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Electrohydrodynamic Patterns in Charged Colloidal Solutions

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Various solutions of charged colloidal particles self-organize under strong ac fields into continuously sheared bands tilted with regard to the direction of the field. We report here that the angle of tilt takes essentially two values, ±45° or ±60°, depending on the amplitude of the periodic electrophoretic drift of the charged aggregate as compared to its width. We propose an electrohydrodynamic model that explains the very striking features of these patterns in colloidal solutions. Numerical solutions show good agreement with the transient and quasistationary structures observed. [S0031-9007(97)02310-7]

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Recent reports have shown that initially homogeneous colloidal suspensions may develop instabilities under strong electric fields leading to surprising *dynamic quasi-stationary* patterns. Among the most striking ones are the chevron structures observed when the solution is confined between two parallel plates, an ac field being applied parallel to the plates: long aggregates of colloidal particles disposed in a zigzag fashion can be observed, as well as the fast recirculation of individual particles within each aggregate. These patterns were observed in solutions of China clay [1], polystyrene latex [2], and DNA [3,4], suggesting that the underlying physics is very general. This phenomenon has dramatic effects on the otherwise very promising capillary electrophoresis technique [3,5], and may also have important consequences (mainly adverse) on other practical applications, such as dielectrophoresis, electroflocculation, or electrorheological fluids [6]. Unfortunately, very limited understanding is available about the mechanisms responsible for both the initial instability and the eventual morphology.

In the present Letter we report progress on the second front. We have developed an electrokinetic theory that takes into account the fact that at the field amplitudes at which these patterns develop, deviations from electroneutrality should occur far beyond the Debye layer. Analysis of the resulting electrical body force on the fluid leads us to predict different morphologies at low and high frequencies in agreement with experiments. For the sake of clarity we report first the experimental observations. We then sketch our theory and show its ability to describe the two regimes. We conclude by comparing our numerical predictions to additional experimental observations of the growth of a zigzag band from a disk-shaped aggregate.

Let us start by briefly describing the key features of electric-field–induced segregation in bacteriophage λ-DNA solutions [7] confined in quasi-2D geometry [Figs. 1(a) and 1(b)]. DNA solutions are particularly well suited to such studies because DNA molecules can be obtained as very monodisperse samples, they are strongly repulsive, and they do not spontaneously aggregate in water solutions containing only monovalent co- and counterions. They also form field-induced patterns at lower fields than other colloids, therefore reducing experimental complications and risks of thermal effects. Above a threshold field depending on the frequency (about 50 V/cm at 10 Hz), segregation into DNA-rich domains and DNA-poor domains occurs. The domains grow by coalescence at a rate increasing with the field strength, and adopt the typical patterns displayed in Figs. 1(a) and 1(b), with elongated aggregates tilted with respect to the (horizontal) field. We report here that two regimes should actually be distinguished. At frequencies lower than about 10 Hz, the aggregates are seen to drift on distances larger than their width over a period of the applied electric field and the tilt angle is $\theta \simeq \pm 45°$ [Fig. 1(a)]. In contrast, we

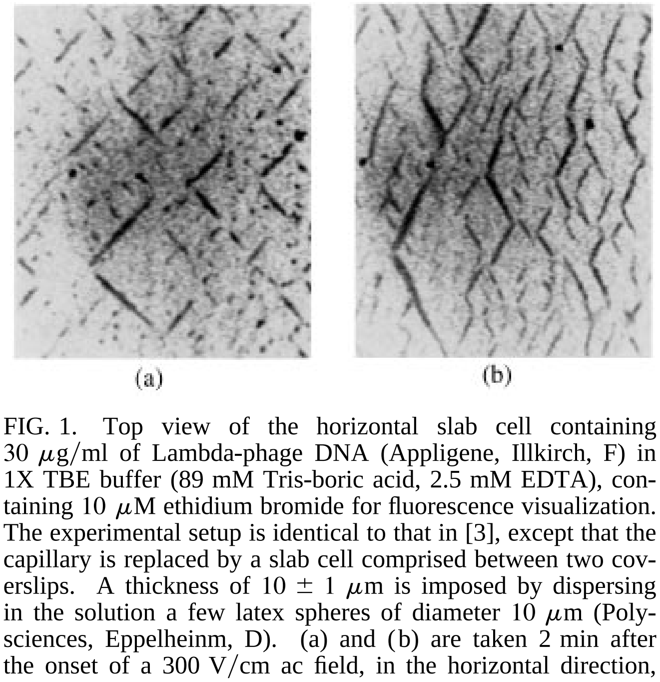

FIG. 1. Top view of the horizontal slab cell containing 30 μg/ml of Lambda-phage DNA (Appligene, Illkirch, F) in 1X TBE buffer (89 mM Tris-boric acid, 2.5 mM EDTA), containing 10 μM ethidium bromide for fluorescence visualization. The experimental setup is identical to that in [3], except that the capillary is replaced by a slab cell comprised between two coverslips. A thickness of 10 ± 1 μm is imposed by dispersing in the solution a few latex spheres of diameter 10 μm (Polysciences, Eppelheinm, D). (a) and (b) are taken 2 min after the onset of a 300 V/cm ac field, in the horizontal direction, at frequencies 2 and 100 Hz, respectively. These are negative images covering 200 μm.

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measure $\theta \simeq \pm 60^\circ$ at higher frequencies [Fig. 1(b), when the periodic drift of the aggregates is a few times smaller than their width. As first recognized by Hu *et al.* for latex suspensions [2], these tilted aggregates are in fact quasistationary (highly) dynamical structures within which individual macroions recirculate continuously as indicated schematically in Fig. 2.

We now outline the general ideas founding our theoretical model. Take a solution of large charged objects (macroions) and monovalent small anions and cations. Applying an electric field $\vec{E}_0$ induces the coupled motion of all species as well as that of the fluid due to the electrical body force term, $\rho_e \vec{E}$, in the Stokes equation: $\eta \Delta \vec{v} - \vec{\nabla} p + \rho_e \vec{E} = 0$, with η the viscosity and $\vec{v}, p, \rho_e, \vec{E}$, respectively, the local fluid velocity, pressure, charge density, and electric field. This situation has been classically analyzed in linearized theories taking the applied field as a small parameter as compared to the equilibrium electric field within the Debye layers [9]. This in fact amounts to assuming that the charge density is essentially that of the equilibrium Debye layers which allows one to evaluate the electrophoretic mobility μ_M for simple shape macroions: $\vec{v}_M = z_M \mu_M \vec{E}_0$, where $z_M = \pm 1$ is the sign of the macroions' charges (i.e., $\mu_M \geq 0$). The excess counterions migrating within the macroions Debye layers also tend to polarize the colloidal particles. However, deviations from electroneutrality at the macroion surfaces do not grow unbounded under electric field, leading instead, after electric relaxation (Debye time $\approx 10^{-9}$ to 10^{-7} s), to nonstationary perturbations of the total salt concentration, S, extending far beyond the Debye layers [9] ($S = c_+ + c_-$, where c_+ and c_- are the supposedly monovalent small cation and anion concentrations). We here argue that these large scale gradients of the salt concentration (and thus of the local conductivity) lead, under electric field, to a charge density which in turn induces large scale shearing of the liquid. As we are interested in electrohydrodynamic phenomena beyond the Debye layers (where the equilibrium electric field vanishes) we cannot resort to the classical "low electric field" approximation to overcome the complexity of the coupled nonlinear electrokinetic equations [9]. Instead we take the concentration of charges on the macroions to be small everywhere compared to the average salt concentration c_s, and assume that it can be described, at length scales much larger than the Debye length, by a smooth continuous concentration profile varying on a scale L, i.e., $c_M(\vec{r}, t) \ll c_s$ with $|\vec{\nabla} c_M| \sim c_M/L$. We then find that the salt concentration, $S(\vec{r}, t) = 2c_s + \delta S$, locally verifies the following linearized conservation equation:

$$\partial_t S - D_s \Delta S - z_M \mu_s \vec{E}_0 \cdot \vec{\nabla} c_M = 0\,, \qquad (1)$$

if $eE_0 L/k_B T \geq 1$, which ensures that the perturbations in electric field are small and scale as $\delta E/E_0 \sim c_M/c_s \ll 1$ [10]. For L in the micron range, this typically holds for $|\vec{E}_0| \geq 100$ V/cm. D_s and μ_s are the diffusion constant and the electrophoretic mobility of the salt ions (taken for simplicity identical for the small counter- and coions). Electroneutrality is also assumed in Eq. (1), which is *here* a good approximation as long as $(eE_0 \kappa^{-1}/k_B T)^2 \ll 1$ (i.e., $E_0 \ll 10^5$ V/cm for a typical Debye length, $\kappa^{-1} \simeq 2$ nm) [10]. The nonuniform salt profile S is then itself "polarized" under the electric field to ensure a quasiuniform current on time scales longer than the ("Debye") electric relaxation time $\vec{\nabla} \cdot (S\vec{E}) \simeq 2c_s \vec{\nabla} \cdot \vec{E} + \vec{E}_0 \cdot \vec{\nabla} S \simeq 0$. This gives rise to a local net charge density, $\rho_e = \varepsilon\varepsilon_0 \vec{\nabla} \cdot \vec{E}$, that extends typically over microns into the electrolyte solution surrounding the macroions. Namely,

$$\rho_e = -\frac{\varepsilon\varepsilon_0}{2c_s} \vec{E}_0 \cdot \vec{\nabla} S\,, \qquad (2)$$

where $\varepsilon\varepsilon_0$ is the dielectric constant of the electrolyte solution. The resulting electrical body force $\rho_e \vec{E}$ generates, within the polyelectrolyte solution, electrohydrodynamic flows that effectively convect the very slowly diffusing macroions, whereas they generally bring a negligible correction to the approximate conservation equation (1) for the much faster diffusing salt ions.

Let us now estimate $\rho_e \vec{E}$ in the vicinity of some arbitrary macroion-rich region, $c_M(\vec{r}, t)$, of electrophoretic mobility μ_M in an ac electric field $\vec{E}_0(t) = \vec{E}_0 \cos(\omega t)$.

It is instructive to start with the case of a *fixed* charged domain, i.e., $\mu_M = 0$, which we assume for concreteness to have a bandlike shape similar to the charged membranes used in electrodialysis [11]. The salt concentration increases at the domain interface towards which the excess counterions migrate, whereas a salt depletion simultaneously forms at the opposite interface. At a given point in the fluid, the gradient of salt is according to Eq. (1) perpendicular to the domain interface and proportionnal to the normal component of the applied electric field $E_0 \cos(\phi)$ (same notation as in Fig. 2). Taking into account a (space dependent) phase shift τ, its amplitude is

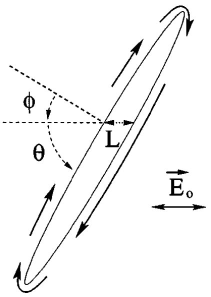

FIG. 2. Sketch of a field-induced quasistationary dynamical aggregate containing typically hundreds of macroions. The direction of circulation (arrows) changes with the sign of the tilt angle, θ. The circulation velocity increases rapidly with increasing field, and can reach 100 μm/s close to the aggregate boundary.

thus formally $|\vec{\nabla}S(t)| \propto E_0(t-\tau)\cos(\phi)$. From Eq. (2) we then obtain $\rho_e(t) \propto E_0(t)E_0(t-\tau)\cos^2(\phi)$. The instantaneous local electric force, $\rho_e\vec{E}_0$, has therefore a component perpendicular to the membrane interface proportional to $E_0^2(t)E_0(t-\tau)\cos^3(\phi)$, and a parallel component proportional to $E_0^2(t)E_0(t-\tau)\cos^2(\phi)\sin(\phi)$. Hence, at first order, both components average to zero over the period, $2\pi/\omega$, since they are proportional to the product of *three* sinusoidal functions of the same frequency.

This is no longer true if we take into account the primary electrophoretic drift of an arbitrary macroion-rich region (i.e., $\partial_t c_M + z_M \mu_M \vec{E}_0 \cdot \vec{\nabla} c_M = 0$) of typical width L along the direction of the field: under electric field, it *moves* in the opposite direction to the (excess) counterions, that is, *towards regions under simultaneous salt depletion process*. To analyze the effect of this periodic oscillation, one must take into account the time dependence of c_M in Eq. (1), and two regimes must be distinguished.

The "low frequency" (LF) regime corresponds to $\omega \ll D_s/L^2 \leq \mu_M E_0/L$. At such frequencies, the salt profile adapts to the quasi-dc drift of the macroin-rich region so that its oscillations are also described by an equation of the form $\partial_t S + z_M \mu_M \vec{E}_0 \cdot \vec{\nabla} S = 0$. Replacing $\partial_t S$ in Eq. (1) now generates a leading contribution to δS scaling as $(-\mu_s/\mu_M)c_M$ and thus *independent* of E_0. This out-of-equilibrium salt depletion develops in the (moving) macroion-rich region to compensate for the macroion contribution to the quasiuniform total electric current. Through Eq. (2) one thus obtains a contribution to the mean local electric force, $\langle \rho_e \vec{E}_0 \rangle$, with nonvanishing components perpendicular and parallel to the interface of the macroion-rich region, scaling, respectively, as $E_0^2\cos^2(\phi)$ and $E_0^2\cos(\phi)\sin(\phi)$. These components simultaneously act to flatten the macroion-rich region perpendicularly to the electric field *and* "facet" it, e.g., into a diamondlike shape, since we predict maximum shearing deformations along the directions $\phi = \pm 45°$, i.e., $\theta = \pm 45°$ [12].

The "high frequency" (HF) regime corresponds to $\omega \gg \mu_M E_0/L$. In this limit, the perturbation of c_M is small: $c_M(\vec{r},t)_{\mu_M \neq 0} \simeq c_M(\vec{r})_{\mu_M=0} + \vec{\nabla} c_{M\mu_M=0} \cdot \delta\vec{r}(t) + ...$ as the electrophoretic drift, $\delta\vec{r}(t) \simeq (z_M \mu_M \vec{E}_0/\omega)\sin(\omega t)$, is smaller than L. Using this expansion in Eq. (1) leads to a correction to S proportional to $\mu_M E_0^2 \cos^2(\phi)$ and thus to a nonvanishing mean electric body force with a normal component scaling as $\mu_M E_0^4 \cos^4(\phi)$, and a component tangent to the aggregate proportional to $\mu_M E_0^4 \cos^3(\phi)\sin(\phi)$. Hence, maximum shearing occurs in this case for $\phi = \pm 30°$, i.e., $\theta = \pm 60°$.

When experimental parameters are used, evaluation of the flow generated by $\langle \rho_e \vec{E}_0 \rangle$ leads to the correct prediction not only for the sign of the recirculation in the aggregates (similar in both regimes and independent of z_M, the sign of the macroions' charges) but also for the order of magnitude of the recirculation velocities. Furthermore, we find $D_s/L^2 \simeq \mu_M E_0/L \simeq 10$ Hz which predicts that the crossover frequency between the HF and LF regimes is indeed close to 10 Hz, corresponding to the observed transition between tilt angles of 60° and 45°, respectively. This concordance between the tilt angle of the elongated aggregates and the direction of maximum shear stress, predicted by our simple model, suggests that these patterns are actually the result of an (electrohydro)dynamical process selecting first the (far-from-equilibrium) quasistationary structures with the maximum shearing amplitude (before they evolve further on longer time scales—typically $t > 10$ min—as reported by Jennings *et al.* [1]).

We confirmed this idea by testing our model against the observation of the transient regime by which a disk-shape λ-DNA aggregate acquires its eventual zigzag structure after the sudden application of a strong ac electric field ($E_0 = 500$ V/cm and $\omega/2\pi = 100$ Hz) corresponding to the HF regime [see Figs. 3(a)–3(d)]. We numerically solved an approximated nonlinear dynamic equation describing the evolution of the density of macroions. In addition to the electrophoretic migration already introduced, this takes into account the macroions' diffusion, the electric field local perturbations, and the macroions' convection due to the flow triggered by $\rho_e\vec{E}$, assuming a quasistatic response of the small ions [10]. The numerical solution is depicted on Figs. 3(e)–3(h) for the HF regime. The deformation process starts with a nonstationary symmetric elongation of the aggregate perpendicularly to the direction of the ac electric field, and evolves, within a few seconds, to form (by spontaneous symmetry breaking) long adjacent quasistationary tilted bands in good agreement with the corresponding experiment of Figs. 3(a)–3(d). The quasistationary numerical solution in the LF limit regime also agrees with the corresponding experimental observation exhibiting a 45° angle of tilt (data not shown).

Although the theoretical elements presented here are barely the first steps in analyzing the complex equations describing the system, the general agreement between the model and the experiments strongly suggests that the dynamic patterns recently observed in several types of colloidal or polyelectrolyte solutions are indeed due to a nonlinear coupling between the macroion density fluctuations and the associated electrohydrodynamic flows [14]. This understanding should allow the development of methods to control this instability, in order, e.g., to delay its appearance during electrophoresis, dielectrophoresis, or in electrorheological fluids.

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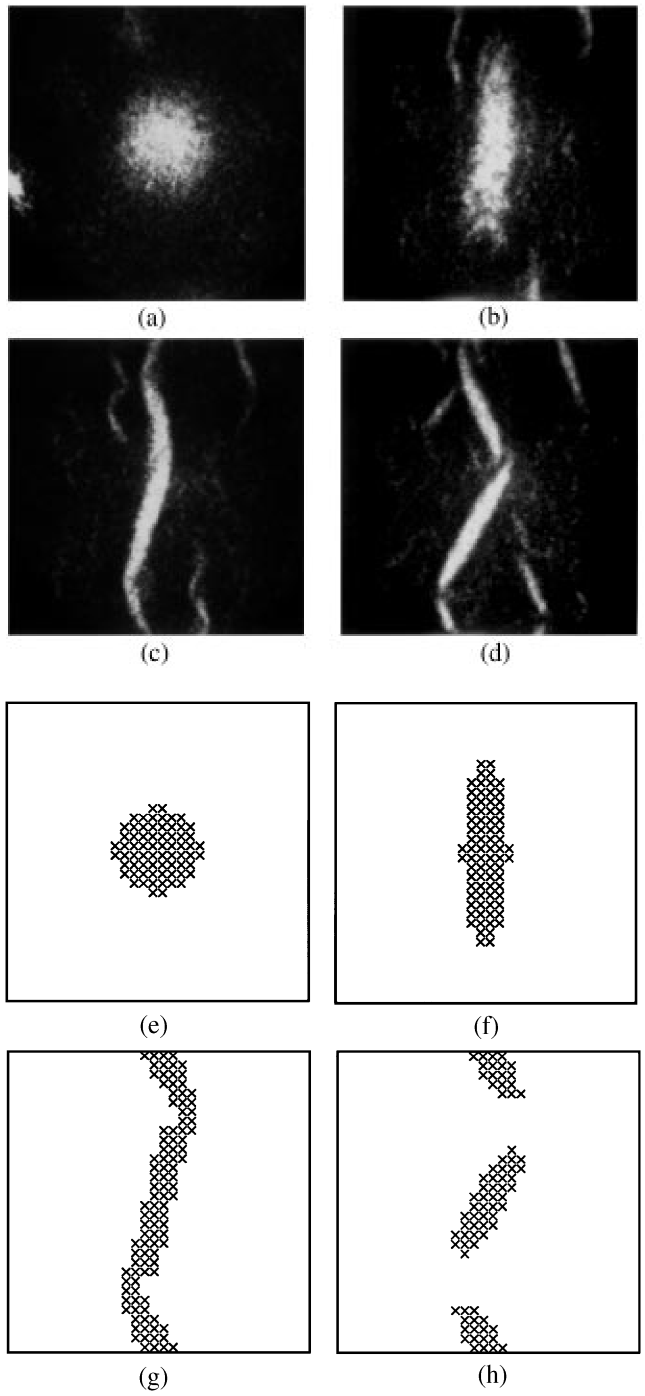

FIG. 3. (a)–(d) An aggregate, formed under a strong electric field, has been left to diffuse for about 1 min after the electric field was turned off (same λ-DNA solution as in Fig. 1). A strong electric field is then suddenly reapplied in the horizontal direction on the disklike macroion-rich region of about 10 μm in diameter ($\omega/2\pi = 100$ Hz and $E_0 = 500$ V/cm). (a) $t = 0$ s; (b) $t = 0.5$ s ; (c) $t = 1.5$ s; (d) $t \geq 3$ s (stationary regime). (e)–(h) Numerical evolution of an initially Gaussian macroion distribution in the analytic electrohydrodynamic HF regime. Spatial periodic boundary conditions are used. Time scales (when the known values of the experimental parameters are used): (e) $t = 0$ s ; (f) $t = 0.1$ s; (g) $t = 1.5$ s; (h) $t = 3$ s. "**x**" indicates that the local probability density is at least one tenth of the maximum of the initial distribution.

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