

New Rectifying Electrohydrodynamic Instability at the Boundary of Charged Gels in Alternating Electric Fields

Benoit Ladoux,¹ Hervé Isambert,² Jean-François Léger,³ and Jean-Louis Viovy^{1,*}

¹Laboratoire de Physicochimie Curie (UMR CNRS 168), Institut Curie, Section de Recherche,
11 Rue Pierre et Marie Curie, 75231 Paris, Cedex 05, France

²Center for Studies in Physics and Biology, The Rockefeller University, Box 25,
1230 York Avenue, New York, New York 10021-6399

³LUDFC, Institut de Physique, 3 Rue de l'Université, F-67084 Strasbourg, France

(Received 22 April 1998)

A new type of electrohydrodynamic instability, induced by ac fields around a charged gel in an electrolyte, is observed. It leads to steady flows parallel to gel surfaces tilted with respect to the field. The flow velocity scales as $v \propto (\text{field strength})^\nu (\text{frequency})^{-\beta} (\text{solution ionic strength})^{-0.8}$, with $\nu = 4.3-2.5$ and $\beta = 0.7-0.9$ depending on conditions. These instabilities, which confirm recent theoretical predictions, may be of importance for understanding colloid electrodynamics and for applications in capillary electrophoresis, dielectrophoresis, and electric micromanipulations. [S0031-9007(98)07431-6]

PACS numbers: 82.70.Gg, 47.65.+a, 66.10.Ed, 82.65.Fr

Extensive research on colloidal suspensions submitted to ac fields is motivated by the spectacular electrodynamic processes they may undergo and by the industrially useful applications of electrorheological fluids [1]. It has also found a new promising domain of application in the micromanipulation of cells or macromolecules [2]. The most famous effect of ac fields on suspensions of charged colloidal particles is the formation of linear *pearl necklace* aggregates aligned parallel to the field [1]. Different and more complex dynamical features, appearing under a strong ac field, have also been reported for suspensions of macroions such as china clay [3], polystyrene spheres [4], DNA molecules [5,6], or charged polysaccharides [7]. The symmetry of the system is broken, and particles organize in elongated aggregates tilted with regard to the direction of the field. A strong recirculation of fluid inside and outside of the aggregates occurs [4-7].

Two theoretical models have been proposed to account for this phenomenon, of practical importance for capillary electrophoresis [5,7,8] dielectrophoresis, electroflocculation, and electrorheological fluids. The first one [4,9] attributes it to a retarded dipole-dipole interaction between neighboring particles. The second model [6,10] suggests that the presence of an inhomogeneity in the distribution of macroions (polyelectrolyte, macroion assembly, or, as in the present study, a charged membrane, all these objects being gathered in the following under the generic name *aggregate*) induces inhomogeneities in the concentration of coions (small ions of same charge) and counterions, as a consequence of Kohlrausch equilibrium. When submitted to a strong electric field, such an inhomogeneity may affect dramatically the surrounding salt concentration [11]. Assuming for definiteness a negative aggregate, the combination of a negative gradient of cations and positive gradient of anions on the cathodic side of the aggregate leads to a transient imbalance of

ion fluxes and to a global salt concentration increase, which is in turn spread by diffusion on distances that exceed the Debye length after typically a few μs . A salt depletion occurs on the anodic side. In the field, these salt gradients induce a slight violation of electroneutrality in the vicinity of the aggregate. The associated charged elements of fluid are therefore subjected to an electrohydrodynamic flow. Solving the evolution of a solution initially at equilibrium (apart from thermal fluctuations) has not yet been fully achieved, but interesting predictions are already available for the case of a steady charged (negatively for definiteness) elongated aggregate in 2D geometry. The model involves the simultaneous solution of ion conservation equations, Poisson equation relating ion transport with electric field, and a generalized electrohydrodynamic Stokes equation relating charge distributions in the fluid with flow. In the limit of low gel charge density c_{gel} (as compared with the bulk salt concentration c_s), one demonstrates analytically that terms nonlinear in field amplitude, coupling the finite electrophoretic mobility of the aggregate with the transport of small ions, are able to yield an imbalance between the *forward* and *backward* electrohydrodynamic drags during one period and, therefore, to induce symmetry-broken macroscopic flow. In the *high frequency* limit, which is of interest for the present work (typically >10 Hz), the following scaling for the velocity of the liquid in the vicinity of the aggregate [10] is predicted:

$$\langle V \rangle \propto (\mu/\omega^2 c_s) E^4 \cos \theta \sin^3 \theta, \quad (1)$$

where E , μ , ω , and θ are, respectively, the field, the mobility of small ions (taken equal for simplicity), the frequency of the field, and the angle between the aggregate and the electric field.

This theory predicts that (i) the shearing velocity increases rapidly with field strength and decreases with

increasing either the buffer concentration or the frequency of the electric field. (ii) The maximal circulation velocity occurs when the aggregate is tilted by $\pm 60^\circ$ with regards to the field (mod 180°). (iii) For an angle comprised between 0° and 90° (the situation depicted in Fig. 1), fluid rotation is clockwise.

As these predictions present several striking qualitative analogies with earlier experimental observations [3–6], we designed an original model experiment to put to the test the main physical mechanisms suggested in [6,10], while ruling out the possibility that the retarded dipole-dipole interaction effects proposed in [4,9] might be responsible for the observations. To this end, we developed an electrohydrodynamic experiment, close to the system theoretically described in [6,10], in which the “aggregate” is an indeformable membrane, thus preventing any local rotation to occur inside the aggregate as invoked in [4,9]. This Letter presents the system, the experimental results, and a quantitative comparison with scaling predictions.

We prepare a negatively charged gel cylinder with a diameter varying from 150 to 250 μm (Seakem HEEO Agarose, FMC, USA) at 2% in buffer. A low-conductivity isoelectric histidine/water buffer (pH 7.6) allowed exploration of a large range in field strength without excessive heat production. The gel was immobilized with a definite angle by a slight compression in a

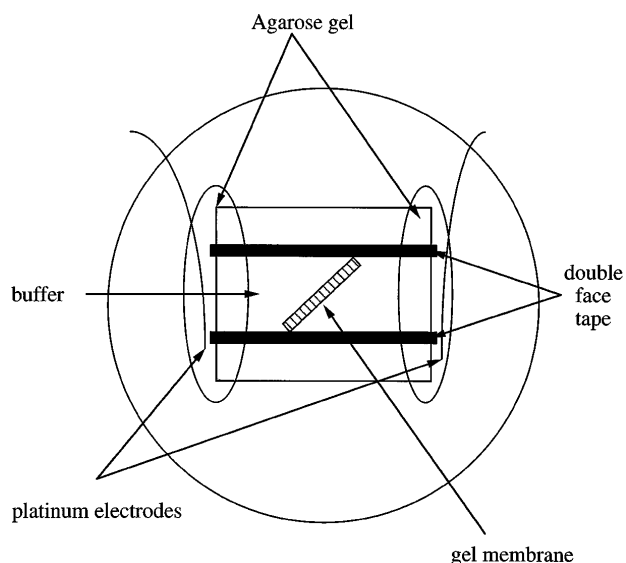


FIG. 1. The cell was placed in a Zeiss Axiovert microscope. Images were collected by a Silicon Intensified Target Camera (LHESA, Cergy, France) and treated using a Hammamatsu Argus 20 processor. ac electric fields were generated by a 0-to-2 MHz function generator (Wavetek, San Diego), driving a Trek Model 610B (Medina, New York) amplifier. Controlling the symmetry of the ac electric field was critical in these experiments: fine adjustment to better than 1 mV was performed by superimposing a small dc bias to the amplifier output to nullify the residual dc component of the field [measured using a wideband electronic voltmeter (Wavetek) connected to a potentiostatic bridge].

channel defined between two coverslides by double-face tape (Fig. 1). The buffer solution was introduced by capillarity, and the extremities of the channel were sealed by neutral agarose plugs (FastLane FMC, USA), allowing electrical connection with two platinum electrodes. Latex spheres (fluospheres, carboxylated, or aminated, 1 μm , Molecular Probes Europe BV, Holland) diluted in the buffer to one bead per $(20 \mu\text{m})^3$ were used as flow tracers for fluorescence microscopy [it was checked that (i) in the conditions used in this study, the suspension of spheres alone did not show any aggregation or instability in the field in the absence of the charged gel and (ii) the results were independent of the sign of the bead's charge]. The cell was thermostated at $12 \pm 3^\circ\text{C}$, and the temperature inside the cell was controlled using a Teflon-coated microthermocouple (Bioblock, Illkirch, France).

The first qualitative observation of this study was that two circulations of fluid, parallel to the gel surface and opposite to each other, appeared for high enough ac fields (Fig. 2). The beads very close to the cell surface underwent a rather chaotic motion, apparently due to collisions with micron-sized corrugations of the gel surface. An accumulation of particles and a maximum in the velocity occurred at a distance of 5–10 μm from the gel. Velocity decayed progressively at larger distances. The cell geometry imposed a slow large-scale recirculation of the fluid.

Bead velocities in ac electric field were measured in the layer of maximum velocity, with an error evaluated as $\pm 10\%$ (below 200 V/cm, the accuracy was smaller due to the low value of the velocity). The velocity increases rapidly with electric field (Fig. 3) and appears to follow a power law $v \propto E^\nu$. The exponent ν depends

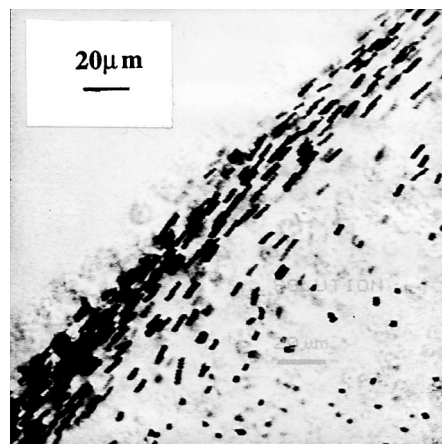


FIG. 2. Videomicrography of the cell (objective $\times 20$): the empty space on the upper left corner is the gel. Only the right bottom interface of the gel is visible. The ac field is horizontal. Latex particles (appearing in dark) are moving from upper right to lower left. For clarity, an exposure time of 0.5 s was chosen to reflect the motion of the particles (however, velocities were measured by particle tracking on the recordings, to avoid ambiguities due to trajectory overlap).

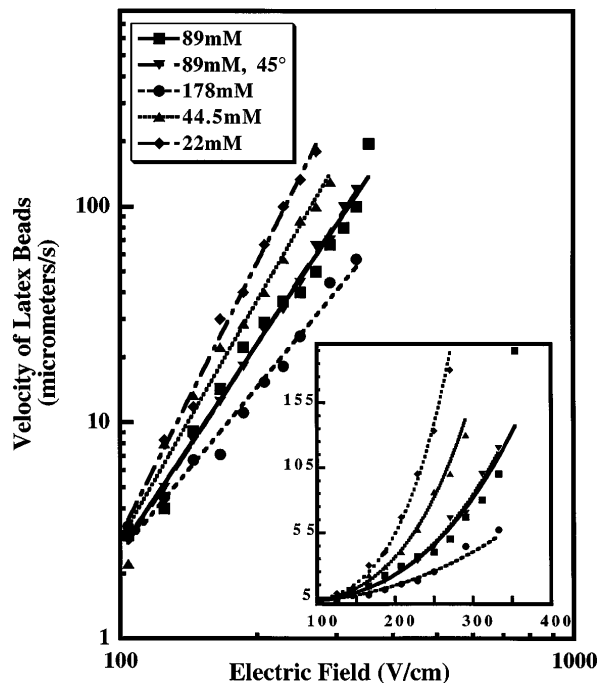


FIG. 3. Velocity of beads vs electric field for histidine concentrations 22, 44.5, 89, 178 mM; $\theta = 60^\circ$ (except for the curve labeled “89mM, 45°,” corresponding to $\theta = 45^\circ$). Inset: Same data on a linear scale.

somewhat on buffer concentration. At an angle of 60° and a frequency of 100 Hz, for instance, ν equals 4.3 ± 0.2 , 3.4 ± 0.2 , 2.7 ± 0.2 , and 2.5 ± 0.1 , respectively, for histidine concentrations of 22, 44, 89, and 178 mM, corresponding to Debye lengths of 14.4, 10.1, 7.2, and 5 nm, respectively) (the theoretical prediction for ν is

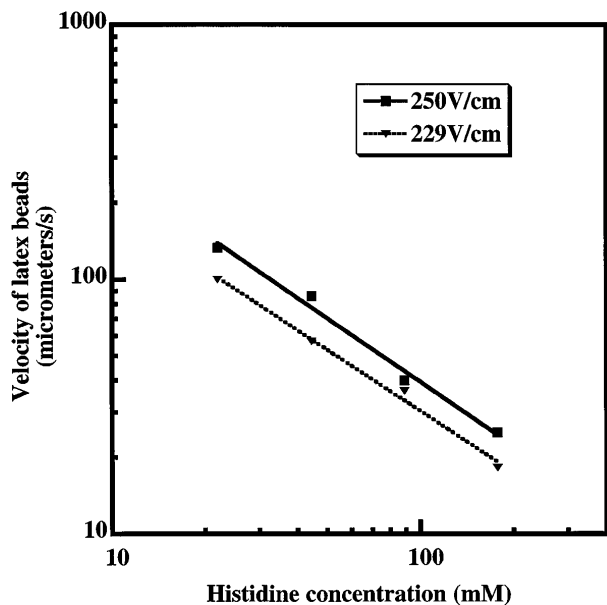


FIG. 4. Velocity of beads vs histidine concentration for two different electric fields.

4). The velocity as a function of buffer concentration, at fixed angle (60°), frequency (100 Hz), and electric field (229 and 250 V/cm) (Fig. 4) scales as $\nu \propto [c]^{-0.8}$ for all histidine concentrations (theoretical exponent -1). Between 100 and 2000 Hz, velocity at fixed field strength (Fig. 5) decreases for increasing frequency with a single scaling exponent β ($\nu \propto \omega^{-\beta}$) equal to 0.7 ± 0.2 and 0.9 ± 0.2 , respectively, for $[\text{histidine}] = 89$ and 22 mM (the theoretical prediction is $\beta = 2$). (Deviations around 2000 Hz and above are probably due to inaccuracies related with the low velocity of beads.) We discarded measurements below 100 Hz, in which latex beads with a $1 \mu\text{m}$ diameter move during one period over distances larger than their size, inducing a risk of perturbation of the flow.

Finally, we compared different angles between the gel and the electric field in 89 mM histidine (Fig. 5). Between 45° and 60° , the experimental difference was not significant within experimental error. For low angles, however (between 15° and 25°), we observed a more complicated flow pattern, which seemed to self-organize in lateral circulations tilted at 60° with regard to the electric field. This suggests that there is indeed a preferred recirculation angle of 60° (as predicted), and that it is not possible to force another geometry beyond certain limits.

These results are overall in very good qualitative agreement with the predictions of [6,10]. The very existence of steady fluid recirculations in ac fields over distances larger than the Debye layer is a strong argument in favor of a salt-depletion mechanism. Moreover, (i) the direction of recirculations is the same as predicted and (ii) the flow velocity quickly increases with field strength and decreases with increasing either the frequency of the field or the buffer concentration.

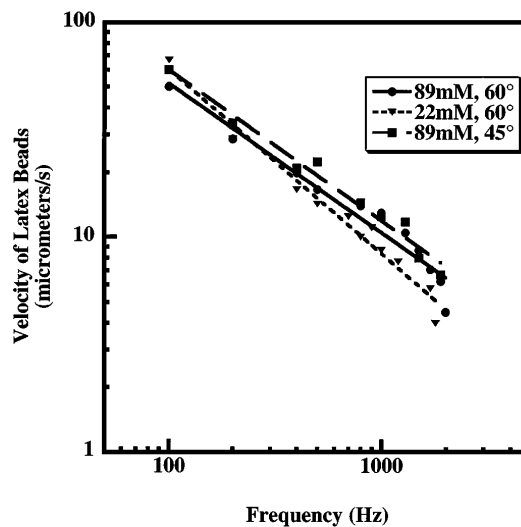


FIG. 5. Velocity of latex beads vs field frequency at two different angles (60° and 45°) in 89 mM histidine, $E = 271$ V/cm; and at 60° , $E = 208$ V/cm in 22 mM histidine.

The predicted and observed scaling exponents are of the same order of magnitude but differ in some cases. The scaling with frequency, in particular, is rather different, and the observed dependence of the field scaling exponent upon buffer concentration is not predicted by the model. Whereas the theory uses a perturbation development on concentrations ($c_{\text{gel}} \ll c_s$), our experiments are performed in the range c_{gel} (of order 3×10^{-3} mol/l) $\cong c_s$ (varying from about 7×10^{-3} to 9×10^{-4} mol/l). Analytical solution of the model in this domain is difficult, but performing experiments at $c_{\text{gel}} \ll c_s$ was impossible with the present experimental setup: decreasing the charge density of the gel would yield very low and hard to measure velocities (for low velocities, Brownian diffusion of particles in and out of the focal plane makes particle tracking impossible). Conversely, increasing the field strength or the salt content of the solution beyond the values used here yields thermally driven hydrodynamic instabilities that obscure the electrohydrodynamic one.

To summarize, we reported here the first observation, to our knowledge, of a rectifying electrohydrodynamic instability in the vicinity of an indeformable charged gel submitted to a strong ac field. Such an instability was anticipated by a recent theoretical model, demonstrating the development of long-ranged space charges in the solution surrounding the gel and of fluid recirculations associated with nonlinearities in the electrokinetic equations. It has been recognized previously that gels and colloidal suspensions may develop nonlinear transport behavior in strong *constant* fields [11]. The instability studied here bears some connections with these earlier ones: both are rooted in the appearance of a concentration polarization zone and in the breakdown of electroneutrality over distances larger than the Debye length. Being specific to ac, however, the instability reported here is connected with other cross terms in the dynamic equations and yields very unique (and less intuitive) rectifying macroscopic behavior. All the qualitative trends observed are consistent with the model's predictions, but some discrepancies exist on the values of the scaling exponents, which probably arise from large salt depletions (i.e., of the same order as the equilibrium bulk salt concentration), not accounted for in the model. The rather extensive agreement nevertheless provides strong support to the theory, and to the assumption that the space charges induced by ion transport play an essential role also in the more complex situation of a colloidal suspension. It also suggests that the physical processes analytically investigated in [6,10] remain relevant for $c_{\text{gel}} \cong c_s$, and that a numerical extension of the model to this range is feasible. The trends observed

here can be of importance for various applications (for instance, the predictions of [10] were used to improve DNA electrophoresis [7]) and might also be useful to increase the applicable field in electrorheological fluids. They also suggest that rectifying instabilities may exert an adverse effect during dielectrophoretic micromanipulation of particles, cells, or macromolecules [2].

This work was supported in part by grants from the EC (BMH4-CT96-1158, and BMH4-97-2627), and from the Association de Recherche Contre le Cancer (ARC). We are indebted to A. Ajdari and J. Prost for illuminating discussions. B. L.'s contribution to this work was part of his military service under DGA-DRET.

*To whom correspondence should be addressed.

Email address: Jean-Louis.Viovy@curie.fr

- [1] H. A. Pohl, *Dielectrophoresis* (Cambridge University Press, Cambridge, England, 1978).
- [2] (a) M. Washizu, *J. Electrostat.* **25**, 109 (1990); (b) G. Fuhr, M. Arnold, R. Hagedorn, T. Muller, W. Benecke, B. Wagner, and U. Zimmermann, *Biochim. Biophys. Acta* **1108**, 215 (1992); (c) H. Kabata, O. Kurosawa, I. Arai, M. Washizu, S. A. Margaron, R. E. Glass, and N. Shimamoto, *Science* **262**, 1561 (1993); (d) C. L. Asbury and G. van den Engh, *Biophys. J.* **74**, 1024 (1998).
- [3] B. R. Jennings and M. Stankiewicz, *Proc. R. Soc. London A* **427**, 321 (1990).
- [4] Y. Hu, J. L. Glass, A. E. Griffith, and S. Fraden, *J. Chem. Phys.* **100**, 219 (1994).
- [5] L. Mitnik, C. Heller, J. Prost, and J. L. Viovy, *Science* **267**, 219 (1995).
- [6] H. Isambert, A. Ajdari, J. L. Viovy, and J. Prost, *Phys. Rev. Lett.* **78**, 971 (1997).
- [7] M. Stefansson and P. Doyle (private communication).
- [8] S. Magnusdottir, H. Isambert, C. Heller, and J. L. Viovy (to be published).
- [9] T. Kiriya, T. Ozawa, T. Akimoto, H. Yoshimura, and T. Mitsui, *Jpn. J. Appl. Phys.* **36**, 7282 (1997).
- [10] H. Isambert, A. Ajdari, J. L. Viovy, and J. Prost, *Phys. Rev. E* **56**, 5688 (1997).
- [11] Ion depletion effects in strong continuous fields are believed to be responsible of nonlinear behavior for various electrodynamic properties, such as the voltage-current responses of ion-exchange membranes [see, e.g., (a) I. Rubinstein and L. Shtilman, *J. Chem. Soc. Faraday Trans. 2* **75**, 281 (1979); (b) I. Rubinstein, *ibid.* **77**, 1595 (1981)]; or the electro-osmotic and electrophoretic mobility of particles [see, e.g., (c) N. A. Mishchuk and P. V. Takhistov, *Colloids Surf. A* **95**, 119 (1995)].