

Electrohydrodynamic Deformation of a Particulate Stream by a Transverse Electric Field

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A theory is presented for the electrohydrodynamic deformation of a thin fluid stream and applied to the experiments of Rhodes, Snyder, and Roberts on colloidal dispersions. The resulting transverse velocity field has a symmetric four-lobe structure and, when the conductivity of the sample is greater than that of the surrounding fluid, the sample deforms into a ribbon whose axis is parallel to the incident field. The ribbon axis is perpendicular to the field if the conductivities are reversed. Electrohydrodynamic velocities are of the order of microns per second and the theory agrees with the qualitative and quantitative features of existing experimental data.

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Sample dispersion caused by various mechanisms limits resolution in electrokinetic techniques used to analyze or purify mixtures of proteins or cellular material; understanding these processes is a prerequisite for developing methodologies with improved resolving power. In a clever set of experiments on a model system, Rhodes, Snyder, and Roberts [1] identified a new electrohydrodynamic dispersion mechanism—deformation of the sample stream into a thin ribbon whose cross-sectional shape depends on conductivities of the stream, σ_s , and the surrounding fluid, σ_b . An ac field was used in these experiments to suppress electrokinetic effects. Figure 1 depicts their apparatus schematically; a buffer fluid carrying a thin stream of a dilute colloidal dispersion moves through a cell of rectangular cross section. The transverse ac field deforms the sample stream into a ribbon whose axis is parallel to the imposed field when $\sigma_s > \sigma_b$; when $\sigma_s < \sigma_b$ the ribbon axis is perpendicular to the imposed field. There is no deformation when the conductivities match. Rhodes, Snyder, and Roberts [1] recognized that the deformation is an electrohydrodynamic effect, proportional to the square of the electric field strength. They used Taylor's leaky dielectric model [2], wherein fluids behave as uniform, polarizable, Ohmic conductors with sharp interfaces, to derive a discriminating function

$$D \equiv \left[\frac{\sigma_s}{\sigma_b} \right]^2 + \left[\frac{\sigma_s}{\sigma_b} \right] + 1 - 3 \left[\frac{\epsilon_s}{\epsilon_b} \right]$$

to classify deformations. ϵ_s and ϵ_b denote dielectric constants of the sample stream and the surrounding fluid. For $D > 0$ the deformation is in the direction of the field, when $D < 0$, the deformation is transverse. Although the dielectric constant of a dilute suspension, ϵ_s , is usually large at low frequencies, it drops towards that of the suspending fluid at high frequencies [3]. Rhodes, Snyder, and Roberts [1] argued that in their high frequency experiments ϵ_s/ϵ_b was near 1 and so theory and experiment agreed.

Nevertheless, there are a number of reasons to doubt the applicability of the leaky dielectric model to the phenomena observed. First, an essential feature of the leaky dielectric model is the appearance of free charge at sharp interfaces because of unequal electrical conductivities and dielectric constants on opposite sides of the surface [2]. The action of the field on the free charge contributes to both normal and shearing stresses. Although the interface between the particulate sample and the surrounding buffer was diffuse in their experiments, Rhodes, Snyder, and Roberts [1] assumed a sharp transition to employ the leaky dielectric model. It is unlikely that free charge would accumulate near the gradual transition between a dilute suspension and clear fluid in the fashion envisioned in the leaky dielectric model, so the stresses calculated with this model will not represent those present in an experiment. Furthermore, experiments at frequencies [4] where the dielectric constants of the sample and buffer differ fail to disclose the dependence on ϵ_s/ϵ_b given by the leaky dielectric discriminating function. Other dc experiments with suspensions or soluble samples [5] exhibit sample mixing which cannot be explained by effects due to the electric charge. Accordingly, another electrohydrodynamic model must be used to explain the dispersion.

The model employed here recognizes that the transition between the sample and the buffer is diffuse and that free charge on the length scale of the sample, *per se*, is absent. Since the length scale characterizing the free charge den-

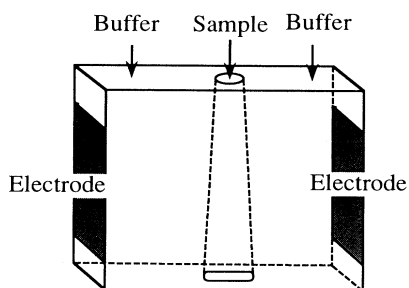


FIG. 1. Schematic diagram of the Rhodes-Snyder-Roberts cell [1]. As shown, the conductivity of the circular sample stream exceeds that of the surrounding fluid so the axis of the deformed stream is parallel to the incident field.

sity in an electrolyte solution is the Debye length, κ^{-1} , free charge effects are negligible when κ^{-1} is small compared to the particle size. According to Landau and Lifshitz [6], the electric force density in rationalized units is

$$\mathbf{f}_e = \frac{1}{2} \nabla \left[e_0 E^2 \rho \left(\frac{\partial \varepsilon}{\partial \rho} \right)_T \right] - \frac{1}{2} \varepsilon_0 E^2 \nabla \varepsilon + \rho_e \mathbf{E}. \quad (1)$$

Here ε_0 stands for the permittivity of free space, ε is the local dielectric constant, ρ is the mass density, ρ_e is the electric free charge density, and \mathbf{E} is the local electric field. The first term is the gradient of a scalar and can be absorbed into the pressure; the free charge density is zero. Thus, fluid motion is described by solutions to the Stokes equations with a distributed electrical body force due to dielectric constant variations, viz.,

$$\mathbf{0} = -\nabla p - \frac{1}{2} \varepsilon_0 E^2 \nabla \varepsilon + \mu \nabla^2 \mathbf{u} \quad \text{and} \quad \nabla \cdot \mathbf{u} = 0. \quad (2)$$

When the axial shear rate is small, buffer and sample move at the same velocity and sample deformation can be studied as a two-dimensional problem in a plane perpendicular to the sample axis.

The current density stemming from the electric field applied transverse to the sample can be expressed as the product of the local conductivity and the field since, in the absence of concentration gradients, the individual ion flux equations can be summed to yield Ohm's law. The argument is as follows. Ions are conserved so the ion fluxes, \mathbf{J}_i , are solenoidal. Next we assume that the individual ionic mobilities ω_i are the same and that the flux relation (the Nernst-Planck relation) is $\mathbf{J}_i = \omega_i [e z_i n_i \mathbf{E} - kT \nabla n_i]$. Here e is the charge on a proton, z_i is the valence of the i th species with concentration n_i , k is Boltzmann's constant, and T is the absolute temperature. Since the solution is electrically neutral on the length scale in question, $\sum z_i n_i = 0$. Accordingly, the current simplifies to $\sum e z_i \mathbf{J}_i = \sum (e z_i)^2 \omega_i n_i \mathbf{E}$. Defining the con-

ductivity as $\sigma \equiv \sum (e z_i)^2 \omega_i n_i$ and noting that the fluxes are solenoidal yields the "macroscopic" equation for the local field strength

$$\nabla \cdot \sigma \mathbf{E} = 0. \quad (3)$$

Of course any transverse motion will deform the sample and alter the conductivity and dielectric constant from their initial distributions. To simplify matters and capture the silent features of the phenomenon, these effects are ignored. Instead, a circular sample configuration of radius a is used to calculate a flow field which represents the initial stages of the deformation process; see Fig. 2. The conductivity and dielectric constant distributions are expressed as

$$\begin{aligned} \sigma &= \sigma_s, \quad \varepsilon = \varepsilon_s, \quad 0 < r < a, \\ \sigma &= \frac{1}{2} \bar{\sigma} + \frac{1}{2} \Delta \sigma \cos \frac{\pi(r-a)}{\delta}, \quad a < r < a + \delta, \\ \varepsilon &= \frac{1}{2} \bar{\varepsilon} + \frac{1}{2} \Delta \varepsilon \cos \frac{\pi(r-a)}{\delta}, \\ \sigma &= \sigma_b, \quad \varepsilon = \varepsilon_b, \quad a + \delta < r < \infty, \end{aligned} \quad (4)$$

to represent the diffuse transition from the properties of the sample to the buffer. Here $\bar{\sigma} \equiv \sigma_s + \sigma_b$, $\Delta \sigma \equiv \sigma_s - \sigma_b$, $\bar{\varepsilon} \equiv \varepsilon_s + \varepsilon_b$, and $\Delta \varepsilon \equiv \varepsilon_s - \varepsilon_b$.

The structure of the velocity and electric field allows the variables to be separated. In polar coordinates the electric potential, ϕ , can be represented as $f(r) \cos \theta$ while for the velocity field the stream function, ψ , is $g(r) \sin 2\theta$. Here θ is the angle between the position vector and the imposed field, \mathbf{E}_∞ , cf. Fig. 2. Clearly the velocity is symmetric with respect to the planes $\theta = 0$ and $\pi/2$. In the regions $0 < r < a$ and $a + \delta < r < \infty$, the electrical body force is zero and the equations have analytical solutions; in the annular ring $a < r < a + \delta$ the coupled ordinary differential equations involve the electrical body force so the equations for $f(r)$ and $g(r)$ were solved numerically. In this example, the velocity scales on $(\pi/2\mu) a \varepsilon_0 \Delta \varepsilon E_\infty^2$ and depends only on the dimensionless ratios $\Delta \sigma / \bar{\sigma}$ and δ/a . Thus, a solution can be constructed which is independent of the velocity scale. The solutions in the three regions were matched to one another by requiring continuity of current, electric potential, velocity, and stress. Results were obtained for several values of $\Delta \sigma / \bar{\sigma}$ and δ/a to explore their effects on the velocity field. To see how the direction of the flow depends on the parameters we look at the radial component for $r > a + \delta$. Here, $g(r) = A + B/r^2$ so the radial component of the velocity field is

$$u_r = \frac{\pi}{2\mu} a \varepsilon_0 \Delta \varepsilon E_\infty^2 [A(r/a)^{-1} + B(r/a)^{-3}] \cos 2\theta \quad (5)$$

for $r \geq a + \delta$.

The direction of the velocity, scaled on $(\pi/2\mu) a \varepsilon_0 \Delta \varepsilon E_\infty^2$,

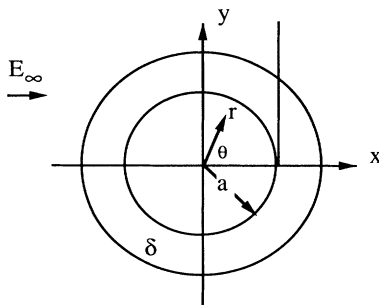


FIG. 2. Definition sketch showing the orientation of the incident field and the polar coordinate system. The inner circle ($r = a$) delineates the beginning of the transition in electrical conductivity and dielectric constant. The transition is complete at the outer circle ($r = a + \delta$). The vertical line at $x = a$ denotes the locus of points where the x component of velocity is calculated for display in Fig. 4.

TABLE I. The constants A and B for different parameter values.

| $\Delta\sigma/\bar{\sigma}$ | δ/a | A | B |
|-----------------------------|------------|--------------|--------------|
| 0.5 | 0.1 | 0.01998 | -0.00763 |
| -0.5 | 0.1 | -0.05842 | 0.02176 |
| 0.5 | 0.5 | 0.02156 | -0.01326 |
| -0.5 | 0.5 | -0.05780 | 0.03221 |
| 0.1 | 0.1 | 0.00705 | -0.00266 |
| -0.1 | 0.1 | -0.00857 | 0.00322 |
| 0.0 | 0.1 | $< 10^{-15}$ | $< 10^{-15}$ |

depends on the signs of A and B ; Table I shows values of A and B for several values of $\Delta\sigma/\bar{\sigma}$ and δ/a .

As expected, the magnitude of the induced velocity increases with the magnitude of the conductivity contrast and the size of the region over which the electrohydrodynamic body force acts. Figure 3 shows streamlines for the scaled velocity field for a typical situation with $\Delta\sigma > 0$ so the ribbon axis is parallel to the imposed field; Fig. 4 shows the x component of the velocity. When the sign of $\Delta\sigma$ is reversed, the flow reverses direction and changes magnitude somewhat. However, the structure of the flow is similar to that shown in Figs. 3 and 4. As the figures indicate, when $\Delta\sigma > 0$, flow stretches the sample in the direction of the field.

The model presented here reproduces all the qualitative features of the Rhodes-Snyder-Roberts experiment [1]: (i) For a sample with $\Delta\epsilon > 0$, the sense of the deformation is in the direction of the applied field when $\Delta\sigma > 0$; (ii) the deformation reverses when $\Delta\sigma$ changes sign; and (iii) the deformation disappears when $\Delta\sigma = 0$, irrespective of the magnitudes of ϵ_s and ϵ_b . The leaky dielectric model, Eq. (1), indicates that the sense of the deformation should be closely tied to the dielectric constant ratio even when the conductivities are matched, which is at variance

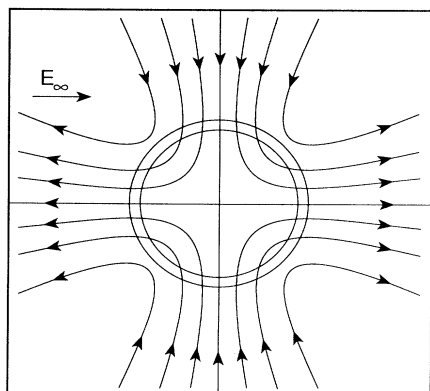


FIG. 3. Streamline pattern for $\Delta\sigma/\bar{\sigma}=0.5$, $\delta/a=0.1$. Contours are shown for the stream function for the dimensionless velocity equal to 0.0, 0.004, 0.008, and 0.012. The concentric circles designate boundaries of the transition region.

with the experimental results.

To estimate an order of magnitude for the velocity using the present theory, we choose representative values of the parameters. DeLacey and White [7] developed a theory to predict the dielectric constant of a dilute suspension. We use their results to estimate $\Delta\epsilon=20$ in a 0.5% suspension of particles with a ζ potential of 100 mV in a 20 mM salt solution at 100 kHz. Note that this value is probably low since experimental results [3] give dielectric increments due to the presence of particles that are often more than an order of magnitude larger. Using the DeLacey-White value gives a characteristic velocity, $a\epsilon_0\Delta\epsilon E_\infty^2/\mu$, slightly larger than $350 \mu\text{m/s}$ with a field strength of 10 V/cm and a sample radius of 0.5 mm. Then using the results for $\Delta\sigma/\bar{\sigma}=0.5$ (Table I) gives a sample deformation rate of approximately $5 \mu\text{m/s}$, in agreement with the results found by Rhodes, Snyder, and Roberts [1]. Predictions made with the new model are also in qualitative accord with the results of electrophoresis experiments using particulate samples in steady fields [5].

Another consequence of the theory is the insight offered into dispersion mechanisms in protein electrophoresis. Protein samples are often analyzed in a gel (gel electrophoresis) or capillary tube (capillary electrophoresis). In these methodologies, a fluid bolus containing the protein is immersed in a buffer solution and exposed to an electric field. Separation is based on the fact that protein molecules migrate at rates determined by their respective electrophoretic mobilities. To see if some of the dispersion observed in such techniques might be due to electrohydrodynamic effects we calculate a representative order of magnitude. Although the dielectric constant difference between sample and buffer is small compared to those found with particulate samples, field strengths may be several hundred volts per centimeter. From data given in Tanford's treatise [8], we estimate $\Delta\epsilon$ to be 0.3 for a 0.1% solution of hemoglobin in

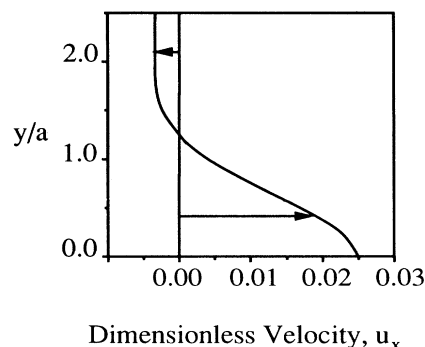


FIG. 4. Dimensionless velocity component (scaled on $\pi a\epsilon_0\Delta\epsilon E_\infty^2/2\mu$) in the field direction at the inner edge of the conductivity-dielectric constant transition, $x=a$ (see Fig. 2) for $\Delta\sigma/\bar{\sigma}=0.5$, $\delta/a=0.1$.

water. For a field strength of 100 V/cm and a sample size of 0.5 mm, the characteristic velocity, $a\epsilon_0\Delta\epsilon E_\infty^2$, is over 100 $\mu\text{m/s}$. Scaling this value using the "constants" derived for the circular sample (Table I) indicates a dispersion velocity of nearly 1 $\mu\text{m/s}$, of the same order of magnitude as the electrophoretic velocity. It should be recognized, however, that the geometric configurations used in protein electrophoresis differ from those on which the numerical constants are derived. Nevertheless, based on this calculation, it appears that electrohydrodynamic dispersion may be an important factor in protein electrophoresis.

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