Measurement of Elastic Forces between Iron Colloidal Particles in a Nematic Liquid Crystal

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(Received 20 January 2006; published 1 June 2006)

The forces that arise between two iron particles in a nematic liquid crystal with a strong homeotropic anchoring were studied. For the first time, the short range repulsive force resulting from the presence of a hedgehog defect between two particles was precisely determined thanks to application of a small magnetic field and observation of the equilibrium position resulting from the balance between the elastic and magnetic forces. Above a given threshold force, the particles stuck together whereas the hedgehog defect was expelled and transformed into a Saturn ring located between the particles. The attractive part of the interparticle force was determined with the same method on the entire range of separation distances; we found that the equilibrium distance between two particles was $r = 1.19 \pm 0.05 \langle d \rangle$ ($\langle d \rangle$ was the average diameter of the pair of particles).

DOI: 10.1103/PhysRevLett.96.217801 PACS numbers: 61.30.−v, 61.30.Jf, 75.50.Bb, 82.70.Dd

Introduction.—In traditional colloidal systems, the solvent is an isotropic fluid. Controlled organization of the colloids can be obtained by application of an external electric or magnetic field: these are the electro- or magnetorheological fluids. When colloidal particles are dispersed in a nematic liquid crystal, they disrupt the nematic order, and minimization of the elastic energy leads to the formation of anisotropic colloidal structures [1].

When the particles are sufficiently large and, depending on the strength and direction of the nematic anchoring on the particle surface, various types of topological defects (such as a hyperbolic hedgehog, a Saturn ring, and boojums) have been reported corresponding to theoretical predictions [2–7]. Past experimental studies have largely focused on dispersions of the liquid microdroplets (water [1,8,9] ferrofluid [10], silicon oil [11–14], etc.) in nematic solvents or the latex particles in lyotropic liquid crystals [9,15]. However, Gu and Abbott described experimental studies of suspensions of glass spheres coated with a thin film of gold in a nematic liquid crystal (NLC) [16].

For the particles mentioned above, if NLC molecules are strongly and perpendicularly anchored at the surface of a spherical particle, this particle acts like a radial hedgehog carrying a topological charge, $Q = 1$. Placed in a uniformly aligned nematic solvent and to satisfy the boundary conditions at infinity, i.e., a total topological charge of zero, the particle should nucleate a further defect in its nematic environment. The dipole is the preferred configuration for large particles and sufficiently strong anchoring, even if quadrupoles were also observed around the glass spheres coated with a thin film of gold, suspended in NLC [16]. This agreed with recent theoretical results [17,18]. The topological dipole is formed by one spherical particle and an accompanying topological defect (known as a hyperbolic hedgehog); these dipoles generate elastic forces that lead to the formation of chains of particles.

The long-range attraction force was measured [10,19], and these experiments confirmed the theoretical predictions for the dipolar character of the interactions between droplets in a nematic solvent [4,20]. The interesting feature of these elastic interactions is that the dipolar attractive force for long distances turns into a repulsive force for short distances and lead to a nonzero separation between the particles.

This Letter will describe the experimental measurements of the elastic force in both the attractive and the repulsive range. A new system made of pure iron particles was employed. The surface of the particles was grafted with octadecyldimethyl(3-trimethoxysilylpropyl)ammonium chlorid (DMOAP) to promote a strong homeotropic (perpendicular) anchoring of the NLC molecules. We believe the experimental system we describe here to be advantageous for two main reasons. First, because the iron particles are solid, therefore even when in contact, they cannot coalesce and fuse. Second, due to their high magnetic permeability, large magnetic forces can be obtained in a low magnetic field. This does not disturb the nematic ordering around the particles, contrary to past experiments under an electric field where the topological dipole transformed into a quadrupole [13,21].

Experimental results.—Details of the chemical treatment of the surfaces of the iron particles will be given elsewhere [22]. This treatment is necessary to obtain a strong homeotropic anchoring of the NLC ($E7$ in this case) at the surface of the particles. The proof of the success of this treatment was obtained by observing a particle dispersed in $E7$ through cross polarizers disposed so that no light was transmitted in the absence of particles.

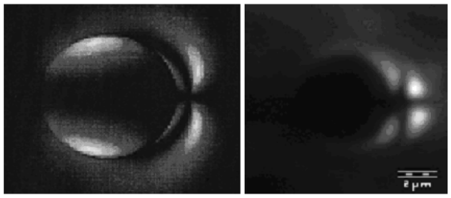

FIG. 1. Left view: numerical simulation [4], right view: observation of an iron particle in a NLC placed between cross polarizers.

The hedgehog defect at the head of the particle induced a rotation of the polarization that broke the extinction between the cross polarizers. Figure 1 on the right shows a photo of this defect obtained with a grafted iron particle. This photo was quite similar to the one predicted by numerical simulation [4] (on the left).

Our aim was to measure the interparticle force, therefore we introduce only a few particles and look for pairs of particles, which were far enough away from other particles. The dispersion of iron particles in NLC was confined between two glass slides, spaced by calibrated sheets of 12 μm, and rubbed on a piece of paper [23] to establish planar anchoring of the NLC at the surface. Different pairs of particles were used; Table I gives their diameter measured by optical microscopy with an objective $\times$ 150.

In the absence of any applied magnetic field, the equilibrium distance, r_0, observed between the centers of the particles was plotted versus the average diameter for the six pairs of particles. The data line up very well on a straight line with a 1.19 ± 0.05 slope. The only other experimental value reported in the literature [1] was 1.3 (separation of 0.3 diameter between the surfaces) for the equilibrium distance between two water droplets in 5CB. A recent numerical calculation of the equilibrium distance between two spherical particles in a NLC, in the same "parallel-dipole" configuration, and using bispherical coordinates and an adaptive grid, predicts $r_0 = 1.23$ diameter [24]; this value well falls within our experimental result (1.19 ± 0.05). On the other hand, several theoretical studies predicted the position of the satellite hedgehog around a single particle between $1.17a$ and $1.25a$ [3,4,7,18] (a is the radius of the particles). The experimental value, $1.2a$, found by Poulin and Weitz [8] agreed with these predictions and we confirm this distance for single iron particles

TABLE I. Radii and average radius of the various pairs of iron particles.

	a_1 (μm)	a_2 (μm)	a (μm)
Pair $n°1$	2.12	1.84	1.98
Pair $n°2$	1.93	1.85	1.89
Pair $n°3$	1.60	1.70	1.65
Pair $n°4$	1.01	0.99	1.00
Pair $n°5$	1.67	1.91	1.79
Pair $n°6$	2.75	2.66	2.70

although the uncertainty for the precise location was much greater than for the distance between two particles; therefore we observe that, within the experimental uncertainty, the position of the defect is the same for a single particle or a pair of particles.

Now, to measure the elastic interparticle force, we only need to apply a magnetic field on a pair of particles. If the magnetic field is parallel to the line joining the centers, then the particles will attract each other and they will come closer until the repulsive elastic force balances the attractive magnetic force. On the other hand, if the magnetic field is perpendicular to the line of centers, they will separate and also find an equilibrium position where the repulsive magnetic force will compensate the attractive elastic force. Therefore if we can calculate the magnetic force as a function of the separation distance in these two situations, then the elastic interparticle force would be known. Two conditions should be fulfilled to obtain reliable results: (1) the influence of the magnetic field on the director should be insignificant (2) the calculation of the magnetic force should be done precisely and certainly not in the dipolar approximation.

The first condition can be realized as long as a small enough field is used. The pertinent parameter is the magnetic coherence length: $\xi_{\mathrm{H}} = \sqrt{K_3/\Delta\chi H^2}$; $\Delta\chi$ stands for the magnetic anisotropy and K_3 the bending elastic constant. This represents the distance needed to line up the director of the nematic on the direction of the magnetic field; we therefore would expect that the magnetic field would have no influence on the director in the region between two particles if $\xi_{\mathrm{H}} \gg a$. Stark [5] calculated the effect of a magnetic field on the free energy of a hedgehog

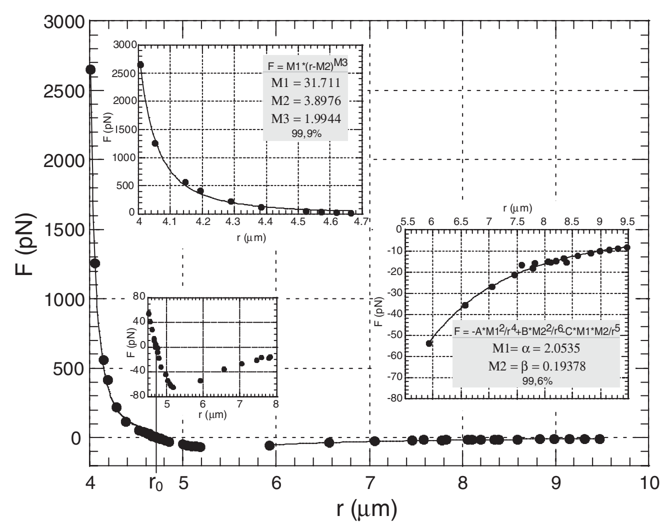

FIG. 2. Elastic force between two iron particles in a liquid crystal. The upper inset shows the repulsive part of the force fitted by a power law. The right inset shows the attractive part of the force fitted by Eq. (1). The last inset is a zoom of the curve around the equilibrium distance r_0.

defect and it appeared to be negligible for $a/\xi_{\mathrm{H}} < 0.1$. Taking $H = 5 \times 10^{-3}$ T (the maximum value used), $K3 = 1.53 \times 10^{-6}$ dyne and $\Delta\chi = 10^{-7}$ we obtain: $a/\xi_{\mathrm{H}} = 2 \times 10^{-3}$, therefore the influence of the magnetic field on the elastic energy can be safely discarded. The second requirement relies on the capacity of numerical methods to solve the equations of magnetostatics between two magnetic spheres characterized by nonlinear magnetization. The parameters used are: initial relative permeability, μ_{i}, and saturation magnetization M_{s}. These values were obtained from a fit of experimental data M (H) for pure iron using the Frolish-Kennelly law: $M = \chi_{\mathrm{i}} H/(1 + \frac{\chi_{\mathrm{i}}}{M_{\mathrm{s}}} H)$, where $\chi_{\mathrm{i}} = \mu_{\mathrm{i}} - 1$. The resulting values were $\mu_{\mathrm{i}} = 7500$ and $M_{\mathrm{s}} = 1332$ kA/m. The field, H_{g}, inside the gap between the particles for a given applied field, H_0, was calculated with a specific finite element code [25] and the force was obtained from the following integral on the midplane separating the two particles: $F_{\mathrm{m}} = \frac{\mu_0}{2} \int_0^a (H_{\mathrm{g}} - H_0)^2 2\pi\rho d\rho$ (where μ_0 is the vacuum permeability). This calculation even worked for spheres in quasicontact and was successfully used to predict the yield stress in magnetorheological fluids [26]. We estimated that the uncertainty was less than 8% for the whole range of separations. The long-range attractive part of the elastic force was derived by Lubensky *et al.* [4]:

$$\frac{F}{4\pi K} = -\alpha^2 a_1^2 a_2^2 \frac{6}{R^4} + \beta^2 a_1^3 a_2^3 \frac{120}{R^6} - \alpha\beta a_1^2 a_2^2 (a_1 - a_2) \frac{24}{R^5} \quad (1)$$

with $\alpha = 2.04$ and $\beta = 0.72$.

The elastic constant $K = 13,7$ pN corresponded to the average of $K1$, for the splay, and $K3$ for the bending, found in the literature [27], (the constant $K2$, corresponding to the twist deformation should have a lower influence with that kind of defect).

The R^{-4} behavior was first observed by Poulin *et al.* [10]. They deduced the force from the measurement of the relative velocities. More recently, Feng *et al.* [18], also verified the dipolar nature of this elastic attractive force, using optical tweezers. However these methods do not allow a precise determination of the constants α and β appearing in Eq. (1).

We have presented in Fig. 2 the entire range of forces between two iron particles (average radius $a = 1.98$ μm). The right insert represents the attractive part of the force, the solid line is the prediction of the Eq. (1), with α and β the parameters of the fit. The other quantities present in Eq. (1) were $a_1 = 2.12$ μm, $a_2 = 1.84$ μm. The parameter of the fit, $\alpha = 2.05$, completely agreed with the theoretical predictions, but the theory appeared to overestimate the quadrupolar contribution since we found $\beta = 0.2 \pm 0.1$ instead of $\beta = 0.72$. It should be noted at this point how our distance measurement between two particles was made. A recent paper [28] showed that systematic errors were found due to an optical determination based on center-to-center measurements. The authors showed that, for Brownian polystyrene particles, this systematic error could give rise to an artificial attractive force. Polystyrene particles do not absorb light and appeared white at their center,whereas their periphery was not well defined. In contrast, in the case of the metallic particles, the edge of the particles showed a sharp transition from black to gray, and the distance between the two opposite sides of the pair of particles could therefore be measured without this error. Furthermore, since we finished the experiment with particles in contact for a high parallel magnetic field, we just substracted this contact distance from the previous ones in order to get the separation distance. This procedure did not give rise to any systematic error. The uncertainty in the force was the one in the distance ($\pm$ 20 nm) multiplied by the derivative of the force; it was less than $\pm 1.5\%$ in the attractive part, but grew steadily as the separation decreased ($\pm$ 13% at $r = 4.2$ μm and $\pm 25\%$ at $r = 4.05$ μm).

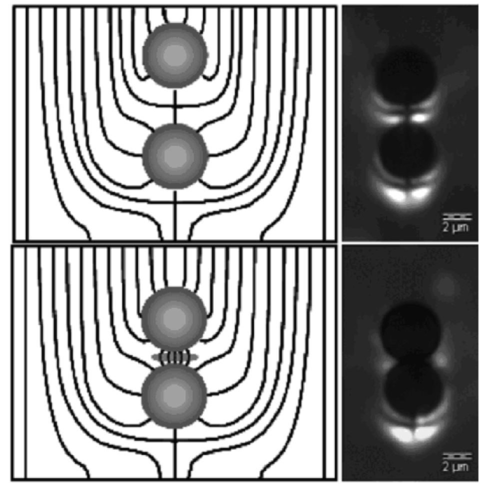

FIG. 3. Top view: separation distance $r = r_0$, the defect is between the particles; lower view: $r \approx 2a$, the defect has transformed into a ring defect.

No predictions were found for comparison in the repulsive part. Our results can be well fitted with an empirical formula: $F = M1 \times (r - M2)^{-M3}$ (see the upper insert in Fig. 2).

In the regime of repulsive forces, the gap between the surfaces of the pair was reduced by increasing the magnetic field parallel to the axis of centers. Each equilibrium position corresponded to a given magnetic field and the relative position of the two spheres was recorded. Then if the field was lowered, the particles moved back. Nevertheless, above a critical magnetic field (corresponding to a critical elastic force) the particles no longer separated when the field was lowered. When this phenomenon happened, the separation of the two particles was close to the resolution of 1 pixel on the image. Furthermore the magnetic force varied quite strongly when the separation distance approached zero. Therefore it was not possible to give a precise estimation of this threshold elastic force.

Now we are going to show that the absence of separation of the particles when the field is turned off implies that the hedgehog defect is expelled from the interparticle gap. The increase of the repulsive elastic force when the particles come closer was due to the increase of the director curvature, as expressed in the Frank free energy [1], to meet the normal anchoring condition on the surfaces (cf. Fig. 3, top view). The minimum distance between the particles would be equal to the core diameter of the defect (typically 10 nm [4]) with a repulsive elastic force estimated from extrapolation of the fit (Fig. 2 top view): $F_{\mathrm{el}} = 3000$ pN. The only two short range attractive forces that could dominate this repulsive force are the van der Waals force (VDW) and the magnetic force due to remnant magnetization. From the remnant magnetization measured on the iron powder after a cycle of induction until saturation, a remnant magnetic moment $m_{\mathrm{r}} = 5.33 \times 10^{-10}$ emu was obtained for a particle of radius 2 μm. The attractive force between two permanent moments at a distance $R = 4$ μm was $F_{\mathrm{rem}} = 6m_{\mathrm{r}}^2/(4\pi\mu_0 R^4) = 0.034$ pN; this is completely negligible. The other attractive force, that could prevent the particles from separating, is the van der Waals force: $F_{\mathrm{VDW}} = \frac{A}{6} \times \frac{a_1 a_2}{a_1 + a_2} \frac{1}{d^2}$; d is the gap between surfaces. The Hamaker constant was estimated for two iron particles in $E7$; we obtained $A = 7.2 \times 10^{-20}$ J. In the presence of the defect with $d = 10$ nm it gives an attractive force, approximately 100 pN, that is still 30 times lower than the elastic repulsive force. We conclude that, if the particles did not move back when the field was turned off, it is because, at some separation below 50 nm, the hedgehog defect was expelled, allowing the van der Waals force to keep the particles together. In this case the situation was close to the one analyzed by Galatola *et al.* [29], where they found a Saturn ring located along the symmetry plane perpendicular to the axis of centers. Our conclusion that the hedgehog defect was expelled and transformed into a ring located between the two particles was confirmed by a careful analysis of the photos obtained between cross polarizers. If the two photos in Fig. 3 are compared, the top photo shows the presence of the defect on the line of centers whereas in the bottom one we distinguish two spots can be identified indicating the presence of the ring defect.

To conclude, let us note that this new system based on iron particles is very well suited to measure elastic forces between particles in a NLC and could be used in other situations. Additionally, by adding a cross-linking polymer, it could be possible to obtain elastic chains of iron particles with easily modulated lengths using a magnetic field. The resulting change of conductivity could be enormous and applications of this type of system may be found (micrometer sized and very sensitive pressure sensor [30]).

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