Application of an Electric Field to Colloidal Particles Suspended in a Liquid-Crystal Solvent

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We study the behavior of colloidal particles suspended in a thermotropic nematic solvent in the presence of an electric field. For normal boundary conditions of the nematic director at the particles' surface, we show experimentally that an electric field applied along the dipolar axis of an elastic dipole induces a transition to an elastic quadrupolar configuration. Turning the field off makes the system go back to the initial state. We also show that it is possible to directly evidence an elastic quadrupolar repulsion between droplets.

The behavior of colloidal suspensions in electric fields is of considerable technological interest with the so-called electrorheological (ER) fluids [1]. The main features of this behavior are now rather well understood. When an external field is applied, particles suspended in an isotropic fluid become polarized. Resultant dipole-dipole interactions between the particles lead to their chaining along the direction of the applied field. When suspended in a liquid-crystal host, colloidal particles are also expected to be polarized upon the application of an electric field. However, new phenomena may take place because of the specific response of the liquid crystal. In this case, the external field is likely to alter the distortions of the liquid crystal alignment around the particles. These distortions induce elastic interactions between the particles and play therefore a crucial role in their stability and the formation of structures. In the absence of any external field, it has been shown, in analogy with electrostatics, that elastic distortions in a nematic liquid crystal can have dipolar or quadrupolar symmetry depending on surface boundary conditions and droplet size [2–9]. Different kinds of distortions and symmetries lead to completely different behaviors and structures. It is thus of critical importance to determine how the electric field affects the distortions around the particles. Stark theoretically predicted that an elastic dipole could be transformed into a quadrupolar configuration known as a Saturn ring in the presence of an electric field [8]. Although this prediction has not yet been experimentally confirmed, Gu and Abbott have recently reported experimental pictures of stable Saturn rings in the absence of a field and the expansion of the ring when the field is applied [10]. These results show the richness of the problem that is still far from being elucidated.

In this Letter, we present experimental results that shed some light on the behavior of liquid crystal suspensions under the action of an external field. We found that application of an electric field on elastic dipoles induces the formation of elastic quadrupoles in accordance with the predictions [8]. This transition occurs for a certain field value that depends on the particle size and the anchoring strength at its surface. Moreover, we were able to directly measure the quadrupolar interaction between quadrupoles

and we show that this interaction is repulsive along a particular direction. These general features contrast with what happens in classical ER fluids. In addition to creating electrostatic dipoles that attract one another when the electric field is on, our experiments reveal the formation of elastic quadrupoles that experience an elastic repulsion.

The system we are interested in consists of silicone oil particles suspended in a thermotropic nematic liquid crystal [11]. In such a medium, it has been shown that particles distort the director field in their vicinity. These elastic distortions lead to distinct configurations that depend on the nature and strength of the anchoring at the drop's surface [2–9]. In the absence of any external field and for a strong normal anchoring of the liquid crystal molecules on the surface, a hedgehog (hyperbolic) defect is created next to the particle to satisfy the nematic far field alignment. The whole configuration has dipolar symmetry. For weaker anchoring or smaller droplet sizes, it is known that the Saturn or surface ring configuration is the favored one [3,4,8,9,12]. The structure has now quadrupolar symmetry. Our experimental systems were all prepared by a thermal-induced phase separation of a binary mixture containing a silicone oil [13] and the liquid crystal [12]. The experiments were performed in thin glass cells fitted with 50-μm-thick spacers which served as electrodes. Their spacing was 1 mm and the electric field was applied in the plane of the cell. At the early stages of the phase separation, small silicone droplets appear in the nematic matrix. They all have the quadrupolar configuration and experience an elastic attraction when r, the vector joining the centers of two droplets, is neither parallel nor perpendicular to the far field alignment of the director [14,15]. This attraction induces the coalescence of the freely floating quadrupoles which then grow in size. However, the coalescence is abruptly stopped when the droplets turn to the dipolar configuration above a critical size R^*. This elastic stabilization originates from the hyperbolic defect which prevents the droplets from coming into contact and fusing. Elastic dipolar interactions give rise to the chaining of particles. The critical radius R^* is a function of both the liquid crystal elasticity K and the anchoring strength W and is given by $R^* \approx K/W$

[12]. Since W is characteristic of the oil, R^* can be varied through the use of different oils. Indeed, the used oils [13] lead to values of R^* of about 1.5 and 3.5 μm approximately, the anchoring being weaker in the latter case.

At this point, we point out that, in the following, terms such as "elastic dipole" and "electric dipole" are going to be used and should not be confused. Elastic dipoles (respectively, quadrupoles) refer only to droplets exhibiting a dipolar (respectively, quadrupolar) symmetry of the liquid-crystal distortions.

If a high electric field is applied along the axis of an isolated elastic dipolar droplet, we observe a transition from the dipole to the quadrupole. Figure 1 shows the dipole point defect opening up into an equatorial ring which consists of a $-\frac{1}{2}$ disclination. This observation is in agreement with the simulations made by Stark [8]. Interestingly, a similar transition has been reported when an electric field is applied to nematic droplets suspended in isotropic phases. A hedgehog defect located at the center of the nematic drop loses its stability in the presence of the field and transforms into a ring at the surface of the drop [2,16]. If we now focus on a chain of elastic dipoles, the droplets do not coalesce because of the in-between hyperbolic defect. Application of a high electric field opens up the defect and makes the droplets coalesce despite a quadrupolar elastic repulsion which is described and measured below. Above the threshold for the dipole to quadrupole transition, the electrostatic force completely overwhelms the elastic one when fields of a few V/μm are applied. We see below that lower fields do not make the droplets coalesce because the elastic repulsion force becomes comparable to the electrostatic one. Turning off the field makes the ring shrink back to the dipole, which is here the stable configuration in the absence of a field. The threshold field (E^*) depends on the droplet size (R), as well as on the anchoring strength. Figure 2 shows the variations of the threshold field as a function of droplet size in the cases of strong and weak normal anchoring. In this latter case, we see that small droplets "switch" to the quadrupolar state at fields lower than that of large droplets. This tendency could be explained the following way. In conditions of weak anchoring, small sizes are known to favor quadrupoles over dipoles [8,12]. It should then be easier to form quadrupoles when the dipoles are small than when they are large. For stronger anchoring, we first notice that the threshold field values are about 3 times higher than in the previous case. Indeed, the dipolar configuration is now significantly more stable and it is much more difficult to form quadrupoles because of a higher energy barrier. In contrast to the previous case, there seems to be a decreasing tendency of E^* with R. But it is difficult to draw more detailed conclusions from the data dispersion.

Finally, we managed to measure the quadrupolar interaction between quadrupoles. At the beginning of the phase separation, all the droplets have the quadrupolar symmetry [12]. Application of a weak electric field (<1 V/μm) at this moment induces the formation of electrostatic dipoles, which drive the elastic quadrupoles to assemble into chains. When r is parallel to the director alignment far from the droplet, the quadrupoles experience a strong elastic repulsion, as predicted [14,15]. We then have a competition between the electric force, $\boldsymbol{F}_{\text{electric}}$, which forces the droplets to come in close contact, and the elastic repulsion force, $\boldsymbol{F}_{\text{elastic}}$, which tends to drive them apart. From the balance of these two effects, it is possible to derive the elastic quadrupolar interaction potential. For each value of the electric field, we can measure the center-to-center distance r between two droplets within a chain and deduce the force profile from the equilibrium condition $\boldsymbol{F}_{\text{electric}} = -\boldsymbol{F}_{\text{elastic}}$. It is worthy to note that, since the electric field is likely to distort the ordering of
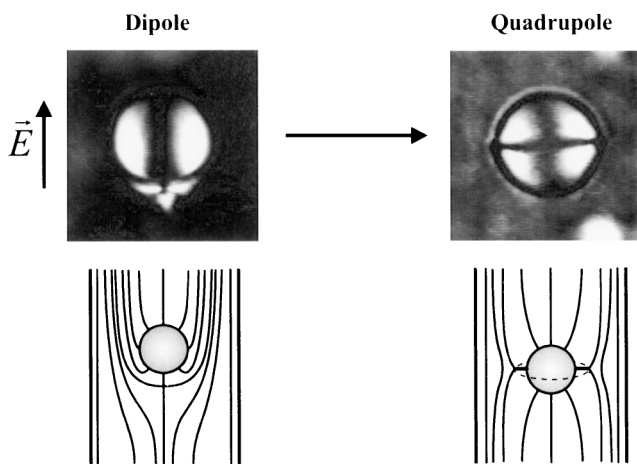

Dipole   **Quadrupole**

$\vec{E}$

FIG. 1. An elastic dipole transforms into an elastic quadrupole under the action of an electric field. The pictures were taken between crossed polarizers. The schematic diagrams below each picture show the director distortions around the droplet. Droplet diameter: 8 μm.
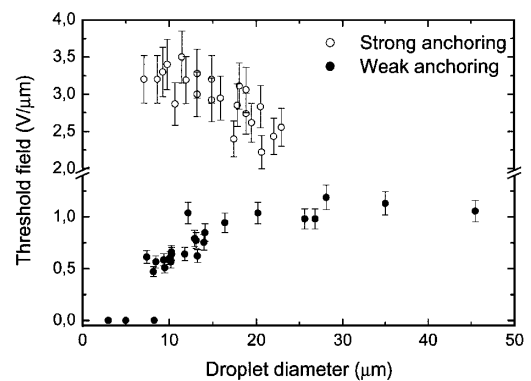

FIG. 2. Threshold field values (E^*) as a function of droplet diameter in the cases of two different anchoring strengths of the liquid crystal molecules at the drop's surface. The letters D and Q stand for dipole and quadrupole, respectively. In the case of the weaker anchoring, the values of E^* do not exceed 1.3 V/μm while they go above 3 V/μm when the anchoring is stronger. In this latter case, it seems that the bigger the droplets, the lower the threshold field while the tendency is reversed when the anchoring weakens.

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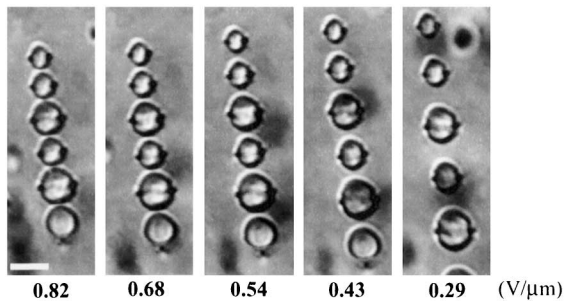
| 0.82 | 0.68 | 0.54 | 0.43 | 0.29 | (V/μm) |

FIG. 3. Series of pictures showing the action of an electric field on quadrupolar droplets. Dipolar electrostatic interactions make the droplets assemble into chains just as in classical ER fluids. The field forces them to be close to one another. However, when the field gets weaker, the elastic repulsion becomes prevalent and the droplets begin to be driven apart. Scale bar: 3.3 μm.

the liquid-crystal molecules in the vicinity of droplets, the measured elastic quadrupolar interaction may intrinsically depend on E. F_{electric} can be roughly estimated using the relation for two spheres immersed in an isotropic fluid [17]:

$$F_{\text{electric}} = 12\pi\varepsilon_0\varepsilon_1\left(\frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + 2\varepsilon_1}\right)^2\frac{R^6 E^2}{r^4}, \qquad (1)$$

where R is the radius of the droplets, ε_0 is the permittivity of free space, and ε_2 is the dielectric constant of the used silicone oil. As a first approximation, we set $\varepsilon_1 = \overline{\varepsilon}_{\text{CL}}$, where $\overline{\varepsilon}_{\text{CL}}$ is the mean dielectric constant of the liquid crystal. Therefore, $F_{\text{elastic}} \propto E^2/r^4$. Figure 3 shows the variations of r with the electric field strength. At the highest fields, the droplets are close to one another but do not contact (far left picture). When the field gets weaker, r increases because of the elastic repulsion. The repulsive force profile is shown in Fig. 4. This graph is the first experimental evidence that elastic quadrupoles actually repel each other when r is along the director align-
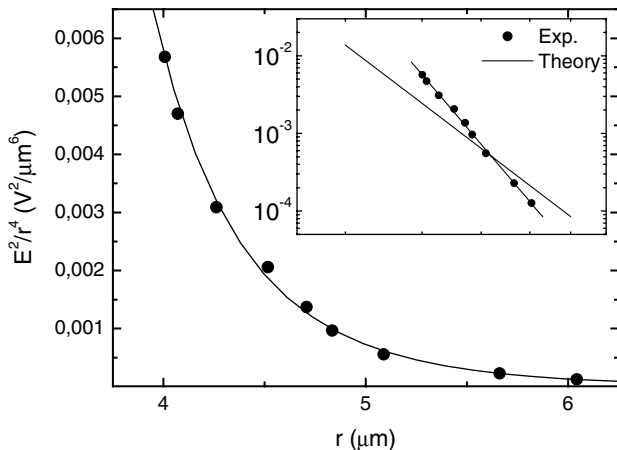
ment. We stress that elastic quadrupoles are quite unstable in the absence of field since they coalesce when they randomly diffuse. Thus, the present result leads to the unexpected conclusion that initially unstable particles can be stabilized by application of an electric field, provided that the particles are driven in a particular direction along which they repel each other. In a classical isotropic fluid, the field would have the opposite effect as it would favor attraction and coalescence of the particles. In the absence of field, previous theoretical predictions based on a long range calculation predicted that the elastic quadrupolar repulsion should follow a $1/r^6$ power law [14,15]. In the present experimental conditions, i.e., in the presence of an electric field, we observe a steeper repulsion that may either arise from the effect of the electric field or from short range effects not considered in [14,15] (see the inset in Fig. 4). The maximum measured separation between two droplets is on the order of a particle diameter. Taking $\varepsilon_2 = 2.24$ and $\overline{\varepsilon}_{\text{CL}} \approx 8.7$ (typical of cyanobiphenyl molecules [18]) into Eq. (1), a crude estimate of the repulsive elastic interaction leads to force values around a few pN.

To conclude, we have investigated the effect of an electric field on particles suspended in a nematic solvent. Our experiments show that elastic dipoles switch to quadrupolar symmetry when the field is applied along the dipole axis. This transition depends on the droplet size and the anchoring strength. More experimental and theoretical work would be needed to better understand this dependence. We further show that chains of quadrupolar particles can be formed when a weak field is applied and that these quadrupoles experience an elastic repulsion. The repulsive force is roughly estimated to be around a few pN. This repulsion unexpectedly stabilizes particles which are initially strongly unstable. On the contrary, application of high enough electric fields along a chain of elastic dipoles makes them coalesce when the defects open up. It is thus a new means to selectively control the coalescence of liquid droplets and thereby their size.

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FIG. 4. Quadrupolar elastic force F_{elastic} ($\propto E^2/r^4$) as a function of the center-to-center distance r in the presence of an electric field. The force profile is repulsive and steeper than the long range prediction in the absence of field (inset). A power law fit leads to a scaling close to $1/r^9$.

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