Electrokinetic Transport of Heterogeneous Particles in Suspension

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Abstract

The Smoluchowski equation for electrophoresis predicts that the electrophoretic velocity of a particle is proportional to its zeta potential but not its size, shape, or orientation. Furthermore, the equation predicts that the rotation rate is identically zero. The Smoluchowski equation fails for *heterogeneous particles* (i.e., those with non-uniform zeta potentials). Recent theories and experiments show that particles with a dipole moment of zeta potential rotate into alignment with an externally applied electric field. For doublets (particles composed of two spheres) the rotation rate depends on 1) whether the spheres are rigidly locked or freely rotating, and 2) the gap distance between the spheres. The relative configuration of two coagulated spheres is determined by the colloidal forces of the system. The goal of our research is to use measurements of electrophoretic rotation to determine the gap between two spheres of a colloidal doublet and also to determine whether or not the doublet is rigid.

Introduction

Almost all colloidal particles immersed in aqueous solution are electrically charged. The electrostatic potential at a particle's surface is called the zeta potential. To maintain electroneutrality oppositely-charged ions (counter-ions) from the solution form a thin layer near the surface. Together the charged solid surface of the particle and the surrounding layer of oppositely-charged fluid compose the electrical *double layer*.

When an electric field is applied to a suspension of colloidal particles, the field interacts with the electrical double layer, and the resulting forces move the particle. This movement is called *electrophoresis*, one of several *phoretic* processes [1]. The Smoluchowski equation predicts

$$U = \frac{\varepsilon \zeta}{\eta} E^{\infty} \qquad \text{(1a)}$$
$$\Omega = 0 \qquad \text{(1b)}$$

where U is the translational velocity of the particle, Ω is its rotation rate, ε is the permittivity of the bulk fluid, η is the viscosity, and E^{∞} is the applied electric field. The Smoluchowski equation requires three main conditions:

1. The particle must be rigid and non-conducting.
2. The double layer thickness (of order κ^{-1}, the Debye screening length) must be much smaller than the size of the particle (i.e., the radius for a spherical particle).
3. The zeta potential must be uniform over the surface.

Equation (1) applies to any particle that satisfies these conditions, independent of its size or shape. Typically, ζ is of order $kT/e = 25.7$ mV at 25 °C, and in water the electrophoretic mobility (U/E^{∞}) for this zeta potential is 2.0 μm s^{-1}/V cm^{-1}.

HETEROGENEOUS PARTICLES

Many particles have non-uniform zeta potentials over their surfaces—they are heterogeneous. Kaolinite clay particles, which have the shape of a disk, may have different zeta potentials on each face and yet a third zeta potential on the edge. Aggregates are nonuniform when the original subunits have different zeta potentials. *Heterogeneous particles (those with a non-uniform zeta potential over their surface) do not obey the Smoluchowski equation.*

Figure 1 shows examples of heterogeneous particles and references to theories describing their electrophoretic motion. Here we summarize the theory for doublets [2]:

$$U_p = \frac{\varepsilon}{\eta}[\zeta_1(1-K^p)+\zeta_2 K^p]E^\infty \qquad (2a)$$

$$U_n = \frac{\varepsilon}{\eta}[\zeta_1(1-K^n)+\zeta_2 K^n]E^\infty \qquad (2b)$$

$$\Omega = -\frac{d\theta}{dt} = \frac{\varepsilon}{\eta}\left(\frac{\zeta_2-\zeta_1}{a_2+a_1}\right)N E^\infty \sin(\theta) \qquad (2c)$$

Equation (2a) describes the translation of a colloidal doublet when its axis is parallel to the electric field, and (2b) describes the translation when the axis is normal to the electric field. Equation (2c) gives the angular velocity of the doublet as a unit. The values of K^p, K^n, and N—three geometric parameters—depend on the ratio of the sphere radii (a_2/a_1) and the dimensionless gap ($\lambda=\delta/(a_1+a_2)$), where δ is the separation between the surfaces of the spheres). In addition these geometric parameters depend on whether the spheres composing the doublet are rigidly locked or freely rotating. Figure 2 shows how the value of N (the rotation rate parameter) depends on λ. Not only is N sensitive to the gap, but N>1 for *freely rotating spheres* and N<1 for *rigid doublets*. The values of N are calculated from the results of Keh and Yang [3].

COLLOIDAL DOUBLETS AND THE GAP BETWEEN TWO COAGULATED SPHERES

The DLVO theory of coagulation predicts two potential energy minima for the two spheres of a doublet [4]. Figure 3 shows the how the potential energy varies with gap distance for two spheres with the same zeta potential. When the spheres touch (i.e., $\lambda=0$), the particles lie in a deep *primary* energy minimum; in this case, the doublet is expected to be rigid.

When the spheres have the same charge, they can also be stable in a *secondary* energy minumum. The secondary minumum lies at distances comparable to the Debye screening length κ^{-1}, and it is not as deep as the primary minumum. The gap is finite ($\lambda>0$) for spheres in a secondary minumum, so not only can the doublet rotate as a unit but each sphere can also rotate independently.

Van de Ven and Mason [5] used shear flows to determine whether colloidal doublets were rigidly locked or freely rotating. They measured the period of rotation (T) of the Jeffrey orbitals of symmetric doublets ($a_2/a_1=1$). Because T is a function of λ, the gap distance could, in principle, be determined from these measurements. Van de Ven and Mason found that a significant number of doublets had $\lambda>0$; that is, the two spheres of a doublet appeared to be freely rotating according to the measured value of T. Unfortunately, the difference between T for a doublet of freely rotating spheres compared to rigidly locked spheres is not as large as one would like in order to make definitive conclusions about the relative configuration of the spheres.

Electrophoretic rotation, on the other hand, appears to be a sensitive probe of the rigidity of doublets—if N>1 then the spheres of the doublet are freely rotating; otherwise the doublet is rigid. In addition, the value of N can provide an estimate for the gap distance.

EXPERIMENTS AND PRELIMINARY DATA

We form aggregates by mixing two dilute suspensions of different polystyrene spheres [6]. The two spheres can have zeta potentials of the same sign but different magnitudes, or zeta potentials of opposite sign. The important distinction between these two cases is that in the former, DLVO theory predicts the existence of a secondary potential minumum which should allow free rotation of the spheres, whereas in the latter case no secondary minumum is predicted. The particle diameters for our experiments are in the range of 1 to 5 μm. Using a VCR and simple imaging analysis, we determine the orientation angle $\theta(t)$ (Figure 4). These data are fit to the integrated form of equation (2c). Figure 5 shows data from one experiment ($a_2/a_1 \approx 1.5$). The best fit between the data and (2c) is $N = 1.68 \pm 0.20$ (95% confidence interval).

Because $N>1$ in these experiments, we conclude that the two spheres in the doublet were *freely rotating*. The curve in Figure 2 (this curve is for equal-sized spheres, but for other size ratios the curve changes little) shows that $N = 1.7$ corresponds to $\lambda=0.001$, or roughly $\delta=2$ nm. For this experiment we measured only $\zeta_2 - \zeta_1$ (i.e., not each zeta potential separately), so we cannot compare the value of δ to the predictions of existing theories of doublet configuration based on colloidal forces.

Future experiments are aimed at measuring N as a function of electrolyte concentration (i.e., Debye screening length). The zeta potentials of the single spheres (i.e., ζ_1 and ζ_2) will be determined *in situ*. Latexes with ζ_1 and ζ_2 of opposite sign and the same sign will be studied. The goal is to probe the configuration of doublets—specifically the gap distance and whether they are rigid or not—and to compare the results with theories for the colloidal forces between the particles.

ACKNOWLEDGEMENT

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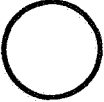
Figure 1: Theory for non-uniformly charged particles

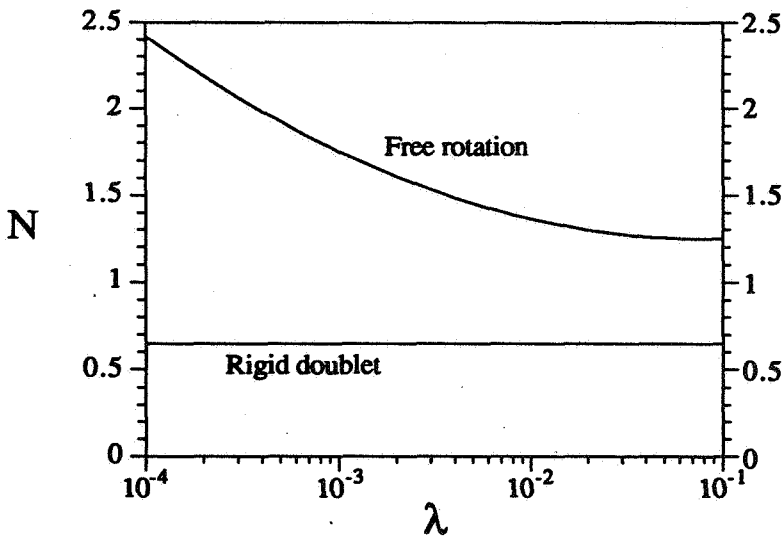|		
Spheres		Anderson *et al.* *JCIS* **105**, 45 (1985) *JCIS* **158**, 1 (1993)
Ellipsoids		Fair and Anderson *JCIS* **127**, 388 (1989)
Doublet		Fair and Anderson *Int. J. Multiphase Flow*, **16**, 663, 1131 (1990) *Langmuir*, **8**, 2850 (1992)
Triplet		Keh and Yang *JCIS* **145**, 362 (1991)
Spherical Macromolecule		B. Yoon *JCIS* **142**, 575 (1991)
Clay disk		Anderson and Fair Proceedings 1991 Coating Conference, TAPPI, Atlanta

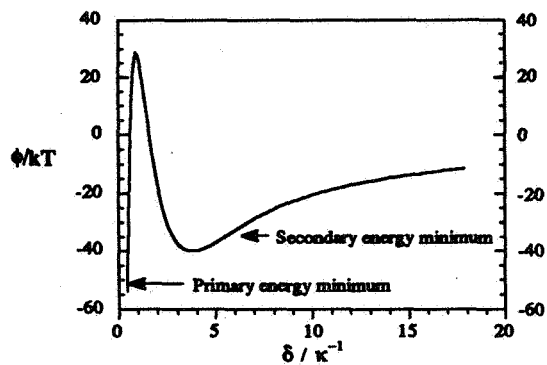Figure 2: Rotation rate parameter N versus gap for a doublet of two equal size spheres.

Figure 3: Potential energy vs. gap distance for two identically charged colloidal particles.
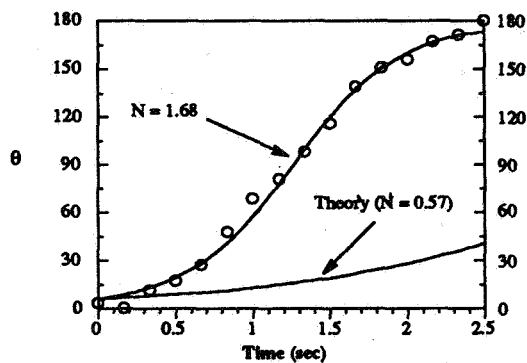

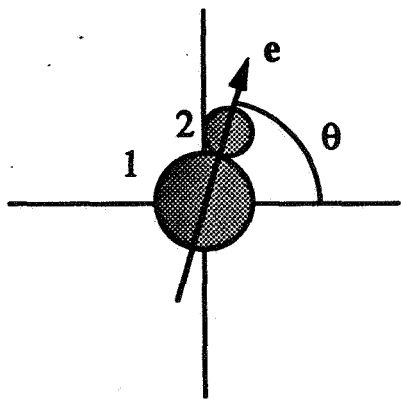Figure 4: Sample data fitted to integrated form of equation (2c).

Figure 5: Orientation of the doublet. Theta is the solid angle between the direction of the applied field and the axis of the doublet.