

Pattern Formation in Nonaqueous Colloidal Dispersions via Electrohydrodynamic Flow

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We describe a new electrohydrodynamic phenomenon observed in inhomogeneous, nonaqueous colloidal dispersions with a spatially varying particle number concentration. In the presence of an external electric field, the dielectric constant and conductivity gradients in these systems engender fluid motion which results in the formation of patterned colloidal structures: columns, disks, and other more complicated structures. Other workers found similar effects in high conductivity systems, where the particles are dispersed in water with dissolved electrolyte. Our experimental results with barium titanate dispersed in low conductivity, apolar liquids indicate that electrical forces due to free charge and dielectric constant variations each play a role in inducing flow. This pattern forming phenomenon differs from previously observed field-induced pattern formation in colloidal dispersions (e.g., colloidal string formation in electrorheological and ferrofluids) largely as a result of the induced fluid flow. A mathematical model has been developed which predicts, qualitatively, the initial flow patterns encountered in our system. The theory may also help explain the formation of more complicated field-induced particle morphologies which have been reported in aqueous and nonaqueous media as well as the observation of dispersion band broadening during electrophoresis.

I. Introduction

The formation of patterned colloidal structures has many applications in materials processing. Examples include catalytic support honeycombs produced by extrusion,¹ hierarchical electronic devices made with ceramic multilayers (e.g., computer multichip modules),² electrorheological fluids,^{3–7} and “smart materials” (e.g., detectors and actuators) formed from patterned composites.⁸ Moreover, nested levels of structural hierarchy in composite materials can impart vastly superior properties over a homogeneously structured material.^{9–11} This is a design feature which is readily exploited in biological materials (e.g., bone, abalone shell, muscles, and tendons) where subtle differences in structure over various length scales can lead to major differences in the performance characteristics. Indeed, these enhanced performance characteristics have sprouted a new field of materials design known as biomimetics, with the goal of mimicking the hierarchical structures found in biological materials.¹² Due to the intrinsic dimensional limitations of mechanical forming, pattern formation in man-made materials has hitherto been restricted to length scales larger than a few tens of micrometers. We have been investigating the use

of forces which act directly on nonhomogeneous regions in a colloidal dispersion so as to manipulate colloidal structure on smaller length scales.¹³ Here we describe a novel example of this approach, to form patterned colloidal dispersions via electrohydrodynamic manipulation, a technique free of many of the limitations of mechanical forming. A brief account of this work recently appeared in a letter to *Nature*.¹³ In this paper, we provide a full account of the experimental techniques, the observations, and the underlying theory.

Electrohydrodynamics is the study of fluid motions which arise as a result of an applied electric field. Electrohydrodynamic deformation of liquid/liquid interfaces, in particular, the deformation of liquid droplets surrounded by a second fluid, has been the subject of extensive studies.^{14–22} The common feature in these systems is the use of weakly conducting organic fluids and the existence of a liquid/liquid interface. Upon application of an electric field, droplets can be deformed into either an oblate or prolate shape, depending on the ratios of the conductivities and dielectric constants between the inner and outer fluid of the droplet. The currently accepted model for this type of deformation was proposed by Taylor in 1966.¹⁴ In his model, known as the “leaky dielectric” model, the liquids are considered to have small conductivities so, when an electric field is applied, free charge appears at the drop interface. The action of the electric field on this charge sets the fluid in motion and toroidal circulation patterns are formed inside and outside the droplet, resulting in deformation. Measure-

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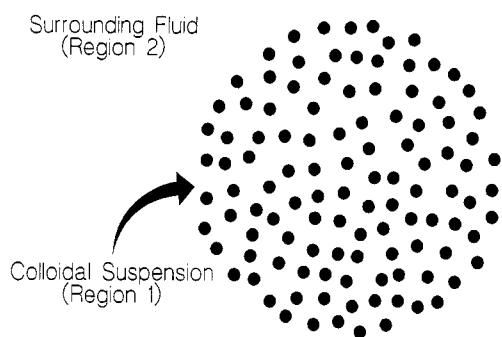


Figure 1. Schematic diagram of our model system. A spherical particle-containing bolus (region 1) nested inside clear ambient fluid (region 2).

ments of the extent of this deformation conform with the Taylor model.²² Electrohydrodynamic motions have also been observed in aqueous colloidal dispersions and our work has been informed by the work of Rhodes *et al.*²³ on polystyrene particles suspended in electrolytes.

We are interested in the electrohydrodynamic deformation of inhomogeneous colloidal dispersions. The simplest example of such a system is that of a spherical, particle-containing region (bolus)—region 1—nested inside clear ambient fluid—region 2 (Figure 1). This system differs from droplets suspended in a second phase in that the boundary layer between regions 1 and 2 is a gradual transition between the suspension and the clear fluid and is devoid of interfacial tension. The thickness of this transition region is determined by a combination of Brownian diffusion and sedimentation. Because of the particles (or the composition of the fluids), the dielectric constant and conductivity of region 1 differ from those of region 2. The mismatch between the dielectric constants of the two regions results from intrinsic differences between particles and fluid and polarization of any diffuse double layer (ion cloud) around each charged particle. Differences in conductivity arise from the following factors: (i) particles impede ion flow and hence reduce the conductivity; (ii) dissolved ions from the particle surfaces increase the local conductivity; (iii) the conductivity of region 1 or 2 may be artificially increased by selectively dissolving a soluble salt. Left on its own and given time to come to equilibrium, the system will become completely mixed via Brownian motion or form a flat layer of particles due to sedimentation. When subject to an electric field, the transition layer between regions 1 and 2 (i.e., the region where ϵ and σ vary spatially) experiences an anisotropic electrostatic body force. This sets the suspension in motion and distorts the shape of the bolus. If the mismatch in conductivity and dielectric constant is large enough, the electrohydrodynamic force will be dominant. It is this force that we exploit to manipulate the structure of a colloidal dispersion. Once colloidal patterns are formed, these structures can be “frozen” in place by solidifying the fluid matrix via gelation or polymerization.^{24,25} Moreover, using electrohydrodynamic flows to manipulate colloid structures prior to solidification offers a new route to advanced ceramic manufacture.

The electrohydrodynamic patterning phenomenon under study here differs significantly from previously observed field-induced pattern formation in homogeneous

colloidal dispersions (e.g., colloidal string formation in electrorheological and ferrofluids).^{3–7,24–28} The commonly accepted patterning mechanism in such systems is via dipole–dipole interactions between suspended particles induced by the presence of either an electric or magnetic field. This is not the mechanism which operates here. Our phenomenon derives from bulk motion brought on by electrical body forces lodged in the suspension, not forces on individual particles. This motion carries particles along with it irrespective of small scale structure, although this structure may affect the details. Bulk motion cannot be explained solely by dipole–dipole interactions between suspended particles.

II. Experimental Section and Discussion

We worked with 100 nm barium titanate (BaTiO_3) particles prepared via a hydrothermal process^{29,30} and dispersed in castor oil (Aldrich). Barium titanate was chosen because it has an extremely high dielectric constant,³¹ typically between 300 and 10 000, depending on its crystalline form, and is a technologically useful material in both the electronic and optical component industries.^{32,33} Castor oil was chosen as the fluid medium because (i) it has a low conductivity ($\sigma = 1.8 \times 10^{-11} \text{ S m}^{-1}$), (ii) fatty-acid based oils are good dispersing media for barium titanate particles,³⁴ (iii) its conductivity may easily be varied over a wide range by doping with small amounts of soluble organic salts (e.g., tetrabutylammonium tetraphenylborate, TBATPB), and (iv) its viscosity is similar to those of polymerizable silicone oils used to prepare colloidal barium titanate structures within a solid silicone polymer matrix.^{24,25} To form a system similar to that depicted in Figure 1, a dilute dispersion of barium titanate particles (0.025 vol %) in castor oil was injected into clear castor oil fluid via a pinhole in a metal electrode. Slow injection of the dispersion into the clear fluid results in a spherical bolus of the dispersion nested within clear castor oil (cf. parts a and e of Figure 2). The $4 \times 4 \text{ cm}$ metal electrodes were 1.5 cm apart; the diameter of the colloidal bolus was approximately 5 mm.

Two experiments were performed to illustrate the importance of the conductivity mismatch in setting the direction of flow. In the first experiment, the conductivity of the dispersion was artificially adjusted to be higher than the conductivity of the clear fluid by dissolving a trace amount of an organic salt (0.2 mM of TBATPB) in the BaTiO_3 dispersion prior to injection. In the second experiment, the conductivity mismatch was reversed by dissolving the organic salt in the clear castor oil prior to injecting the dispersion. The measured conductivity of a 0.2 mM solution of TBATPB in castor oil was $2.28 \times 10^{-9} \text{ S m}^{-1}$, approximately 100 times higher than that of neat castor oil. Figure 2 illustrates the results for both experiments as two series of video images taken after the application of a 2000 V cm^{-1} electric field and separated by a time interval of approximately 0.2 s. In sequence a–d (with higher conductivity on the inside), the spherical bolus deforms immediately in the direction of the applied

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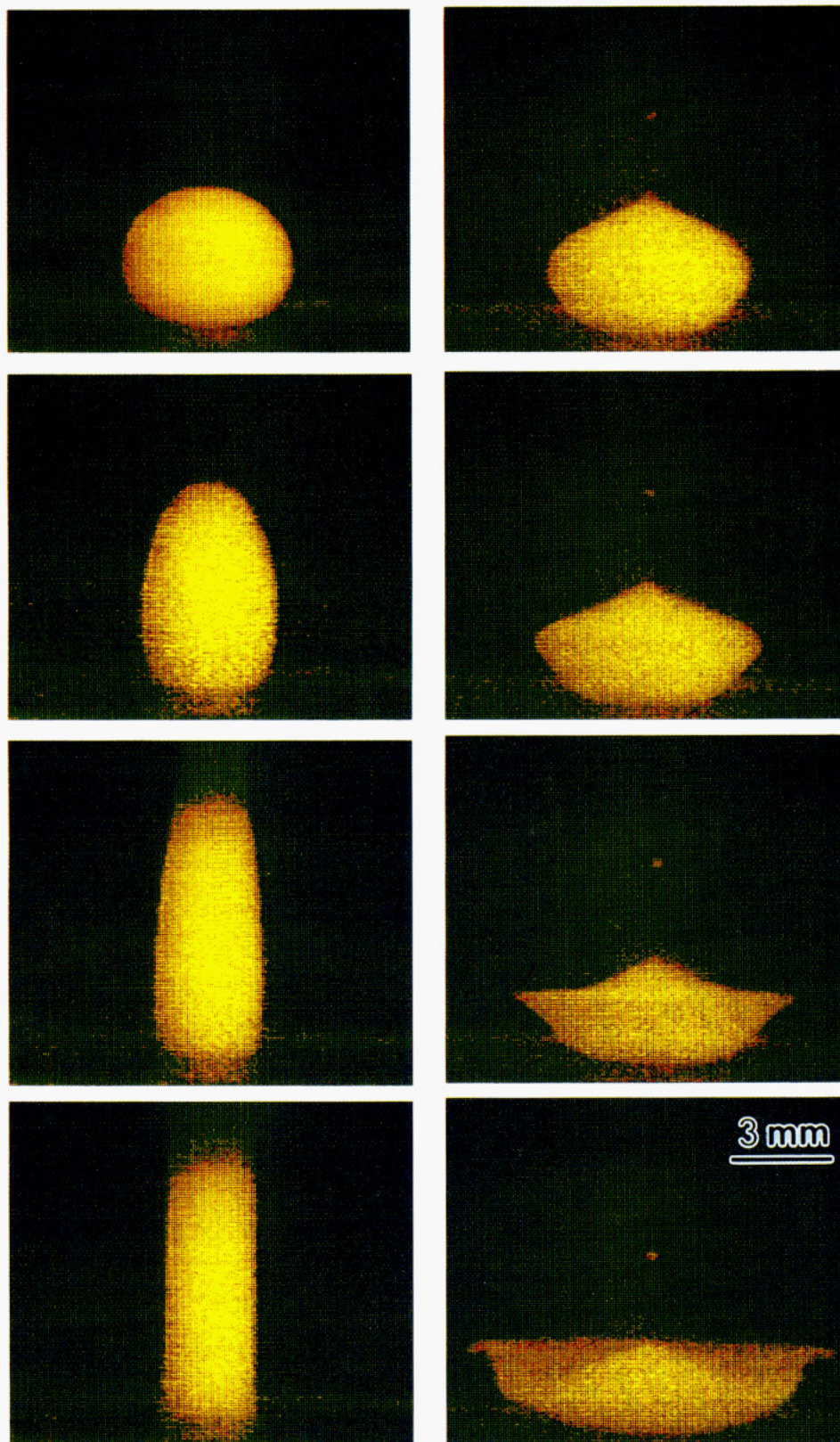


Figure 2. Two examples of the deformation of a colloidal dispersion via an applied electric field. Panels a–d (left) and e–h (right) are video image sequences taken after a steady dc field was applied to a spherical cloud of BaTiO_3 dispersion nested inside clear castor oil fluid. The BaTiO_3 dispersion was comprised of 100 nm BaTiO_3 particles dispersed in castor oil at 0.025% volume fraction. The resulting photographs have been artificially colorized to enhance the contrast between particle containing regions and clear fluid. In the two experiments the conductivity mismatch between the inner and outer bolus region was reversed by selectively dissolving a trace amount of tetrabutylammonium tetraphenylborate ($0.2 \times 10^{-3} \text{ mol dm}^{-3}$) either in the inner region, sequence a–d, or in the surrounding clear fluid, sequence e–f. In both cases the magnitude of the applied field was 2000 V cm^{-1} , applied in a vertical direction. The time interval between panels is approximately 0.2 s.

field and continues to stretch out until it collides with the top electrode to form a near-perfect column. The column remains intact for several seconds until the disturbance

generated at the top of the column (see Figure 2d) propagates down the entire length of the column. In the part e–h sequence, a dramatically different flow pattern

is engendered by the field. Here the spherical bolus deforms orthogonal to the applied field, forming a disklike shape which continues to expand laterally. After some time, a film forms across the bottom electrode. Steady (dc) fields were used to generate all of the patterns shown in Figure 2 but the direction and speed of the motion are insensitive to field polarity. Similar flow patterns are induced by applying low frequency ac fields (approximately 100 Hz) which shows that the particle motions are not the result of electrokinetic phenomena.

Similar flow patterns are also induced if the effective dielectric constant of the dispersion is made to be less than that of the surrounding fluid. This is done by dispersing silica particles (100 nm in diameter with $\epsilon \sim 2$, Bangs Laboratories) in castor oil ($\epsilon = 4.43$) and injecting this mixture into clear castor oil fluid as before. The conductivity of the inner region of the resulting spherical dispersion bolus can be adjusted to be higher or lower than the surrounding clear fluid in an identical manner to that of the previous experiment. Upon application of the electric field the spherical bolus undergoes a deformation identical with that observed with the barium titanate dispersion (i.e., prolate for higher and oblate for lower inner conductivity). This result suggests that the dielectric constant mismatch in these systems is overwhelmed by effects due to the conductivity contrast. This differs from behavior predicted for nonuniform colloidal dispersions subject only to the dipole force.³⁵ There the bolus flow pattern should *reverse* direction when the dielectric constant mismatch is reversed. To explain the observed behavior, we postulate the influence of an additional electrical force which results from the accumulation of free charge in the transition layer between the suspension and clear fluid. A theory which takes this effect into account is presented in the next section. To further test this hypothesis, an experiment was performed with no colloidal particles present in the spherical bolus (i.e., no dielectric constant mismatch between the inner and outer region). The inner region contained only dissolved salt (tetrabutylammonium tetraphenylborate) and an inert dye ("Oil Red", Aldrich) used to visualize the flow. Application of the electric field in this experiment resulted in a flow pattern identical with that shown in Figure 2. The combination of all three experiments demonstrates that the electrical body force resulting from gradations in dielectric constant is not the only force responsible for the observed electrohydrodynamic flow in these systems.

These results illustrate how the flow pattern around a bolus can be manipulated by adjusting the conductivity mismatch between the inner and outer regions. To achieve useful pattern formation in these systems, however, the deliberate manipulation of colloidal structure over long periods of time is of much greater interest. For this technique to be useful for any of the applications mentioned earlier, it must be capable of two functions: first, colloidal patterning must be achieved on small (mesoscopic) length scales; second, these colloidal structures must remain stable for a sufficiently long time to enable the surrounding fluid to be solidified via, for example, polymerization or gelation techniques. Unfortunately, the long-time evolution of such patterns is extremely difficult to predict for a number of reasons: (i) any fluid motion will deform the sample and alter the conductivity and dielectric constants from their initial values; (ii) the morphology of the transition layer (i.e., both the ion and particle concentration profiles) will change as a result of electrohydrodynamic, diffusion, and sedimentation induced flow. Gen-

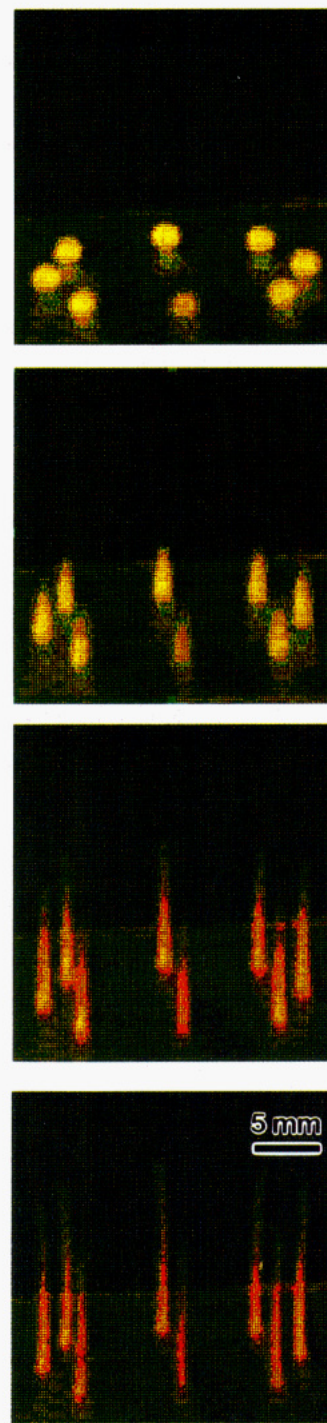


Figure 3. Formation of multiple colloidal columns/spikes via electrohydrodynamic flow. Parts a–d (top to bottom) represent a sequential series of video images taken after a steady dc field (500 V cm^{-1}) was applied to eight identical spherical boli of the BaTiO_3 dispersion described in Figure 2. The separation distance between columns is 7 mm. The slight bow in these columns is thought to be due to a hydrodynamic interaction between the columns and the vessel wall or between adjacent columns.

erally, the transition layer will become more diffuse with time. Given these difficulties, a detailed theoretical analysis for long-time pattern evolution has not yet been attempted. Preliminary experiments, however, look promising in view of the above application requirements. Figure 3 shows the simultaneous deformation of eight identical spherical BaTiO_3 suspension boli into a ringed columnar structure via the application of a steady dc field (500 V cm^{-1}). This type of slow deformation results in a

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columnar structure from each individual bolus. At the tip of each column a sharp spike forms, which continues to sharpen parallel to the direction of the field, stretching the column to a gradually finer diameter. Shortly after the formation, the sharpness of this spike is beyond the resolution of the human eye. An attempt to measure the thickness of the colloidal spike was made by focusing a green argon-ion laser beam ($\lambda = 488$ nm, approximately 200 mW, Lexel, Inc.) onto the spike tip and recording the resulting diffraction line spacings, projected onto a screen 4 m from the sample. Laser diffraction is a standard method used for the determination of fiber thicknesses in the diameter range of 1–100 μm .³⁶ The sensitivity of the method is limited by the refractive index mismatch between the fiber, in this case the colloidal column, and the surrounding medium. Given the low volume fraction of particles in our suspension, this mismatch is expected to be quite small and hence limit the sensitivity of the measurement. In our samples, the thinnest part of the colloidal fiber which gave rise to a detectable diffraction pattern corresponded to a thickness of 30 μm . We concluded that the thicknesses of the colloidal spikes produced in this manner were less than 30 μm . By applying a low frequency ac field (e.g., 4000 V cm^{-1} , 100 Hz), the colloidal spikes shown in Figure 3 are formed over a much larger time period and remain stable for periods greater than 3 h before any evidence of dissipation. This time is sufficient to enable polymerization of the ambient fluid, as previously described,^{24,25} so as to permanently retain the colloidal structure formed via the electrohydrodynamic flow. Obviously, the formation of such structures is not limited to forming only eight columns at a time. Since each of the columns shown in Figure 3 is similar, it should be easy to extrapolate this process to form large numbers of colloidal columns/fibers simultaneously. Multiple thin films may also be formed in this manner.

Another simple approach to forming complicated colloidal patterns is to change the initial shape of the colloidal region nested within the clear fluid. The structures formed by the electrohydrodynamic flow depend on the initial configuration of the dispersion, and with other arrangements complex, sometimes disordered, structures ensue. This is illustrated in Figure 4, which shows the plan view of a flat layer of a 0.025 vol % BaTiO_3 dispersion in castor oil covered with clear castor oil fluid. Glass electrodes are used so as to view the colloidal dispersion. Upon application of a steady dc field (500 V cm^{-1} , directed out of the page) a regular cellular structure forms, which evolves into a more complex pattern as a result of the electrohydrodynamic flow. This experiment clearly illustrates the complex nature of the process and more detailed analysis of this situation is needed in order to predict the evolution of such structures with time.

We believe that the "pancake" experiment displayed in Figure 4 may be similar to the Rayleigh–Bernard instability,^{37,38} where an unstable stratification of liquid density is set up in a fluid by heating uniformly from below. In such systems, patterned convective flow is observed, usually with a hexagonal cellular structure, once a critical temperature gradient is established. In Figure 4b, similar "hexagon-like" convection patterns are observed at the initial stages of the electrohydrodynamic flow once a field is applied. The motion in this case results from electrostatic (i.e., Coulombic and polarization) rather than gravitational body forces acting on the fluid. In this

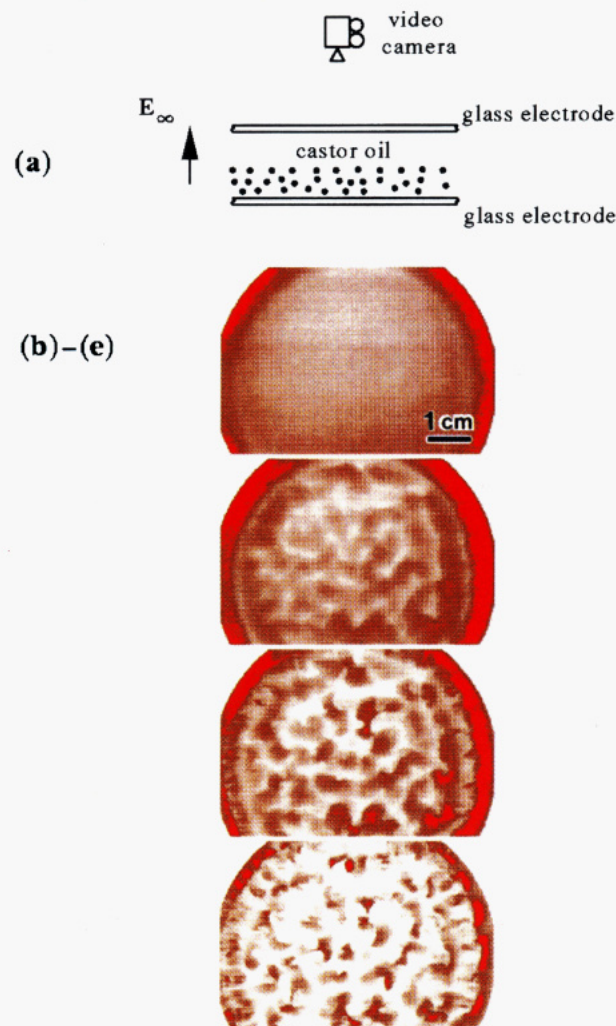


Figure 4. (a) Schematic representation of the apparatus used to obtain a plan view of the BaTiO_3 dispersion layer. (b) Sequential video images of the dispersion layer after the application of a steady dc field (500 V cm^{-1}).

problem there may be a critical value for the electrostatic field strength, rather than the temperature gradient, which sets the fluid in motion. Nevertheless, much of the similarity between these two systems ends here, because as soon as the liquid is set into motion, the evolution of the conductivity and dielectric constant distributions differs from that of the density distribution in the Rayleigh–Bernard problem.

III. Electrohydrodynamic Theory

In the situations just described, motion arises from two sorts of electrical body forces, one stemming from a polarization force derived from gradations in the dielectric constant and the other due to the action of the applied field on induced free charge. To synthesize a theoretical description, we link Maxwell's theory for electrical phenomena to the equations describing the mechanics of the flow. Our analysis builds on those of Rhodes et al., who considered the deformation of a cylinder with a sharp interface,²³ and Saville,³⁵ who analyzed an object with a diffuse interface. Differences with these two approaches arise from (i) considering a diffuse interface and (ii) accounting for the generation of a volumetric free charge whenever there is a gradation in conductivity and dielectric constant. Electric forces can be described in

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terms of Maxwell's stress tensor or as a body force,³⁹ i.e.

$$\mathbf{f}_e = -\frac{1}{2}\epsilon_0 \mathbf{E} \cdot \nabla \mathbf{E} + \rho_e \mathbf{E} \quad (1)$$

The symbols are $\mathbf{f}_e$, the electric body force per unit volume, ϵ_0 , the permittivity of free space, $\mathbf{E}$, the electric field strength, ∇ , the gradient of the local dielectric constant, and ρ_e , the free charge per unit volume. Gradations in the dielectric constant arise from the factors mentioned earlier. Free charge stems from the action of the applied field on ions that carry the current. To calculate the flow field arising from these electrical body forces when the flow is slow, the Stokes equations must be solved for the velocity, $\mathbf{u}$, and pressure, p , in a fluid with viscosity, μ , viz.

$$\mathbf{0} = -\nabla p + \mathbf{f}_e + \mu \nabla^2 \mathbf{u} \quad \nabla \cdot \mathbf{u} = 0 \quad (2)$$

Clearly, one must know how the electric field is distributed to solve these equations. The field is governed by

$$\nabla \cdot \epsilon_0 \mathbf{E} = \rho_e \quad (3)$$

and the charge density is related to the ion concentrations by

$$\rho_e \equiv \sum_{k=1}^N e z^k n^k \quad (4)$$

Here e is the charge on a proton and z^k is the valence of the k th ionic species whose concentration is n^k . Ions are carried by the flow and move in response to gradients in the electrochemical potential, so if we denote the mobility of the k th ionic species by ω^k , the conservation equation is

$$\mathbf{u} \cdot \nabla n^k = \nabla \cdot [-\omega^k e z^k n^k \mathbf{E} + \omega^k k_B T \nabla n^k] \quad (5)$$

$$k = 1, \dots, N$$

Here k_B is Boltzmann's constant and T is the absolute temperature. Since magnetic effects are small, the electric field is irrotational and we can write the field as the gradient of a potential, ϕ

$$-\nabla \phi = \mathbf{E} \quad (6)$$

These equations are too complex to solve in any general sense but useful insight can be gained by studying simplified forms. Our objective is to decide how a nonuniform dispersion will deform so tractability is important. To help decide on the elements of the simplified model, we analyze an equation for charge conservation and restrict attention to situations where the mobilities of all ions are the same, as denoted by ω , and the dielectric constant distribution is known. Upon multiplying eq 5 by $e z^k$ and adding the equations for each ion species, we obtain the charge conservation equation as

$$\mathbf{u} \cdot \nabla \rho_e = \nabla \cdot [\sigma \nabla \phi + D \nabla \rho_e] \quad (7)$$

where $\sigma \equiv \sum_{k=1}^N (e z^k)^2 \omega n^k$ is the conductivity and D is the ion diffusivity, $\omega k_B T$. Now if the contributions from convective transport, $\mathbf{u} \cdot \nabla \rho_e$, and diffusive transport, $\nabla \cdot [D \nabla \rho_e]$, are small compared to conduction, $\nabla \cdot [\sigma \nabla \phi]$, then the structure of the electric field will be determined by conduction and the charge distribution follows from Gauss'

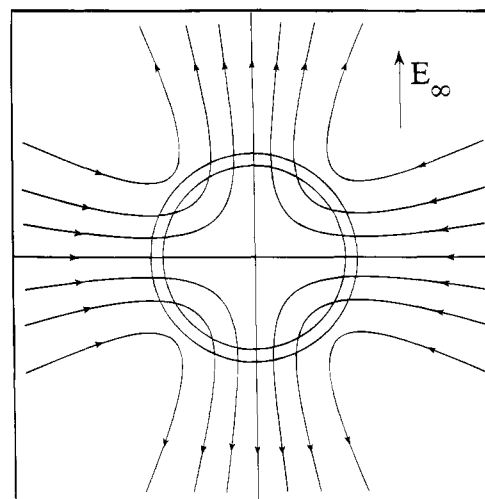


Figure 5. Streamline pattern for flow engendered by a circular shaped cloud of a dispersion immersed in a clear fluid with a lower conductivity and dielectric constant calculated from the model set here.

law, eq 3. An order-of-magnitude analysis can be used to assess the relative magnitudes.

The situation under study differs from those commonly encountered in electrokinetics where free charge exists in the equilibrium state due to the presence of charged interfaces. Here we study systems on a length scale where, in the absence of an external field, there is no free charge; free charge is induced in the bulk by the field as it adjusts itself to ensure conservation of charge. Denoting the magnitude of the applied field as E_∞ and the length scale as l , it follows from eq 3 that the charge density is $\mathcal{O}(\epsilon_0 E_\infty / l)$. From the Stokes equation we see that the velocity is $\mathcal{O}(\epsilon_0 E_\infty^2 l / \mu)$ so that the convective term in eq 7 is $\mathcal{O}(\epsilon_0^2 E_\infty^2 / \sigma \mu)$ relative to the term representing current carried by conduction. The diffusive term is $\mathcal{O}(\epsilon_0 D / \sigma l^2)$ compared to conduction. To estimate the orders-of-magnitude we choose $l \approx 1$ mm, $E_\infty \approx 10^5$ V/m, $D \approx 10^{-10}$ m²/s, $\sigma \approx 10^{-9}$ S/m, and $\mu \approx 10^{-2}$ kg/ms, typical values for the phenomena under study in low dielectric constant liquids. Thus $(\epsilon_0^2 E_\infty^2 / \sigma \mu) \approx 10^{-1}$ and $(\epsilon_0 D / \sigma l^2) \approx 10^{-6}$. Accordingly, we can approximate the electric potential by solutions of

$$\nabla \cdot [\sigma \nabla \phi] = 0. \quad (8)$$

In a general model one would need to track the ion densities to calculate the local electric conductivity and have an evolution equation for the dielectric constant. In situations involving dispersions, the particle distribution must be calculated as it evolves due to electrical and hydrodynamic forces. However, a qualitative picture can be obtained from a simple model where the dielectric constant and conductivity distributions are prescribed. This has been done for situations where a uniform transverse electric field, E_∞ , acts on a circular region of radius a with dielectric constant ϵ_s and conductivity σ_s , surrounded by a region with properties σ_∞ and ϵ_∞ . Each property varies smoothly in the transition zone of thickness δ (see Figure 5). Since the situation is two-dimensional, the solution is relatively straightforward. First, eq 8 can be converted to an ordinary differential equation for the potential since the field varies as $\cos \vartheta$ for one that is uniform at infinity; here ϑ is the angle measured from the direction of the field. Thus

$$\phi = R(r) \cos \vartheta \quad (9)$$

and the differential equation for $R(r)$ is

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$$R'' + [r^{-1} + S(r)]R' - r^{-2}R = 0 \quad (10)$$

with

$$S(r) \equiv \frac{1}{\sigma(r)} \frac{d\sigma}{dr} \quad (11)$$

To represent the conductivity distribution we choose

$$\begin{aligned} \sigma &= \sigma_s & 0 < r < a \\ \sigma &= \frac{1}{2} \left[\bar{\sigma} + \Delta\sigma \cos \left[\frac{\pi(r-a)}{\delta} \right] \right] & a < r < a + \delta \\ \sigma &= \sigma_\infty & a + \delta < r < \infty \end{aligned} \quad (12)$$

with $\bar{\sigma} \equiv \sigma_s + \sigma_\infty$ and $\Delta\sigma \equiv \sigma_s - \sigma_\infty$. Accordingly, the potential can be seen to depend on the independent and parametric variables as

$$\phi = aE_\infty \Phi \left[\frac{r}{a}, \vartheta, \frac{\Delta\sigma}{\bar{\sigma}}, \frac{\delta}{a} \right] \quad (13)$$

Equation 10 can be solved numerically to obtain the potential and field strength for a given conductivity distribution.

To obtain the flow field, the known potential distribution is used to solve eq 2 numerically for situations where the dielectric constant is distributed as

$$\begin{aligned} \epsilon &= \epsilon_s & 0 < r < a \\ \epsilon &= \frac{1}{2} \left[\bar{\epsilon} + \Delta\epsilon \cos \left[\frac{\pi(r-a)}{\delta} \right] \right] & a < r < a + \delta \\ \epsilon &= \epsilon_\infty & a + \delta < r < \infty \end{aligned} \quad (14)$$

with $\bar{\epsilon} \equiv \epsilon_s + \epsilon_\infty$ and $\Delta\epsilon \equiv \epsilon_s - \epsilon_\infty$. Since the gradient in the dielectric constant is radial, the Stokes' equation becomes

$$\mathbf{0} = -\nabla p - \frac{1}{2}\epsilon_0 \mathbf{E} \cdot \frac{d\epsilon}{dr} \mathbf{e}_r + \rho_e \mathbf{E} + \mu \nabla^2 \mathbf{u} \quad (15)$$

with $\mathbf{e}_r$ representing a unit vector in the radial direction. From eq 3, the charge density is calculated as

$$\rho_e = -\epsilon_0 \nabla^2 \phi - \epsilon_0 \frac{d\epsilon}{dr} \frac{\partial \phi}{\partial r} = \epsilon_0 \epsilon \left[\frac{1}{\sigma} \frac{d\sigma}{dr} - \frac{1}{\epsilon} \frac{d\epsilon}{dr} \right] \frac{\partial \phi}{\partial r} \quad (16)$$

Note that the sense of the free charge force is controlled by the relative magnitudes of the conductivity and dielectric constant variations and one may outweigh the other. On the other hand, the sense of the body force arising from dielectric constant variations is set by the difference between the dielectric constant inside of and outside of the cylindrical region.

Since the problem is two-dimensional, a stream function, ψ , can be used to represent the flow field, viz.

$$u_r = \frac{1}{r} \frac{\partial \psi}{\partial \vartheta}, \quad u_\vartheta = -\frac{\partial \psi}{\partial r} \quad (17)$$

$$\psi(r, \vartheta) = \frac{a^2 \epsilon_0 \epsilon_\infty E_\infty^2}{\mu} G \left[\frac{r}{a}, \frac{\delta}{a}, \frac{\Delta\sigma}{\bar{\sigma}}, \frac{\Delta\epsilon}{\bar{\epsilon}} \right] \sin(2\vartheta) \quad (18)$$

This leads to a fourth order ordinary differential equation for the G function. Note that here the scaling for the velocity has been modified slightly to reduce the number of parameters.

Table 1. Deformation in the Absence of Free Charge Effects

$\Delta\epsilon$	$\Delta\sigma$	deformation
>0	>0	prolate
<0	<0	prolate
>0	<0	oblate
<0	>0	oblate

Table 2. Fluid Speed at the Edge of the Transition Region^a

δ/a	u	δ/a	u
0.001	13.3	0.5	1.36
0.01	2.83	1.0	1.93
0.1	1.11	2.0	3.38

^a Calculations for $\sigma_s/\sigma_\infty = 100$ and $\epsilon_s/\epsilon_\infty = 1$; the scale factor is $a\epsilon_0 E_\infty^2/\mu$.

The equations for the potential and stream functions have been solved for several choices of σ_s , σ_∞ , ϵ_s , and ϵ_∞ . Figure 5 depicts the situation and shows the streamlines of the velocity field calculated when the dielectric constant and conductivity of the interior exceed those in the exterior. In this case the dispersion would be drawn out into a prolate ellipsoidal shape with its major axis parallel to the field. According to the theory, and in agreement with our experimental observations, the flow direction reverses when the conductivity of the interior is less than that of the exterior. Here the sample takes up the shape of an oblate ellipsoid with its axis orthogonal to the field. In our experiments with barium titanate the conductivity ratio, σ_s/σ_∞ , is $\approx 10^2$ when the dispersion is doped with TBATPB and $\approx 10^{-2}$ when the TBATPB is added to the suspending oil. Under these conditions, the effects of conductivity contrast overwhelm the relatively small effects of dielectric constant variation. In the previous section, we described experiments with a silica dispersion and an organic dye bolus in clear fluid. These experiments confirmed the negligible effects of dielectric constant variation in the above experiment. Once again theory and experiment were in qualitative agreement; prolate deformations for a high conductivity bolus and an oblate deformation when the suspending fluid had the higher conductivity. No deformation was observed when the dyed bolus had the same conductivity as the suspending oil.

The relation between the direction and strength of the flow is complicated by the large number of parameters involved. Most of the results discussed below are for $\delta/a = 0.1$. Changing this ratio does not seem to affect matters qualitatively. First, if free charge effects are suppressed, i.e., $\rho_e = 0$, then the sense of the deformation depends on $\Delta\sigma$ and $\Delta\epsilon$ as shown in Table 1.³⁵ Two other special cases are of interest. When $\Delta\epsilon = 0$ but $\Delta\sigma \neq 0$, the deformation is due to free charge effects and it is prolate when $\Delta\sigma > 0$ and oblate when $\Delta\sigma < 0$. On the other hand, when $\Delta\epsilon \neq 0$ but $\Delta\sigma = 0$, the deformation is oblate when $\Delta\epsilon > 0$ and prolate when $\Delta\epsilon < 0$. Rhodes et al.²³ derived an analytical *discriminating function* for a sharp interface, viz.

$$\left[\frac{\sigma_s}{\sigma_\infty} \right]^2 + \frac{\sigma_s}{\sigma_\infty} + 1 - 3 \frac{\epsilon_s}{\epsilon_\infty} \begin{cases} > 0 \text{ prolate deformation} \\ < 0 \text{ oblate deformation} \end{cases}$$

which gives the sense of the deformation when $\delta = 0$; our numerical results agree with this expression when δ/a is small.

The speed of the deformation is strongly dependent on the δ/a ratio, as Table 2 illustrates. Note that with the characteristic values quoted earlier, the deformation speed is several millimeters per second. The nonmonotonic

change of velocity with δ/a reflects the complex interplay between the body forces and the transition layer thickness.

Finally, we note that the effects of a variable frequency can be obtained by including the Maxwell current, $\partial \mathbf{P}/\partial t$, where $\mathbf{P}$ is the polarization.⁴⁰ Although the general case is complicated, the high frequency limit offers some insight. Here, free charge effects are negligible and the expression for the conductivity in eq 11 contains only effects from dielectric constant variations across the transition region, viz.

$$S(r) \equiv \frac{1}{\sigma(r)} \frac{d\sigma}{dr} = -\frac{\pi}{\delta} \frac{\Delta\epsilon/\bar{\epsilon} \sin[\pi(r-a)/\delta]}{1 + \Delta\epsilon/\bar{\epsilon} \cos[\pi(r-a)/\delta]} \quad (19)$$

Accordingly, at high frequencies the fluid behaves as a perfect dielectric and solution of the equations shows that the deformation is always prolate. However, for this approximation to hold, the oscillation frequency must be substantially larger than the highest relaxation frequency, $\sigma/\epsilon\epsilon_0$; for the oily systems studied here this frequency ranges from (roughly) 1 Hz for the neat castor oil to 50 Hz for the doped fluid. The highest frequency used in our experiments with dispersions was 100 Hz, probably not large enough to produce perfect dielectric behavior. However, we did carry out experiments with a dyed, particle-free bolus. Here effects due to dielectric constant variations should be negligible. There was no deformation when the frequency was above 300 Hz, indicating that free charge effects had been nullified because the free charge force was unable to keep pace with the field. At lower frequencies, deformations gradually appeared and conformed with the sense dictated by the conductivity contrast.

IV. Conclusions

We have demonstrated a new phenomenon in inhomogeneous, nonaqueous colloidal dispersions. In such systems, the intrinsic difference in dielectric constant and conductivity ($\Delta\epsilon$ and $\Delta\sigma$) between regions of differing particle number concentration engenders fluid motion

upon the application of an external electric field. For apolar fluids, with low conductivity, electrical forces due to free charge and dielectric constant variation each play a role in inducing flow. By tailoring $\Delta\epsilon$, $\Delta\sigma$, and the initial configuration of the dispersed particles, many intricate colloidal patterns and shapes can be produced in a controlled manner. With appropriate choice of suspending fluid, these patterns can be made to remain stable for sufficient periods to enable solidification of the fluid matrix by conventional means (e.g., gelation or polymerization). Although the experiments presented here have been performed solely on BaTiO₃/castor oil and SiO₂/castor oil dispersions, this technique is in no way restricted to these system. Indeed, provided that $\Delta\epsilon$ and/or $\Delta\sigma$ is large enough, any colloidal dispersion nested within any ambient fluid may be manipulated in a similar manner. Another example of such an effect is the observation of dispersion bands during protein electrophoresis.²³ In such experiments, protein solution is initially injected as a fluid bolus and subsequently separated electrophoretically via the application of an external electric field. During separation, the protein bands are observed to broaden in a direction orthogonal to the electric field. The formation of such bands can be explained by similar electrohydrodynamic processes to the ones considered here. Analysis of the phenomenon may also provide insight into the formation of complicated field-induced particle morphologies which have been reported in aqueous²⁸ and nonaqueous^{6,7,24,25} systems. More fully understood, the electrohydrodynamic manipulation of colloids may be put to use in the manufacture of materials with patterns that cannot be formed by mechanical means.

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