Colloidal Interactions and Transport in Nematic Liquid Crystals

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We describe a new nematic liquid-crystal colloid system which is characterized by both charge stabilization of the particles and an interaction force. We estimate the effective charge of the particles by electrophoretic measurements and find that in such systems the director anchoring energy W is very low and the particles have little director distortion around them. The interaction force is created by producing a radial distribution of the nematic order parameter around a locally isotropic region created by ir laser heating. We theoretically describe this as being due to the induced flexoelectric polarization, the quadrupolar symmetry of which provides the required long-range force acting on charged particles.

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It is well known that directed diffusion cannot occur in systems in equilibrium; however, if the thermodynamic balance is disturbed then a net transport of particles can emerge. It has been shown that particle motion can be induced by, for example, external optically induced patterns. Here we describe a new observation of the motion of colloidal particles in a nematic liquid crystal and a local isotropic area produced by heating from a laser. We postulate that the interaction is produced by the gradient of the order parameter radially from the isotropic area and theoretically describe this via the flexoelectric effect. However, before we describe these interactions further, a critical part of our work which allows the above effects to be manifest, and which distinguishes our work from previous studies, is the fact that we have produced a charged stabilized of colloidal particles in a thermotropic liquid crystal, which in itself is a new result. We therefore describe this part of our work first.

A large volume of studies is dedicated to variations of ‘‘nematic colloids,’’ where the boundary conditions on particle surface generate long-range distortions and topological defects around them and the nematic-mediated interactions between the particles. A recent review of this area can be found in [1]. When a spherically symmetric particle is brought into the nematic medium with its locally quadrupolar symmetry, one expects the same nature of deformations around the particle. This is indeed the case for planar director anchoring on the particle surface, with two boojum singularities at its poles. For strong radial anchoring energy W there is sometimes an additional symmetry breaking into a polar configuration with a single (-1) point defect [2], which arises for larger particles in order to reduce the ‘‘Saturn ring’’ energy contained in a singular core of a $(-1/2)$ disclination loop [3]. Of course, when the director anchoring on particle surface is weak, i.e., below the characteristic ratio $WR/K = 1$ with K the curvature elastic constant of a nematic, no topological singularities arise and the director distortion $\boldsymbol{n}(\boldsymbol{x})$ always retains the natural quadrupolar symmetry [3]. Nematic colloids is an increasingly important area of study, partly for academic reasons, but also due to new application prospects such as self-assembly of particles in aligned strings [4] and other aggregation patterns [5,6], and even as biological sensors [7,8].

Charge stabilization in a hydrophobic nematic matrix has never been observed before. Classically, colloid particles suspended in a liquid matrix have to be stabilized against flocculation that occurs when, e.g., hard spheres come into contact and become locked in the primary van der Waals potential well. Two main methods are used: steric and charge stabilization. In the first case, a polymer brush is ‘‘grown’’ on the particle surface and in the second, charge can be made to uniformly cover the particle surface and the molecules on this surface dissociate. The counterions leave the particles, which now repel each other via electrostatic Coulomb forces. If the liquid has the native ions and counterions, then a double layer is formed near the particle surface and the range of electrostatic repulsion is screened at distances above the Debye length. All of this is very well known, except that the charge stabilization is meant to work in water; the cases of colloid charge dissociation in the hydrophobic phase are extremely rare [9,10]. The work [9] is particularly important since hydroxylated silica spheres were used, similar to our case.

We used plain silica particles with natural hydroxyl or Si-OH surface groups (Bangs Labs, Fishers, IN; particle diameters 0.98, 2.56, and 4.09 μm; refractive index 1.37 for $\lambda = 589$ nm) supplied in dry powder. These are classical charge-stabilized hydrophilic colloid particles. We have instead dispersed them in typical (hydrophobic) nematic liquid crystals: 4′-pentyl-4-cyanobiphenyl (5CB), with $T_{\mathrm{ni}} \approx 36\,^\circ$C and refractive indices $n_o = 1.53$ and $n_e = 1.73$ at room temperature, and a cyanobiphenyl mixture E7 with $T_{\mathrm{ni}} \approx 58\,^\circ$C, obtained from Merck (Darmstadt, Germany). An ordinary stirring of particles achieved a reasonably stable colloid. We believe this is due to the high polarizability of the π electrons and the large CN dipole of cyanobiphenyl: the OH groups on particle surface dissociate to some degree in spite of the overall hydrophobic nature of cyanobiphenyls. It is also possible that some surface charges can be due to the absorption of ions. Measurements of electrophoretic mobility add strength to our conjecture. First we filled a 500 μm thick, planar cell with water with particles suspended in it. Applying a dc voltage in the plane of the cell, with electrodes 8 mm apart, and monitoring the motion of a selected particle close to the center (in depth) of the cell we measured the constant velocity of electrophoretic drift. Then the same experiment was performed with a particle in similar sized unaligned liquid-crystal matrix. The results are as follows.

Water matrix.—The field $E = 0.625$ kV/m (5 V), the velocity of a 2.56 μm particle was measured as $v = 24\ \mu\mathrm{m/s}$. For water viscosity $\eta = 0.001$ Pa s we obtain the Stokes drag $6\pi\eta R v \approx 5.8 \times 10^{-13}$ N. Equating this to qE we obtain the total (negative) charge on the particle $q \approx 9.3 \times 10^{-16}$ C, which approximately equals that of $\sim 5800e$.

LC matrix.—The field $E = 3.75$ kV/m (30 V), the velocity of 2.56 μm particle was measured as $v = 0.9\ \mu\mathrm{m/s}$. For the average 5CB-E7 viscosity $\eta = 0.08$ Pa s we obtain the Stokes drag $6\pi\eta R v \approx 1.7 \times 10^{-12}$ N. Equating this to qE we obtain the total charge on the particle $q \approx 4.6 \times 10^{-16}$ C, or approximately $\sim$2900 electrons. This means the surface coverage of $\sim 1.410^{14} e/\mathrm{m}^2$. In physical chemistry it is common to express the colloid surface charge via the so-called ζ potential [11]; however, we prefer to use the effective charge as this will be essential later in the discussion of flexoelectric forces.

Charge dissociation in a hydrophobic liquid, and the resulting stabilization of colloid particles in a matrix of nematic LC, is a very unusual finding. We also notice a second unexpected consequence of double layer formation. Figure 1 demonstrates that there are no relevant director distortions around such particles, even the biggest 4.09 μm diameter ones. This means that the effective nematic colloid ratio $WR/K \rightarrow 0$, i.e., that the effective anchoring energy W vanishes. This is in great contrast to most previous studies of particles in liquid crystals (where sterically stabilized particles were used and various director textures observed). The only explanation we can offer is that the nematic order parameter Q drops to zero near the particle surface (and $W \propto Q$, of course). This assertion is difficult to test experimentally [but see below, when we do test and exploit the $Q(r)$ variation in a different experiment]. On the one hand, it is easy to accept because the concentration of effective impurities rapidly rises in the ionic double layer—its thickness (the Debye length) must be much wider in 5CB than in water because of the much lower concentration of counterions. One could have expected an opposite effect: an increase in Q due to the radial local electric field in the double layer "capacitor." Apparently this is not the case. Since these particles do not interact at long distances and do not cost significant Frank elastic energy, their dispersion in the LC matrix is possible and their aggregation does not occur unless they are forced into direct contact (in which case they stick permanently, not being sterically stabilized).

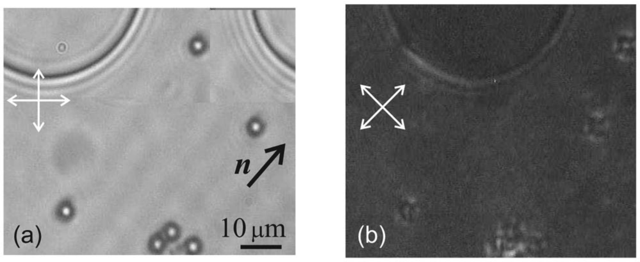

FIG. 1. Silica particles in 10 μm-thick 5CB cell with homogeneous planar alignment. (a) Polars crossed at 45° to the director, providing a bright field and showing no director distortions; (b) same image at crossed polars aligned with $\boldsymbol{n}$. Images also show a part of the overheated isotropic "bubble."

We now move to our second result which is to induce particle motion by restructuring the nematic matrix. We should first mention that there have been several accounts in recent literature of laser-heating induced particle motion in liquid crystals [12,13] in which case very short (a few microns) range interactions were produced by director deformations around the particles and the heated areas ("ghosts"). Our results are different, both in terms of the geometry of the resulting forces, which are quadrupolar and not radial, and our proposed mechanism, which is based on a variation in the order parameter and not the director.

We irradiate the planar LC cell with a focused infrared (ir) laser beam to induce a locally overheated spot where the 5CB is in the isotropic phase. The experimental setup is typical for optical tweezing, with a single microscope objective in an inverted microscope configuration. We used a ×50 objective lens with a numerical aperture of 0.55 (MPlan Apo, Mitutoyo) objective lens. A 1 W 1064 nm laser beam was expanded to fill the back aperture of the objective and focused onto a $\sim 1\ \mu$m spot. A second objective was used to illuminate the sample with white light. Crossed polarizers were used so that changes in birefringence could be visualized as shown in Fig. 2(a). Around the central bright spot (which is the laser beam) there is an approximately circular zone in which the 5CB has been heated to the isotropic phase (in the steady state of heat flux) and there it appears dark between crossed polarizers. This isotropic region ("bubble") is separated from the nematic by a well-defined boundary. We see the characteristic pattern of Newton colors around a circular isotropic "bubble," which are in direct correlation with the local birefringence $\Delta n \propto Q(r)$. The prevalent green color far from the "bubble" represents the regular nematic order in 5CB at $T_0 = 24\,^\circ\mathrm{C}$, $Q \approx 0.6$; $\Delta n = 0.2$, when viewed in a 10 μm-thick cell between crossed polars. Continuously reducing $Q(r)$ on approaching the overheated iso-

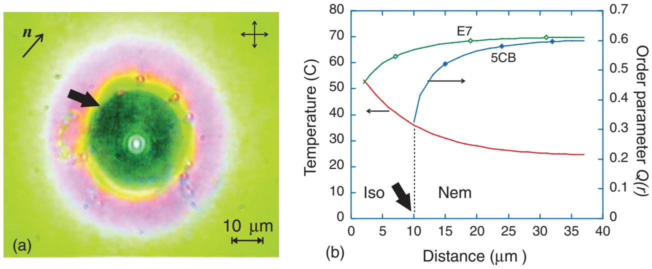

FIG. 2 (color). (a) The image of a 10 μm planar cell with 5CB viewed between crossed polars in white light on transmission. The arrow points at the edge of the isotropic region. Newton colors indicate the change of local birefringence, while the absence of dark or bright brushes confirms the uniformly homogeneous director field. (b) The plot of the temperature $T(r)$ (red line) and order parameter $Q(r)$ variation [for 5CB (green line) and E7 (blue line)] with distance from the laser beam spot.

tropic region produces the color change via the shift of the principal maximum in the transmission spectrum. Figure 2(b) shows the variation of local temperature $T(r)$, obtained by solving the steady-state 2D diffusion equation with an added heat loss through cell walls: $D\nabla^2 T = b(T - T_0)$. Matching the ambient T_0 at $r = \infty$ and T_{ni} at the isotropic boundary, we obtain the decay length $\xi = \sqrt{D/b} \sim 9\ \mu$m and the profile $T(r) \propto K_0(r/\xi)$, the solution in terms of the Bessel K function of zero order. Mapping $T(r)$ to the well-documented $Q(T)$ gives the change of the nematic order $Q(r)$ with distance from the overheated beam spot, Fig. 2(b), which matches the Newton color map.

The main observation is that our charge-stabilized colloid particles experience a force and are driven to move when an isotropic "bubble" is present in the cell. Importantly, the force on the particles is long ranged. The sketch in Fig. 3(a) illustrates the trajectories traced by different particles, which started at different distances and orientation with respect to the isotropic region. The velocity depends on the distance and the particle size, but in all cases we observed an order of magnitude $v \sim 0.1\ \mu$m/s, see Fig. 4.

How can we rationalize these observations? Let us first of all reiterate the different facts that require simultaneous explanation. (i) When a circular isotropic region is formed due to the steady-state thermal gradient around the overheated beam spot, distant particles experience a force that appears to have a quadrupolar symmetry—attraction towards the bubble along the nematic director axis, repulsion from the bubble when at 90° with respect to the director, and sideways motion at medium angles $\sim 45°$. (ii) When a different liquid crystal was used (E7), with a higher clearing temperature so that no isotropic bubble or significant color rainbow was observed, the particles experienced no detectable long-range force. (iii) When a particle happens to be inside the isotropic bubble, in most cases there is no detectable long-range force or induced motion (apart from the ordinary dielectric repulsion very close to the laser beam, since the particles have lower refractive index than the medium). We detected no relevant Soret effect [14] on the length scales involved when particles were dispersed in water. (iv) When observed between crossed polarizers, the nematic director around the isotropic bubble appears to remain uniform. The same applies to the director field $\boldsymbol{n}(\boldsymbol{x})$ around colloid particles—even if there are director distortions, their range does not spread far enough from the particle to be detected with our resolution.

The fact that we see no distortions even around the large "bubble" means that to maintain $WR/K \ll 1$ we must have $W \to 0$. The only possible explanation for that is an extended region of the low nematic order parameter and the associate gradient dQ/dr. The full uniaxial nematic ordering is described by the traceless second-rank tensor $Q_{ij} = Q[n_i n_j - \frac{1}{3}\delta_{ij}]$, which has a principal axis called the nematic director $\boldsymbol{n}$ and a magnitude of order characterized by the scalar parameter Q. Usually the value of Q is constant (apart from the cores of topological defects), but in our case the situation is the opposite. The wide region of temperature gradient ensures a significant and long-range variation $Q(r)$. The director gradients would cost an additional free energy and so matching between the director field outside the "bubble" with its interface is achieved by the variation of Q, while keeping $\boldsymbol{n}$ constant. A similar

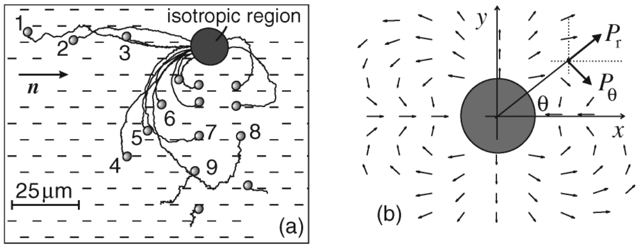

FIG. 3. (a) The sketch of particle tracks, depending on their original position with respect to the isotropic region (shaded circle). (b) Orientations of local flexoelectric polarization around the region with axially symmetric dQ/dr and uniform director $\boldsymbol{n} = n_x$, Eq. (2).

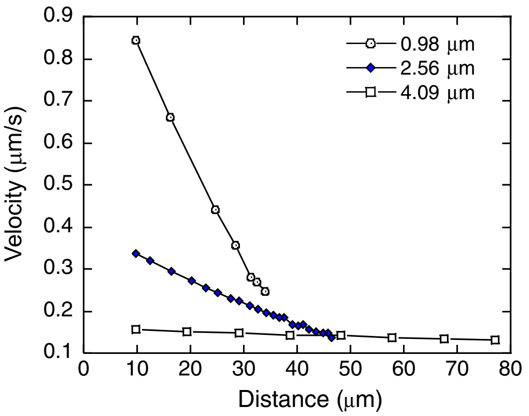

FIG. 4 (color online). Measured velocity as function of distance from the beam, for particles of different sizes (labeled on plot).

argument has been invoked for smaller colloid particles, whose charge stabilization in a weakly ionic matrix requires a broad double layer and thus a region of vanishing Q due to the concentration gradient.

Clearly, the presence of the isotropic bubble, with its strong and long-range order parameter variation $Q(r)$, causes the force on our particles. Such a force seems to be unexpected, since usually one looks for director gradients between objects to couple and produce a long-range interaction. There is, however, a physical mechanism that could account for our findings. The flexoelectric effect is a property of all nematic liquid crystals [15]. Its origin lies in the quadrupolar symmetry breaking described by the order parameter Q_{ij} and the observation that gradients of this order can generate local dielectric polarization [16]. Although the original theory and experiment only looked at possible director gradients, the subsequent analysis has firmly established that four independent terms contribute to the local polarization in the distorted nematic [17,18]:

$$\boldsymbol{P}_{\text{fl}} = e_1 Q \boldsymbol{n} \text{div} \boldsymbol{n} + e_3 Q[\boldsymbol{n} \times \text{curl} \boldsymbol{n}] + e_2 \boldsymbol{n}(\boldsymbol{n} \cdot \boldsymbol{\nabla} Q) + e_0 \boldsymbol{\nabla} Q. \tag{1}$$

In the literature, the pair of terms e_0-e_2 is often called "order electricity," although there is a unique physical mechanism behind all forms of flexoelectricity. If we assume the director remains uniform at all times, $n = n_x$, then the two components of flexoelectric polarization become:

$$P_r = (e_2 \cos^2\theta + e_0)\frac{dQ}{dr}; \qquad P_\theta = e_2 \sin\theta \cos\theta \frac{dQ}{dr}. \tag{2}$$

We can already see the quadrupolar symmetry, which is illustrated in more detail by a map in Fig. 3(b). In order to account for the force acting on particles we need to recall that they are effectively charged, and are subjected to an electric field, $\varepsilon_0 \boldsymbol{\chi} \cdot \boldsymbol{E} = \boldsymbol{P}$, with the principal axis of dielectric susceptibility tensor constant along x. The resulting force will naturally reproduce the observed pattern of particle movement. As an example, for the particle aligned along x, particles 1-2-3 in Fig. 2(a):

$$F = \frac{q(e_2 + e_0)}{\varepsilon_0 \chi_\parallel} \frac{dQ}{dr}. \tag{3}$$

What remains is to determine the value of the order parameter gradient dQ/dr. In principle, we could extract its values from the data in Fig. 2(b). However, a crude estimate may be obtained by observing that a change $\Delta Q \sim 0.3$ occurs over a distance $\sim 20\ \mu$m, giving $|dQ/dr| \sim 2 \times 10^4\ \text{m}^{-1}$. We now can estimate the force acting on the particles. Taking the earlier estimate of charge q and using the literature values for the typical flexoelectric coefficients, $e_i \sim 10$ pC/m [17,18], we obtain an attractive force of the order $F \sim 7$ pN. Balancing this against the friction drag $6\pi\eta R v$ (and ignoring the noncentral anisotropic nature of nematic drag [19], irrelevant for this estimate), we obtain the order of magnitude of particle velocity $v \sim 1.5\ \mu$m/s for $2.56\ \mu$m diameter particle. Considering approximations involved, especially the fact that $|dQ/dr|$ is actually much lower at some distance away from the "bubble," this in good agreement with velocity measurements in Fig. 3.

As a side remark, we note that in the analysis of particle motion we did not consider the anisotropy of the viscous force [19]. The trajectory of the motion will be additionally curved due to the resulting "lift force"; however, the overall symmetry of the flexoelectric force map and the order of magnitude of velocity remains valid.

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