Reports

Hydrodynamic Measurement of Double-Layer Repulsion Between Colloidal Particle and Flat Plate

DENNIS C. PRIEVE AND BARBARA M. ALEXANDER

Electrostatic repulsion acting across an electrolyte solution lends stability to paints and printing inks and influences cell adhesion, aggregation, and fusion. A new technique is used to measure this interaction when one of the bodies has colloidal dimensions. The potential energy profile of interactions between a 15-micrometer polystyrene sphere and a glass plate is determined by observing the distribution of separation distances (0.2 to 0.4 micrometer) that the particle samples by Brownian motion. Measurements of the speed with which the sphere is carried by linear shear flow along the wall are used to calculate separation distance. Although evidence for hydrodynamic lift is found, it is not included in the potential profile.

THE ELECTROSTATIC INTERACTION of charged bodies across electrolyte solutions is profoundly different from the interaction across a vacuum. The presence of mobile ions in the intervening media weakens the interaction by a process known as Debye screening. At equilibrium, a diffuse cloud of counterions forms in the solution next to a charged surface, which has a net charge equal and opposite to that of the surface. The thickness of this cloud is the Debye length

$$\lambda = \left(\frac{\epsilon kT}{8\pi I e^2}\right)^{1/2} \qquad (1)$$

where ϵ is the dielectric constant, I is the ionic strength, e is the charge on a proton, and kT is the thermal energy. The Debye length varies from about 1 nm in physiological saline to 1 μm in deionized water. This diffuse cloud, together with the layer of fixed charges on the surface, is called the double layer. When two charged surfaces are brought together so that their double layers overlap, the resulting electrostatic interaction is called the double-layer force.

Double-layer repulsion retards the aggregation of aqueous colloidal dispersions which, for example, make up foodstuffs, paints, printing inks, photographic films, and blood (*1*). Double-layer repulsion can also prevent the deposition of red blood cells on an electrode; when the repulsion is weakened, these cells adhere because of long-range van der Waals attraction (*2, 3*). Other biological phenomena affected by electrostatic repulsion include cell adhesion and fusion. Parsegian (*4*) has discussed the importance of long-range forces in the initial stages of approach of biological membranes.

We report here a new experimental technique for measuring the interaction between a colloidal particle and a flat wall. It is based on the principle that, at equilibrium, the probability of finding a particle at a given distance h from the wall is related to the potential energy $\phi(h)$ at that distance by Boltzmann's equation

$$p(h) = A \exp[-\phi(h)/kT] \qquad (2)$$

where $p(h)dh$ is the probability of finding the particle between h and $h + dh$, k is Boltzmann's constant, T is absolute temperature, and A is the normalization constant. By repeatedly observing the distance between the particle and the wall over a long period of time, one can determine the probability density $p(h)$; the potential energy profile can be calculated from Eq. 2.

Results obtained by this technique should complement results obtained from direct measurements of the interaction between crossed-mica cylinders (*5–7*). Although it does not have the subnanometer resolution of that method for determining the separation distance, this new technique has the advantage of reducing one of the surfaces studied to colloidal dimensions (the bodies used for direct measurements are 10^3 to 10^6 times as large as a colloidal particle).

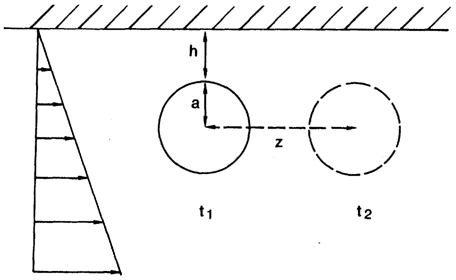

Fig. 1. Side view of a polystyrene sphere (which is less dense than the glycerol-water solution) near the glass optical flat at two different times, t_1 and t_2. The fluid velocity profile is shown at the left. From the distance traveled, z, in time $t_2 - t_1$, the separation distance, h, can be deduced. From a histogram of many such measurements, one can calculate the potential-energy profile using Boltzmann's equation.

The changes in particle-wall separation are too small to be measured by direct observation with a light microscope. Instead, the fluid is occasionally made to undergo steady laminar motion through the flow cell (see Fig. 1), and the speed with which the particle is carried with the fluid can be observed with the microscope. Multiple images of the sphere, produced by strobe lighting through a dark-field condenser, are recorded on each frame of film.

Very near the walls, the fluid's speed increases linearly with the distance from the wall. A rigid sphere entrained in such a flow field will undergo rotation and translation parallel to the wall at a speed that is somewhat less than the speed of the undisturbed fluid at the same distance from the wall as the particle's center. The relation between the speed of the sphere and its distance from the wall was determined by Goldman *et al.* (*8*) who solved Stokes equation for this situation. Thus, the instantaneous distance of the sphere from the wall was deduced from the measured translational velocity.

The upper and lower walls of the flow cell are glass optical flats, 3 cm by 3 cm by 1 cm, separated by 1 mm of fluid. Providing a constant fluid flow rate is essential, if changes in particle velocity are to be interpreted as changes in particle-wall separation. A gravity feed system was used. We maintained constant head pressure throughout the experiments by allowing atmospheric air to enter the otherwise sealed reservoir through a tube inserted beneath the fluid surface. To avoid flow rate changes caused by the temperature dependence of fluid viscosity, we installed the apparatus in a constant-temperature room. The small remaining temperature changes of the fluid were recorded, so that viscosity corrections could be made during data analysis.

To determine if changes in flow rate contributed significantly to changes in measured particle speed, we observed two particles simultaneously. An increase in flow rate would increase the speed of both particles, producing a correlation between their speeds, whereas Brownian motion of either

---

D. C. Prieve, Department of Chemical Engineering, Carnegie-Mellon University, Pittsburgh, PA 15213.
B. M. Alexander, Procter & Gamble Company, Ivorydale Technical Center, Cincinnati, OH 45217.

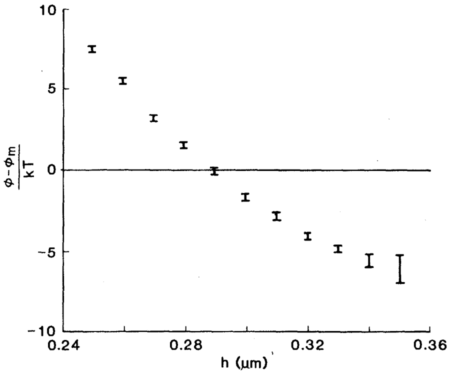

Fig. 2. Potential energy of a polystyrene sphere, relative to the most probable particle-wall separation distance, after the gravitational contribution has been subtracted.

of the two widely spaced particles is independent of that of the other. In the first of the results presented below, the correlation coefficient was less than 0.001, an indication that any flow rate changes contribute negligibly to changes in the particles' speed.

Particles 8 to 18 μm in diameter were studied in aqueous solutions of 37 to 98 percent glycerol (by weight). As received from the manufacturer, the American Chemical Society grade glycerol contained a significant quantity of ionic material. Solutions of lower ionic strength were obtained by treatment with mixed-bed, ion-exchange resin. The ionic strength could then be adjusted from 0.03 to 0.2 mol/m^3 by the addition of a small quantity of NaCl. We used the measured solution conductivity to calculate the ionic strength of all solutions, assuming the electrolyte to be NaCl. For the conditions encountered below, the double-layer repulsion is expected to be much stronger than the van der Waals attraction.

Figure 2 shows the interaction energy profile of colloidal forces for a particular sphere, 14.7 μm in diameter, in a 37.5 percent glycerol solution having an ionic strength of 0.079 mol/m^3 and a *p*H of 6.3 (*9*). This plot is based on 221 observations of the particle-wall separation distance. To deduce the potential energy from the histogram of separation distances using Eq. 2, we first eliminated the constant A by dividing Eq. 2 evaluated at h by Eq. 2 evaluated at h_m, where h_m is the location of the maximum of the function $p(h)$ (the most probable separation distance). The ratio $p(h)/p(h_m)$ was then approximated as the ratio of the number of observations of separation distances in the small interval centered at h to the maximum number of observations in any interval, all intervals having the same width. This procedure yields $\phi(h) - \phi(h_m)$, the total potential energy of the sphere due to gravity and colloidal forces. This function has a minimum at $h = h_m = 0.29$ μm, which was determined as the center of the interval containing the largest number of observations. We obtained the contribution of colloidal forces alone (Fig. 2) by subtracting the gravitational contribution calculated from the size of the particle and the densities of the fluid and particle. The error bars show the effect of adding or subtracting one observation to the total in each interval.

At these large distances, current theories predict that the double-layer energy should decay exponentially with distance, where the decay length equals the Debye length. The data presented in Fig. 2 could be described in terms of such a model. The decay length determined by a logarithmic regression of the data in Fig. 2 is within 30 percent of 45 nm, the Debye length estimated from the solution conductivity. Israelachvili and Adams (*5, 10*) also observed exponential decay at such low ionic strengths, with a decay length equal to the Debye length.

To show that the repulsion of Fig. 2 is electrostatic, we repeated the experiments in solutions of five different ionic strengths. The effect of increasing salt concentration is to decrease the most probable separation distance (Fig. 3). This decrease reflects either a weakening of double-layer repulsion through Debye screening or a strengthening of attractive forces. Since van der Waals attraction can only be decreased by ionic screening of the low-frequency contribution (*11*) while the buoyancy force is relatively insensitive to ionic strength, this result indicates that the interaction determined by this technique includes double-layer repulsion.

To show that hydrodynamic forces do not contribute to the interaction shown in Fig. 2, we made additional observations, using different flow rates. About 100 observations of a 12.6-μm particle were obtained for each of two flow rates that differed by a factor of 2.9. No shift in the most probable separation distance was discernible.

Hydrodynamic forces are present during the period of fluid motion and can also be measured if the procedure is modified. To obtain each value of separation distance for Fig. 2 or Fig. 3, we allowed the fluid to flow for about 30 seconds; this was followed by a 10-minute rest period with no flow. If the rest period is omitted, the results become strongly dependent on flow rate. For example, in a solution of 98.1 percent glycerol, the most probable separation distance for a 9.2-μm particle increased from 0.2 to 1.2 μm when the flow rate was increased by a factor of 1.7. Apparently the increment in separation that occurs during a single 30-second interval of flow is insignificant compared with the amount of random Brownian motion that occurs during the 10-minute rest period; but, if the rest period is omitted, these small increments accumulate to produce a significant change in separation distance.

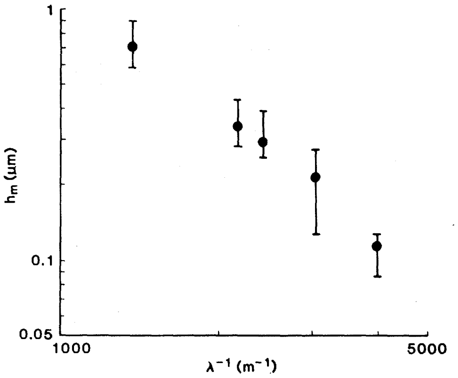

Fig. 3. Effect of salt concentration on the most probable particle-wall separation distance. The bar denotes the range of h_m observed for a number of different particles, and the point denotes their mean. The abscissa is proportional to the square root of the salt concentration. A decrease in the most probable separation indicates a weakening of double-layer repulsion.

When the fluid is in motion a sufficiently small fraction of the time, hydrodynamic forces do not significantly change the distribution of particle-wall separation distances determined by this technique, as demonstrated by the insensitivity of the measured distribution to changes in flow rate. On the other hand, increasing the salt concentration significantly decreases the most probable separation distance, an indication that double-layer repulsion does contribute to the interaction.

REFERENCES AND NOTES

1. E. J. W. Verwey and J. Th. G. Overbeek, *Theory of the Stability of Lyophobic Colloids* (Elsevier, New York, 1948).
2. D. Gingell and J. Fornes, *Nature (London)* **256**, 210 (1975).
3. ———, *Biochem. J.* **16**, 1131 (1976).
4. V. A. Parsegian, *Annu. Rev. Biophys. Bioeng.* **2**, 221 (1973).
5. J. N. Israelachvili and G. E. Adams, *J. Chem. Soc. Faraday Trans. 1* **74**, 975 (1978).
6. R. M. Pashley, *J. Colloid Interface Sci.* **83**, 531 (1981).
7. ——— and J. N. Israelachvili, *ibid.* **97**, 446 (1984).
8. A. J. Goldman, R. G. Cox, H. Brenner, *Chem. Eng. Sci.* **22**, 653 (1967).
9. Other fluid properties at 25°C include a viscosity of 2.88 cpoise, a density of 1.09 g/cm^3, and a dielectric constant of 69.50.
10. J. N. Israelachvili and G. E. Adams, *Nature (London)* **262**, 774 (1976).
11. V. A. Parsegian, in *Physical Chemistry: Enriching Topics from Colloid and Surface Science,* H. Van Olphen and K. J. Mysels, Eds. (Theorex, La Jolla, CA, 1974), p. 27.
12. B.M.A. was supported by a fellowship from Calgon Corporation. The results summarized here were taken from her thesis (Carnegie-Mellon University, 1985). Financial support was also provided by the National Science Foundation.

23 July 1985; accepted 8 November 1985