamic interactions reduce the gravity-induced relative motion more than the electrophoretic relative motion. At a separation distance of about 1.5 average radii, then, the oppositely directed relative velocities balance, and the relative motion along the line of centers is arrested. Thus, the different behavior of pairwise hydrodynamic interactions for gravitational and electrophoretic motion prevents the two spheres from becoming sufficiently close to aggregate.

In the absence of interparticle attractive and repulsive forces, the stability condition of zero relative velocity along the line of centers is, from equation (6),

$$-V_{12}^{G,o}/V_{12}^{E,o} = L^E(s)/L^G(s) \quad .$$

For widely separated spheres ($s \rightarrow \infty$), $L^E \rightarrow 1$ and $L^G \rightarrow 1$, and so $-V_{12}^{G,o}/V_{12}^{E,o} = 1$ is the lower limit of the stable region of parameter space. As the separation distance s decreases, L^G decreases faster than does L^E, so that L^E/L^G increases, and the upper limit of the stable region occurs for very small critical separations at which the relative velocity is arrested. In this case, L^E/L^G approaches a constant provided by lubrication theory [2]. The results are shown in Figure 3 as a function of the size ratio, λ, for buoyant density ratios of $\gamma = 0$ and $\gamma = 1$. A rather large range of relative magnitudes of gravitational and electrophoretic motion is encompassed by the stable or "collision-forbidden" zone, indicating that undesirable aggregation during sedimentation to separate particles by size or density may be eliminated by applying an electric field, if the particles also differ in surface charge or potential.
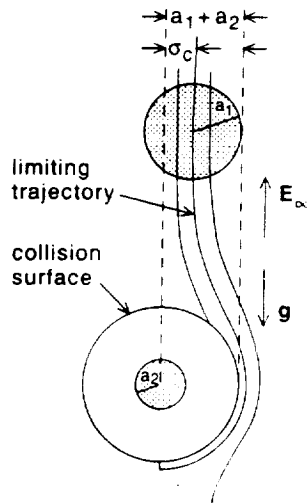

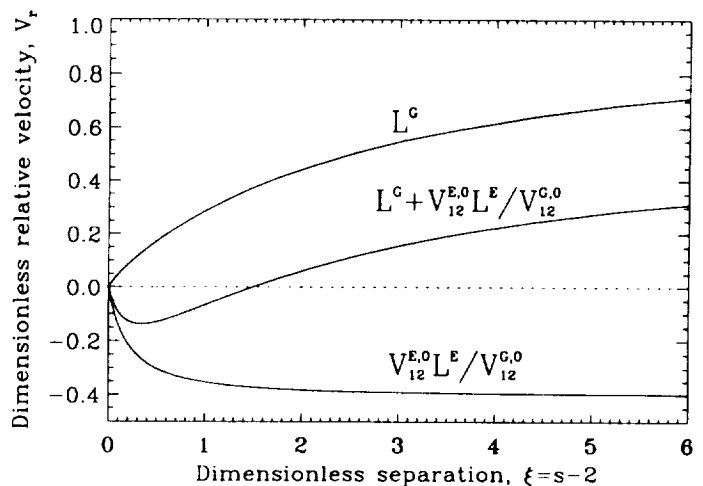Fig. 1 - Schematic of relative trajectories of two spheres due to gravity and electrophoresis.

Fig. 2. - Dimensionless relative velocity along the line of centers due to gravity, electrophoresis, and combined effects.

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A typical plot of the collision efficiency as a function of the relative velocity parameter $V_{12}^{G,o} / V_{12}^{E,o}$ is shown in Figure 4 for $\gamma = 2$, $\beta = 0.5$, $\lambda_L/a = 0.044$, $\kappa a = 10^3$, $N_A = 10^4$, and $N_R = 10^2$. The collision rate per unit volume in the suspension is then given by equation (8). For $\left| V_{12}^{G,o} / V_{12}^{E,o} \right| \gg 1$ and $\left| V_{12}^{G,o} / V_{12}^{E,o} \right| \ll 1$, the previous results for gravitational aggregation and electrophoretic aggregation, respectively, acting alone are recovered [4,5]. In general, the collision efficiencies for electrophoresis exceed those for sedimentation because of the weaker hydrodynamic interactions for electrophoresis. Also, the collision efficiencies are reduced for small size ratios, because the smaller particle then tends to follow the streamlines around the larger particle and not collide with it.

Varying the parameter $V_{12}^{G,o} / V_{12}^{E,o}$, which is the ratio of the relative velocity due to gravity to that due to the electric field for well-separated spheres, reveals some provocative phenomena. When this parameter is positive, electrophoresis and gravity aid each other. In this case, the collision efficiency decreases as $V_{12}^{G,o} / V_{12}^{E,o}$ increases, due to the stronger hydrodynamic interactions (which inhibit approach and aggregation) for gravity. The downturn for $V_{12}^{G,o} / V_{12}^{E,o} \rightarrow 0$ is a consequence of the attractive van der Waals forces becoming negligible in this limit with fixed N_A. When $V_{12}^{G,o} / V_{12}^{E,o} < 0$, electrophoresis and sedimentation are in opposite directions. For $-1 < V_{12}^{G,o} / V_{12}^{E,o} < 0$, the collision efficiency increases as $V_{12}^{G,o} / V_{12}^{E,o}$ decreases, and may even exceed unity (implying that hydrodynamic interactions *increase* the collision rate!). In this case, the net relative velocity is dominated by electrophoresis but reduced by gravity; as one particle approaches the other, hydrodynamic interactions cause the gravitational relative velocity to decrease more than electrophoretic relative velocity, so that the net relative velocity *increases*, and the spheres are drawn together at an enhanced rate. In contrast, when $V_{12}^{G,o} / V_{12}^{E,o} < -1$, the net relative velocity is dominated by gravity and reduced by electrophoresis. Then as one particle approaches the other, the gravitational velocity is reduced by hydrodynamic interactions to a greater extent, so that the relative velocity decreases. This causes the collision efficiencies to be reduced, and the collision-forbidden zone described earlier is apparent.
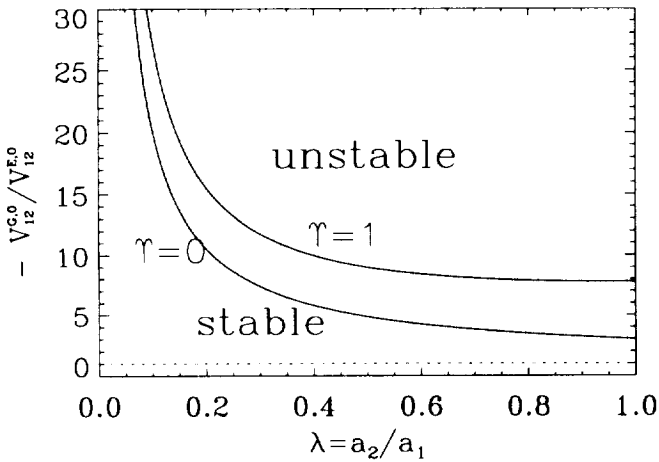

Fig. 3 - Stability diagram showing the collision-forbidden (stable) region of parameter space for antiparallel alignment of gravitational and electrophoretic motion of two different particle species.
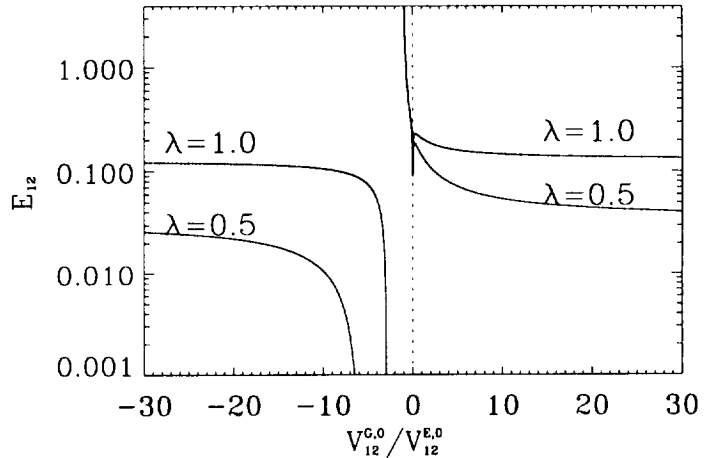

Fig. 4 - Collision efficiency for combined gravitational and electrophoretic motion.

CONCLUSIONS AND FUTURE WORK

A trajectory analysis employing hydrodynamic mobility functions has been employed to predict pairwise aggregation rates of small spherical particles in a heterogeneous suspension subject to both gravitational and electrophoretic particle motion. Depending on the relative orientation and magnitude of the gravity vector and the electric field, aggregation may be enhanced or retarded. Due to the stronger hydrodynamic interactions for

gravitational motion, a "collision-forbidden" region is predicted for antiparallel alignment of the gravitational and electrophoretic velocities over a broad range of the relative magnitude of these velocities.

Experiments are planned to test the theoretical predictions. Bidisperse mixtures of small particles with different surface charges will be allowed to sediment under normal gravity, with and without an electric field applied. Both parallel and antiparallel orientations of the electric field and gravity will be employed, including within the collision-forbidden region, to determine the conditions for which aggregation, and hence the sedimentation rate, is enhanced or suppressed. A shallow density gradient will be employed to suppress free convection in the suspending fluid.

Zone electrophoresis experiments, in which the motion and interaction of bands of particles are observed, will also be performed. It is hoped that these will allow direct observation of aggregates, as illustrated in Figure 5 and simulated in Figure 6, where a band of faster-moving particles pass through a band of slower-moving particles to generate a band of aggregates with intermediate mobility.
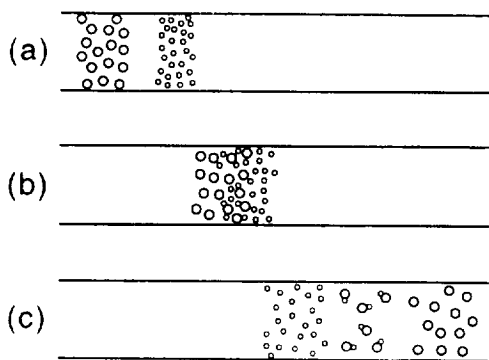

Fig. 5 - Schematic of aggregation during zone electrophoresis of a high-mobility band passing through a low-mobility band.
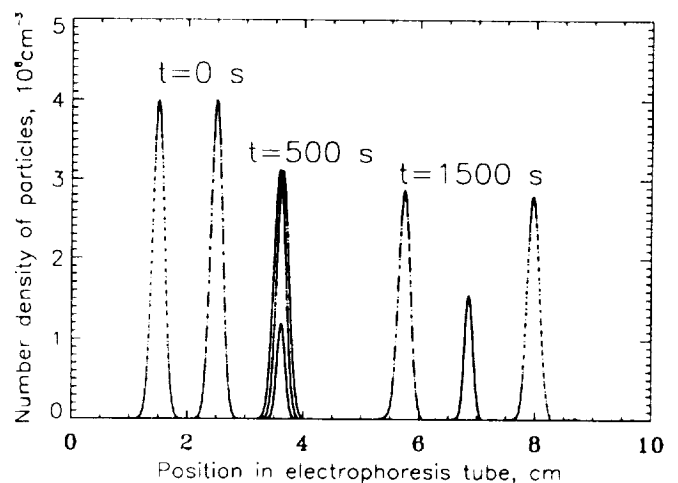

Fig. 6 - Simulation of aggregation during zone electrophoresis of a high-mobility band passing through a low-mobility band.

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